This thesis is presented for the Degree of Doctor of Philosophy of the Australian National University.

The work described in this thesis was carried out under the supervision of Professor A. J. Parker during the period of February 1968 to February 1971.

[Signature]
Acknowledgments

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David John Lloyd
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- Elimination reactions promoted by strong hydrogen bonds which are strong donor chelates.

**Factors which affect and determine the nature of the variable E2 transition state:**

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SUMMARY

The character of the $E_2C$ transition state has been studied with respect to charge development, double bond development and atomic arrangement about $C\alpha$ and $C\beta$.

The properties of the $E_2C$ transition state determined by this work were consistent for an $E_2C - E_2H$ spectrum of transition states suggested by Winstein and Parker. The results for $E_2C$ 'like' $\beta$-elimination reactions were as anticipated from the description of the $E_2C$ 'like' transition state initially proposed by Winstein and Parker.

Several systems were analysed to elucidate the various properties of the transition state. This was achieved by comparison of the behaviours of the $E_2C$ 'like' transition state, $S_N2$ transition state, solvolysis transition state and $E_2H$ transition state to parallel changes in $\alpha$ and $\beta$ substituents.

The rate constants and olefinic product distributions for dehydrobromination of 1-bromo-1-R propane promoted by $\text{NBu}_4\text{Br}$ in acetone was compared to the $S_N2$ substitutions of the same compounds with $\text{NBu}_4\text{Cl}$ in DMF, the solvolysis of the same materials in acetone-water solvent mixtures and the $E_2H$ dehydrobrominations promoted by $\text{KO-tBu}$ in $\text{t}$-butanol. Hammet $\rho - \sigma^+$ graphs were constructed for the $E_2C$ 'like', $S_N2$ and solvolysis reactions of the 1-bromo-1-R propanes. The $\rho$ values determined indicated the $E_2C$ 'like' transition state to have only slight, if any, positive charge at $C\alpha$. The Hammett $\rho - \sigma^+$ graph for the $S_N2$ transition state produced the normal U shape curve for $S_N2$ reactions at benzylic carbon atoms.

The same form of treatment was applied for $E_2C$ 'like', $S_N2$, $E_2H$ and solvolysis reactions of 2-bromo-1-R propanes. The Hammett $\rho - \sigma$ graphs for these reactions, together with an examination of the kinetic results, indicated that there was very little, if any, negative charge development at $C\beta$ in the $E_2C$ 'like' transition state.

Olefinic product distributions resulting from $E_2C$ reactions of several substrates were measured so as to show the extent of double bond development in the $E_2C$ 'like' transition. The trans:cis olefin ratios...
were used to show that there is considerable double bond development in the E₂C 'like' transition state by assuming that the transition state was olefin like if the olefinic product distributions resembled the equilibrium proportions. This assumption was shown to hold for simple alkyl substrates but deviations were found when unsaturated α or β substituents were bonded to C_α or C_β. On the basis of kinetic evidence, it is suggested that conjugation of p orbitals in the reaction centre of E₂C and SN₂ transition states with unsaturated α or β substituents does not occur.

An analysis of the leaving group tendencies in E₂C 'like' elimination reactions indicated a large degree of C_α-leaving group bond breaking in the E₂C 'like' transition state; which agrees with the findings of Bunnett and Cromwell. The existence of large London dispersion force attractions between vicinal polar substituents in cis and trans-1,2-disubstituted cyclohexanes was demonstrated and found to be of the order of 5-6 Kcals/mole for vicinal bromine groups.

A full description of the E₂C - E₂H spectrum of transition states proposed by Winstein and Parker is provided as well as the critical evidence leading to such a proposal. A resume is also given describing the predicted movement within the E₂C - E₂H spectrum for variations in base, leaving groups, α and β substituents and solvent.
INTRODUCTION

Into the garden I brought it to read
And under the arbute and lauristine
Read it, so help me grace in my need,
   From title-page to closing line.
Chapter on chapter did I count,
   As a curious traveller counts Stonehenge;
Added up the mortal amount;
   And then proceeded to my revenge

Sibrandus Schafnaburgensis

Robert Browning
Many carbon compounds undergo elimination reactions. An obvious statement which poses several questions. What are elimination reactions? How do they happen? Why do they exist? And when do they occur? The search for answers to these questions has extended through decades, but even now questions remain unanswered. The discussion of all these topics is of interest but the subject is too vast to be fully discussed within this text. If a chemist is so fortunate as to provide a solution to only part of one of the above topics, then surely he is a privileged scientist. Many chemists are responsible for development of an understanding of elimination reactions. Few are more revered than Hughes and Ingold. In more recent times Bunnett has made a substantial contribution. Their ideas were naturally challenged during this period. However, the basic foundation of a mechanistic approach to bimolecular \( \beta \) elimination reactions was laid down by Hughes and Ingold, and the construction continued by others.
Elimination reactions represent the majority of methods by which unsaturation is introduced into organic molecules. Due to the importance of olefinic carbon compounds, it is essential that organic chemists fully understand the mechanisms of the methods used to obtain alkenes. An excellent treatment of all methods of performing elimination reactions has been compiled and edited by Patai.

This thesis is limited to a discussion of bimolecular β-elimination reactions as carried out in homogeneous solvent-solute systems, as represented in eqn (1). If a synthetic organic chemist acquires a complete understanding of the mechanism of bimolecular β-elimination reactions, it will allow him to predict the olefinic products of an elimination reaction and also synthesise alkenes which are otherwise unobtainable.

\[ Y^- + H-CR_β-C_R-X \rightarrow Y-H + CR=CR + X^- \]

\[ \ldots \text{eqn. (1)} \]

The extensive studies of the mechanism of β elimination reactions first performed by Hughes and Ingold and later reviewed by Bunnett, Saunders and Banthorpe were very thorough and searching. Their conclusions best represented the known experimental data. Unfortunately, the experimental examinations were almost universally limited to elimination reactions promoted by strong hydrogen bases in alcoholic solvents, e.g. sodium ethoxide in ethanol (NaOEt/CH3CH2OH) and potassium t-butoxide in t-butanol (KO-t-Bu./t-BuOH).

These reviewers recognised a spectrum of transition states in which there were two main variable properties -

(1) Non synchronisation of bond breaking and bond forming,

(2) Variable double bond formation within the spectrum.
Excellent correlation between theory and results was obtained for the reactions of alkoxide bases in alcoholic solvents. There were inadequacies in the spectrum proposed and these were recognised and expounded by Winstein. Winstein was at first uncertain of the nature of the changes required. After further consideration Parker and Winstein suggested that a third dimension should be added to the spectrum. They suggested that for elimination reactions promoted by strong carbon nucleophiles which are weak hydrogen bases, varying degrees of interaction of the base with $C_\alpha$ should be incorporated in the spectrum of transition states.

Bunnett treated the earlier ideas of Winstein with scepticism. However, Bunnett highlighted the problem of a mechanistic approach to bimolecular elimination reactions when he considered changes in base strength and how they might affect movement through the spectrum. "No prediction is ventured, because of uncertainty as to what measure of base strength to heed and as to whether a stronger base would call for a transition state with increased or decreased C-H rupture".

Credit must be given to Bunnett for his criticism of theories proposed from ambiguous results, for he has certainly inspired other physical organic chemists to search for more conclusive evidence.

The purpose of this thesis is to attempt to describe the character of the $E_2C$ transition state and examine the proposal that there is interaction of the base (or nucleophile) with $C_\alpha$ in the transition state spectrum for $\beta$-elimination reactions. It is not intended to replace the spectrum described by Bunnett but to add a third dimension to the spectrum. No one experiment has elucidated this problem and it is only by a detailed analysis of current and previous results that the position may be clarified.

B Transition State Spectra for $\beta$-Elimination Reactions

(a) Elimination Reactions Promoted by Strong Hydrogen Bases:

The description of the spectrum of transition states recognised as applicable to elimination reactions promoted by strong hydrogen bases is well documented, e.g. alkoxides in alcohols.

This is represented in structures I, II and III which vary
mainly in non-synchronous bond breaking and bond forming.

The characteristics of each of these transition states are:

(1) The $\text{C}_a\text{-X}$ bond is well broken and far ahead of $\text{C}_\beta\text{-H}$ bond breaking. There is little $\text{B}\text{-H}$ bond formation, considerable negative charge on $\text{X}$ and $\text{B}$, considerable positive charge on $\text{C}_a$ and only slight double bond formation. This extreme structure closely resembles the transition state for the $\text{E}_1$ mechanism.$^4$

(II) All bonds are equally broken, or equally formed, with small negative charge at $\text{C}_\beta$ and small positive charge at $\text{C}_a$. Within this structure it was recognised$^4$ that there could be varying degrees of double bond formation.

(III) The $\text{C}_a\text{-X}$ bond is only slightly broken and far behind the $\text{C}_\beta\text{-H}$ bond breaking. There is almost complete $\text{B}\text{-H}$ bond formation, considerable negative charge at $\text{C}_\beta$ and little double bond formation.

(b) **Elimination Reactions promoted by weak H bases which are strong C nucleophiles.**

This class of reaction has been extensively studied by Winsstein and Parker$^9$-13, Kevill and Cromwell$^{15}$ and more recently by others$^{14,16}$. The remarkable facet of this collection of work is the disagreement between authors as to which transition state structure is utilised by these elimination reactions.
Figure 1. The Parker-Winstein spectrum of transition states for \(\beta\)-elimination reactions
Kevill and Cromwell prefer the earlier merged mechanism proposed by Winstein. This has been discarded by Winstein and Parker, who now prefer the spectrum of transition states I - V in figure 1 as representative of the spectrum utilised by β-elimination reactions.

For β-elimination reactions which Winstein and Parker would classify as E2C 'like' (IV) Bunnett and McLennan suggested that they utilise a paene-carbonium structure (I) which would fall within Bunnett's spectrum and not require Cα-Y interaction. More recently Bunnett has suggested a structure more like II which has a large degree of double bond character, which again does not require Cα-Y interaction.

The characteristics of the proposed transition states in figure 1 are -

I - III, essentially the same as described in Bunnett's spectrum and there is no interaction between Y and Cα.

V. There is a well developed double bond, well broken Cα-X and Cβ-H bonds and interaction between Cα and Y. Y and X carry considerable negative charge and H considerable positive charge. It is unreasonable to propose that there would not be at least an electrostatic interaction between Y and H, let alone some covalent bonding, since they both carry almost full charges.

IV can be termed as E2C'like' or E2H 'like', depending upon where, for a specific case, the transition state lies in the spectrum. Winstein and Parker believe, in general, that no β-elimination reactions lie at either the E2H or E2C extremes and IV, varying between II and V, best represents the known experimental data. It is only possible to suggest that one elimination reaction is more E2H'like' or more E2C 'like' than another elimination reaction.

It seems inevitable that the controversy over inclusion of Cα-Y interaction in the transition state spectrum will continue for some time. It seems undesirable to enter this controversy, but unfortunately it is not possible to study the mechanism of β-elimination reactions without forming an opinion either way. Consideration of all evidence available, most of which has not been published, suggests to me that
C_s - Y interaction does take place in $E_2$ transition state.

It must be emphasised, however, that this thesis was not designed to prove the existence of an $E_2 C'_\text{like} \transition$ state. The intention was to study the character of the transition state utilised, with respect to charge distribution, bond formation and bond breaking by comparison with transition states of known character. No comprehensive review of the data available has been published, therefore a summarised version of the case for inclusion of $C_s - Y$ interaction as part of the transition state spectrum will be presented.

(c) The Merged Mechanism

Results obtained by Winstein revealed inadequacies of the Bunnett $E_2$ spectrum of $E_2$ transition states to explain certain kinetic effects. It was found that bases which were weak H bases but strong C nucleophiles (e.g. $\text{Cl}^-$, $\text{Br}^-$, $\text{PhS}^-$) produced significant amounts of olefin (see eqn. (2)) more rapidly than stronger H bases (e.g. $\text{t}-\text{butoxide}$). Winstein considered it necessary to invoke $C_s - Y$ interaction in the transition state and the structure he proposed as an intermediate VI was considered the partition to $\text{SN}_2$ and $E_2 \transition$ products, thus the "merged mechanism".

\[
\text{RCH}_1 \text{CHR}_2 + \text{Y}^- \quad \rightarrow \quad \text{RCH} \quad \text{C} \quad \text{CHR} \quad \text{Y} \quad \text{H} \\
\text{merged intermediate} \\
\text{RCH} = \text{CHR} \\
\]


His initial proposals were supported by several workers\textsuperscript{15, 26}. VI can be likened to the SN\textsubscript{2} transition state where C\textsubscript{a} is Sp\textsuperscript{2} hybridised and Y and X are perpendicular to the plane of C\textsubscript{a}.

Winstein's\textsuperscript{7, 8} structure VI was applied to dehydrotosylation reactions (loss of p-toluene sulphonate acid from a carbon skeleton) of cis and trans-4-t-butyl cyclohexyl p-toluene sulphonate, promoted by halide ions in acetone and t-butanol.

Winstein and Parker\textsuperscript{11, 23} later rejected the "merged mechanism" after application of two test cases -
(a) the chloride ion promoted dehydrochlorination of erythro and threo-3-p-anisyl-2-butyl chloride in acetone in the presence of 2,6-lutidine,
(b) the chloride ion promoted dehydrochlorination of menthyl chloride and neomenthyl chloride in acetone in the presence of 2,6-lutidine.

The reasoning applied was that in reactions (a) and (b) above the intermediate (VI) should be symmetrical, i.e. the asymmetry of C\textsubscript{a} in the ground state should be destroyed. For each isomer in either (a) or (b) the intermediate should therefore be identical, i.e. each isomer should give the same olefinic product distributions. This criterion was not fulfilled as the product ratios were different. Therefore VI was rejected.

In fact the eliminations were found to be the most stereo-specific anti elimination reactions known. The merged mechanism has been further disproved by other steric and electronic evidence\textsuperscript{17, 20-22}. It is of academic interest to note that it satisfied all known experimental data at the time of proposal.

If the evidence is analysed with respect to the E\textsubscript{2}C - E\textsubscript{2}H spectrum no anomalies occur. There is still the same C\textsubscript{a} -base interaction and the conclusion that the transition states for anti \textsubscript{aa} and anti \textsubscript{ee} elimination are similar still holds.

Considering structures I, II and IV with regard to this conclusion, we find II and IV very like olefins in the transition state and, since the same olefin is produced from both anti \textsubscript{aa} and anti \textsubscript{ee}
elimination, then II and IV are in accordance with the above results.
Clearly I, which is like the carbonium ion produced from both the axial and equatorial isomers during solvolysis, is acceptable.

(C) Orientation and Stereochemistry in the Variable E₂ Spectrum of Transition States

There are three important aspects of this section -

1. Positional Orientation deals with the position of the double bond within an alkyl structure when two or more locations are available. This refers to the whole classical question of Hofmann vs. Saytzeff tendencies.

2. Geometrical Orientation deals with the stereochemistry of the product olefin, i.e. all factors affecting the cis:trans olefin ratios.

3. Stereochemistry of the β-elimination transition state. The relationship of the leaving group, and β proton to the plane of the developing double bond is the important criterion. They may depart from opposite sides (anti elimination) or from the same side (syn elimination).

(1) Hofmann-Saytzeff Tendencies

The determination of reasons why bases cause elimination into different carbon chains (as in eqn (2)), when one or more positions are available for double bond formation has been one of the most controversial problems of the early mechanistic approach to β elimination reactions. 

Hofmann-Saytzeff tendencies is a major section of the following discussions of the effects associated with the stereochemistry of the systems. At this time the previous work dealing with stereochemistry in and stereochemistry of adjacent systems will be summarized. 

Winston and Packer have shown that stereochemistry of the systems is important in understanding the stereochemistry of adjacent systems. At this time the previous work dealing with stereochemistry in and stereochemistry of adjacent systems will be summarized.
The Saytzeff olefin was initially recognised as the most substituted olefin, but is now generally accepted as the more stable olefin while the Hofmann therefore became the least substituted or least stable olefin.

This subject has been thoroughly reviewed and it seems apparent that there are three factors controlling positional orientation in $\beta$-elimination reactions:

(i) Electronic effects of substituents in the inductive sense.
(ii) Conjugative effects of substituents which refers to both conjugation of charge and conjugation of the developing double bond.
(iii) Steric effects associated with the changes in hybridisation can arise by relative steric stabilisation or destabilisation of the transition states for formation of Hofmann or Saytzeff olefins.

The major disagreement was the assignment of which effect was the dominating influence for formation of the Hofmann olefin. Brown advocated steric considerations while Hughes, Ingold and Banthorpe favoured polar and conjugative effects. Hughes, Ingold and Banthorpe maintained that steric effects only come into consideration when overly large substituents, nucleophiles and leaving groups are present. It seems evident that all factors must be taken into consideration as it is difficult to isolate a single factor.

However, it is not intended to discuss this controversy but only to show how a study of Hofmann-Saytzeff tendencies helped to elucidate the character of the $E_2C'\text{like}'$ transition state. The analysis of Hofmann-Saytzeff tendencies is a major section of this thesis. A full discussion of results and their implications will be produced in a later section. At this time the previous work relevant to this study will be summarised.

Winstein and Parker found that $E_2C'\text{like}'$ dehydrobrosylations of erythro and threo-3-$p$-anisyl-2-butyl $p$-bromobenzene sulphonate with chloride ion in acetone gave no detectable Hofmann olefin. They were able to deduce that the Saytzeff-Hofmann ratio was at least 1000:1. Also, the dehydro tosylation of neomethyl tosylate by chloride ion in acetone gave a Saytzeff:Hofmann ratio of 97:3 while with ethoxide ion
the Saytzeff:Hofmann ratio was 4:1. It should be noted that dehydro­
tosylation of menthyl tosylate by chloride ion in acetone produced only
the Hofmann olefin ($\Delta^2$-menthene). The Saytzeff olefin can only arise
by syn elimination or other pathways (solvolysis, dehydrochlorination of
the SN$_2$ product neomenthyl chloride).

This work illustrated that for E$_2$ 'like' eliminations there exists a marked preference for Saytzeff elimination products,
except when the required anti stereochemistry is unobtainable.

(2) Geometrical Orientation

Winstein and Parker$^{9-13}$ have previously suggested
that the E$_2$ 'like' transition state has a large degree of double bond
character. Bunnett$^{4,14a,54}$ and McLeman$^{16}$ originally disagreed with
this suggestion, but Bunnett$^{14b}$ has recently conceded that $\beta$-elimination
reactions promoted by weak H-bases do pass through a transition state
which contains a large degree of double bond character.

The doubt as to the amount of double bond developed
in the transition state was due to the fact that Winstein and Parker had
compiled evidence which inferred this to be the case but no research
had been implemented to directly show this assertion to be true.
Therefore part of this thesis has been an analysis of olefinic product
distributions carried out with the intention of elucidating this aspect.

For any elimination reaction the cis:trans olefinic
product ratio can vary between two extremes. The first extreme is
that expected for a transition state with a fully developed double bond.
This can be best represented by determination of the relative stabilitites
of the cis and trans olefins. This can be measured by equilibration of
the olefins concerned. Consideration of structures VII and VIII shows
that the substituents $R_1$ and $R_2$ can be eclipsed on the same side of
the double bond VII or lie on opposite sides VIII.

Clearly it is the result of the various possible interactions
of $R_1$ and $R_2$ which governs the relative stabilities of VII and VIII.
The second extreme is that expected for a transition state with no double bond development, i.e. like the starting reactants. The best representation of this form is the starting reactant $R_1\text{CH}_2\text{CHXR}_2$ which can produce both VII and VIII by elimination of HX.

IX and X are the Newman Projection Formulae of the reactant configurations which give rise to VII and VIII respectively. It is the relative free energies of IX and X which govern the \textit{cis:trans} olefin ratio for this extreme and it is the interactions of $R_1$, $R_2$ and X in IX and X which will determine their relative free energies.

Therefore a \textit{cis:trans} olefinic product ratio may vary from the result predicted for a transition state with a well developed double bond to that predicted for a transition state which is reactant-like. This whole treatment completely depends on the type and influence of the various interactions $R_1$ and $R_2$ can have on their surrounding environments both in the ground state and the transition state.
The description of these interactions is more appropriately described as Substituent Effects; but, since they affect the geometrical orientation of the transition state, they will be introduced here. Ingold\textsuperscript{3} has provided an excellent description at the level understood by most organic chemists, of the interactions within and between molecules and it is only intended to produce a short summary of the relevant sections.

There are three main interactions between non-reacting molecules:

(a) \textbf{Electrostatic Interactions} which refers to attractions and repulsions which arise from charge localised on a molecule whether it is a full charge (e.g. carboxylate groups) or a dipole (e.g. a carbon chlorine covalent bond) or a quadrupole (e.g. hydrogen molecule). The strength of the interactions varies greatly with forces between ions as the strongest and quadrupole-quadrupole forces the weakest.

(b) \textbf{London Dispersion Forces}. Ingold\textsuperscript{3} refers to these interactions as electrokinetic interactions as they arise by reason of the motion of electrons. They can best be described as the synchronised motion of electrons about a group of atoms within a molecule, i.e. fluctuating dipole induced dipoles. Thus there will always be attraction.

(c) \textbf{Exchange Interactions}. For two atoms which are short distances apart covalency formation may take place when the Pauli principle allows.

However, repulsions will be experienced at very small interatomic distances due to violation of the same principle. Generally, at very short distances these are a dominating force.

Ingold\textsuperscript{3} has shown that intramolecular forces exist and are derived basically from the same forces mentioned for intermolecular interactions. They can be shown to affect physical properties, free energy of reactants and products and activation energy of reactions.

These can be either direct interactions or transmitted interactions (refers to inductive and conjugative effects).
(3)  **Syn vs Anti Elimination of β-proton and Leaving Group**

It has long been recognised that syn elimination was generally less favourable than anti elimination. Exceptions were known, especially where a β-proton was strongly activated by acidifying substituents. This implies that in a paene carbanion type transition state syn elimination was not strictly disadvantageous.

Apparently anti elimination was more favourable, but the reasons were not clear. This was exemplified by Bunnett - "It is not well understood from theory why this geometry is so good."

Bunnett has suggested that the anti requirement could be due to either the electrons released from the Cβ-H bond to form the double bond; favouring entry into the Cα octet from the back side with respect to the leaving group, or due to eclipsing effects which destabilise the syn elimination transition state.

The E2C 'like' transition state IV provides an excellent reason for β-elimination reactions strongly favouring anti stereochemistry. The interaction of the base Y with the β-proton and Cα (as in the Walden Inversion) excludes the possibility of the β-proton departing from the same side of the plane of the double bond as the leaving group.

Therefore a criterion of IV is that E2C 'like' reactions show marked anti stereochemistry. Winstein and Parker have shown that this is the most stringent stereochemical requirement of E2C 'like' reactions. They studied this in several systems by comparing the rate constants for elimination, using weak H-bases.

The dehydrotosylation of neomenthyl tosylate by tetra n-butyl ammonium chloride in acetone to form Δ²-menthene (anti aa elimination) proceeds fourteen times faster than the dehydrotosylation of menthyl tosylate to form the same olefin under the same conditions (anti ee elimination). Formation of Δ³-menthene from neomenthyl tosylate by dehydrotosylation with chloride ion in acetone (anti aa elimination) proceeds at least 20,000 times faster than formation of Δ³-menthene from menthyl tosylate and chloride ion in acetone (syn ee elimination).
The anti:syn elimination ratio of greater than 20,000 is indeed a very marked preference.

Another isomer pair which confirms this result is cis, cis-2, 6-dimethyl-cis-4-t-butyl cyclohexyl tosylate and trans, trans-2, 6-dimethyl-trans-4-t-butyl cyclohexyl tosylate. Dehydrotosylation of the cis isomer by tetrabutyl ammonium chloride in acetone proceeds at least 20,000 times faster than dehydrotosylation of the trans isomer under the same conditions. In fact the trans isomer gives 100 ± 2% substitution and the cis isomer gives 100 ± 2% elimination. Therefore the value of 20,000 is a lower limit set by the limits of detection of the instruments used for analysis. This result shows that the free energy of the transition state for syn elimination is at least 6 Kcal/mole higher than the transition state for anti elimination.

It would be anticipated that syn elimination with chloride ion would only be found in a system in which elimination could not proceed through an \( E_2 \) "like" transition state except where strong acidification of the \( \beta \) proton compensated for the weak H basicity of chloride ion, i.e. the elimination utilises an \( E_2^H \) transition state.

There are other systems where anti elimination shows marked enhancement over syn elimination and systems such as the dehydrobrosylation reactions of trans-2-phenyl cyclopentyl p-bromo benzenesulphonate (brosylate) which gives anti:syn ratios from 0.08 to 110 depending on the base-solvent system.

In summary, reactions of strong H bases can be forced by substrate modifications to react via a syn elimination transition state, whereas the \( E_2 \) "like" reactions of weak H bases cannot pass through a syn elimination transition state.

D Factors which Affect and Determine the Nature of the Variable \( E_2 \) Transition State

(a) The effect of changing \( \alpha \) and \( \beta \) substituents

Bunnett has analysed and predicted the effect of \( \alpha \) and \( \beta \) substituents on the variable \( E_2 \) transition state as described by him for reactions of alkoxide type bases, i.e. \( E_2^H \) reactions. It is not intended
to repeat his description in detail but only to mention it for comparison with $E_2C$ reactions.

The study of electronic and steric effects of a substituents, especially, and $\beta$ substituents is a major part of this thesis. The results and analysis will be presented later in the discussion section.

Preliminary studies of $\beta$ substituent effects on $E_2C$ reactions have been reported\(^{12}\). They involved the effect of $\beta$-bromine, methyl and carboxymethyl relative to $\beta$ hydrogen. Parker, Cook and Ruane\(^{12}\) found several trends in their results. They studied the dehydrobromination reactions of the 2-bromo propyl compound $\text{XI (CH}_3\text{-CHBr-CHR}_1\text{R}_2\text{)}$ induced by chloride ion and acetate ion both in acetone as solvent. The rate of dehydrobromination by both chloride ion and acetate ion in acetone is greatly enhanced by substitution of two $\beta$ protons by either $\beta$ methyl, bromine or carboxymethyl. However, the rate of chloride ion promoted dehydrobromination is little affected by the nature of the $\beta$ substituent (whether methyl, bromine or carboxy). Any differences are small enough to be explained in terms of eclipsing effects. This shows that the chloride promoted dehydrobromination is insensitive to acidifying or conjugative effects of $\beta$ substituents. This would be expected if chloride ion utilised on $E_2C$ 'like' transition state.

The acetate ion promoted dehydrobromination is accelerated $\times 10^5$ by changing from two $\beta$ methyl substituents to a $\beta$ bromine plus a $\beta$ carboxymethyl. Therefore, the acetate ion elimination is strongly affected by the acidifying substituents. Clearly there must be some difference in the transition state utilised by chloride ion and acetate ion. Parker\(^{12,17}\) considers that the chloride ion eliminations utilise an $E_2C$ 'like' transition state, while acetate ion eliminations (acetate is a relatively strong H base in acetone\(^{17}\)) becomes more $E_2H$ 'like' and thus more sensitive to acidifying effects of $\beta$ substituents.

The rate difference between SN\(^2\) reactions of chloride ion and acetate ion is approximately one log unit\(^{12}\) and the rate difference for dehydrobromination of 2-bromo-3-methyl butane with chloride ion and acetate ion in acetone is of the same order of magnitude\(^{12}\). This
implies that the rate of reaction correlates with carbon nucleophilicities of the two bases and for this compound both acetate ion and chloride ion eliminations utilise $\text{E}_2\text{C 'like'}$ transition states.

The difference in pKa of the two acids HCl and HOAc in DMF is approximately 9 units. Therefore, if a strongly acidified compound was found in which both chloride ion and acetate ion utilised $\text{E}_2\text{H 'like'}$ transition states then a rate difference of $10^9$ would not be unexpected, i.e. the rates of reaction would correlate with the H basicity of the two bases.

The reactions of cyclohexyl compounds are also instructive. It was found that substitution of a $\beta$ proton by a $\beta$-methyl or phenyl greatly enhances the rate of $\text{E}_2\text{C 'like'}$ reactions but there is little difference in the rates of $\text{E}_2\text{C 'like'}$ eliminations from $\beta$ methyl and $\beta$ phenyl compounds. This earlier work indicated that there were significant differences between the substituent effects on $\text{E}_2\text{C 'like'}$ reactions and the substituent effects on alkoxide promoted $\beta$-eliminations as described by Bunnett.

A recent effort was made by Eck and Bunnett to test the idea of including C-a-base interaction in the spectrum of $\beta$-elimination transition states. They predicted that a neopentyl steric effect of bulky $\alpha$ substituents should slow $\text{E}_2\text{C 'like'}$ reactions as they do $\text{SN}_2$ reactions. Cook and Parker showed that their argument was somewhat distorted by three factors:

(a) It is hardly reasonable to compare two totally distinct transition states such as the $\text{SN}_2$ and $\text{E}_2\text{C 'like'}$ transition states. In the $\text{SN}_2$ reaction there is no well developed double bond, i.e. no $sp^2$ hybridisation at $C_\beta$ and no base-$\beta$ proton interaction in the transition state. This means that it is difficult to separate steric effects of $\beta$ substituents from consideration of electronic and conjugative effects of $\beta$ substituents in the $\text{E}_2\text{C 'like'}$ transition state.

(b) They also considered that steric deceleration by $\alpha$ substituents in an $\text{SN}_2$ reaction at primary carbon was representative of the steric situation of an $\text{E}_2\text{C 'like'}$ transition state for attack at tertiary carbon. Cook and Parker showed that the 'neopentyl' effect fell away drastically for $\text{SN}_2$ reactions on going from $1^\circ$ to $2^\circ$ to $3^\circ$, i.e. from 16,000 to
500 to 3. This fall off was due to changes in the character of the \( \text{SN}_2 \) transition state. The 'looseness' of the \( \text{SN}_2 \) transition state increases from \( 1^\circ \), to \( 2^\circ \), to \( 3^\circ \) and it is known that non-bonding interactions of the type which retard \( \text{SN}_2 \) reactions fall off strongly with distance \( 3^\circ, 30^\circ \).

(c) Closely related to part (b) is the third consideration which they ignored. Winstein and Parker \( 9-13, 17-22 \) have maintained that the \( \text{E}_2 \) 'like' transition state is very 'loose' (more so than the \( \text{SN}_2 \) transition state). Since it is only possible to study the 'neopentyl' effect at \( 2^\circ \) and \( 3^\circ \) carbon, the greatest effect expected would be 500 [from (b)] for \( \text{E}_2 \) reactions at \( 2^\circ \) carbon. However, the \( \text{E}_2 \) 'like' transition state at \( 2^\circ \) carbon needs only to be as loose as the \( \text{SN}_2 \) transition state at \( 3^\circ \) carbon and no 'neopentyl' effect will be observed. It is hardly unexpected, therefore, that Bunnett \( 14b \) observes no 'neopentyl' effect for \( \text{E}_2 \) 'like' reactions at \( 3^\circ \) carbon.

(b) The effect of changing Base or Nucleophile

The effect of changes from one strongly H basic alkoxide base to another strong H base is well understood from past \( 4-6 \) reviews.

The rapid rates of elimination reactions promoted by weak H bases, especially in dipolar-aprotic solvents (e.g. chloride ion and mercaptides in acetone) relative to strong H bases in protic solvents (e.g. \( t \)-butoxide in \( t \)-butanol) was the initial result which caused Winstein \( 7, 8 \) to doubt the adequacies of the spectrum of \( \text{E}_2 \) transition states described by Bunnett \( 4 \).

Winstein and Parker \( 20 \) actually found that dehydrotosylation reactions of variously substituted cyclohexyl \( p \)-toluene sulphonates was up to 40 times faster when promoted by chloride ion in \( t \)-butanol than when promoted by \( t \)-butoxide in \( t \)-butanol. It is hard to reconcile this fact in terms of Bunnett's \( 4 \) \( \text{E}_2 \) transition state spectrum. \( t \)-Butoxide is \( \approx 10^{15} \) times more H-basic than chloride ion, and a transition state with exclusive \( \beta \)-proton attack is hard put to explain this enormous factor.

There seems to be some consideration unaccounted for by Bunnett \( 4 \). Winstein and Parker maintain that this is interaction of the base with \( C_a \) in an \( \text{E}_2 \) 'like' transition state. Clearly structures I and
Il cannot provide an explanation for so large an enhancement of the rate of chloride ion promoted elimination.

This was not an isolated effect. Comparison of p-nitro thiophenoxide and p-nitro phenoxide show that in acetone p-nitro thiophenoxide is approximately $10^6$ times less basic than p-nitro phenoxide, but approximately 4 times more effective for reactions at a carbon centre, e.g. SN$_2$ reactions. In the dehydrotosylation of cis-2-methyl cyclohexyl p-toluene sulphonate, p-nitro thiophenoxide is 5 times more effective but in the dehydrobromination of cis-1,2-dibromo cyclohexane p-nitro thiophenoxide is 25 times less effective than p-nitro phenoxide.

A further example of this is found when acetate ion and chloride ion in acetone are compared. In pure C attack transition states the chloride and acetate have approximately the same rate. Since the chloride is $10^9$ less basic than acetate in acetone as solvent, it would be expected that the acetate:chloride rate ratio for elimination reactions should vary through a range of $10^9$.

For dehydrotosylation of cis-2-methyl cyclohexyl p-toluene sulphonate the acetate:chloride rate ratio is 0.5 while for dehydrobromination of erythro-methyl-2,3-dibromo butanoate the acetate:chloride rate ratio is $3 \times 10^6$.

Winstein and Parker considered this to be one of the most important criteria of C$_a$-base interaction in the E$_2$ transition state. They proposed not only to find qualitative trends but also to find quantitative correlations. If a model system were found where the number of variables was limited, as far as possible, to one (i.e. variation of the attacking base) and changes of base did not cause changes in the position along the E$_2$C - E$_2$H spectrum, then it would be predicted that the ratio of E$_2$C 'like' reactions would correlate directly with the carbon nucleophilicity of the attacking base. To test this hypothesis a Swain-Scott type of relationship was applied [eqn (3)].

$$\log k_y^E = \eta^S \log k_y^S + \text{Const}$$

where $k_y^S$ is the rate constant for SN$_2$ substitution by Y and $\eta^S$ is a correlation coefficient.
A further prediction is that a Bronsted correlation (correlation of rate of elimination with H basicity of the base - eqn (4)) should also be found in a model system for E, H 'like' reactions. It uses H-basicity as a model for H nucleophility.

$$\log k_e^y = \beta pK_a(HY) + \text{Const}$$  
.eqn (4)

The pKa of the acid HY should be determined in the solvent used for the elimination reactions.

Winston and Parker found Swain-Scott correlations for dehydrotosylations of cyclohexyl p-toluene sulphonate in acetone and dehydrobromination reactions of t-butyl bromide in acetone. However, no Swain-Scott relation was found for dehydrobrominations of cyclohexyl bromide in acetone, and dehydrobrominations of cis-1,2-dibromo cyclohexane in acetone.

Winston and Parker found Bronsted correlations for dehydrobrominations of cis-1,2-dibromo cyclohexane in acetone but no Bronsted correlation for dehydrobrominations of cyclohexyl bromide or t-butyl bromide in acetone and no correlation for dehydrotosylations of cyclohexyl p-toluene sulphonate in acetone.

Therefore the correlations that have been observed are:

(a) Correlation of elimination rate with C nucleophilicity but not with H nucleophilicity.
(b) No correlation of rate of elimination with either C or H nucleophilicities.
(c) Correlation of rate of elimination with H nucleophilicity and no correlation with C nucleophilicity.

Since all these results are obtained for reactions of the same group of bases with different substrates then surely this is clear evidence for the spectrum of transition states as proposed by Winston and Parker. It is hard to envisage variations of $10^6 - 10^{15}$ from predicted rate values (from H basicity considerations) and the quantitative correlations of rate of elimination with carbon nucleophilicity, ever being explained in terms of a transition state which does not include C-base
interaction\textsuperscript{4, 14, 16}. The least these results provide is clear evidence that the spectrum of transition states for bimolecular $\beta$ elimination proposed by Bunnett\textsuperscript{4} needs re-evaluation.

(c) **The effect of changing solvent**

As is found with all other effects previously described, the solvation of E\textsubscript{2}C 'like' transition states is very different from solvation of E\textsubscript{2}H 'like' transition states.

Parker\textsuperscript{13, 20, 33} has described the effects of solvation of anions, cations, dipolar molecules, and transition states, on the rates of several reactions. An analysis of the solvent activity coefficients (\gamma_+^{O-}) for the transition state anions of E\textsubscript{2}C 'like', E\textsubscript{2}H 'like' and SN\textsubscript{2} reactions enables determination of charge distribution in these three transition states. He has found that SN\textsubscript{2} transition states can be 'tight' or 'loose' but that the E\textsubscript{2}C 'like' transition state is very 'loose',\textsuperscript{13} and that the E\textsubscript{2}H 'like' transition state is 'tight'.\textsuperscript{33}

This indicates that for E\textsubscript{2}C 'like' transition states the nucleophile, leaving group and $\beta$ proton have well developed charges similar to the product conditions. However, in the E\textsubscript{2}H 'like' transition state the base and leaving group are very unlike free anions. This difference is indicative of the existence of a spectrum of transition state structure for $\beta$ elimination reactions.

Other features arise from Parker's treatments. The rate of E\textsubscript{2}C 'like' reactions are relatively independent of the solvent used, i.e. independent of ionising power or basicity of the solvent. In practice, ion pairing does lower the observed rate of elimination except where tetra-n-butyl ammonium salts are used. This property of tetra alkyl ammonium salts has also been discussed by Parker\textsuperscript{18}. The effect is derived from the relative interactions of the tetra-n-butyl ammonium salt with the ground state anion and the transition state anion. The tetra-n-butyl ammonium cation has only a general anion-cation interaction with both the ground state anion and transition state anion. The alkali metal cations (e.g. Li\textsuperscript{+}, Na\textsuperscript{+}, K\textsuperscript{+}) have both general and specific cation-anion interactions which can give rise to different stabilities of ground state and transition state ion pairs.
This observation has obvious synthetic implications. A bi-
molecular reaction between an anion and a neutral molecule is almost
as fast in benzene as in ethanol or DMF, whereas side reactions such
as solvolyses are significantly decelerated on changing to less polar
solvents.

(d) **The effect of changing leaving group**

After the initial success of Winstein and Parker\(^9,18,20\) in
obtaining quantitative correlations of elimination rates of \(E_2C\) 'like'
reactions with carbon nucleophilicity of the attacking base an attempt
was made to apply the same treatment to changes in leaving group\(^10,55\).
The same difficulty arose in choice of a model system, which can force
each separate compound to utilise the same transition state structure
(i.e. \(E_2C\) 'like' or \(E_2H\) 'like').

The reactions chosen for comparison were the \(SN_2\) and \(E_2C\) 'like'
reactions of mono-substituted cyclohexyl compounds with tetra ethyl
ammonium chloride in DMF. An excellent linear correlation was
obtained for a plot of \(\log k_2^E\) vs \(\log k_2^S\) for this reaction\(^10,55\).
Various other correlations were attempted to test the extent of this
type of application. Parker and Lloyd\(^10,55\) found that \(E_2H\) 'like' reactions
correlated with other \(E_2H\) 'like' reactions for changes in leaving group
(i.e. \(\log k_2^E\) vs \(\log k_2^E\)) for a large variety of leaving groups and alkyl
substrates. Also \(SN_2\) reactions correlated with other \(SN_2\) reactions
(i.e. \(\log k_2^S\) vs \(\log k_2^S\)).

As expected, \(SN_2\) transition states behave in a parallel fashion
for changes of leaving groups, independent of the nucleophile used and
\(E_2H\) 'like' transition states promoted by strong H-bases also parallel
each other for changes in leaving group. The anomaly occurs with \(\beta\)
elimination reactions promoted by \(E_2C\) bases. The behaviour of the
transition state for thio phenoxide and chloride promoted \(\beta\)-elimination
does not correlate with the behaviour of the transition state for \(\beta\)-
elimination promoted by strong H bases (e.g. ethoxide or \(\tau\)-butoxide).
Since the \(E_2C\) 'like' transition state closely parallels the \(SN_2\) transition
state for variations of leaving group, then this indicates that of the
influences the leaving group can exert, that which is apparent in the
SN$_2$ transition state is apparent in the E$_2$C 'like' transition state. It
was considered that this indicated C$_a$-base interaction in the transition
state.$^{10,55}$(e) \textbf{Primary Hydrogen Isotope Effects}

Bunnett has reviewed and analysed the effect of Primary
Hydrogen Isotope effects in E$_2$H 'like' reactions, assuming a linear
relationship of C$_\beta$-H-B. However, this did not include an assessment of
isotope effects expected for a non-linear arrangement of C$_\beta$-H-B.

More O'Ferrall$^{34}$ treated this aspect from a theoretical stand-
point and assessed values expected for various angles of the C$_\beta$-H-B
arrangement.

Parker and Weinstein$^{19}$ showed that the Hydrogen Isotope Effect
for E$_2$C 'like' reactions fell within the range predicted by More O'Ferrall
for a C$_\beta$-H-B angle of 90°. Although they acknowledged that this evidence
did not conclusively prove the transition state to be E$_2$C 'like', it was
considered that the Primary Hydrogen Isotope Effects were as predicted
for an E$_2$C 'like' transition state (IV). Also, the small Hydrogen
Isotope Effect for SN$_2$ reactions ($k_H : k_D = 1.0$) showed that the E$_2$C
'like' and SN$_2$ transition states are distinct and there is no merged
intermediate or transition state.

E SUMMARY of Introduction

Since a complete review of all work on E$_2$C 'like' reactions
has never been compiled, it was attempted in this introduction to
collect and correlate results determined prior to and concurrent with
this thesis. However, this was limited to work which was not directly
involved with this thesis. The literature relevant to this thesis is
presented in the discussion.

The Introduction has indicated several major features of
bimolecular $\beta$-elimination reactions -
(a) The necessity for a spectrum of variable $E_2$ transition states.
(b) The need for invoking base - $C_a$ interaction in the transition state.
(c) Only the products of anti elimination have been observed from $E_2C$ 'like' reagents. Where syn elimination products were observed, solvolysis or other mechanistic pathways were significant.
(d) The rate of $E_2C$ 'like' reactions is only weakly affected by acidifying $\beta$-substituents.
(e) The rate of $E_2C$ 'like' reactions is relatively unaffected by changes of solvent.

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A1. Kinetics - Mathematical background

(a) Dethyroamination of allyl bromides with tertiary amines

Eqn. 1

Dethyroamination would not take place if 2,6-toluidine were not present, because of rapid back addition of HBr. However, the toluene deactivates the bromide ion produced by forming tight ion pairs of toluenide anion - bromide. The toluene does not change the rate of reaction and therefore does not alter the free energy of the transition state of the reaction. The toluene allows the reaction to proceed by lowering the free energy of the products. For solvents which solvate the hydrogen bromide better than amines, e.g., DME, no toluene need be added to facilitate the reaction.

Since hydrogen bromide is a tight ion pair, the reaction of one mole of allyl bromide and one bromide ion in acetone to produce one mole of chloride does not alter the initial concentration of electrically active bromide ion, although the "isolated" concentration increases.
RESULTS

During the course of this thesis, rate constants were determined for various types of reactions. These included $E_2$ reactions, $E_2^2$ reactions, $SN_2$ reactions, solvolysis reactions, and $E_2$ reactions.

Each type of reaction was analysed by different methods, both mathematically and chemically. The description of the experimental techniques falls within the scope of the experimental section while the results will be described in this section.

(A) Kinetics - Mathematical background

(a) Dehydrobromination of alkyl bromides with tetra-$n$-butyl ammonium bromide in the presence of 2,6-lutidine in acetone solution ($E_2C$ Reaction).

\[ RBr + Br^- \rightarrow R\text{olef.} + \text{Lut}^+\cdot\text{Br}^- + \text{Br}^- \quad \text{Eqn 5} \]

Dehydrobromination would not take place if 2,6-lutidine were not present, because of rapid back addition of HBr. However, the lutidine deactivates the bromide ion produced by forming tight ion pairs of lutidinium bromide. The lutidine does not change the rate of reaction and therefore does not alter the free energy of the transition state or reactants. The lutidine allows the reaction to proceed by lowering the free energy of the products. For solvents which solvate the hydrogen bromide better than acetone, e.g. DMF, no lutidine need be added to facilitate the reaction.

Since lutidinium bromide is a tight ion pair, the reaction of one mole of alkyl bromide and one bromide ion in acetone to produce one mole of olefin does not alter the initial concentration of kinetically active bromide ion, although the "titrated" concentration increases.
Rate = \( k_E \ \text{alkyl bromide} \ [\text{active bromide ion}] \)

\( a = \) Initial RBr \( x = \) RBr lost.

\( b = \) Initial active bromide ion.

\( k_E^2 \) is the second order rate constant for dehydrobromination of the alkyl bromide in units of litre/mole/sec.

Rate = \( \frac{dx}{dt} = k_E^2 b (a - x) \) Eqn 6

Rearrangement gives

\( \frac{1}{b} \cdot \frac{dx}{a - x} = k \cdot dt. \)

Integration gives

\[ k_E^2 \cdot t = \frac{1}{b} \cdot \ln \frac{1}{a - x} \]
\[ = \frac{2.203}{b} \cdot \log \frac{1}{a - x} \]

\[ \therefore k_E^2 \cdot \frac{b}{2.303} = \log \frac{1}{a - x} / t. \]

For a plot of \( \log \frac{1}{a - x} \) vs time the slope = \( k_E^2 \cdot \frac{b}{2.303} \)

i.e. \( k_E^2 = \frac{2.303}{b} \cdot \text{slope}. \) volume of sample

\( \frac{\text{concentration of titrant}}{\text{Eqn 7}} \)

(b) General bimolecular reaction with competing substitution, and elimination.

These reactions fall in the class where the \( \beta \)-elimination reaction deactivates one or zero molecules of nucleophile (\( \text{SN}_2 + \text{E}_2 \) reactions).

The general form is -

\[ \text{RX} + Y^- \rightarrow \text{R olefin} + \text{RY} + H^+ \cdot Y^- + X^- \]

\( a = \) Initial concentration of RX

\( x = \) Loss of RX

\( b = \) Initial concentration of \( Y^- \)
\[ Fs = \text{Fraction of substitution (SN}_2) \]
\[ Fe = \text{Fraction of elimination} \]
\[ k_{E+S} = \text{Sum of the second order rate constants for } SN_2 \text{ and } E_2 \text{ reactions.} \]
\[ Fs + Fe = 1. \]
\[ \text{Rate} = k_{E+S} [RX][Y^-] \]
\[ = \frac{dx}{dt} = k_{E+S} \left( \frac{a - x}{2} \right) \left( b - Fsx \right) \]

Integration and rearrangement gives
\[ k_{E+S} \cdot t = \frac{1}{b - aFs} \cdot \ln \frac{b - Fsx}{a - x} \]
\[ = \frac{2.303}{b - aFs} \cdot \log \frac{b - Fsx}{a - x} \]
After plotting \( \frac{b - Fsx}{a - x} \) vs. \( t \) a straight line results with
\[ \text{slope} = k_{E+S} \frac{b - aFs}{2.303} \]
i.e.
\[ k_{E+S} = \frac{2.303}{b-aFs} \cdot \text{slope} \]

which corrects to
\[ k_{E+S} = \frac{2.303}{b-aFs} \cdot \text{slope} \cdot \text{volume of sample} \text{ concentration of titrant} \]

Eqn 9

This form of kinetic equation is applied for \( SN_2 \) and \( E_2 \) reactions of \( NBu_4Cl \) and \( NBu_4OAc \) in DMF, \( SN_2 \) and \( E_2 \) reactions of \( NBu_4CN \) (see also part (d) following) and \( NBu_4Cl \) (in the presence of 2,6-lutidine) in acetone, \( SN_2 \) and \( E_2 \) reactions of KOt-Bu in t-BuOH and NaOEt in EtOH. However, for reactions of NaOEt and KOt-Bu the kinetics hold only if \( Fs \) is artificially assigned as 1.00. This is necessary because one mole of base is lost by substitution and elimination.

(c) Bimolecular substitution and \( \beta \)-elimination reactions of \( NBu_4OAc \) in acetone. This system is different from the previous [(b)] in that for each mole of acid produced two moles of "active" acetate ion are removed due to formation of biacetate ion \( (H(OAc)^-) \).
The general form is

\[ RX + OAc^- \xrightarrow{\text{E+S}} \text{R olefin} + R OAc + H, (OAc)^-_2 + X^- \]

\[ a, x, b, \text{Fe} \text{ and } k^E+S \text{ are as defined in part (b)} \]

\[ \text{Rate} = k^E+S [RX] [OAc^-] \]

\[ = \frac{dx}{dt} = k^E+S (a - x)(b - (1 + \text{Fe})x) \]  

Eqn 10

Integration and rearrangement gives

\[ k^E+S \cdot t = \frac{1}{b-(1+\text{Fe})a} \ln \frac{b-(1+\text{Fe})x}{a - x} \]

\[ = \frac{2.303}{b-(1+\text{Fe})a} \log \frac{b-(1+\text{Fe})x}{a - x} \]

\[ \text{i.e. When plotting } \log \frac{b-(1+\text{Fe})x}{a - x} \text{ vs. } t \text{ a straight line results with} \]

\[ \text{slope} = k^E+S \frac{b-(1+\text{Fe})a}{2.303} \]

\[ \text{i.e. } \frac{k^E+S}{2} = \frac{2.303}{b-(1+\text{Fe})a} \cdot \text{slope} \cdot \frac{\text{volume of sample}}{\text{concentration of titrant}} \]  

Eqn 11

(d) Bimolecular, debromination reactions, in competition with dehydrobromination and substitution, remove two moles of nucleophile for debromination of each mole of alkyl substrate. This class of reaction is represented in this work by the reactions of \( \text{NBu}_4 \text{ArS} \) and \( \text{NBu}_4 \text{CN} \) in acetone as solvent.

In the general form there are three competing bimolecular reactions.

\[ \text{R Br}_2 + Y^- \]

Substitution

Dehydrobromination

Debromination

\[ \text{R Br}_2 Y + \text{Br}^- \]

\[ \text{R Br olefin} + \text{Br}^- + \text{HY} \]

\[ \text{R olefin} + 2\text{Br}^- + \text{Y}^- \]
\[ a = \text{Initial RBr}_2 \text{ concentration} \]
\[ b = \text{Initial } Y^- \text{ concentration} \]
\[ x = \text{Loss of RBr}_2 \]
\[ F_d = \text{Fraction of debromination and } F_s \text{ and } F_e \text{ are as in part (b)} \]

\[ \text{i.e. } F_s + F_e + F_d = 1 \]
\[ \text{. . . Rate } = k_2^{E+S+D} [\text{RBr}_2] [Y^-] \]
\[ \frac{dx}{dt} = k_2^{E+S+D} (a - x)(b - (1 + F_d)x) \]
\[ \text{Eqn 12} \]

This is essentially the same eqn as in (c) and reduces to the same final form except F_d replaces F_e.

\[ \text{i.e. For a plot of log } \frac{b - (1 + F_d)x}{a - x} \text{ vs. } t, \]
\[ k_2^{E+S+D} = \frac{2.303}{b - (1 + F_d)a} \cdot \text{slope} \cdot \frac{\text{volume of sample}}{\text{concentration of titrant}} \]
\[ \text{Eqn 13} \]

(e) Solvolysis reactions of alkyl halides.

The kinetic equation for this class of reaction is clearly independent of salt or base in the media so that the same form holds for all solvolysis conditions.

The general form is

\[ \text{Rate } = k_1 [RX] \]

\[ a \text{ and } x \text{ are as defined in part (b)} \]

\[ k_1 \text{ is the first order rate constant for solvolysis of the alkyl substrate} \]

\[ \text{. . . Rate } = \frac{dx}{dt} = k_1 (a - x) \]

\[ \text{Eqn 14} \]

Integration and rearrangement gives

\[ k_1 t = \ln \frac{1}{a - x} \]
\[ = 2.303 \log \frac{1}{a - x} \]

Plotting \( \frac{1}{a - x} \) versus time a straight line results with

\[ \text{slope } = \frac{k_1}{2.303} \]

\[ \text{. . . } k_1 = 2.303 \times \text{slope} \]

\[ \text{Eqn 15} \]
Kinetics of pseudo 1st order reactions studied with U. V. spectroscopy (E, H).

The general form is as for 2nd order reactions

\[ RX + Y^- \rightarrow \text{olefin} + \text{RY} + \text{H}_2 \text{Y} + X^- \]

\[ \text{Rate} = k_2 [RX] [Y^-] \]

for \([Y^-] \gg [RX]\)

Then \( k_2 [Y^-] = k_1 \)

If \( x \) = RX present at time \( t \).

\[ k_2 = \text{overall 2nd order rate constant} \]

\[ k_1 = \text{pseudo 1st order rate constant} \]

\[ \text{OD} = \text{E} \text{l} \text{c} \text{w} \text{h} \text{e}r \text{e} \text{E} = \text{extinction coefficient} \]

\[ c = \text{concentration} \]

\[ \text{OD} = \text{optical density} \]

\[ l = \text{cell length} = 1.00 \text{ cms} \]

\[ c = \frac{\text{OD}}{E} \]

\[ \text{Rate} = - \frac{dx}{dt} = k_1 x \]

Integration and rearrangement gives

\[ - \ln x = k_1 t \]

\[ -k_1 = \frac{\ln x}{t} \]

i.e.

\[ = \frac{\ln x_1 - \ln x_0}{t_1 - t_0} \]

\[ = \frac{\ln \frac{\text{OD}}{0} - \ln \frac{\text{OD}}{0}}{t - t_0} \]

for \( \text{OD}_0 = 0 \)

\[ -k_1 = \frac{\ln \text{OD}}{t} \]

\[ \therefore -k_1 = 2.303 \frac{\log \text{OD}}{t} \]

Eqn 16
A plot of log OD versus t gives

\[ \text{a slope} = \frac{-k_1}{2.303} \]

\[ k_1 = -2.303 \times \text{slope.} \]

It should be realised that the kinetic equations in parts (a), (b), (c) and (d) are all different forms of the same equation which can be written as follows -

\[ \text{Rate} = \frac{dx}{dt} = k_2 (a - x) (b - mx) \quad \text{Eqn 17} \]

where \( m = 0, F_s, 1, 1+F_e \) or \( 1+F_d \).

Examples of typical runs and other associated experimental detail are described in the experimental section.

(B) Kinetic results

(a) Dehydrobromination reactions of alkyl bromides promoted by \( \text{NBu}_4 \text{Br} \) in Acetone.

The general form of the reaction studied is in Eqn 18.

\[ R_-\text{C}H_2\text{Br}-\text{CH}-R_\beta + Br^-/\text{Lut} \rightarrow R_a-\text{C}H=\text{CH}-R_\beta + Br^- + \text{Lut.H}^+\text{Br}^- \]

(\text{XI})

(i) Rate constants were determined for dehydrobromination of several compounds. The results which were determined are presented in Table I. The accuracy of the method of determination was \( \pm 5\% \) of the value quoted. This error does not affect the theoretical consideration of the results.
TABLE I

Rate constants for dehydrobromination of substituted bromo ethanes (XI) by NBu₄Br in acetone in the presence of 2, 6-lutidine at 75°Cᵃ,ᵇ,c

<table>
<thead>
<tr>
<th>No.</th>
<th>Rα</th>
<th>Rβ</th>
<th>( \log k_2 ) (^{d,e,})</th>
<th>[trans]</th>
<th>( \log k_2 ) (^{(t)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H</td>
<td>CH₃</td>
<td>-5.94</td>
<td>-</td>
<td>-6.24</td>
</tr>
<tr>
<td>2</td>
<td>CH₃</td>
<td>CH₃</td>
<td>-4.68</td>
<td>-4.69</td>
<td>82</td>
</tr>
<tr>
<td>3</td>
<td>C₆H₅</td>
<td>CH₃</td>
<td>-3.36</td>
<td>-3.36</td>
<td>99</td>
</tr>
<tr>
<td>4</td>
<td>4-NO₂-C₆H₄</td>
<td>CH₃</td>
<td>-3.58</td>
<td>-3.59</td>
<td>99</td>
</tr>
<tr>
<td>5</td>
<td>4-CH₃-C₆H₄</td>
<td>CH₃</td>
<td>-2.83</td>
<td>-2.83</td>
<td>-i</td>
</tr>
<tr>
<td>6</td>
<td>C₆H₅</td>
<td>C₆H₅</td>
<td>-3.14</td>
<td>-3.17</td>
<td>98</td>
</tr>
<tr>
<td>7</td>
<td>CH₃</td>
<td>C₆H₅</td>
<td>-4.39</td>
<td>-4.39</td>
<td>93</td>
</tr>
<tr>
<td>8</td>
<td>CH₃</td>
<td>4-NO₂-C₆H₄</td>
<td>-3.77</td>
<td>-3.77</td>
<td>-i</td>
</tr>
<tr>
<td>9</td>
<td>CH₃</td>
<td>4-CH₃OC₆H₄</td>
<td>-4.43</td>
<td>-</td>
<td>-i</td>
</tr>
</tbody>
</table>

(ii) Footnotes TABLE I

a The concentration of reactants except where otherwise stated were NBU₄Br = 0.1 M; alkyl bromide = 0.02 M; 2, 6-lutidine = 0.05 M.

b The rate constants quoted are for formation of trans olefin. V.P.C. analysis verified the identity of the olefin (see TABLE XXXV for exact details).

c The rate constants were determined using Eqn 7 and are expressed as logarithms of the 2nd order rate constant which are in units of litres/mole/sec.

d All rate constants in TABLE I were determined by analysis for the bromide ion produced. Nos. 2, 3, 4, 6 and 7 were also determined by analysing for the acid produced and the result agreed with the bromide ion analysis. When two results are quoted this represents duplicate runs with freshly prepared solutions.
The concentration of NBu$_4$Br = 0.1 M; n-propyl bromide = 1.0 M; 2,6-lutidine = 0.25 M.

The value quoted is the log $k_E^E$ after correction for the salt assisted solvolysis of the alkyl bromide in the presence of NBu$_4$ClO$_4$ and 2,6-lutidine (see Controls following).

Corrected for two equivalent hydrogens.

The trans olefin was verified to be the major product by V.P.C. and shown to be >95% of the total products. Any small corrections to the final rate constant would not in any way affect the theoretical analysis of the results.

(iii) Controls

(a) Materials used. 1-Bromo propane; 2-bromo butane; 1-bromo-1-phenyl propane; 1-bromo-1-(4-nitrophenyl) propane; 1-bromo-1,2-diphenyl ethane; 2-bromo-1-(4-nitrophenyl) propane were all prepared as described in the experimental section and were verified to be >99% pure by N.M.R. analysis, bromide analysis and the reaction infinities.

The two following compounds were prepared but, unfortunately, efforts to remove the trans olefin by any purification method were thwarted by dehydrobromination of the alkyl bromide during all attempted purification procedures.

2-Bromo-1-phenyl propane was used 92% pure.

1-Bromo-1-(4-methylphenyl) propane was used 93% pure.

By analogy of the N.M.R. of the alkyl bromide with the other similar alkyl bromides the ratio of alkyl bromide to trans olefin was established. This compared exactly with the value determined by bromide analysis and reaction infinities. The procedure was tested with artificial mixtures of trans-1-phenyl propene and 1-bromo-1-phenyl propane and proved to be valid.

All other materials (NBu$_4$Br, 2,6-lutidine and acetone solvent) were purified by standard procedures described in the Experimental section.
(b) Analytical Methods

It was demonstrated that the analytical procedures used accurately determined the concentration of the bromide ion and acid produced. The acid was titrated by quenching the sample into acetone and titrating with NaOMe in MeOH under a N₂ atmosphere, using thymol blue as an indicator. The bromide ion was determined in 1, 2 and 4 (TABLE I) by quenching the sample into 50% acetone/water and titrating the bromide ion potentiometrically with aqueous AgNO₃ solution. In 3, 5, 6, 7, 8 and 9 the sample was quenched into toluene, extracted into water and the water extract titrated potentiometrically with aqueous silver nitrate solution. The exact details are in the experimental section.

It was verified by experiment that none of the alkyl bromides in TABLE I decomposed during the analyses.

(c) Solvolysis reactions

All the alkyl bromides were tested to determine whether there was any significant competition of solvolysis with the bimolecular dehydrobromination. Where there was significant solvolytic reaction the rate constant for solvolysis was determined and the observed second order rate constant corrected to allow for this (TABLE I, footnote i). In TABLE II are the results of each test of the solvolysis rates.

TABLE II

Solvolysis tests on the reaction systems in TABLE I

<table>
<thead>
<tr>
<th>No.</th>
<th>Rₐ</th>
<th>Rₜ</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H</td>
<td>CH₃</td>
<td>log k₁ = -7.52, approx. 25% of total reaction</td>
</tr>
<tr>
<td>2</td>
<td>CH₃</td>
<td>CH₃</td>
<td>Undetected during one half life</td>
</tr>
<tr>
<td>3</td>
<td>C₆H₅</td>
<td>CH₃</td>
<td>1.6% solvolysis in one half life</td>
</tr>
<tr>
<td>4</td>
<td>4NO₂-C₆H₄</td>
<td>CH₃</td>
<td>&lt;1% solvolysis in two half lives</td>
</tr>
<tr>
<td>5</td>
<td>4CH₃-C₆H₄</td>
<td>CH₃</td>
<td>log k₁ = -4.55, approx. 10% of total reaction</td>
</tr>
<tr>
<td>6</td>
<td>C₆H₅</td>
<td>C₆H₅</td>
<td>6% solvolysis in one half life</td>
</tr>
<tr>
<td>7</td>
<td>CH₃</td>
<td>C₆H₅</td>
<td>Undetected during one half life</td>
</tr>
<tr>
<td>8</td>
<td>CH₃</td>
<td>4NO₂-C₆H₄</td>
<td>&quot; &quot; &quot; &quot; &quot; &quot;</td>
</tr>
<tr>
<td>9</td>
<td>CH₃</td>
<td>4CH₃-O-C₆H₄</td>
<td>&quot; &quot; &quot; &quot; &quot; &quot;</td>
</tr>
</tbody>
</table>
Footnotes  TABLE II

a  The concentration of reactants except where otherwise stated was alkyl bromide = 0.02 M, NBu$_4$ClO$_4$ = 0.1 M, and 2,6-lutidine = 0.05 M. The NBu$_4$ClO$_4$ was present so as to approximately allow for the salt effect of NBu$_4$Br on the reaction.

b  The first order rate constant (in sec$^{-1}$) was determined using Eqn 14 when the solvolysis represented a significant part of the total reaction. The observed second order rate constant was corrected for solvolysis using equation 19 -

$$k_{E}^{2} = k_{2}^{E\text{ obs}} - \frac{k_{1}}{[Br]}$$

Eqn 19

$E_{2}^{k}$ = derived second order rate constant

$E_{2}^{k\text{ obs}}$ = observed second order rate constant

$k_{1}$ = measured solvolysis rate constant

$[Br^{-}]$ = concentration of Br$^{-}$ in second order dehydrobromination

c  The concentration of reactants was NBu$_4$ClO$_4$ = 0.1 M, n-propylbromide = 1.0 M, and 2,6-lutidine = 0.25 M.

d  The amount of solvolysis was determined by analysis of the bromide ion produced using the same analytical procedures as for the second order dehydrobromination reactions.

It was also verified that the NBu$_4$Br did not decompose under the conditions of the reaction. That is, a solution of 0.1 M NBu$_4$Br in the presence of 2,6-lutidine, warmed for one half life at 75°C did not produce any acid or lose any bromide ion.

(d) Infinities

Reaction infinities were determined for all the reactions in TABLE I and the results are presented in TABLE III.


### TABLE III

Infinity titrations determined for Reactions in TABLE I

<table>
<thead>
<tr>
<th>No.</th>
<th>$R_a$</th>
<th>$R_b$</th>
<th>Calc. Inf. (^b)</th>
<th>Titrated Inf.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H</td>
<td>CH(_3)</td>
<td>420.48(^c)</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>CH(_3)</td>
<td>CH(_3)</td>
<td>11.15</td>
<td>11.12</td>
</tr>
<tr>
<td>3</td>
<td>C(_6)H(_5)</td>
<td>CH(_3)</td>
<td>11.85</td>
<td>11.85</td>
</tr>
<tr>
<td>4</td>
<td>4NO(_2)·C(_6)H(_4)</td>
<td>CH(_3)</td>
<td>8.30</td>
<td>8.30</td>
</tr>
<tr>
<td>5</td>
<td>4CH(_3)·C(_6)H(_4)</td>
<td>CH(_3)</td>
<td>7.63</td>
<td>7.52</td>
</tr>
<tr>
<td>6</td>
<td>C(_6)H(_5)</td>
<td>C(_6)H(_5)</td>
<td>9.42</td>
<td>9.25</td>
</tr>
<tr>
<td>7</td>
<td>CH(_3)</td>
<td>C(_6)H(_5)</td>
<td>7.77</td>
<td>7.75</td>
</tr>
<tr>
<td>8</td>
<td>CH(_3)</td>
<td>4NO(_2)·C(_6)H(_4)</td>
<td>7.59</td>
<td>7.60</td>
</tr>
<tr>
<td>9</td>
<td>CH(_3)</td>
<td>4CH(_3)·O·C(_6)H(_4)</td>
<td>8.25</td>
<td>8.17</td>
</tr>
</tbody>
</table>

**Footnotes TABLE III**

\(^a\) The accuracy of the determination is ± 0.10. The figure quoted is the number of mls of standard AgNO\(_3\) solution required to titrate the bromide ion produced.

\(^b\) The calculated infinity is the value calculated from determination of the purity of the starting alkyl bromide.

\(^c\) Due to the slow reaction rate the titrated infinity was not determined. The time required to react a sample to infinity would have been 560 days. However, the n-propyl bromide was analysed for bromine content and this, together with the single peak V.P.C. trace of the n-propyl bromide, verified the compound as greater than 99.7% purity. Therefore the calculated infinity derived from this figure was used in the kinetic equation.

(b) **Solvolysis Reactions of alkyl halides in acetone-water mixtures**

The general form of the reactions studied in this class is presented in eqn 20 and the kinetics used are in eqn 14.

$$R_aCHXCH_2R_b \rightarrow R_aCH^+CH_2R_b \rightarrow \text{Products} \quad \text{Eqn 20}$$

XII
Rate constants were determined for solvolysis reactions of several alkyl halides by determination of the rate of halide ion production \( \frac{d[Br^-]}{dt} \). The results are presented in TABLE IV and the estimated error in the values quoted is \( \pm 5\% \). The results are expressed as logarithms of the first order rate constant which is in units of sec\(^{-1}\).

### TABLE IV

First order rate constants for solvolysis of substituted halo ethanes (XII) in acetone-water mixtures\(^a, c\)

\[
R_a CHX CH_2 R_b
\]

<table>
<thead>
<tr>
<th>No.</th>
<th>(R_a)</th>
<th>(R_b)</th>
<th>X</th>
<th>% Acetone</th>
<th>Temp. (^\circ)C</th>
<th>(\log k_1)</th>
<th>(\log k_1)</th>
<th>(\log k_1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H</td>
<td>CH(_3)</td>
<td>Br</td>
<td>50</td>
<td>100</td>
<td>-4.25</td>
<td>-4.25</td>
<td>-4.25</td>
</tr>
<tr>
<td>2</td>
<td>CH(_3)</td>
<td>&quot;</td>
<td>&quot;</td>
<td>75</td>
<td>75</td>
<td>-4.27</td>
<td>-4.25</td>
<td>-4.26</td>
</tr>
<tr>
<td>3</td>
<td>C(_6)H(_5)</td>
<td>&quot;</td>
<td>&quot;</td>
<td>0</td>
<td>-4.62</td>
<td>-4.62</td>
<td>-4.62(^d)</td>
<td>-4.62(^d)</td>
</tr>
<tr>
<td>4</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>25</td>
<td>-3.29</td>
<td>-3.29</td>
<td>-3.29</td>
<td>-3.29</td>
</tr>
<tr>
<td>5</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>75</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-1.16(^b)</td>
</tr>
<tr>
<td>6</td>
<td>4NO(_2)-C(_6)H(_4)</td>
<td>&quot;</td>
<td>&quot;</td>
<td>75</td>
<td>-4.39</td>
<td>-4.37</td>
<td>-4.38</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>CH(_3)</td>
<td>C(_6)H(_5)</td>
<td>&quot;</td>
<td>75</td>
<td>-5.15</td>
<td>-5.15</td>
<td>-5.15</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>&quot;</td>
<td>4NO(_2)-C(_6)H(_4)</td>
<td>&quot;</td>
<td>75</td>
<td>-5.25</td>
<td>-5.25</td>
<td>-5.25</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>C(_6)H(_5)</td>
<td>CH(_3)</td>
<td>90</td>
<td>75</td>
<td>-4.04</td>
<td>-4.04</td>
<td>-4.04</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>&quot;</td>
<td>C(_6)H(_5)</td>
<td>&quot;</td>
<td>75</td>
<td>-4.41</td>
<td>-4.41</td>
<td>-4.41</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>4CH(_3)-C(_6)H(_4)</td>
<td>CH(_3)</td>
<td>&quot;</td>
<td>25</td>
<td>-4.65</td>
<td>-4.65</td>
<td>-4.65</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>50</td>
<td>-3.48</td>
<td>-3.48</td>
<td>-3.48</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>75</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-2.47(^b)</td>
</tr>
<tr>
<td>14</td>
<td>C(_6)H(_5)</td>
<td>&quot;</td>
<td>Cl</td>
<td>100</td>
<td>-4.59</td>
<td>-4.59</td>
<td>-4.59</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>4CH(_3)O-C(_6)H(_4)</td>
<td>&quot;</td>
<td>&quot;</td>
<td>0</td>
<td>-4.22</td>
<td>-4.22</td>
<td>-4.22</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>25</td>
<td>-3.05</td>
<td>-3.05</td>
<td>-3.05</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-0.49(^b)</td>
</tr>
</tbody>
</table>

\(\text{(II) Footnotes \quad \text{TABLE IV}}\)

\(^a\) Except where stated the concentration of alkyl halide was 0.02 M.

The solvent mixtures are expressed as % volume-volume.
Extrapolated via an Arrhenius plot of $\log k_1$ vs. $\frac{1000}{T}$ from results at other temperatures.

All rate constants in TABLE IV were determined by analysis of the halide ion produced using potentiometric AgNO$_3$ titrations. All determinations were carried out in duplicate with freshly prepared solutions.

The concentration of 1-bromo-1-phenyl propane was 0.01 M.

(III) Controls
(a) Materials used

All compounds described under the corresponding sections succeeding TABLE I were all used as previously described.

The two new compounds in TABLE IV are 1-chloro-1-phenyl propane, which was used > 99% pure (NMR, chloride analysis and infinities as previously described) and 1-chloro-1-(4-methoxyphenyl) propane, which, similar to 2-bromo-1-phenyl propane and 1-bromo-1-(4-methylphenyl) propane could not be purified by any technique available due to dehydrochlorination to the trans olefin which is the initial contaminant. The material used was verified to be 88% pure alkyl chloride by the same agreement of NMR analysis, chloride analysis and reaction infinities.

(b) Analytical methods

It was demonstrated that the analytical procedures used accurately determined the concentration of halide ion. The bromide ion in 1 and 2 (TABLE IV) was determined by quenching the reaction sample in water and titrating potentiometrically with AgNO$_3$, while in 6, 7, 8 and 14 the sample was quenched in 50% acetone-water and titrated with the AgNO$_3$ solution. In 3, 4, 9, 10, 11, 12, 15 and 16 the sample was quenched into toluene, extracted into water and titrated with the AgNO$_3$ solution. It was also verified by experiment that none of the alkyl halides in TABLE IV decomposed during the analyses.

In this section the important information was the rate constant for formation of a carbonium ion ($\log k_1$ in TABLE IV). Therefore no
quantitative product analyses were performed to determine the amount or nature of the olefinic products or similarly observe substitution products (alcohols of the same or rearranged structures of the parent alkyl bromide). However, qualitative tests on several solvolyses using V.P.C. showed the major product to be the trans conjugated olefin.

(c) Infinites

Titration infinites were determined for all the reactions in TABLE IV. All titration infinites correlated with the corresponding calculated infinity to within ± 3%, e.g. see the Infinites section following TABLE I.

(d) Extrapolations

Since the reactions reported in TABLE IV could not all be carried out on alkyl bromides in the same acetone-water mixture and at the same temperature, various extrapolations were necessary to obtain results which could be compared in a theoretical analysis.

(i) Temperature extrapolations. In TABLE IV, 5, 13 and 17 were determined by extrapolation of results at lower temperatures. This was carried out using the Arrhenius equation\(^9\) below (eqn 21)

\[
k = A e^{-\frac{E_a}{R T}}
\]

which reduces to

\[
\log k \frac{1}{T} = -\frac{E_a}{2.303R} + \text{Const.}
\]

i.e. a plot of \(\log k \text{ vs.} \frac{1}{T}\) should be a straight line of slope \(-\frac{E_a}{2.303R}\).

By a reading at any \(\frac{1}{T}\) value on the resulting graph the value of \(\log k\) was determined for the required temperature.

Following are the results for the extrapolation of the rate constants for solvolysis of 1-chloro-1-(4-methoxyphenyl) propane in 90% acetone-water at 0°C and 25°C to the rate constant at 100°C.

\[\text{(eqn 21)}\]
TABLE V

Arrhenius Results for solvolysis of 1-chloro-1-(4-methoxyphenyl) propane in 90% acetone-water

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Temp. °A</th>
<th>$\frac{1000}{T}$</th>
<th>$10^5k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>273</td>
<td>3.6630</td>
<td>6.02</td>
</tr>
<tr>
<td>25</td>
<td>298</td>
<td>3.3557</td>
<td>88.6</td>
</tr>
<tr>
<td>75</td>
<td>348</td>
<td>2.8736</td>
<td>6080</td>
</tr>
<tr>
<td>100</td>
<td>373</td>
<td>2.6810</td>
<td>32500</td>
</tr>
</tbody>
</table>

(ii) Changes in solvent mixture and leaving group

There was a great range in solvolysis rate constants in TABLE IV which depended on the structure of the compound. The range of results was large for comparison of p-substituted l-halo-l-phenyl propane derivatives where the p-nitro compound was approximately $10^3$ slower than the p-hydrogen compound which was approximately $10^4$ slower than the p-methoxy compound. This range of $10^7$ could not be accommodated by varying the temperature. Two other variations were possible and these were to change the solvent to a less solvolysing media (i.e. from 50% acetone-water to 90% acetone-water) or to change to a poorer leaving group (from bromide to chloride).

The effect of changing solvent was computed by determining the solvolysis rate of one reference compound in both solvent mixtures and comparing the rate of a second compound to it. The rate differences could then be calculated and the assumption is made that the rate difference in 90% acetone is approximately equal to the rate difference in 50% acetone. Theoretical justification for this assumption is found in the Winstein-Grunwald equation for solvolysis. The compounds are very similar, varying only in aromatic substituents. Therefore, changing the solvent mixture should not greatly distort the rate difference between two para substituted phenyl propane derivatives. The same rationalisation can be used for changes in leaving group. It should be emphasised that,
although this aspect has not been comprehensively investigated in this thesis, similar forms of extrapolations have been applied successfully elsewhere \(^9\)-\(^{13}, \(^{17}-\(^{20}, \(^{25}, \(^{33}\).

However, the magnitude of any possible error could not be anywhere as large as the rate differences of up to \(10^7\) observed for changes in para substituents in the 1-halo-1-phenyl propanes. A valid test of this approach is the linearity of the Hammett \(\rho - \sigma\) plot of the solvolysis results [figure (5)] and comparison of the \(\rho\) value determined to other \(\rho\) values for similar solvolyses reported by Leffler and Grunwald \(^{40}\) which demonstrate that any errors are insignificant.

\(c\) Bimolecular substitution and elimination reactions of alkyl bromides with \(\text{NBu}_4\text{Cl}\) in DMF

The general form of the reactions studied is in equation 22

\[
\begin{align*}
\text{R}_a\text{CHBrCH}_2\text{R}_b + \text{Cl}^- & \rightarrow \text{R}_a\text{CH} = \text{CHR}_b + \text{R}_a\text{CHCl-CH}_2\text{R}_b \\
& \quad + \text{Cl}^- + \text{Br}^- + \text{H}^+ \\
\text{Eqn 22}
\end{align*}
\]

The overall rate constant \(k_{E+S}^2\) was determined and split into components of dehydrobromination \((k_{E}^2\)) and substitution \((k_{S}^2\)). The results are presented in TABLE VI. They are expressed as logarithms of the rate constant \((\log k_{E+S}^2\text{ etc.})\) and the accuracy of determination is estimated at \(\pm 5\%\) of the value quoted. The rate constants were calculated using Eqn 8.
<table>
<thead>
<tr>
<th>No.</th>
<th>$R_a$</th>
<th>$R_b$</th>
<th>Temp $^\circ$C</th>
<th>$\log k$</th>
<th>$E+S$</th>
<th>$Fe$</th>
<th>$\log k$</th>
<th>$E+S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CH$_3$</td>
<td>CH$_3$</td>
<td>25</td>
<td>-3.44</td>
<td>d</td>
<td>0</td>
<td>-3.43</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>C$_6$H$_5$</td>
<td>CH$_3$</td>
<td>&quot;</td>
<td>-2.20</td>
<td></td>
<td>0.86c</td>
<td>-4.2</td>
<td>-2.17</td>
</tr>
<tr>
<td>3</td>
<td>4CH$_3$C$_2$H$_4$</td>
<td>CH$_3$</td>
<td>&quot;</td>
<td>-1.75</td>
<td></td>
<td>-1.76</td>
<td>0</td>
<td>-1.76</td>
</tr>
<tr>
<td>4</td>
<td>4NO$_2$C$_2$H$_4$</td>
<td>CH$_3$</td>
<td>&quot;</td>
<td>-1.74</td>
<td></td>
<td>-1.74</td>
<td>0</td>
<td>-1.74</td>
</tr>
<tr>
<td>5</td>
<td>CH$_3$</td>
<td>C$_6$H$_5$</td>
<td>&quot;</td>
<td>-4.10</td>
<td>d</td>
<td>-</td>
<td>-4.24</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>CH$_3$</td>
<td>4NO$_2$C$_2$H$_4$</td>
<td>&quot;</td>
<td>-3.70</td>
<td>d</td>
<td>17</td>
<td>-4.47</td>
<td>-3.78</td>
</tr>
<tr>
<td>7</td>
<td>CH$_3$</td>
<td>4CH$_3$OCC$_2$H$_4$</td>
<td>&quot;</td>
<td>-4.58</td>
<td>d</td>
<td>14</td>
<td>-5.07</td>
<td>-4.24</td>
</tr>
<tr>
<td>8</td>
<td>C$_6$H$_5$</td>
<td>C$_6$H$_5$</td>
<td>50</td>
<td>-1.79</td>
<td></td>
<td>18</td>
<td>-2.55</td>
<td>-1.89</td>
</tr>
</tbody>
</table>

Footnotes TABLE VI

a The concentration of reactants was NBu$_4$Cl = 0.04 M and alkyl bromide = 0.02 M. Reactions were followed by analysis for bromide ion produced and chloride ion lost. In all cases the acid produced was measured and this agreed with the chloride ion lost.

b Except where stated, the fraction of elimination ($Fe$) was determined titrimetrically by measurement of the acid and bromide produced. The uncertainty in the measurement is estimated as ±2.0%. The result is expressed as a percentage of the total elimination plus SN reactions.

c The $Fe$ was determined by V.P.C.

d The titrimetric analyses were performed by Mr. R. I. Tilley.

Controls

(a) Materials Used

The purity of the alkyl bromides and difficulties in handling some of them have been described in the Controls Section following TABLES I and IV.
(b) Analytical Methods

Analysis of artificial mixtures demonstrated that the analytical procedures accurately determined the concentration of bromide ion, chloride ion and acid produced. The concentration of bromide ion and chloride ion was measured by potentiometric titration with aqueous AgNO₃ solution. The mixed halide titration was performed in saturated barium nitrate solution which decreases co-precipitation of chloride ion and bromide ion so that two end points were observed\(^{27,55}\) (The first for complete titration of the bromide ion present and the second for complete titration of the bromide plus chloride ion.)

The acid produced was determined by titration with NaOMe/MeOH solution (described in control section after TABLE I). The acid production was not measured for all reactions reported in TABLE VI. However, in all cases where the fraction of elimination was determined by both chloride ion lost and acid produced the results agreed to within \(\pm 2\%\)

In all the reactions in TABLE VI the potentiometric titration was carried out by quenching a 5 ml sample of reaction mixture into 20 mls of toluene, extracting with water and titrating the aqueous solution with standard AgNO₃ solution. It was verified by experiment that none of the alkyl bromides or the NBu₄ Cl reacted or decomposed during the analysis.

The fraction of elimination was determined by V. P. C. in No. 2. However, the technique will be described later in the V. P. C. section.

c) Solvolysis reactions

All the alkyl bromides were tested to determine whether there was any significant competition of solvolysis with the bimolecular substitution and dehydrobromination. In the corresponding section following TABLE I it was reported that with two compounds the rate of solvolysis was significant and the bimolecular reaction had to be corrected because of the relatively rapid rate of solvolysis.

In all the reactions reported in TABLE VI solvolysis of the alkyl bromide was negligible or undetectable. As expected from TABLE IV, the solvolysis reaction was greatest for 1-bromo-1-(4-methylphenyl) propane (No. 3). Even in this case the solvolysis was less than 2% in
one half life of the bimolecular reaction. Since the reaction of interest in this section was the $\text{SN}_2$ reaction of chloride ion and not the dehydrobromination reaction, then this amount of solvolysis was negligible.

(d) **Infinites**

Titration infinites were determined for all the reactions in TABLE VI. All titration infinites agreed to within $\pm$ 3% with the calculated infinites.

(d) **Bimolecular substitution and elimination reactions of substituted bromo ethanes (XI) with $\text{NBu}_4\text{OAc}$ in DMF and $\text{KOT-Bu}$ in $t$-butanol**

The general form of the reactions studies are in Eqns 23 and 24

$$
\begin{align*}
\text{R}_a\text{CHBrCH}_2\text{R}_p + \text{OAc}^- & \rightarrow \text{R}_a\text{CH} = \text{CHR} + \text{HOAc} - \text{CHR}_2\text{R}_p \\
+ \text{Br}^- & + \text{HOAc}
\end{align*}
$$

**Eqn 23**

$$
\begin{align*}
\text{R}_a\text{CHBrCH}_2\text{R}_p + \text{t-BuO}^- & \rightarrow \text{R}_a\text{CH} = \text{CHR}_p + \text{Br}^- + \text{t-BuOH}
\end{align*}
$$

**Eqn 24**

The overall rate constant $k_{E+S}^2$ was determined and split into components of dehydrobromination ($k_E^2$) and substitution ($k_S^2$).

The results are presented in TABLE VII. They are expressed as logarithms of the rate constant ($\log k_{E+S}^2$ etc.) and the accuracy of determination is estimated at $\pm$ 5% of the value quoted. The rate constants were calculated using eqn 8.
### TABLE VII

Bimolecular rate constants for dehydrobromination and substitution ($\frac{d\text{Br}}{dt}$) reactions of substituted bromoethanes (XI) with $\text{NBu}_4\text{OAc}$ in DMF and $\text{KO}_t\text{-Bu}$ in $t$-butanol $^a,b$

$$R_\alpha\text{CHBrCH}_2R_\beta$$

<table>
<thead>
<tr>
<th>No.</th>
<th>$R_\alpha$</th>
<th>$R_\beta$</th>
<th>Base</th>
<th>Temp. $^\circ$C</th>
<th>$\log k_{E+S}$ (1)</th>
<th>$\log k_{E+S}$ (2)</th>
<th>$\log k_2^d$</th>
<th>$\log k_2^e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C$_6$H$_5$</td>
<td>CH$_3$</td>
<td>KO$_t$-Bu</td>
<td>75</td>
<td>-2.84</td>
<td>-2.86</td>
<td>100</td>
<td>-2.92</td>
</tr>
<tr>
<td>2</td>
<td>C$_6$H$_5$</td>
<td>C$_6$H$_5$</td>
<td>&quot;</td>
<td>25</td>
<td>-2.84</td>
<td>-2.87</td>
<td>100</td>
<td>-2.85</td>
</tr>
<tr>
<td>3</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>46.3$^g$</td>
<td>-2.01</td>
<td>-2.01</td>
<td>100</td>
<td>-2.01</td>
</tr>
<tr>
<td>4</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>75</td>
<td>-</td>
<td>-</td>
<td>100</td>
<td>-1.06</td>
</tr>
<tr>
<td>5</td>
<td>CH$_3$</td>
<td>C$_6$H$_5$</td>
<td>&quot;</td>
<td>75</td>
<td>-1.66</td>
<td>-1.67</td>
<td>100</td>
<td>-1.67</td>
</tr>
<tr>
<td>6</td>
<td>C$_6$H$_5$</td>
<td>CH$_3$</td>
<td>NB$_4$OAc</td>
<td>25</td>
<td>-0.93</td>
<td>-0.89</td>
<td>8</td>
<td>-2.00</td>
</tr>
<tr>
<td>7</td>
<td>C$_6$H$_5$</td>
<td>C$_6$H$_5$</td>
<td>&quot;</td>
<td>0</td>
<td>-2.13</td>
<td>-</td>
<td>78</td>
<td>-2.24</td>
</tr>
</tbody>
</table>
Footnotes TABLE VII

a The concentration of reactants was KOt-Bu = 0.04 M, alkyl bromide = 0.02 M and NBu₄OAc = 0.04 M, except where otherwise stated.

b \( k_2^{E+S} \) is the overall second order rate constant and \( k_2^E \) is the second order rate constant for dehydrobromination and \( k_2^S \) is the second order rate constant for substitution (all in units of litre/mole/sec).

c Fe is the fraction of elimination expressed as a percentage of the total bromide production. It was determined titrimetrically and by V.P.C.

d Corrected for the small amount of salt assisted solvolysis in the presence of NBu₄ClO₄.

e Extrapolated by means of an Arrhenius plot from the results at lower temperatures.

f The rate constant \( k_E \) quoted for dehydrobromination is for formation of trans olefin only. Some reactions were carefully analysed for cis, trans and Hoffman olefins. The results of this are quoted in a following table.

g The concentration of alkyl bromide was 0.000128 M and the KOtBu = 0.04 M. The result was determined by U.V. spectroscopy and followed at 255 m\( \mu \) and 309 m\( \mu \). The kinetics used are shown in eqn 16.

h Where two results are quoted this represents duplicate runs with freshly prepared solutions.

Controls

(a) Materials

The handling of all the materials used in this section has been described previously or is treated in the experimental section.

(b) Analytical Methods

All the reactions in TABLE VII were analysed for base by quenching a 5 ml sample of reaction mixture into excess p-toluene
sulphonic acid and back titrating with NaOMe in MeOH (see Experimental section). The neutral solution was quenched into toluene and extracted with water. The aqueous layer was titrated for halide ion potentiometrically with aqueous AgNO₃ solution. In all cases the base consumed was equal to the halide ion liberated. The fraction of elimination could not be easily determined titrimetrically because the acid produced and SN₂ substitution each remove the base. Therefore the proportions of substitution and elimination products were determined by V.P.C.

The methods of analysis were tested on blanks to show that they accurately determined the bromide ion and acid produced. It was also found that none of the reactants decomposed during the analysis.

(c) Extrapolations

The only extrapolation in TABLE VII was result no. 4 which was arrived at through a simple Arrhenius temperature extrapolation.

(d) Solvolysis reactions

Except for result No. 1 in TABLE VII, the solvolysis reaction was indetectable in the presence of NBu₄ClO₄ (lutidine was also added in t-BuOH). In No. 1 the bimolecular rate constant was corrected for solvolysis using the equation

\[ k_2^E = k_2^{obs} - k_1 [\text{Base}] \]

The solvolysis accounted for 20% of the total reaction and the rate constant was determined (\( \log k_1 = 1.08 \times 10^{-5} \text{ sec}^{-1} \)). Also 9.5% substitution products was found and verified. However, this was accounted for by the unimolecular solvolysis so that the Fe of the bimolecular reaction was effectively 100%.

(e) Infinites

Titration infinities were determined for all the reactions in TABLE VII except for No. 3 which was measured using U.V. spectroscopy. All titrated infinities agreed to within 3% of calculated values.
Salt assisted solvolysis reactions of substituted halo ethanes (XII)

The general form of the reactions studied is in eqn 25

\[
R_a CHX CH_2 R_b \rightarrow R_a CH^+ CH_2 R_b + X^- \quad \text{(XII)}
\]

solvolysis products

Eqn 25

Rate constants were determined for solvolysis reactions of several alkyl halides by determination of the rate of halide ion production \( \frac{dX^-}{dt} \). The results are presented in TABLE VIII and the estimated error in the values quoted is \( \pm 5\% \). When strongly basic or nucleophilic anions are used it is assumed that there is no competing bimolecular reaction because the unreactive anion perchlorate ion causes faster salt assisted ionisation. The results were calculated using eqn 14 and are expressed as logarithms of the first order rate constant which is in units of sec\(^{-1}\).

**TABLE VIII**

First order rate constants for salt assisted solvolysis of substituted halo ethanes\(^{a,d}\) (XII)

<table>
<thead>
<tr>
<th>No.</th>
<th>R(_a)</th>
<th>R(_b)</th>
<th>X</th>
<th>Temp °C</th>
<th>Salt</th>
<th>(10^2 M) Conc.</th>
<th>Solvent</th>
<th>log k (_1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4CH(_3) -C(_6)H(_4)</td>
<td>CH(_3)</td>
<td>Cl(_e)</td>
<td>75</td>
<td>NBu(_4) Cl</td>
<td>3.89</td>
<td>Me CO (_2)</td>
<td>-4.33 (_b)</td>
</tr>
<tr>
<td>2</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>7.88</td>
<td>&quot;</td>
<td>-4.17</td>
</tr>
<tr>
<td>3</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>NBu(_4) ClO(_4)</td>
<td>4.61</td>
<td>&quot;</td>
<td>-4.21</td>
</tr>
<tr>
<td>4</td>
<td>4CH(_3) -C(_6)H(_4)</td>
<td>&quot;</td>
<td>Br</td>
<td>&quot;</td>
<td>&quot;</td>
<td>9.22</td>
<td>&quot;</td>
<td>-4.55</td>
</tr>
<tr>
<td>5</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>4.80</td>
<td>(_t)-BuOH</td>
<td>-3.64</td>
</tr>
<tr>
<td>6</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>KO (_t)-Bu</td>
<td>4.28</td>
<td>&quot;</td>
<td>-3.60 (_b)</td>
</tr>
<tr>
<td>7</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>-3.88</td>
</tr>
<tr>
<td>8</td>
<td>C(_6)H(_5)</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>NBu(_4) ClO(_4)</td>
<td>4.80</td>
<td>&quot;</td>
<td>-4.97</td>
</tr>
</tbody>
</table>
Footnotes TABLE VIII

a The concentration of alkyl halide was 0.02 M and 2,6-lutidine = 0.05 M.

b The result was duplicated with freshly prepared solutions and the two results agreed to within $\pm$ 2%.

c The magnitude of the salt assisted solvolysis was indicated by carrying out this determination in the presence of 2,6-lutidine with no salt present.

d A prime purpose of these results was to show the rate of salt assisted ionisations more closely correlated with ion pair association rather than nucleophilicity or basicity of the anion.

e This value was used to estimate a rate constant for bromide promoted dehydrobromination of 1-bromo-1-(4-methoxy phenyl) propane which could not be synthesised. A value was determined from the chloro derivative in its reaction with chloride ion by allocating no more than 50% of acid production (a very generous amount) to an $E_2$ C reaction and assuming that chlorine is removed not more than 100 times more rapidly than bromine in $E_2$ C reactions. This is a generally accepted figure for the difference between chloride promoted dehydrochlorination and bromide promoted dehydrobromination.\textsuperscript{8,9,14c,17-22}

Controls

(a) Materials used

1-Chloro-1-(4-methoxyphenyl)propane and 1-bromo-1-(4-methylphenyl)propane were both used as 90% pure compounds, the major impurity being trans-1-arylpropene. This method of handling this type of mixture was discussed previously in the sections following TABLEs I and IV.

(b) Analytical methods

The important aspect of this work was the rate of formation of the carbonium ion intermediate. Therefore the production of chloride or bromide ion was followed analytically as this is a direct measure of the rate of formation of carbonium ion.

All reactions in TABLE VIII were followed by quenching a 5 ml sample of reaction mixture into toluene and extracting the solution with water and titrating the aqueous solution potentiometrically with standard $\text{AgNO}_3$. 
Although the products were not important in terms of the kinetic study, they were checked by V. P. C. In acetone the solvolysis gave > 98% trans-1-aryl propene, while in t-BuOH up to 30% substitution product was found. It should also be noted that the 2,6-lutidine was added to stop back addition of the hydrogen halide to the olefin. It has already been reported that 2,6-lutidine does not change the rate of reaction.

(e) Infinites

Infinity titrations were determined for all reactions reported in TABLE VIII and all values agreed to within ± 3% of calculated values.

(f) Bimolecular rate constants for dehydrobromination, dehydrotosylation and substitution reactions of cis-1,2-disubstituted cyclohexanes (XIII)

The reactions studied in this section gave a multiplicity of products. There were many possible reaction pathways, several of which gave the same products. The scheme for two specific cases are presented in Figure (2) and Figure (3).

The overall rate constant \( k_{E+S} \) was determined and split into components of dehydrobromination and dehydrotosylation \( k_{E} \) and substitution \( k_{S} \). The results are presented in TABLE IX. They are expressed as logarithms of the rate constant \( k_{E+S} \) etc. which is in units of litres mole\(^{-1}\) sec\(^{-1}\).

The accuracy of the determination is not as good as for reactions in TABLES I, IV, VI, VII and VIII because of the multiplicity of the reaction pathways available and analytical difficulties associated with identification of these pathways. The estimated error is ± 20% of the value quoted, which includes uncertainties in the kinetic and product analyses as well as the previously mentioned complications.
TABLE IX

Bimolecular rate constants for dehydrobromination, dehydrotosylation and substitution reactions of cis-1,2-disubstituted cyclohexanes (XIII)

<table>
<thead>
<tr>
<th>No.</th>
<th>X</th>
<th>Y</th>
<th>Base</th>
<th>Solvent</th>
<th>Temp. °C</th>
<th>$\log k_{E^S}^b$</th>
<th>$\log k_{E^S}^b$</th>
<th>$\log k_{E^S}^b$</th>
<th>$\log k_{E^S}^b$</th>
<th>$\log k_{E^S}^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Br</td>
<td>Br</td>
<td>NaOEt&lt;sup&gt;c&lt;/sup&gt;</td>
<td>EtOH</td>
<td>50</td>
<td>-1.7</td>
<td>&gt; 98</td>
<td>-0.8&lt;sup&gt;d&lt;/sup&gt;</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>Br</td>
<td>OTos</td>
<td>&quot; &quot;&lt;sup&gt;c&lt;/sup&gt;</td>
<td>&quot; &quot;&lt;sup&gt;c&lt;/sup&gt;</td>
<td>75</td>
<td>-3.4</td>
<td>&gt; 90</td>
<td>-3.0&lt;sup&gt;d&lt;/sup&gt;</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot; &quot;&lt;sup&gt;c&lt;/sup&gt;</td>
<td>&quot; &quot;&lt;sup&gt;c&lt;/sup&gt;</td>
<td>75</td>
<td>-3.4</td>
<td>&gt; 90</td>
<td>-2.5&lt;sup&gt;g&lt;/sup&gt;</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>&quot;</td>
<td>&quot;</td>
<td>NBu&lt;sub&gt;4&lt;/sub&gt;Cl</td>
<td>Acetone</td>
<td>100</td>
<td>-2.5</td>
<td>-</td>
<td>&lt; -4.3&lt;sup&gt;d&lt;/sup&gt;</td>
<td>-</td>
<td>f</td>
</tr>
<tr>
<td>5</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot; &quot;&lt;sup&gt;c&lt;/sup&gt;</td>
<td>&quot; &quot;&lt;sup&gt;c&lt;/sup&gt;</td>
<td>50&lt;sup&gt;i&lt;/sup&gt;</td>
<td>-2.5</td>
<td>-</td>
<td>-3.6&lt;sup&gt;g&lt;/sup&gt;</td>
<td>-</td>
<td>f</td>
</tr>
<tr>
<td>6</td>
<td>&quot;</td>
<td>&quot;</td>
<td>NBu&lt;sub&gt;4&lt;/sub&gt;OAc&lt;sup&gt;c&lt;/sup&gt;</td>
<td>&quot; &quot;&lt;sup&gt;c&lt;/sup&gt;</td>
<td>50&lt;sup&gt;i&lt;/sup&gt;</td>
<td>-2.5</td>
<td>-</td>
<td>&lt; -2.5&lt;sup&gt;d&lt;/sup&gt;</td>
<td>-</td>
<td>f</td>
</tr>
<tr>
<td>7</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot; &quot;&lt;sup&gt;c&lt;/sup&gt;</td>
<td>&quot; &quot;&lt;sup&gt;i&lt;/sup&gt;</td>
<td>75&lt;sup&gt;i&lt;/sup&gt;</td>
<td>-1.7</td>
<td>-</td>
<td>-1.7&lt;sup&gt;g&lt;/sup&gt;</td>
<td>-</td>
<td>f</td>
</tr>
<tr>
<td>8</td>
<td>OTos</td>
<td>OTos</td>
<td>NBu&lt;sub&gt;4&lt;/sub&gt;Cl</td>
<td>&quot; &quot;&lt;sup&gt;h&lt;/sup&gt;</td>
<td>100</td>
<td>-2.8</td>
<td>45</td>
<td>-4.1&lt;sup&gt;g&lt;/sup&gt;</td>
<td>-4.0</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>&quot;</td>
<td>&quot;</td>
<td>NBu&lt;sub&gt;4&lt;/sub&gt;OAc&lt;sup&gt;c&lt;/sup&gt;</td>
<td>&quot; &quot;&lt;sup&gt;c&lt;/sup&gt;</td>
<td>75&lt;sup&gt;i&lt;/sup&gt;</td>
<td>-1.5</td>
<td>30</td>
<td>-2.1&lt;sup&gt;g&lt;/sup&gt;</td>
<td>-1.6</td>
<td></td>
</tr>
</tbody>
</table>
Footnotes TABLE IX

a Concentration of reactants, except where otherwise stated, were base = 0.04 M, RXY = 0.02 M and 2,6-lutidine = 0.04 M. Results were determined by following bromide ion production, acid production, loss of base and production of organic products by V.P.C.
b Extrapolated to 75°C from results at other temperatures.
c No lutidine present.
d Rate constant for dehydrobromination.
e Verified by V.P.C. analysis. The fraction of elimination is expressed as a percentage of total reactions.
f Due to multiple pathways leading to the same product, no attempt has been made to estimate log k₂ or Fe.
g Rate constant for dehydrotosylation.
h OTos represents p-toluene sulphonate (tosylate).
i Concentration of NBu₄ OAc = 0.03 M and RXY = 0.015 M.

Specific reaction schemes

The rate constants quoted for cis-2-bromocyclohexyl p-toluene sulphonate and cis-1,2-di-p-toluene sulphonate in TABLE IX are not as accurate as previous rate constants. This is due to the many reaction pathways open to the two compounds. These are shown in figure (2) and figure (3).

However, it should be noted that the errors involved in determination of the rate constants are not of significant magnitude to affect their theoretical discussion presented in later sections.
Figure 2

Bimolecular Reaction Pathways available to the reaction of \textit{cis}-2-bromo cyclohexyl p-toluene sulphonate (XIV) with a nucleophile Y.
Figure 3

Bimolecular Reaction pathways available to the reaction of cis-cyclohexyl-1,2-di-p-toluene sulphonate (XV) with a nucleophile Y⁻
The reactions were analysed by V.P.C., titration of acid, bromide ion and base. The results presented in TABLES X and XI were used to determine two of the rate constants quoted in TABLE IX. The SN$_2$ substitution by Y$^-$ accounted for up to 30% of the total reaction with cis-2-bromo cyclohexyl p-toluene sulphonate and up to 70% in reactions of cis-cyclohexyl-1,2-di-p-toluene sulphonate.

TABLE X

Proportions of products from bimolecular reactions of cis-2-bromo cyclohexyl p-toluene sulphonate with various bases.

<table>
<thead>
<tr>
<th>Base</th>
<th>Solvent</th>
<th>Temp. °C</th>
<th>O$_{Tos}$</th>
<th>Br</th>
<th>Y</th>
<th>% Y$^-$ consumed</th>
<th>% Br$^-$ produced</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOEt$^c$</td>
<td>EtOH</td>
<td>50</td>
<td>26$^g$</td>
<td>66$^a$</td>
<td>8$^c$</td>
<td>108</td>
<td>35</td>
</tr>
<tr>
<td>NBu$_4$OAc$^d$, Me$_2$CO</td>
<td>&quot;</td>
<td>&lt;15$^e$</td>
<td>85$^a$</td>
<td>-</td>
<td>23</td>
<td>58</td>
<td></td>
</tr>
<tr>
<td>NBu$_4$Cl$^b$, $^d$</td>
<td>&quot;</td>
<td>100</td>
<td>&lt;19$^e$</td>
<td>81$^a$</td>
<td>-</td>
<td>30</td>
<td>28</td>
</tr>
</tbody>
</table>

Footnotes TABLE X

a By V.P.C. analysis of 0.05 M reaction mixtures after 10 half lives, using authentic materials as standards.
b Containing excess 2,6-lutidine.
c Expressed as a percentage of total organic products by V.P.C.
d Expressed as a percentage of the acid produced. There are also substitution products as in figure (2).
e Calculated by assuming that this is the only source of acid in addition to that produced from formation of 1-bromo cyclohexene and 3-Y-cyclohexene, as in figure (2).
f This compound was not detected, i.e. <1%.
g Calculated by assuming that this is the only other source of bromide ion and noting the absence of any other products by V.P.C.
h Determined titrimetrically by potentiometric halide determination or acid-base titrations.
### TABLE XI

Proportions of products from reactions of cis-cyclohexyl-1,2-di-p-toluene sulphonate with various bases in acetone

<table>
<thead>
<tr>
<th>Base</th>
<th>Temp. °C</th>
<th>( \text{Otos} )</th>
<th>( \text{Y} )</th>
<th>( \text{H}^+ )</th>
<th>( % \text{Y}^- ) consumed</th>
<th>( % \text{H}^+ ) produced</th>
</tr>
</thead>
<tbody>
<tr>
<td>NBu Cl(^a)</td>
<td>100</td>
<td>48(^d)</td>
<td>4(^b)</td>
<td>6(^b)</td>
<td>42(^d)</td>
<td>56(^c)</td>
</tr>
<tr>
<td>NBu OAc</td>
<td>75</td>
<td>27(^d)</td>
<td>5(^b)</td>
<td>28(^b)</td>
<td>40(^d)</td>
<td>78(^c)</td>
</tr>
</tbody>
</table>

#### Footnotes TABLE XI

- **a** Containing excess lutidine
- **b** By V. P. C. analysis of 0.05 M reaction mixtures after 1 half life. Starting material does not decompose.
- **c** By titration. Recorded as a percentage of the total products.
- **d** Calculated from **b** and **c** assuming that these are the only other organic products as in figure (3). They cannot be analysed by V. P. C.

Clearly the study of 1,2-disubstituted cyclohexyl systems is very complex. Although much information can be gained from the results in TABLE IX, the level of uncertainty in the results restricts their theoretical treatment to discussion of large effects and trends. Therefore, because of these limitations and the analytical difficulties associated with the systems, it is recommended that this system should not be used to investigate the simple aspects of bimolecular transition states.

#### Controls

(a) **Materials used**

All materials were used at > 98% purity as verified by V. P. C., N. M. R., elemental analysis and comparison of melting points and boiling points to values recorded in the literature.

(b) **Analytical methods**

Several methods of analysis were employed. Halide ions were titrated potentiometrically with standard AgNO\(_3\) solution and acid-base
titrations to determine acid and base present were carried out in acetone solution using standard sodium methoxide in methanol and p-toluene sulphonic acid in 80% acetone-ethanol.

For nos. 1, 2, 3, 4, 5 and 8, 5 ml samples of reaction mixture were quenched into excess p-toluene sulphonic acid, back titrated with sodium methoxide in methanol using thymol blue as indicator. The mixture was then poured into 25 mls methanol and titrated potentiometrically with standard aqueous AgNO₃ solution.

5 ml samples of nos. 6, 7, and 9 were quenched into acetone, titrated for acid present with sodium methoxide in methanol (thymol blue) and then back titrated for base present with p-toluene sulphonic acid in 80% acetone-ethanol (bromo phenol blue). The mixtures in nos. 6 and 7 were poured into 25 mls of methanol and titrated with AgNO₃. V.P.C. analyses were performed at various stages of the reaction as described following TABLES X and XI.

(c) Solvolysis reactions

No significant solvolysis was detected in any reaction in TABLE IX. A remarkable feature of these compounds was their marked stability relative to the mono-substituted compounds. This aspect is discussed in detail in the Discussion section of this thesis.

(d) Infinites

Titration infinites were not used as a verification of purity on complete reaction, because the figure measured is only a reflection of the partitioning of the reactants along the many reaction pathways available.

(e) Extrapolations

In TABLE IX the log $k^E_2$ and log $k^S_2$ values quoted are all correct to the same temperature (75°C). The extrapolations were made by assuming a tenfold change in rate for a 25°C change in temperature. This assumption has been justified previous as the normal temperature coefficient for an anion-neutral molecule type of reaction. Also, no evidence was found to suggest that such an assumption does not hold for reactions of cyclohexyl compounds.
Bimolecular rate constants for the debromotosylation reactions of trans-2-bromo cyclohexyl p-toluene sulphonate

The general form of the reactions studied is in eqn. 26

$$\text{Br} + 2Y^- \rightarrow \text{Br}^- + \text{OTos}^- + Y^- Y$$

The overall rate constants for debromotosylation, dehydrobromination, dehydratosylation and substitution reactions of trans-2-bromo cyclohexyl p-toluene sulphonate with NBu$_4$CN and NBu$_4$ArS were determined by following the production of bromide ion and the loss of cyanide ion and p-nitro thiophenoxide ion. The results are presented in TABLE XII and are expressed as logarithms of the overall rate constants which are in units of litres/mole/sec and the accuracy of the determination is estimated at $\pm$ 5% of the value quoted. The rate constants were calculated using eqn 12.

**TABLE XII**

Bimolecular rate constants for debromotosylation of trans-2-X cyclohexyl p-toluene sulphonate (XVI) with NBu$_4$ArS and NBu$_4$CN in DMF at 75°C

<table>
<thead>
<tr>
<th>No.</th>
<th>X</th>
<th>Base a, b</th>
<th>log $k_{E+S}^2$</th>
<th>%D c</th>
<th>log $k_{D}^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>(1)</td>
<td>(2)</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Br</td>
<td>NBu$_4$ArS</td>
<td>-2.66</td>
<td>-2.62</td>
<td>92.5</td>
</tr>
<tr>
<td>2</td>
<td>&quot;</td>
<td>NBu$_4$CN</td>
<td>-1.49</td>
<td>-1.51</td>
<td>86</td>
</tr>
<tr>
<td>3</td>
<td>OTos</td>
<td>NBu$_4$ArS</td>
<td>-d</td>
<td>-d</td>
<td>0</td>
</tr>
</tbody>
</table>
Footnotes  TABLE XII

(a) Concentration of reactants were base = 0.04 M and trans-2-X cyclohexyl p-toluene sulphonate = 0.01 M.

(b) OTos represents p-toluene sulphonate and ArS represents 4-nitro thiophenoxide.

(c) D represents that part of the total reaction which gives debromosylation and therefore produces cyclohexene.

(d) The reaction was analysed by V. P. C. after the infinity amount of 4-nitro thiophenoxide ion had been removed and it was found that no cyclohexene was produced. Therefore it was not of any interest to determine rate constants.

Controls

(a) Materials used

The trans-2-bromo cyclohexyl p-toluene sulphonate and trans-cyclohexyl-1,2-di-p-toluene sulphonate were prepared and purified by methods reported in the literature and described in the Experimental section.

Care must be exercised in the handling of NBu₄ArS because the p-nitro thiophenoxide is rapidly oxidised by atmospheric oxygen to the disulphide. Therefore all analyses and reaction samples were handled beneath an inert nitrogen atmosphere.

(b) Analytical methods

Since p-nitro thiophenoxide is readily oxidised, the analytical methods must be carefully controlled. For result No.1, at each time of analysis, two 5 ml samples were cooled and one was quenched into excess p-toluene sulphonate acid and titrated with methoxide in methanol using thymol blue indicator. The second sample was quenched into toluene, acidified, extracted with water and titrated with standard AgNO₃ solution.

For No. 2 samples were quenched into acetone, titrated with p-toluene sulphonate acid (bromophenol blue) and poured into toluene.
They were then extracted with water and titrated with AgNO₃.

It was demonstrated that neither the reactants nor the products decomposed during the analysis procedure.

The V. P. C. analyses were performed, using standard techniques described in the Experimental section. It was also shown that the products did not react further with any species in the medium.

(c) Solvolysis reactions

Both compounds tested in this section showed indetectable solvolysis in one half life of the slowest reaction.

(d) Infinities

Infinity titrations agreed to within ±3% of the calculated values.

(c) V. P. C. PRODUCT ANALYSES

All titrimetric and V. P. C. product analyses should be included in this section. However, the methods used for the analyses are repetitive. The results described here are those which were determined with the intention of closely following the olefinic product distribution and where a kinetic result was of secondary importance. Therefore the only results included in this section are those olefinic product determinations which were used to elucidate the aspect of double bond character in the E₂C transition state.

The olefinic products from dehydrobromination reaction of substituted bromo ethanes (XI) are presented in TABLE XIII. The exact experimental techniques used for each analysis are described in the Experimental section. For each analysis either an internal standard or another product as reference was used to allow for variation in sensitivity of the V.P.C. and variation of the injection volume. This technique proved most satisfactory and the estimated error in each result quoted in TABLE XIII is ±2% of the value quoted. All the olefins were identified by comparison with authentic samples and in several cases the major product was isolated, purified and its physical properties checked to verify its identity. Also artificial mixtures of the analysis result were made and tested by U.V. and N.M.R. spectroscopy for comparison with the analysis result.
TABLE XIII

Olefinic product distributions determined after dehydrobromination of various substituted bromo ethanes (XI) for elimination towards R_β or into R_a

\[
R_a \text{CHBrCH}_2R_\beta
\]

<table>
<thead>
<tr>
<th>No.</th>
<th>R_a</th>
<th>R_β</th>
<th>Base^b</th>
<th>Solvent</th>
<th>Temp. °C</th>
<th>% Olefins^e</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>cis-stilbene</td>
</tr>
<tr>
<td>1</td>
<td>C_6H_5</td>
<td>C_6H_5</td>
<td>NBu_4 Br^c</td>
<td>Me_2CO</td>
<td>75</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>&quot;</td>
<td>&quot;</td>
<td>NBu_4 OAc</td>
<td>DMF</td>
<td>25</td>
<td>0.4</td>
</tr>
<tr>
<td>3</td>
<td>&quot;</td>
<td>&quot;</td>
<td>KOT-Bu</td>
<td>t-BuOH</td>
<td>25</td>
<td>0.6</td>
</tr>
<tr>
<td>4</td>
<td>&quot;</td>
<td>&quot;</td>
<td>NaOMe</td>
<td>80% DMSO-MeOH</td>
<td>25</td>
<td>0.7</td>
</tr>
<tr>
<td>5</td>
<td>&quot;</td>
<td>CH_3</td>
<td>NBu_4 Br^c</td>
<td>Me_2CO</td>
<td>75</td>
<td>2</td>
</tr>
<tr>
<td>6</td>
<td>&quot;</td>
<td>&quot;</td>
<td>KOT-Bu</td>
<td>Me_2CO</td>
<td>75</td>
<td>98.5</td>
</tr>
<tr>
<td>7</td>
<td>&quot;</td>
<td>&quot;</td>
<td>NBu_4 Br^c</td>
<td>Me_2CO</td>
<td>75</td>
<td>98.8</td>
</tr>
<tr>
<td>8</td>
<td>CH_3</td>
<td>C_6H_5</td>
<td>&quot;</td>
<td>Me_2CO</td>
<td>75</td>
<td>92.7</td>
</tr>
<tr>
<td>9</td>
<td>&quot;</td>
<td>&quot;</td>
<td>KOT-Bu</td>
<td>t-BuOH</td>
<td>75</td>
<td>98.1</td>
</tr>
<tr>
<td>10</td>
<td>CH_3</td>
<td>CH_3</td>
<td>NBu_4 Br^c</td>
<td>Me_2CO</td>
<td>75</td>
<td>82</td>
</tr>
<tr>
<td>11</td>
<td>(CH_3)_2CH^d</td>
<td>CH_3</td>
<td>NBu_4 Br^c</td>
<td>Me_2CO</td>
<td>75</td>
<td>92.5</td>
</tr>
</tbody>
</table>

^a: Elimination towards R_β or into R_a

^b: Base

^c: NBu_4 Br

^d: (CH_3)_2CH
Footnotes TABLE XIII

a The most significant aspects of this table are the analysis of cis and trans olefins and the determination of the relative % Hofmann and % Saytzeff olefins in the product.

b Except where otherwise stated the concentration of reactants were Base = 0.05 M and RBr = 0.02 M.

c The concentration of reactants was NBu$_4$Br = 0.1 M, 2,6-lutidine = 0.05 M and RBr = 0.02 M.

d There was considerable work in the literature for reactions of the p-toluene sulphonate derivative. Therefore, so that this result could be directly compared to the literature results, the reaction and analysis were performed on the alkyl tosylate rather than the alkyl bromide.

e The results quoted are expressed as a percentage of the total olefinic products resulting from the bimolecular reaction of the base and alkyl substrate.

Controls

Several methods of analysis were used, i.e. in terms of the relation of olefin to solvent and to column used on the V.P.C. These are all documented in the experimental section. They can be represented by the following possibilities -

(1) A reaction sample was analysed for only one compound and, because of the presence of salts, this compound was extracted into a solvent more volatile than itself and an internal standard was added to allow for minor technical variations.

(2) A reaction sample was analysed for two or more compounds and was extracted into a solvent more volatile than both compounds. The ratio of one compound to another was carefully measured.

(3) Where very volatile olefins such as the butenes and methylpentenes were studied the mixtures were extracted into a solvent of less volatility and the ratio of one compound to another analysed.
(4) Some olefins were rapidly lost into the atmosphere and so these were analysed by direct injection of the reaction sample into the V.P.C. which contained a glass wool filled, glass injector insert which could be readily cleaned.

(b) Reaction infinity analyses vs half life analyses

Generally infinity samples were analysed by V.P.C. However, in some cases this was unsatisfactory because products reacted further to give a new product composition. This was mainly experienced with the 1,2-disubstituted cyclohexyl derivatives.

Another difficulty which arose was the problem of dehydrobromination of the reactant alkyl bromide to the product olefins, by a pyrolytic mechanism in the V.P.C. injectors. This made essential the analysis of infinity reaction samples (i.e. samples reacted 10 or more half lives) which required further controls. These controls, however, were common to all reactions analysed at infinity and some to reactions analysed at other reaction times.

(i) Isomerisation of products. This can be coupled with decomposition of reactants. Isomerisation could be tested for in two ways, which involved testing the stability of an artificial olefin mixture or testing the stability of the product mixture with time (so long as that mixture did not correspond to the equilibrium concentrations). The test to demonstrate the absence of a reactant which decomposed involved the combination of these two tests. That is, the products were shown not to isomerise and the infinity analysis to remain stable.

(ii) Solvolysis of Reactants. When a small amount of one product was present it was important to show that this product was formed via a bimolecular elimination and not via a unimolecular solvolysis. The proof of this involved two tests which were the measurement of the relative rate of solvolysis in the presence of an inert salt such as NBu₄ClO₄ and the analysis of products from this reaction to show that the amount of the minor reaction product from the bimolecular reaction could not have arisen by a unimolecular mechanism.
In the case of the butenes this also involved measurement of the butenes formed from the tetra-n-butyl ammonium cation.

(c) A typical test analysis

The volume of V.P.C. analytical work carried out for this thesis is too large for all the results to be described. Therefore only a typical analysis will be described.

V.P.C. product analyses of the dehydrobromination of 1-bromo-1,2-diphenyl ethane with Bu₄Br in acetone at 75°C were carried out in the presence of 2,6-lutidine.

4.80 ml samples of .0987 M NBu₄Br, .0196 M RBr and .05 M 2,6-lutidine in acetone were warmed at 75°C for varying times and quenched into 20 mls of pentane, washed with water and the pentane layer made up to 25 mls. 2 µl of this solution was then injected into the P.E. 900 onto a 5% Apiezon L column at 170°C and the cis-stilbene was studied at 4X and the trans-stilbene at 40X.

TABLE XIV

V.P.C. analytical results for dehydrobromination of 1-bromo-1,2-diphenyl ethane with NBu₄Br in acetone in the presence of 2,6-lutidine at 75°C.

<table>
<thead>
<tr>
<th>No.</th>
<th>Time</th>
<th>Wt trans</th>
<th>Wt cis</th>
<th>C cis</th>
<th>% cis</th>
<th>trans/cis</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30 hr</td>
<td>.69970gm</td>
<td>.15745gm</td>
<td>.16888</td>
<td>2.3</td>
<td>42</td>
</tr>
<tr>
<td>2</td>
<td>65 &quot;</td>
<td>.70585&quot;</td>
<td>.12805 &quot;</td>
<td>.13735</td>
<td>1.6</td>
<td>62</td>
</tr>
<tr>
<td>3</td>
<td>137 &quot;</td>
<td>.50773 &quot;</td>
<td>.11867 &quot;</td>
<td>.12728</td>
<td>2.0</td>
<td>50</td>
</tr>
<tr>
<td>4</td>
<td>161 &quot;</td>
<td>.56445 &quot;</td>
<td>.11790 &quot;</td>
<td>.12656</td>
<td>2.1</td>
<td>47</td>
</tr>
<tr>
<td>Aver.</td>
<td></td>
<td>-</td>
<td></td>
<td>-</td>
<td>-</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Footnotes TABLE XIV

a The period of time the sample was warmed at 75°C.

b This value was determined by tracing the peak onto tracing paper, cutting out the peak and weighing it.
The value represents the weight of the cis peaks multiplied by a correction factor (1.0726) which was predetermined by measuring the relative molar responses of cis-stilbene and trans-stilbene.

The percentage of cis-stilbene in the total olefinic products.

(D) Equilibration of olefins

It was necessary, for comparison with the results in the previous Product Analyses section, to determine the equilibration mixtures of several olefinic systems. The results of the equilibration reactions performed for this thesis are presented in TABLE XV

<table>
<thead>
<tr>
<th>No.</th>
<th>Rα</th>
<th>Rβ</th>
<th>Solvent</th>
<th>Temp. °C</th>
<th>cis-stilbene</th>
<th>trans-stilbene</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C₆H₅</td>
<td>C₆H₅</td>
<td>DMFα</td>
<td>37</td>
<td>0.05</td>
<td>99.95</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>trans-1-phenyl</td>
<td>cis-1-phenyl</td>
<td>3-phenyl propene</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>propene</td>
<td>propene</td>
<td>98.4</td>
</tr>
<tr>
<td>2</td>
<td>C₆H₅</td>
<td>CH₃</td>
<td>DMSOβ</td>
<td>50</td>
<td>trans-2-butene</td>
<td>cis-2-butene</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>64</td>
<td>27</td>
<td>9</td>
</tr>
<tr>
<td>3</td>
<td>CH₃</td>
<td>CH₃</td>
<td>DMSOβ, c</td>
<td>55</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Footnotes TABLE XV

a Equilibration of cis-stilbene and trans-stilbene by iodine, irradiated by U.V. light in DMF solution by the method of Fischer.

b Equilibration was performed using KOt-Bu in DMSO by the method of Schriesheim.

c To verify the accuracy of our techniques we repeated the determination reported in reference 38.
The estimated error in the determination is $\pm 2\%$ of the result quoted. Each value quoted represents the percentage of that component in the total olefinic product mixture.

**Comparison of techniques**

Two techniques were used for the equilibrations. The first method was to irradiate an iodine solution in DMF, with a narrow band of U.V. light which caused activation of the iodine, causing it to add to the olefin, and allow free rotation about the two carbon atoms terminating the double bond. The iodine is then removed and the olefin reformed.

The second method is to react the olefins with KOt-Bu in DMSO. The strong base removes an allylic proton to give a carbanion which can isomerise the double bond along the carbon chain and allow free rotation about the former double bond position. The carbanion may then protonate again and form any one of the olefins possible from that carbanion.

The two methods both give good results and both have their advantages and disadvantages. The first method is applicable only when the double bond is located in a fixed position and cannot migrate along a carbon chain, whereas the second method is ideal for olefins which are attached to alkyl chains, but cannot be used for olefins which do not have an allylic proton. The two methods cannot be interchanged because they have different mechanisms of isomerisation and are therefore applicable to different olefinic systems.

**Controls**

It is necessary to establish that the values which are measured are representative of the true equilibrium proportions. This necessitates several tests -

1. The equilibrations must be left to react for long periods during which time regular analyses are performed. The mixture was considered to have reached equilibrium when several successive analyses gave the same result.

2. The equilibrium was approached from two directions and the equilibrium constant from each direction agreed to $\pm 5\%$. 

It was verified that no decomposition of the olefins took place under the reaction conditions by checking the total olefinic concentration as well as the olefinic distributions.

The normal V.P.C. controls were also performed to show the olefins did not react or decompose during analysis or that they did not change proportions on quenching of the equilibration mixture. Most of these tests were checked by subjecting known mixtures of olefins to the analytical procedures and checking the final results.

**A typical equilibration determination**

The analysis of samples from the equilibration of cis-stilbene and trans-stilbene in DMF was carried out by direct injection of the DMF solution into the P.E. 900 gas chromatograph fitted with a 5% Apiezon L column. Direct injection techniques were used because they enable rapid, accurate analyses and the only other contaminant, iodine, was easily removed by reaction with copper mesh before injection into the V.P.C.

(i) Proportional response of cis-stilbene and trans-stilbene

2 microlitres of 0.0926 M cis-stilbene and 0.0943 M trans-stilbene in DMF was injected on Apiezon L column at 150°C and 1000 times attenuation

<table>
<thead>
<tr>
<th>No.</th>
<th>Weight of cis-peak</th>
<th>Weight of trans-peak</th>
<th>cis/trans ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.43425 gms</td>
<td>0.48260 gms</td>
<td>0.8998</td>
</tr>
<tr>
<td>2</td>
<td>0.43700</td>
<td>0.47010</td>
<td>0.9296</td>
</tr>
<tr>
<td>3</td>
<td>0.45705</td>
<td>0.49825</td>
<td>0.9173</td>
</tr>
<tr>
<td>Aver.</td>
<td>0.44277</td>
<td>0.48365</td>
<td>0.9155</td>
</tr>
</tbody>
</table>

Correcting the cis/trans ratio for the difference in concentration

\[
\text{cis/trans response} = 0.9323
\]

\[
\therefore \text{cis gives 0.9323 the response of trans, or trans gives 1.0726 the response of cis.}
\]
(ii) Analysis of the equilibration mixture.

400 mls of 0.0463 M cis-stilbene and 0.0119 M iodine in DMF was irradiated with a Hanovia, medium pressure, mercury arc-lamp through a U.V. light filter solution at 37°C. 4.80 ml samples were treated with copper mesh and 2 microlitre samples were injected into the V.P.C. at 150°C. Trans-stilbene was studied at attenuation 200X and cis-stilbene at attenuation 10X.

<table>
<thead>
<tr>
<th>No.</th>
<th>Irradiation time</th>
<th>Weight of cis</th>
<th>Weight of trans</th>
<th>( \frac{[\text{cis}]}{[\text{trans}]} \times 10^3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>18 hours</td>
<td>0.04360</td>
<td>1.41425</td>
<td>1.54</td>
</tr>
<tr>
<td>2</td>
<td>21 &quot;</td>
<td>0.02200</td>
<td>1.27925</td>
<td>0.80</td>
</tr>
<tr>
<td>3</td>
<td>24 &quot;</td>
<td>0.01660</td>
<td>1.40630</td>
<td>0.59</td>
</tr>
<tr>
<td>4</td>
<td>43 &quot;</td>
<td>0.01250</td>
<td>1.35095</td>
<td>0.46</td>
</tr>
<tr>
<td>5</td>
<td>119 &quot;</td>
<td>0.00945</td>
<td>1.17495</td>
<td>0.40</td>
</tr>
<tr>
<td>6</td>
<td>126 &quot;</td>
<td>0.00888</td>
<td>1.14485</td>
<td>0.39</td>
</tr>
<tr>
<td>7</td>
<td>126 &quot;</td>
<td>0.00938</td>
<td>1.05595</td>
<td>0.44</td>
</tr>
<tr>
<td>8</td>
<td>126 &quot;</td>
<td>0.00790</td>
<td>1.14875</td>
<td>0.34</td>
</tr>
<tr>
<td>Aver.</td>
<td></td>
<td></td>
<td></td>
<td>0.40 ± 0.06</td>
</tr>
</tbody>
</table>

Correcting for the proportional response

\[
\text{actual} \frac{[\text{cis}]}{[\text{trans}]} = 0.40 \times 10^{-3} \times 1.0726
\]

\[
= 0.42 \times 10^{-3} \pm 0.06
\]

The determination from the opposite direction, i.e. high purity trans-stilbene, gave the result

\[
\frac{[\text{cis}]}{[\text{trans}]} = 0.50 \times 10^{-3} \pm 0.06
\]

Ave.

\[
\frac{[\text{cis}]}{[\text{trans}]} = 0.46 \times 10^{-3}
\]

i.e.

\[
\frac{[\text{trans}]}{[\text{cis}]} = 2,200
\]
All the N.M.R. spectra for compounds mentioned in the results section, except for cyclohexyl derivatives, are listed in TABLES XXX, XXXI, XXXII, XXXIII.

N.M.R. analyses are not a major part of this thesis and were only used to show how, by an analysis of a large cross-section of related compounds, it is possible to establish normal $\tau$ values and $J$ values (chemical shift and coupling constants). Comparison of the spectrum of an unknown compound with the spectra of identified compounds gives very good evidence for the structure of the unknown compound.

If the N.M.R. data in TABLE XXX is examined it can be readily observed that a regular pattern is present. One of the most unstable compounds handled was 1-chloro-1-(4-methoxy phenyl) propane which could not be distilled, recrystallised, or purified by solution chromatography or V.P.C. The only method which afforded some purification was to rapidly filter a pentane solution through active carbon and evaporate the pentane under reduced pressure.

N.M.R. analysis of the colourless oil indicated that the oil was a mixture of the alkyl chloride and anethole (1-(4-methoxy phenyl) propene) in the ratio of 9:1, i.e. the alkyl chloride was 90% pure. This conclusion was arrived at by examination of the N.M.R. integration of the distant methyl groups labelled C in TABLE XXX and TABLE XXXIII which was a triplet in the alkyl chloride at 9.04 $\tau$ and a doublet with the olefin at 8.19 $\tau$.

This analysis was verified by both the chloride analysis and the reaction infinities which, for the reaction with chloride ion in acetone, gave only one peak on the V.P.C. which corresponded to anethole. Also, if enough anethole was added to the oil to make a supposedly 80%-20% combination of alkyl chloride and anethole, the N.M.R. spectrum of this mixture changed from the original in only one aspect, that being the integration of the distant methyls (labelled C) changed in ratio to 4:1.
Examination of the synthetic procedure elucidates the problem even further. When hydrogen chloride is reacted with the known alcohol several materials are possible in the final mixture but some are unlikely and others can be eliminated. The only possible components are unreacted alcohol (eliminated by the absence of deuterio exchangeable peaks as well as other characteristic signals), rearrangement products (unlikely because the carbonium formed is already the most stable isomer and the absence of extraneous signals), olefinic products (anethole - by dehydrochlorination of the product and dehydration of the reactant), and the required alkyl chloride.

It is quite clear that evaluation of an N.M.R. spectrum of an alkyl chloride, combined with various N.M.R. tests, halide analysis, infinity reaction analyses, and V.P.C. analysis of reaction products verifies without any doubt the identity of the starting alkyl chloride.

This technique of identification was used for several alkyl halides because they were either secondary benzylic halides (under-stably unstable) or alkyl halides which rearranged on distillation and so were not readily purified. N.M.R. spectroscopy was not utilised as the prime identification method but only to substantiate results from other techniques. This approach was utilised only with 1-chloro-1-(4-methoxyphenyl) propane; 1-bromo-1-(4-methylphenyl) propane and 2-bromo-1-phenyl propane.
DISCUSSION

A  Charge distribution at the α carbon atom

The problem of establishing the character and extent of charge development at Cα was approached by using the transition state for a distinctly different type of reaction as a model for the E2C 'like' transition state.

Therefore, comparison of the rates of E2C 'like' reactions and solvolysis reactions was used to identify the extent of positive charge development at Cα, while comparison of the rates of E2C 'like' reactions and SN2 reactions was used to infer Cα-base bonding in the E2C 'like' transition state. Also the rates of E2C 'like' and E2H 'like' reactions were compared to show the individuality of the E2H 'like' and E2C 'like' transition states.

(i) Comparison of transition states for solvolysis reactions and E2C 'like' β-elimination reactions.

Bunnett4,14a and McLennan16 have implied that β-elimination reactions induced by weak hydrogen bases, but strong carbon nucleophiles (e.g. halide and mercaptide ions), proceed through a carbonium ion 'like' (paene-carbonium) E2 transition state. This necessitates considerable positive charge at Cα and very little negative charge at Cα or positive charge at Hβ. Weinstein and Parker9-13,17-22 designate the β-eliminations induced by these bases as E2C 'like', i.e. Cα and Cβ both have considerable sp2 character, little charge and the double bond well formed. The differences between the rate constants for E2C 'like' and solvolysis reactions of various 1-para substituted phenyl-1-bromo propanes clarify the aspect of charge development at Cα in the E2 transition state. The results are presented in TABLE XVI and the reaction schemes are shown in Figure 4.
TABLE XVI

Rate constants (log k) for $E_2$ dehydrobromination induced by NBu$_4$Br in acetone and solvolysis reactions of 1-R-1-bromopropanes (XVIII)

\[ R-\text{CHBrCH}_2\text{CH}_3 \]

(XVIII)

<table>
<thead>
<tr>
<th>R</th>
<th>$E_2 C^a$ log k$_2$</th>
<th>$SN_1 + E_1^c$ log k$_1$</th>
<th>$\sigma^+ f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>-5.94</td>
<td>-8.1$^d$</td>
<td>-</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>-4.68</td>
<td>-7.2$^d$</td>
<td>-</td>
</tr>
<tr>
<td>4NO$_2$C$_6$H$_4$</td>
<td>-3.58</td>
<td>-7.3$^d$</td>
<td>0.790</td>
</tr>
<tr>
<td>C$_6$H$_5$</td>
<td>-3.36</td>
<td>-4.04</td>
<td>0.0</td>
</tr>
<tr>
<td>4CH$_3$C$_6$H$_4$</td>
<td>-2.91</td>
<td>-2.47</td>
<td>-0.311</td>
</tr>
<tr>
<td>4CH$_3$OOC$_6$H$_4$</td>
<td>$&lt;-1.4^b$</td>
<td>+0.1$^e$</td>
<td>-0.778</td>
</tr>
</tbody>
</table>

Footnotes TABLE XVI

a  Results from TABLE I at 75°C.
b  This result is estimated by the method described in Footnote e TABLE VII.
c  Results are from TABLE IV and are for solvolysis in 90% acetone water at 75°C.
d  Extrapolated from results in 50% acetone water in TABLE IV by assuming the same solvent effect as observed for 1-phenyl-1-bromopropane.
e  Extrapolated from results in TABLE IV for the chloro derivative, assuming the same substituent effect for solvolysis of chlorides as for bromides.
f  The $\sigma^+$ values were reprinted from Ref, 40.
Figure 4

Products for the reactions of 1-R-1-bromopropanes XVIII with NBu₄Cl in DMF at 25°C (SN₂); NBu₄Br in acetone at 75°C (E₂C 'like'); KO₂Bu in t-butanol (E₂H'like') and their solvolysis in acetone water mixtures (SN₁+E₁).

\[
RCHCICICH_3 + Br^- 
\]

SN₂

\[
RC\alpha H Br C\beta H_2 CH_3
\]

XVIII

\[
RCH=CHCH_3 + Br^-
\]

e₁

RCH=C=CHCH_3

solvolysis products

R = H, CH₃, C₆H₅, 4-CHOCH₃, 4-NO₂CH₃, 4-C₆H₅CH₃
Rate constants for the E$_2$C 'like' dehydrobromination reactions of bromide ion in acetone vary by only a factor of 5 times from R = 4-nitro phenyl to R = 4-methyl phenyl. However, the same change in substituents causes a rate increase of $10^5$ for the solvolysis reaction. If the 4-methoxy derivative is included the solvolysis range is $10^8$. Unfortunately, the rate constant for E$_2$C 'like' dehydrobromination could not be determined but a generous estimate is made in TABLE XVI which gives an E$_2$C 'like' range of $10^2$. The comparison of the R = methyl to R = phenyl result also illuminates the large differences between the E$_2$C 'like' and solvolysis transition states. The E$_2$C 'like' rate constant increases 20 times while the solvolysis rate constant increases by $10^3$.

A Hammet $\rho$-$\sigma$ plot can also be constructed as in Figure 5 using rate constants in TABLES XVI and XVII. The graph consists of a plot of log k vs $\sigma$ for solvolysis, E$_2$C 'like' and SN$_2$ reactions. The $\rho$ value determined for solvolysis is -5.30 which compares favourably with $\rho = -4.54$ for the solvolysis of 2-phenyl-2-chloropropane in 90% acetone water at $25^\circ C$. The $\rho$ value of $< -0.6$ for the E$_2$C 'like' reaction is clearly very much less than the $\rho$ values usually obtained for solvolysis of benzylic compounds.

According to the Hammond Postulate the transition state for the endoenergetic first step of the solvolysis reaction must be very much like the energetic carbonium ion intermediate involved in the solvolysis reaction. Therefore the transition state for the solvolysis reaction is a good model for a "paene carbonium" E$_2$ transition state, if it exists. The comparative electronic effects of $\alpha$ substituents on the rate of the E$_2$C
Figure 5

Hammett Plot of log k vs $\sigma^+$ for $E_2\ C$ 'like' dehydrobromination $SN_2$ substitution and solvolysis reactions of para substituted 1-aryl-1-bromopropanes as in Figure 4. The results are taken from TABLES XVI and XVII.

The Hammett equation, $log k = \rho \sigma + C$, is further illustrated graphically in Figure 5. The value of $\rho$ for $E_2\ C$ 'like' reactions is approximately -0.6. The solvolysis mechanism (as in Figure 5) is clearly indicated by the higher values of $\rho$ for solvolysis reactions (Table XVII). The $E_2\ C$ 'like' mechanism is utilized for bromide promoted dehydrobromination of l-bromo l-phenylpropanes.
'like' reaction and the rate of the solvolysis reaction is, therefore, a measure of the amount of positive charge at $C_a$ in the $E_2$ 'like' transition state.

The $E_2$ 'like' transition state is very insensitive to electronic effect of substituents relative to the solvolysis transition state as exemplified by the rate constants in TABLE XVI and the Hammet p values of $-5.30$ for solvolysis and $<-0.6$ for $E_2$ 'like' dehydrorbomira tion of 1-bromo-1-aryl propanes. Clearly the $E_2$ 'like' transition state has very little, if any, positive charge at $C_a$, i.e. the "paene carbonium" $E_2$ transition state is not utilised for bromide promoted dehydrorbomira tions of 1-bromo-1-aryl propanes.

(ii) Comparison of transition states for $SN_2$ substitution reactions and $E_2$ 'like' $\beta$-elimination reactions.

The nature of the charge distribution and bonding arrangement about $C_a$ is further identified by comparison of the electronic and steric effects of a substituents on the $E_2$ 'like' transition state to their effects on the $SN_2$ and $E_2H$ transition states. The rate constants needed for such a comparison are presented in TABLE XVII

**TABLE XVII**

Rate constants ($\log k_2$) for $SN_2$, $E_2$ 'like' and $E_2H$ 'like' reactions of 1-R-1-bromo propanes (XVIII), as in Figure 6 and rate constants ($\log k_2$) for the $SN_2$ reaction of $RCH_2Br$ (XIX) with $NBu_4Cl$ in acetone at $0^\circ C$.

<table>
<thead>
<tr>
<th>R</th>
<th>$SN_2$ (XIX)$^a$</th>
<th>$SN_2$ (XVIII)$^b$</th>
<th>$E_2C$(XVIII)$^c$</th>
<th>$E_2H$(XVIII)$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\log k_2$</td>
<td>$\log k_2$</td>
<td>$\log k_2$</td>
<td>$\log k_2$</td>
</tr>
<tr>
<td>H</td>
<td>-0.8$^g$</td>
<td>-2.0$^g$</td>
<td>-5.94$^h$</td>
<td>-5.64$^h$</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>-3.4$^f$</td>
<td>-3.43</td>
<td>-4.68$^h$</td>
<td>-6.18$^h$</td>
</tr>
<tr>
<td>C$_6$H$_5$</td>
<td>-1.81</td>
<td>-2.18</td>
<td>-3.36</td>
<td>-4.72$^i$</td>
</tr>
<tr>
<td>4NO$_2$-C$_6$H$_4$</td>
<td>-0.96</td>
<td>-1.75</td>
<td>-3.58</td>
<td>-</td>
</tr>
<tr>
<td>4CH$_3$-C$_6$H$_4$</td>
<td>-</td>
<td>-1.76</td>
<td>-2.91</td>
<td>-</td>
</tr>
<tr>
<td>4CH$_3$O-C$_6$H$_4$</td>
<td>-1.41</td>
<td>-</td>
<td>&lt;-1.41$^e$</td>
<td>-</td>
</tr>
</tbody>
</table>
The rate constants for SN₂ reactions of para substituted 1-aryl-1-bromo propanes in Table XVII show the same trends as the rate constants for SN₂ reactions of para substituted phenyl bromo methanes. Electron withdrawal and electron donation both give increases in rate. The reasons for this are well understood \(^{13}\), and are due to the rate enhancement by both 'loosening' and 'tightening' of the SN₂ transition state. Although this effect is apparent, it is by no means a large effect. In fact, the SN₂ transition state is relatively insensitive to the electronic effects of para aromatic substituents. The 4-methoxy benzyl bromide substitutes 3 times faster than benzyl bromide while in the solvolysis reactions the 4-methoxy derivative accelerates the rate \(10^4\) times relative to the 4-hydro derivative (Tables XVI and XVII).

The E₂C 'like' reactions of 1-aryl-1-bromo propanes are similarly insensitive to electron donation and withdrawal. In Figure 5 the Hammett \(\rho - \sigma^+\) plot is a slight curve, similar to the slight curve for the SN₂ reaction. The evaluation of these results and the conclusions arising must be viewed with cautious reservation due to two inherent problems. The charging of a substituent may cause a shift in the position that the transition
state occupies in a given mechanistic spectrum, e.g. the $\text{SN}_2$ reactions of benzylic systems. Secondly, small variations in rate constant which involve only small free energy changes may be caused by slight differences in other aspects of the ground state and transition state, e.g. solvation of the ground state and transition state. It is certainly preferable to be considering large effects as found with solvolysis reactions of 1-aryl-1-bromo propanes in TABLE XVI.

Irrespective of these problems, it is clear that both the $\text{SN}_2$ and $\text{E}_2\text{C}'$ like' transition states are only slightly sensitive to electronic effects of $\alpha$ substituents. A measure of this relative insensitivity is the comparison of rate increments on changing $R$ = methyl to $R$ = phenyl in 1-R-1-bromo propanes for $\text{SN}_2$, $\text{E}_2\text{C}'$ like' and solvolysis reactions. For $\text{SN}_2$ and $\text{E}_2\text{C}'$ like' reactions there is a 20-fold increase in rate while for the solvolysis reactions there is a $10^3$ increase in rate. When it is considered that all systems pass through $sp^2$ hybridised transition states and within the spectrum of transition state structures available to $\text{SN}_2$ reactions there exists a structure which has almost as much charge at $C_\alpha$ as the solvolysis intermediate, and this structure is postulated as very 'loose' with markedly decreased steric considerations, the difference between the 20-fold and $10^3$ increments is even more remarkable.

It is not clear why the $\text{SN}_2$ transition state on changing $R$ from methyl to phenyl to 4-methoxy phenyl in 1-R-1-bromo propane does not move towards the very 'loose' extreme of the $\text{SN}_2$ transition state spectrum and undergo the large rate accelerations experienced for the solvolysis transition state. A simple explanation of the insensitivity of $\text{SN}_2$ and $\text{E}_2\text{C}'$ like' reactions to electronic effects of $\alpha$-substituents could be that the interactions of the leaving group and nucleophile on opposite sides of $C_\alpha$ with both lobes of the developing $p$-orbital inhibits strong conjugation of the $p$-orbital with the $\pi$ system of the benzene ring. This explanation infers $C_\alpha$ - base interaction in the $\text{E}_2\text{C}'$ like' transition state.

It is when steric effects are considered that the distinct differences between the $\text{E}_2\text{C}'$ like' and $\text{SN}_2$ transition states is apparent. Clearly this is because the $\text{SN}_2$ transition state involves a one carbon
reaction centre and the $E_2C$ 'like' transition state involves a two carbon reaction centre. The $E_2C$ 'like' transition state is 'looser' than the $SN_2$ transition state. Since non-bonding interactions fall off rapidly with distance, it would be expected that the steric retardation experienced in the $SN_2$ reactions should not be found with $E_2C$ 'like' reactions. In TABLE XVII the rate of the $SN_2$ reaction of XVIII decreases by 30 times on changing from $R = H$ to $R = \text{methyl}$ while the rate of the $E_2C$ 'like' reaction of XVIII increases 20 times. In the tight $SN_2$ transition state steric hindrance is increased with increasing carbon substitution whereas in the 'loose' $E_2C$ 'like' transition state steric compression is decreased relative to the ground state both at $C_a$ and $C_\beta$. Therefore the individuality of the $SN_2$ and $E_2C$ 'like' transition states is established.

Therefore, in their response to electronic effects of a substituents, the $SN_2$ and $E_2C$ 'like' transition states are very similar but in their response to steric effects they are vastly different. Bunnett used the difference in steric effects of substituents as evidence to discard the $E_2C$ 'like' transition state. However, he failed to consider other major factors.

(iii) Comparison of transition states for $E_2C$ 'like' and $E_2H$ 'like' β-elimination reactions.

It was not possible to determine the rate constants for the KO-t-bu promoted dehydrobromination of any para substituted 1-aryl-1-bromo propanes other than the parent hydro compound. The para-methyl and para-methoxy derivatives solvolysed too fast in t-butanol while in the para-nitro derivative the nitro group reacted rapidly with the t-butoxide. However, the results for variation of $R = \text{hydrogen, methyl and phenyl}$ in 1-$R$-1-bromo propanes in TABLE XVII are sufficient to establish the distinction between the $E_2H$ and $E_2C$ 'like' transition states.

The $E_2H$ 'like' transition state, as described by Weinstein and Parker, is "paene carbanion like" with relatively small charge developed at $C_a$. Therefore the rate of $E_2H$ 'like' reactions should not be greatly affected by changes in the electronic effect of a substituents or by 'normal'
steric changes in a substituents. As pointed out previously, the rate of $E_2C$ 'like' eliminations of 1-R-1-bromo propanes in TABLE XVII are increased 20 times on changing from $R = \text{hydrogen}$ to $R = \text{methyl}$ and increased 20 times by changing $R = \text{methyl}$ to $R = \text{phenyl}$. The rate of $E_2H$ 'like' reactions are decreased 4 times on changing from $R = \text{hydrogen}$ to $R = \text{methyl}$ but increased 30 times by changing $R = \text{methyl}$ to $R = \text{phenyl}$. Certainly it is difficult to separate steric and electronic effects on rate when such small rate differences are apparent but the trends for both reactions are clear. The rate variations for changing $\alpha$-alkyl substituents in $E_2H$ eliminations are in accordance with a tight "paene carbonion" transition state while the results for $E_2C$ 'like' eliminations are as expected for a product like transition state and have been thoroughly analysed previously.$^4,17$

For eliminations promoted by KO-$t$-Bu in $t$-butanol the introduction of aromatic $\alpha$-substituents as $R$ in 1-R-1-bromo propanes, because of the ability of phenyl groups to conjugate charge, moves the transition state towards Bunnett's$^4$ central $E_2$ mechanism. Such movement is in agreement with olefin product ratios for phenyl substituted compounds as discussed in a later section.

The character of the $E_2C$ 'like' transition state as determined by comparison of a substituent effects in $E_2C$ 'like', $SN_2$, solvolysis and $E_2H$ reactions is -
(a) only slight positive charge at $C_\alpha$,
(b) similar arrangement of groups about $C_\alpha$ in both the $SN_2$ transition state and $E_2C$ 'like' transition state,
(c) an $E_2C$ transition state is a different total structure from both the $SN_2$ and $E_2H$ transition states,
(d) the results are consistent with a loose product like transition state.

B Charge distribution at the $\beta$ carbon atom

The major question to be answered concerns the nature and extent of charge development at the $\beta$ carbon atom. In view of the success
achieved, for the α carbon atom, by testing $\text{SN}_2^*$, $E_2^*$, and solvolysis transition states as models for the $E_2^*$ 'like' transition state, a similar survey was carried out for changes in β substituents. This aspect has been considered superficially by other workers $^4, 12, 14c, 15, 16c, d, 17, 20, 41$. However, analysis of the results in terms of an $E_2^*$ 'like' transition state and use of other transition states as models to determine charge distribution of the transition state has not been previously reported. Discussion of some of the earlier work is found in the Introduction.

(i) Electronic effects of substituents at the β carbon atom.

The alkyl systems studied for this analysis were the 1-R-2-bromo propanes (XX) where $R = \text{methyl, phenyl, 4-nitro phenyl and 4-methoxy phenyl}$. The $\text{SN}_2^*$, $E_2^* \text{C 'like'}, E_2^* \text{H}$ and solvolysis reaction schemes, for which rate constants were determined, are set out in Figure 6.

There are three possible olefinic products, from the elimination reaction and these are cis and trans-1-R propenes and 3-R propene. It should be noted that this system was chosen because the major product (trans-1-R propene) is the same as the major olefin from the study of α-substituent effects and predominates at greater than 95% of the total olefins. The rate constants for $\text{SN}_2^*$, $E_2^* \text{C 'like'}$ and solvolysis reactions in Figure 6 are presented in TABLE XVIII.

| TABLE XVIII |
| Rate constants ($\log k$) for the $E_2^* \text{C 'like'}, \text{SN}_2^*$ and solvolysis reactions of 1-R-2-bromo propane (XX) presented in Figure 6 |

<table>
<thead>
<tr>
<th>R</th>
<th>$E_2^* \text{C 'like}^{\text{a}}$</th>
<th>$\text{SN}_2^* + E_2^* \text{C 'like}^{\text{b}}$</th>
<th>$\text{SN}_2^* \text{C 'like}^{\text{c}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$</td>
<td>-6.3$^b$</td>
<td>-4.26</td>
<td>-3.3$^f$</td>
</tr>
<tr>
<td>C$_6$H$_5$</td>
<td>-4.39</td>
<td>-4.62</td>
<td>-4.24</td>
</tr>
<tr>
<td>4NO$_2$-C$_6$H$_4$</td>
<td>-3.77</td>
<td>-5.25</td>
<td>-3.78</td>
</tr>
<tr>
<td>4CH$_3$-O-C$_6$H$_4$</td>
<td>-4.53</td>
<td>-0.268</td>
<td>-4.24</td>
</tr>
</tbody>
</table>
The rate constants in TABLE XVIII show that the E₂C 'like' dehydrobrominations, like the solvolysis reactions and SN₂ reactions, are relatively insensitive to changes in the electronic effects of β-substituents. Since there can be no negative charge localised at the β carbon atom in either the SN₂ transition state or the carbonium ion like transition state, it is therefore indicated that little, if any, negative charge is localised at C₂ in the E₂C 'like' transition state.

Electron withdrawing β-substituents increase slightly the rates of E₂C 'like' dehydrobrominations in TABLE XVIII but slightly decrease the rates of both SN₂ and solvolysis reactions. Presumably the decrease in rate of SN₂ and solvolysis reactions is due to a long range inductive effect on the reaction centre.

Kevill and Cromwell¹⁵ also observed a slight rate enhancement in E₂C 'like' reactions. They used a Hammett ρ - σ⁻ plot for dehydrobrominations of para substituted 2-benzyl-2-bromo-1-indanones in acetonitrile, and determined ρ values of +.42 for chloride ion promoted dehydrobromination and +.16 for bromide ion promoted dehydrobromination. They also noted that these values were much less than the ρ values of +2 to +3 for β-elimination reactions of para substituted β-phenyl ethyl compounds with ethoxide in ethanol and with t-butoxide in t-butanol.⁴²,⁴³,⁶¹ They therefore concluded that there was very little charge at C₂ in bromide and chloride promoted dehydrobromination but considered the mechanism of elimination was the "Merged Mechanism"⁷,⁸.
Figure 6

The reaction pathways of 1-R-2-bromo propane (XX) with NBu$_4$Br and lutidine in acetone (E$_2$C 'like') at 75°C; NBu$_4$Cl in DMF at 25°C (SN$_2$); KO t-Bu in t-BuOH at 50°C and solvolysis in 50% acetone-water and 90% acetone-water.

\[
\text{R C} H_2 C_2 H Br \quad \text{CH}_3
\]

\[
\begin{align*}
\text{SN}_2 & \quad \text{NBu}_4 \text{Cl} \\
\text{R C} & \text{HCHC} \text{HClC} \text{H} \quad \text{CH}_3 \\
& \quad \text{Br}^{-} \\
\text{E}_2 \text{C like} & \quad \text{NBu}_4 \text{Br} \\
\text{R C} & \text{HCHCH} \quad \text{CH}_3 \\
& \quad \text{trans} \\
& \quad + \text{KBr} + t-\text{BuOH} \\
\text{Solvoly s} & \\
\text{R C} & \text{HCH}+ \text{CH} \quad \text{trans} \\
& \quad \text{CH}_3 \\
& \quad + H^+ + \text{Br}^{-} \\
\text{solvolysis products} & \\
\text{R} & = H, C_3 \text{H}_4 \text{O} \text{C} \text{H}_2 \quad 4 \text{C} \text{H}_3 \text{C} \text{H}_4 \\
& 4 \text{C} \text{H}_3 \text{C} \text{H}_4
\]

Since the benzyl indanone system and β-phenyl ethyl system are vastly different, both stereochemically and in their α substituents, it was considered that a better, relative indication of charge development at C$_\beta$ would be comparison of E$_2$C 'like' and E$_2$H 'like' reactions of the same substrate. Figure 7 is the Hammett ρ - σ plot of log $k_E^2$ vs σ for
E₂C 'like' bromide promoted dehydrobromination of para substituted 1-aryl-2-bromo propanes where \( \rho = +0.48 \). De Puy et al. have determined \( \rho \) values for E₂H 'like' dehydrobromination and dehydrotosylation of the same substrate system and report \( \rho \) values of +1.37 with ethoxide in ethanol and +1.84 with t-butoxide in t-butanol.

Clearly the E₂C 'like' transition state has less negative charge at C\( \beta \) than has the E₂H transition state. However, the \( \rho \) values for the E₂H 'like' \( \beta \) elimination reactions studied by De Puy are not as positive as may have been expected. These \( \rho \) values for E₂H 'like' elimination may be compared to the \( \rho \) values for the disproportionation reaction of para substituted benzaldehydes (\( \rho = +3.7 \)) to benzyl alcohols and benzoic acids and to the aromatic substitution reactions of para substituted 2-nitro phenyl fluorides with ethoxide ion in ethanol (\( \rho = +4.07 \)). Clearly, even in the E₂H 'like' transition state, there is not a fully developed negative charge at C\( \beta \).

(ii) Steric effects of substituents at the \( \beta \) carbon atom

Further evidence of the existence of a spectrum of transition states for bimolecular \( \beta \)-elimination reactions is found in TABLE XIX which contains rate constants for the SN₂ and E₂ reactions of 1-bromo-1-phenyl-2-R-ethanes with various bases (\( R = \)methyl or phenyl).

The bases range from E₂C 'like' bases such as chloride and bromide ion; to acetate ion which can utilise either E₂C 'like' or E₂H 'like' transition states and finally t-butoxide ion which is a strong E₂H 'like' base.

In TABLE XIX the \( \Delta \log k_{\text{Me}}^{\text{Me}} \) is +0.2 and +0.5 for E₂ 'like' bases, which indicates that the E₂C 'like' transition state is insensitive to both conjugative and electronic effects of the \( \beta \) phenyl substituent relative to the \( \beta \) methyl group. The \( \Delta \log k_{\text{Me}}^{\text{Me}} \) for t-butoxide is +1.9 indicating that the E₂H transition state is considerably stabilised by conjugative and electronic effects at C\( \beta \). The \( \Delta \log k_{\text{Me}}^{\text{Me}} \) for acetate ion is +0.8 which is between the E₂C 'like' and E₂H extreme values.
Figure 7
Hammet $\rho - \sigma^-$ plot of $\log k_2^E$ vs $\sigma^-$ for dehydrobromination of 1-aryl-2-bromo propane with $\text{NBu}_4\text{Br}$ in the presence of lutidine in acetone at $75^\circ\text{C}$ (Aryl = 4-Y phenyl).
This spectrum of values of $\Delta \log k^\text{Me} \text{E}_2 / \log k^\text{Me} \text{Ph}_2$ is further evidence for the occurrence of a variable amount of negative charge localized at C$_\beta$ as the transition state shifts from E$_2$C 'like' to E$_2$H 'like'. It is remarkable that the E$_2$C 'like' dehydrobrominations are insensitive to the conjugative effects of a $\beta$-phenyl substituent, considered in the light of Winston-Parker's description of the E$_2$C 'like' transition state (containing considerable double bond development). This result is rather perplexing.

### TABLE XIX

Effect of $\beta$ substituents on SN$_2$ and E$_2$ rates of reaction of 1-bromo-1-phenyl-2-R ethane (XXI)$_2^a,h$

<table>
<thead>
<tr>
<th>R</th>
<th>NBu$_4^+$ Br$^-$/Acetone 75°C</th>
<th>NBu$_4^+$ Cl$_2$/DMF 25°C</th>
<th>NBu$_4^+$ OAc/DMF 75°C</th>
<th>KOt-Bu$_4^+$ BuOH 75°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>log k$^E$</td>
<td>log k$^S$</td>
<td>log k$^E$</td>
<td>log k$^S$</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>-3.38</td>
<td>-4.2</td>
<td>-2.18</td>
<td>-2.0</td>
</tr>
<tr>
<td>C$_6$H$_5$</td>
<td>-3.16</td>
<td>-3.7$^e$</td>
<td>-2.9$^e$</td>
<td>-1.2$^f$</td>
</tr>
</tbody>
</table>

$\Delta \log k^\text{Me} \text{E}_2 / \log k^\text{Me} \text{Ph}_2$

- +0.22
- +0.5
- +0.8

Footnotes TABLE XIX

a The values of the $\beta$ elimination rate constants are in units of 1/mole/sec and are for production of trans olefin.
b Results are from TABLE I.
c Results are from TABLE VI.
d Results are from TABLE VII.
e Extrapolated from Results at 50°C by allowing a 10-fold rate decrease for a 25°C decrease in temperature.
f. Extrapolated from a result at 0°C using the same factor as in g.

g. Extrapolated using an Arrhenius plot from results at 25°C and 46.3°C.

h. $\Delta \log k_{Me}^{Ph}$ is the increment difference in $\log k_2$ between the result for $R = \text{methyl}$ and $R = \text{phenyl}$.

Since the rate of $E_2C$ 'like' reactions are largely insensitive to electronic effects of β-substituents, then for changes in simple alkyl β-substituents it would be expected that variations in rate would be due mainly to steric effects.

In TABLE XX a series of rate constants are presented for bromide ion promoted β elimination reactions of a series of alkyl structures (XXII) where $R_1$ and $R_2$ in XXII are varied from hydrogen to methyl to phenyl and para anisyl. Changing from a β-hydrogen to either a β-methyl, phenyl or p-anisyl in XXII causes increases in rate of up to 100-fold. However, it is noticeable that the β-methyl, phenyl and p-anisyl derivatives all have comparatively similar enhancements relative to β-hydrogen. This observation is apparent for cases when the C$\beta$ substitution level is changed from primary to secondary or from secondary to tertiary.

**TABLE XX**

Steric effects of β-substituents on rates of $E_2C$ 'like' dehydrobrominations and dehydratosylation of XXII with $\text{NBu}_4\text{Br}$ in acetone in the presence of 2,6-lutidine at 75°C

<table>
<thead>
<tr>
<th>$R_1$</th>
<th>$R_2$</th>
<th>$X$</th>
<th>$\log k_2$ $E_{c, d}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>H</td>
<td>OTos$^a$</td>
<td>-6$^b$</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>H</td>
<td></td>
<td>-3.7</td>
</tr>
<tr>
<td>C$_6$H$_5$</td>
<td>H</td>
<td></td>
<td>-3.6</td>
</tr>
<tr>
<td>4CH$_3$OC$_6$H$_4$</td>
<td>H</td>
<td></td>
<td>-3.81</td>
</tr>
<tr>
<td>4CH$_3$OC$_6$H$_4$</td>
<td>CH$_3$</td>
<td></td>
<td>-2.71</td>
</tr>
<tr>
<td>C$_6$H$_5$</td>
<td>C$_6$H$_5$</td>
<td></td>
<td>-2.7</td>
</tr>
<tr>
<td>H</td>
<td>H</td>
<td>Br</td>
<td>-7.1$^b$</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>H</td>
<td></td>
<td>-5.1$^c$</td>
</tr>
<tr>
<td>C$_6$H$_5$</td>
<td>H</td>
<td></td>
<td>-4.7$^e$</td>
</tr>
</tbody>
</table>
Footnotes TABLE XX

a OTos = p-toluene sulphonate.
b The rate constant is corrected for the statistical number of hydrogens available.
c Log $k_2^E$ is the rate constant for formation of trans olefin and is in units of 1/mole/sec.
d Results are from Reference 17.
e Results are from Table I.

Changes in $\beta$ substituents in the solvolysis transition state to a more bulky $\beta$-substituent would be expected to have only a slight accelerating effect on the rate of reaction. This is predicted because the reaction centre is one carbon removed from the substituent and therefore cannot fully take part in the steric decompression of the solvolysis transition state relative the ground state. In the SN$_2$ transition state rate decelerations are experienced due to steric compression in the transition state. However, this only becomes of major importance with very bulky $\beta$-substituents in a tight transition state, e.g. the "neopentyl effect"$^{25,27}$.

The situation is different in an E$_2$ transition state because $C_\beta$ is part of the reaction centre. If we consider the steric requirements of reactants and products of elimination, it should be possible to observe steric acceleration. In the reactants, bulky groups are in a tetrahedral configuration about $C_a$ and $C_\beta$ but in the olefinic product the groups are in a trigonal arrangement about both $C_a$ and $C_\beta$. If only the trans olefin is considered (so that eclipsing effects of vinyl groups may be neglected), then clearly, on bulk considerations alone, the product olefin is more stable than the reactants.

In a 'loose' olefin like E$_2$C transition state, because non-bonding interactions fall off rapidly with distance$^3$, there should be insignificant repulsive interactions of $a$ and $\beta$ substituents with either the leaving group or base. Therefore steric acceleration is predicted and has been observed in E$_2$C 'like' reactions in TABLE XX$^{17,20}$. 
The attractive effects of vicinal polar substituents

It is of interest to discuss $\beta$ substituent effects in the cyclohexyl compounds presented in TABLE XXI. An effect is observed where polar, vicinal groups on a cyclohexyl ring interact with each other and stabilise the 1,2-disubstituted compound. The existence of stabilisation by dispersion force interactions between polarisable groups like bromine, phenyl, $p$-toluene sulphinyl or $p$-toluenesulphonyl has been acknowledged previously $^3, ^4$.

### TABLE XXI

$\beta$-Substituent effects on $\text{SN}_2$ (log $k_2S$) and $\text{E}_2$ 'like' (log $k_2E$) reactions of 2-R cyclohexyl $p$-toluene sulphonates$^a$

\[
Y^- + \begin{array}{c}
\text{O} \\
\text{Tos}
\end{array} \xrightarrow{\text{R}} \begin{array}{c}
\text{R} \\
\text{H}
\end{array} + \begin{array}{c}
\text{R} \\
\text{R}
\end{array} + \begin{array}{c}
\text{R} \\
\text{Y}
\end{array}
\]

<table>
<thead>
<tr>
<th>R</th>
<th>$\text{NBu}_4\text{Cl, Me}_2\text{CO, }75^\circ\text{C}$</th>
<th>$\text{NBu}_4\text{OAc, Me}_2\text{CO, }75^\circ\text{C}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\text{cis-2-R}$</td>
<td>$\text{trans-2-R}$</td>
</tr>
<tr>
<td></td>
<td>log $k_E$</td>
<td>log $k_S$</td>
</tr>
<tr>
<td>H</td>
<td>-2.57$^c$</td>
<td>-2.57$^c$</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>-1.2</td>
<td>-3.25</td>
</tr>
<tr>
<td>(CH$_3$)$_2$CH</td>
<td>-0.6$^f$</td>
<td>-3.3$^g$</td>
</tr>
<tr>
<td>(CH$_3$)$_3$C</td>
<td>-0.2$^b$</td>
<td>-1.55$^b$</td>
</tr>
<tr>
<td>C$_6$H$_5$</td>
<td>-0.7$^e$</td>
<td>-3.81</td>
</tr>
<tr>
<td>Br</td>
<td>-3.64</td>
<td>-</td>
</tr>
<tr>
<td>4CH$_3$C$_6$H$_4$SO$_2$</td>
<td>-1.03$^b$</td>
<td>-4.05$^b$</td>
</tr>
<tr>
<td>4CH$_3$C$_6$H$_4$SO$_3$</td>
<td>-4.4$^d$</td>
<td>-4.3$^d$</td>
</tr>
</tbody>
</table>

Footnotes TABLE XXI

a Rate constants are in l/mole/sec. and are from Reference 20 except where otherwise stated. Dehydrotosylation forms 1-R cyclohexene from cis isomers and 3-R cyclohexene from trans isomers. In some cases rate constants have been extrapolated from values at lower temperature using activation energies determined directly for the reaction or from a closely related reaction.
The product olefin was not analysed by V.P.C., but is assumed to be that of anti Saytzeff elimination.

The rate has been adjusted to allow for two equivalent anti hydrogens.

The rate has been adjusted to allow for two equivalent leaving groups. Results are from TABLE IX.

Rates for dehydrobrosylation were converted to rates for dehydrotosylation by subtracting 0.6

Results are from Reference 11. Estimated from reaction of neomenthyl p-toluene sulphonate by assuming the 4-methyl substituent has negligible effect on rate.

Estimated from rates of reaction of menthyl tosylate (see footnote f).

4-Methyl phenyl sulphone.

Changing R, in the reactions of cis-2-R compounds with NBu₄Cl in acetone, from hydrogen to either methyl, phenyl, iso-propyl or t-butyl, gives a rate increase of 30 to 100-fold. This is comparable to the result in alicyclic systems, and the reasons for this have been previously expounded. However, for R = bromine and p-toluene sulphonate there is a marked deceleration of 10³ - 10⁴ in rate. This occurs not only for Saytzeff elimination but also for Hoffman elimination and bimolecular substitution. There is little possibility of some factor equally affecting the three different transition states for these reactions. Therefore it is considered that the rate deceleration is due to stabilisation of the ground state of the substrate which, of course, is the same for each reaction.

A rate deceleration is also experienced in the elimination and substitution reactions of the trans-2-R compound with chloride ion and the cis-2-R compound with acetate ion.

Clearly a rate deceleration would be predicted if an attractive interaction between the vicinal polar groups is postulated, as the relationship of the groups to each other are similar for both the cis and trans configuration. These interactions have been noted previously as
several examples of this are found in the literature, e.g. cis-1,2-dibromo ethene is more stable than the trans isomer.47

Also 1-bromo-1,2-diphenyl ethane dehydrobrominates with chloride ion in DMF 50 times faster than 1,2-dibromo-1,2-diphenyl ethane.48 From our understanding of steric effects on E2C'like' reactions it would be expected that the mono bromide should dehydrobrominate 50 - 100 times slower than the dibromide. Therefore the combined kinetic effects indicate a stabilisation interaction of the vicinal bromines which has a 2,000 to 5,000-fold effect on rate of elimination.

The energy involved in such a rate deceleration is 4 to 5 Kcal/mole. The reason for this effect becoming apparent lies in the nature of the SN2 and E2C'like' transition states. As the leaving group departs and forms the 'loose' transition state, the distance between the vicinal groups is increased and the orientation changed so that this stabilisation energy must necessarily be lost.

In summary, the β-substituent effects have elucidated several characteristics of the E2C 'like' transition state -

(a) There is only slight, if any, negative charge at Cβ in the E2C 'like' transition state, 

(b) The insensitivity of the E2C 'like' transition state to electronic effects allows a study of steric effects which suggest that the transition state is 'loose' and has a large degree of double bond character.

C Double bond development in the E2C 'like' transition state

If the E2C 'like' transition state is very product like (well developed double bond) then the logical prediction was that the olefinic product distribution would, without exception, closely parallel the equilibrium proportions. This infers, in saturated alkane systems, simple steric control of the relative free energies of the transition states leading to each olefin. However, when a double bond develops adjacent to some form of unsaturation, an important aspect to consider is conjugation of either the π system of the developing double bond, or any charge developed at Cα or Cβ. Investigation of both situations is
warranted because product distributions in both types illuminate characteristics of the $E_2C$ 'like' transition state.

Even in the simple alkyl systems there are factors which can distort the product distribution. The presence of the leaving group, nucleophile and proton, even in a 'loose' transition state, cannot be ignored. Their presence would increase the free energy difference between cis and trans arrangements in the transition state. Also solvation effects on the transition states will be different for comparisons of protic and aprotic solvents. Generally the trans : cis ratio should be increased by the steric effects of other atoms in the transition state and by changing from aprotic to protic solvents.

Simple steric considerations in the $E_2H$ 'like' transition state suggest that olefinic product distributions should follow relative free energies of reactant configurations. However, the 'tight' $E_2H$ transition state is markedly affected by inductive and conjugative effects of substituents. Therefore it is uncertain what the product distribution should be from any single reaction system. It is only possible to indicate the large differences between the product analyses for $E_2H$ and $E_2C$ 'like' reactions and use these differences to illuminate the double bond development in the $E_2C$ 'like' transition state.

(i) Saturated alkyl substrates

In TABLE XXII are presented the product distributions for various elimination and equilibration reactions of simple saturated alkyl systems.
<table>
<thead>
<tr>
<th>Substrate</th>
<th>Reaction type</th>
<th>Base</th>
<th>Temp °C</th>
<th>% Hof.</th>
<th>% Trans</th>
<th>% cis</th>
<th>[Hof.] [Sayt.]</th>
<th>[Trans] [cis]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-bromo butane</td>
<td>E2</td>
<td>NBu₄Br/Me₂CO</td>
<td>75</td>
<td>4m</td>
<td>82</td>
<td>14</td>
<td>0.042</td>
<td>5.9</td>
</tr>
<tr>
<td></td>
<td>E₂</td>
<td>NBu₄F/CH₃CN</td>
<td>50</td>
<td>11.6</td>
<td>68.9</td>
<td>19.5</td>
<td>0.131</td>
<td>3.53</td>
</tr>
<tr>
<td></td>
<td>E₂</td>
<td>NaOEt/DMSO</td>
<td>25</td>
<td>27.2</td>
<td>56.8</td>
<td>16</td>
<td>0.374</td>
<td>3.54</td>
</tr>
<tr>
<td></td>
<td>E₂</td>
<td>KOT- Bu/DMSO</td>
<td>50</td>
<td>30</td>
<td>54</td>
<td>16</td>
<td>0.429</td>
<td>3.4</td>
</tr>
<tr>
<td></td>
<td>E₂</td>
<td>KOT- Bu/t-BuOH</td>
<td>50</td>
<td>54</td>
<td>28</td>
<td>18</td>
<td>1.17</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td>Equil</td>
<td>KOT- Bu/DMSO</td>
<td>55</td>
<td>9m</td>
<td>64</td>
<td>27</td>
<td>0.099</td>
<td>2.4</td>
</tr>
<tr>
<td>2-methyl-3-butyl tosylate</td>
<td>E₂</td>
<td>NBu₄Br/Me₂CO</td>
<td>75</td>
<td>0.3n</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>E₂</td>
<td>KOT₄Bu/t-BuOH</td>
<td>50</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>E₁</td>
<td>Solv/t-BuOH</td>
<td>25</td>
<td>0.2j</td>
<td>-</td>
<td>-</td>
<td>0.002</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Equil</td>
<td>-</td>
<td>25</td>
<td>50n</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2-bromo-2-methyl butane</td>
<td>E₂</td>
<td>NBu₄Cl/Me₂CO</td>
<td>50</td>
<td>9n</td>
<td>-</td>
<td>-</td>
<td>0.099</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>E₂</td>
<td>KOT₄Bu/t-BuOH</td>
<td>50</td>
<td>73</td>
<td>-</td>
<td>-</td>
<td>2.70</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>E₁</td>
<td>Solv/Me₂CO</td>
<td>50</td>
<td>8.2j</td>
<td>-</td>
<td>-</td>
<td>1.00</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Equil</td>
<td>-</td>
<td>25</td>
<td>8.2j</td>
<td>-</td>
<td>-</td>
<td>0.09</td>
<td>-</td>
</tr>
<tr>
<td>2-methyl-3-pentyl tosylate</td>
<td>E₂</td>
<td>NBu₄Br/Me₂CO</td>
<td>75</td>
<td>7.5m</td>
<td>7.4</td>
<td>1.1</td>
<td>0.081</td>
<td>70-20</td>
</tr>
<tr>
<td></td>
<td>E₂</td>
<td>KOT₄Bu/t-BuOH</td>
<td>50</td>
<td>48.9</td>
<td>32.6</td>
<td>16.3</td>
<td>0.957</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>E₂</td>
<td>KOT₄Bu/t-BuOH</td>
<td>50</td>
<td>49.8</td>
<td>47.9</td>
<td>1.9</td>
<td>1.0</td>
<td>25.2</td>
</tr>
<tr>
<td></td>
<td>E₁</td>
<td>Solv/t-BuOH</td>
<td>50</td>
<td>7.0</td>
<td>7.0</td>
<td>0</td>
<td>0.91</td>
<td>730</td>
</tr>
<tr>
<td></td>
<td>Equil</td>
<td>KOT₄Bu/DMSO</td>
<td>55</td>
<td>8.4l</td>
<td>7.2</td>
<td>1.2</td>
<td>0.105</td>
<td>6.0</td>
</tr>
</tbody>
</table>
Footnotes TABLE XXII

a Determined by VPC analysis.
b Solvent contains excess 2,6-lutidine.
c Represents that portion of total olefinic products which was the less substituted (Hofmann) olefin from β-elimination of HX. Unless otherwise stated, the Saytzeff olefin was the only other product.
d Percentages of cis and trans isomers from β-elimination.
e The ratio of the total less substituted (Hofmann) olefin to total more substituted (Saytzeff) olefin.
f From Reference 28b.
g From Reference 38b. See also TABLE XV footnotes b and c.
h From Reference 29
i In gas phase from Reference 49. Equilibration of related olefins in DMSO and on activated alumina gives similar proportions.
j The equilibration product contains 8.2% 2-methyl-1-butene and 0.2% 3-methyl-1-butene.
k From Reference 50.
l Contained 16% 2-methyl-1-pentene.
m From TABLES XIII and XV.
n From Reference 17.
o From Reference 51.
p From Reference 52.

The olefinic ratios in TABLE XXII for E₂C 'like' reactions are very close to the equilibrium values (as predicted) and show the E₂C 'like' reactions to be the most trans Saytzeff oriented, bimolecular β-eliminations known, provided the requirement of anti geometry is not violated. Since the E₂C 'like' transition state is 'loose' and only slightly charged (if at all) at Cβ and Cα, then the best explanation of this close correlation is that the known transition state has a large degree of double bond character.

This correlation is not universal to all elimination reactions.

The olefinic product distribution in E₂H reactions of KOTBu in t-buOH with
all substrates in TABLE XXII show a large deviation away from the equilibrium distributions. It is apparent that a well developed double bond does not occur within the $E_2H$ transition state of simple alkyl system. For elimination reactions of strong H-bases in aprotic solvents (where solvation effects are decreased) passing through an $E_2H$ transition state, the base is not in close proximity to either $C_\beta$ or $C_\alpha$. Therefore it is not unexpected to find for elimination reactions of 2-bromo butane that the trans:cis ratio is relatively independent of changes from one strong H-base to another. Although the reservations previously mentioned, such as electronic and conjugative effects of substituents, need careful consideration, a pattern of steric effects emerges which is consistent with the structural description of the $E_2H$ transition state.

(ii) Unsaturated alkyl substrates

The analysis of olefinic product distributions is complicated by unsaturated $\alpha$ and $\beta$ substituents. For $E_2H$ reactions the conjugative and inductive effects are markedly increased. In fact, conjugative dispersion of charge and conjugative interactions with the developing double bond seem to dominate steric considerations in the $E_2H$ transition state.

In TABLE XXIII are presented the olefinic product distributions for reactions of several $\alpha$ and $\beta$ aryl substituted alkyl compounds with $E_2C$ and $E_2H$ bases.
### TABLE XXIII

Proportions of olefins from dehydrobromination of α and β aryl substituted alkyl bromides

<table>
<thead>
<tr>
<th>Substratea</th>
<th>Reaction type</th>
<th>Base/Solvent</th>
<th>Temp °C.</th>
<th>% Hof.</th>
<th>% Trans</th>
<th>% cis</th>
<th>[Hof.] [Sayt.]</th>
<th>[Trans] [cis]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Br-1,2-diphenyl ethane</td>
<td>E₂C</td>
<td>NBu₄Br/Me₂COᵇ</td>
<td>75</td>
<td>-</td>
<td>trans stilbene</td>
<td>cis-stilbene</td>
<td>-</td>
<td>49</td>
</tr>
<tr>
<td>E₂H</td>
<td>NBu₄OAc/DMF</td>
<td>25</td>
<td>-</td>
<td>98.6</td>
<td>2</td>
<td>0.4</td>
<td>-</td>
<td>250</td>
</tr>
<tr>
<td>E₂H</td>
<td>KO't-Bu/t-BuOH</td>
<td>25</td>
<td>-</td>
<td>99.4</td>
<td>0.6</td>
<td>0.7</td>
<td>-</td>
<td>170</td>
</tr>
<tr>
<td>E₂H</td>
<td>NaOCH₂/80%DMSO</td>
<td>25</td>
<td>-</td>
<td>99.3</td>
<td>0.7</td>
<td>-</td>
<td>-</td>
<td>140</td>
</tr>
<tr>
<td>-</td>
<td>Equil/DMF</td>
<td>37</td>
<td>-</td>
<td>99.05</td>
<td>0.05</td>
<td>-</td>
<td>-</td>
<td>2000</td>
</tr>
<tr>
<td>1-Br-1-phenyl propane</td>
<td>E₂C</td>
<td>NBu₄Br/Me₂COᵇ</td>
<td>75</td>
<td>-</td>
<td>trans-1-phenyl propene</td>
<td>cis-1-phenyl propene</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td>E₂H</td>
<td>KO't-Bu/t-BuOH</td>
<td>75</td>
<td>-</td>
<td>99</td>
<td>1.0</td>
<td>1.5</td>
<td>-</td>
<td>65</td>
</tr>
<tr>
<td>-</td>
<td>Equil/DMF</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1-Br-1-Ard propane</td>
<td>E₂C</td>
<td>NBu₄Br/Me₂COᵇ</td>
<td>75</td>
<td>-</td>
<td>trans-1-Ar propene</td>
<td>cis-1-Ar propene</td>
<td>-</td>
<td>80</td>
</tr>
<tr>
<td>-</td>
<td>Equil/MeCN</td>
<td>55</td>
<td>ca. 5</td>
<td>98.8</td>
<td>1.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2-Br-1-phenyl propane</td>
<td>E₂C</td>
<td>NBu₄Br/Me₂COᵇ</td>
<td>75</td>
<td>-</td>
<td>trans-1-phenyl propene</td>
<td>cis-1-phenyl propene</td>
<td>0.005</td>
<td>14</td>
</tr>
<tr>
<td>E₂H</td>
<td>KO't-Bu/t-BuOH</td>
<td>75</td>
<td>-</td>
<td>92.7</td>
<td>6.8</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>-</td>
<td>Equil/DMSO</td>
<td>50</td>
<td>0.03</td>
<td>98.4</td>
<td>1.6</td>
<td>0.0003</td>
<td>62</td>
<td></td>
</tr>
<tr>
<td>2-Br-2-cmethyl-1-phenyl propane</td>
<td>E₂C</td>
<td>NBu₄Br/Me₂COᵇ</td>
<td>60</td>
<td>-</td>
<td>22.0</td>
<td>-</td>
<td>-</td>
<td>0.28</td>
</tr>
<tr>
<td>E₂C</td>
<td>NBu₄Cl/Me₂COᵇ</td>
<td>60</td>
<td>-</td>
<td>13.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.16</td>
</tr>
<tr>
<td>-</td>
<td>Equil/MeOH</td>
<td>55</td>
<td>ca. 5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.05</td>
</tr>
</tbody>
</table>
Footnotes TABLE XXIII

a Results, except where stated, are taken from TABLES XIII and XV.
b Contains excess 2,6-lutidine.
c From Reference 14c.
d Ar = 4-nitro phenyl.
e From Reference 35. Determined by refluxing the mixture of olefins in methanol-hydrochloric acid mixtures.
f See TABLE XV for methods of equilibration.

A rather perplexing feature of TABLE XXIII is the difference in olefin proportions resulting from $E_2C$ reactions and proportion of olefins from equilibration reactions. However, the proportions of olefins from $E_2H$ reactions do closely parallel the equilibrium proportions.

Clearly it is difficult to separate aromatic stabilisation of a transition state either by mesomeric dispersion of developed charge or conjugative interaction with the π system of a double bond. Therefore it is difficult to interpret rate enhancement effects of aromatic substituents on $E_2H$ reactions as being due to either dispersion of charge or increasing the double bond character in the $E_2H$ transition state.

$\beta$-Elimination reactions with strong H-bases have previously been shown to involve a significant degree of conjugation of charge to unsaturated α and β substituents \cite{4, 12, 17, 20}. If aromatic conjugation of charge is to occur, the phenyl ring must become coplanar to the developing double bond, i.e. in the case of 1-bromo-1,2-diphenyl ethane, trans stilbene stereochemistry may be obtained. It may be argued that both conjugation with charge and conjugation with a developing double bond (similar to conjugation in free trans stilbene) will give the same stereochemistry in the transition state. However, it is felt that conjugation with a well developed double bond in a transition state is not greatly significant.

The reasons for this proposal are -

(i) It is difficult to visualise a transition state with both considerable
charge at $\alpha$ and $\beta$ and a well developed double bond.

(ii) For reasons discussed later, there is a lack of conjugation of the well developed double bond in the $E_2C$ 'like' transition state which suggests that a double bond in a transition state does not experience the same conjugative stabilisation as the product olefin.

Winftein and Parker have always considered that in the $E_2C$ 'like' transition state there is considerable double bond development. If it is considered, by analogy with the product olefins, that there should be conjugation of this developing double bond with aromatic substituents in the transition state, then the kinetic olefin proportions resulting should parallel the equilibrium olefin proportions as determined experimentally with some slight deviation due to the presence of leaving group, base and $\beta$-protons.

However, if it is considered that the $E_2C$ 'like' transition state and the product olefin are different, then it is probable that the transition state shall have some distinctive characteristics such as a lack of conjugation of the double bond with unsaturation in $\alpha$ and $\beta$ substituents. If this last postulate is true, then the olefin proportions should be governed by the steric requirements of the $\alpha$ and $\beta$ substituents so that the same pattern found in TABLE XXII should emerge for $E_2C$ 'like' reactions in TABLE XXIII.

This trend is found for dehydrobromination reactions promoted by bromide ion in acetone and is shown in TABLE XXIV. Included is the equilibrium olefin proportion for cis and trans-2-butenes and 1-butene as an example of steric control operating in an $E_2C$ 'like' transition state.
TABLE XXIV

Olefins proportions from dehydrobromination of substituted bromo ethanes \( R_1 CHBrCH_2 R_2 \) with \( NBu_4 Br \) in acetone

<table>
<thead>
<tr>
<th>( R_1 )</th>
<th>( R_2 )</th>
<th>Reaction</th>
<th>( % ) Hofmann</th>
<th>( % ) trans</th>
<th>( % ) cis</th>
</tr>
</thead>
<tbody>
<tr>
<td>( CH_3 )</td>
<td>( CH_3 )</td>
<td>E_2 C 'like'</td>
<td>4</td>
<td>82</td>
<td>14</td>
</tr>
<tr>
<td>( CH_3 )</td>
<td>( C_6H_5 )</td>
<td>&quot;</td>
<td>0.5</td>
<td>92.7</td>
<td>6.8</td>
</tr>
<tr>
<td>( C_6H_5 )</td>
<td>( CH_3 )</td>
<td>&quot;</td>
<td>-</td>
<td>99</td>
<td>1.0</td>
</tr>
<tr>
<td>( C_6H_5 )</td>
<td>( C_6H_5 )</td>
<td>&quot;</td>
<td>-</td>
<td>98</td>
<td>2.0</td>
</tr>
<tr>
<td>( CH_3 )</td>
<td>( CH_3 )</td>
<td>Equil</td>
<td>9</td>
<td>64</td>
<td>27</td>
</tr>
<tr>
<td>( C_6H_5 )</td>
<td>( C_6H_5 )</td>
<td>&quot;</td>
<td>-</td>
<td>99.05</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Footnotes TABLE XXIV

a Results taken from TABLES XXII and XXIII.

b Equilibration results from TABLES XXII and XXIII. The result for the butene system is considered as representative of steric control of olefin proportions whereas the stilbene system is considered representative of combined steric control and conjugative control.

Dehydrobromination of 2-bromo butane gives 14\% cis-2-butene while the equilibrium proportion is 27\% cis-2-butene. This is expected because of the presence of the base, leaving group and \( \beta \)-proton. If the \( E_2 C \ 'like' \) reactions of the compounds with \( R_1 \) or \( R_2 \) as phenyl have insignificant conjugation of the phenyl group with the double bond, then the kinetic olefin proportions should deviate from the result for 2-bromo-butane by an amount equivalent to the difference in steric requirements of a phenyl group relative to a methyl group in the transition state. In TABLE XXIV this effect is apparent and it should also be noticed that the proportion of cis olefin differs greatly from the combined conjugative and steric control of the stilbene system.
This evidence therefore indicates that there is little, if any, conjugation of the developing double bond with phenyl substituents, although this does not exclude conjugation with developed charge as found in the E₂ transition state.

The structure of the E₂ 'like' transition state as pertaining to double bond development is therefore described as having a well developed double bond which is insensitive to inductive and conjugative effects of substituents. This idea was then tested by making a prediction of kinetic olefinic proportions resulting from a model reaction.

In the β-elimination of tosyllic acid from 3-methyl-1-phenyl-2-butyl tosylate it was predicted that for elimination using bromide ion in acetone, 1-phenyl-3-methyl-2-butene should be the major olefinic product whereas the most stable olefin (due to conjugation) is trans-1-phenyl-3-methyl-1-butene. The conjugated olefin was also predicted as the major product from KOTBu/t-BuOH promoted elimination of tosyllic acid from the same substrate. The results are presented in TABLE XXV.

<table>
<thead>
<tr>
<th>Base/Solvent</th>
<th>cis</th>
<th>trans</th>
<th>2-ene</th>
<th>[trans]</th>
<th>[1-ene]</th>
</tr>
</thead>
<tbody>
<tr>
<td>RCH₂CHOTosCH₃</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NBu₄Br/Me₂CO₂⁻</td>
<td>0.4</td>
<td>8.65</td>
<td>90.1</td>
<td>22</td>
<td>0.10</td>
</tr>
<tr>
<td>KOTBu/t-BuOH</td>
<td>1.5</td>
<td>95.5</td>
<td>2.8</td>
<td>0.016</td>
<td>35</td>
</tr>
<tr>
<td>Equil/DMSO¹</td>
<td>0.15</td>
<td>63.1</td>
<td>33.0</td>
<td>420</td>
<td>1.92</td>
</tr>
<tr>
<td>RCH₂CHOTosCH₃</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NBu₄Br/Me₂CO₂⁻</td>
<td>0.1</td>
<td>7.4</td>
<td>92.5</td>
<td>74</td>
<td>0.081</td>
</tr>
<tr>
<td>KOTBu/t-BuOH</td>
<td>16.3</td>
<td>32.6</td>
<td>51.1</td>
<td>2.0</td>
<td>0.97</td>
</tr>
<tr>
<td>Equil/DMSO¹</td>
<td>1.2</td>
<td>7.2</td>
<td>80</td>
<td>6.0</td>
<td>0.105</td>
</tr>
</tbody>
</table>
The results in TABLE XXV are exactly as predicted from the prior description of the $E_2$ 'like' transition state. The olefin proportions from dehydrotosylation by bromide ion are similar for both $R = \text{methyl}$ and phenyl and both are comparable with the olefinic equilibrium proportions for $R = \text{methyl}$. This suggests, in agreement with the previous evidence, that the phenyl ring is only utilising steric control of orientation in a similar way to a methyl group.

Another way of conveying this idea is to consider the equilibrium proportions for $R = \text{methyl}$ represents steric control of orientation and the proportions for $R = \text{phenyl}$ represents steric plus conjugative control of orientation. It is apparent, using this standard, that dehydrotosylation with bromide ion more closely correlates with steric control, without interference from other effects. In fact the $[1\text{-ene}]:[2\text{-ene}]$ ratios are remarkably similar with values of $0.10$ ($R = \text{C}_6\text{H}_5$ for $-\text{HOTos}/\text{Br}^-$), $0.081$ ($R = \text{CH}_3$ for $-\text{HOTos}/\text{Br}^-$) and $0.105$ ($R = \text{CH}_3$, equilibration).

Probably the most important aspect of TABLE XXV is not the mechanistic information derived from the results but the synthetic implications. Strong C-bases are now able to perform $\beta$-elimination reactions to give products which were previously unobtainable via a $\beta$-elimination reaction using a strong H-base. An example of this is 1-phenyl-3-methyl-2-butene as the major product from 1-phenyl-3-methyl-2-butyl tosylate and bromide.
ion in acetone. Other predictions can also be made. 3-Bromo-4-methyl methyl pentanoate would be expected to give predominantly 4-methyl methylpent-3-enoate with bromide ion in acetone but predominantly 4-methyl methylpent-2-enoate with any strong H-base.

In summary, the analysis of β-elimination reaction transition states as reactant or product like, because of its sensitivity to various unconnected factors, is indicative but not definitive of how product like a transition state is. However, several different approaches give results in agreement with the approach used in this section (e.g. substituent effects, leaving group effects, and solvation effects). Therefore several conclusions can be drawn.

(i) There is a considerable amount of double bond development in the E₂C 'like' transition state. This is greater than is found in E₂H reactions of simple saturated alkyl substrates.

(ii) There is only slight, if any, conjugation of the developing double bond with a or β aryl substituents.

D Leaving group tendencies in β-elimination reactions

Hoffman used tosylate-bromide rate ratios to study the character of the SN₂ transition. This form of approach was later extended to elimination reactions. (A tosylate-bromide rate ratio is defined as the ratio of the rate constant for an alkyl tosylate to the rate constant for the related alkyl bromide where the same type of reaction is studied and the products are the same.)

Hoffman maintained that for SN₂ reactions a low tosylate-bromide rate ratio indicated small Cₐ-leaving group bond breaking and high tosylate bromide rate ratios indicated large Cₐ-leaving group bond breaking. Hofmann then attempted to extrapolate this treatment to the β-elimination transition state as proof of Cₐ-base interaction even with strong H-bases. Although his basic premise is tenable, his treatment of the β-elimination transition state can best be considered inconclusive. The problem associated with his treatment is the complexity of the spectrum of
E₂ transition states. Therefore the restriction must be placed on leaving
group analyses using tosylate-bromide rate ratios that they represent
the degree of C₁-leaving group bond breaking in the transition state.

It was previously recognised¹⁰,⁵⁵ that the 'looseness' of a
transition state can vary with several factors, notably the degree of sub­
stitution. Therefore it was considered that more information about relative
degrees of 'looseness' in an E₂ transition would be available from a
comparison of tosylate-bromide rate ratios for simultaneous SN₂ and E₂
reactions. In TABLE XXVI are presented various tosylate-bromide rate
ratios [log k (OTos) - log k (Br)] for SN₂ and E₂ reactions.

**TABLE XXVI**
Leaving group tendencies of tosylates and bromides in
SN₂ and E₂ reactions

<table>
<thead>
<tr>
<th>Reactants</th>
<th>T°C</th>
<th>Solvent</th>
<th>log k(OTos) - log k (Br)</th>
<th>SN₂</th>
<th>E₂</th>
<th>Δ(SN₂-E₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃₂CH₂CH₂X</td>
<td>75</td>
<td>Me₂CO</td>
<td>0.00</td>
<td>0.41</td>
<td>-0.41</td>
<td></td>
</tr>
<tr>
<td>CH₃₂CH₂CH₂X</td>
<td>75</td>
<td>Me₂CO</td>
<td>0.78</td>
<td>0.97</td>
<td>-0.19</td>
<td></td>
</tr>
<tr>
<td>CH₃₂CH₂CH₂X</td>
<td>75</td>
<td>Me₂CO</td>
<td>0.79</td>
<td>0.69</td>
<td>+0.10</td>
<td></td>
</tr>
<tr>
<td>CH₃₂CH₂CH₂X</td>
<td>55</td>
<td>EtOH</td>
<td>1.06</td>
<td>0.95</td>
<td>+0.11</td>
<td></td>
</tr>
<tr>
<td>CH₃₂CH₂CH₂X</td>
<td>75</td>
<td>EtOH</td>
<td>0.48</td>
<td>0.13</td>
<td>+0.35</td>
<td></td>
</tr>
<tr>
<td>CH₃₂CH₂CH₂X</td>
<td>75</td>
<td>EtOH</td>
<td>0.70</td>
<td>0.12</td>
<td>+0.58</td>
<td></td>
</tr>
<tr>
<td>CH₃₂CH₂CH₂X</td>
<td>75</td>
<td>EtOH</td>
<td>0.53</td>
<td>-0.26</td>
<td>+0.79</td>
<td></td>
</tr>
<tr>
<td>CH₃₂CH₂CH₂X</td>
<td>75</td>
<td>t-BuOH</td>
<td>1.28</td>
<td>0.00</td>
<td>+1.28</td>
<td></td>
</tr>
<tr>
<td>CH₃₂CH₂CH₂X</td>
<td>75</td>
<td>t-BuOH</td>
<td>&gt;1.6</td>
<td>0.38</td>
<td>&gt;+1.2</td>
<td></td>
</tr>
<tr>
<td>CH₃₂CH₂CH₂X</td>
<td>55</td>
<td>EtOH</td>
<td>0.57</td>
<td>-1.10</td>
<td>+1.67</td>
<td></td>
</tr>
<tr>
<td>CH₃₂CH₂CH₂X</td>
<td>40</td>
<td>t-BuOH</td>
<td>1.04</td>
<td>-0.80</td>
<td>+1.84</td>
<td></td>
</tr>
<tr>
<td>CH₃₂CH₂CH₂X</td>
<td>50</td>
<td>Me₂CO</td>
<td>0.25</td>
<td>0.24</td>
<td>+0.01</td>
<td></td>
</tr>
<tr>
<td>CH₃₂CH₂CH₂X</td>
<td>30</td>
<td>EtOH</td>
<td>1.00</td>
<td>-1.00</td>
<td>+2.00</td>
<td></td>
</tr>
<tr>
<td>cis OThs +Cl⁻</td>
<td>75</td>
<td>Me₂CO</td>
<td>ca. .5</td>
<td>k</td>
<td>+0.3</td>
<td>+0.1</td>
</tr>
<tr>
<td>cis OThs +Cl⁻</td>
<td>75</td>
<td>Me₂CO</td>
<td>ca. .5 k</td>
<td>k</td>
<td>+0.4</td>
<td>+0.0</td>
</tr>
<tr>
<td>cis Br +Cl⁻</td>
<td>75</td>
<td>Me₂CO</td>
<td>k</td>
<td>k</td>
<td>+0.8</td>
<td>-0.3</td>
</tr>
<tr>
<td>cis Br +Cl⁻</td>
<td>75</td>
<td>Me₂CO</td>
<td>k</td>
<td>k</td>
<td>-1.84</td>
<td>+2.3</td>
</tr>
<tr>
<td>cis Br +Cl⁻</td>
<td>75</td>
<td>Me₂CO</td>
<td>ca. .9 k</td>
<td>k</td>
<td>-1.8</td>
<td>+2.7</td>
</tr>
<tr>
<td>cis Br +Cl⁻</td>
<td>75</td>
<td>Me₂CO</td>
<td>ca. .9 k</td>
<td>k</td>
<td>-1.8</td>
<td>+2.7</td>
</tr>
</tbody>
</table>
Footnotes TABLE XXVI

a  Ar = 4-nitrophenyl; Ph = phenyl; OAc = acetate; OTos = p-toluene sulphonate.

b  Log k for reaction with X = tosylate minus log k for same reaction with X as bromine.

c  Data for cyclohexyl tosylate is from Reference 9 and results for cyclohexyl bromide is from Reference 58.

d  From Reference 55.

e  From Reference 16b.

f  From References 9 and 59.

g  From Reference 57.

h  From Reference 17.

i  From TABLE IX. Due to the complexity of the reaction schemes no rate could be exactly determined.

j  Tosylate result from TABLE IX. Bromide result from Reference 12.

k  The average value for all the other SN₂ ratios in the same solvent.

The results for the disubstituted cyclohexyl derivatives in TABLE XXVI are made a little uncertain by attractive forces between the vicinal polar substituents, and by the complexity of the reaction pathways available. Log k (OTos) - log k (Br) values for SN₂ reactions were unable to be determined accurately so that the average ratio for all the other SN₂ reactions in the same solvent in TABLE XXVI (0.5 in Me₂CO and 0.9 in EtOH) were assigned as representative of the actual value.

Despite the obvious doubts associated with this average value, the differences in Δ (SN₂-E₂) of up to ±3.0 log units are in excess of the maximum errors anticipated and therefore do not alter the theoretical analysis of the results.

It has previously been established from a study of solvent effects that the E₂H transition state was tighter than both the E₂C 'like' and SN₂ transition states, which are of comparable 'looseness'. From
Hoffman's study of tosylate-bromide rate ratios it would therefore be expected that there would be only small differences in ratios for SN₂ and E₂C 'like' transition states (i.e. $\Delta (SN₂-E₂) \approx 0$). However, for the E₂H transition state the tosylate-bromide rate ratio would be expected to be much less than for the SN₂ transition state. This is certainly observed in TABLE XXVI where $\Delta (SN₂-E₂) \approx 0$ for reactions of chloride and thio-phenoxide but $\Delta (SN₂-E₂) = 1 - 3$ for reactions of t-butoxide and ethoxide.

It is also apparent in TABLE XXVI that there is a whole range of $\Delta (SN₂-E₂)$ values between the E₂C 'like' and E₂H extremes. In fact, the $\Delta (SN₂-E₂)$ values increase as the H-base strength increases, i.e. as the E₂H character of the transition state increases. This suggests that the E₂C 'like' transition state described by Weinstein and Parker exists and also that there is a whole spectrum of transition states between the E₂C 'like' and E₂H extremes. As a tosylate-bromide rate ratio only measures the C⁻-leaving group bond breaking in the transition, it is not a criterion for other properties of the transition state. These trends could be explained in terms of Bunnett's E₂ spectrum of transition states. However, they closely parallel the trends which would be predicted for an E₂C-E₂H spectrum.

It was previously established that a β-bromine substituent is very acidifying and increases the E₂H character of the β-elimination transition state. Since $\Delta (SN₂-E₂)$ is more positive for acetate ion than for chloride ion, it is considered that the acetate promoted elimination is more E₂H like when a β bromine substituent is present. As expected, the transition state for the chloride ion elimination is relatively insensitive to changing from a β-hydrogen substituent to a β-bromine substituent. It is also apparent that a β-tosylate substituent is not as acidifying as a β-bromine substituent. The $\Delta (SN₂-E₂)$ for the β-tosylate derivative with acetate ion in acetone lies in the range of values found for E₂C like transition states.

A similar analysis of leaving group effects by Bunnett for dehydrohalogenations of 1-phenyl-2-X-2-methyl propane (where X is bromine or chlorine) led him to the conclusion that the transition state for β-eliminations promoted by weak H-bases had a large degree of C⁻-
leaving group bond breaking. He found the highest bromide-chloride rate
ratios ever observed for dehydrohalogenations promoted by bromide ion
and chloride ion in acetone. His values agreed with the results of Kevill\(^{15b}\)
for dehydrohalogenations of indanone derivatives in acetonitrile.

In summary, the study of leaving group effects on \(\beta\)-
elimination reactions has illustrated the following characteristics of the
\(E_2C\) 'like' transition state -

(a) The quantitative parallel of changes in free energy of the \(SN_2\)
transition state and \(E_2C\) 'like' transition state for changes in leaving group
and the pattern of correlations for \(E_2H\) reactions\(^{10,55}\) suggests that
base - \(C\) interaction takes place in the \(E_2C\) 'like' transition state.

(b) The arrangement of atoms about \(C\) in the \(E_2C\) 'like' transition
state is very 'loose', i.e. the leaving group - \(C\) bond is well broken in
the transition state.

E Comparison of aromatic substituent effects in \(SN_2\) and solvolysis
reactions.

In earlier sections of this discussion it was proposed that
in \(E_2C\) 'like' reactions, aromatic \(a\) and \(\beta\) substituents do not conjugate
with the double bond in the transition state. Also it was suggested that
aromatic substituents only interact inductively (not conjugatively) with
charge development. The reasons for this suggestion are not immediately
obvious. One possible reason for no conjugation at \(C\) could be that the
leaving group and nucleophile are both interacting with the developing \(p\)-
orbital at \(C\) and the \(a\) substituents are therefore unable to interact with
the developing \(p\)-orbital.

The best model to test this supposition is the comparison of
the substituent effects in \(SN_2\) and solvolysis reactions.

In TABLE XXVII are presented the rate constants for \(SN_2\)
and solvolysis reactions of para-substituted benzyl bromides. In Figure 5
is presented the Hammett \(\rho - \sigma^+\) plot for the solvolysis of para substituted
1-bromo-1-aryl propanes (where \(\rho = \text{-5.30}\)) and the Hammett \(\rho - \sigma^+\) plot
for the SN₂ reactions of chloride ion on para substituted 1-bromo-1-aryl propanes. In figure 8 are presented the Hammett ρ-σ plot for the SN₂ reactions of chloride ion, on para substituted 1-bromo-1-aryl propanes and para substituted benzyl bromides. Figures 5 and 8 both show the typical U-shaped Hammett plot for SN₂ reactions at benzylic carbon.

**TABLE XXVII**

<table>
<thead>
<tr>
<th>para subst.</th>
<th>+σᵃ</th>
<th>σᵃ</th>
<th>log kᵇ</th>
<th>log k²ˢᶜ</th>
<th>log k²ˢᵈ</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO₂</td>
<td>+ .79</td>
<td>+ .778</td>
<td>- 7.3</td>
<td>- 1.75</td>
<td>- 0.96</td>
</tr>
<tr>
<td>H</td>
<td>0</td>
<td>0</td>
<td>- 4.04</td>
<td>- 2.18</td>
<td>- 1.81</td>
</tr>
<tr>
<td>CH₃</td>
<td>- .391</td>
<td>- .170</td>
<td>- 2.47</td>
<td>- 1.76</td>
<td>-</td>
</tr>
<tr>
<td>CH₃O</td>
<td>- .778</td>
<td>- .268</td>
<td>+ 0.1</td>
<td>-</td>
<td>- 1.41</td>
</tr>
</tbody>
</table>

Footnotes TABLE XXVII

*a* Rates constants for solvolysis of 1-bromo-1-aryl propanes in 90% acetone water at 75°C. Results from TABLE IV.

*b* Rate constants for SN₂ reactions of chloride ion in DMF at 25°C with 1-bromo-1-aryl propanes. Results are from TABLE VI.

*c* Rate constants for SN₂ reactions of para substituted benzyl bromides with chloride ion in acetone at 0°C. Results from TABLE XVII.

If it is considered that the solvolysis transition state is the optimum situation for conjugation of aromatic substituents with the reacting centre, then the ρ value of -5.30 for solvolysis of 1-bromo-1-aryl propanes is the result of combined inductive and conjugative effects. The transition state is very like a carbonium ion, so that any conjugation is with vacant p-orbitals rather than occupied p-orbitals. The existence and magnitude of this conjugative effect is demonstrated by comparison of
Figure 8

The Hammett $\rho - \sigma$ plot for SN$_2$ reactions of 1-aryl-1-bromopropanes with chloride ion in DMF and 1-aryl-1-bromomethanes (benzyl) with chloride ion in acetone

\[ \begin{align*}
O &= 4XC_6H_4CH_2Br + Cl^- \\
X &= 4XC_6H_4CHBrCH_2CH_3 + Cl^-
\end{align*} \]
Hammett $\rho - \sigma$ and $\rho - \sigma^*$ graphs for solvolyses of 2-bromo propanes as in TABLE XIII

$\rho = -0.73$
figures 5 and 9. Figure 9 is a Hammett $\rho - \sigma$ and $\rho - \sigma^*40$ plot for the solvolysis reactions of 2-bromo-1-aryl propanes and 2-bromo butane. A good linear correlation is obtained for both plots with $\rho = -0.73$.

It would be unexpected that the inductive effect of the para substituted aromatic substituents should decrease greatly on changing from RCHXCH$_2$CH$_3$ to RCH$_2$CHXCH$_3$ so that the $\rho$ value for the 2-bromo-1-aryl propanes is probably representative of the inductive component in the 1-bromo-1-aryl propanes$^{60}$. If this is acceptable then the majority of the large difference between $\rho = -0.73$ and $\rho = -5.3$ is due to the conjugative interactions in the 1-bromo-1-aryl propanes. These values are comparable with other results in related systems, e.g. the solvolysis of 2-aryl-2-chloro propanes in 90% acetone water at 25°C has a $\rho = -4.54^{40}$ and the solvolysis of 1-aryl-2-chloro-2-methyl propanes in methanol at 66.5°C has a $\rho = -1.15^{60}$. Therefore it is observed that the decrease in $\rho$ value is due to the disappearance of a conjugative effect$^{60}$ caused by the insertion of a methylene group between the aryl substituent and the reaction centre.

This form of treatment can be applied to SN$_2$ reactions. If a conjugative interaction were taking place in the SN$_2$ transition state of benzylic systems then this would be revealed by the comparison of the effects of $\alpha$-aromatic substituents and $\beta$-aromatic substituents on rates of reaction.

In TABLE XXVIII are presented the rate constants for (i) the SN$_2$ reactions of 2-bromo-1-R propanes with chloride ion in DMF at 25°C, (ii) the solvolysis reactions of the same compounds in 50% acetone water at 75°C, and (iii) the SN$_2$ reactions of 1-R-2-ethyl $p$-toluene sulphonates with ethoxide in ethanol at 30°C.
TABLE XXVIII

Rate constants, for $\text{SN}_2$ reactions of 1-R-2-bromo propanes with chloride ion in DMF at 25°C ($\log k^{2S}$), the $\text{SN}_2$ reactions of 1-R-2-ethyl $p$-toluene sulphonates with ethoxide in ethanol at 30°C ($\log k^{2S}$), and the rate constants for solvolysis of 1-R-2-bromo propanes in 50% acetone water at 75°C.

<table>
<thead>
<tr>
<th>R</th>
<th>$\log k^{2S}_a$ DMF</th>
<th>$\log k^{2S}_b$ EtOH</th>
<th>$\log k^a$</th>
<th>$\sigma^c$</th>
<th>$\sigma^{*c}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$</td>
<td>-3.43</td>
<td>-3.7</td>
<td>-4.26</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>C$_6$H$_5$</td>
<td>-4.17</td>
<td>-4.13</td>
<td>-4.62</td>
<td>0</td>
<td>+0.6</td>
</tr>
<tr>
<td>4NO$_2$C$_6$H$_4$</td>
<td>-3.69</td>
<td>-5.25</td>
<td>+.778</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>4CH$_3$OC$_6$H$_4$</td>
<td>-4.0</td>
<td>-4.12</td>
<td>-.268</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>4ClC$_6$H$_5$</td>
<td>-3.99</td>
<td>-</td>
<td>+.227</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>3BrC$_6$H$_4$</td>
<td>-3.74</td>
<td>-</td>
<td>+.391</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

Footnotes TABLE XXVIII

a Reactions of 1-R-2-bromo propanes. Results are from TABLES IV and VI.

b Rate constants for $\text{SN}_2$ reactions of 1-R-2-ethyl $p$-toluene sulphonates. Values are from Reference 61, 42

c From Reference 40.

The results in TABLE XXVIII are presented graphically in figure 10 which is the Hammett $\rho - \sigma$ and $\rho - \sigma^*$ plot for the $\text{SN}_2$ Reactions of 1-R-2-bromo propanes with chloride ion in DMF and in figure 11 which is the Hammett $\rho - \sigma$ and $\rho - \sigma^*$ plot for the $\text{SN}_2$ reactions of 1-R-2-ethyl $p$-toluene sulphonates with ethoxide ion in ethanol.

The results in TABLE XXVII show that the rates of $\text{SN}_2$ reactions are relatively insensitive to changes in para substituent in an aryl group compared to the effect of the same changes in para substituent on the rate of solvolysis reactions. This is further exemplified by the change from
Figure 10

Hammett $\rho - \sigma$ and $\rho - \sigma^*$ graphs of an SN$_2$ reaction of 1-R-2-bromo propane with chloride ion in DMF as in TABLE XXVIII
Figure 11

Hammet $\rho - \sigma$ and $\rho - \sigma^*$ graphs for $\text{SN}_2$ reactions of 2-R ethyl $p$-toluene sulphonate with ethoxide ion in ethanol as in TABLE XXVIII
R = methyl to R = phenyl. The rate of solvolysis is increased by 1000 times while the rate of SN$_2$ reactions are increased only 20-40 times (see TABLES XVI and XVII).

If it is considered that conjugative interactions exist in the SN$_2$ transition states of benzylic compounds, then a criterion for the occurrence of this interaction would be a large decrease in the sensitivity of the SN$_2$ transition state, to para aromatic substituents when changing from an α aryl to a β aryl substituent. Comparison of the kinetic results in TABLES XXVII and XXVIII as well as comparison of figures 10 and 11 with figures 5 and 8 show that this is not the situation. In fact it is remarkable how similar the Hammett ρ - σ plots for SN$_2$ reactions are on changing from α aryl to β aryl substituents.

The gentle U shaped curve for α aryl substituents has been discussed before\textsuperscript{13, 33}. The U shaped curve for β aryl substituents is probably due to the same cause. This has been observed before\textsuperscript{42}; however, the curve was represented as a very poor linear correlation.

This treatment suggests that there is only relatively small conjugative interactions in the SN$_2$ transition state. If the extension is made to E$_2$ 'like' reactions then the same method of analysis can be applied. The Hammett ρ value is -0.61 for the dehydrobromination of 1-aryl-1-bromo propanes with bromide ion in acetone at 75°C (figure 5) and for the dehydrochlorination of 1-aryl-2-chloro-2-methyl propanes with sodium methoxide in methanol to give the Hofmann olefin the Hammett ρ value is -0.10\textsuperscript{14}. Therefore it appears that there is no conjugation of charge development or double bond development in the E$_2$ 'like' transition state. This form of approach can therefore be described as a measure of conjugation of α aryl substituents with a reaction centre.

In summary, this Hammett ρ - σ analysis, and product analysis all suggest that the double bond does not conjugate with aromatic substituents in the E$_2$ 'like' transition state. A possible reason for the lack of conjugation of α aryl substituents has already been proposed, but
it is still not clear why β aryl substituents show only slight, if any, conjugation with the developing double bond. This is the only aspect of E₂C 'like' reactions which has not been investigated and the need for further work is obvious.

F Debromination and debromotosylation reactions

Only a small number of results have been determined with the intention of supplementing work by other researchers. It was considered by Parker that a spectrum of transition states, similar to the E₂C-E₂H spectrum, may exist for debromination and debromotosylation reactions. Although they have not observed any evidence suggesting Cₐ-base interaction for debrominations promoted by mercaptides or iodides, this does not exclude the possibility that such a spectrum exists.

In TABLE XXIX are presented some tosylate-bromide rate ratios (log $k_2^\text{OTos}$ - log $k_2^\text{Br}$) for debromination and debromotosylation reactions promoted by cyanide ion and 4-nitro thiophenoxide ion in acetone. In the debromotosylation reactions the carbon bonding to the tosylate is assigned as the a-carbon atom. This is possible because the tosylate leaving group cannot act as an electrophilic centre, which is evidenced by the fact that cyclohexyl-trans-1,2-ditosylate does not produce cyclohexene when treated with 4-nitro thiophenoxide. The assignment of tosylate:bromide rate ratios for SN₂ reactions is made by using the same assumption as in TABLE XXVI (see footnote k).

<table>
<thead>
<tr>
<th>Base</th>
<th>log $k(\text{OTos})$-log $k(\text{Br})$</th>
<th>log $k(\text{OTos})$-log $k(\text{Br})$</th>
<th>$\Delta(\text{SN}_2-\text{E}_2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CN⁻</td>
<td>+.5 ⁓</td>
<td>+0.87 ⁓</td>
<td>-0.4 ⁓</td>
</tr>
<tr>
<td>ArS⁻</td>
<td>+.5 ⁓</td>
<td>-0.37 ⁓</td>
<td>+0.84 ⁓</td>
</tr>
</tbody>
</table>
Footnotes

**TABLE XXIX**

a  ArS⁻ = 4-nitro thiophenoxide and X represents the leaving groups tosylate and bromide.

b  Assigned using the convention in TABLE XXVI, footnote k.

c  Results for debromination from Reference 20 as determined by Mr. M. Ruane.

The analysis of leaving group effects for E₂C 'like' reactions, presented in the Discussion, Section D, can be extended to E₂Hal reactions. It has already been shown that E₂Hal reactions, similar to E₂C 'like' reactions, strongly favour anti orientation of leaving groups. Also, from transition state solvent activity coefficients it is suggested that debromination reactions promoted by 4-nitro thiophenoxide pass through a transition state which is of comparative 'tightness' to the E₂H transition state. The Δ(SN₂⁻E₂) value for 4-nitro thiophenoxide in TABLE XXIX when compared with the Δ(SN₂⁻E₂) values for dehydrobromination and dehydrotosylation in TABLE XXVI correlate remarkably well with this observation.

The interesting result, therefore, is the cyanide ion result which gives a Δ(SN₂⁻E₂) value closely comparable with that which is observed for E₂C 'like' reactions. The direct suggestion from this is that the transition state for cyanide ion promoted debromination is very 'loose', similar to the E₂C 'like' transition state. Although the inference that Ca-base interaction is taking place cannot be made from these results, it is interesting to note that this base substrate system is utilising a 'loose' transition state which would be expected for an E₂C 'like' type of transition state for debrominations.

G  The E₂C 'like' transition state

At this stage of this thesis it is pertinent to provide a complete description of the E₂C 'like' transition state. Winstein and Parker in their earlier publications described a structure which they felt best represented the known facts about β-elimination reactions promoted by
weak H-bases. However, it remained at that time to test the validity of their description by experiment. The main objection to the $E_2C'$ like' structure was the inclusion of C-base interaction as an essential quality of the $E_2C'$ like' structure $^{4,14,16}$.

The character of the $E_2C'$ like' transition state as determined by the evidence presented in the Introduction and Discussion sections of this thesis is as follows:

(a) There is some form of Base-$C_a$ interaction in the $E_2C'$ like' transition state.

(b) There is a strict requirement of anti arrangement of the $\beta$ proton and the leaving group in the transition state.

(c) There is a well broken $C_a$ leaving group bond in the transition state.

(d) There is a large degree of double bond development in the transition state.

(e) There is only slight, if any, development of positive charge at $C_a$ in the transition state.

(f) There is only slight, if any, development of negative charge at $C_\beta$ in the transition state.

(g) The transition state is very 'loose'. The ionic species produced have an almost fully developed charge.

(h) The double bond developed in the transition state does not conjugate with unsaturated $\alpha$ or $\beta$ substituents.

H The $E_2C'$ like' spectrum of transition state structures

Bunnett $^4$ has described and predicted the effect of base, $\alpha$ and $\beta$ substituents, leaving group and solvent on the type of transition state utilised by strong H bases when they promote $\beta$-elimination reactions.

A preliminary analysis of the effect of the above factors on movement through the $E_2C'$ like' - $E_2H$ spectrum has recently been submitted for publication $^6$, and is the result of work carried out by a number of chemists.
(a) The effect of base

Previously\(^4\), there was some difficulty in interpreting the effect of base, due to the uncertainty as to what criterion of basicity should be used. With the advent of the \(E_2^2\)-\(E_2^H\) spectrum it has now become clear that both the carbon nucleophilicity and hydrogen nucleophilicity (or basicity) of the attacking base must be considered.

For a simple alkyl substrate each base will occupy a position in the \(E_2^2\)-\(E_2^H\) spectrum where both properties of the base are balanced. This has been illustrated by an analysis of variation of leaving group effects for changes of base\(^1^0\). If from any position in the spectrum we change to a stronger carbon nucleophile, without greatly increasing the H-basicity, then a shift in transition state character towards more \(E_2^2\) 'like' is predicted. For a change to a stronger H-base, a shift in character towards the \(E_2^H\) side of the spectrum is predicted. Also, development of some paene carbanion character\(^4\) would not be unexpected depending on the interplay of all other factors.

(b) The effect of leaving group

There are considerable differences in the 'tightness' (or 'looseness') of the \(E_2^H\) and \(E_2^2\) transition states, i.e. different amounts of \(C_\alpha\) leaving group bond breaking. It is expected that leaving groups which facilitate bond breaking, or vice versa, would cause the transition state character to change for changes in leaving group.

For changes to poorer leaving groups, e.g. tri-methyl ammonium or sulphones, a shift towards more \(E_2^H\) character would be predicted. For changes to more labile leaving groups a shift towards more \(E_2^2\) 'like' character is predicted. This is well demonstrated by the existence of linear free energy relationships (parallel of \(SN_2\) and \(E_2^2\) 'like') for reactions of cyclohexyl tosylate with various bases\(^9,20\). For reactions of cyclohexyl bromide with these bases there is no such linear free energy relationship. This is because bromide is a poorer leaving group than tosylate and for elimination reactions promoted by slightly stronger H bases there is a shift in transition state character towards the more \(E_2^H\) 'like' side of the spectrum.
(c) **The effect of α substituents**

Increasing substitution of the α carbon atom from $1^\circ$ to $2^\circ$ to $3^\circ$ causes a 'loosening' of the transition states utilised by the substrate. Therefore, changing to non polar and bulky α substituents will, because the $E_2C'$like' transition state is 'loose', cause a shift towards more $E_2C'$like' character.

Polar α substituents in so much as they affect the strength of the $C\alpha$ leaving group bond, may (depending on their electron withdrawing or electron donating ability) cause a shift in either direction. Electron withdrawing α substituents should cause a 'tightening' of the transition state and therefore a shift towards more $E_2H'$like' character. Electron donating α substituents should cause a 'loosening' of the transition state, and therefore a shift towards more $E_2C'$like' character.

(d) **The effect of β substituents**

Bulky, non polar, β substituents have the same loosening effect on the transition state as do α substituents. This is probably due to the fact that the bulky substituents have less steric compression about a trigonal carbon atom in an olefin than they have about a tetrahedral carbon in the reactants. Therefore, for changes to bulky, non polar β substituents, there is a shift towards more $E_2C'$like' character.

Electron withdrawing β substituents, because they acidify the β proton, will increase the $E_2H'$ character of the transition state by facilitating $\beta_C-H$ bond breaking. Electron donating β substituents cause the reverse shift because of the decreased acidity of the β proton.

(e) **Solvent effects**

Protonic solvents strongly solvate anions by H-bonding interactions. In a 'loose' $E_2C'$like' transition state the nucleophile is well solvated, and any destabilisation of the transition state, caused by slight desolvation of the nucleophile, is amply reimbursed by solvation of the leaving group. An $E_2H'$ type of transition state, where the charge is almost lost by the nucleophile, and dispersed evenly over the charged transition state, experiences a destabilisation effect in protonic solvents due to the necessary desolvation of the nucleophile. Therefore the
E₂C 'like' transition state is favoured in protic solvents. Aprotic solvents have no stabilising solvation of anionic species by H-bonding. The E₂C 'like' reactions go from an anionic reaction through a transition state resembling free anions to products which contain an anion. Therefore solvent effects are not expected to stabilise or destabilise the E₂C 'like' transition state.

The E₂H transition state, because the negative charge is dispersed over a larger centre, is destabilised by protic solvents relative to the ground state reactions. Therefore changing from protic solvents to dipolar aprotic solvents causes a shift towards more E₂H character.

The situation is complicated by the fact that changing from protic to aprotic solvents also changes the activity of the nucleophile and it is not certain that the H-nucleophilicity and C-nucleophilicity are equally affected by the change since each is an independent property of the nucleophile.

(f) Additivity of all the effects

It must be remembered as an overriding consideration of each of the previous sections that the combined effect of all the factors determines the type of transition state utilised in a bimolecular β-elimination reaction.

The character of the E₂ transition state utilised need not change when one of the above variables is altered, as the combined effect of other factors may more than compensate for the change.

Examples of this can be found for each factor. For the reactions of cyclohexyl tosylate with NBu₄X salts, in acetone, a linear free energy relationship exists which was used as evidence for Cₐ base interaction. This would not have occurred had the E₂C or E₂H character varied greatly on changing from one base to another. The reasons for this are in the system chosen. The tosylate leaving group is very labile and favours 'loose' transition states and the cyclohexyl system also favours loose transition states. Since the E₂C 'like' transition state is 'loose' then the effect of leaving group and substrate structure overrides the effect of changing the base. However, for reactions of cyclohexyl bromide no linear free energy relationship was obtained because the change from
tosylate to bromide leaving group made the transition state more susceptible to changes in H basicity of the base.

In the study of leaving group tendencies of $E_2C$ 'like' reactions, another linear free energy correlation was obtained, which demonstrated parallel changes between $E_2C$ 'like' reactions and $SN_2$ reactions for changes of leaving group from tosylate through chloride to dimethyl sulphonium $^{10, 20}$. This inferred there were only slight changes in the character of the transition state for changing the leaving group. The reason why this occurred is the same as above. The elimination reactions promoted by chloride ion in the cyclohexyl system were chosen to show this correlation, i.e. the base and substrate structure both favour 'loose' transition states and dominate changes in leaving group.

The study of the effect of changes in β substituents was also subject to such dominance $^{12, 17}$. It was found that on changing a β substituent from methyl to bromo to carboxymethyl hardly affected the character of the transition state for chloride ion promoted dehydrobromination reactions in acetone. The same reason is, of course, apparent. The nature of the leaving group and the base both favour $E_2C$ 'like' transition states, so much so that they dominate changes in β substituents. However, with acetate ion as a base, a $10^5$ increment in rate is observed, demonstrating that the acidification of the β proton has markedly affected the position of the $E_2$ transition state in the $E_2C-E_2H$ spectrum.

The question of whether or not the proposal of an $E_2C-E_2H$ spectrum of transition states is acceptable to the Physical Organic Chemist is going to be the origin of much controversy in the future. However, certain undeniable facts arise from the data presented in the Introduction and Discussion sections of this thesis. Firstly, the Variable $E_2$ transition state spectrum proposed by Bunnett $^4$ cannot adequately explain the experimental results obtained for β-elimination reactions promoted by weak H-bases. Secondly, the application of β-elimination reactions promoted by bases such as chloride ion, bromide ion, mercaptides and acetate ion has opened a completely new dimension for synthetic organic chemists. The criteria of reaction feasibility and reaction products differ from the β-elimination reactions promoted by the "classical" alkoxides.
EXPERIMENTAL

A General

1 Determination of physical constants etc.

Melting points were determined using a Kofler micro hot stage. They are uncorrected and expressed in degrees centigrade (°C).

Nuclear magnetic resonance (NMR) spectra were recorded using a Varian Associates HA-100 spectrometer and a Japan Electronics Company C60-HL spectrometer. Analysis was carried out in deuterchloroform solution (except where otherwise stated) using tetramethylsilane (TMS) as an internal standard. All chemical shifts quoted are relative to TMS and are reported on the δ scale.

Quantitative ultraviolet spectra were determined on a Gilford Model 2400 spectrophotometer.

Elemental analyses were carried out by the A.N.U. Microanalytical Division, Australian National University, Canberra, and are accurate to ± 0.3%.

2 Purification of solvents

Acetone was purified according to the method of Vogel (Ref. 63) by refluxing over potassium permanganate, drying over anhydrous potassium carbonate and fractionation at BP = 56° (lit. 64 BP = 56.2°C).

tert.-Butanol (t-BuOH) was purified according to the method of Vogel (Ref. 63) by drying over potassium carbonate, filtering, dissolving 20 gms of sodium metal in the solvent, refluxing 24 hrs with 50 mls of tertiary butyl benzoate and fractionating, BP = 82°C (lit 64 BP = 82.8°C).

Dimethyl formamide (DMF) was purified according to method of Moe 65 by standing over molecular sieves, passing the DMF through a column of alumina under a nitrogen atmosphere, bubbling nitrogen through the solvent and rapid distillation under high vacuum, BP = 40°/8 mm. The purified solvent was stored in a dark bottle over molecular sieves.
Ethanol (EtOH) was purified by the magnesium ethylate method as outlined by Vogel (Ref. 63) and fractionated, BP = 78°C (lit. 64 BP = 78.5°C). The purified solvent was stored under a nitrogen atmosphere.

Water (H₂O) was purified by bubbling nitrogen through the solvent and then distillation with a constant nitrogen stream, BP = 100°C. The purified solvent was stored under a nitrogen atmosphere.

Methanol (MeOH) was purified by the magnesium methylate method as outlined by Vogel (Ref. 63) and fractionated, BP = 64°C (lit. 64 BP = 64.2°C).

Dimethyl sulphoxide (DMSO) was purified by standing over molecular sieves for one day, fractionating under reduced pressure with a nitrogen bleed, and rapid distillation at reduced pressure with a nitrogen bleed, BP = 63°C/4 mm. The purified solvent was stored in a dark bottle under a nitrogen atmosphere and over molecular sieves.

3 Preparation and purification of nucleophilic reagents

Tetra-n-butyl ammonium bromide (NBu₄Br). Commercial samples were recrystallised from acetone-ether mixtures, filtered under nitrogen and dried for 24 hrs at 0.2 mm and 25°C.

Tetra-n-butyl ammonium chloride (NBu₄Cl). Commercial samples were recrystallised from acetone-ether mixtures, filtered under nitrogen and dried for 2 days at 0.2 mm and 25°C.

Tetra-n-butyl ammonium perchlorate (NBu₄ClO₄). A solution of 38 gms of sodium perchlorate mono hydrate in 800 ml of water was added slowly with stirring to a solution of 50 gms of NBu₄Br in 600 ml.

* All salts were analysed to be greater than 98% pure. They are all handled under a nitrogen atmosphere as most are either hygroscopic or react with oxygen or carbon dioxide.
of water. The precipitated solid is filtered, washed with water and recrystallised from methanol-water and from acetone-ether. The crystals were then dried at 0.2 mm and 25°C for 12 hours.

**Tetra-n-butyl ammonium p-nitrothiophenoide (NBu₄ArS).**

35.25 gms of 4,4'-dinitro diphenyl disulphide is added to a solution of 14 gms of potassium hydroxide and 27.5 gms of thiophenol in 300 mls of ethanol and the suspension is stirred for two hours. The mixture is poured into one litre of water, filtered, acidified, filtered and the residue dissolved in 2 molar potassium hydroxide. The solution is acidified, filtered, and the residue dissolved in ether, dried with anhydrous magnesium sulphate and the p-nitrothiophenoide recrystallised from ether, MP = 75-77°C (lit. MP = 77°C).

A solution of NBu₄OMe was prepared by reacting a slight excess of silver oxide with tetra-n-butyl ammonium iodide (NBu₄I) in methanol until no iodide ion is left. A slight excess of p-nitrothiophenol is then added to this solution which is filtered, evaporated and the solid residue recrystallised from acetone, MP = 109-110°C (lit. MP = 110°C).

**Tetra-n-butyl ammonium acetate (NBu₄OAc).** A slight excess of silver acetate was added to a solution of NBu₄I in methanol and the suspension stirred for 2 hours. Complete reaction was verified by a negative test for iodide ion. The solution was filtered, evaporated, benzene added, evaporated and more benzene added. The solution was applied to an Activity I basic alumina column packed in benzene and eluted. The pure crystalline salt left after evaporation of solvent may be recrystallised from 40% benzene-40% n-pentane-20% ethyl acetate or used in its present form after drying for 3 days at 0.2 mm and 25°C as it is > 98% pure when analysed for acetate ion.

**Tetra-n-butyl ammonium cyanide (NBu₄CN).** A solution of 36.5 gms of NBu₄ClO₄ in 200 mls of methanol was added to 6.8 gms of potassium cyanide in 500 mls of refluxing MeOH. The suspension was refluxed for 3 hours, cooled, filtered and evaporated, benzene added
and evaporated again. The yellow oil in benzene solution is applied to an Activity I basic alumina column packed in benzene and eluted with benzene. The crystalline solid residue left after evaporation of the solvent is > 98% pure. However, this may be recrystallised from acetone-ether mixture and dried for 3 days at 0.2 mm and 25°C.

Potassium tert.-butoxide (KOT-Bu) solution in t-BuOH was prepared by dissolving potassium metal in t-BuOH.

Sodium ethoxide (NaOEt) solution in ethanol was prepared by dissolving sodium metal in ethanol.

Sodium methoxide (NaOMe) solution in methanol was prepared by dissolving sodium metal in methanol.

4 Preparation and purification of organic compounds.

The N.M.R. spectrum of all compounds prepared was determined and structural determinations were based mainly on this information and physical constants reported in the literature. The relevant N.M.R. detail is reported later on pp. 137-143.

Simple olefins. Commercial samples of simple olefins were analysed by Vapour Phase Chromatography and shown to be > 99% pure. These were distilled and used without further purification for synthetic and product analysis work. The boiling points obtained were: cis-2-butene, BP = 3.0°C (lit. 66, BP = 3.7°C); trans-2-butene, BP = 0°C (lit. 66, BP = 0.9°C); 2-methyl-2-pentene, BP = 67°C (lit. 66, BP = 67.5°C); cis-4-methyl-2-pentene, BP = 58°C (lit. 66, BP = 57.7 - 58.5); trans-4-methyl-2-pentene, BP = 54°C (lit. 66, BP = 54.2 - 55.2°C); 2-methyl-1-pentene, BP = 61°C (lit. 66, BP = 61.5 - 62.0°C); cis-stilbene, BP = 130/8 mm (lit. 66, BP = 136-7/10 mm); cyclohexene, BP = 82°C (lit. 66, BP = 83°C).

Trans-stilbene was recrystallised from ethanol, MP = 124 - 125°C (lit. 66, MP = 124°C).

2-Bromo butane. A commercial sample was fractionated, BP = 91°C (lit. 66, BP = 91.2°C) and used without further purification.
1-Bromo propane. Commercial samples were fractionated and used without further purification, BP = 70°C (lit. 66 BP = 70.8°C).

2,6-Lutidine. Commercial reagent was fractionated before use, BP = 142°C (lit. 66 BP = 143°C).

1-Butene. 11 gms of potassium metal was dissolved in 250 mls of t-BuOH and 36 gms of 1-bromo butane was added. The solution was refluxed and the gas evolved collected in an acetone-dry ice trap. The crude olefin was distilled and analysed by vapour phase chromatography and shown to be > 98% pure, BP = -6°C (lit. 66, BP = -6.3°C).

trans-1-Phenyl propene. 7.5 gms of 1-bromo-1-phenyl propane and 20 gms of NBu4Br were dissolved in 100 mls of DMF and refluxed for 30 mins. The solution was poured into 300 mls water, extracted with pentane, dried over anhydrous magnesium sulphate, filtered, evaporated and distilled. V.P.C. analysis showed > 98% purity, BP = 40°C/1 mm (lit. 64, BP = 176-7°C).

3-Phenyl propene. Prepared as in Ref. 67 by the reaction of phenyl magnesium bromide with allyl bromide in ether, BP = 156°C (lit. 66, BP = 156°C).

Trans-1-(4-nitrophenyl)-1-propene. 10 mls of 0.02 molar 1-(4-nitro phenyl)-1-bromo propane, 0.1 molar NBu4Br and 0.05 M 2,6-lutidine in acetone was warmed for 8 hours at 100°C in a sealed ampoule under a nitrogen atmosphere. The solution was poured into water, extracted with hexane, dried over anhydrous magnesium sulphate, filtered, evaporated and recrystallised from EtOH, MP = 94°C (lit. 68, MP = 94-95°C).

Trans-stilbene. High purity trans-stilbene > 99.96% pure was required for equilibration experiments. 99.98% pure trans-stilbene was obtained from preparative Vapour Phase Chromatography using a Pye Series 105 Automatic Preparative Chromatograph installed with a 27 ft. 3/8" OD glass column packed with 20% SE-30 on Chromosorb W. AW. DMCS. at 210°C with a flow rate of 60 mls per minute. 500 microlitre samples in chloroform were injected and collected automatically until 4 gms of purified product had been collected.
2-Methyl-3-pentanol (Ref. 69, supplied by Mr. R. I. Tilley). Iso propyl magnesium bromide prepared from 25 gms of iso propyl bromide and 5 gms of magnesium in 500 mls ether is reacted rapidly with 11 gms of propionaldehyde in 50 mls ether. 150 mls of saturated ammonium chloride in water is added. The ether layer is separated, washed with water, dried over anhydrous magnesium sulphate, filtered, evaporated and distilled, BP = 128 - 130°C (lit. 66, BP = 129.30).

2-Methyl-3-pentyl p-toluene sulphonate (prepared by the Tipson method, Ref. 70). 6.5 gms of 2-methyl-3-pentanol and 13.2 gms of p-toluene sulphonyl chloride is stirred in 75 mls of A.R. pyridine for 3 hours at room temperature until complete precipitation of pyridinium chloride has been observed. The mixture is poured into ether, washed with concentrated hydrochloric acid in water until pH = 2. The ether extract is washed with water, dried over anhydrous magnesium sulphate, filtered, evaporated and the oil recrystallised from methanol at -70°C and dried at 0.2 mm/20°C for 1 hr and stored at -10°C, MP = 21-22°C (no melting point was obtained in Ref. 50).

1-Phenyl-1-propanol. 160 gms of ethyl bromide and 35 gms of magnesium were reacted in 2 litres of ether. 156 gms of benzaldehyde in 300 mls of ether was added to the mixture and refluxed for 1 hour. The complex was destroyed with 100 mls of water and 2 molar hydrochloric acid was added until all the magnesium hydroxide dissolved. The ether layer was washed with water, dried over anhydrous magnesium sulphate, filtered, evaporated and the liquid distilled, BP = 92°C/4 mm (lit. 64, BP = 105.8/10 mm).

1-Phenyl-2-propanol. 33.6 gms of benzyl methyl ketone in 100 mls ether is added dropwise to 4.75 gms of lithium aluminium hydride, stirred in 500 mls of ether. The complex is destroyed with 50 mls of saturated sodium sulphate solution and the white precipitate dissolved by the addition of 2 molar hydrochloric acid. The ether layer is washed with water, dried over anhydrous magnesium sulphate, filtered, evaporated and the oil distilled, BP = 68°C/1 mm (lit. 64, BP = 125°/25mm).
1-Phenyl-1-propyl acetate. 5 gms of 1-phenyl-1-propanol, 6 mls of acetic anhydride and 50 mls of acetic acid are refluxed for 3 hours. The solution is cooled, poured into n-pentane, extracted with water, 5% sodium bicarbonate and water again. The pentane layer was dried over anhydrous magnesium sulphate, filtered, evaporated and the oil distilled, BP = 77°C/1 mm (lit. 64, BP = 115°C/16 mm).

1-Phenyl-2-propyl acetate was prepared by the method of Vogel (Ref. 63). x moles of alcohol was refluxed in 3x moles of acetic anhydride for 3 hours, poured into water and stirred. 5% solution of sodium bicarbonate is slowly added with vigorous stirring until pH > 7. Ether is added and the ether layer is washed with H₂O, dried over anhydrous magnesium sulphate, filtered, evaporated and the oil distilled, BP = 84°C/2 mm (lit. 64, BP = 115°/16 mm).

1-Phenyl-1-bromo propane was prepared as in Ref. 71 by saturating x mls of 1-phenyl-1-propanol in 2x mls of benzene with dry hydrogen bromide. The benzene solution was washed with water twice, dried over anhydrous calcium chloride, filtered, evaporated and distilled, BP = 92-94°C/3 mm (lit. 71, BP = 94-95°C/5 mm).

1-Phenyl-2-bromo propane. 1-Phenyl-2-propyl tosylate was made by the Tipson (70) method as in Ref. 72. 20 gms of 1-phenyl-2-propyl tosylate and 40 gms of NBut₄Br are warmed in 500 mls of acetone at 75°C for 4 hours (see Ref. 89). The solution was cooled, poured into ether, washed with water, dried over anhydrous magnesium sulphate, filtered, evaporated and distilled, BP = 89-90°C/8 mm (lit. 71, BP = 92-93°C/10 mm).

1-Phenyl-1-chloro propane. x mls of 1-phenyl-1-propanol in 2x mls of benzene were saturated with hydrogen chloride until precipitation of water was complete. The solution was poured into hexane, washed with water twice, dried over anhydrous magnesium sulphate, filtered, evaporated and distilled, BP = 86°C/15 mm (lit. 64, BP = 87-8°C/15 mm).

1-(4-nitrophenyl)-1-propanol was prepared as in Ref. 73 by the nitration of 1-phenyl-1-propanol. A mixture of α-isomer and β-isomer results which was separated by fractionation through a Nester Faust Annular Teflon Spinning Band Distillation column, BP = 165°C/.2 mm (lit. 73 BP = 161-162°C/1 mm). V.P.C. of each fraction showed no
contamination by the other isomer.

1-(4-nitrophenyl)-2-propenol. 25 mls of 1-phenyl-2-propyl acetate was added dropwise to a mixture of 180 mls of conc. nitric acid (SG = 1.42) and 45 mls of conc. nitric acid (SG = 1.50) at 0°C. and stirred for 2 hours at 0°C. The reaction was monitored by V.P.C. and was complete after 2 hours at 0°C. The mixture was poured onto 500 gms of ice, extracted with ether and the ether layer was washed with water twice, dried over anhydrous magnesium sulphate, filtered, evaporated and the yellow oil was analysed by V.P.C. This showed two major peaks (o and p isomer) and a third small peak, presumably the meta isomer.

The mixture of oils was refluxed in a mixture of 150 mls of 90% EtOH and 35 mls of conc. hydrochloric acid for 6 hours. The reaction was worked up as previously and the yellow oil was separated into pure ortho and para isomer by spinning band distillation. The para isomer was recrystallised from ether, MP = 65-66°C.

Analysis: Expected C = 59.66, H = 6.12, N = 7.73
Found C = 59.79, H = 6.13, N = 7.53

1-(4-nitro phenyl)-1-bromo propane. 1 gm of 1-(4-nitro phenyl)-1-propanol and 6 gms of hydrobromic acid (SG = 1.49) were refluxed for 10 minutes and cooled. The solution was poured into ether and extracted with water. The ether layer was washed with water twice, dried over anhydrous magnesium sulphate, filtered and evaporated. The oily residue was rapidly filtered through activated charcoal while in n-hexane solution. The product recrystallised from n-hexane on cooling, MP = 60-61°C.

Analysis Expected C = 44.28, H = 4.13, N = 5.74
Found C = 44.03, H = 3.96, N = 5.74

1-(4-nitro phenyl)-2-bromo propane. 9 gms of 1-(4-nitro phenyl)-2-propanol and 100 mls of hydrobromic acid (SG = 1.49) were refluxed for 15 minutes, cooled, extracted into ether, washed with water, dried over anhydrous magnesium sulphate, filtered, evaporated and N.M.R. on the oil showed 90% alkyl bromide and 10% olefin. The oil was fractionated and the fraction, BP = 142°/2.5 mm analysed as > 98% pure by N.M.R. and analysis.

Analysis expected: Br = 32.74%, Found: Br = 32.25%.
1-(4-methyl phenyl)-1-propanol. 8.8 gms of propionaldehyde in 50 mls of ether was added dropwise to the Grignard complex formed from 26 gms of 4-bromo toluene and 4 gms of magnesium metal in 500 mls of ether. The reaction was quenched with 100 mls of saturated ammonium chloride solution. The ether layer was washed with water, dried over anhydrous magnesium sulphate, filtered, evaporated and the oil distilled. BP = 100°C/6 mm \((\text{lit.} 64, \text{BP} = 118-120°C/23 \text{mm})\).

1-(4-methyl phenyl)-1-bromo propane. x mls of 1-(4-methyl phenyl)-1-propanol and 2x mls of benzene at 0°C were saturated with hydrogen bromide until precipitation of water was complete. The solution was poured into n-pentane, washed with water and the n-pentane layer dried over anhydrous magnesium sulphate, filtered, evaporated and the oil, which was analysed by N.M.R. and bromide analysis, was 90% pure alkyl bromide with the corresponding trans-(4-methyl phenyl)-1-propene as the only impurity. Physical attempts to separate this mixture were unsuccessful because (a) the alkyl bromide decomposes on distillation, V.P.C. or column chromatography, and (b) filtration through activated charcoal in pentane solution gave only slight improvement in the purity. Therefore the mixture of 90% 1-(4-methyl phenyl)-1-bromo propane and 10% trans-1-(4-methyl phenyl)-1-propene was used for all kinetic work.

1-(4-methoxy phenyl)-1-propanol was prepared as in Ref. 74 by the reaction of 4-methoxy phenyl magnesium bromide with propionaldehyde in ether. BP = 118-120°C/2 mm \((\text{lit.} 74, \text{BP} = 120.5-121°C/4 \text{mm})\).

1-(4-methoxy phenyl)-1-chloro propane. x mls of 1-(4-methoxy phenyl)-1-propanol in 2x mls of n-pentane at 0°C was saturated with hydrogen chloride until complete precipitation of water. The pentane layer was washed with water twice, dried over anhydrous magnesium sulphate, filtered, evaporated and the oil analysed by N.M.R. and chloride analysis which showed the oil as 75% alkyl chloride and 25% anethole. Identical problems of purification were found with this compound as with 1-(4-methyl phenyl)-1-bromo propane so that this mixture was used for all kinetic work.
1-(4-methoxy phenyl)-2-propanol, prepared as in Ref. 78 by the reaction of 1-(4-methoxy phenyl) propene with N-bromo succinimide, dehydrobromination of the bromohydrin formed and reduction of the ketone. The product oil was fractionated, BP = 112°C/3.5 mm (lit. 78, BP = 119°C/4 mm).

1-(4-methoxy phenyl)-2-bromo propane. 2 mls of 1-(4-methoxy phenyl)-2-propanol was mixed with 20 mls of hydrobromic acid (SG = 1.49) and refluxed for 10 mins. The mixture was poured into n-pentane, washed twice with water, the pentane layer dried over anhydrous magnesium sulphite, filtered and evaporated. N.M.R. showed the product to be 90% pure. Careful fractionation at reduced pressure gave a clear, colourless oil, BP = 110-111°C/1 mm. N.M.R. and bromide analysis showed the product to be 99% pure. Br calculated = 34.9%, Br found = 34.5%.

1,2-diphenyl ethanol was prepared as in Ref. 75 by the reaction of benzyl magnesium chloride with benzaldehyde and recrystallised from pentane-benzene. MP = 67°C (lit. 64, MP = 67°C).

1-Bromo-1,2-diphenyl ethane was prepared as in Ref. 76 by the reaction of 1,2-diphenyl ethanol with hydrogen bromide in n-pentane at -70°C. The clear oil was filtered through activated charcoal which removed all contaminating cis and trans stilbenes. This was verified by U.V. analysis.

1,2-Diphenyl ethyl acetate was prepared as in Ref. 77 by the acetylation of 1,2-diphenyl ethanol in refluxing acetic anhydride and acetic acid. The oil isolated was distilled, BP = 202°C/9.5 mm (lit. 64, BP = 202-205°C/10 mm).

3-Bromo cyclohexene was prepared as in Ref. 79 by the reaction of N-bromo succinimide with cyclohexene in carbon tetrachloride. BP = 78°C/30 mm (lit. 64, BP = 74°C/28 mm).

3-Chloro cyclohexene was prepared as in Ref. 80 by the reaction of cyclohexene and t-butyl hypochlorite in the presence of benzoyl peroxide. BP = 49.5°C/12 mm (lit. 64, BP = 65-66°C/40 mm).
3-Acetoxy cyclohexene was prepared by Vogel's (Ref. 63) standard method of acetylation with acetic anhydride. BP = 67-68°C/11 mm (lit. 64, BP = 35°C/0.4 mm).

3-Ethoxy cyclohexene. 11.5 gms of trans-1,2-dibromo cyclohexane was refluxed with 200 mls of 1 molar sodium ethoxide in ethanol for 24 hours. 150 mls of ethanol was removed by distillation. The remaining solution was neutralised with 2 molar hydrochloric acid, poured into 300 mls of water and extracted with n-pentane. The pentane layer was washed with water, dried over anhydrous sodium sulphate, filtered, evaporated and the oil distilled. BP = 60°C/20 mm (lit. 64, BP = 154°C).

4-Nitrophenyl cyclohex-2-ene sulphide. 1.5 gms of 4-nitrothiophenol, 10 mls of pyridine and 3.2 gms of 3-bromo cyclohexene in 40 mls of DMF were warmed until the colour faded, poured into ether, washed with water, neutralised to pH = 2 with 2M hydrochloric acid, washed with water, dried over anhydrous magnesium sulphate, filtered, evaporated and the residue recrystallised from methanol. MP = 54-55°C. Analysis: Expected C 61.25 H 5.57 N 5.95 C 61.55 H 5.68 N 5.80

2,3-Dibromo cyclohexene was prepared as in Ref. 81 by the reaction of cyclopentene with bromoform and potassium t-butoxide in t-butanol. The product isolated was thermally rearranged and distilled. BP = 76°C/8 mm (lit. 81, BP = 94°C/4.5 mm).

1-Bromo cyclohexene. 25 gms of 2,3-dibromo cyclohexene and 5 gms of lithium aluminium hydride were mixed in 250 mls of ether and refluxed for 24 hours. 100 mls of saturated sodium sulphate solution was added slowly. The ether layer was washed with water, dried over anhydrous sodium sulphate, filtered, evaporated and the oil was distilled. BP = 54-56°C/20 mm (lit. 64, BP = 48°C/14 mm).

cis-1,2-Dibromo cyclohexane was prepared as in Ref. 82 by the photolysis of 1-bromo cyclohexene and anhydrous hydrogen bromide in n-hexane. The oil was distilled. BP = 100°C/8 mm (lit. 64, BP = 115°C/14 mm).
trans-1,2-Dibromo cyclohexane. To 30 gms of cyclohexene in 150 mls of carbon tetrachloride at 0°C was added 58.5 gms of bromine in 150 mls of carbon tetrachloride. The solution was washed with 10% sodium bicarbonate solution and water. The CCl₄ layer was dried over anhydrous magnesium sulphate, filtered, evaporated and the oil distilled. BP = 72°C/2.5 mm (lit. 64, BP = 101°C/14 mm).

cis-1,2-Dichloro cyclohexane was prepared as in Ref. 83 by the reaction of cis-2-chloro cyclohexanol with thionyl chloride in pyridine. The oil was distilled. BP = 91°C/20 mm (lit. 66, BP = 93.5°C/22 mm).

cis-1,2-Cyclohexane diol was prepared by the method of Vogel (Ref. 63) by the reaction of cyclohexene with osmium tetroxide, and hydrogen peroxide in t-BuOH. The product was recrystallised from ethyl acetate. MP = 96°C (lit. 63, MP = 96°C).

cis-1,2-Diacetoxycyclohexane was prepared by Vogel's (Ref. 63) standard method of acetylation with acetic anhydride and distilled. BP = 118°C/13 mm (lit. 64, BP = 118°C/13 mm).

cis-2-Bromo cyclohexanol was prepared as in Ref. 84 by the aluminium iso-propoxide reduction of 2-bromo cyclohexanone in iso-propanol. The liquid was distilled. BP = 62°C/1.5 mm (lit. 64, BP = 60°C/1 mm).

cis-2-Bromo cyclohexyl-p-toluene sulphonate was prepared as in Ref. 85 by using the Tipson method of reacting cis-2-bromo cyclohexanol with p-toluene sulphonyl chloride in pyridine. The product was recrystallised from n-pentane-benzene. MP = 78-79°C (lit. 85, MP = 79-80°C).

cis-1,2-Cyclohexane diol di p-toluene sulphonate. cis-1,2-Cyclohexane diol was esterified by the Tipson method as in Ref. 86 and recrystallised from methanol. MP = 128-129°C (lit. 86, MP = 128.5 -129.5°C).

trans-1,2-Cyclohexane diol di p-toluene sulphonate. trans-1,2-Cyclohexane diol was esterified by the Tipson method and recrystallised from methanol. MP = 108°C -109°C (lit. 86, MP = 108-109°C).
trans-1,2-Cyclohexane diol was prepared as in Vogel (Ref. 63) by the reaction of cyclohexene with formic acid and 30\% hydrogen peroxide. The solid was recrystallised from ethyl acetate. MP = 102.5 - 103°C (lit. 66, MP = 103°C).

trans-2-Bromo cyclohexanol was prepared as in Ref. 87 by the reaction of N-bromo succinamide and cyclohexene in water. The liquid was distilled. BP = 73°C/5 mm (lit. 87, BP = 73-75°C/5 mm).

trans-2-Bromo cyclohexyl p-toluene sulphonate was prepared as in Ref. 85 by the Tipson method and recrystallised from methanol. MP = 44-45°C (lit. 85, MP = 44-45°C).

5 Apparatus for kinetic measurements
(a) Thermostats

Kinetic measurements were carried out at set temperatures from 0°C to 100°C. All thermostat temperatures were measured with previously calibrated precision thermometers.

0°C. Two methods were used to maintain temperatures at 0°C. The first method used was to place the container in a melting ice bath. Variation in the temperature control was ±0.2°C. The second method was to set a Haake-Kryo thermat model KT41, containing ethanol at 0°C. Variation in the temperature control was ±0.1°C.

25°C. An insulated stainless steel bath containing 50\% polyethylene glycol and 50\% water was maintained at 25°C by a Braun-Melsungen Immersion Thermostat Unit model Thermomix II. Variation in temperature control was ±0.1°C which was the same for all baths controlled by Braun Units.

50°C. An insulated stainless steel bath containing 100\% polyethylene glycol was maintained at 50°C by two Braun Melsungen Immersion Thermostat Units model Thermomix II. Variation in temperature was the same as for 25°C.

75°C and 100°C. Insulated stainless steel baths containing liquid paraffin, BP WM2 were maintained at 75°C and 100°C by Braun Melsungen Immersion Thermostats model Thermomix-universal. Variation in temperature control was ±0.1°C.
(b) **Constant Volume Pipettes**

Pipettes of different volumes were constructed with a two-way tap, fitted above the bulb of the pipette. The device enabled samples of a constant volume to be withdrawn quickly from reaction mixtures. The pipette was calibrated for various solvents at 20°C, using a standard drainage time.

**B Nuclear Magnetic Resonance Spectra (N.M.R.)**

N.M.R. spectra have been determined for all compounds mentioned in section 3. All spectra not reported were as predicted from a prior understanding of N.M.R. No detail is given for any cyclohexyl compounds because all compounds prepared have been previously reported in the literature and in all cases the expected boiling point (or melting point) was obtained. Physical constants for several compounds could not be determined so that elemental analysis and N.M.R. were the methods used to determine or verify structures. The N.M.R. spectra of these compounds and all other compounds in their systems are recorded.
### TABLE XXX

N.M.R. spectral data for 1-aryl-1-propyl system

\[
Y = H \quad \text{NO}_2 \quad \text{CH}_3 \quad \text{CH}_3O \\
X = \text{OH} \quad \text{Br} \quad \text{Cl} \quad \text{OOCCH}_3(\text{OAc})
\]

![Diagram of molecular structure]

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Footnotes TABLE XXX

a All spectra determined in deuterio chloroform solution at 20°C.

b \( \tau \) values are accurate to \( \pm 0.01 \)

c \( J \) values are accurate to \( \pm 0.5 \) cps.

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TABLE XXXI
N.M.R. spectral data for the 1-aryl-2-propyl system

\[ Y \quad H \quad NO_2 \quad CH_3O \]
\[ X \quad OH \quad Br \quad O-COCH_3(OAc) \quad SO_3 \quad CH_3(Otos) \]

\[ Y - CH_2CHXCH_3 \]
\[ Ar \quad A \quad B \quad C \]

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a. All spectra were determined in deuterio chloroform solution.

b. $\tau$ values are accurate to $\pm$ 0.01

c. $J$ values are accurate to $\pm$ 0.5 cps.

d. The signal of the methylene adjacent to the aromatic (A) was often a broad multiplet composed of 4-7 lines. The reason for this is considered to be due to restricted rotation about the $\text{-CH}_2\text{-CHX}$ bond so that the two protons of the multiplet are not exactly identical.

e. The aromatic signals were slightly overlapped. However, it was possible to distinguish the different character of the two aromatic signals.
### TABLE XXXII

N. M. R. spectral data for the 1,2-diphenyl ethyl system$^a$

![Diagram of the 1,2-diphenyl ethyl system](image)

$X = \text{OH, Br, OCOCH}_3(OAc)$

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<td>broad band</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td></td>
<td>A</td>
<td>4.05</td>
<td>triplet</td>
<td>1</td>
<td>7 cps</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>6.90</td>
<td>broad multiplet</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>OCOCH$_3$</td>
<td>8.02</td>
<td>singlet</td>
<td>3</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ All spectra determined in deuterio chloroform solution.

$^b$ $\tau$ values accurate to $\pm$ 0.01

$^c$ $J$ values accurate to $\pm$ 0.5 cps.

$^d$ As in the 1-phenyl-2-propyl system (TABLE XXX) the methylene adjacent to the aromatic ring is not a simple doublet.
### TABLE XXXIII

N.M.R. spectral data for the trans-1-phenyl propene system

![Chemical Structure](https://example.com/structure.png)

\[ Y - C H = C H - C H_3 \]

**Ar** A B C

\[ Y = H, CH_3O, NO_2 \]

<table>
<thead>
<tr>
<th>Compound Y</th>
<th>Proton</th>
<th>( \tau ) value</th>
<th>Description</th>
<th>Integration</th>
<th>( J_{BC} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>Ar</td>
<td>2.78</td>
<td>broad multiplet</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>A</td>
<td>3.50</td>
<td>2nd order multiplet</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>4.02</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>8.15</td>
<td>doublet</td>
<td>3</td>
<td>6 cps</td>
</tr>
<tr>
<td>CH₃O</td>
<td>Ar</td>
<td>3.02</td>
<td>typical para disubstituted</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>A</td>
<td>3.56</td>
<td>2nd order multiplet</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>4.18</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>8.19</td>
<td>doublet</td>
<td>3</td>
<td>6 cps</td>
</tr>
<tr>
<td>CH₃O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO₂</td>
<td>Ar</td>
<td>2.24</td>
<td>typical para disubstituted</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>A</td>
<td>3.57</td>
<td>narrow multiplet</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>B</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>8.08</td>
<td>doublet</td>
<td>3</td>
<td>5 cps</td>
</tr>
</tbody>
</table>

\( a \) All spectra were determined in deutero chloroform. \( \tau \) values are accurate to \( \pm 0.01 \tau \). \( J \) values are accurate to \( \pm 0.5 \) cps.

\( b \) \( J_{AB} \) could not be read directly from the spectrum as the combined signal of the A and B protons was 2nd order.

\( c \) The signal from the A and B protons was a multilined 2nd order spectrum.

\( d \) The signal from the A and B protons was a narrow multiplet from 3.50 \( \tau \) - 3.66 \( \tau \).
C Analytical techniques

1 Potentiometric titrations

Chloride and bromide ions were estimated by potentiometric titration versus standardised silver nitrate solution, using a Copenhagen Radiometer (Type PHM 26) equipped with silver and calomel (mercury/mercurous chloride) electrodes. The calomel electrode was not immersed directly into the titrated solution but connected to the solution by a salt bridge containing saturated potassium nitrate solution. Titration end points were characterised by sharp changes in electrode potential.

Titration of bromide ion in the presence of chloride ion was possible in the presence of 5% barium nitrate solution, added to reduce co-precipitation of the silver halides (Ref. 88). The mixed halide titration gave two end points, the first corresponding to the complete precipitation of the more insoluble silver bromide and the second corresponding to the total halide content of the solution sample. All halide titrations were carried out in acidic media to prevent interference from acetate ion, cyanide ion, or 2,6-lutidine.

Several organic bromides solvolysed rapidly in water or reacted rapidly with silver nitrate. In the presence of these molecules titrations were carried out in 50% acetone-water solutions or the organic molecule was extracted into toluene, after which the water washings could easily be titrated with silver nitrate.

The necessity and validity of the above titration procedures were confirmed by controlled blank experiments. Acidification and extraction procedures are described in more detail in the later sections devoted to specific reactions.

2 Acid-base titrations

In all cases the titration of hydrogen ion or base was carried out in non-aqueous media. All titrations were corrected for a small blank indicator titration. The validity of all titrimetric analyses was verified by control titrations with standard solutions of these ions.
(a) For hydrogen ion: samples were poured into acetone and titrated versus sodium methoxide in methanol beneath a N₂ atmosphere, using thymol blue as an indicator.

(b) For cyanide and acetate ion: samples were poured into acetone and titrated versus p-toluene sulphonic acid in 80% acetone - 20% ethanol, using bromophenol blue as indicator.

(c) For p-nitro thiophenoxide ion: this anion was estimated by titration versus p-toluene sulphonic acid in 80% acetone - 20% ethanol using thymol blue as an indicator.

3 Analytical Vapour Phase Chromatography (V.P.C.)

Gas Chromatographs. The V.P.C. identification and quantitative analysis of substrates and products was carried out using -

(i) Perkin Elmer 881 Flame Ionisation Gas Chromatograph, connected to a Hitachi Perkin Elmer Recorder (model 159).

(ii) Perkin Elmer 900 Flame Ionisation Gas Chromatograph connected to a Hitachi Two-pen Recorder QPD 73.

(iii) Perkin Elmer 880 Flame Ionisation Gas Chromatograph connected to a T.O.A. Electronic Ltd. Electronic Polyrecorder (model EPR-2TB).

Columns. Several different columns were used for the analyses.

(a) A 5% UCON Polar 50-HB 200 on NAW Chromosorb W, 80/100 mesh, 10 ft. long, 1/8" O.D. with a nitrogen carrier gas flow of 30 ml/min. This was used on the Perkin Elmer 880.

(b) A 5% APIEZON L Column on NAW Chromosorb W, 80/100 mesh, 10 ft. long, 1/8" O.D. with a nitrogen carrier gas flow of 30 ml/min. This was used on the Perkin Elmer 880.

(c) A 1.5% SE-30 Methyl Silicone Rubber Gum Liquid Phase on 80-100 mesh Chromosorb W-A.W.-D.M.C.S. in a 6 ft. long, 1/4" O.D. glass column with a carrier gas flow of 30 ml/min. This was used on the Perkin Elmer 881.

(d) An 8% UCON oil, LB-550X Liquid Phase on 60-80 mesh, Chromosorb W - A.W. - D.M.C.S. in a 6 ft. long, 1/4" O.D. Glass column with a carrier gas flow rate of 30 ml/min. This was used on the Perkin Elmer 881.
(e) A 10% APIEZON L Liquid Phase on 60-80 mesh Chromosorb W-N.A.W. in a 6 ft. long, 1/8" O.D. stainless steel column with a carrier gas flow of 60 mls/min. This was used on the Perkin Elmer 900.

(f) A 5% SQUALANE Liquid Phase on 60-80 mesh Chromosorb W-A.W.-D.M.C.S. in a 20 ft. long, 1/8" O.D. stainless steel column with a carrier gas flow of 15 mls/min. This was used on the Perkin Elmer 900.

(g) A 15% 50:50 ETHYLENE GLYCOL - SILVER NITRATE Liquid Phase on 30-60 mesh Chromosorb W-N.A.W. in a 12 ft. long, 1/4" O.D. stainless steel column with a carrier gas flow of 15 mls/min. This was used on the Perkin Elmer 900.

Techniques

A large variety of compounds was studied and therefore a variety of V.P.C. conditions was necessary. It was impossible to use the same sampling technique for each analysis.

When a single compound was analysed quantitatively an internal standard was added to minimise errors in injection volume and variations in the sensitivity of the chromatograph. When two or more compounds were studied an internal standard was unnecessary as the ratio of one compound to the other is invariable on changing the above conditions. It is generally advisable not to inject non-volatile material into the V.P.C., therefore reaction mixtures should have salts removed by extraction. However, the Perkin Elmer 900 injector block assembly can be adapted for direct injection of a reaction mixture.

All the necessary controls were carried out on authentic samples of products to ensure that the analysis was not in error due to isomerisation or decomposition of the products, or losses due to gas leaks at joints.

(i) A 5 ml infinity sample of reaction mixture was poured into 15 mls of n-pentane, washed twice with water and rinsed into a 25 ml volumetric flask. 5 mls of a solution of internal standard was added and the volume made up to 25 mls. A one to four micro litre sample of this solution was then injected into the gas chromatograph.
(ii) A 5 ml infinity sample of reaction mixture was poured into 15 mls of toluene, washed twice with water, rinsed into a 25 ml volumetric flask, and the level was made up to 25 ml. A 1-4 microlitre sample of this solution was injected into the gas chromatograph.

(iii) 1-4 Microlitres of an infinity sample of a reaction mixture was injected directly into the Perkin Elmer 900. This was possible because of the use of a glass insert (inside the injector block) which was lightly packed with glass wool. Deposited salts and the glass wool were later removed from the glass insert.

Generally techniques (ii) and (iii) were used when quantitatively analysing for highly volatile products. Technique (i) was the method of choice for low volatility products.

Peak areas of products were measured by tracing the peak onto tracing paper (Arcus Tracing Paper No. 309) cutting the peak from the sheet and weighing the peak. The same analytical technique would be used for a standard solution of the products and compared to the result from the reaction mixture to determine the accurate product analysis.

**TABLE XXXIV**

General conditions used for V.P.C. analysis of the various substrate systems

<table>
<thead>
<tr>
<th>System</th>
<th>Technique of Analysis</th>
<th>Column</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenyl propane</td>
<td>(i) - pentane ext.</td>
<td>e - Apiezson L</td>
</tr>
<tr>
<td>Stilbene</td>
<td>(i) and (iii) direct</td>
<td>e</td>
</tr>
<tr>
<td></td>
<td>- toluene ext.</td>
<td>f - squalane</td>
</tr>
<tr>
<td>Butane</td>
<td>(ii) and (iii)</td>
<td>f alone and f and g - silver nitrate - in series.</td>
</tr>
<tr>
<td>Methyl pentane</td>
<td>(ii) and (iii)</td>
<td>a, b, c, d - Ucon, Apiezson L and SE-30</td>
</tr>
<tr>
<td>Cyclohexyl</td>
<td>(i)</td>
<td></td>
</tr>
</tbody>
</table>
TABLE XXXV
Reactions studied quantitatively by V. P. C. analysis

<table>
<thead>
<tr>
<th>Compound</th>
<th>Nucleophile</th>
<th>Solvent</th>
<th>Column Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;CHCHOTos&lt;sup&gt;a&lt;/sup&gt;CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>NBu&lt;sub&gt;4&lt;/sub&gt;Br&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Acetone</td>
<td>Squalane and silver nitrate</td>
</tr>
<tr>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;CH=CH&lt;sub&gt;2&lt;/sub&gt;C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;</td>
<td>Equilibration</td>
<td>DMF</td>
<td>Apiezon L.</td>
</tr>
<tr>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;CHBrC&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;</td>
<td>NBu&lt;sub&gt;4&lt;/sub&gt;Br&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Acetone</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>NBu&lt;sub&gt;4&lt;/sub&gt;Cl</td>
<td>DMF</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>NBu&lt;sub&gt;4&lt;/sub&gt;Ac</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>KO&lt;sub&gt;t&lt;/sub&gt;-Bu</td>
<td>t-BuOH</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>NaOMe</td>
<td>80% DMSO-MeOH</td>
<td>&quot;</td>
</tr>
<tr>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;CH=CH-Ch&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Equilibration</td>
<td>DMSO</td>
<td>&quot;</td>
</tr>
<tr>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;-CHBrCH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>NBu&lt;sub&gt;4&lt;/sub&gt;Br&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Acetone</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>NBu&lt;sub&gt;4&lt;/sub&gt;Cl</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>NBu&lt;sub&gt;4&lt;/sub&gt;Ac</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>KO&lt;sub&gt;t&lt;/sub&gt;-Bu</td>
<td>t-BuOH</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>NBu&lt;sub&gt;4&lt;/sub&gt;Br&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Acetone</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>KO&lt;sub&gt;t&lt;/sub&gt;-Bu</td>
<td>t-BuOH</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>NBu&lt;sub&gt;4&lt;/sub&gt;Br&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Acetone</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>NBu&lt;sub&gt;4&lt;/sub&gt;Cl</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>NBu&lt;sub&gt;4&lt;/sub&gt;Ac</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>KO&lt;sub&gt;t&lt;/sub&gt;-Bu</td>
<td>t-BuOH</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>NBu&lt;sub&gt;4&lt;/sub&gt;Br&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Acetone</td>
<td>&quot;</td>
</tr>
<tr>
<td>4NO&lt;sub&gt;2&lt;/sub&gt;C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;CHBrCH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>NBu&lt;sub&gt;4&lt;/sub&gt;Br&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Acetone</td>
<td>&quot;</td>
</tr>
<tr>
<td>CH&lt;sub&gt;3&lt;/sub&gt;CH=CHCH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Equilibration</td>
<td>DMSO</td>
<td>Squalane</td>
</tr>
<tr>
<td>CH&lt;sub&gt;3&lt;/sub&gt;CHBrCH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>NBu&lt;sub&gt;4&lt;/sub&gt;Br&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Acetone</td>
<td>&quot;</td>
</tr>
<tr>
<td>trans</td>
<td>Br&lt;sup&gt;a&lt;/sup&gt;</td>
<td>NBu&lt;sub&gt;4&lt;/sub&gt;CN</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>OTo&lt;sub&gt;s&lt;/sub&gt;</td>
<td>&quot;</td>
<td>&quot; or SE-30</td>
</tr>
<tr>
<td>cis</td>
<td>Br</td>
<td>NBu&lt;sub&gt;4&lt;/sub&gt;Cl&lt;sup&gt;b&lt;/sup&gt;</td>
<td>&quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>OTo&lt;sub&gt;s&lt;/sub&gt;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>cis</td>
<td>OTo&lt;sub&gt;s&lt;/sub&gt;</td>
<td>NBu&lt;sub&gt;4&lt;/sub&gt;Cl&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Acetone</td>
</tr>
<tr>
<td>&quot;</td>
<td>OTo&lt;sub&gt;s&lt;/sub&gt;</td>
<td>NBu&lt;sub&gt;4&lt;/sub&gt;Ac</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

---

<table>
<thead>
<tr>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>a OTos represents p-toluene sulphonate</td>
</tr>
<tr>
<td>b 2,6-Lutidine added to react with HBr produced</td>
</tr>
<tr>
<td>c ArS represents 4-nitro thio phenoxide.</td>
</tr>
</tbody>
</table>
4 Preparative Gas Chromatography

High purity trans stilbene (> 99.96%) was required for equilibration experiments. This was obtained by preparative V. P. C. using a Pye, Series 105, Automatic Preparative Chromatograph installed with a 22 ft, 3/8" O. D. glass column packed with 20% SE-30 silicone methyl rubber gum on 60-80 mesh Chromosorb W-AW-DMCS at 210°C with a flow rate of 60 ml/min.

1-Phenyl-1-propyl t-butyl ether was a possible product in the reaction of 1-phenyl-1-bromo propane with potassium t-butoxide in t-butanol. A small sample of a V. P. C. peak assigned as the ether was collected from a Varian Aerograph series 200 fitted with 5% SE-30 on 60-80 mesh Chromosorb W-NAW packed in a 5 ft long, 1/4" O. D. stainless steel column. A sample of the liquid collected was submitted for a mass spectral determination of the structure.

5 Mass Spectrometry

Structural determination of one compound was carried out. This was 1-phenyl-1-propyl t-butyl ether (see previous section 4). The mass spectrum was determined on an A. E. I. MS 902 Mass Spectrometer, using a heated inlet system. The spectrum was run at 70 ev and 12 ev.

The sample was proven to be the ether and not the only other possible product, cis-1-phenyl propene, by several features -

(a) Occurrence of a molecular ion (small) m/e = 168
(b) " M-28 ion (McLafferty loss of CH₂=CH₂)
(c) " M-57 ion (Loss of tBu· radical)
(d) The presence of major ions with m/e > 118 which is mass number of 1-phenyl propene.

D Determination of rate constants

The kinetic methods described in the Results Section were used repeatedly. However, only one example of a typical run will be given for each type of kinetic analysis.
**Typical Run I**

The reaction of $1-(4$-nitro phenyl)$-1$-bromo propane with $\text{NBu}_4\text{Br}$ in the presence of 2,6-lutidine, in acetone as solvent, at $75.0^\circ\text{C}$. 4.80 ml samples of 0.0174 molar alkyl bromide, 0.0987 molar $\text{NBu}_4\text{Br}$ and 0.0505 molar 2, 6-lutidine in acetone were warmed at $75.0^\circ\text{C}$ for various times. The samples were cooled and quenched into 30 mls acetone and titrated with sodium methoxide in methanol (0.0101 M) using thymol blue as an indicator. The titrant mixture was washed into 30 mls of water, acidified with 5 mls of 2 molar nitric acid and titrated potentiometrically with silver nitrate (0.01006 M).

Run Results - All units in mls $\text{AgNO}_3$ 0.01006 molar

<table>
<thead>
<tr>
<th>No.</th>
<th>Time</th>
<th>mls NaOMe</th>
<th>mls AgNO$_3$</th>
<th>$a - x (\text{RBr pres.})$</th>
<th>log $\frac{1}{a - x}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Zero</td>
<td>0.31</td>
<td>47.95</td>
<td>8.30</td>
<td>$1.0810$</td>
</tr>
<tr>
<td>2</td>
<td>2 hrs</td>
<td>1.46</td>
<td>49.30</td>
<td>6.95</td>
<td>$1.1581$</td>
</tr>
<tr>
<td>3</td>
<td>4 &quot;</td>
<td>2.81</td>
<td>50.53</td>
<td>5.72</td>
<td>$1.2425$</td>
</tr>
<tr>
<td>4</td>
<td>6 &quot;</td>
<td>4.02</td>
<td>51.50</td>
<td>4.75</td>
<td>$1.3232$</td>
</tr>
<tr>
<td>5</td>
<td>8 &quot;</td>
<td>5.77</td>
<td>52.33</td>
<td>3.92</td>
<td>$1.4067$</td>
</tr>
<tr>
<td>6</td>
<td>11 &quot;</td>
<td>5.80</td>
<td>53.15</td>
<td>3.10</td>
<td>$1.5087$</td>
</tr>
<tr>
<td>7</td>
<td>12 &quot;</td>
<td>6.25</td>
<td>53.76</td>
<td>2.49</td>
<td>$1.6037$</td>
</tr>
<tr>
<td>8</td>
<td>$\infty$</td>
<td>8.69</td>
<td>56.25</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

See Eqn 7 and figure 12 for $\log \frac{1}{a - x}$ vs time which gives a slope $= \frac{0.45}{11x60x60\text{sec}^{-1}}$

$$k_2 = \frac{2.303}{b} \times \text{slope} \times \frac{\text{vol. of sample}}{\text{concentration of titrant}}$$

$$k_2 = \frac{2.303}{47.95} \times \frac{0.450}{11x60x60} \times \frac{4.80}{0.01006} \text{1/mole/sec.}$$

$$k_2 = 2.60 \times 10^{-4} \text{1/mole/sec.}$$

For a repeat Run with freshly prepared solutions the result was $2.64 \times 10^{-4} \text{1/mole/sec.}$

The amount of bromide ion produced by the solvolysis reaction after 12 hrs at $75^\circ\text{C}$ in the presence of lutidine and $\text{NBu}_4\text{ClO}_4$ was 0.10 mls.

This was representative of all the reactions in TABLE I. Except where stated, all solvolyses were found to be less than 0.5% after two half lives of the bimolecular reaction.
Figure 12. The reaction of 1-(4-halo phenyl)-1-bromo propane with NaN₄ in the presence of 2,6-toluene in acetone at 75°C.
Typical Run II

The reaction of 1-(4-nitro phenyl)-1-bromo propane with tetra-n-butyl ammonium chloride in DMF solution at 25.0°C.

4.80 ml samples of 0.0212 molar alkyl bromide and 0.0425 molar NBu₄Cl in DMF were warmed at 25.0°C for various times and quenched into toluene and water. The ions were extracted into the water and titrated with silver nitrate solution (0.00962 M) in the presence of barium nitrate.

Run Results - All units in mls AgNO₃ (0.01006 molar).

<table>
<thead>
<tr>
<th>No.</th>
<th>Time</th>
<th>1st end point</th>
<th>2nd end point</th>
<th>Cl⁻ present</th>
<th>RBr present</th>
<th>log ( \frac{b-Fs_x}{a-x} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0 secs</td>
<td>.10</td>
<td>20.88</td>
<td>20.78</td>
<td>10.00</td>
<td>.3177</td>
</tr>
<tr>
<td>2</td>
<td>78 &quot;</td>
<td>.90</td>
<td>20.90</td>
<td>20.00</td>
<td>9.20</td>
<td>.3373</td>
</tr>
<tr>
<td>3</td>
<td>193 &quot;</td>
<td>1.70</td>
<td>20.90</td>
<td>19.20</td>
<td>8.40</td>
<td>.3589</td>
</tr>
<tr>
<td>4</td>
<td>313 &quot;</td>
<td>2.31</td>
<td>20.94</td>
<td>18.64</td>
<td>7.79</td>
<td>.3790</td>
</tr>
<tr>
<td>5</td>
<td>433 &quot;</td>
<td>2.90</td>
<td>20.95</td>
<td>18.04</td>
<td>7.20</td>
<td>.3981</td>
</tr>
<tr>
<td>6</td>
<td>553 &quot;</td>
<td>3.47</td>
<td>20.95</td>
<td>17.48</td>
<td>6.63</td>
<td>.4211</td>
</tr>
<tr>
<td>7</td>
<td>733 &quot;</td>
<td>4.13</td>
<td>20.97</td>
<td>16.84</td>
<td>5.97</td>
<td>.4504</td>
</tr>
<tr>
<td>8</td>
<td>9000 &quot;</td>
<td>10.10</td>
<td>21.12</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

See Eqn 8 and figure 13 for \( \log \frac{b-Fs_x}{a-x} \) vs time which gives a slope

\[ \frac{\text{volume of sample}}{\text{concentration of titrant}} \times \text{slope} = \frac{.13}{750 \text{ sec}} \]

\[ k_{2}^{ES} = \frac{2.303}{b-aF_s} \times \text{slope} \times \frac{4.80}{0.00962} \]

\[ = 1.85 \times 10^{-2} \text{ l/mole/sec.} \]

Note: For this calculation Fs was assumed to be .98 ± .02 as derived from the titration figures. The later V.P.C. analysis showed the value to be .99 ± .005.

In all cases except where stated in TABLE VI solvolysis was checked and found to be less than 5% in two half lives of the bimolecular reaction.
Figure 13: The reaction of 1-(4-nitrophenyl)-1-bromo propane with tetra-n-butyl ammonium chloride in DMF at 25°C.
In TABLE XXXVI are the reactions for which the general form in b, c, d was used.

**TABLE XXXVI**

General bimolecular reactions where the nucleophile and leaving group are not equivalent.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Nucleophile</th>
<th>Solvent media</th>
<th>Temp. °C</th>
<th>M b</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆H₅CHBrCH₂CH₃</td>
<td>NBu₄Cl</td>
<td>DMF</td>
<td>25</td>
<td>Fs</td>
</tr>
<tr>
<td>4CH₃C₆H₄CHBrCH₂CH₃</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4NO₂C₆H₄CHBrCH₂CH₃</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₆H₅CHBrCH₂C₆H₅</td>
<td></td>
<td></td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>CH₃CHBrCH₂CH₃</td>
<td></td>
<td></td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>CH₃CHBrCH₂C₆H₅</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₆H₅CHBrCH₂CH₃</td>
<td>NBu₄OAc</td>
<td></td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>C₆H₅CHBrCH₂C₆H₅</td>
<td></td>
<td>t-Butanol</td>
<td>25, 46</td>
<td>1</td>
</tr>
<tr>
<td>C₆H₅CHBrCH₂CH₃</td>
<td>KOt-Bu</td>
<td></td>
<td>75</td>
<td>1</td>
</tr>
<tr>
<td>cis</td>
<td>NaOEt</td>
<td>Ethanol</td>
<td>75</td>
<td>1</td>
</tr>
<tr>
<td>cis</td>
<td></td>
<td></td>
<td>50</td>
<td>1</td>
</tr>
<tr>
<td>cis</td>
<td>NBu₄Cl</td>
<td>Acetone-lutidine (.04)</td>
<td>100</td>
<td>1</td>
</tr>
<tr>
<td>cis</td>
<td></td>
<td>(.04)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>cis</td>
<td>NBu₄OAc</td>
<td>Acetone</td>
<td>75</td>
<td>1 + Fe</td>
</tr>
<tr>
<td>cis</td>
<td></td>
<td></td>
<td>50</td>
<td>1 + Fe</td>
</tr>
<tr>
<td>trans</td>
<td>NBu₄ArS</td>
<td></td>
<td>75</td>
<td>1 + Fd</td>
</tr>
<tr>
<td>trans</td>
<td>NBu₄CN</td>
<td></td>
<td>75</td>
<td>1 + Fd</td>
</tr>
</tbody>
</table>
Footnotes

TABLE XXXVI

a Except where otherwise stated, concentration was 0.02 molar.
b M in equation 17.
c Except where otherwise stated, concentration was 0.04 molar.
d Determined by Mr. R. I. Tilley.
e A significant amount of solvolysis was encountered. The bimolecular rate constant was corrected for this.
f OTos is p-toluene sulphonate.
g Figures in parenthesis represent the concentration of the reactants.
h Concentration of compound was 0.013 molar.
i OAc is acetate ion. Concentration of NBu₄OAc was 0.03 molar.
j ArS is 4-nitro thiophenoxide.
k Concentration of compound was 0.01 molar.
l Control experiments were carried out to show that 3-bromo-cyclohexene rapidly reacts with cyanide and 4-nitro thiophenoxide to give substitution product.

Typical run III

The solvolysis of 1-(4-nitro phenyl)-1-bromo propane in 50% acetone-water at 75°C

4.16 ml samples of 0.0228 molar alkyl bromide in 50% acetone water were warmed at 75°C for various times, cooled and poured into 30 mls of 50% acetone and titrated with silver nitrate (0.01025 molar).

Run - all units in mls AgNO₃ (0.01025).

<table>
<thead>
<tr>
<th>Number</th>
<th>Time</th>
<th>mls AgNO₃</th>
<th>RBr pres.</th>
<th>log ( \frac{1}{a-x} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Zero</td>
<td>.09</td>
<td>9.47</td>
<td>1.0236</td>
</tr>
<tr>
<td>2</td>
<td>30 min.</td>
<td>.86</td>
<td>8.70</td>
<td>1.0594</td>
</tr>
<tr>
<td>3</td>
<td>92 &quot;</td>
<td>2.15</td>
<td>7.41</td>
<td>1.1302</td>
</tr>
<tr>
<td>4</td>
<td>135 &quot;</td>
<td>2.95</td>
<td>6.61</td>
<td>1.1799</td>
</tr>
<tr>
<td>5</td>
<td>180 &quot;</td>
<td>3.66</td>
<td>5.90</td>
<td>1.2292</td>
</tr>
<tr>
<td>6</td>
<td>225 &quot;</td>
<td>4.24</td>
<td>5.32</td>
<td>1.2741</td>
</tr>
<tr>
<td>7</td>
<td>270 &quot;</td>
<td>4.87</td>
<td>4.69</td>
<td>1.3288</td>
</tr>
<tr>
<td>8</td>
<td>∞</td>
<td>9.56</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
By plotting \( \log \frac{1}{a - x} \) vs time (see figure 14) a straight line results with

\[
\text{slope} = \frac{.225}{200 \times 60} \text{ sec}^{-1}
\]

\[
k_1 = 2.303 \times \frac{.225}{200 \times 60} \text{ sec}^{-1}
\]

\[
= 4.32 \times 10^{-5} \text{ sec}^{-1}
\]

A repeat run gave the result

\[
4.04 \times 10^{-5} \text{ sec}^{-1}
\]

The solvolysis rates studied were accurate to \( \pm 5\% \). Other compounds for which solvolysis rates were determined are listed in TABLE XXXVII.
Figure 14: Solvolysis of 1-(4-nitro phenyl)-1-bromo propane in 50% acetone water at 75°C.
**TABLE XXXVII**

Compounds and conditions for which solvolysis rates were determined

<table>
<thead>
<tr>
<th>Compound</th>
<th>Medium&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Temp&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>4NO&lt;sub&gt;2&lt;/sub&gt;C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;CHBrCH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>50% acetone-water</td>
<td>75°C</td>
</tr>
<tr>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;CHBrCH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>CH&lt;sub&gt;3&lt;/sub&gt;CHBrCH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>CH&lt;sub&gt;2&lt;/sub&gt;BrCH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;CHBrCH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>90% acetone-water</td>
<td>75°C</td>
</tr>
<tr>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;CHBrCH&lt;sub&gt;2&lt;/sub&gt;C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>4CH&lt;sub&gt;3&lt;/sub&gt;64H&lt;sub&gt;4&lt;/sub&gt;CHBrCH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;CHClCH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Acetone-lutidine (.06)NBu&lt;sub&gt;4&lt;/sub&gt;Cl (.08)</td>
<td>75°C</td>
</tr>
<tr>
<td>4CH&lt;sub&gt;3&lt;/sub&gt;64CHClCH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;3&lt;/sub&gt; &quot;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>4CH&lt;sub&gt;3&lt;/sub&gt;64CH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;3&lt;/sub&gt; &quot;</td>
<td>t-Butanol-lutidine (.04)</td>
<td>&quot;</td>
</tr>
<tr>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;CHBrCH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

Footnotes **TABLE XXXVII**

<sup>a</sup> Figures in parenthesis represent the concentration of the compound or salt in the medium.

<sup>b</sup> Where two temperatures are reported this indicates that the rate was determined at both temperatures and an Arrhenius extrapolation of rate to other temperatures was carried out in order to directly compare results for different compounds.
Typical Run IV

The reaction of 1-bromo-1,2-diphenylethane with potassium t-butoxide at 46.3°C as determined using the Gilford U.V. spectrometer. 0.00128 molar alkyl bromide and 0.0358 molar potassium t-butoxide in t-butanol was warmed at 46.3°C and the Gilford machine set to follow the change in optical density at 295 mµ with respect to time.

A reference cell containing t-BuOH was used as the blank.

Two controls carried out simultaneously were standard trans-stilbene and potassium t-butoxide in t-butanol (which showed no change) and 0.00128 M alkyl bromide in t-butanol (this showed no solvolysis).

Run at 295 mµ \( \infty OD = 1.82 \)

<table>
<thead>
<tr>
<th>Time</th>
<th>OD</th>
<th>OD( _\infty - OD)</th>
<th>( \log (OD\infty - OD))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zero</td>
<td>.57</td>
<td>1.25</td>
<td>.0969</td>
</tr>
<tr>
<td>10.1 min.</td>
<td>.83</td>
<td>.99</td>
<td>1.9956</td>
</tr>
<tr>
<td>20.2 &quot;</td>
<td>1.02</td>
<td>.80</td>
<td>1.9031</td>
</tr>
<tr>
<td>30.3 &quot;</td>
<td>1.20</td>
<td>.62</td>
<td>1.7924</td>
</tr>
<tr>
<td>40.4 &quot;</td>
<td>1.32</td>
<td>.50</td>
<td>1.6990</td>
</tr>
<tr>
<td>50.5 &quot;</td>
<td>1.42</td>
<td>.40</td>
<td>1.6021</td>
</tr>
<tr>
<td>60.6 &quot;</td>
<td>1.50</td>
<td>.32</td>
<td>1.5051</td>
</tr>
<tr>
<td>70.7 &quot;</td>
<td>1.56</td>
<td>.26</td>
<td>1.4151</td>
</tr>
</tbody>
</table>

\[-k_1 = \frac{2.303 \log (OD\infty - OD)}{time} \]

Plotting \( \log (OD\infty - OD) \) (see figure 15) vs time a straight line results with

slope = \( \frac{-k_1}{2.303} \)

\[-k_1 = 2.303 \times \text{slope} \]

\[= \frac{2.303}{1} \times \frac{-.195}{20 \times 60} \]

\[k_1 = 3.74 \times 10^{-4} \]

\[k_2 = \frac{k_1}{[tBuO^-]} \]

\[= \frac{.000374}{.0358} \]

\[= 1.05 \times 10^{-2} \text{ l/mole/sec.} \]
A repeat reaction following 309 mµ gave the result
\[ k_2 = 1.15 \times 10^{-2} \text{ l/mole/sec.} \]

Therefore the result obtained is accurate to within ±5%. This was the only reaction followed by U.V. spectroscopy because -

(1) Other solvents interfered with absorptions.

(2) Reactions were generally so slow that they would need to be determined at 100°C which is far too high a temperature for the U.V. spectrometer.

(3) Absorptions of reactants and other products overlapped greatly with the desired product olefin.
Figure 15  The Reaction of 1-bromo-1, 2-diphenyl ethane with potassium t-butoxide in t-butanol at 46.3°C.
SCIENTIFIC PAPERS RELEVANT TO THIS WORK

"The E₂C Mechanism in elimination Reactions. Part II. Substituent effects on rates of elimination from acyclic systems."

"The E₂C Mechanism in elimination reactions. Part V. Elimination from five and six membered alicyclics."

"The E₂C Mechanism. Charge distribution at C_a in E₂C, SN₂ and solvolysis transition states."


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(b) A. Schriesheim and C. A. Rowe, J. Amer. Chem. Soc., 84, 3160 (1962).


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58 Unpublished results privately communicated from Mr. M. Ruane. See also Reference 20.


Results determined by Mr. R. I. Tilley.


K. Ziegler, A. Spath, E. Schaaf, W. Schumann and E. Winkelmann, Annalen, 551, 80, (1942).


