

THE AUSTRALIAN NATIONAL UNIVERSITYFACULTY OF SCIENCEDEPARTMENT OF CHEMISTRYANNUAL REPORT 1966

Professor and Head of Department	A.N. Hambly, M.Sc., Dip. Ed. (Melb.), F.R.A.C.I. (on leave May 1966 to January 1967)
Associate Professor (Organic Chemistry)	W.D. Crow, M.Sc. (Syd.), Ph.D. (Sheff.), F.R.A.C.I. (Acting Head of Department)
Visiting Professor	A.G. Anderson, Jr., M.S., Ph.D. (Mich.)(May to December 1966)
Reader (Physical Chemistry)	J.H. Bradbury, M.Sc. (Melb.) Ph.D. (Birm.), F.R.A.C.I.
Senior Lecturers	R.F.C. Brown, M.Sc. (Syd.), Ph.D. (Cantab.), F.R.A.C.I. (on leave 1966) N.S. Gill, M.Sc., Ph.D. (Syd.) J.A. Broomhead, B.Sc. (Syd.), Ph.D. R.N. Warrenner, M.Sc. (Syd.), Ph.D. (N.S.W.)
Lecturers	N.J. Daly, B.Sc., Ph.D. (W. Aust.) D.L. Scott, B.Sc., Ph.D. (Tas.) B.K. Selinger, M.Sc. (Syd.), Dr. rer. nat. (Stuttgart)
Temporary Lecturer	C.P. Whittle, B.Sc., Ph.D. (Adel.)
Senior Demonstrators	G.F. Kolar, B.Sc. (Tas.) M. Sterns, M.Sc., Ph.D. (Melb.) M.L. Tonnet, M.Sc. (Syd.), Ph.D. J.G. Wilson, M.Sc. (Syd.), Ph.D. (Nott.)
Demonstrator	M.P. Henry, B.Sc.
Research Assistants	P.W. Atkinson, B.Sc. (Reserve Bank Fund) K.H.J. Bryant, B.Sc. (Adel.) G.V. Chapman, B.Sc. (Wool Research Fund) J.J. Foster, B.Sc. (Syd.) N.L.R. King, B.Sc. (Q'ld.) (Wool Research Fund) R.K. Solly, B.Sc. (W.A.) M.Sc. (resigned 23.9.66)
Head Technician	A.T. Miles, A.W.A.S.M.

Developments in the undergraduate area have been largely confined to final year courses. The new Chemistry III course to be delivered for the first time in 1967, will consist of a large number of lecture topics from which the student will select suitable courses. In this way it is hoped to present a more flexible course and at the same time permit more rigorous treatment of some areas. With the change of intake pending in First Year, major course experiments did not seem profitable, and attention has been largely directed to improvement and diversification of the laboratory courses. Arrangements have been made with A.N.U. Press to produce a loose-leaf laboratory manual for 1967.

During 1966, visitors to the Department who lead seminars in the weekly programme for senior undergraduate and graduate students were:

Professor A.G. Anderson, Jr., University of Washington (Seattle).
 Professor A.J. Birch, University of Manchester.
 Professor A. Maccoll, University of London.
 Dr. E.A. Magnusson, Avondale College.
 Dr. M.F.R. Mulcahy, C.S.I.R.O. Coal Research, Sydney.
 Professor M. Szwarc, New York State University, Syracuse.
 Professor E. Wenkert, Indiana University.

Professor A.N. Hambly was on leave for portion of the year, which was spent at the State University of New York (Buffalo) as Visiting Professor.

Dr. R.F.C. Brown was also on study leave for 1966 at the University of Southampton, carrying out research on photo-chemistry with Professor R.G. Cookson. In addition to visits to U.K. universities, Dr. Brown attended the I.U.P.A.C. Congress on Chemistry of Natural Products at Stockholm.

Professor A.G. Anderson, Jr., (University of Washington, Seattle, U.S.A.) spent a period of six months in the Department as Visiting Professor. Quite apart from the formal post-graduate lectures which he gave, Professor Anderson contributed greatly to the Department's activities through his discussions with staff and students, and his participation in seminars.

Student Enrolment and Performance

The rate of increase in student enrolment fell from the high value of 35% to 5% in 1966, probably due largely to the fact that many students chose to repeat their last school year, thus taking advantage of the "Wyndham" year (1967). The relevant statistics are given below:

Unit	Enrolled	Examined	Passed	Classified
General Chemistry	79	65	49	1 HD, 6 D, 10 Cr
Chemistry I	95	81	56	3 HD, 7 D, 10 Cr
Chemistry II	33	32	22	1 HD, 3 D, 6 Cr
Chemistry IIIA	16	16	12	1 HD, 1 D, 5 Cr
Chemistry IIIB	23	23	19	2 HD, 1 D, 5 Cr
Chemistry IV	3	3	3	1 HI, 2 HIIA
M.Sc. (Qual.)	3	3	3	-
M.Sc. (Thesis)	10	3	3	-
Ph.D.	12	2	2	-

Research Activities(a) General

The Department was for the first time eligible to apply for funds to the Australian Research Grants Committee. Despite the short notice, four projects were nominated and resulted in a total grant of \$21,600. The accepted projects were two in number - a combined project on NMR of proteins, insect attractants and ^{13}C -compounds (Bradbury, Crow and Warrener) and a study of time-resolved spectroscopy (Selinger).

The Rural Credits Division of the Reserve Bank made a grant of \$20,000 over a three-year period to support a study of naturally occurring insect attractants in timber species (Crow). Portion of the funds were used to purchase an A.E.I. MS10C2 mass spectrometer, which has been functioning well and has proved a valuable addition to departmental equipment.

The NMR facilities have now been extended to cover ^{13}C resonance and variable temperature work, and arrangements have been made to use a PDP-8S computer as a C.A.T. on the instrument.

(b) Inorganic Chemistry

Pure Cs_2MnCl_4 containing the octahedral species MnCl_4^{2-} has been prepared by dehydration of $\text{Cs}_2\text{MnCl}_4 \cdot 2\text{H}_2\text{O}$. Reported methods of preparation for K_4MnCl_6 were found unsatisfactory, but the compound can be prepared by fusion of KCl with MnCl_2 under suitable conditions. Ligand field parameters for these compounds have been calculated from their reflectance spectra.

The UV absorption spectra of some Mn(II) halide compounds have been obtained from single crystals and agreement found with calculated band positions. A preliminary study of Mn(III) halide compounds has also been made.

(Gill and Foster)

Compounds resulting from the reaction between 4-picoline and copper(II) chloride are under investigation. Of the three products isolated, only one has been previously described.

Formulae have been assigned to the new compounds, and X-ray diffraction studies are being employed to determine the structures.

(Gill and Sterns)

A number of new ruthenium(III) dihalobis(ethylenediamine) complexes have been synthesised and their geometrical configurations established as cis by resolution of the racemate. Detailed kinetic studies show that the mechanisms of substitution are characterised by a marked base catalysis accompanied by retention of configuration. Various infra-red criteria used for the detection of cis-trans isomers have been critically evaluated in conjunction with this work and all but one method found to be unreliable.

(Broomhead and Kane-Maguire)

An erroneous literature report concerning the synthesis of cis and trans dihalobis(1,10-phenanthroline)iridium(III) compounds has been corrected and several new methods for the synthesis of iridium complexes developed. Studies of substitution reactions show these iridium compounds to be extremely inert but susceptible to catalysis by light.

(Broomhead and Grumley)

The reaction between ammonia and iodine under various conditions is being examined with a view to establishing the mode of formation of the explosive "nitrogen iodide". The various products of the reaction have yielded some copper derivatives which are under examination.

(Scott)

(c) Organic Chemistry

The mechanism of S-N bond fission in 3-isothiazolone by nucleophiles was further investigated. It proved possible, by the utilisation of appropriate carbanions, to synthesise a series of glutaconimides - an unusual case of sulphur extrusion.

(Crow and Gosney)

Acylation studies on 3-isothiazolone lead to O-acylation, followed more or less readily by migration of the acyl group to N. In the case of the mesyl and tosyl derivatives, however, N-substitution occurs, followed by migration to O. The mechanism of the migration is under examination.

(Chan and Crow)

The study of thermally excited molecules has been continued with a view to establishing the existence of a prismane intermediate structure in the aromatic migrations; the well known isomerisation of the xylenes is being more closely investigated. Work on the production of hetarynes continues.

(Crow and Wentrup)

Callitris hugelii volatiles have been isolated and subjected to separation by gas-liquid chromatography. Identification and structural work are in progress while awaiting field tests against Diadoxus spp. ("Jewel Beetle").

(Atkinson and Crow)

Cleavage of the dimeric and trimeric procyanidins in Vitis has been achieved by heating in water at 90°. Catechin and epicatechin are produced, as well as unidentified products. Attempts to label the site of cleavage by working in deuterium oxide were foiled by a facile exchange of the aromatic hydrogens in the methylated phloroglucinol ring. A number of aromatic ethers were also studied, and a general explanation for the exchange (or lack of exchange) has been suggested.

(Crow and Kolar)

The previous failure of the mycelianamide synthesis has been ascribed to an unexpected cyclic elimination of a sulphoxide intermediate, leading to deoxygenation at one of the hydroxamic acid functions. Alternative methods are still under examination.

(Brown and Meehan)

The products obtained from the action of acetic anhydride on cyclic ketonitrones have been shown to be butenolides, not α -pyrones as originally thought. The mechanism of their formation has been elucidated.

(Brown and Subrahmanyam)

Studies on the synthesis of pyrimidines from 1,3-thiazines have led to successful production of either N-alkylated uracils or N-alkylated 2-thiouracils. The method has been extended to a general synthesis of orotic acid derivatives.

(Cain and Warrenner)

Photoaromatisation of 3,6-dimethyl-4,5-diphenylcyclohexadiene dicarboxylic anhydride is even more facile than was previously observed for the 3,4,5,6-tetramethyl derivative. The 3,4,5,6-tetraphenyl anhydride undergoes rearrangement on photoaromatisation, and this is believed to involve a benzvalene intermediate. The pyrolysis and mass spectral fragmentation of these compounds have also been studied for comparison.

(Anderson, Barnes*, Bremner and Warrenner)

Possible synthetic routes to 3,3'-dipyridylmethane have been investigated. The reaction of 2-aminopyridine derivatives with formic acid and formaldehyde affords methylated compounds in most cases. In some cases 5-hydroxymethyl derivatives are formed. However, these fail to condense further to give the 3,3-dipyridylmethane system.

(Whittle)

Desulphurisation of thiophen derivatives with nickel boride catalysts has indicated that these catalysts are capable of selective desulphurisation in the presence of unsaturated linkages.

(Whittle)

It was found that pyridine derivatives could not be prepared from 6-membered cyclic α -keto-nitrones.

(Brown, Subrahmanyam and Whittle)

The reaction between 2-aminopyridine and methyl propiolate has been re-investigated in some detail, and a correction has been made to the structure of one of the products.

(Wilson)

(d) Physical Chemistry

Measurement of the conductance of solutions in D_2O under pressures of 1-2000 atmospheres shows that the increase in conductivity with pressure is less than for the corresponding H_2O solutions.

(Hambly and Tonnet)

A special burner was constructed to allow accurate measurement of the number of atoms in the light path for atomic absorption spectroscopy. The results indicated that the present theory does not predict the experimental results. A theory has been developed which allows for Doppler and pressure broadening of the spectral line profile for both the emitting and absorbing atoms, and has been used in the development of a computer programme. Excellent agreement between predicted and experimental values has been obtained.

(Hambly and Rann)

Polarographic studies were continued on the reduction of nitroanilines at the dropping mercury cathode. Values of the diffusion current and the half-wave potential have been observed for a series of o-, m- and p-nitroanilines as a function of pH and temperature.

(Bryant and Hambly)

Previous studies on the solvation of hydrogen halides in halobenzenes have been extended to include a study of the base strength of the solvents. Rotation of the smaller molecules (HCl, HBr, DCl) have been observed in all solvents where the presence of a methyl group does not obscure the IR bands.

(Hambly and Henry)

Studies have been continued on the interfacial polycondensation reaction between terephthaloyl chloride and piperazine in heptane/water. Both hydrolysis and polyamidation are shown to be first order with respect to acid chloride, and to have activation energies of 12 and 4 k.cal.mole⁻¹ respectively.

(Bradbury and Crawford)

The presence of citrulline and 3,4-dihydroxyalanine in unmedullated keratin has been confirmed. The latter is known to be implicated in the formation of melanin granules which cause pigmentation of the fibres.

The so-called epicuticle membrane of wool fibres (ca. 10^{-6} cm thick) has been separated; analysis shows it to be about 80% protein, and aminoacid analysis indicates that it probably forms part of the cuticle membrane. Some progress has also been made in separation of the ortho-cortex and para-cortex components of wool fibres.

(Bradbury, Chapman and King)

Work on the conformation of the synthetic polypeptide poly- γ -benzyl-L-glutamate has continued. Viscosity studies in mixed solvents have been aided by a range of samples of different known molecular weights (kindly supplied by Prof. P. Doty, Harvard University), and these measurements are now being extended to lower M.W. with samples prepared in these laboratories.

(Bradbury and Fenn)

Peptides and proteins containing histidine are being examined by NMR with a view to determining the pKa's of the histidine residues. It is hoped to obtain valuable information about the active sites where histidine is involved.

(Bradbury and Wilairat)

The kinetics of thermal decomposition of t-butyl methyl and ethyl ethers have been studied in the range 433-495°. Both reactions are essentially first order, the products being isobutene and the corresponding alcohol; no alkanes or ketones are produced. The appropriate rate equations are

$$\text{t-butyl methyl ether: } k_1 = 10^{14.55} \exp(-61,600/RT) \text{ sec}^{-1}$$

$$\text{t-butyl ethyl ether: } k_1 = 10^{4.22} \exp(-59,700/RT) \text{ sec}^{-1}$$

Both reactions are concluded to be homogeneous eliminations.

(Daly and Wentrup)

The reactions of naphthalenes in the excited (single) state (excimer fluorescence, proton transfer reactions, kinetics of photodimer formation) are being studied by spectroscopic methods. Photochromic changes in other aromatic systems are being examined.

(Selinger and Wilairat)

Spectral changes over intervals in the nanosecond region are being probed with high speed detection equipment.

(Selinger and Speed)

Molecular orbital calculations on the 3-hydroxyisothiazole molecule, and others, have been completed.

(Christie and Selinger)

Other Activities

The Third National Convention of the R.A.C.I. was held in Canberra in August; both academic and technical staff were heavily involved in the organisation and day-to-day administration. Staff and students of the department presented a total of ten lectures on a wide variety of topics. Mrs. Lalitha Subrahmanyam (a recent M.Sc. graduate) being awarded the R.A.C.I. Prize for the best student lecture.

Dr. C.P. Whittle and Dr. B.K. Selinger continued to act as Deputy Wardens in Garran and Burton Halls respectively. Both will be getting married in early 1967 and will not be continuing with their duties. Dr. N.S. Gill left the Department in December to take sabbatical leave at the University of East Anglia. She will be working with Professor S.F. Mason on aspects of spectroscopy, and will be absent for the whole of 1967.

Developments in 1967

The increase in student numbers, post-graduate research workers and staff members has already reached the stage where little expansion is possible. Extensions to the Department, originally expected to be commenced in 1967, have now been set back by some two years. The expected fall in first year numbers in 1967 will hopefully permit unlimited entry in that year, but restrictions to enrolment in subsequent years now seem unavoidable.

The Research School of Chemistry will be in operation in late 1967, and it is possible that some participation in the teaching programme may be arranged with interested staff members.

Publications by the Staff and Students of the Department during 1966

BRADBURY, J.H., CHAPMAN, G.V., and KING, N.L.R.

"The chemical composition of wool. II. Analysis of the major histological components produced by ultrasonic disintegration." Aust. J. biol. Sci., 18, 353-64 (1965).

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BRADBURY, J.H., and SCHERAGA, H.A.[†]

"Structural studies of ribonuclease. XXIV. The application of nuclear magnetic resonance spectroscopy to distinguish between the histidine residues of ribonuclease." J. Am. Chem. Soc., 88, 4240-4246 (1966).

BROOMHEAD, J.A.^{**}

"Resolution of oxalatobis(ethylenediamine) cobalt (III) bromide by a preferential induced crystallisation." Nature, 211, 741-2, (1966).

BROWN, R.F.C., CROW, W.D. and SOLLY, R.K.^{*}

"Formation and fission of 2,3-dehydropyrazine by pyrolysis of pyrazine-2,3-dicarboxylic anhydride." Chem. and Ind., 1966. 343.

BROWN, R.F.C., RAE, I.D.^{*}, SHANNON, J.C.[†], STERNHELL, S.[†] and SWAN, J.M.[†]

"Synthetic studies in the 1,2-dithiole series. IV. The methylation of 4-benzamido-1,2-dithiole-3-thione." Aust. J. Chem., 19, 503-511, 1966.

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"The pyrolysis of polycarbonyl compounds. I. Mass spectral and pyrolysis fragmentation of indanetrione." Aust. J. Chem., 19, 1045-57, 1966.

CHAN, A.W.K. and CROW, W.D.

"Chemical constituents of Eriococcus confusus Maskell. I. The quinonoid pigments." Aust. J. Chem., 19, 1701-8, 1966.

CROW, W.D. and GOSNEY, I.

"Isothiazole chemistry. III. Kinetics and mechanism of cyclization of cis-3-thiocyanoacrylamide." Aust. J. Chem., 19, 1693-9, 1966.

CROW, W.D., and SOLLY, R.K.

"Reactions of excited molecules. I. A thermal four-centre migration in phenylhydrazones." Aust. J. Chem., 19, 2119-26, 1966.

DALY, N.J.^Ø and STIMSON, V.R.[‡]

"The thermal decomposition of diisopropyl ether." Aust. J. Chem., 19, 239-50, 1966.

GILL, Naida S. and KINGDON, Hilary J.*

"The infrared spectra of complexes of transition metal halides with substituted pyridines". Aust. J. Chem., 19, 2197-211, 1966.

HAMBLY, A.H.

"The concept of stability in chemistry." Approach to Chemistry, 1966, 1-19.

SELINGER, B.K.**

"The photoassociation of some substituted naphthalenes. I. Rate constants and thermodynamic data for excited dimer formation." Aust. J. Chem., 19, 825-34, 1966.

WARRENER, R.N.

"Synthesis of 1-substituted-6-alkyl-5-cyanouracils, including the N(1)-amino and N(1)-hydroxy-derivatives." Chem. and Ind., 381, 1966.

WARRENER, R.N. and BREMNER, J.B.

"Excited-state reactions of 1,2,4,5-tetramethyl-3,5-cyclohexadiene-cis-1,2-dicarboxylic anhydride." Angew. Chem., 78, 305 (1966); internat. edit., 5, 311-2 (1966).

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WARRENER, R.N. and CAIN, E.N.

"Synthesis of 1-hydroxy-2-thiouracils." Angew. Chem., 78, 491 (1966); internat. edit., 5, 511-2 (1966).

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"1-Thiapyrimidines : Sulphur analogues of nucleic acid bases." Tetrahedron Letters, 3225-9, 1966.

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"The synthesis and rearrangement of 1,3-oxazines." Tetrahedron Letters, 3251-5, 1966.

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"A novel synthesis of 1,2-dithiol-3-thione." Chem. and Ind., 289-290, 1966.

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"A one-step synthesis of fused pyrimidine dithiones." Angew. Chem., 78, 333, (1966); internat. edit., 5, 309-10 (1966).

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DARNALL, K.R.[†], LEUTZINGER, E.[†], PAN, Y.H.[†] and TOWNSEND, L.B.[†]

"The preparation of Deoxynucleosides via the Fusion Procedure".
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American Chemical Society, Sept. 1965, Atlantic City, New Jersey.