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Demystifying the dendralenes*

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Abstract: We present herein an overview of our ongoing studies with dendralenes. The first synthetic routes to this fundamental family of compounds have revealed long-hidden secrets in hydrocarbon chemistry and set the scene for synthetic and materials chemistry applications.

Keywords: cycloadditions; dendralenes; domino reactions; hydrocarbons; organic synthesis; polycyclic compounds; polyenes.

INTRODUCTION

There are four main classes of conjugated polyalkenic hydrocarbons: the linear polyenes, annulenes, dendralenes, and radialenes (Fig. 1). As originally identified by Hopf [1], the distinction between these structures comes from the connectivity of the parent ethylene units. Linear polyenes are unbranched and acyclic, and their cyclic counterparts are the annulenes. Dendralenes are a family of branched, acyclic oligoalkenes, whereas their cyclic forms are termed "radialenes". Additionally, there exist hybrid families of both linear and branched connectivity, most notably the fulvenes.

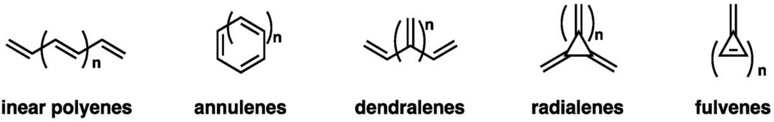

Fig. 1

Both the linear conjugated polyenes and the annulenes have received much attention in the literature [2]. Radialenes and fulvenoid compounds, while less popular, have also been the subject of several reviews [3]. Until last year, the dendralenes had been the subject of only one comprehensive review from almost 30 years ago [1]. Prior to their synthesis in 2000 [4], the dendralenes had remained largely neglected. With neglect, however, comes opportunity for scientific discovery [5].

The dendralenes are trivially named by placing the number of alkene units in brackets before the word "dendralene" (Fig. 2). Early synthetic studies towards the [*n*]dendralenes were primarily focused on the preparation of the triene and tetraene [1]. These approaches included classical methods of alkene synthesis, such as high-temperature eliminations [6], which often required rather harsh reaction conditions [1]. Furthermore, none of these approaches were conducive to the preparation of members higher than the tetraene.

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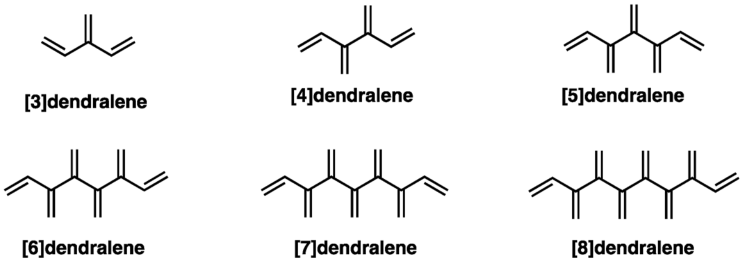
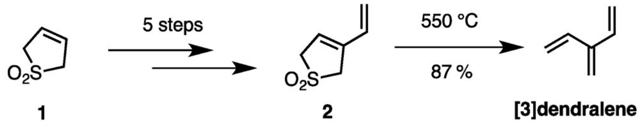


Fig. 2

SYNTHESIS OF THE PARENT DENDRALENES

Due to the widely anticipated instability of the dendralenes [1,7], initial work towards their synthesis involved the use of 1,3-butadiene masking groups. An important contribution in dendralene synthesis came from Cadogan and co-workers in 1991, who were able to prepare [3]dendralene in 6 steps from 3-sulfolene **1** [8] (Scheme 1). In the final step, [3]dendralene was prepared in 87 % yield from 3-vinyl-3-sulfolene **2** via pyrolysis at 550 °C. This result was key to the development of the first general [*n*]dendralene synthesis, which was reported by our group in 2000 [4].

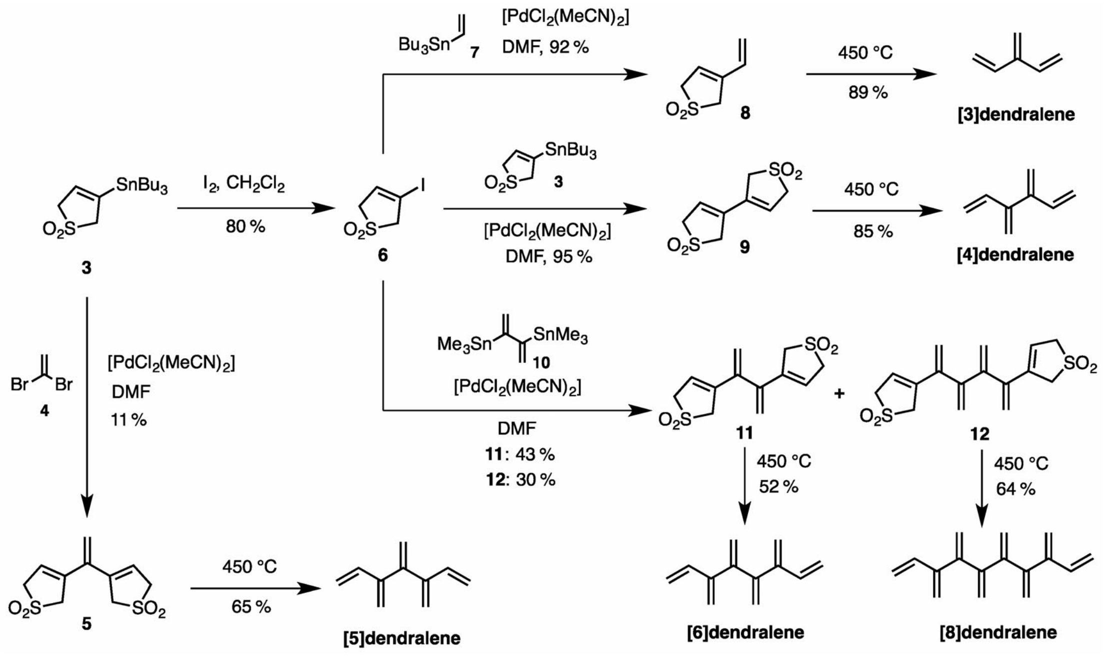


Scheme 1

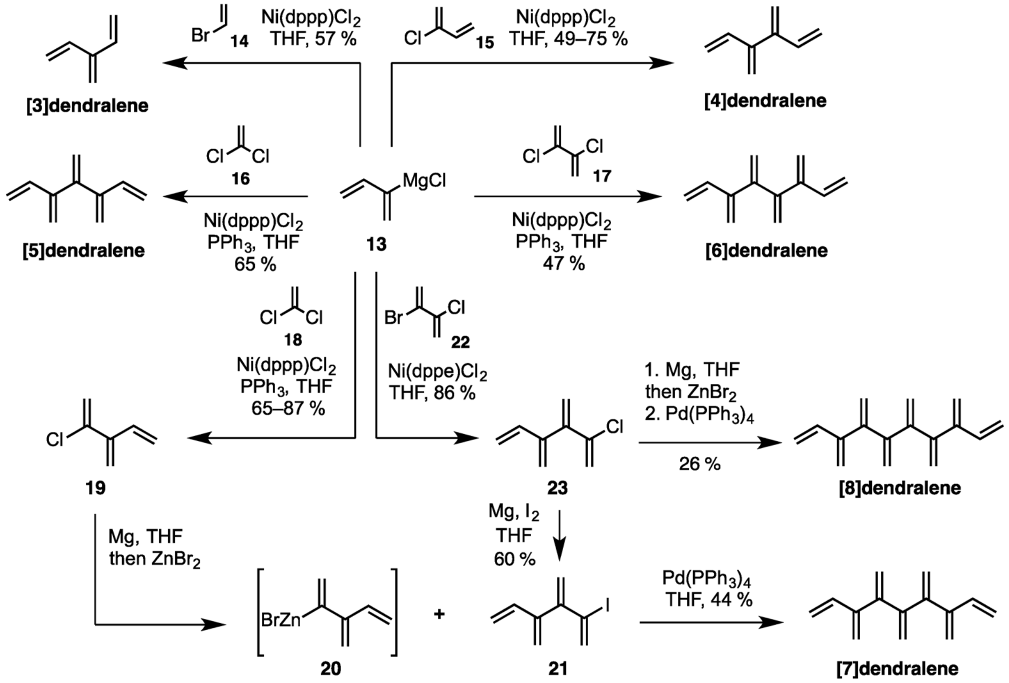
Our general synthetic approach involved a more modern method for the formation of C(sp^2)–C(sp^2) bonds than those used in previous dendralene syntheses. Thus, a series of Stille cross-coupling reactions were used to generate our sulfolene-masked [*n*]dendralene precursors from the previously reported 3-tributylstannyl-3-sulfolene **3** [9] (Scheme 2). A two-fold Stille coupling between alkenylstannane **3** and 1,1-dibromoethylene **4** generated our [5]dendralene precursor **5**, albeit in low yield. The remaining [*n*]dendralene precursors were prepared via iodinolysis of stannane **3** to produce iodide **6**, which then participated in a series of Stille reactions with suitable alkenic or sulfolenic stannanes to produce the precursors to [3]-, [4]-, and [6]dendralene, as well as the precursor to [8]dendralene **12**, which was produced fortuitously, as an unexpected by-product in the generation of [6]dendralene precursor **11**.

The sulfolene-masked dendralenes depicted in Scheme 2 were found to be stable white solids, exhibiting generally poor solubility in common organic solvents. For this reason, pyrolysis of these stable precursors was performed directly on the solids (rather than in solution) to give the parent dendralenes in yields in the 50–90 % range on 1–8 mg scale [4]. The dendralenic products were trapped neat at low temperature and diluted with solvent before full characterization. This publication represented the first report of any member of the family higher than [4]dendralene [10].

Despite the success of this original approach published in 2000, the small scale of the synthesis precluded a study into the properties of the dendralenes beyond NMR, IR, UV–vis, and MS characterization. The discovery that the dendralenes could be handled in neat form at ambient temperature came later, through a concerted effort to achieve a multiple gram scale, *direct* synthesis of [4]dendralene [11]. Following this, the first cross-coupling approach to the family of parent [3]- to [8]dendralenes that avoided the use of masking groups was quickly devised. While the literature of cross-coupling reactions to form C(sp^2)–C(sp^2) is vast, relatively few papers describe polyene synthesis and only a tiny number



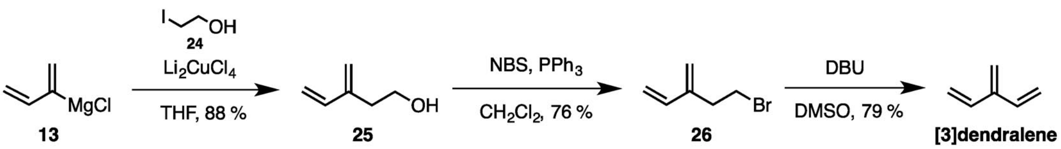
Scheme 2



Scheme 3

are concerned with branched polyenes. After many failed attempts to apply methods developed for arene coupling partners, we eventually found success with a combination of Ni(0)-catalyzed Kumada couplings and Pd(0)-catalyzed Negishi couplings [12] (Scheme 3). The chloroprene Grignard reagent **13** was used as our key starting material for this sequence. The lower members of the dendralene family, namely, [3]- through [6]dendralenes, can be generated in one step from the chloroprene Grignard reagent using suitable mono-electrophiles **14** and **15**, or bis-electrophiles **16** and **17**. Synthesis of the higher dendralenes is currently less facile. The two building blocks required for [7]- and [8]dendralene (**19** and **23**) are prepared from chloroprene Grignard reagent **13**, in one step. [7]Dendralene is prepared via a Kumada coupling of the organozinc species **20** and iodide **21**. [8]Dendralene is prepared via an oxidative Pd(II)-catalyzed homo-coupling of the organozinc reagent derived from chloride **23**.

While the direct cross-coupling approach is efficient in producing the dendralenes, we are limited to the production of [3]dendralene as a solution in tetrahydrofuran (THF). (This solvent is required for generation of the chloroprene Grignard reagent, and the boiling points of THF and [3]dendralene are very similar.) In order to procure [3]dendralene as a neat liquid, we first treated the chloroprene Grignard reagent **13** with 2-iodoethanol **24** to form alcohol **25**, which was then converted into bromide **26** [13] (Scheme 4). Slow addition of diazabicycloundecene (DBU) to a solution of bromide **26** in dimethyl sulfoxide (DMSO) allows [3]dendralene to be distilled out of the reaction mixture as it is produced, and collected in a cold trap. This simple method has granted us access to [3]dendralene in up to 5 g batches.



Scheme 4

The highest dendralene reported so far is [8]dendralene, with the main hurdle towards the generation of higher analogs being access to the requisite bifunctional dendralene building blocks. Efforts are underway to address this issue. Our reported procedures did, however, allow the preparation of synthetically useful amounts (200 mg to 10 g) of the complete series from [3]- to [8]dendralene. The completion of this work placed us in a unique position: We were able to explore the properties of this fundamental polyene family for the first time.

SPECTROSCOPIC PROPERTIES OF THE PARENT DENDRALENES: ALTERNATION IN BEHAVIOR

With increasing numbers of –CH=CH– units, the increased conjugation in the all-*E* linear polyenes (Fig. 1) is observed in UV spectra as an increase in wavelength (λ_{max} increases by ca. 25 nm per alkene), as well as an increase in molar extinction coefficient of a *group* of absorption peaks of similar appearance [14]. Interestingly, in all except [3]dendralene, the dendralenes show a *single* UV–vis absorption maximum (λ_{max} = 215–217 nm, hexane) [12]. This absorption maximum is reminiscent of that of 1,3-butadiene. [3]Dendralene has two absorption maxima (λ_{max} = 206, 231 nm, hexane).

When the molar extinction coefficients are plotted against the number of C=C units in the dendralene, a pattern becomes apparent (Fig. 3). The even dendralenes demonstrate a linear increase in molar extinction coefficient, which rises by ca. 10 000 units as each additional 1,3-butadiene is added. The odd dendralenes, however, exhibit lower extinction coefficients, and do not show a linear correlation.

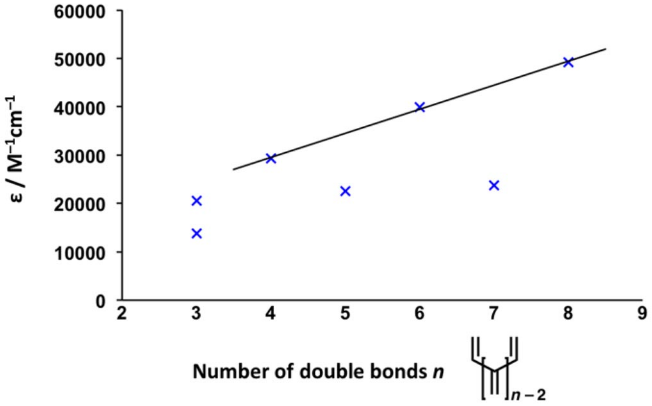
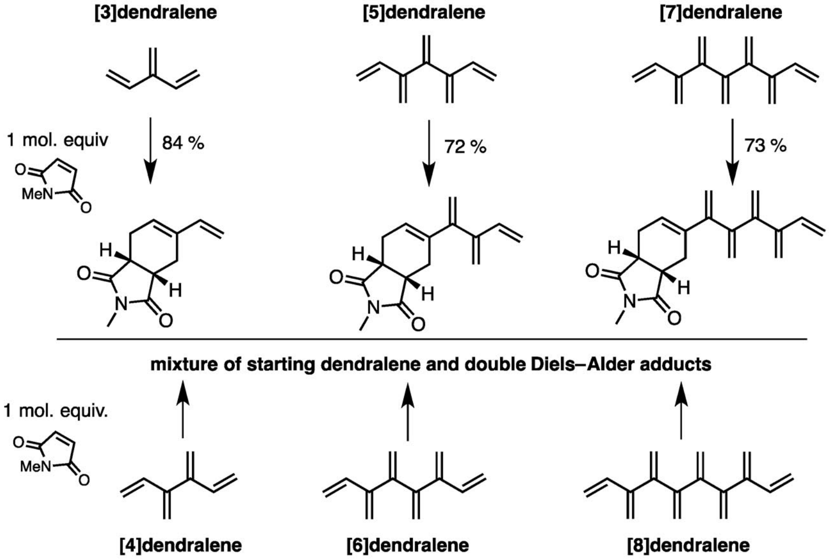


Fig. 3

STABILITY AND REACTIVITY OF THE PARENT DENDRALENES: ALTERNATION IN BEHAVIOR

After preparing these hydrocarbons on the hundreds of milligrams to several grams scale, we began to realize that the dendralenes show an alternating pattern of stability [12]. The odd dendralenes are less stable than their even counterparts, dimerizing and oligomerizing readily. This behavior is most pronounced in the triene and the tetraene. [3]Dendralene, for example, has a half-life of only 10 h as a neat liquid at 25 °C. [4]Dendralene, on the other hand, can be stored neat at room temperature for months without decomposition. [5]Dendralene and [7]dendralene are more stable, but still exhibit half-lives less than an order of magnitude higher than that of the triene. The higher even-parity dendralenes are less stable than the tetraene but can still be stored neat for extended periods of time.

This pattern of stability also translates to their reactivity (Scheme 5). The odd dendralenes react rapidly with 1 molar equivalent of *N*-methylmaleimide (NMM) to generate the mono-adducts cleanly and in good yields [12]. In contrast, when subjected to 1 molar equivalent of NMM, the even den-



Scheme 5

dralenes are slower to react, and generate mixtures of unreacted starting material and double Diels–Alder adducts.

These experimental findings have been supported and explained by density functional theory (DFT) calculations by Prof. Paddon-Row [15] (Fig. 4). The even-parity dendralenes show a clear preference for one conformation. The lowest-energy conformations of the even dendralenes are comprised of conjugated *s-trans* 1,3-butadienyl units, which sit almost orthogonal to their neighbors. The odd-parity dendralenes also prefer conformations containing conjugated *s-trans* 1,3-butadienyl units, but have an additional, less conjugated alkene. There is a slight preference for the "odd one out" alkene to be at the end of the chain, in an orientation that is closer to an *s-cis* relationship with its neighbor than *s-trans*.

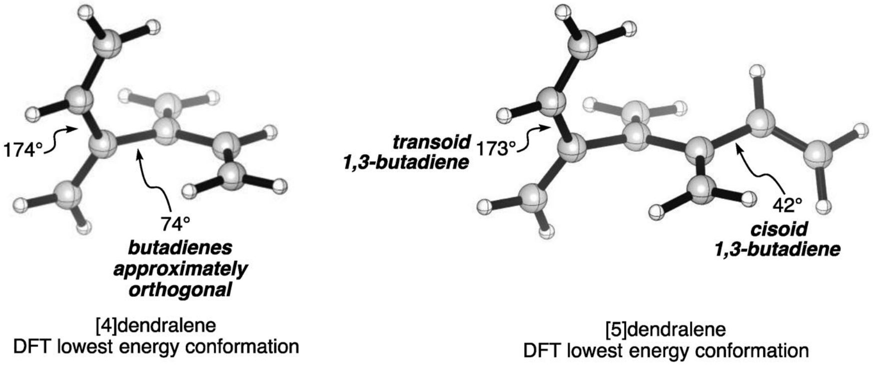


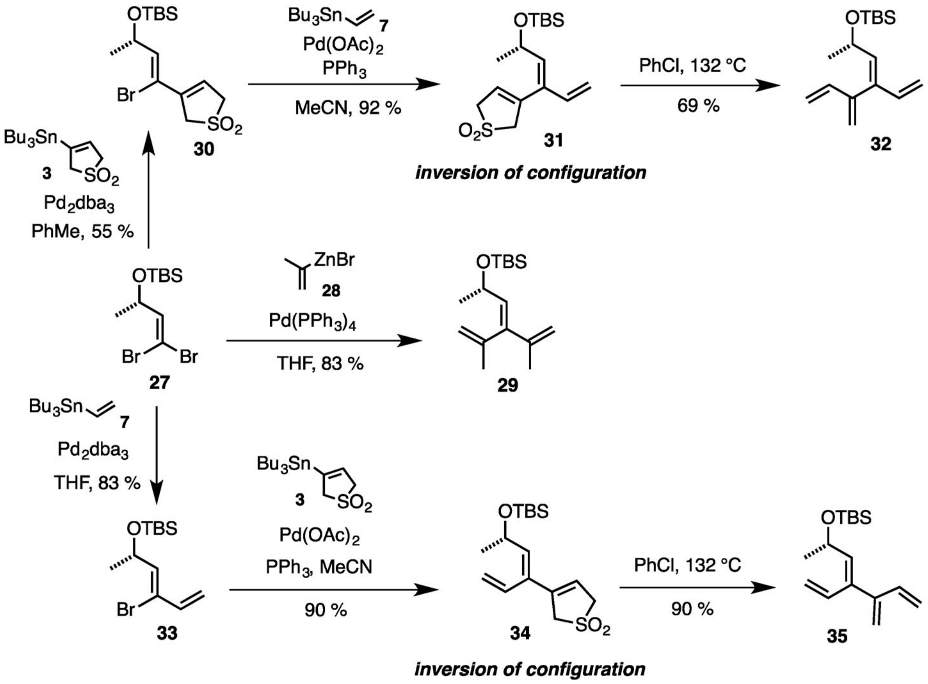
Fig. 4

The differential reactivity of the odd and even dendralenes towards dienophiles can now be explained. When an odd dendralene undergoes a Diels–Alder reaction, it reacts at the terminal diene site since this has a cisoid conformation (which is required for a concerted Diels–Alder reaction). The cycloaddition generates a substituted even dendralene, which is more stable than the starting odd dendralene. Conversely, the even dendralenes, which are more sluggish to react, will generate a substituted odd dendralene when they react at the terminal diene site. This is more reactive than the starting material, and will rapidly participate in a second Diels–Alder reaction.

SYNTHESIS OF SUBSTITUTED DENDRALENES

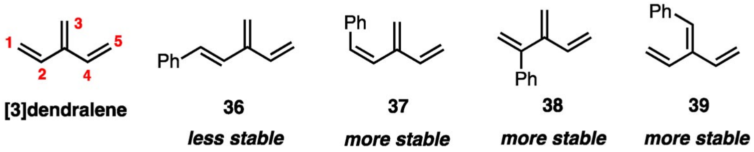
While the synthesis and analysis of the parent systems is essential in understanding their fundamental reactivity, applications will require access to substituted dendralenes. Numerous syntheses of substituted [3]dendralenes have been reported [16], and over the past decade or so we have developed our own methods for the preparation of substituted dendralenes and related cross-conjugated systems [17]. These studies have uncovered interesting and unusual aspects of reactivity in polyenic systems.

Much of our work has focused on the development of cross-coupling methods for the synthesis of cross-conjugated systems. 1,1-Dibromoalkenes are particularly convenient precursors to substituted dendralenes, since they are readily prepared through Ramirez dibromo-olefination of aldehydes [17b]. Thus, a double Negishi cross-coupling reaction between dibromoalkene **27** and two molar equivalents of propen-2-yl zinc bromide **28** gave substituted [3]dendralene **29** (Scheme 6). This approach also allows access to substituted [4]dendralenes, such as **32**, via a series of two Stille reactions, followed by pyrolysis of sulfolene **31**. Curiously, the second Stille reaction proceeds with inversion of configuration at the electrophilic sp^2 carbon site. This phenomenon has also been noted by Negishi in coupling reactions between organozinc species and 2-bromo-1,3-dienes [18]. By changing the order of the two Stille reactions, we are able to access compound **35**, a geometrical isomer of the tetraene **32**.



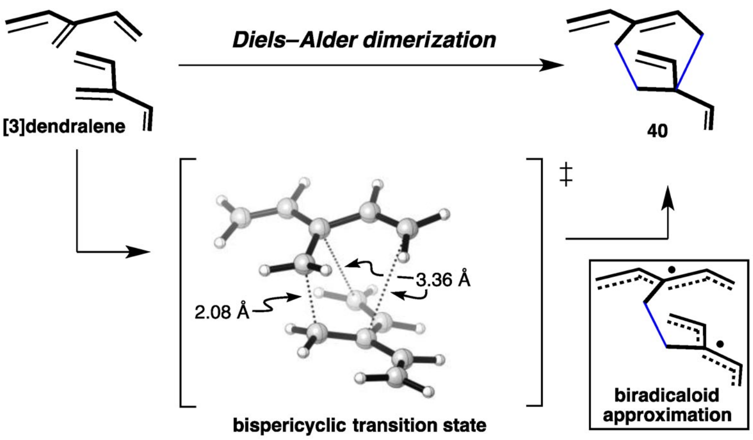
Scheme 6

We have carried out the first systematic investigations into the influence of substituents on the properties of cross-conjugated systems, with surprising results. For example, the incorporation of the same substituent can have either a stabilizing or destabilizing effect, depending upon the position of attachment. The mono-substituted [3]dendralene system is a case in point. Of the four possible regioisomeric mono-phenyl [3]dendralenes (Scheme 7), it was found that a phenyl substituent at the 1-*Z* (**37**), 2- (**38**), or 3-position (**39**) conferred increased stability relative to the parent [3]dendralene. Conversely, 1-*E*-phenyl [3]dendralene **36** is much less stable, undergoing Diels–Alder dimerization at a rate of up to 200 times greater than that of the parent [3]dendralene [17c].



Scheme 7

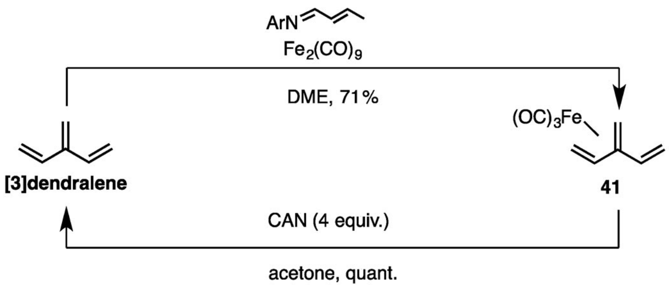
These experimental findings were explained by DFT calculations performed by Prof. Paddon-Row [17c]. The dimerization of [3]dendralene occurs via a bispericyclic transition state, with one short-forming bond and two degenerate long-forming bonds (Scheme 8). This transition structure can be approximated to a bis-pentadienyl radical. The presence of a radical-stabilizing substituent at the 1-*E*-position (such as a phenyl goup) stabilizes the transition state, thus causing acceleration of the dimerization reaction.



Scheme 8

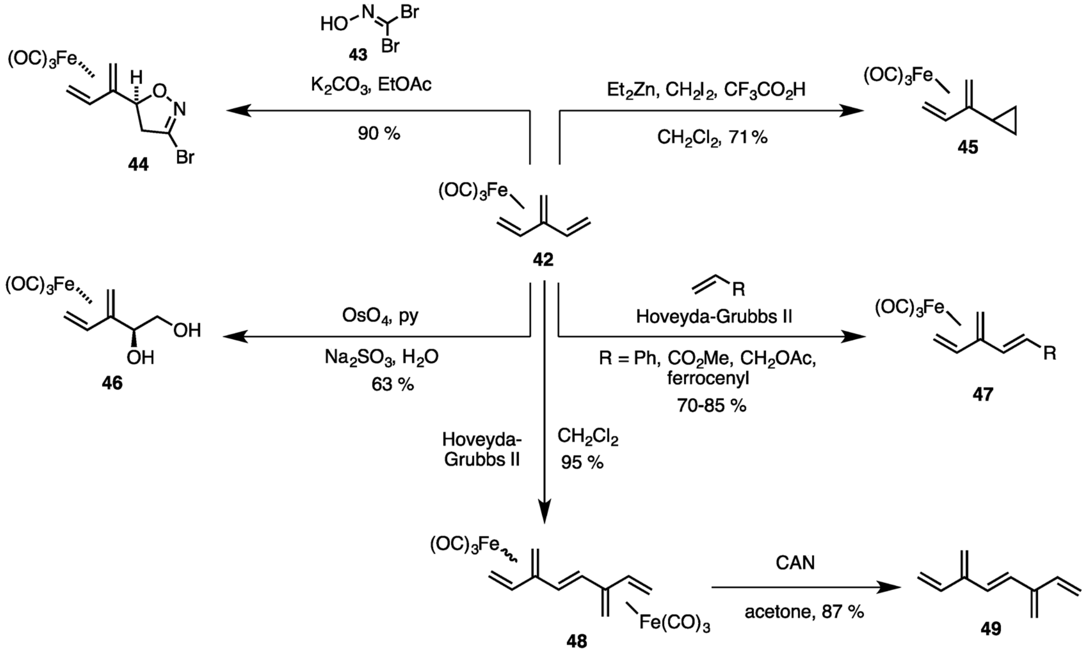
REACTIONS OF THE DENDRALENES

While we have had significant success in the functionalization and reactions of the dendralenes, we have occasionally encountered selectivity issues. In an effort to gain more control over the reactivity of the dendralenes, we turned to iron tricarbonyl complexes as 1,3-butadiene masking groups [19]. For example, we found that [3]dendralene can be converted into iron tricarbonyl complex **41** in good yield (Scheme 9). Treatment of the iron complex **41** with ceric ammonium nitrate (CAN) resulted in decomplexation and high-yielding recovery of the hydrocarbon.



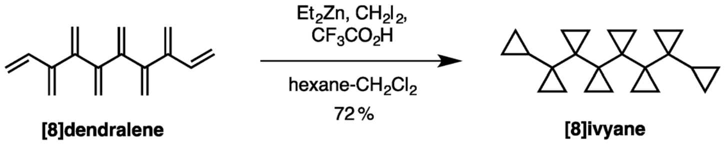
Scheme 9

This complexation allows selective mono-1,3-dipolar cycloaddition, as well as mono-cyclopropanation and -dihydroxylation, feats that had proved unattainable on the parent dendralene [19] (Scheme 10). This gave us an array of functionalized 1,3-butadienes **44**, **45**, and **46** in complexed form, which could be decomplexed and reacted further. Cross-metathesis reactions allowed a very straightforward synthesis of substituted dendralenes **47** (in complexed form), and self-metathesis of the iron tricarbonyl complex of [3]dendralene generated compound **48**. Decomplexation with CAN allowed the first synthesis of pentaene **49**, one of the simplest possible structures containing both through- and cross-conjugation.



Scheme 10

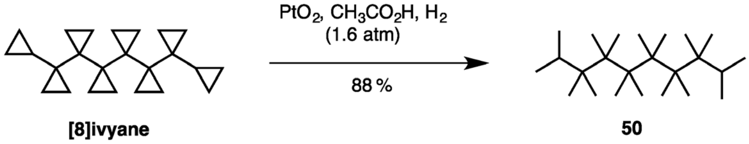
The dendralenes are turning out to be superb starting materials for fundamental hydrocarbons that had previously not succumbed to synthesis. Thus, an exhaustive Simmons–Smith cyclopropanation of [3]- through [8]dendralene generated the ivyane family of 1,1-linked oligocyclopropanes [20]. While more traditional cyclopropanation methods gave incomplete conversions, the Shi trifluoroacetic acid-activated zinc carbenoid protocol gave clean transformation into the desired compounds [21]. Synthesis of [8]ivyane is illustrated in Scheme 11, a reaction sequence that forms 16 carbon–carbon bonds in one pot.



Scheme 11

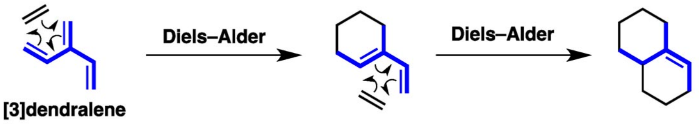
The ivyane family, which exhibit an interesting chiral helical molecular structure, have some other unexpected properties. [6]Ivyane has one of the highest reported experimental heats of combustion of any hydrocarbon [20]. Hydrogenolysis reactions performed on the ivyanes generate yet more interesting hydrocarbons, such as acyclic system **50** carrying all carbon quaternary centers at six contiguous sites on the main chain (Scheme 12). Such structures have not been accessed previously.

Perhaps the most useful synthetic attribute of the dendralenes is their Diels–Alder reactivity. The Diels–Alder reaction is, of course, one of the most important and powerful organic reactions, forming two new bonds, one new ring, and up to four contiguous stereocenters in one operation. Domino sequences of Diels–Alder reactions are therefore incredibly efficient ways to construct complex multicyclic systems. The dendralenes are unique in their ability to perform diene-transmissive Diels–Alder (DTDA) reaction sequences.



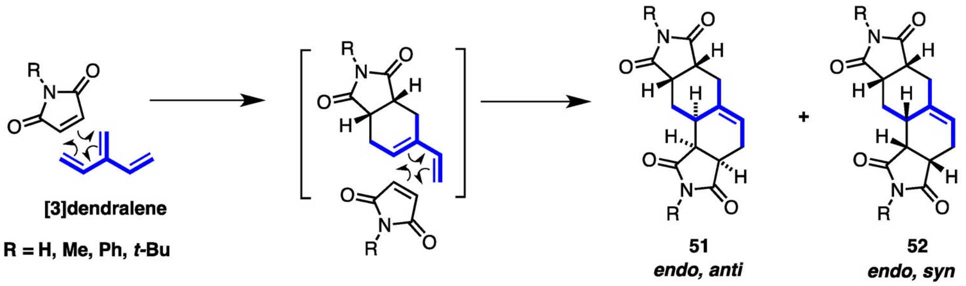
Scheme 12

The simplest DTDA sequence of the simplest dendralene is illustrated in Scheme 13. In this process, [3]dendralene reacts as a diene in a Diels–Alder reaction with ethylene, generating 1-vinylcyclohexene, another 1,3-butadiene. This "transmitted" semicyclic diene can then undergo a second Diels–Alder reaction with ethylene, to generate a mono-unsaturated decalin system. The term "diene-transmissive" was coined by Tsuge and co-workers, who carried out important early work in this area [22].



Scheme 13

We are by no means the first group to explore DTDA sequences of dendralenes [6,23]. We have, however, attempted to study DTDA reactivity in a systematic manner with a view to specific synthetic applications and an extension of the concept to higher polyenic systems. We are particularly interested in controlling the outcomes of these reactions. The DTDA cascade of [3]dendralene with *N*-substituted maleimides, for example, generates a mixture of diastereomers **51** and **52** [11] (Scheme 14). The stereoselectivity of the process improves significantly with increasing size of the *N*R substituent.

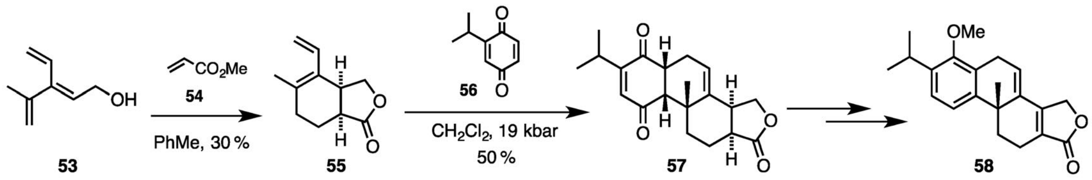


Scheme 14

We have also performed this Diels–Alder reaction sequence using [4]- and [5]dendralene [24]. While the increased number of double bonds present in the higher dendralenes means that the Diels–Alder sequence becomes increasingly powerful, it also becomes increasingly complex. These reactions give mixtures of single, double, and triple Diels–Alder adducts, as mixtures of diastereomers. Evidently, the key to unlocking the true synthetic potential of the dendralenes lies in the development of methods to control the outcomes of these reactions.

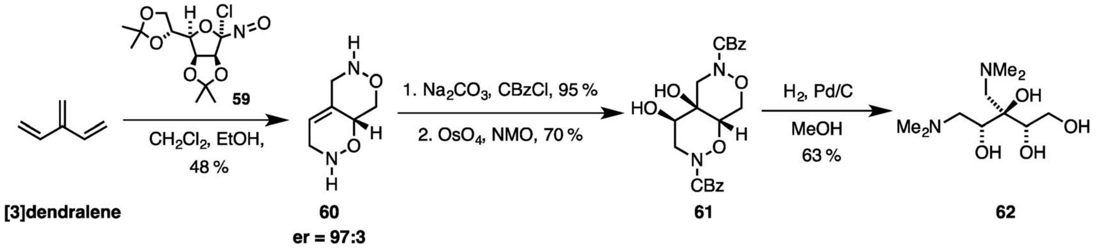
APPLICATIONS OF THE DENDRALENES IN SYNTHESIS

Despite the synthetic utility of the dendralenes, until recently only one target synthesis application had been reported, specifically our 2008 formal total synthesis of triptolide [25]. The synthesis employed the DTDA cascade of a substituted [3]dendralene **53** (Scheme 15), which was prepared in three steps using cross-coupling chemistry. This substituted [3]dendralene underwent an initial Diels–Alder reaction with methyl acrylate, the cycloadduct from which lactonized in situ to generate bicycle **55**. A second Diels–Alder reaction with substituted benzoquinone **56** generated tetracycle **57**, completing the formation of the carbon framework of triptolide. A series of functionalization reactions gave compound **58**, an intermediate from the 1982 synthesis by Brechtold and co-workers [26]. The second example of a dendralene in total synthesis came in late 2012, when Shenvi and co-workers published the synthesis of an antimalarial amphilectane natural product [27].



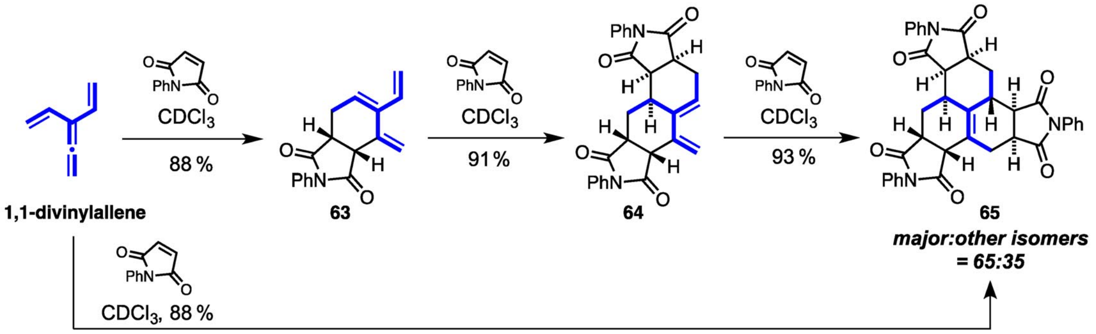
Scheme 15

We have also employed the dendralenes in the synthesis of natural product-like frameworks. Thus, with Vasella's nitrososugar reagent **59** [28], we were able to perform a hetero-Diels–Alder reaction with [3]dendralene in high enantioselectivity [29] (Scheme 16). Following *N*-protection of isoxazolidine **60** as the benzyloxycarbonyl (CBz) derivative, we performed a dihydroxylation, generating diol **61** as a single diastereomer. Global hydrogenolysis proceeded with concomitant *N*-methylation to generate branched-chain diamino tetrol **62**, reminiscent of (but distinct from) naturally occurring branched-chain amino sugars.



Scheme 16

In order to further expand the horizons of polyene chemistry, we set our sights on the "allenic dendralene", 1,1-divinylallene. This π-bond rich hydrocarbon was prepared and characterized by our research group for the first time in 2011 [30]. The hydrocarbon undergoes a diene-transmissive sequence of three Diels–Alder reactions using *N*-phenylmaleimide as the dienophile (Scheme 17). We can either perform this sequence in a stepwise manner, or perform all three Diels–Alder reactions in a "one-pot" manner, by controlling reaction stoichiometry. This reaction sequence demonstrates the huge (and generally untapped) synthetic potential of π-bond rich hydrocarbons: no fewer than six of 1,1-divinylallene's seven carbon atoms participate in new bond formations in this reaction. Thus, in one synthetic operation, six new carbon–carbon bonds, three new rings, and eight stereocenters are gener-



Scheme 17

ated in high yield and high diastereoselectivity. Studies into total synthesis applications of this and related sequences are underway in our laboratories.

CONCLUSIONS

The examples presented in this report highlight the incredible synthetic utility of the dendralenes and related π-bond rich systems in synthetic organic chemistry. Having demonstrated the ease with which these compounds can be synthesized using cross-coupling chemistry, it is our hope that others will be inspired to employ them in synthesis.

ACKNOWLEDGMENTS

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