

# $\pi$ -Bond-Rich Hydrocarbons

## 1,1-Divinylallene\*\*

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Studies into fundamental hydrocarbon structures have led to a deeper understanding of structure, reactions and mechanism. Such investigations have also led to the invention of new synthetic methods, strategies and tactics.<sup>[1]</sup> While many families of designed molecules have succumbed to synthesis, a significant number have not yet been made. Members of the dendralene family (**1** and **2**, Figure 1) of branched acyclic oligoalkenic hydrocarbons higher than the tetraene, for example, were prepared for the first time in 2000.<sup>[2]</sup> More recently, practical syntheses of the dendralenes allowed the unexpected alternation in behavior in odd and even members of the family to be uncovered.<sup>[3]</sup> It has recently been shown that [4]- and [5]dendralenes have significant synthetic potential in the rapid generation of polycyclic systems.<sup>[4,5]</sup> Herein we report the first synthesis of a considerably less stable relative of the dendralenes and one of the most C=C bond-rich small molecules, 1,1-divinylallene **3**. We also demonstrate that it surpasses the dendralenes—on a “bonds formed per atom” basis—in its ability to generate structural complexity.

Only a small number of 1,1-divinylallenes have been reported in the literature.<sup>[6–11]</sup> Most are highly substituted<sup>[6–9]</sup> and information on their physical and chemical properties is scant. Only one study has been reported with a less

substituted derivative. Thus, Hopf and co-workers prepared a methyl-substituted analogue of **3** but its instability precluded isolation and characterization.<sup>[10,11]</sup>

The Hopf group has also attempted to prepare the parent 1,1-divinylallene **3**.<sup>[10,11]</sup> In one unsuccessful approach, flash vacuum pyrolysis of diacetate **4** gave the ethynyl-1,3-butadiene **5**, a result that was ascribed to a sigmatropic 1,5-hydrogen shift of the presumed divinylallene intermediate **3** (Scheme 1). Ethynyl-1,3-butadiene **5** is the only reported decomposition product of a 1,1-divinylallene. We suspected that the sigmatropic rearrangement was a result of the high temperature involved in the pyrolysis experiment. Nevertheless, much lower temperatures have been employed to bring about related thermal hydrogen shifts in allenes,<sup>[12]</sup> so we thought it prudent to calculate the activation parameters for this transformation using the very accurate multilevel ab initio G4 method<sup>[13]</sup> before devising a synthetic plan to the hydrocarbon. The lowest-energy G4 transition state<sup>[14]</sup> for the 1,5-H shift exhibits a C–C–C bond angle bent significantly (131°) from the linear geometry of the starting allene and a long (1.55 Å) developing C–H bond. The computed activation parameters,  $\Delta H^\ddagger_{298\text{K}}$  and  $\Delta G^\ddagger_{298\text{K}}$  are 177.0 and 184.4 kJ mol<sup>−1</sup>, respectively, which are sufficiently large to guarantee thermal stability of 1,1-divinylallene towards the 1,5-H sigmatropic shift at temperatures as high as 250 °C.

Our computational results indicate that, under standard laboratory conditions (i.e. < 250 °C), 1,1-divinylallene **3** should be stable towards the only decomposition pathway that has been previously documented. Nevertheless, alternative, highly facile, intermolecular pathways for degradation of **3**, such as Diels–Alder dimerization—as seen previously with [3]dendralene<sup>[15]</sup>—could necessitate special care with the isolation of **3**. G4 calculations provided valuable insight into this problem. The G4  $\Delta G^\ddagger_{298\text{K}}$  value for the Diels–Alder dimerization of **3** is 90.3 kJ mol<sup>−1</sup>, which is substantially

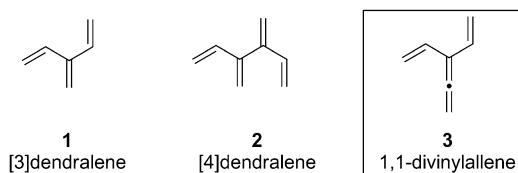


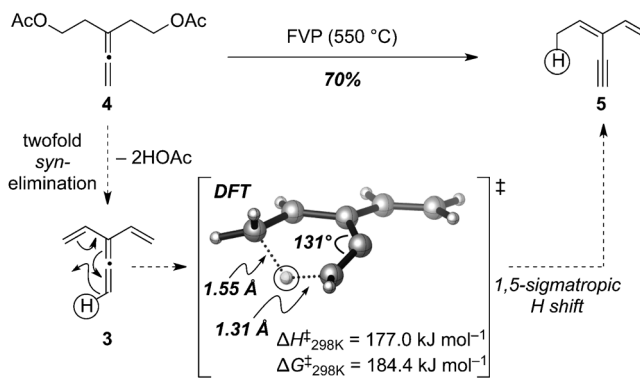
Figure 1. Branched hydrocarbons that are rich in C=C bonds.

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[\*\*] Funding from the Australian Research Council (ARC) is gratefully acknowledged. M.N.P.-R. acknowledges computing time from the Australian Partnership for Advanced Computing (APAC) awarded under the Merit Allocation Scheme. The authors thank Alan D. Payne and Ryan W. Cox (ANU) for preliminary experiments.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/ange.201105541>.

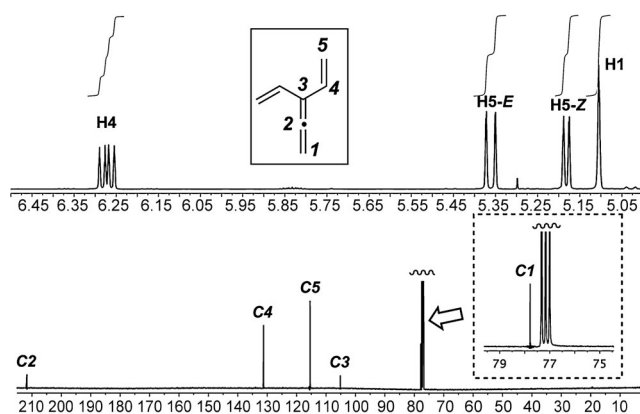


Scheme 1. The G4 TS for Hopf's sigmatropic rearrangement of **3**.

smaller than the G4  $\Delta G_{298K}^{\ddagger}$  value of 110.8 kJ mol<sup>-1</sup> for the Diels–Alder dimerization of cyclopentadiene, neat solutions of which have a lifetime in the order of days at room temperature. Our calculations suggest that concentrated solutions of **3** should have lifetimes three orders of magnitude shorter than those for cyclopentadiene, on the timescale of only minutes at room temperature. In light of this issue, we elected to pursue an approach that would generate the hydrocarbon in dilute solution.

Several of the more obvious approaches to **3**, involving cross-coupling reactions<sup>[16]</sup> or S<sub>N</sub>2'-type reactions<sup>[10,11,17]</sup> were investigated. Frustratingly, none delivered the target. The approach that was ultimately successful (Scheme 2) involved Grieco–Sharpless elimination<sup>[18]</sup> of the selenide **10**, derived from alcohol **8**, which was conveniently prepared on multi-gram scale by nucleophilic addition of the Grignard reagent derived from 2-chloro-[3]dendralene **6**<sup>[19]</sup> to formaldehyde. The addition proceeds with overall allylic transposition of the Grignard reagent, presumably on account of the cyclic nature of the mechanism of this process (see **7**).<sup>[20]</sup> In fact, none of the un-transposed isomer **9** could be detected in the reaction mixture.<sup>[21]</sup>

We have prepared samples of 1,1-divinylallene **3** in CDCl<sub>3</sub> and [D<sub>6</sub>]DMSO through the Grieco–Sharpless elimination reaction of selenide **10**. As predicted through our calculations, the hydrocarbon proved to be highly unstable. To minimize loss of the hydrocarbon through decomposition and evaporation, we find it most convenient to use these solutions directly in further reactions. Nevertheless, for characterization purposes, direct bulb-to-trap distillation (0 °C; 1 mmHg) of the reaction mixture gave a dilute solution of 1,1-divinylallene **3** in CDCl<sub>3</sub> free of other impurities. A ca. 0.02 M concentration solution of 1,1-divinylallene **3** has a half-life of around 43 h at 25 °C. The decomposition pathway of **3** is opaque at present, since a complex mixture of products is generated. We suspect that Diels–Alder dimerizations are involved. The hydrocarbon **3** was characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, IR, UV spectroscopic and mass spectrometric



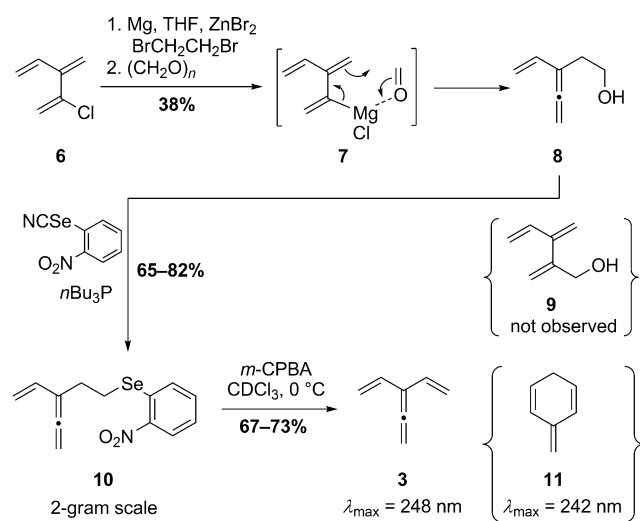
**Figure 2.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of 1,1-divinylallene **3** (800 MHz and 200 MHz, respectively, CDCl<sub>3</sub> solvent, assignments from HSQC experiments).

analysis<sup>[22]</sup> (see Figure 2 for <sup>1</sup>H and <sup>13</sup>C NMR spectra). 1,1-Divinylallene **3** exhibits a single UV absorption maximum at 248 nm, a longer wavelength than that seen for vinylallenol **8** (215 nm), [3]dendralene **1** (two maxima, 206 and 231 nm)<sup>[3]</sup> and closer in value to that of isotoluene **11** (242 nm).<sup>[23]</sup>

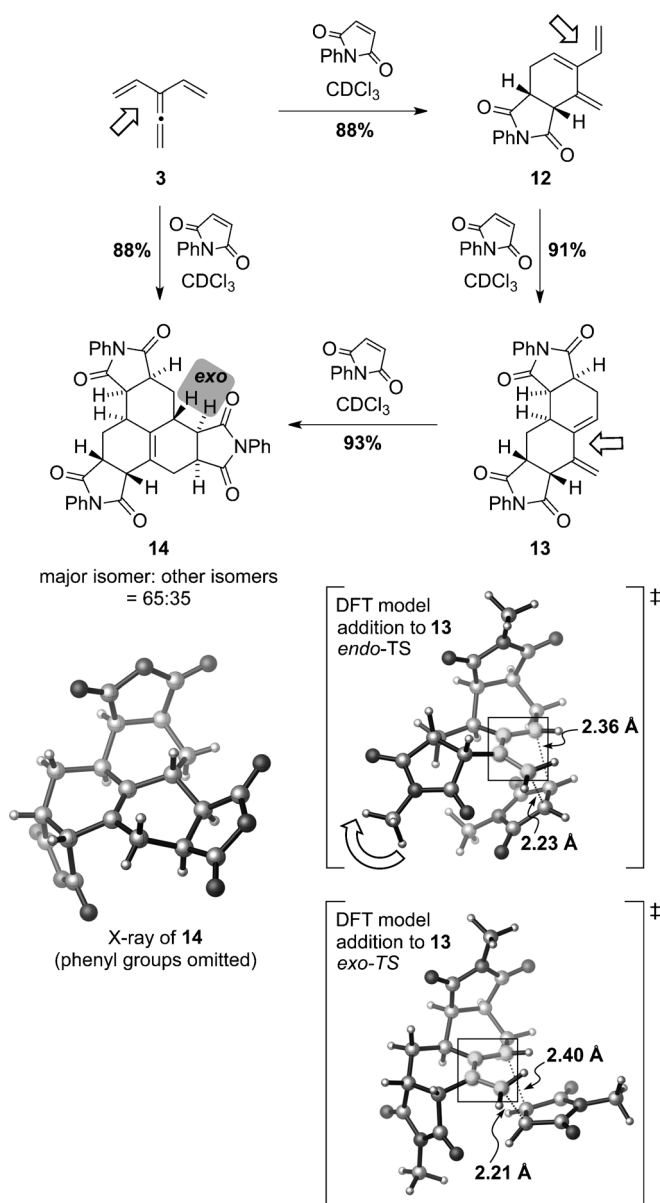
Hopf et al. reported an MP2/cc-pVTZ computational study of the conformational analysis of 1,1-divinylallene and concluded that the C<sub>2</sub> conformation, with each vinyl group approximately *s-trans* with respect to the allenic moiety, was the most stable.<sup>[11]</sup> However, using the same MP2/cc-pVTZ method, we find the *s-cis,s-trans* conformation—depicted in the inset of Figure 2 (the MP2 dihedral angles made between the vinyl groups with the allenic moiety are –35° and 173°)—to be the most stable conformation and not the C<sub>2</sub> conformation, as stated by Hopf et al., the former being enthalpically 3.9 kJ mol<sup>-1</sup> more stable than the C<sub>2</sub> *s-trans,s-trans* conformation. A variety of other methods—B3LYP, M06-2X, CBS-QB3, G4—also predict the *s-cis,s-trans* conformation to be the most stable. We conclude, therefore, that, of the four conformations of **3** that we have located,<sup>[24]</sup> the global minimum energy conformation is the *s-cis,s-trans* conformation.<sup>[25]</sup>

One molecule of 1,1-divinylallene **3** reacts with three dienophile molecules to generate the tricyclic decahydrophenalene ring system **14** (Scheme 3). This unprecedented triple diene-transmissive<sup>[26,27]</sup> sequence generates six new C–C bonds. It is striking that such a small cross-conjugated hydrocarbon, with only four C=C bonds, can generate such a high degree of structural complexity so rapidly. Using *N*-phenylmaleimide as dienophile, the overall triple cycloaddition sequence is high yielding and proceeds with the generation of eight new stereocenters. The first and second cycloadditions each give a single diastereomeric product, within the limits of detection. The third gives a mixture but with one diastereomeric product clearly dominating (major diastereomer:other isomers = 65:35). The stereochemistry of the major triple adduct **14** was determined through single crystal X-ray analysis.<sup>[28]</sup>

The first cycloaddition occurs at either one of the two equivalent vinylallene “diene” sites of **3** to give mono-adduct **12**, a cyclic cross-conjugated triene.<sup>[29]</sup> The second addition



**Scheme 2.** First synthesis of the parent 1,1-divinylallene **3**.



**Scheme 3.** A triple diene-transmissive Diels–Alder sequence involving 1,1-divinylallene **3**. Lower right: the diene is boxed in the DFT model TSs and developing bond lengths are shown.

must occur at the semicyclic diene site of **12**, with the dienophile approaching from the less hindered  $\pi$ -diastereoface of the diene (i.e. *anti* with respect to the succinimide ring of **12**) and through the expected *endo*-mode. This *endo,anti* product of the second addition, **13**, carries a conformationally restricted diene. Unexpectedly, **13** underwent cycloaddition with *N*-phenylmaleimide predominantly through the *exo*-mode and to the same face as the first dienophile, to form the final product **14**. In order to understand the origin of this surprising stereochemical outcome, the third cycloaddition was investigated computationally using B3LYP/6-31G(d) theory. Calculations were carried out on the smaller *N*-methyl analogue, which proved to be a good simulacrum. The transition structure of the Diels–Alder reaction leading to the major isomer, along with the corresponding (and anticipated)

*endo*-diastereomer, are depicted in Scheme 3. The calculated TS energies are consistent with experimental observations, with the one leading to the *exo*-isomer lower in energy by 5.3 kJ mol<sup>−1</sup>.<sup>[30]</sup> The strain in the *endo*-TS is apparent from the twisting of the succinimide ring introduced in the first cycloaddition (curved arrow in *endo*-TS, Scheme 3).

In conclusion, 1,1-divinylallene **3** has been prepared for the first time. The synthesis employs standard laboratory equipment and techniques. In light of its volatility and tendency towards decomposition, the hydrocarbon is best handled in solution. 1,1-Divinylallene **3** is one of the most  $\pi$ -bond rich hydrocarbons prepared, with only seven carbons but four C=C bonds. The arrangement of C=C bonds in **3** permits a controlled sequence of three cycloaddition reactions and the rapid construction of the phenalene framework. The ability to isolate mono- and bis-adducts invites future synthetic applications, which will undoubtedly mandate different dienophiles for each of the three Diels–Alder reactions. Studies into the application of this sequence in total synthesis are underway.

Received: August 5, 2011

Published online: September 14, 2011

**Keywords:** 1,1-divinylallene · cycloaddition · Diels–Alder reactions · hydrocarbons

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