

Diphenylmethylenecyclobuta[*a*]-
cyclopropa[*d*]benzene: Synthesis
and Spectral Characterization

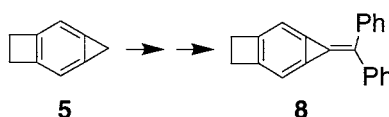
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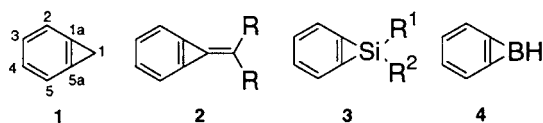
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ABSTRACT



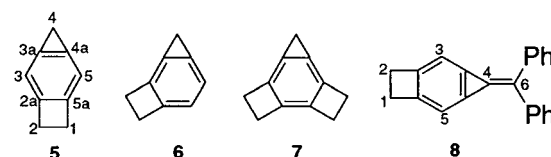
The first derivative of the novel and highly strained rocketene (cyclobuta[*a*]cyclopropa[*d*]benzene) **5**, namely, the C4 diphenyl-substituted exocyclic alkene **8**, has been prepared in 16% overall yield as a yellow oil with properties fully consistent with its highly strained nature.

The class of strained aromatic hydrocarbons known as the cycloproparenes and illustrated by the parent molecule 1*H*-cyclopropabenzene **1** has provided much fascinating chemistry¹ since Anet and Anet² reported the first authenticated derivative in 1964. In particular, the pK_a of **1** is estimated³ to be ca. 36, and thus the C1 cyclopropabenzene anion and its naphthalenyl analogue can be generated with ease and used in synthesis, e.g., in Peterson olefination to give exocyclic alkenes **2**.^{1,4,5}



Recently searches for more elusive heteroatom derivatives have seen successes most notably with the stable silacyclopropabenzene,⁶ e.g., **3**, and the transient benzoborirane **4**.⁷

Imposition of further strain into the cycloproparene frame has been achieved through synthesis of the ring fused



cyclobutane derivatives **5** (“rocketene”⁸),^{9,10} **6**,¹¹ and **7**,¹² and detailed theoretical, structural, and spectroscopic studies of these have appeared.^{13,14} Despite such physicochemical investigations, there has been no report of further chemical

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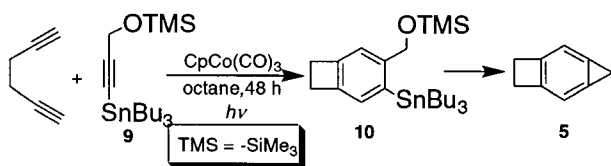
(8) Rocketene is indexed as tricyclo[5.2.0.0^{3,5}]nona-1,3(5),6-triene; CAS Registry No. 57867-58-0.

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transformation of any one of these highly strained compounds into another with the same fundamental hydrocarbon framework. We report here the synthesis and spectroscopic properties of the first rocketene derivative, namely, the exocyclic diphenyl-substituted olefin **8**.

The original syntheses of **5** date to 1975 from routes that were visionary at the time but had notably low overall yields, which were never greater than 5%.^{9,10} The shorter Saward and Vollhardt route¹⁰ depended upon $\text{CpCo}(\text{CO})_2$ -catalyzed $[2 + 2 + 2]$ cycloaddition of a propyne with hexa-1,5-diyne to provide an ortho-disubstituted cyclobutabenzene, from which subsequent 1,3-(α,o)-elimination gave rocketene (see Scheme 1). However, the authors employed $-\text{OMe}$ as the

Scheme 1



benzylic leaving group with the result that the ring closure proceeded in 5% yield only. As $-\text{OSiMe}_3$ is a better leaving group in electrophilic aromatic substitution reactions than $-\text{OMe}$,¹⁵ McNichols and Stang¹⁶ found that its use here also improved the overall yield of **5** to 32% some 10 years ago as illustrated in Scheme 1. Thus, cobalt-catalyzed co-oligomerization of hexa-1,5-diyne with 1-tributylstannyl-3-trimethylsilyloxypropyne **9** paralleled the Saward and Vollhardt reaction efficiency and gave the ortho-difunctionalized cyclobutabenzene **10** in 50% yield. Subsequent 1,3-elimination of the stannyl and trimethylsilyl groups was effected in 65% yield with BuLi at -78°C , thus making rocketene easily available for subsequent chemical examination.¹⁶

In our hands, all attempts to prepare cyclobutarene **10** based upon the conditions described by King and Efraty¹⁷ and by Macomber¹⁸ and following precisely the described procedure¹⁶ failed. On each occasion, alkynylstannane **9** was recovered in 15–25% yield with no evidence gained for either (volatile) hexa-1,5-diyne or the sought after cyclobutabenzene **10**. As the cobalt catalyst can require photodecarbonylation to become efficient,¹⁹ external irradiation

of the reaction mixture with a Phillips Innova heat lamp was employed, but it had no beneficial effect. However, unlike the former reactions, a black precipitate within the reaction vessel appeared to be consistent with observations made by King²⁰ for $\text{CpCo}(\text{CO})_2$, and moved Vollhardt et al.²¹ to suggest that some progress had been made. It was found that only upon irradiation with an air-cooled halogen slide projector bulb mounted ca. 5 cm from the reaction vessel was the desired cyclotrimerization effected,¹⁹ whereupon **10** was isolated in 46% yield under conditions that constitute a notable variation to those described in 1992.¹⁶ The spectroscopic data recorded for **10** are fully consistent with the literature, and two-dimensional NMR correlation spectroscopy has confirmed the assignment of all ^1H and ^{13}C resonances.

Subsequent synthesis of **5** via the 1,3-elimination was straightforward. Thus, with a slight excess of butyllithium, **10** gave a pale yellow oil that was immediately taken to be a cycloproparene from its characteristic unpleasant pungent odor! The ^1H and ^{13}C NMR resonances assigned to **5** have been confirmed by two-dimensional correlation experiments and agree with the literature, but there has been no prior analysis.^{9,10,13} Notable for **5** is the clear separation of the singlets for the cycloproparenyl H4 (δ 2.99 ppm), cyclobutarenyl H1/2 (δ 3.15 ppm), and aromatic H3/5 (δ 6.80 ppm) protons, while the ^{13}C spectrum displays spectral features of both **1** and cyclobutabenzene. The cycloproparenyl sp^3 center C4 (δ 19.3 ppm) and its fusion sites C3a/4a (δ 122.1 ppm) compare well with those of **1** (δ 18.4 and 125.4 ppm, respectively), while a similar relationship pertains for C1/2 (δ 29.4 ppm) and C2a/5a (δ 145.2 ppm) with cyclobutabenzene (δ C1/2, 30.0 ppm; C1a/5a, 145.6 ppm).¹ The diagnostic shielding¹ of the arene carbon atoms C3/5 (δ_{C} 110.1 ppm; $\Delta\delta$ ²² 18.6) adjacent to the sites of ring fusion is greater than that observed for **1** (δ_{C} 114.7 ppm) by ca. 4.6 ppm, as a result of the additional ring distortion present in **5**. It compares appropriately with the sum of the shieldings from **1** ($\Delta\delta$ 14.0) and cyclobutabenzene (δ_{C} 122.1 ppm; $\Delta\delta$ 6.4).

Sequential treatment of **10** with BuLi and interception of the derived anion **11** with Me_3SiCl gave, via **12** and **13**, the disilane **14** as a clear, odorless oil (47%)²³ in direct analogy to the synthesis of 1,1-bis(trimethylsilyl)cyclopropa[*b*]naphthalene.^{1,4} That initial proton abstraction is from the doubly benzylic cycloproparenyl C4 center and not from a four-membered ring methylene group follows from the symmetry of the ^1H and ^{13}C NMR spectra of **14**. Thus, **14** displays only three proton singlets (δ 0.01, 2.88, and 6.38 ppm) in the expected 9:2:1 ratio, and the six ^{13}C resonances are as shown in Figure 1, which provides a visual comparison of the data for **5** and **14** with those of **1** and its disilane **15**.^{1,4}

The route from disilane **14** to diphenylmethyldidenerocketene **8** (Scheme 2) is directly analogous to that used for the

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(22) $\Delta\delta$ is the shielding relative to δ_{C} PhH at 128.7 ppm.

(23) All new compounds gave satisfactory spectroscopic and microanalytical data.

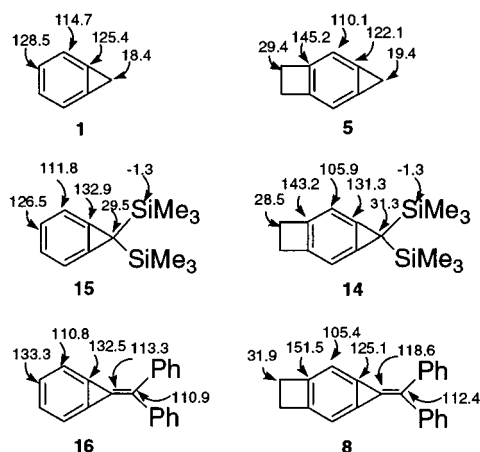


Figure 1. ^{13}C NMR data for selected cyclopropabenzene and rocketene derivatives (in parts per million and recorded for CDCl_3 solutions).

less strained cycloproparenes, viz., removal of a silyl group by potassium *tert*-butoxide and Peterson olefination of resulting α -silyl anion **13** with benzophenone.^{24,25} Exocyclic alkene **8** was isolated in 34% as a yellow oil.^{22,25} All attempts to crystallize the compound for X-ray analysis in the freezer (over a period of six months) resulted instead in slow decomposition. The ^1H NMR spectrum of **8** displays the 16

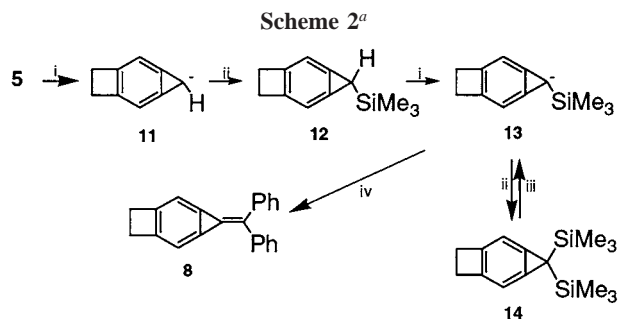
protons in a 2:2:2:1:1 ratio with singlets for H1/2 (δ 3.21 ppm) and H3/5 (δ 7.61 ppm) and coupled signals due to the protons of the exocyclic phenyl substituents as expected. Comparisons of the ^{13}C NMR data of **8** with those its precursors **14** and **5** match well those between the benzenoid analogue **16**²² and its progenitors **15**²² and **1**¹ (Figure 1), with the exception of the three-membered ring atoms. Here, the exocyclic fusion site (C4) of **8** is expected to be somewhat less shielded than that of **16** (δ 118.6 vs 113.3 ppm) by virtue of the ca. 2 ppm downfield shift of C4 in **14** vs **15**. However, the bridge bond atoms (C3a/4a) are more shielded in **8** than in **16** or **14** (δ 125.1 vs 132.5 and 131.3 ppm) and, in fact, lie closer to those of the cyclopropa[*b*]naphthalene analogue (δ 127.4 ppm).²⁶ In the absence of additional information, it would be speculative to suggest reasons for this save to point out that exocyclic alkene fusion should impact more upon the more highly strained **5** than **1**. Differences in δ_{C} for the external center C6 are smaller. In addition to these data, the electronic absorption spectrum of **8** shows a 6 nm negative solvatochromy between cyclohexane and acetonitrile that is characteristic of the polar alkylidenecycloproparene hydrocarbons,^{4,5d} implying **8** to be polar in analogy to **16** (μ 1.0 D).^{1,24,26}

We remain fascinated by the imposition of strain on the aromatic framework, and studies of these and related compounds will form the subject of future publications.

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Supporting Information Available: Experimental and analytical details for all new compounds described as well ^1H and ^{13}C spectra of **8**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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^a Reagents: (i) BuLi; (ii) TMSCl; (iii) KOBu-*tert*; (iv) Ph₂CO.

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