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Communications

Reaction of 1,2-Dehydro-*o*-carborane with Acetylenes. Ene Reactions and Cycloaddition To Give an Analogue of Benzocyclobutadiene[1,2]

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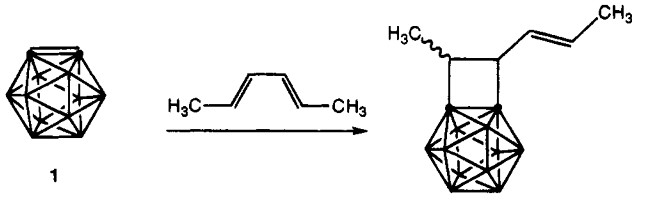
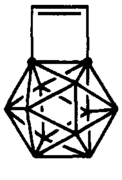
1,2-Dehydro-*o*-carborane (**1**), has been shown to undergo many of the same reactions as its two-dimensional relative, 1,2-dehydrobenzene, or benzyne.[3] In particular, Diels–Alder reactions,[4] 2 + 2 cycloadditions,[4] and ene reactions[5] have been investigated. As for benzyne, the Diels–Alder and ene reactions appear to be concerted. However, the loss of stereochemistry in the 2 + 2 cycloaddition demands a stepwise reaction.



1

Reactions of **1** with acetylenes have not been described, but the analogy to benzyne would lead one to suspect that ene reactions to give allenes would dominate.[6] However, the known[4] relative efficiency of 2 + 2 cycloadditions of **1** permitted us to hope that derivatives of **2**, carborane versions of benzocyclobutadienes, would be among the products. If they were, the properties of such molecules would allow us to comment on the connection between the cage and external orbitals and any resulting antiaromaticity in **2**. Data from EPR spectra of carboranylcarbenes and nitrenes[7] reveal no evidence of overlap, but the properties of "naphthalenes" such as **3** and **4** are still a matter of some controversy,[8] and the stability or instability of **2** seemed well worth determining. All that was required was a reasonable synthetic route.



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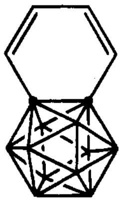

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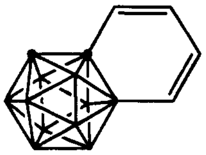

4

Generation of **1** in the presence of 3-hexyne led to a single ($\sim$99%) major product isolated in approximately 30% yield by preparative gas chromatography. Precise mass spectrometry showed it to be a 1:1 adduct of **1** and 3-hexyne. The ^{1}H NMR spectrum showed single hydrogens attached to the carborane cage (δ 3.72) and to a double bond (δ 5.52). A methyl doublet appeared at δ 1.72, as well as an ethyl group at δ 0.94 and 2.08. Although the infrared spectrum reveals no strong allene band (weak band at 1955 cm^{-1}), there can be little doubt that the structure of the product is **5**. There is an isomeric compound formed, but only in $<1\%$ relative yield, and we cannot comment on its structure. A similar reaction with 4-octyne leads to **6** in $>99\%$ relative yield.

This provides a quite convenient synthesis of carboranylallenes, but it is clear that no useful amounts of 2 + 2 adducts are formed. The problem now becomes one of minimizing the ene reaction and maximizing cycloaddition. The use of 1-alkynes is of no avail, as the presence of an acidic terminal hydrogen shortcircuits our base-induced generation of **1**. We hoped that a phenyl group would both block one possible ene reaction and make the stepwise 2 + 2 cycloaddition more favorable by stabilizing the intermediate diradical. In the event, this strategy proved effective. Two major products are formed

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(1) This work is taken from the A.B. Thesis of R.J.C., Princeton University, 1994.

(2) Support from the National Science Foundation through Grants CHE-9024996 and CHE-9322579 is gratefully acknowledged.

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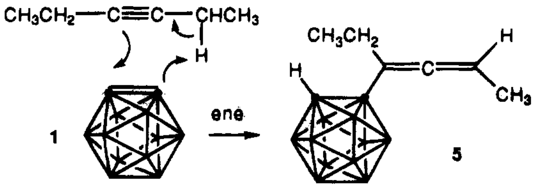
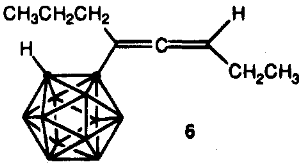
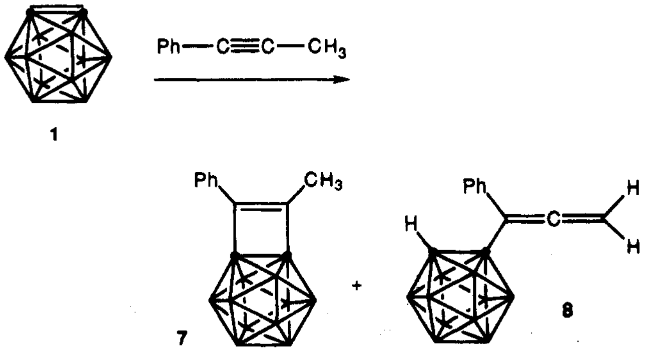




6

from the reaction of **1** with methylphenylacetylene, **7** (18% yield[9]) and **8** (~6% yield) in the ratio 3:1.



Pure **7** could be obtained by preparative gas chromatography, but we could not separate compound **8** from **7** by this method. However, spectra of enriched samples leave no doubt that **8** is the ene product. For example, the terminal methylene hydrogens of **8** appear as a singlet at δ 5.15, and the cage hydrogen is at δ 3.6. The major product **7**, mp 112−114 °C, is more interesting. Precise mass spectrometry establishes it as a 1:1 adduct of **1** and the acetylene. Neither a cage hydrogen nor olefinic hydrogens can be found in the ^{1}H NMR spectrum. Aromatic hydrogens are visible as a multiplet (augmented AB pattern) centered at δ 7.25, and a singlet methyl group appears at δ 1.98. The ^{13}C NMR spectrum ($CDCl_3$) showed the required nine signals at δ 141.1, 138.6, 129.4, 129.1, 129.0, 125.5, 73.9, 75.3, and 14.3,[9] and the proton-decoupled ^{11}B NMR spectrum consisted of three signals at δ −51.18 (br s, 4B), −44.76 (br s, 2B), and −32.42 (br s, 2B) and a broader signal centered roughly at δ −22 (2B). The structural assignment of **7** seems secure.

Compound **7** is the first example of a carborane fused to an unsaturated four-membered ring. It is not inordinately reactive and is clearly far more stable than benzocyclobutadiene, a molecule that dimerizes at low temperature and requires special techniques for observation.[10] Some 1,2-substituted benzocyclobutadienes are stable to dimerization but nonetheless react rapidly with oxygen unless extraordinary precautions are taken.[11] We hope to carry out a detailed study of the properties of **7**, but already it is clear that it is much more stable than its two-dimensional relatives. No special care needs to be taken in its handling, and it neither dimerizes at room temperature nor reacts rapidly with oxygen. There is surely no strong destabilizing interaction between the cage and the p orbitals on the adjacent carbons.

These results are in accord with our expectations based on the EPR spectra of carboranylcarbenes and carboranylnitrenes[7] and lead one to predict that **3** and **4** are best described as conventional dienes, not exotic naphthalenes.

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(9) We thank Judson A. Brewer for this measurement.

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