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A New Source of 1,2-Dehydro-*o*-carborane[1]

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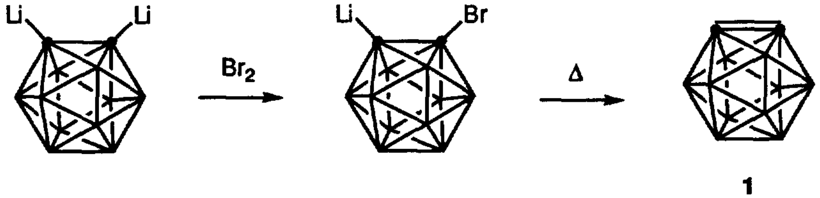
Abstract: 1,2-Dehydro-*o*-carborane adds to naphthalene and benzene to give Diels-Alder adducts. Treatment of the benzene adduct at 230-260 °C in the presence of acceptors leads to transfer of 1,2-dehydro-*o*-carborane.

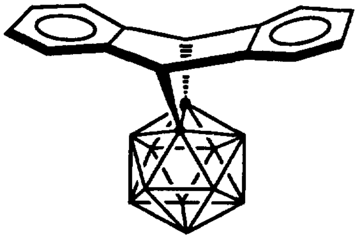
Some years ago, we reported the properties of a three-dimensional analogue of benzyne, 1,2-dehydro-*o*-carborane, **1**.[2,3] Our recipe[2a] involved mono-bromination of 1,2-dilithio-*o*-carborane, and thus several intermediates preceded formation of **1**. Although we believe we have eliminated these intermediates as sources of the products attributed to **1**,[2a] we continued to seek a less problematic precursor to **1**.



1

In this and succeeding figures, the dots represent carbons. All other vertices are borons, and there is an unshown hydrogen at every unoccupied vertex.

We first attempted to use **2**, the known adduct of **1** and anthracene,[2a] hoping that we could induce either a photochemical or thermal reverse Diels-Alder reaction. Photolysis has so far not been successful. Although anthracene can be detected after pyrolysis of **2** at ~800 °C, one can scarcely regard such a reaction as useful![2a,4] However, the formation of anthracene provides the energetic advantage of forming only the third ring of the aromatic system. We reasoned that substantially more energetic impetus might be found in the formation of the second aromatic ring of naphthalene or, best of all, of a simple benzene ring itself. Accordingly, we sought to make adducts **3** and **4**.



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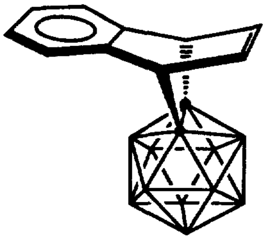

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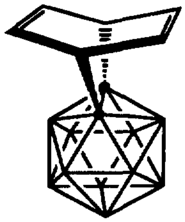
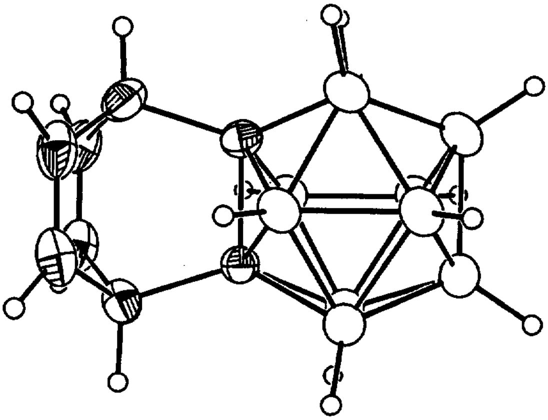
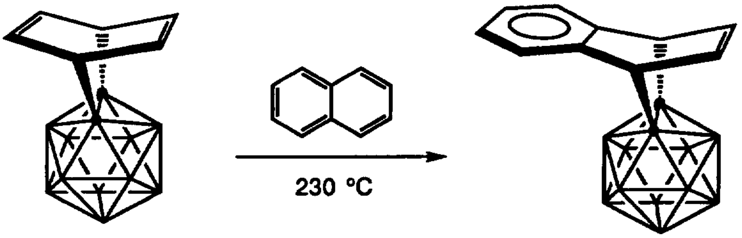


4

Addition of **1** to naphthalene in the standard fashion[2a] gave **3** in 15% isolated yield. In close analogy to the known ^{1}H and ^{13}H NMR spectra of **2**,[2a] compound **3**, mp 154-155 °C, showed a 2H multiplet at δ 4.5 (**2**: δ 4.78) for the bridgehead hydrogens. In addition there was a 2H multiplet at δ 6.9 for the hydrogens attached to the unconjugated double bond. The ^{13}C NMR spectrum showed the expected five non-cage carbon resonances. Addition of **1** to benzene took place at 80 °C in cyclohexane. Isolation was by preparative gas chromatography followed by crystallization from 2-propanol to give **4** (mp 100 °C, dec) in ~ 8% yield. Although the ^{1}H NMR spectrum seemed definitive, (**4**: δ 1.2-3.5, br m, 10H; 4.15, d, 2H; 6.70 d, 4H), the parent peak in the mass spectrum was at *m/z* 218 not 220. Accordingly, we analyzed a single crystal of **4** by X-ray diffraction. A colorless chunk of **4** cut to roughly 0.38 mm x 0.45 mm x 0.50 mm was mounted on a glass fiber with epoxy cement and transferred to a Siemens P4 diffractometer equipped with an LT-2 low temperature device and graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å).[5] The structure was solved in the orthorhombic space group $P2_12_12_1$ (No. 19) by direct methods (SHELXTL-PLUS)[6] and refined by full matrix least-squares on F^2 (SHELXL-93).[7] The structure is clearly that of **4**.



The question is whether the reverse Diels-Alder reaction of **3** and/or **4** will occur in a reasonable temperature range. For **3** the answer is no, as we are only able to observe naphthalene when **3** is heated in the gas phase at > 400 °C. However, when we heated an ether solution of **4** and naphthalene at 190 °C or 230 °C (sealed tube) for 12 hours we obtained **3** in 8% and 14% yield, respectively. Reaction at 260 °C was much less clean, but provided even more **3**. Thus we are able to transfer **1** under reasonable reaction conditions.



4 **3**

We must still resolve questions of the details of the transfer of **1**. In particular, we must rule out stepwise processes. However, the absence of isomeric "2 + 2" products in the reaction with naphthalene makes us confident that **1** is a real intermediate in the transfer process.

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1. We thank the National Science Foundation for support of this work through grant NSF CHE-9322579. Portions of this work are taken from the A.B. Thesis of JHA, Princeton University, 1996. We especially thank Henry L. Gingrich for encouragement and advice.

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