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Photolysis of naphthocarborane and benzocarborane in oxygen

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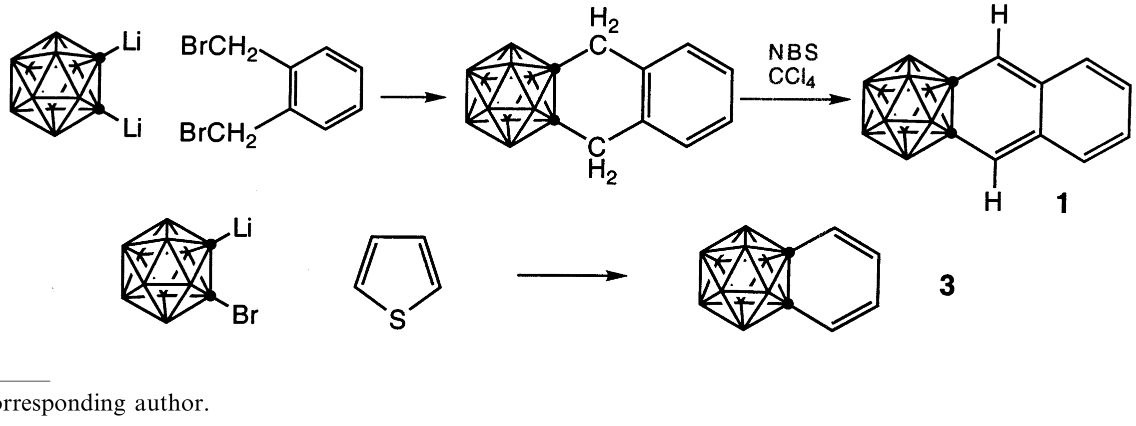
Abstract

Photolysis of 'naphtho-*o*-carborane' under oxygen leads to the quinone, 5,8-diketonaphthocarborane. Photolysis in the presence of hydrogen donors such as acetonitrile or 1,4-cyclohexadiene leads both to the quinone and 5-ketodihydronaphthocarborane. By contrast, photolysis of 'benzocarborane' under similar conditions leads only to a highly stereo- and regiospecific dimerization. © 2000 Elsevier Science Ltd. All rights reserved.

We recently reported the photolysis of 'naphthocarborane' (**1**), and ascribed the resultant hydrogen abstraction to the formation of an intermediate diradical, **2**.[1] The diradical can be detected spectroscopically, and is an efficient abstractor of hydrogen from a variety of sources. Here we intercept the diradical with oxygen, and contrast the photolysis of **1** with that of benzocarborane, **3**. As shown below, **1** was made by a slight modification of the simple synthesis developed many years ago by Matteson and Davis,[2] and **3** was made by our cycloaddition/sulfur extrusion route.[3]



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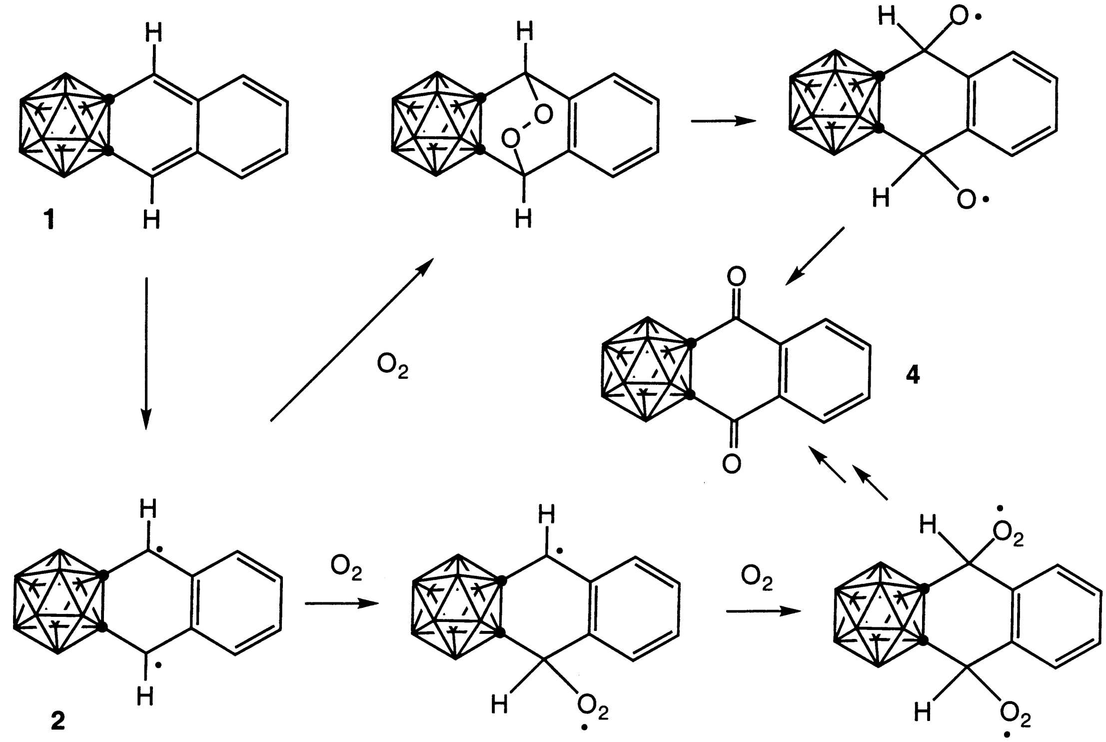
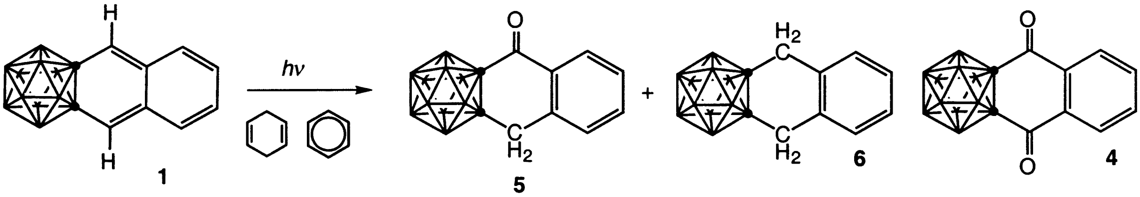
Photolysis of a benzene solution of **1** saturated with oxygen with a medium pressure Hanovia mercury arc through Pyrex led to a single product, quinone **4**, isolated conveniently by HPLC (90% CH_3CN/10% chloroform). This product was shown to be $C_{10}H_{14}B_{10}O_2$ by high resolution mass spectrometry, and showed a doublet of doublets at δ 7.90 and 8.26 in its 500 MHz ^1H NMR spectrum ($CDCl_3$, $J = 5.9$, 3.3 Hz). In addition, the ^{13}C NMR spectrum ($CDCl_3$) consisted of the appropriate five signals at δ 71.5, 129.5, 130.8, 136.1 and 177.9. The carbonyl group absorbed in the infrared at 1707 cm^{-1} (CH_3CN).

We cannot be certain of the mechanism of quinone formation, but two possibilities are shown below. Each process involves capture of the diradical **2** by oxygen, one in a single step to give an *endo* peroxide, the other in two steps.

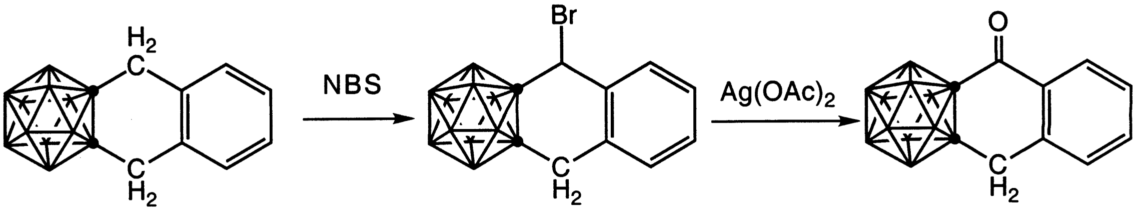


When solvent benzene, a poor hydrogen donor, is augmented with better sources of hydrogen such as 1,4-cyclohexadiene, a new product, ketone **5** is formed along with **6**, the product of double hydrogen abstraction.



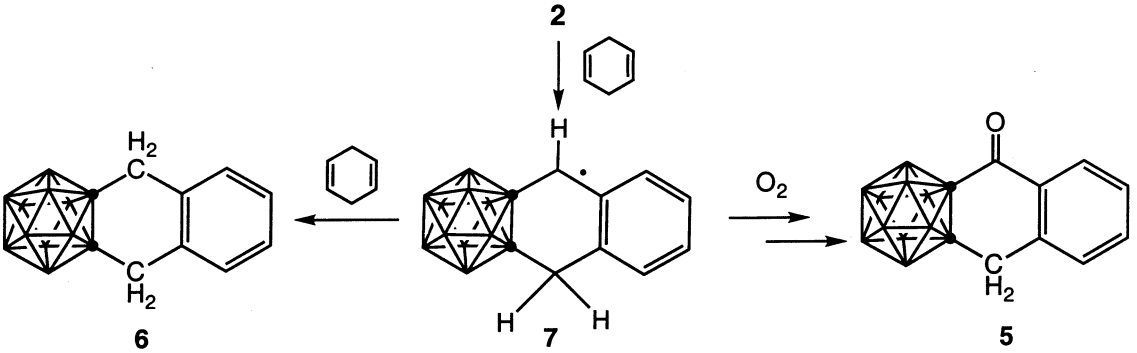
Known[2] ketone **5** (mp 145°C) was synthesized conveniently by the following route [IR (CH_3CN, KBr) 1698, 1692 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3^-$) δ 3.90 (s, 2H), 7.21 (d, 1H,

$J = 7.9$ Hz), 7.47 (t, 1H, $J = 7.9$ Hz), 7.65 (t, 1H, $J = 7.9$ Hz), 8.20 (d, 1H, $J = 7.9$ Hz); ^{13}C NMR (500 MHz, $CDCl_3$) δ 36.2, 68.9, 72.7, 126.2, 128.5, 128.8, 129.4, 135.5, 138.1, 179.7].



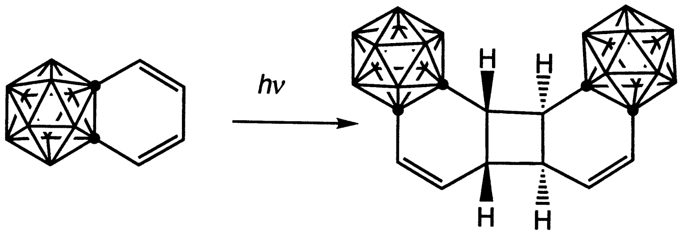
6 **5**

Even a small amount of 1,4-cyclohexadiene was sufficient to alter the product ratio sharply. Thus, photolysis of **1** in 1 mL benzene doped with 6 mg 1,4-cyclohexadiene led to a 3:2:1 ratio of **5**:**6**:**4**. Addition of 12 mg led to suppression of both carbonyl compounds, and exclusive formation of **6**. We take this result to mean that the presence of a hydrogen donor leads to the interception of radical **7**, which partitions between further hydrogen abstraction to give **6** and capture by oxygen, ultimately to produce **5**. Ketone **5** was largely unaffected on photolysis, although some particulate matter appeared. Quinone **4** is more sensitive, and is degraded on photolysis to what appears to be polymeric material.



6 **7** **5**

In contrast to the diradical and radical chemistry shown by **1**, benzocarborane is neither oxygenated nor hydrogenated on photolysis through Pyrex in the presence of hydrogen sources and/or oxygen in hexane. Instead, a highly efficient (ca. 90% yield) regiospecific and stereospecific dimerization gives **8**. Thus, it appears that diradical formation from **1** critically benefits from generation of the benzene ring in **2**.



8

The structure of **8** was secured by X-ray diffraction of a single crystal obtained by recrystalization from toluene (see Fig. 1). The B–B, B–C, and C–C carborane distances are 1.752(3)–1.783(3), 1.702(2)–1.735(2), and 1.654(2) Å, respectively, and are comparable to values reported for related molecules. The most notable feature is the pair of cyclobutane bonds connecting the two halves of the dimer. The cyclobutane bond in the cleft of the molecule is 1.556(3) Å, whereas that on the exterior edge is significantly longer at 1.568(4) Å. The elongated bond is associated with the two allylic carbons within the dimer. Thus, the structure is consistent with little or no aromatic character in the C–C carborane bond. The formation of the *trans* dimer is the result of the energetic advantage of keeping the carborane cages remote from each other. The head-to-head nature of the dimer recapitulates the regiochemistry found in the dimerization of indene,[4] and presumably reflects the increased delocalization of developing radicals in the transition state for the head to head process over that for the head to tail dimerization.

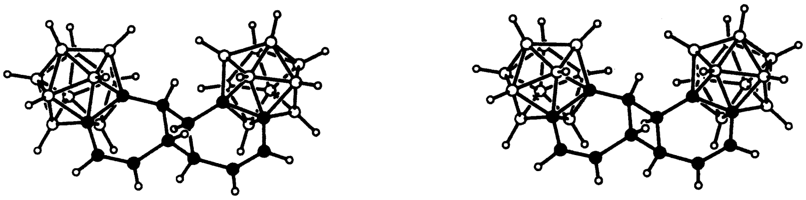


Figure 1. Stereoview of the X-ray diffraction derived structure of **8**

Acknowledgements

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