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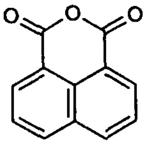
# The Singular Reduction of 1,8-*bis*-Hydroxymethylnaphthalene to a Benzonorcaradiene by $LiAlH_4$

Janeta V. Popovici-Müller and Thomas A. Spencer*

Department of Chemistry, Burke Laboratory, Dartmouth College, Hanover, NH 03755, USA

**Abstract:** Reduction of 1,8-naphthalic anhydride (**1**) with $LiAlH_4$ in THF (or DME, but not $Et_2O$) affords, in addition to diol **2**, benzonorcaradiene **3**. Extended treatment of **2** or lactone **4** also leads to **3**, in 66% and 65% yield, respectively. Reduction of **4** with $LiAlD_4$ established that formation of **3** proceeds via a symmetrical intermediate. No significant norcaradiene formation is observed upon comparable $LiAlH_4$ treatment of **14**, **15**, **16** or **17**. This novel reduction of a naphthalene derivative to a benzonorcaradiene appears to be unique to **2** or its precursors. © 1997 Elsevier Science Ltd.

Reduction of 1,8-naphthalic anhydride (**1**) with $LiAlH_4$ has been used by a number of investigators[1-6] as a source, in yields ranging from 61-92%, of 1,8-*bis*-hydroxymethylnaphthalene (**2**), which we also required. When we ran this reaction in refluxing THF, according to the procedure of Beyler and Sarett,[1] we noticed that diol **2** was accompanied by a single major, less polar, byproduct which intriguingly displayed a $^1H$ NMR signal at δ -0.20 ppm ($CDCl_3$). When this reaction was allowed to run for 30 h instead of 3 h, there could be isolated, in addition to 33% of **2**, 46% of this other compound, which was identified as benzonorcaradiene **3**, mp 108-109°C, on the basis of elemental analysis, mass spectrum, $^{13}C$ NMR spectrum, and the $^1H$ NMR spectrum shown in Figure 1, featuring the *endo*-cyclopropane proton signal at very high field. The $^1H$ NMR data for the norcaradiene portion of **3** are consistent with those reported for the parent benzonorcaradiene.[7]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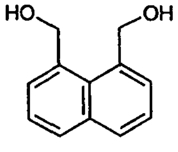
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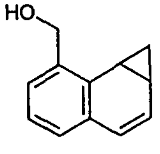
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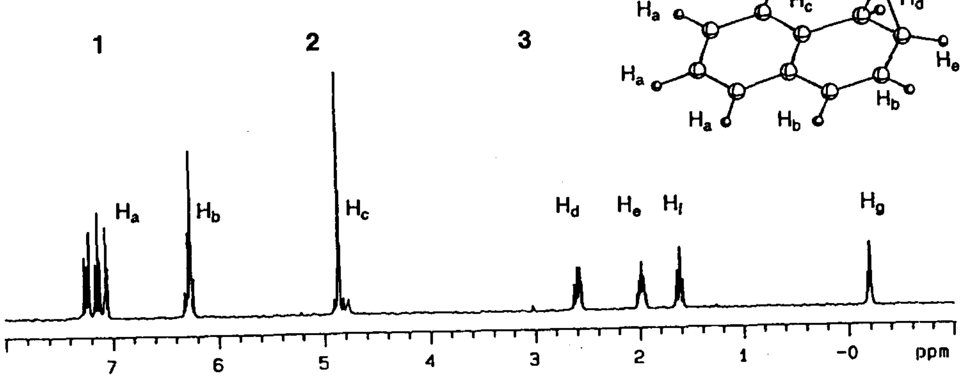
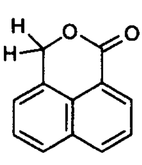


Figure 1. $^1H$ NMR Spectrum of 7-(Hydroxymethyl)-1a,7b-dihydro-1H-cyclopropa[a]naphthalene (**3**) in $CDCl_3$ (with $D_2O$ added).

To try to elucidate the pathway leading from **1** to **3**, reductions of possible intermediate species were explored. Upon treatment with two equivalents of $LiAlH_4$ in THF at reflux for 23 h, according to the procedure of Boekelheide and Vick[2] with Beyler and Sarett workup[1], lactone **4**[5] afforded 65% of **3**, but ether **5**[5] gave no trace of **3**. Reduction of lactone **4** with $LiAlD_4$ produced **6** ($d_2$-**2**)[4] and 61% of a 1:1 mixture of **7** and **8**, readily identified by $^1$H NMR. In Figure 2 are given the $^1$H NMR data in DMSO-$d_6$ for **3** and the 1:1 mixture of **7** + **8**. Analogous reduction of dideuteriolactone **9**[4] with $LiAlH_4$ afforded **6** and a 1:1 mixture of **10** and **11**, similarly identified. These results establish that formation of benzonorcaradiene **3** occurs via a symmetrical intermediate, or an equilibrating mixture of energetically equivalent intermediates, presumably related to diol **2**. Similar treatment of diol **2** itself with $LiAlH_4$ afforded up to 66% of **3**, but the yields were quite variable.[8]



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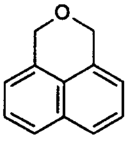

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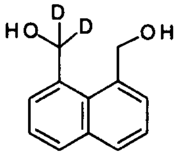

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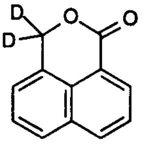

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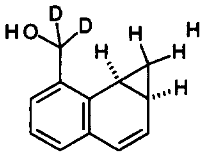

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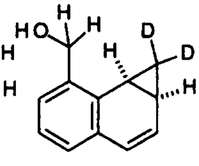

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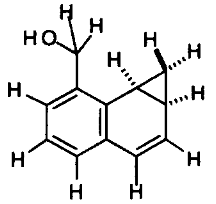
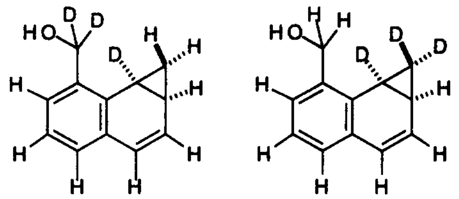


**3**

7.25-7.00 (3H), 6.31-6.22 (2H), 5.13 (t,1H), 4.76-4.60 (q of d, 2H), 2.55-2.47 (1H),1.98-1.89 (1H), 1.64-1.57 (1H), -0.41- -0.46 (1H)

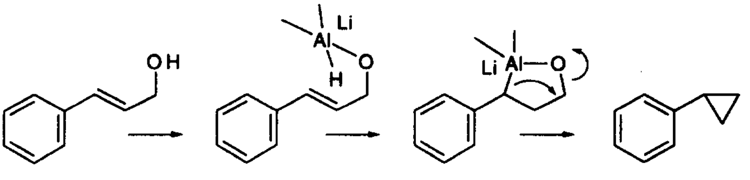


**7 + 8** (1:1)

7.25-7.00 (3H), 6.31-6.22 (2H), 5.13 (t) and 5.08 (s) (1H), 4.76-4.60 (q of d, 1H), 1.96-1.91 (1H), 1.62-1.58 (0.5H), -0.43- -0.46 (0.5H)

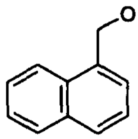
**Figure 2.** $^1$H NMR Data in DMSO-$d_6$ for **3** and the 1:1 Mixture of **7** and **8**

The formation of **3** is reminiscent of earlier observations[9,10] of cyclopropane formation upon extended treatment of certain allylic alcohols with $LiAlH_4$, as in the conversion of **12** to **13**.[9] These unusual reductions were found to occur in THF but not in ether,[11-13] and formation of **3** likewise was observed in THF or DME but not in ether. A mechanism was proposed,[9,10] essentially like that shown below for the conversion of **12** to **13**. The requirement for THF was ascribed to its being a stronger Lewis base than ether, resulting in greater coordination to aluminum and enhancement of both hydride transfer and cyclopropane formation,[12] although activation through more effective solvation of lithium by THF seems to be a reasonable alternative explanation.

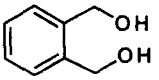


**12** **13**

To determine if this novel method for norcaradiene formation could be extended to different types of compounds, prolonged treatment with $LiAlH_4$ in refluxing THF or DME was applied to 1-naphthalenemethanol (**14**) and 1,2-bis(hydroxymethyl)benzene (**15**),[14] but no reaction was observed. To test whether the 1,8-*peri* strain in **2** is responsible for its peculiar susceptibility toward reduction, 8-methyl-1-naphthalenemethanol (**16**)[15] was subjected to the same treatment, but again, no cyclopropane formation could be detected. Finally, monomethyl ether **17**, mp 53-54°C, was prepared (NaH, then $CH_3I$; 91%) and heated with $LiAlH_4$ in THF for 45 h. In addition to recovered **17**, there was obtained 10% of **16** and a very small amount (<<1%) of a non-polar chromatographic fraction which showed a trace of a peak at $\delta$ -0.2 in its $CDCl_3$ $^1H$ NMR spectrum.



**14**



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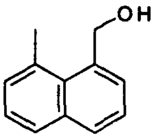
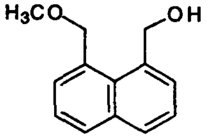
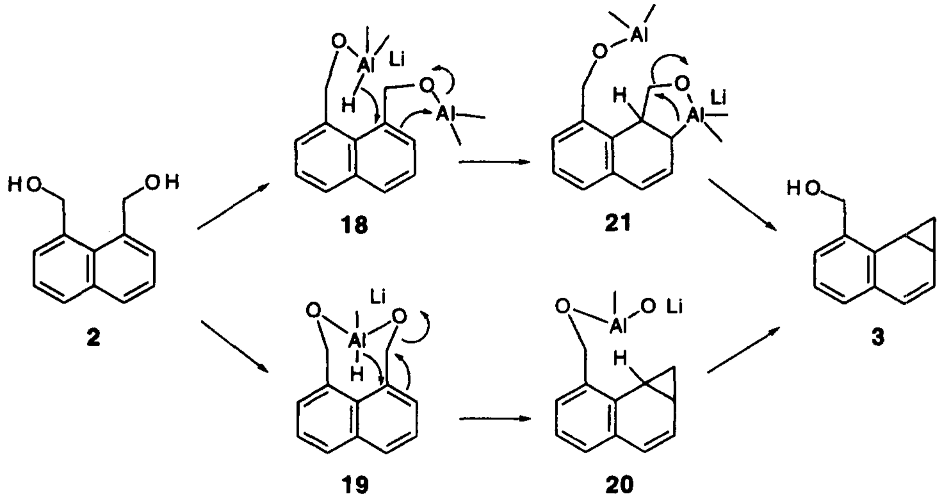


**16**



**17**

These observations indicate that this unprecedented reduction of a naphthalene derivative to form a benzonorcardiene requires the presence of both hydroxymethyl groups found in **2**, which apparently is uniquely suited to this type of reaction. Plausible pathways consistent with this requirement can be envisioned through either **18** or **19**. Conversion of **19** to **3** could occur directly via **20**, as shown, or via **21**, as in the case of **18**. Molecular modeling[16] indicates that either **18** or **19** can adopt a geometry in which a hydride on aluminum is close enough to be transferred to the appropriate carbon atom.



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7. $^1$H NMR data for benzonorcaradiene are listed in: Vogel, E.; Wendisch, D.; Roth, W.R. *Angew. Chem. Int. Ed. Engl.* **1964**, *6*, 443 (solvent not specified); Kato, M.; Kobayashi, H.; Yamamoto, H.; Seto, K.; Ito, S.; Miwa, T. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3523-3532 ($CCl_4$). The signals for the cyclopropane H's in **3** at $\delta$ 1.6 and -0.2 ppm have spin-spin splitting patterns essentially identical to those shown for the analogous H's of benzonorcaradiene by Roth, H.D.; Manion Schilling, M.L. *Can. J. Chem.* **1983**, *61*, 1027-1035.
8. For example, when the $LiAlH_4$ reduction of **2** is conducted using the Soxhlet extraction procedure of ref. 1, the yield of **3** is negligible to very low. The yields of **3** reported are of material separated from **2** by column chromatography on silica gel (2:3 ethyl acetate:hexane); this **3** still contains traces of impurities removable by recrystallization from $CH_2Cl_2$:hexane. Efforts to increase the yield of **3** from **1**, **4** or **2** by attempting to force complete conversion of **2**, e.g., by extended reaction time or intermittent addition of fresh portions of $LiAlH_4$, failed.
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16. Dreiding models (using S as Al) indicate that either **18** or **19** can readily be manipulated to bring H on "Al" to within 2.0 Å of the receptor C. The distance 2.0 Å was chosen as an appropriate approximation of H-C distance in the transition state on the basis of calculations of the H-C distance in the transition state for addition of LiH to carbonyl groups: Wu, Y.-D.; Tucker, J.A.; Houk, K.N. *J. Am. Chem. Soc.* **1991**, *113*, 5018-5027 and Eksterowicz, J.E.; Houk, K.N. *Tetrahedron Lett.* **1993**, *34*, 427-430. Semiempirical computations at the AM1 level on **19** and **18** support the conclusion that only a modest increase in energy (10-15 kcal/mol) is required for **19** and **18** to adopt such a geometry. These computations were performed using Spartan, version 4.1, Wavefunction, Inc.: Irvine, CA 92715, 1997. We thank Professor R. Ditchfield for advice concerning these computations.

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