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FACILE RETRO DIELS-ALDER REACTION OF A VINYL LITHIUM COMPOUND

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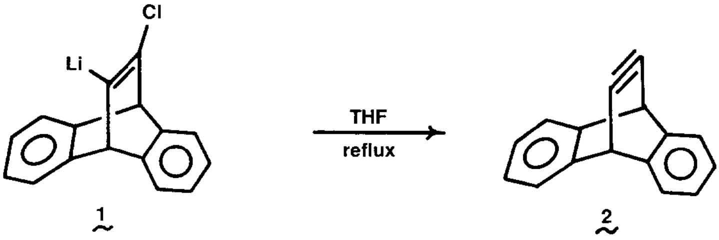
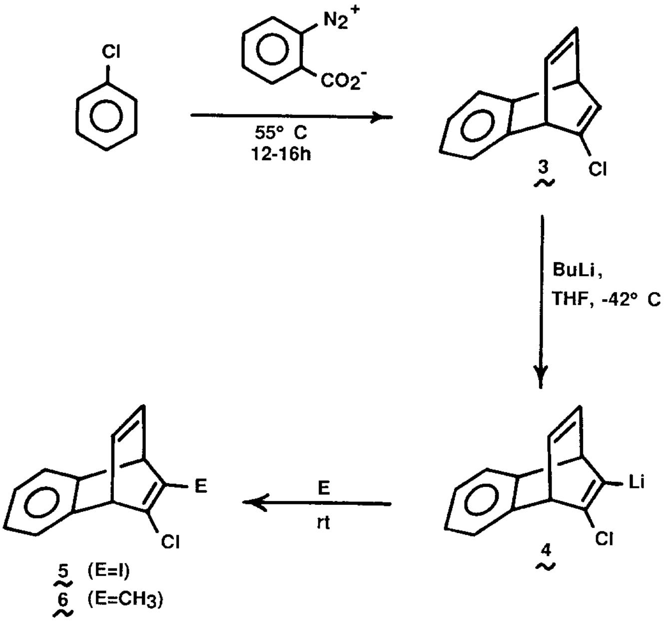
Abstract: Attempts to generate benzobarrelyne **8** by loss of lithium chloride from **4** resulted in a facile retro Diels-Alder reaction of the "dimeric" adduct formed by addition of **4** to **8**.

A few years ago, we presented evidence for the existence of the bicycloalkyne dibenzobarrelyne **2**, generated by the elimination of lithium chloride from **1**[1,2] and trapped by cycloaddition to various dienes.[2] In attempting to extend this work to benzobarrelyne **8**, we discovered an unusual and unanticipated retro Diels-Alder reaction of considerable interest.



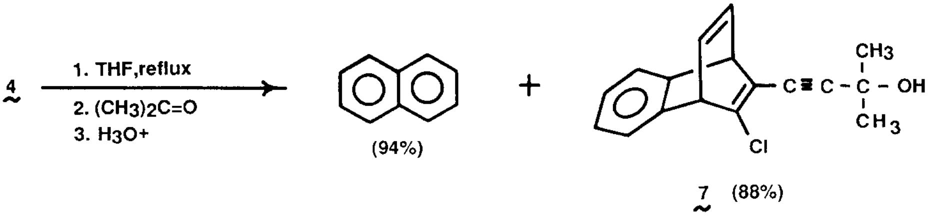
2-Chloro-1,4-dihydro-1,4-ethenonaphthalene **3** was prepared in 30-40% yield and multigram quantities through the addition of benzyne to chlorobenzene.[3] Lithiation of **3** with *n*-BuLi in THF at -42°C gave a nearly quantitative yield of **4**, as shown by quenching with I_2 to give **5** in 93% isolated yield, mp 85-86°C,[4] and by quenching with methyl iodide to give **6** in 86% yield, mp 62-63°C.[5] THF solutions of **4** are reasonably stable up to room temperature.

Whereas vinyl chloride **3** required temperatures of 350°C for pyrolytic decomposition and gave a mixture of naphthalene, 1-chloronaphthalene and 2-chloronaphthalene (1:0.8:2),[6-8] its lithio derivative **4** decomposed at a much lower temperature (refluxing THF) and gave naphthalene as the only volatile product. Thinking that the latter reaction might involve an anion-

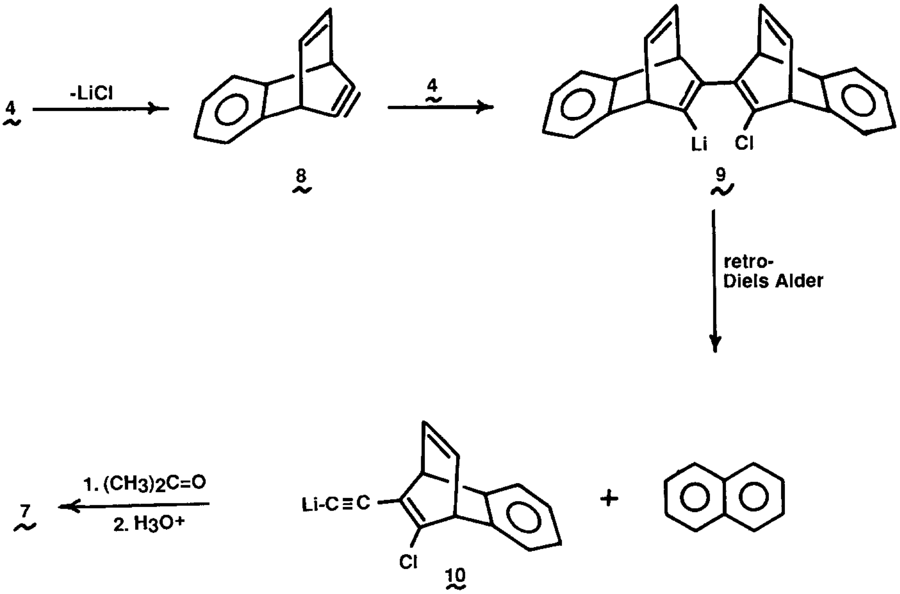


assisted retro Diels-Alder reaction,[9] with the elimination of the unknown species {Li-C≡C-Cl}, we heated a THF solution of **4** at reflux for 2 h, then added acetone, hoping to trap this species. The products were a nearly quantitative yield of naphthalene and the unexpected tertiary acetylenic alcohol **7**.

Evidence for the structure of **7** is spectroscopic. In particular, its ^1H NMR spectrum showed a six-proton singlet at δ 1.48 for the methyl protons, a broad O-H singlet at δ 2.16 (removed with D_2O), two bridgehead protons at δ 4.71 and 4.78, and aromatic and vinyl multiplets at δ 6.90 (4H) and 7.18 (2 H). The infrared spectrum showed bands for the hydroxyl group (3592 cm^{-1}) and the triple bond (2205 cm^{-1}).[10]



A plausible route to **7** is shown. Elimination of lithium chloride from **4** produces benzobarrelyne **8** which then reacts rapidly with the starting material **4** to give the "dimeric" adduct **9**. A retro Diels-Alder of **9** would give naphthalene and acetylide **10** which reacts with



the subsequently added acetone to give the observed **7** after an aqueous quench. Possible driving forces for the facile retro Diels-Alder reaction of **9** are the formation of an aromatic system (naphthalene) and the conversion of an *sp*^{2} to an *sp* lithio derivative (**9** ⟶ **10**). In the previous study on dibenzobarrelyne **2**,[2] a similar addition of **1** to **2** was observed, but the analogous retro Diels-Alder reaction did not occur under comparable conditions, probably because of the lesser resonance energy to be gained by forming the central aromatic ring in anthracene vis-a-vis the second aromatic ring of naphthalene.

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References and Notes

1. Huebner, C. F.; Puckett, R. T.; Brzechfta, M.; Schwarts, S. L. *Tetrahedron Lett.* **1970**, 359.
2. Hart, H.; Shamouilian, S.; Takehira, Y. *J. Org. Chem.* **1981**, *46*, 4427.
3. Tabushi, I.; Yamada, H.; Yoshida, Z.; Oda, R. *Bull. Chem. Soc. Japan* **1977**, *50*, 285.
4. Bridgehead protons at δ 4.85 and 4.95, vinyl and aryl protons (2 each) at δ 6.78, 6.90 and 7.16; *Anal.* Calcd for $C_{12}H_8ClI$: C, 45.80; H, 2.56. Found: C, 45.68; H, 2.51.
5. Methyl protons at δ 1.84, bridgehead protons at δ 4.56 and 4.67; vinyl and aryl protons at δ 6.90–7.17; *Anal.* Calcd for $C_{13}H_{11}Cl$: C, 77.03; H, 5.47. Found: C, 76.94; H, 5.43.

6. The reaction was performed by heating a neat sample of 3 in a sealed tube at 350°C for 5 min; volatiles were separated from polymeric products by preparative tlc and were analyzed by gas chromatography. Flash pyrolysis of 3 (short residence times) at 400°C gave only recovered starting material.
7. Pyrolysis of indanetrione at 500°C in a large excess of chlorobenzene gave the same products, presumably via the formation and decomposition of 3; Brown, R. F. C.; Solly, R. K. *Chem. and Ind.* **1965**, 181.
8. The acid-catalyzed isomerization of 1- and 2-chloronaphthalenes on alumina silica at 355-365°C is known; Vorozhtsov, N. N., Jr.; Koptyug, V. A. *J. Gen. Chem. USSR, Engl. Transl.* **1958**, *28*, 368.
9. Oku, A.; Kakihana, T.; Hart, H. *J. Am. Chem. Soc.* **1967**, *89*, 4554; Bowman, E. S.; Hughes, G. B.; Grutzner, J. B. *J. Am. Chem. Soc.* **1976**, *98*, 8273; Neukam W.; Grimme, W. *Tetrahedron Lett.* **1978**, 2201; Papies, O.; Grimme, W. *Tetrahedron Lett.* **1980**, *21*, 2799; Vara Prasad, J. V. N.; Iyer, P.; Pillar, C. N. *J. Org. Chem.* **1982**, *47*, 1380.
10. *Anal.* Calcd for $C_{17}H_{15}ClO$: C, 75.41; H, 5.58. Found: C, 75.32; H, 5.60. The mass spectrum showed parent peaks at *m/e* 272 and 270, intensity ratio 1:3, showing the presence of one Cl atom.

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