FORMATION OF 1,2-DEHYDROBENZENE FROM 1-CHLOROBENZVALENE BY STRONG BASES:

EVIDENCE FOR THE REARRANGEMENT OF 1,6-DEHYDROBENZVALENE TO BENZYNE

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Summary: Treatment of 1-chlorobenzvalene with n-butyllithium or with lithium diiso-
propylamide in the presence of dimethylfuran and furan led to butylbenzene and to the
adducts 12a and b, respectively.

We have recently demonstrated that tricyclo[4.1.0.0^{2,7}]hept-1(7)-ene ($\underline{1}$) at room tem-
perature and above rearranged to 1,2,3-cycloheptatriene ($\underline{2}$) [1]. We have tried to extend
this reaction to the lower homologue $\underline{3}$ and found that $\underline{3}$, even at 80°C, did not show any pro-
pensity to isomerize to 1,2,3-cyclohexatriene ($\underline{4}$). When $\underline{3}$ was generated from the silane $\underline{5}$ by
desilylation with CsF in DMSO at 80°C in the presence of diphenylisobenzofuran, only the
known [2] [3.1.1]propellane $\underline{6}$ was isolated in 43% yield. The different behavior of $\underline{1}$ and $\underline{3}$
with respect to the bicyclo[1.1.0]but-1(3)-ene 1,2,3-butatriene rearrangement probably rests
on the fact that the reaction $\underline{1} \rightarrow \underline{2}$ is considerably more exothermic than the isomerization
$\underline{3} \rightarrow \underline{4}$ and, therefore, proceeds at lower temperature [3]. In this connection it seemed of in-
terest to find out, if the isomerization of 1,6-dehydrobenzvalene ($\underline{7}$) to benzyne ($\underline{8}$) could
be brought about, and at what temperature this orbital symmetry-allowed [4] conversion would
take place.

Solutions of 1-chlorobenzvalene ($\underline{9c}$) in ether were obtained, when $\underline{9a}$ [5] was metalated
to $\underline{9b}$ with n-butyllithium (BuLi) at room temperature, followed by addition of $\underline{9b}$ to p-tolu-
enesulfonyl chloride (TsCl) in ether at -78°C. The precipitate was filtered off with a glass
frit at -78°C and the resulting filtrate contained $\underline{9c}$ in a yield of 35%. $\underline{9c}$ was character-
ized by ^{1}H and ^{13}C NMR spectroscopy [6,7].

$\underline{9c}$ proved to be less stable than $\underline{9a}$. When a mixture of $\underline{9a}$ and $\underline{9c}$ in ether was warmed to
room temperature, ^{1}H NMR analysis showed that the concentration of $\underline{9a}$ was unchanged, whereas
$\underline{9c}$ had completely rearranged to chlorobenzene [8]. At -78°C $\underline{9c}$ was stable for several days.

The addition of $\underline{9c}$ in ether to a solution of BuLi (4.0 equiv.) in ether at -105°C fol-

lowed, after 15 minutes, by aqueous work-up, led to a 45% yield of butylbenzene (10). 1-Butyl-benzvalene (9d) or 1-butyl-6-lithiobenzvalene (9e) could not be detected, even when the components were mixed at -105°C and the solution was analyzed by ^{1}H NMR spectroscopy at -60°C. 1-Methylbenzvalene [9] and 1-lithio-6-methylbenzvalene were prepared as model compounds for 9d and 9e and were found to be stable at room temperature in ether in the presence of lithium chloride. In a further control experiment it was ascertained that a mixture of BuLi (4.0 equiv.) and chlorobenzene in ether at -105°C, followed by aqueous work-up after 15 minutes, did not lead to 10 in a yield exceeding 0.5%.


9	a	b	c	d	e	f
X	H	Li	Cl	Bu	Bu	Cl
Y	H	H	H	H	Li	Li
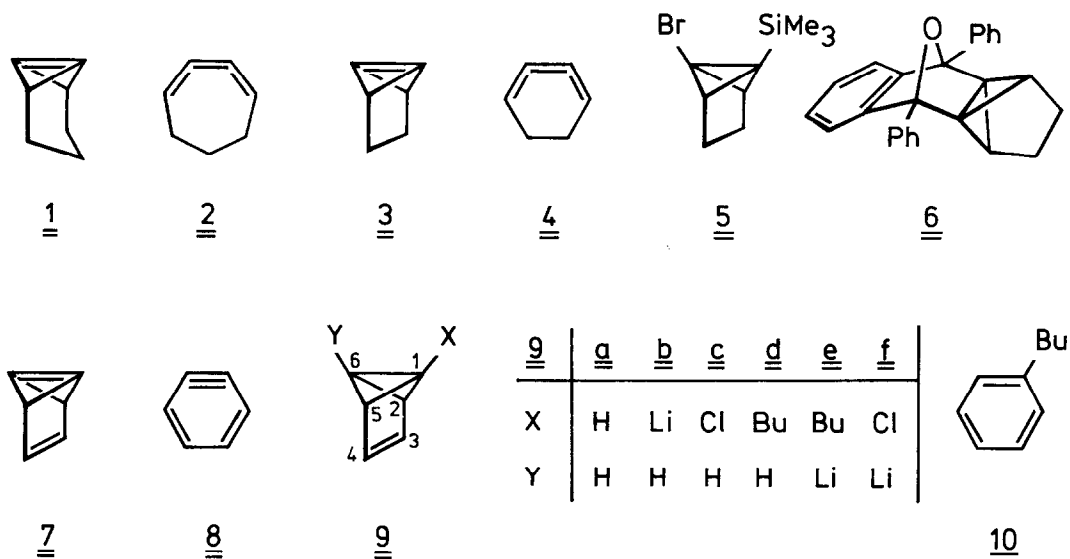
From these results we conclude that the reaction of 9c with BuLi does not produce 10 via the route 9c → 9f → 7 → 9e → 9d → 10 and not via the sequence 9c → chlorobenzene → → 8 → 10. However, the mechanism depicted in the Scheme is consistent with all our observations.

Scheme
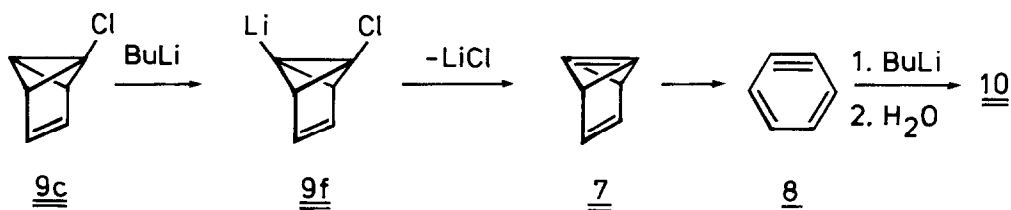
According to the Scheme, the reaction of BuLi with 9c affords, via 9f, 1,6-dehydro-benzvalene (7), which, even at -105°C, rearranges faster to benzyne (8) than it adds BuLi to form 9e [10].

The result of a further experiment indicated that 8, and not 7, was the reactive species that had been trapped. When LDA was added to 9c in ether at -70°C in the presence of a mixture of 2,5-dimethylfuran (11a) and furan (11b) (20 equiv. of each), a 2.0:1.0 mixture of the Diels-Alder adducts 12a and b was produced (total yield 17%). The same 2.0:1.0 ratio of 12a and b was obtained on combining BuLi and 1-bromo-2-chlorobenzene in ether at -70°C together with 11a and b (20 equiv. of each; total yield of 12a/b 20%). The identical values for the competition constants of the adduct formation in both experiments ensure that 8 is the reactive intermediate in the first mentioned reaction.

13	a	b	c	d
X	H	Li	Cl	Br
Y	H	H	H	SiMe$_3$
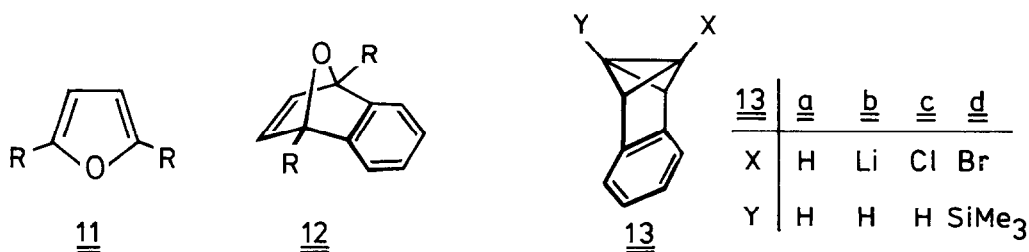
11, 12, 14: a: R = Me; b: R = H
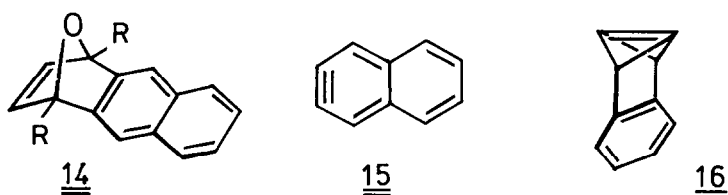
Using 1-chloronaphthvalene (13c) instead of 9c led to similar results. 13c was obtained from 13a [5] by treatment first with BuLi (to give 13b), then with TsCl, in a yield of 68% [11]. Unlike 9c, 13c is stable at room temperature. Again, the reaction of 13c with BuLi in ether at -90°C, after aqueous work-up, gave only 2-n-butylnaphthalene in a yield of about 60%. In addition, when 13d was allowed to react with CsF at room temperature in DMSO in the presence of 11a and b (10 equiv. of each), a 2.0:1.0 mixture of 14a and b was formed (total yield 27%). The same ratio of 14a and b was produced (total yield 32%), when the same reaction was carried out with 2-bromo-3-trimethylsilylnaphthalene [12] instead of 13d. Evidently, the 1,6-dehydro-naphthvalene (16), when generated from 13c by BuLi or from 13d by CsF, rearranges quickly to 2,3-dehydronaphthalene (15) and cannot be trapped by BuLi or 11a and b.

References and Notes:

1) H.-G. Zoch, G. Szeimies, R. Römer, and R. Schmitt, Angew. Chem. 93, 894 (1981); Angew. Chem., Int. Ed. Engl. 20, 877 (1981). H.-G. Zoch, G. Szeimies, R. Römer, G. Germain, and J.-P. Declercq, Chem. Ber., in print.

2) H. Legner, Diplomarbeit Univ. München 1980.

3) The thermal rearrangements 1 → 2 and 3 → 4 appear to be orbital symmetry-forbidden: R. B. Woodward and R. Hoffmann, Angew. Chem. 81, 797 (1969); Angew. Chem., Int. Ed. Engl. 8, 781 (1969).

4) N. J. Turro, C. A. Renner, T. J. Katz, K. B. Wiberg, and H. A. Connon, Tetrahedron Lett. 1976, 4133. J. J. Mulder, J. Am. Chem. Soc. 99, 5177 (1977).

5) T. J. Katz, E. J. Wang, and N. Acton, J. Am. Chem. Soc. 93, 3782 (1971). T. J. Katz, R. J. Roth, N. Acton, and E. J. Carnahan, Org. Synth. 53, 157 (1973). It is noteworthy that, occasionally, solutions of 9b in ether decomposed violently without apparent cause

6) 9c: ^{1}H NMR (CCl$_4$): δ = 2.63 (m; 2 H, 2-H, 5-H), 4.33 (t; 1 H, 6-H), 6.02 (t; 2 H, 3-H, 4-H). - ^{13}C NMR (CDCl$_3$/Et$_2$O): δ = 44.6 (d; C-2, C-5), 54.7 (d; C-6), 70.9 (s; C-1), 133.5 (d; C-3, C-4).

7) In addition to 9c, the following benzvalene derivatives were obtained from 9b: with chlorotrimethylsilane 1-trimethylsilyl-benzvalene (50%), with methyl chloroformate methyl benzvalene-1-carboxylate (33%), with p-toluenesulfonyl bromide 1-bromobenzvalene (30%), with p-toluenesulfonyl fluoride 4-tolyl-1-tricyclo[3.1.0.0^{2,6}]hex-4-enyl sulfone (60%).

8) At this point it is not clear, if catalysis played a role in the rearrangement of 9c to chlorobenzene. In general, bridgehead halogen substituted bicyclo[1.1.0]butanes are, according to our experience, less prone to rearrangement by electrophilic catalysts than the corresponding hydrocarbons.

9) U. Burger and G. Gandillon, Tetrahedron Lett. 1979, 4281. U. Burger, G. Gandillon, and J. Mareda, Helv. Chim. Acta 64, 844 (1981).

10) The intermediacy of 7 is not proven. Our experiments do not exclude a concerted reaction of 9f to 8.

11) 13c: ^{1}H NMR (CDCl$_3$): δ = 2.94 (d; 2 H, 2-H, 5-H), 4.31 (t; 1 H, 6-H). - ^{13}C NMR (CDCl$_3$): δ = 43.7 (d; C-2, C-5), 49.1 (d; C-6), 64.9 (s; C-1), 120.3 (d), 124.5 (d), 145.8 (s; C-3, C-4).

12) Obtained from 13d by thermal rearrangement.

(Received in Germany 17 December 1982)