

THE CHEMISTRY OF PHENALENIUM SYSTEM. XII¹⁾
NAPHTHO[1,8]TRICYCLO[4.1.0.0^{2,7}]HEPTENE. SYNTHESIS AND REARRANGEMENT TO
PLEIADIENE

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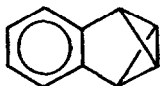
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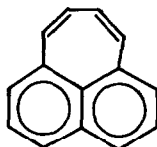
The most important synthesis of the valence isomer of benzenoid hydrocarbon, benzvalene (1) and naphthovalene (benzobenzvalene) (2) involves cyclization of the intermediate carbene species resulting from the cyclopentadienyl and/or the indenyl anion with dichloromethane in the presence of alkyl lithium to form the bicyclo[1.1.0]butane system.²⁾



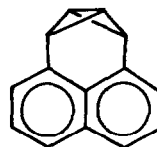
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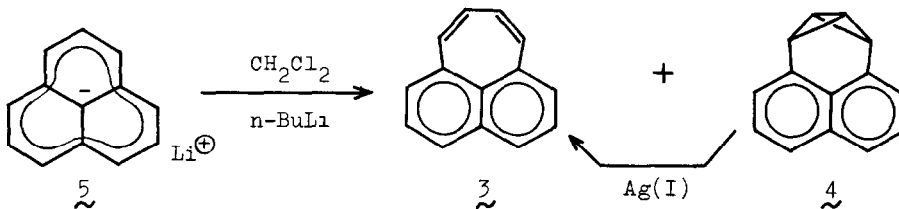


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In conjunction with our studies on the chemistry of the phenalenyl system, we have found that the "valene" type valence isomer of pleiadiene (3), naphtho[1,8]tricyclo[4.1.0.0^{2,7}]heptene (4), also accessible from the analogous reaction³⁾ of phenalenyl anion (5). The formation of 4 is the first example for the existence of the "valene" type valence isomer⁴⁾ of nonalternant hydrocarbon.

In a typical experiment, a solution of 1.0 g (6.0 mmol) of phenalene in 70 ml of absolute ether was treated with 6.5 mmol of n-butyllithium at 0° for 20 min, and then a solution of 1.1 g (13 mmol) of dichloromethane in 5 ml of absolute ether and 13 mmol of n-butyllithium in absolute ether were added at -50~-40° during 40 min. The reaction mixture was allowed to stir at this temperature for additional 2 hr, quenched by water and extracted with ether. The ethereal layer was washed with water and dried over anhydrous magnesium sulfate. Removal of the solvent in vacuo afforded an orange oil which was chromatographed repeatedly on a

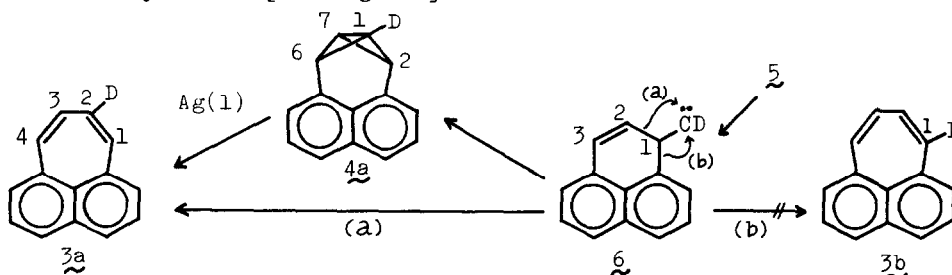
column of alumina deactivated with 5% of water (elution with light pet. ether) to give 0.102 g (10%) of 3 and 0.420 g (40%) of 4 along with two other thermally labile unidentified products. The pleiadene 3, reddish orange prisms (recrystallized from light pet. ether) with mp 92-93° (Lit.⁵⁾ 87-90°), anal. found, C, 94.20; H, 5.64%, m/e, 178(M⁺, 100%), 152(M-26, 74%), 76(36%), was identified by comparison of its melting point,⁵⁾ uv-visible spectrum⁵⁾ and nmr spectrum⁴⁾ with those reported.



The structure of the major product 4, colorless needles, mp 76-78° (after three times recrystallization from light pet. ether), anal. found, C, 94.43; H, 5.59, calcd. for C₁₄H₁₀, C, 94.34; H, 5.66%, is supported by the following spectroscopic evidences. Its mass spectrum shows a striking resemblance to that of 3. The abundant ions appear at m/e 178(100%, molecular ion) and 152(46%), indicating a facile loss of acetylene to give an ion formulated as acenaphthylene ion. The uv spectrum of 4 (in cyclohexane), 217 nm (log ε, 4.51), 234(4.47), 284(3.84), 295(3.91), 304(3.76), 310(3.71), 319(3.07) and 323(2.97), is similar to that of naphtho[1,8]tricyclo[4.3.0.0^{2,7}]nonene reported by Nelson and Gillespie.⁶⁾ The nmr spectrum of 4 (CCl₄, 60 MHz) [see Fig. 1] is compatible with the proposed bicyclobutane structure. It shows, in addition to a low-field multiplet at δ 6.93-7.52 due to the six aromatic protons, a sharp pair of two-proton triplets at δ 2.48 and 3.17 with the coupling constant of 2.5 Hz.⁷⁾ The ir spectrum of 4 in CCl₄ consists bands at 3100-2960 (four bands), 1605, 1510, 1415, 1385, 1180, 1110, 1030, 985, 915, 840, 720 and 660 cm⁻¹.

Chemical evidence for the structure of 4 was provided by its Ag(I) ion induced isomerization⁸⁾ to pleiadene 3. Thus, as would be expected, upon treatment with silver perchlorate (0.1 mmol) in benzene, 4 (0.2 mmol) was isomerized to afford pleiadene 3. This conversion proceeded smoothly at room temperature during 1 hr and the isolated yield of 3 was more than 70%.

The formation of $\underline{3}$ would reasonably be interpreted by the ring enlargement of the carbene intermediate ($\underline{6}$). The question of possible migratory preferences for the intramolecular bond shift of $\underline{6}$ [either route (a) or (b)] is of interest. In this connection we have examined the reaction of $\underline{5}$ with dideuteriodichloromethane. Migration of C-2 from C-1 to the carbene center would give pleiadene-2-d ($\underline{3a}$) whereas migration of the aromatic carbon from C-1 to the carbene center would give pleiadene-1-d ($\underline{3b}$). The reaction of $\underline{5}$ with CD_2Cl_2 in the presence of n-butyllithium was carried out as previously described affording labeled products. In the bicyclobutane derivative, the deuterium present was completely at a bridge-head position (C-1) of the bicyclobutane moiety ($\underline{4a}$), nmr (CCl_4 , 60 MHz) δ 2.43 (b.t., 1H, H-7), 3.13(d, $J=2.5$ Hz, 2H, H-2,6), 6.92-7.50(m, 6H), as expected from the method of synthesis [see Fig. 1].



The site of deuterium in labeled pleiadene is obtainable from its nmr spectrum [see Fig. 2]. In addition to the six-proton multiplet for the aryl hydrogens, the spectrum showed two sets of vinyl hydrogens at δ 5.23 and 5.86 as an AB-

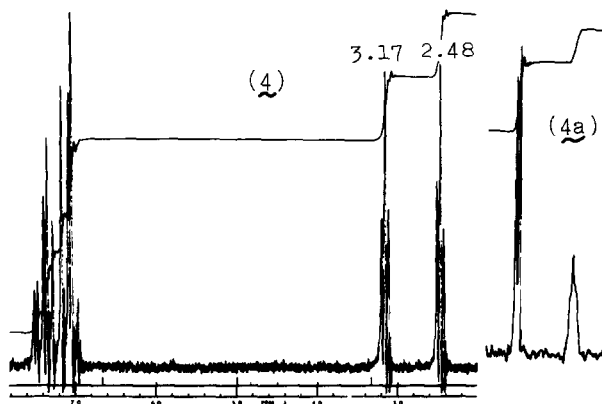


Fig. 1 Nmr spectra of $\underline{4}$ and $\underline{4a}$

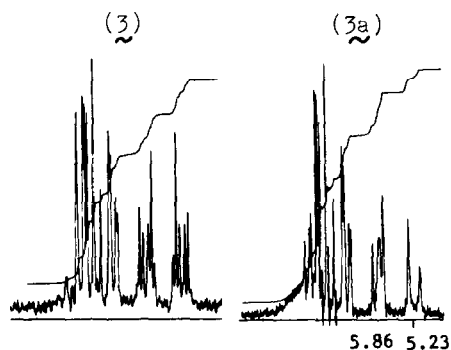
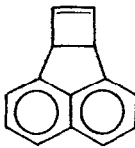


Fig. 2 Nmr spectra of $\underline{3}$ and $\underline{3a}$

quartet ($J_{AB}=13$ Hz) attributed to H-3 and H-4 respectively and an one hydrogen singlet at δ 5.85 which was assigned to H-1. Furthermore, the reaction of the labeled bicyclobutane (4a) with Ag(I) gave the same deuterated pleiadiene ($\underline{3a}$).⁹⁾ In view of these data, it is clear that the resulting pleiadiene was labeled exclusively as in ($\underline{3a}$) and the reaction proceeds through vinyl migration of an intermediate carbene species $\underline{6}$ [route-(a)].¹⁰⁾ Further studies on the chemistry of this bicyclobutane system are currently in progress.

REFERENCES AND FOOTNOTES

- 1) Part XI of this series, see : I. Murata, T. Nakazawa and T. Imanishi, Tetrahedron Letters, in the press.
 - 2) T. J. Katz, E. J. Wang and N. Acton, J. Amer. Chem. Soc., 93, 3782 (1971). Benzvalene has already been synthesized by photolyzing benzene; cf. K. E. Wilzbach, J. S. Ritsher and L. Kaplan, ibid., 89, 1031 (1967); L. Kaplan and K. E. Wilzbach, ibid., 90, 3291 (1968); H. R. Ward and J. S. Wishnok, ibid., 90, 1085 (1968).
 - 3) Isobullvalene has also been prepared by the analogous reaction using the cyclononatetraenide ion: (a) K. Hojo, R. T. Seidner and S. Masamune, J. Amer. Chem. Soc., 92, 6641 (1970); (b) T. J. Katz and J. J. Cheung, ibid., 91, 7772 (1969); (c) T. J. Katz, J. J. Cheung, and N. Acton, ibid., 92, 6643 (1970).
 - 4) Synthesis of the other valence isomer of pleiadiene, naphtho[1,8]bicyclo[3.2.0]hepta-2,6-diene (1), and its rearrangement to pleiadiene has recently been reported by J. Meinwald et. al.: J. Meinwald, G. E. Samuelson and M. Ikeda, J. Amer. Chem. Soc., 92, 7604 (1970).
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(1)
- 5) V. Boekelheide and G. K. Vick, ibid., 78, 653 (1956).
 - 6) S. F. Nelson and J. P. Gillespie, ibid., 94, 6237 (1972).
 - 7) Naphthovalene showed nmr signals at δ 6.82 (sym. m. 4H), 3.83 (t, $J=1.5$ Hz, 2H) and 2.40 (t, $J=1.5$ Hz, 2H).²⁾
 - 8) Recent review on the Ag(I) promoted isomerization of the strained sigma-bond: see, L. A. Paquette, Account Chem. Research, 4, 280 (1971).
 - 9) The labeled bicyclobutane derivative (4a) should yield pleiadiene-2-d ($\underline{3a}$) on Ag(I) promoted isomerization, since tricyclo[4.1.0.0^{2,7}]heptane-1,7-d₂ was isomerized exclusively to cis,cis-1,3-cyclohexadiene-2,3-d₂ on the same treatment; see L. A. Paquette, G. R. Allen, Jr., and R. P. Henzel, J. Amer. Chem. Soc., 92, 7002 (1970).
 - 10) It is well known that a vinyl migration to a carbenoid center is a favored process. cf. P. G. Gassman, T. J. Atkins and F. J. Williams, ibid., 93, 1812 (1971).