

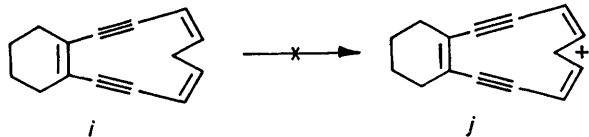
## Concerning the 1,5-Didehydro[10]annulene System

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**Summary** Attempted syntheses of 1,5-didehydro[10]annulene derivatives led to an intriguing isomerization which shows that any thermodynamic stability associated with this  $10\pi$ -electron system is at most comparable to that associated with benzene.

Much effort has been expended in recent years on the question of the aromaticity of conjugated  $10\pi$ -electron systems. Elegant work by Vogel *et al.*, on bridged annulene systems<sup>1a</sup> lent support to the validity of "Huckel's



$4n + 2$  rule"; however, the non-planarity of 1,6-methano[10]annulene<sup>1b</sup> modifies these compounds to the extent that they are *not rigorously* demonstrative of the properties of the planar  $10\pi$ -systems. Moreover, recent work has

shown<sup>2</sup> that two [10]annulenes are puckered molecules undergoing rapid conformational changes, and are not aromatic by any criteria associated with this term.<sup>3</sup> However, factors causing the nonplanarity in both classes of compounds are eliminated in 1,5-didehydro[10]annulene (1); thus this compound is especially suited for the investigation of planar  $10\pi$ -electron systems.<sup>4,5</sup> We report attempted syntheses of 1,5-didehydro[10]annulene derivatives and record intriguing properties of this system that have, in part, contributed to the difficulty of this synthetic problem.

The dilithium salt prepared from 1,2-diethynylcyclohexene (2)<sup>6</sup> and *n*-butyl-lithium was treated with ditosylate (3) to afford in *ca.* 10% yield the desired cyclized product (4), m.p. 154.5–155.5°. The successful removal of the protective group under neutral conditions (acidic conditions always led to preferential attack by the proton at the acetylenic bond) was achieved by hydride abstraction from the benzylidene position.<sup>7</sup> Trityl fluoroborate in acetonitrile converted (4) into the corresponding carbonium ion, which was hydrated in buffered solution to provide (80% yield) a hydroxybenzoate (5), m.p. 145° (dec.), which was transformed into dimesylate (6) through diol (7) (dec. at *ca.* 100°) in the usual way.

Treatment of (6) with sodium methoxide gave, in addition to 1,2,3,4-tetrahydroanthracene (8),<sup>8</sup> C<sub>14</sub>H<sub>14</sub>, a new hydrocarbon (9), m.p. 73.0—74.5° (30—40% yield), calc. mass for C<sub>14</sub>H<sub>12</sub>, 180.0939; found, *m/e* 180.0937 (base peak). Catalytic hydrogenation of (9) over Rh at -80°<sup>9</sup> and then over

cyclohexane) 223 nm (log ε 4.61), 234 (4.85), 262 (3.98), 267 (3.93), 276 (3.89), 290 (2.56), and 323 (2.12)]. This information and the synthetic scheme were compatible with the formulation 3,4-tetramethylene-1,5-didehydro[10]annulene (structure A) for compound (9). However, some doubt was cast on this assignment in comparing these data with those obtained in previous studies (*vide infra*).

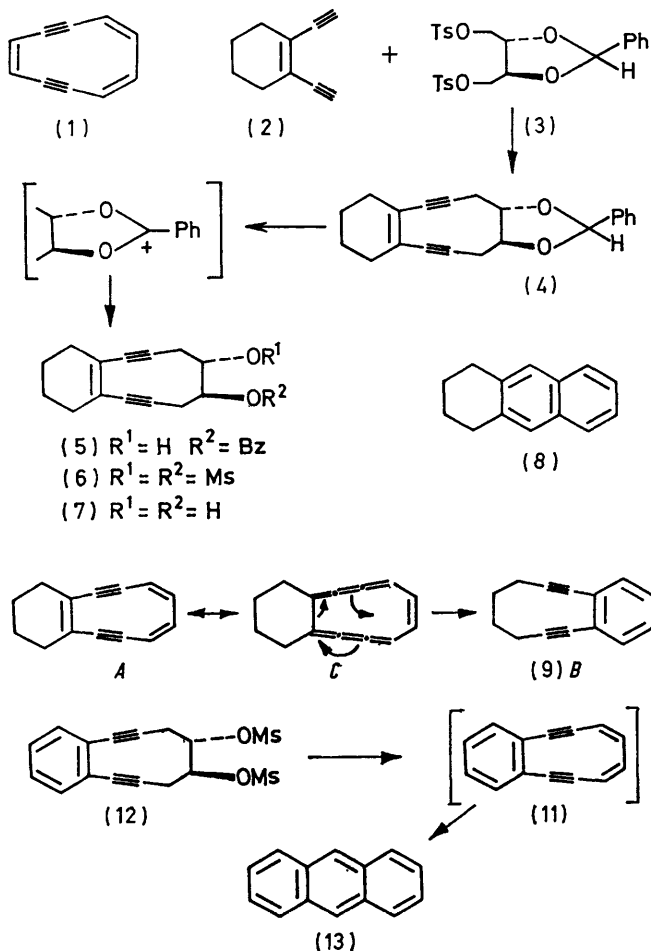
Our earlier work involved attempted syntheses of 1,5-didehydro-3,4-benz[10]annulene (11). The dimesylate (12), m.p. 113°, was prepared in a manner similar to that for (6). Compound (12) invariably provided anthracene (13) under various elimination conditions. (Use of deuteriated solvents in the elimination reaction showed that the two additional protons in anthracene entered at the 9,10 positions.) All of the intermediates possessing the 1,2-diethynylbenzene moiety had u.v. spectra similar to that of (9), which suggested the possibility that (9) could possess structure B (3,4-benzocyclodec-3-ene-1,5-diyne). Because chemical and spectral data could not differentiate rigorously between the two possible isomers (the results of catalytic hydrogenation under various conditions were inconclusive), and because B could not be synthesized directly from dilithio-1,2-diethynylbenzene and 1,4-dibromobutane, an X-ray analysis of compound (9) was undertaken. Some problem of disorder was presented, but the main features were those of structure B, although the possibility of the presence of a small amount of A is not excluded at this time.

The formation of B can be most readily (if not uniquely) explained by considering the other resonance form of the 1,5-didehydro[10]annulene system, C. A "Cope-like" rearrangement as depicted would lead directly to B. The distance (or interaction) between the in-plane π-electrons in structure A (or C) is little different from that in B, and molecular models indicate not a large difference in the strain associated with the respective ten-membered rings. Thus, if the rearrangement does indeed occur as shown (*vide supra*), then one can conclude that any stability associated with the 10π-electron system is at most comparable to that associated with benzene.†

It is readily apparent that replacement of the tetramethylene bridge of dimesylate (6) with a trimethylene moiety would enhance the energy barrier of the above rearrangement because of the large strain expected in the product. As such, the didehydro[10]annulene system may survive. Studies are underway to elucidate further the chemistry of this intriguing planar 10π-system.

We are indebted to M. J. Bennet and R. Smith of this department for the X-ray analysis of compound (9) and to the National Research Council for financial support.

(Received, September 8th, 1971; Com. 1575.)



PtO<sub>2</sub> in acetic acid afforded in 85% yield a bicyclic compound, C<sub>14</sub>H<sub>26</sub>, which was identical with *cis*-bicyclo[8,4,0]-tetradecane prepared in an unambiguous manner.† The proton signals in the low-field region of the n.m.r. spectrum of (9) constituted an AA'BB' system ( $\tau$  2.80 and 2.89;  $J_{A,B}$  7.5,  $J_{A,B'}$  1.4,  $J_{B,B'}$  8.8,  $J_{A',B'}$  0.0), and additional signals appeared at  $\tau$  7.82 (m, 4H) and 8.04 (m, 4H). The u.v. spectrum of (9) showed absorption maxima [ $\lambda_{\text{max}}$  (in

† From *o*-phenylene dibutyrate through a sequence of acyloin condensation, removal of OH and C=O, and catalytic hydrogenation over PtO<sub>2</sub>.

‡ Studies concurrent with those reported here led to the synthesis of compound *i*. Treatment of this compound with trityl fluoroborate in acetonitrile at 25° for 19 h did not produce the corresponding cation *j*, although formation of triphenylmethane was evident.

<sup>1</sup> (a) E. Vogel, *Proc. Robert A. Welch Found. Conf. Chem. Res.*, 1968, **12**, 215; (b) M. Dobler and J. D. Dunitz, *Helv. Chim. Acta*, 1965, **48**, 1429. An X-ray analysis of 1,6-methano[10]annulene shows that the distance between C-1 and C-6 is 2.26 Å and that the distortion from coplanarity is 20°.

<sup>2</sup> S. Masamune, K. Hojo, Kiyomi Hojo, G. Bigam, and D. L. Rabenstein, *J. Amer. Chem. Soc.*, in the press.

<sup>3</sup> F. Sondheimer, I. C. Calder, J. A. Elix, Y. Gaoni, P. J. Garratt, K. Grohmann, G. di Maio, J. Mayer, M. V. Sargent, and R. Wolovsky, *Chem. Soc. Spec. Publ.*, No. 21, 1967, p. 75.

<sup>4</sup> T. J. Sworski, *J. Chem. Phys.*, 1948, **16**, 550.

<sup>5</sup> For a summary of attempted syntheses, see F. Sondheimer, *Proc. Robert A. Welch Found. Conf. Chem. Res.*, 1968, **12**, 125.

<sup>6</sup> G. M. Pilling and F. Sondheimer, *J. Amer. Chem. Soc.*, 1971, **93**, 1970.

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<sup>8</sup> D. I. Davies and C. Waring, *J. Chem. Soc. (C)*, 1968, 1865.

<sup>9</sup> S. Masamune and R. T. Seidner, *Chem. Comm.*, 1969, 542.