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BENZO$(CH)_{10}$ INTERCONVERSIONS. THE SYNTHESIS AND THERMAL ISOMERIZATION OF *anti*-7,8-BENZOTRICYCLO$[4.2.0.0^{2,5}]$DECA-3,7,9-TRIENE

Leo A. Paquette and John C. Stowell*

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

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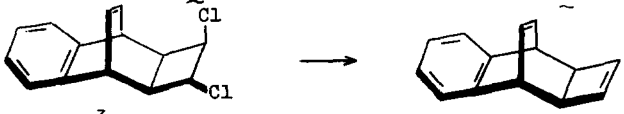
Although the multifarious nature of $(CH)_{10}$ hydrocarbon chemistry has engendered much recent interest in these molecules, no attention has yet been paid to the stereoelectronic control which benzo fusion could exert on the various bond reorganizations characteristic of the parent systems.[1] In this preliminary report, we describe a convenient synthesis of the title compound (4) and provide the first indication that mechanistically significant information can be derived from structural modifications of this type.

Addition of benzyne (from diazotized anthranilic acid) to 7,8-dichlorobicyclo[4.2.0]-octa-2,4-diene (1)[2] afforded (40% yield) 2 (mp 181-182°)[3] and 3 (mp 134-135°)[3] which were readily separated by alumina chromatography. Treatment of these dichlorides with sodium anthracene in anhydrous tetrahydrofuran gave 4 (mp 51-52°)[3] in quantitative yield. The *anti* stereochemistry of 4 follows from steric considerations,[4] energetically favorable secondary orbital interactions expected in the transition state of the benzyne cycloaddition, and spectral data [$\delta_{TMS}^{CDCl_3}$ 7.11 (A_2B_2, 4H, aryl), 6.22 (3 lines, 2H, vinyl), 6.05 (s, 2H, cyclobutene vinyl), 3.6-3.9 (m, 2H, methine), and 2.65 (m, 2H, cyclobutene methine)].

1 2



3 4

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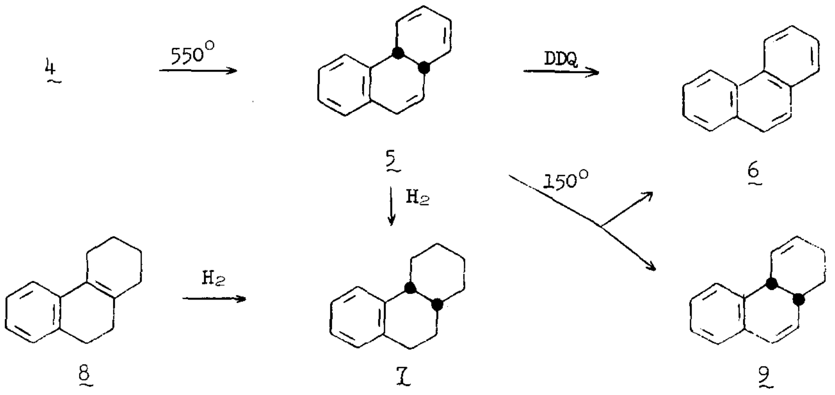
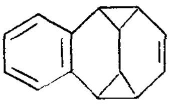
Pyrolysis of 4 in the vapor phase at 550° and 1 mm (N_2 flow, residence time ~ 2 sec) proceeded in high (> 95%) yield to afford a lone isomeric hydrocarbon which has been characterized as cis-4b,8a-dihydrophenanthrene (5);[3] $\lambda_{max}^{isooctane}$ 248 nm (ϵ 15,000); $\delta_{TMS}^{CDCl_3}$ 3.28 (m, 1, H_{8a}), 3.70 (m, 1, H_{4b}), 5.45-6.05 (m, 5, vinyl), 6.45 (dd, 1, H_{10}), and 6.9-7.3 (m, 4, aryl). Triple resonance studies at 100 M Hz revealed the following coupling constants: $J_{4b,8a}$ = 11 Hz; $J_{9,10}$ = 10 Hz; $J_{8a,10}$ = 3 Hz. A trace of phenanthrene (6) invariably accompanied the formation of 5. The gross structure of 5 was established by DDQ oxidation to 6, whereas the cis stereochemistry of the ring juncture was confirmed by catalytic hydrogenation to 7 which was prepared in unequivocal fashion by reduction of 8.[5] Benzo$(CH)_{10}$ derivative 5 is itself unstable to prolonged heating in the liquid phase at 150°. Upon being heated for 3 hrs at this temperature, 5 was seen to suffer disproportionation to 6 and tetrahydrophenanthrene 9[3] (ratio 1:1).



It is clear that the formation of 5 cannot be rationalized by any sequence which would involve intermediate 10 (the result of intramolecular cycloaddition), since the anthracene nucleus would most certainly eventuate. This is in marked contrast to 11 which is the key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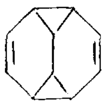
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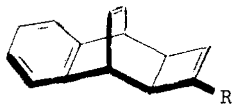
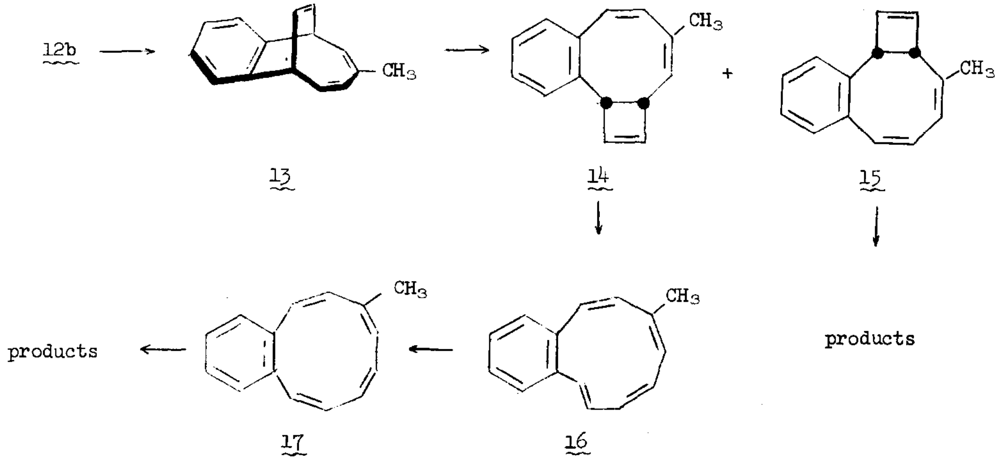


12a, R = Cl
b, R = CH_3

intermediate in several related thermal $(CH)_{10}$ rearrangements.[6] Rather, the observed transformation demands benzo or ethylene bridge migration and thereby sets the stage for a novel competitive phenomenon. To resolve this question and in fact establish that the ethylene bridge migrates to the apparent exclusion of the alternative pathway, dichlorides 2 and 3 were dehydrochlorinated[7] to give 12a[3] (mp 55-56.5°, 92%), which was subsequently converted in 71% yield to 12b[3] with lithium dimethylcuprate.[8]

Pyrolysis of 12b as above at 550° and 0.15 mm afforded a pale yellow oil which was oxidized directly with DDQ in benzene solution. Chromatography of the crude reaction mixture on alumina (elution with benzene) led to the isolation of a hydrocarbon fraction which consisted (vpc analysis) of phenanthrene (18%),[9] methylphenanthrenes (61%), naphthalene (7%), recovered 12b (10%), and two unknown substances (2% and 1%, respectively). The methylphenanthrene fraction was collected by preparative scale vpc and analyzed quantitatively by infrared and nmr spectroscopy.[10] This mixture was seen to consist solely of the 1-methyl (20%), 2-methyl (50%), and 3-methylphenanthrenes (30%). This striking positional selectivity suggests that the thermal rearrangement of 12b may involve initial cyclobutene ring cleavage to 13, followed by [1,5]sigmatropic shift of the ethylene bridge to give 14 and 15.[11] Conrotatory opening of the four-membered ring in these attractive intermediates would then give rise to four different methylated trans(cis)[4] benz[10]annulenes which serve as the likely precursors of the dihydrophenanthrenes.



However, by analogy to Masamune's observations with cis-bicyclo[6.2.0]deca-2,4,7,9-tetraene,[12] trans-fused dihydrophenanthrenes are expected from such intermediates. Rather, the cis isomer (e.g., 5) is produced essentially in quantitative yield, perhaps because the added stability introduced by the fused aromatic ring permits *trans* → *cis* isomerization (e.g., **16** → **17**) to occur prior to electrocyclization. Current experiments are concerned with the verification of these conclusions.[13]

REFERENCES AND FOOTNOTES

(1) The synthesis of only two benzo$(CH)_{10}$ hydrocarbons has been described to date; however, no chemistry of these systems has yet been reported: E. Vedejs, *Tetrahedron Lett.*, 2633 (1968). Professor L. Friedman has informed us privately that he also has succeeded in preparing **4**.

(2) R. Huisgen, G. Boche, W. Hechtl, and H. Huber, *Angew. Chem.*, **78**, 595 (1966); *Angew. Chem. Intern. Ed. Engl.*, **5**, 585 (1966).

(3) Satisfactory elemental analyses (± 0.3%) were obtained for all new compounds.

(4) L. A. Paquette and J. C. Stowell, *Tetrahedron Lett.*, 4159 (1969).

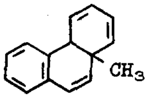
(5) H. Christol, Y. Pietrasanta, and J.-L. Vernet, *Ann. Chim.*, 145 (1968).

(6) (a) W. von E. Doering and J. W. Rosenthal, *J. Am. Chem. Soc.*, **88**, 2078 (1966); (b) S. Masamune, R. T. Seidner, H. Zenda, M. Wiesel, N. Nakatsuka, and G. Bigam, *ibid.*, **90**, 5286 (1968); (c) M. Jones, Jr., and B. Fairless, *Tetrahedron Lett.*, 4881 (1968); (d) W. Grimme, H. J. Riebel, and E. Vogel, *Angew. Chem.*, **80**, 803 (1968); *Angew. Chem. Intern. Ed. Engl.*, **7**, 823 (1968); (e) J. S. McConaghy, Jr., and J. J. Bloomfield, *Tetrahedron Lett.*, 1121 (1969); (f) R. T. Seidner, N. Nakatsuka, and S. Masamune, *Can. J. Chem.*, **48**, 187 (1970).

(7) W. Metzner and W. Hartmann, *Chem. Ber.*, **101**, 4099 (1968).

(8) E. J. Corey and G. H. Posner, *J. Am. Chem. Soc.*, **89**, 3911 (1967); **90**, 5615 (1968).

(9) The production of phenanthrene appears to be the result of the demethylation of **i** during the DDQ oxidation [*cf.*, for example, J. F. Bagli, P. F. Morand, K. Wiesner, and R. Gaudry, *Tetrahedron Lett.*, 387 (1964)].



i

(10) Under conditions of infinite dilution, the chemical shift of a methyl group is very characteristic of its position on the phenanthrene ring: P. Durand, J. Parello, and N. P. Buu-Hoï, *Bull. Soc. Chim. France*, 2438 (1963); R. J. Ouellette and B. G. van Leuwen, *J. Org. Chem.*, **34**, 62 (1969). For example, in carbon tetrachloride the following δ values were observed: 1-methyl (164.5 Hz), 2-methyl (152.4 Hz), 3-methyl (156.3 Hz), 4-methyl (188.4 Hz), and 9-methyl (162.2 Hz).

(11) It should be pointed out that, if benzo migration were operative, the 3-, 4-, and 9-methylphenanthrenes would have been produced in addition to the parent aromatic system. The conclusions are founded on the assumption that the methyldihydrophenanthrenes do not interconvert under the reaction conditions.

(12) S. Masamune, C. G. Chin, K. Hojo, and R. T. Seidner, *J. Am. Chem. Soc.*, **89**, 4804 (1967).

(13) We are grateful to Badische Anilin und Soda Fabrik for providing us with a generous sample of cyclooctatetraene.