

Communications TO THE EDITOR

9,10-Dihydro-9,10-Methanoanthracene

Sir:

We wish to report the synthesis of 9,10-dihydro-9,10-methanoanthracene (I). The existence of I was stated as fact by Whitmore¹ but no experimental evidence for this statement is traceable; and while preparations of derivatives of this system have been reported in the literature from time to time,²⁻⁴ subsequent work has shown that two^{2,4} of the three substances do not possess the assigned structures.^{5,6} The remaining substance³ is still in doubt since no unequivocal procedure for its preparation has appeared and no conclusive disproof of its structure has been attempted. Consequently the hydrocarbon system in question (I) must be regarded as hitherto unknown. Our interest in I derives from studies on the chemistry and molecular rearrangements of the 9,10-dihydro-9,10-ethanoanthracene (II) system (dibenzobicyclo[2,2,2]-octadiene) where the ethano bridge carries carboxyl and halogen or hydroxyl substituents.⁷⁻¹⁰

The synthesis of I was accomplished by the following reactions: bicyclo[2,2,1]heptadiene¹¹ was treated in benzene, containing a trace of hydroquinone, with excess butadiene for 24 hr. at 200–205° to yield 9.4% of 1,4,4a,5,8,8a,9,9a,10,10a-decahydro-9,10-methanoanthracene (III), m.p. 54.0–55.5° (uncorr.) from ethanol.

Anal. Calc'd for C₁₅H₂₀: C, 89.94; H, 10.06. Found:¹² C, 89.68; H, 10.10. Mol. wt. Calc'd, 200. Found, 197 (bromination¹³). Conversion of III to

I was achieved in 19% yield by dehydrogenation in benzene over 5% palladium-charcoal catalyst under an initial nitrogen pressure of 450 p.s.i. at 230° for 14 hr.;¹⁴ glistening white plates (from ethanol), m.p. 154.5–155.5° (uncorr.).

Anal. Calc'd for C₁₅H₁₂: C, 93.71; H, 6.29. Found:¹⁵ C, 93.54; H, 6.27.

The following chemical evidence supports the correctness of our structure for I. III, which possesses a single band in its infrared spectrum at 1640 cm.⁻¹, indicating the absence of two different types of double bonds, absorbs hydrogen smoothly in glacial acetic acid over Adams' catalyst, with no break in the curve of uptake *vs.* time, to give a perhydro-9,10-methanoanthracene (IV), long white needles (from ethanol), m.p. 76.5–77.8° (uncorr.).

Anal. Calc'd for C₁₅H₂₄: C, 88.16; H, 11.84. Found:¹² C, 88.14; H, 11.77.

Thus the alternative structure for III, 1,4,4a,5,8,8a,9,9a,10,10a-decahydro-1,4-methanoanthracene, is rendered improbable. The methylanthracenes isomeric with I are eliminated by the behavior of I on chromic acid oxidation from which, as from similar treatment of an authentic sample of II,¹⁶ no anthraquinone (or anthraquinone derivative) could be isolated—or even detected in minute amounts.¹⁷

A formal resemblance between the ultraviolet spectra of I and II affords spectrophotometric support for the structure of I and also rules out the methylanthracenes and naphthalenic structures.¹⁸ The principal bands for I and II are given in Table I.

TABLE I
ULTRAVIOLET ABSORPTION BANDS OF I AND II IN 95% ETHANOL

	λ_{\max} (Å)	log ϵ
I	2640 ^a	3.07
	2720	3.30
	2780	3.41
II	2590 ^a	2.93
	2650	3.18
	2720	3.30

^a Shoulder.

(14) H. Adkins, L. M. Richards, and J. W. Davis, *J. Am. Chem. Soc.*, **63**, 1320 (1941).

(15) Spang Microanalytical Laboratory, Plymouth, Michigan.

(16) S. J. Cristol and N. L. Hause, *J. Am. Chem. Soc.*, **74**, 2193 (1952).

(17) L. F. Fieser, *Experiments in Organic Chemistry*, 2nd ed., D. C. Heath and Co., New York, N. Y., 1941, p. 190.

(18) D. D. Phillips and J. Cason, *J. Am. Chem. Soc.*, **74**, 2934 (1952).

(1) F. C. Whitmore, *Organic Chemistry*, D. Van Nostrand Co., Inc., New York, N. Y., 1937, p. 867.

(2) E. B. Barnett, J. W. Cook, and M. A. Matthews, *Ber.*, **60**, 2353 (1927).

(3) C. Dufraisse and L. Enderlin, *Bull. soc. chim.*, [5] **1**, 267 (1934).

(4) A. Müller, *J. Org. Chem.*, **12**, 815 (1947).

(5) J. W. Cook, *Ber.*, **60**, 2366 (1927); *J. Chem. Soc.*, 2798 (1928).

(6) W. E. Doering and J. A. Berson, *J. Am. Chem. Soc.*, **72**, 1118 (1950).

(7) W. R. Vaughan and K. M. Milton, *J. Am. Chem. Soc.*, **74**, 5623 (1952).

(8) W. R. Vaughan, M. V. Andersen, Jr., and R. Q. Little, Jr., *J. Am. Chem. Soc.*, **76**, 1748 (1954).

(9) W. R. Vaughan and R. Q. Little, Jr., *J. Am. Chem. Soc.*, **76**, 2952, 4130 (1954).

(10) W. R. Vaughan and A. C. Schoenthaler, Unpublished research. Cf. A. C. Schoenthaler, Ph.D. Dissertation, University of Michigan, 1955.

(11) We are indebted to the Shell Development Company for a generous supply of this material.

(12) Microanalysis by Anna Griffen, University of Michigan.

(13) S. Siggia, *Quantitative Organic Analysis via Functional Groups*, 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1954, p. 69.

Final confirmation for the structure of I is available from the high resolution nuclear magnetic resonance spectra of I and II.¹⁹ The spectra of both substances show no mutual C—H and CH₂ splitting, thus confirming similar rigid structures. Only aromatic, methine and methylene protons are detectable, thus ruling out a methyl group in I as well as ethylenic protons which would be present in the isomeric 1,4-dihydro-1,4-methanoanthracene. The lines attributable to the aromatic protons lie at lower fields than in toluene: I ($\delta = -2.1$)²⁰; II ($\delta = -2.6$)²⁰; toluene ($\delta = -1.58$).²⁰ Thus

(19) Kindly obtained by Dr. Edward B. Baker of the Physical Research Laboratory, Dow Chemical Company, Midland, Michigan.

(20) $\delta = (H_c - H_r)/H_r \times 10^6$ (shift in parts per million referred to water); frequency 30 Mc. Cf. L. H. Meyer, A. Saika, and H. S. Gutowsky, *J. Am. Chem. Soc.*, **75**, 4567 (1953).

fewer electrons per proton are available in I and II than in toluene. Finally, the line at $\delta = -2.1$ in the spectrum of I shows evidence of unresolved structure, while the corresponding line at $\delta = -2.6$ in the spectrum of II is very sharp. Thus equivalence of all aromatic hydrogens in II is indicated while in I non-equivalence is suggested. This difference is not surprising in view of the expected greater distortion of the aromatic rings in I. It is clear from the spectrum of I that the numbers of methine and methylene protons are equal, as expected.

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