

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MICHIGAN]

9,10-Dihydro-9,10-methanoanthracene and Its Perhydro DerivativesWYMAN R. VAUGHAN AND MASAO YOSHIMINE^{1,2}*Received Aug. 6, 1956*

The synthesis of 9,10-dihydro-9,10-methanoanthracene (dibenzobicyclo[2,2,1]heptadiene), I, is described. The preparations of a number of potential as well as actual intermediates containing the same tetracyclic system are described, and the conversion of two of these to two stereoisomeric perhydro derivatives, XVI and XX, is discussed. Ultraviolet spectra of I and related compounds are considered to afford evidence for interaction of nonadjacent (nonconjugated) chromophores.

In a preliminary communication³ we have reported the synthesis of 9,10-dihydro-9,10-methanoanthracene (I), which despite a number of earlier claims for preparation of various of its derivatives, must be considered the parent and unique member of a new system of compounds. Our interest in this system stems from a suggestion⁴ that the lactone produced by the action of 48% hydrobromic acid on 2-hydroxy-3-methyldibenzobicyclo[2,2,2]octadiene-*trans*-2,3-dicarboxylic acid⁵ might be derived from I. Subsequent degradation⁶ showed this hypothesis to be in error but thereby raised intriguing questions as to what might be the chemical nature of methylene substituted derivatives of I.

Discounting such reports of derivatives of I as have appeared in experimental literature^{7,8,9} on the basis of subsequent disproofs^{10,11} of all but one,⁸ there remained the positive statement¹² that I was known and that oxidation removed the methylene bridge to give anthraquinone. Certain preliminary studies appeared to confirm the nature of the oxidation of the system in question (as stated in ref. 6, p. 1749), but, as will appear in the sequel, there is no basis for such a statement when I is subjected to oxidation.

Two potential routes to the synthesis of I were considered and investigated, one of which was completely unsuccessful but yielded new information on the benzylic acid rearrangement, wherein an at-

tempt was made to contract the ethylene bridge of dibenzobicyclo[2,2,2]octadiene-2,3-dione. This will be reported elsewhere. The other route involved construction of the system about a preformed bicyclo[2,2,1]heptane system by means of the Diels-Alder reaction. A number of possibilities were considered, and two independent approaches were undertaken and are reported herewith.

The initial and less equivocal synthesis is outlined in Chart I and is patterned after the elegant synthesis of triptycene by Bartlett, Ryan, and Cohen.¹³

The starting material (II) for this series of reactions was readily prepared from 1,4-benzoquinone and cyclopentadiene,¹⁴ and its conversion to III was effected at room temperature in order to avoid the difficulties encountered by others who were unable to bring about effective aromatization.^{14,15} The structure of III was related to the quinone, obtained in poor yield by Diels and Alder¹⁵ from II with ferric chloride in hydrobromic-acetic acid mixture, by reductive acetylation of the quinone to give III.

The desired ring system was completed by conversion of III to IV with butadiene, and aromatization was then attempted without success. Consequently IV was hydrolyzed to V and smoothly oxidized to VI which was oximated to VII. Conversion of VII to VIII was effected, but the latter proved to be extremely unstable, and the projected conversion to IX was not achieved. Instead, VII was catalytically reduced to X which was then deaminated to give XI, which unfortunately resisted aromatization. This route was then abandoned, with XI being reserved for comparison with products accessible by the successful alternative but more equivocal route outlined in Chart II.

The availability of XII¹⁶ made this approach especially attractive, since the dienophilic character of the double bond in bicyclo[2,2,1]heptene has been established.¹⁷ However, the *bis*-adduct of XII

(1) Abstracted from the Ph.D. dissertation of Masao Yoshimine, University of Michigan, 1955.

(2) Edgar C. Britton Fellow in Organic Chemistry, 1954-1955.

(3) W. R. Vaughan and M. Yoshimine, *J. Org. Chem.*, **21**, 263 (1956).

(4) K. M. Milton, Dissertation, University of Michigan, 1951.

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

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

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

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

(9) A. Muller, *J. Org. Chem.*, **12**, 815 (1947).

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

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

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

(13) P. D. Bartlett, M. J. Ryan, and S. G. Cohen, *J. Am. Chem. Soc.*, **64**, 2649 (1942).

(14) W. Albrecht, *Ann.*, **348**, 31 (1906).

(15) O. Diels and K. Alder, *Ber.*, **62**, 2337 (1929).

(16) A generous supply of this substance was kindly donated by the Shell Development Company, Emeryville, Calif.

(17) K. Alder and G. Stein, *Ann.*, **496**, 204 (1932).

CHART I

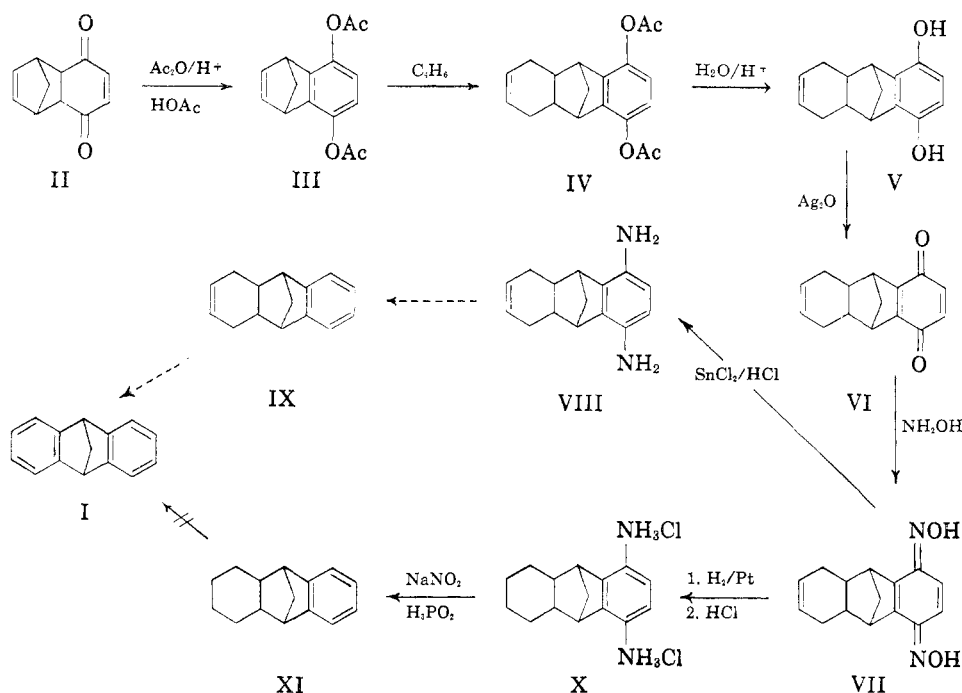
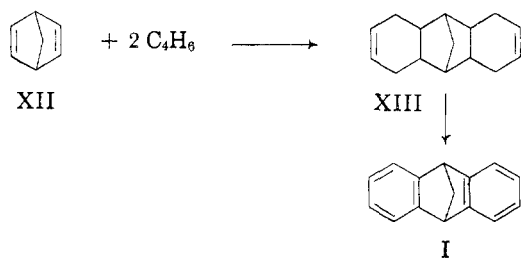
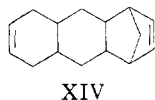


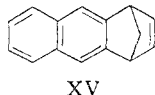
CHART II



with butadiene (XIV), isomeric with XIII, must be considered and would lead to an equivocal structure (XV) for the dehydrogenation product.



Nevertheless, the reaction between XII and excess butadiene was carried out, and a product with an



appropriate analysis for XIII (or XIV) was obtained in 9.4% yield. It seemed improbable that the second molecule of butadiene would add to the monoadduct at the cyclohexene double bond as long as there remained the intrinsically more reactive bicyclic double bond, and support for this hypothesis was obtained upon examination of the infrared spectrum of the product wherein there appears but one absorption band in the double bond region—and that at 1640 cm^{-1} corresponding to a normal unconjugated double bond. On the other

hand, XII shows a weak absorption at 1550 cm^{-1} , which is close to the Raman assignment¹⁸ of 1568 cm^{-1} for the bicyclic double bond of dicyclopentadiene. With this encouragement aromatization of XIII was investigated.

Several attempts to dehydrogenate XIII with sulfur, with and without solvent, afforded only unidentifiable high-melting material. Next catalytic dehydrogenation over palladium charcoal in refluxing cymene was attempted, but only starting material and a trace of perhydrogenated XIII, m.p. $76.5\text{--}77.8^\circ$ (XVI) were isolable. Thus, it seemed desirable to provide a hydrogen acceptor for the catalytic reaction, and the procedure of Adkins, Richards and Davis,¹⁹ using 5% palladium on charcoal in benzene at 230° , with an initial nitrogen pressure of 450 p.s.i., was employed. Under these conditions there was isolated a 19% yield of material corresponding in analysis to I (or XV). The substance melted at $154.5\text{--}155.5^\circ$, which eliminated the isomeric methylanthracenes from consideration, as did the ultraviolet spectrum (Table I) and the failure to produce even a trace of anthraquinone on vigorous oxidation.

The correctness of assigning to the dehydrogenation product the desired structure I rather than XV is established by the dissimilarity of the ultraviolet spectrum to that of naphthalenic systems (no absorption maxima above $300 \text{ m}\mu$) and its formal resemblance to that of 9,10-ethano-9,10-dihydroanthracene (XVII), (Table I) and by the high resolu-

(18) K. W. F. Kohlrausch and R. Seka, *Ber.*, **69**, 729 (1936).

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

TABLE I
 ULTRAVIOLET ABSORPTION MAXIMA

Com- pound	Max. (m μ)	Log ϵ	Max. (m μ)	Log ϵ	Max. (m μ)	Log ϵ
I ^a	264 ^b	3.07	272	3.30	278	3.41
XI ^a	259	2.89	265	3.06	272	3.10
XVII ^a	259 ^b	2.93	265	3.18	272	3.30
XVIII ^{a,c}	266 ^b	3.03	272	3.34	279	3.58
XIX ^d			264	3.06	272	3.00
Tripty- cene ^e	263 ^b	3.25	271	3.66	278	3.56

^a 95% ethanol; Cary Quartz Recording Spectrophotometer, Model II. ^b Shoulder. ^c Sample kindly supplied by A. C. Schoenthaler. ^d D. D. Phillips and J. Cason, *J. Am. Chem. Soc.*, **74**, 2934 (1952). ^e P. D. Bartlett and E. S. Lewis, *J. Am. Chem. Soc.*, **72**, 1005 (1950).

tion NMR spectra²⁰ of I and XVII: Only aromatic, methine, and methylene (no ethylenic) protons are detectable, and there is no mutual C—H and CH₂ splitting, confirming similar rigid structures possessing no ethylenic double bonds. Furthermore there are equal numbers of methine and methylene protons in I and twice as many methylene as methine hydrogens in XVII.

It is interesting to note that while chromic anhydride attacks both I and XVII, no trace of anthraquinone can be detected whereas 9,10-etheno-9,10-dihydroanthracene²¹ (XVIII) readily affords anthraquinone under similar conditions. No attempt was made to characterize the oxidation products of I and XVII, but the implied preferential susceptibility to oxidation of the aromatic rings is reminiscent of triptycene¹³ which affords anthraquinone on mild chromic anhydride oxidation. In triptycene this has been attributed to a possible Mills-Nixon effect^{13,22} and in the present compounds an analogous situation would seem to obtain. The chemical shifts (δ) for the aromatic protons in I and XVII are greater than for toluene (-1.58), indicating fewer electrons per proton than in toluene, which is consistent with their structures; and while the line at $\delta = -2.6$ (XVII) is very sharp, indicating complete equivalence of all aromatic protons, that at $\delta = -2.1$ (I) shows evidence of unresolved structure and hence nonequivalence of the aromatic protons. This is indicative of increased distortion in I, which is to be expected, and is consistent with an increased susceptibility to oxidation and with a true Mills-Nixon effect.

ULTRAVIOLET SPECTRA

The resemblance of I to triptycene is observable in their ultraviolet spectra, and for purposes of

(20) Kindly obtained by Dr. E. B. Baker of the Physical Research Laboratory, Dow Chemical Company, Midland, Mich.

(21) S. J. Cristol and N. L. Hause, *J. Am. Chem. Soc.*, **74**, 2193 (1952); A. C. Schoenthaler, Dissertation, University of Michigan, 1955.

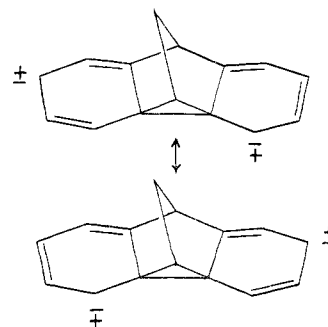
(22) Cf. G. W. Wheland, *Resonance in Organic Chemistry*, John Wiley & Sons, Inc., New York, N. Y., 1955, p. 497 f.

discussion, the principal absorption bands of several of the dihydroanthracenes mentioned above, as well as those for XI and 9,10-dimethyl-9,10-dihydroanthracene (XIX) are presented in Table I.

If XIX is considered a model compound for the 9,10-dihydroanthracene system, it will be noted that XI and XVII have spectra which resemble that of XIX closely, except for a generally increased intensity for XVII. Thus, the methano bridge in XI and the ethano bridge in XVII do not appear to influence the absorption characteristics of the adjacent aromatic ring(s). On the other hand, I, XVIII, and triptycene show more intense absorption by a factor of 2 to 3, and their maxima occur at from 4 to 7 m μ longer wave lengths than their apparent equivalents in XIX, XI, and XVII.

The wave lengths of the absorption maxima as well as the intensities of absorption for hydroaromatic compounds such as XIX are greater than for benzene, and this may be attributed to hyperconjugation, as for alkylbenzenes.²³ However, XI and XVII, which like triptycene (Table I, ref. e), are probably incapable of hyperconjugation on stereochemical grounds, spectroscopically resemble XIX. Friedel and Orchin²⁴ have suggested that the spatial overlap of two methyl groups in 4,5-dimethylphenanthrene and 4,5-dimethylchrysene introduces strain in the aromatic nucleus, causing an increased absorption maximum and intensity. Since there is undoubtedly strain imposed on the aromatic nuclei of XI and XVII by the 9,10-bridges (cf. NMR shifts for I and XVII aromatic protons, above), it is reasonable to attribute the resemblance of their spectra to that of XIX to this strain phenomenon.

While there is no other obvious phenomenon to account for the "abnormal" spectrum of XI, all of the remaining compounds (except the model, XIX) are capable of increased conjugation by interaction between nonadjacent chromophores as suggested by Bartlett and Lewis (Table I, ref. e) for triptycene and considered by Cram and Steinberg for the paracyclophanes²⁵: e.g.,

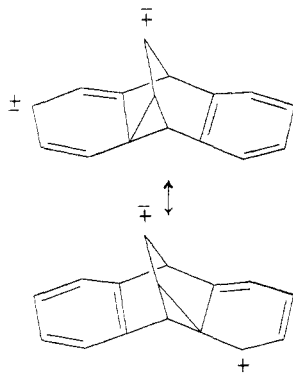


(23) F. A. Matsen, W. W. Robertson, and R. L. Chuoke, *Chem. Revs.*, **41**, 273 (1947).

(24) R. A. Friedel and M. Orchin, *Ultraviolet Spectra of Aromatic Compounds*, John Wiley and Sons, Inc., New York, N. Y., 1951, pp. 23, 25.

(25) D. J. Cram and H. Steinberg, *J. Am. Chem. Soc.*, **73**, 5691 (1951).

However, all of these systems also contain highly strained structures, and consequently the strain and nonadjacent chromophores interaction effects cannot be separated. One might expect the increase in strain in I over that in XVIII (bicyclo[2,2,1]heptane *vs.* bicyclo[2,2,2]octane)²⁸ to produce the increasing wavelength and intensity order, triptycene < XVIII < I. But the observed order is triptycene < I < XVIII, and therefore it is possible that in addition to interaction between the aromatic rings, there is interaction between the rings and the etheno or vinylene bridge: *e.g.*,



STERIC RELATIONSHIPS

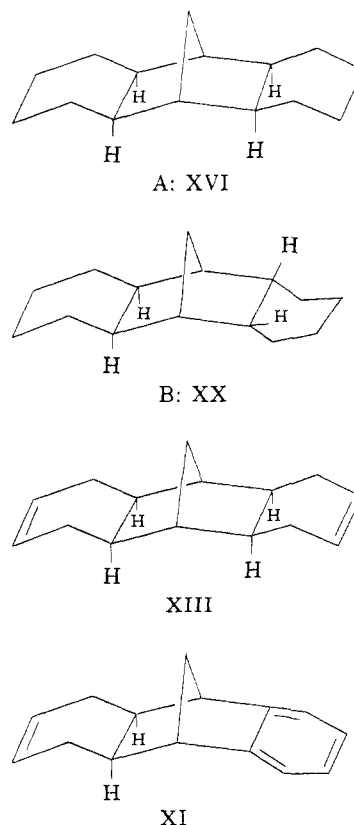
It was originally thought that the skeletal structure of I might be established by relating the perhydro derivative of XI (XX) to the perhydro compound (XVI) derived from XIII. Accordingly, a sample of XVI, m.p. 76.5–77.8° (*vide supra*), was prepared by hydrogenation of XIII (Adams' catalyst), and XI was similarly reduced to give XX, m.p. 47.3–48.3°. Obviously, isomers rather than identical substances were produced. The mode of synthesis leaves no room to doubt the structure of XX, and the arguments advanced concerning the structure of I, above, establish by implication an identical structure for XVI; thus, stereoisomers are at hand. Of the numerous possibilities all but three can be eliminated by invoking the principles of *cis* addition in the Diels-Alder reaction and of one-side hydrogenation advanced by Linstead²⁷: those remaining have exclusively *cis* ring junctions and may be represented as (A), *exo:exo*; (B), *exo:endo*; and (C), *endo:endo*, all configurations with respect to the methylene bridge. A consideration of Courtauld models²⁸ indicated clearly that spatial requirements prohibit two *endo* cyclohexane rings attached to the bicyclo[2,2,1]heptane system, and thus the existence of configuration C is rendered improbable. Consequently it is reasonable to as-

sume that the two stereoisomers XVI and XX represent the remaining configurations A and B.

If one disregards for the moment the configuration produced by the synthesis of XI (*i.e.*, III → IV, Chart I) and considers only the hydrogenation of XI to XX, there is ample precedent for preferential *exo* hydrogenation.^{29,30,31} This, then, will lead to *endo* ring junction for the new hydroaromatic ring, and XX will possess the *exo:endo* configuration, since the *endo:endo* configuration (C) has been eliminated on steric grounds.

Now if the initial Diels-Alder reaction had produced an *endo* ring junction, either the improbable *endo:endo* system would result from *exo* hydrogenation of the aromatic ring, or the hydrogenation would have had to be *endo*. The latter would be as improbable as the existence of the *endo:endo* system, since the original *endo* cyclohexane ring would effectively exclude the necessary quasiplanar contact of the aromatic ring with the catalytic surface (*cf.* ref. 27).

These arguments lead to the conclusions that the initial Diels-Alder reaction (III → IV, Chart I) must have produced an *exo* ring junction and that the reaction of XII with two molecules of butadiene must have produced two *exo* ring junctions (Chart



(26) P. D. Bartlett and F. D. Greene, *J. Am. Chem. Soc.*, **76**, 1088 (1954).

(27) R. P. Linstead, W. E. Doering, S. B. Davis, P. Levine and R. R. Whetstone, *J. Am. Chem. Soc.*, **64**, 1985 (1942).

(28) G. S. Hartley and C. Robinson, *Trans. Faraday Soc.*, **48**, 847 (1952).

(29) K. Alder and G. Stein, *Ann.*, **525**, 183 (1936).

(30) R. B. Woodward and H. Baer, *J. Am. Chem. Soc.*, **70**, 1161 (1948).

(31) K. Alder and W. Roth, *Ber.*, **87**, 161 (1954).

(32) G. Stork, E. E. van Tamelen, L. J. Friedman and A. W. Burgsthaler, *J. Am. Chem. Soc.*, **75**, 384 (1953).

II). In both Diels-Alder reactions, then, butadiene has added to a bicyclo [2,2,1]heptene (or heptadiene) system in the *exo* manner, for which there is again ample precedent.^{29,31,32} Accordingly, XIII, and therefore XVI, have the *exo:exo* configuration (A) and XI, and therefore XX, have the *exo:endo* configuration (B).

It remains to comment upon the hydrogenation of XIII as it bears upon its structure as compared with XIV. The uptake of hydrogen plotted as a function of time gives a smooth curve, no break being observed. Taken by itself this fact is only suggestive of two sterically identical double bonds; but taken in concert with the infrared spectrum of the compound, which, as stated above shows but one double bond absorption—and that in the normal rather than bicyclic double bond region—it constitutes presumptive support for the assigned structure (XIII) and the assigned configuration.

EXPERIMENTAL

All melting points are uncorrected. Infrared spectra were obtained from Nujol mulls, unless otherwise noted, by means of a Perkin-Elmer Infrared Spectrophotometer, Model 21. Microanalyses were run by Goji Kodama (K) and Anna Griffin (G) University of Michigan, Department of Chemistry and Spang Microanalytical Laboratory, Ann Arbor, Mich. (S).

5,8-Diacetoxy-1,4-dihydro-1,4-methanonaphthalene (III). To a solution of 50.0 g. (0.287 mole) of 1,4,4a,8a-tetrahydro-1,4-methanonaphthalene-5,8-dione (II)¹⁴ in 88.0 g. (0.862 mole) of acetic anhydride and 50 ml. of glacial acetic acid was added, with stirring, 4 ml. of concentrated hydrochloric acid. A slight temperature rise and darkening of the reaction mixture was noted. After standing overnight at room temperature the mixture was cooled, several ml. of water was added, and the sides of the flask were scratched to induce crystallization. White crystals were collected and washed with a small portion of water. The diluted filtrate was cooled and a second crop of white crystals was collected and washed with water. The two crops were combined and dried in a vacuum desiccator to give 47.5 g. (64%) of white crystals, m.p. 102–105°. Three recrystallizations from petroleum ether (b.p. 60–75°) yielded white crystals, m.p. 105–106°.

Anal. Calc'd for C₁₅H₁₄O₄: C, 69.75; H, 5.49. Found (K): C, 69.47; H, 5.49.

*Reductive acetylation of 1,4-dihydro-1,4-methanonaphthalene-5,8-dione.*¹⁵ To a suspension of 0.0140 g. (0.0000804 mole) of 1,4-dihydro-1,4-methanonaphthalene-5,8-dione¹⁵ in ten drops of acetic anhydride were added 0.05 g. of zinc dust and 0.02 mg. of sodium acetate and the mixture was heated to 70° for 10 min., thereby discharging the initial yellowish color.³³ One milliliter of glacial acetic acid was added and the hot solution was filtered from the zinc and zinc acetate. The filtrate was boiled and water was added to destroy the excess acetic anhydride, forming a slightly turbid mixture. After cooling the mixture in the refrigerator for an hour, 0.0030 g. (14%) of white crystals, m.p. 102.5–104.0°, was collected. A mixed m.p. with 5,8-diacetoxy-1,4-dihydro-1,4-methanonaphthalene, III, showed no depression.

1,4-Diacetoxy-5,8,8a,9,10,10a-hexahydro-9,10-methanoanthracene (IV). To 5.2 g. (0.096 mole) of butadiene condensed in a borosilicate glass combustion tube was added

2.50 g. (0.00968 mole) of III and 10 ml. of sodium dried benzene. The sealed tube was heated for 14 hr. at 205°, yielding a tan reaction mixture which was concentrated under an air jet to a tan gummy mass. The crude product was sublimed at 125° at 0.04 mm. for 4 hr., giving 2.34 g. of white crystalline material, m.p. 80–115°. The continued sublimation of the residue for 12 hr. yielded 0.40 g. of a white powder, m.p. 108–117°. The combined sublimes were crystallized from petroleum ether (b.p. 40–60°) to obtain 1.65 g. (54%) of white glistening plates, m.p. 116.5–119.0°. Several recrystallizations from petroleum ether (b.p. 40–60°) afforded white glistening plates, m.p. 119–120°.

Anal. Calc'd for C₁₉H₂₀O₄: C, 73.06; H, 6.45. Found (K): C, 72.89; H, 6.77.

5,8,8a,9,10,10a-Hexahydro-1,4-dihydroxy-9,10-methanoanthracene (V). A solution of 0.190 g. (0.000608 mole) of IV in a mixture of 25 ml. of 5% hydrochloric acid and 150 ml. of 95% ethanol was heated under reflux for 2 hr. After one half of the solvent was stripped off at water pump pressure in a nitrogen atmosphere, the reaction mixture was cooled, and 0.125 g. (90%) of white glistening plates, m.p. 213–215° d., was collected. The analytical sample, white glistening plates, m.p. 215.0–215.5° d., was obtained after two recrystallizations from benzene.

Anal. Calc'd for C₁₅H₁₆O₂: C, 78.92; H, 7.06. Found (G): C, 78.94; H, 6.86.

5,8,8a,9,10,10a-Hexahydro-9,10-methano-1,4-anthraquinone (VI). To a solution of 2.40 g. (0.0105 mole) of V in 150 ml. of absolute ether were added 5.40 g. (0.0244 mole) of freshly prepared silver oxide and 5.40 g. of anhydrous magnesium sulfate. This mixture was shaken for 45 min. and then was filtered. The filtrate was concentrated under an air jet, yielding 2.40 g. of deep yellow crystals, m.p. 119.0–123.5°. One crystallization from petroleum ether (b.p. 40–60°) gave 1.80 g. (75%) of fine yellow needles, m.p. 123–124°. The analytical sample was prepared by several recrystallizations from petroleum ether (b.p. 40–60°), yielding fine yellow needles, m.p. 125.0–125.5°.

Anal. Calc'd for C₁₅H₁₄O₂: C, 79.62; H, 6.24. Found (K): C, 79.32; H, 6.27.

5,8,8a,9,10,10a-Hexahydro-9,10-methano-1,4-anthraquinone dioxime (VII). A solution of 2.08 g. (0.00920 mole) of VI and 6.39 g. (0.00920 mole) of hydroxylamine hydrochloride in 75 ml. of ethanol was refluxed for ten hours and then was poured into 800 ml. of water. After 12 hr., a brownish precipitate was collected by filtration and dried. The dioxime, 1.95 g. (79%) of light brown powder, was obtained after two washings with benzene. The dioxime darkened at 195° and decomposed completely at 208°. The decomposition temperature was dependent on the rate of heating. Two recrystallizations from benzene yielded a light yellow powder. The melting point capillary was placed in the bath at 195° and heated at the rate of 10° per minute. The dioxime darkened at 205° and decomposed instantaneously at 211°.

Anal. Calc'd for C₁₅H₁₆N₂O₂: C, 70.29; H, 6.29; N, 10.93. Found (S): C, 70.33; H, 6.21; N, 10.77.

1,4-Diamino-5,8,8a,9,10,10a-hexahydro-9,10-methanoanthracene (VIII). To a solution of 0.200 g. (0.000760 mole) of VII in 4 ml. of ethanol was added a solution of 0.65 g. of stannous chloride dihydrate in 4.7 ml. of concentrated hydrochloric acid. The reddish reaction mixture was heated at 80° for 5 min., discharging the color. From the cooled reaction mixture, white crystalline material was collected by filtration, washed with an ethanol-hydrochloric acid mixture and with ether. A sample of the product was burned leaving a white residue; therefore, to a solution of the crystals in water was added several drops of 5% sodium hydroxide, producing a white turbid mixture. Upon cooling and scratching the sides of the flask, a white precipitate was obtained which was quickly filtered, washed with boiled water, and dried. Nearly white crystals, 0.050 g. (29%), m.p. 103–108° d. were obtained. All attempts to purify the diamine further were unsuccessful.

(33) L. F. Fieser, *Experiments in Organic Chemistry*, 2nd ed., D. C. Heath and Company, New York, N. Y., 1941, p. 399.

Anal. Calc'd for $C_{15}H_{18}N_2$: C, 79.60; H, 8.02; N, 12.38. Found (S): C, 79.29; H, 8.15; N, 12.28.

1,4-Diamino-5,6,7,8,8a,9,10,10a-octahydro-9,10-methanoanthracene dihydrochloride (X). To a suspension of 0.04 g. of platinum oxide reduced in 10 ml. of absolute ethanol was added a solution of 0.500 g. (0.00195 mole) of VII in absolute ethanol. The theoretical volume of hydrogen was absorbed in 30 min. The platinum residue was filtered off and the filtrate was dried over Drierite, treated with Norit, and filtered. The brownish filtrate was saturated with dry hydrogen chloride and then 400 ml. of sodium dried ether was added, precipitating a tan material. The mixture was cooled. The resulting precipitate was collected by filtration and was dried in a vacuum desiccator. The reduction yielded 0.561 g. (95%) of tan crystals, m.p. 288–293° d. with previous darkening. No attempts to purify diamine hydrochloride were made.

Anal. Calc'd for $C_{15}H_{22}Cl_2N_2$: C, 59.79; H, 7.36; N, 7.30. Found (G): C, 59.52; H, 7.12; N, 7.43.

1,2,3,4,4a,9,9a,10-Octahydro-9,10-methanoanthracene (XI). This compound was prepared by the deamination procedure of Bartlett and Greene.²⁶ A solution of 1.00 g. (0.00320 mole) of X in 50 ml. of 50% hypophosphorous acid was added dropwise, with stirring, to a solution of 1.375 g. of sodium nitrite in 100 ml. of 50% hypophosphorous acid cooled to below -15° . In 5 min. a frothing of the yellow reaction mixture began. The addition required 1.5 hr., and the mixture was stirred for an additional hour at -15° . The reaction mixture was placed in the cold room at -5° for 5 hr., causing the formation of an orange precipitate. After adding 100 g. of ice to the reaction mixture, it was allowed to stand in the cold room for an additional 10 hr. The reaction mixture was then extracted with several portions of ether, totaling 300 ml. The combined ethereal extracts were washed with 5% sodium hydroxide, 5% hydrochloric acid, and water. The resulting orange ethereal solution was dried over anhydrous magnesium sulfate, filtered, and the ether blown off under an air jet to give a dark red sticky oil. The crude mixture was sublimed at 0.5 mm., at 50–55° for 10 hr., yielding 0.352 g. (55%) of white crystals, m.p. 59.5–61.0°. Crystallization from methanol gave 0.281 g. (44%) of fine white needles, m.p. 60.5–61.5°.

Anal. Calc'd for $C_{15}H_{18}$: C, 90.85; H, 9.15. Found (G): C, 90.62; H, 8.88.

1,4,4a,5,8,8a,9,9a,10,10a-Decahydro-9,10-methanoanthracene (XIII). To 41.0 g. (0.760 mole) of c.p. butadiene condensed in a stainless steel bomb was added a mixture of 5.00 g. (0.0530 mole) of bicyclo[2,2,1]hepta-2,5-diene (XII)^{16,34} and a trace of hydroquinone in 50 ml. of benzene. The sealed bomb was heated for 24 hr. at 200–205°. After cooling, the light brown reaction mixture was concentrated on the steam bath under an air jet to give a yellowish brown gummy oil. The crude mixture was placed in a short path distillation apparatus and was heated at 100° under water pump pressures for one hour to remove low boiling components. The resulting gummy residue was heated between 105–120° at 0.05 mm. to give a colorless oil. The distillate was dissolved in ethanol and cooled to 0° in the refrigerator overnight. Long white plates, 1.02 g. (9.4%), m.p. 50–53°, were collected by filtration. The analytical sample, m.p. 54.0–55.5°, was prepared by two recrystallizations from ethanol.

Anal. Calc'd for $C_{15}H_{20}$: C, 89.94; H, 10.06. Found (K): C, 89.68; H, 10.10.

Molecular weight (bromination³⁵) Calc'd: 200. Found: 197.

The infrared spectrum has medium bands at 3030 cm^{-1} and 1640 cm^{-1} .

9,10-Dihydro-9,10-methanoanthracene I. The method of

Adkins, Richards and Davies¹⁹ was used to dehydrogenate XIII. To a solution of 0.500 g. (0.00200 mole) of XIII in 10 ml. of benzene in a glass lined stainless steel bomb was added 0.50 g. of 5% palladium-charcoal catalyst. The bomb was flushed with nitrogen, then put under an initial pressure of 450 p.s.i. of nitrogen, and heated at 230° for 14 hr. with shaking. The catalyst was filtered off and washed with 70 ml. benzene and 100 ml. of acetone. The solvent was stripped from the filtrate at water pump pressure at 40–50°, leaving a white oily mass. The crude product was crystallized from ethanol to yield 0.075 g. (19%) of white crystals, m.p. 151.5–153.0°. Two crystallizations from ethanol gave the analytical sample glistening white plates, m.p. 154.5–155.5°.

Anal. Calc'd for $C_{15}H_{12}$: C, 93.71; H, 6.29. Found (S): C, 93.54; H, 6.27.

Partial oxidation of 9,10-dihydro-9,10-methanoanthracene I. To a solution of 0.020 g. (0.00010 mole) of 9,10-dihydro-9,10-methanoanthracene, I, in 5 ml. of glacial acetic acid was added 0.040 g. (0.00040 mole) of chromic anhydride which was heated on a steam bath for 1 hr., giving a clear green solution. The cooled reaction mixture was poured into 25 ml. of water, forming a white precipitate which was filtered off, washed with water, and dried. The white crystals, 0.013 g., m.p. 151–153°, gave no anthraquinone vat test.³⁶ A sample crystallized from ethanol gave no m.p. depression with starting material. No attempt was made to isolate the oxidation products.

Oxidation of 9,10-dihydro-9,10-methanoanthracene I. To a solution of 0.20 g. (0.00010 mole) of 9,10-dihydro-9,10-methanoanthracene, I, in 5 ml. of glacial acetic acid was added 0.100 g. (0.00010 mole) of chromic anhydride which was heated on a steam bath for 24 hr. resulting in a clear green solution. The reaction mixture was poured into 50 ml. of water and cooled in a refrigerator for two weeks. No precipitate was formed. No attempt was made to identify the oxidation products and no anthraquinone could be detected.³⁶

Oxidation of 9,10-dihydro-9,10-ethanoanthracene (XVII). To a solution of 0.050 g. (0.00024 mole) of XVII²¹ was added 0.113 g. (0.00113 mole) of chromic anhydride in 10 ml. of glacial acetic acid; the mixture was heated for 2 hr., resulting in a clear green solution. The reaction mixture was poured into 50 ml. of water forming a white precipitate which was filtered off, washed with water, and dried. The white crystals, 0.0036 g., m.p. 138.0–140.5°, gave no anthraquinone vat test.³⁶ A sample recrystallized from ethanol gave no m.p. depression with starting material.

Perhydro-9,10-methanoanthracene (XVI). To a suspension of 0.20 g. of platinum oxide reduced in 10 ml. of glacial acetic acid was added a solution of 0.0902 g. (0.000451 mole) of XIII in 10 ml. of glacial acetic acid. The theoretical volume of hydrogen was absorbed in 15 min. and no break in the curve of hydrogen uptake *vs.* time was observed. The platinum residue was filtered off, and the filtrate was poured into 20 ml. of water to form a turbid mixture. After a week in the refrigerator, 0.0710 g. (77%) of white crystals, m.p. 75–77°, was collected by filtration and dried. Crystallization from ethanol yielded 0.0413 g. (45%) of long white needles, m.p. 76.5–77.8°.

Anal. Calc'd for $C_{15}H_{24}$: C, 88.16; H, 11.84. Found (G): C, 88.14; H, 11.77.

Perhydro-9,10-methanoanthracene (XX). To a suspension of 0.05 g. of platinum oxide reduced in 10 ml. of glacial acetic acid was added a solution of 0.100 g. (0.000505 mole) of 1,2,3,4,4a,9,9a,10-octahydro-9,10-methanoanthracene (XI) in 5 ml. of glacial acetic acid. The theoretical volume of hydrogen was absorbed in 4 hr. The platinum residue was filtered from the reduction mixture and the solvent was stripped off at 40–50° under water pump pressure, yielding 0.087 g. (84%) of white crystals, m.p. 45–48°. Crystalliza-

(34) Julius Hyman and Co., Belg. pat. 498,176, Jan. 15, 1951; *C. A.*, 49, 372 (1955).

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

(36) Ref. 33, p. 190.

tion from methanol afforded 0.55 g. (53%) of white needles, m.p. 46.8–48.0°. The analytical sample was obtained by one further recrystallization from methanol yielding white needles, m.p. 47.3–48.3°.

Anal. Calc'd for $C_{15}H_{24}$: C, 88.16; H, 11.84. Found (G): C, 88.02; H, 11.73.

ANN ARBOR, MICH.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

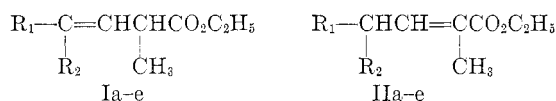
Olefinic Stability and Tautomeric Equilibria. I. Branched-Chain Unsaturated Esters¹

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The equilibria between conjugated and unconjugated isomers in two highly branched γ -alkyl unsaturated ester systems have been investigated. The proportion of unconjugated olefin has been shown to decrease with increasing branching in the γ -substituent. These results have been correlated with a number of earlier data and evidence has been presented supporting an interpretation in terms of steric interactions.

It was recently reported that the alkoxide-catalyzed isomerization of ethyl 4-ethyl-2-methyl-3-octenoate (Ib) leads to an equilibrium mixture containing approximately one third of this ester (or its glycol analog) and two thirds of the corresponding conjugated ester, ethyl 4-ethyl-2-methyl-2-octenoate (IIb).² The substitution of other n -alkyl groups for ethyl or n -butyl in the γ -position exerted little effect on the position of equilibrium in this system (Ic–IIc). However, when ethyl was replaced by methyl, the proportion of unconjugated isomer (Ia) in the equilibrated mixture with IIa was reported to be 56%.

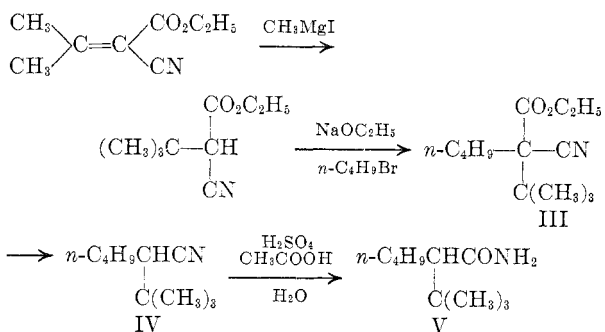


Ia, IIa: $R_1 = n-C_{10}H_{21}$, $R_2 = CH_3$
 Ib, IIb: $R_1 = n-C_4H_9$, $R_2 = C_2H_5$
 Ic, IIc: $R_1 = n-C_7H_{15}$, $R_2 = n-C_7H_{15}$
 Id, IIc: $R_1 = n-C_4H_9$, $R_2 = iso-C_3H_7$
 Ie, IIe: $R_1 = n-C_4H_9$, $R_2 = tert-C_4H_9$

Enhanced hyperconjugative stabilization of the β, γ -double bond by the methyl group and reduced strain of the *cis*-type about the β, γ -double bond were considered as alternative explanations of the higher proportion of unconjugated isomer found in the equilibrated γ -methyl compounds. To examine these alternatives in systems containing more highly branched substituents, the corresponding esters with γ -isopropyl and γ -*tert*-butyl substituents (Id–IIc and Ie–IIe, respectively) have been synthesized and the equilibrium mixtures of the two isomers determined after isomerization.³

SYNTHESIS

Unsaturated esters required for these studies were prepared by dehydration of the β -hydroxy esters (VIIIa, VIIIb) formed in the Reformatsky reaction of the corresponding α -alkyl aldehydes (VIIa, VIIb) with ethyl α -bromopropionate. The aldehydes were obtained by Rosenmund reduction of the corresponding acid chlorides. Branched acids were prepared *via* modifications of the malonic ester synthesis. Thus, the synthesis of 2-*tert*-butylhexanoic acid (VIb) *via* ethyl isopropylideneacyanoacetate, ethyl *tert*-butylcyanoacetate and the dialkylcyanoacetate (III) is shown in the series of equations below. The corresponding 2-isopropylhexanoic acid (VIa) was prepared by a reaction sequence which is not shown, but which involved successive alkylations of malonic ester with isopropyl bromide and n -butyl bromide, followed by alkaline hydrolysis, acidification and decarboxylation.



(3) The α -methyl substituent has been retained both as a point of reference throughout the series and to prevent thermal equilibration of the two isomers during distillation of the isomerized mixtures. Such equilibration is known to occur in the absence of an α -alkyl group [J. Cason, N. L. Allinger, and C. F. Allen, *J. Org. Chem.*, **18**, 857 (1953)]. The α, γ -dialkyl system is further convenient in that no addition of alkoxide to the double bond has been found to occur for these compounds [*cf.* R. P. Linstead and E. G. Noble, *J. Chem. Soc.*, 610 (1934); R. P. Linstead, *J. Chem. Soc.*, 2498 (1929)].

(1) Presented in part at the 130th National Meeting of the AMERICAN CHEMICAL SOCIETY, Atlantic City, Sept. 16–21, 1956.

(2) J. Cason and K. L. Rinehart, Jr., *J. Org. Chem.*, **20**, 1591 (1955).