orange-red 2,4-dinitrophenylhydrazone of 2,8-diketo-4a-methyl - 1,2,3,4,4a,5,6,7,8,9,10,10a - dodecahydrophenanthrene (XIII), m.p. 228–230°; $\lambda_{max}^{CHCl_3}$ 2590 Å. (ϵ 27400); $\lambda_{max}^{CHCl_3}$ 3710 Å. (ϵ 48000).

Anal. Calcd. for $C_{27}H_{28}N_8O_8$: C, 54.72; H, 4.76; N, 18.91; CH_3O–, 0. Found: C, 55.26; H, 5.21; N, 17.80; CH_3O–, 0.3.

RAHWAY, N. J.

[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY, THE OHIO STATE UNIVERSITY]

The Synthesis and Resolution of Hexahelicene[1]

BY MELVIN S. NEWMAN AND DANIEL LEDNICER[2]

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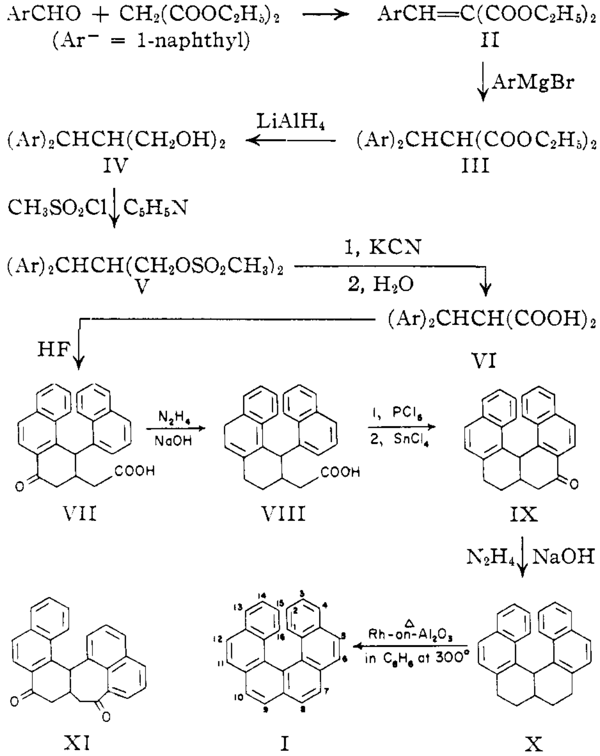
The synthesis and resolution of hexahelicene (I) is described.

In continuation of work on the synthesis and resolution of compounds which owe their asymmetry to intramolecular overcrowding[3] we report the synthesis and resolution of hexahelicene (I).[4] This compound represents the first example of a purely aromatic hydrocarbon which owes its asymmetry to intramolecular overcrowding. The preferred synthesis is outlined in the chart.



The condensation of 1-naphthaldehyde with ethyl malonate afforded II in 70% yield. The yields of III by addition of the Grignard reagent from 1-bromonaphthalene to II varied unpredictably between 35 and 56%. Reduction of III afforded pure IV in 90% yield. Conversion of the latter to VI was carried out in high over-all yield without purification of V or the corresponding dinitrile. Interestingly, the hydrolysis of the dinitrile by sulfuric in acetic acid was incomplete even after prolonged refluxing. However, alkaline hydrolysis for one hour in ethylene glycol at reflux afforded the acid VI in high yield. Cyclization of VI to VII by anhydrous hydrogen fluoride proceeded in 65–70% yield, the remaining product being a neutral glass. When pure VII was dissolved in hydrogen fluoride it could be quantitatively recovered. The only fair yield obtained in this type of cyclization which ordinarily proceeds in high yield foreshadowed the increasing difficulties which were to be met in the synthesis because of the increasing steric strains gradually being introduced into the molecule.

The ketoacid VII was reduced to VIII in 87% yield by the Huang-Minlon procedure. We have found in this case, as well as in several others, that the long periods of heating often recommended[5] are not necessary. After the water is distilled and the temperature begins to rise rapidly, if the apparatus is connected to an azotometer, it is seen that the gas evolution, usually nearly theoretical, is complete in 15–30 minutes. Further heating after this point is useless or harmful.

The cyclization of the reduced acid VIII proved difficult. The ring closure of the acid chloride of VIII to IX in 55% yield was finally accomplished by heating at 90° for one hour with stannic chloride in *o*-dichlorobenzene. When one contrasts this with the rapid cyclization of substituted γ-phenylbutyryl chlorides using stannic chloride[6] (2–12 minutes at about 5°) the great resistance toward formation of the hydrohexahelicene ring system is illustrated.

The conversion of IX to hexahelicene (I) was effected by several different routes, the best of which comprised reduction to the hexahydro derivative X followed by hydrogen transfer to benzene[7] over 5% rhodium-on-alumina[8] at 300°. The

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[1] A systematic name is phenanthro[3,4-c]phenanthrene. However, a proposal to create the systematic name *helicene* for nuclei of the continuously coiled type is at present being considered by American and International nomenclature committees. The prefixes, penta, hexa and hepta, etc., would be used for five, six and seven, etc., ring compounds. The numbering preferred by the authors is shown on I.

[2] Holder of National Science Foundation Predoctoral Fellowships during the years 1952–1955. The material herein presented is taken from the Ph.D. thesis, O.S.U., 1955.

[3] For a review of recent accomplishments in this field see M. S. Newman and R. M. Wise, THIS JOURNAL, **78**, 450 (1956).

[4] For a preliminary communication see M. S. Newman, W. B. Lutz and D. Lednicer, *ibid.*, **77**, 3420 (1955).

[5] D. Todd, "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1948, Vol. IV, p. 385.

[6] M. S. Newman, H. V. Anderson and K. H. Takemura, THIS JOURNAL, **75**, 347 (1953).

[7] Compare H. Adkins, L. M. Richards and J. W. Davis, *ibid.*, **63**, 1320 (1941).

[8] Catalyst supplied by the Baker Company, Philadelphia, Pa.

ultraviolet absorption spectra of hexahelicene, dibenzo[c,g]phenanthrene and phenanthrene are shown in Fig. 1. The hydrogen transfer over a palladium catalyst[7] went in poor yield. The difficulty of dehydrogenation to the aromatic I was further illustrated by the fact that when X was refluxed for nine hours with 2,3-dicyano-4,5-dichloroquinone[9] (DDQ) in refluxing xylene a dihydrohexahelicene, XIV, was formed which was inert to further similar treatment under the same conditions. On the other hand tetralin is converted to naphthalene almost quantitatively by the same quinone in two hours in boiling benzene.[9] Similarly, tetrahydrohexahelicene (XIII), prepared by dehydration of the carbinol XII prepared by reduction of IX, was converted only to XIV by treatment with excess DDQ in refluxing xylene for 24 hours. The dihydro compound XIV could be converted to I by heating with sulfur at 255°. Compound I could also be made by hydrogen transfer from XIII, but to no advantage since the yield of XIII and IX was not good.

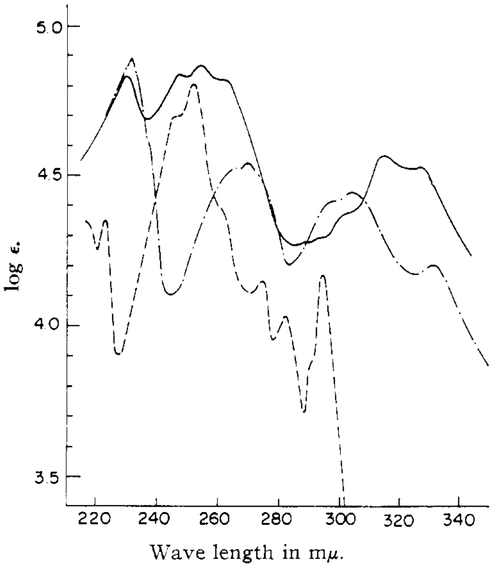
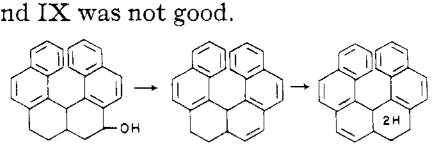


Fig. 1.—Ultraviolet absorption spectra: ———, hexahelicene; ·—·—, dibenzo[c,g]phenanthrene from E. D. Bergmann and J. S. Szmuszkovicz, THIS JOURNAL, 73, 5153 (1951); ----, phenanthrene, from R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951, structure 341.



XII XIII XIV

The position of the hydrogen atoms in XIV is uncertain. If they were in positions 8a and 16c, the absorption spectrum of XIV would be expected to resemble that of XIII. However, the curves shown in Fig. 2 show little resemblance. If the hydrogens were at positions 7 and 8, it is difficult to see why they would not be removed in the vigorous treatment with DDQ. If the hydrogens were *trans* and at positions 8a and 16c, the failure to be removed by DDQ would be understandable in terms of the mechanisms proposed for dehydrogenation[10] by DDQ. Possibly the hydrogens in XIV are not adjacent.

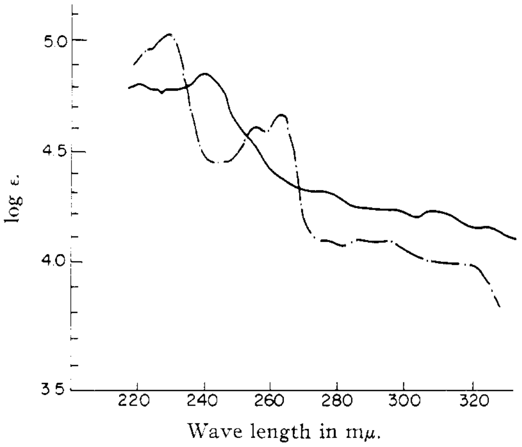
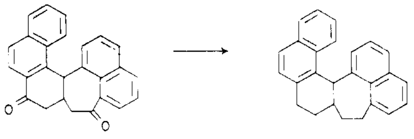


Fig. 2.—Ultraviolet absorption spectra: ———, (?) dihydrohexahelicene (XIV); ·—·—, 7,8,8a,16c-tetrahydrohexahelicene (XIII).

At first glance the great resistance of XIV to dehydrogenation by all reagents tried might seem surprising. However, it should be borne in mind that the increase in resonance energy which might be expected to result from the conversion of dihydrohexahelicene (XIV), to I probably does not take place. Because of the non-planar structure of I (see below) the resonance energy in XIV may be almost the same as that in I. In addition, the gain in resonance energy in going from XIV to I may be offset by increased internal strain in I as compared to XIV.

When the acid chloride of VII was cyclized with aluminum chloride in *sym*-tetrachloroethane at 90–95° for 90 minutes, a diketone presumably of structure XV was obtained. On reduction the hexahydro compound XVI was produced which proved different from X.



XV XVI

Since we were unable to obtain an aromatic hydrocarbon comparable to I from XVI,[11] XV or the glycol XVII, corresponding to XV, we believe that XV has the structure shown. If XVI were a stereoisomer of X, it should have been possible to obtain I from XVI. Furthermore, since both XVI and X

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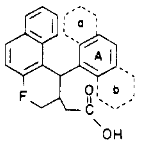
[9] E. A. Braude, A. G. Brook and R. P. Linstead, *J. Chem. Soc.*, 3569 (1954).

[10] E. A. Braude, L. M. Jackman and R. P. Linstead, *ibid.*, 3548 (1954).

[11] L. F. Fieser, THIS JOURNAL, **55**, 4963 (1932), was unable to prepare a fully aromatic pleiadene from a dihydropleiadene by heating with sulfur. Similarly P. D. Gardner and W. J. Horton, *ibid.*, **74**, 657 (1952), were unable to effect the transformation by a variety of methods. V. Boekelheide and G. K. Vick, *ibid.*, **78**, 653 (1956), have recently prepared the bright red fully aromatic pleiadene by means of a double Hoffman degradation.

arise from VII, they must have the same stereochemistry unless isomerism occurred during the reactions of VII, a possibility that is unlikely.[12]

Normally, γ-1-naphthylbutyric acids cyclize to give ketotetrahydrophenanthrene derivatives.[13] In the formation of VII from VI an example of such a ring closure is seen. However, the cyclization of VII to XV exemplifies closure at the *peri* position. On the other hand, cyclization of VIII occurs normally to yield IX. An explanation for this interesting contrast may best be obtained from a study of molecular models. Consider the generalized structure XVII.



XVII

When F represents the ketone function C=O the left hand portion of the molecule is more rigid than when F is the methylene function CH_2. This increased rigidity aided by carbonyl conjugation with the ring makes the transition state for ring closure at the *peri* position (naphthalene ring in position A-b), easier to attain than the transition state for ring closure at the 2-position (naphthalene ring in position A-a) because in the latter position the a-ring interferes with the other naphthalene ring in the molecule. When F represents the methylene function, the molecule is less rigid and the normal tendency toward ring closure in the 2-position (naphthalene ring in position A-a) prevails (compound IX formed).

The resolution[4] of hexahelicene (I) was accomplished with the aid of 2-(2,4,5,7-tetranitro-9-fluorenylideneaminoöxy)-propionic acid, TAPA,[14] by a method which appears never to have been observed before. When a solution of I and (−)-TAPA, each pale yellow, in benzene was concentrated a deep red color was produced from which solid or liquid complexes (see Experimental) were difficult to separate. However, judicious addition of ethanol caused active I to crystallize. Conventional recrystallization then afforded (−)-I,[15] $[\alpha]^{24}\mathrm{D}$ −3640°, $[\alpha]^{24}_{546}$ −4820°. By using (+)-TAPA the (+)-I compound was obtained, $[\alpha]^{25}\mathrm{D}$ 3707°. The method of resolution is new because it represents the separation of a compound in active form from an optically inactive solvent. The phenomenon is possible because the complexing agent, (−)-TAPA, must form complexes of different stability with (+)- and (−)-I. Racemic I melts at 230° whereas (−)-I melts at 266°. After remelting, the sample of (−)-I melted at 234–250°, which indicates that partial racemization occurred during the melting point determination. It is obvious, therefore, that the optical stability of I is similar to that of 1,12-dimethylbenzo[c]phenanthrene-5-acetic acid.[3] We hope to study the racemization of this and related compounds in more detail.

A sample of hexahelicene (I) was sent to Prof. H. S. Gutowsky, University of Illinois, who is interested in nuclear magnetic resonance phenomena. He reports the following concerning I.

> "The proton magnetic resonance of hexahelicene was observed (L. H. Meyer, A. Saika and H. S. Gutowsky, THIS JOURNAL, **75**, 4567 (1953)) in chloroform and in carbon tetrachloride solutions. The spectrum consisted of two main components, with relative integrated intensities of 3:2, located at δ-values of +0.325 and +0.391, respectively. The weaker of these components was broader and appeared to contain two sub-components of unequal intensity. On the basis of intensities, as well as by their chemical shifts, the main component at +0.325 can be assigned to the 10 peripheral protons (4–13, incl.) and the weaker double line at +0.391 to the 6 terminal protons at the 'split' in the polycyclic ring (1, 2, 15, 16 and 3, 14). The chemical shift in the resonance of the peripheral protons from the resonance of the terminal protons is comparable to that found (H. J. Bernstein and W. G. Schneider, *J. Chem. Phys.*, **24**, 468 (1956)) in compounds such as phenanthrene. There do not appear to be any sizable effects due to the 'helical type' overlap of the rings."

Experimental

Diethyl 1-Naphthylmethylenemalonate (II).—In the best run, a solution of 500 g. (3.21 moles) of 1-naphthaldehyde,[16] 610 g. of diethyl malonate (3.81 moles) and 500 ml. of dry benzene was brought to a reflux. A solution of 35 g. of benzoic acid and 41.5 g. of piperidine in 50 ml. of benzene was added in portions over a period of 5 hours, at which time 60 ml. (103%) of the theoretical water had been collected. Distillation of the crude product isolated in the usual way[17] afforded 811 g. of a fraction b.p. 180–200° at 2.5 mm. This was redistilled to yield 752 g. (70%) of I as an extremely viscous light yellow oil, b.p. 203–205° at 2 mm. The middle cut of a redistilled sample from a previous run constituted the analytical sample.

Anal. Calcd. for $C_{18}H_{18}O_4$: C, 72.4; H, 6.1. Found[18]: C, 73.2, 73.6; H, 5.9, 6.0.

Diethyl Di-1-naphthylmethylmalonate (III).—A solution of 310 g. (1.03 moles) of II in 300 ml. of benzene was added to an initially ice-cold solution of one mole (by titration) of 1-naphthylmagnesium bromide in 600 ml. of tetrahydrofuran and 400 ml. of benzene at such a rate that a gentle reflux ensued (45 minutes). One hour after the addition was complete the Grignard complex was decomposed with water followed by 50% hydrochloric acid and the mixture worked up in the usual manner.

Treatment of the residual amber oil with 50 ml. of ether and enough low boiling petroleum ether to yield a just homogeneous solution produced on standing a crystalline mass. This was drained of solvent and oil by filtration and recrystallized from ethanol to yield 238.2 g. (55.8%) of the ester

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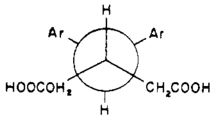
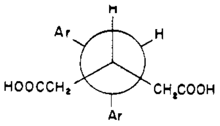
[12] The stereochemistry of X and XV is determined in the ring closure of VI to VII. The ring fusion is assumed to be *trans* since the product should be derived from rotamer VIa which is less strained than rotamer VIb.



VIa (to *trans* VII)



VIb (to *cis* VII)

[13] A. L. Green and D. H. Hey, *J. Chem. Soc.*, 4307 (1954); R. P. Linstead, *Ann. Repts. on Progr. Chem.* (*Chem. Soc. London*), **33**, 336 (1936); H. D. Springall, *ibid.*, **36**, 301 (1939).

[14] M. S. Newman and W. B. Lutz, THIS JOURNAL, **78**, 2469 (1956).

[15] The optical rotation of this compound was calculated to be 3000° by D. D. Fitts and J. G. Kirkwood, *ibid.*, **77**, 4940 (1955).

[16] Eastman Kodak Co. White Label Grade, used as obtained.

[17] Ether–benzene was added to the total mixture and the organic layer washed with 10% hydrochloric acid, water, 10% aqueous sodium bicarbonate and saturated sodium chloride. The solution was then filtered through anhydrous sodium sulfate and the solvent taken off under reduced pressure.

[18] Carbon, hydrogen analyses were performed by the Galbraith Laboratories, Knoxville, Tenn., unless otherwise stated.

III, m.p. 109–113°.[19] Further recrystallization (ethanol) yielded a sample, m.p. 113.4–114.2° (cor.).

In several other attempts in which the usual variables were varied smaller yields (32–49%) were obtained. The addition of an extra mole of magnesium bromide to II or the use of di-1-naphthylmagnesium (free of halide) gave smaller yields (in the latter case no product was obtained).[20]

Anal. Calcd. for $C_{23}H_{26}O_4$: C, 78.8; H, 6.2. Found: C, 78.8; H, 6.4.

2,2-Di-1-naphthyl-1,3-propanediol (IV).—A solution of 10 g. of III in 50 ml. of benzene and 150 ml. of dry ether was slowly added to a well stirred suspension of 2.34 g. of lithium aluminum hydride in dry ether. The reaction mixture was stirred for one hour after addition was complete, the excess reagent destroyed with 50 ml. of water and the complex broken up by the addition of 50 ml. of 50% sulfuric acid. The reaction mixture was treated in the usual manner, though enough benzene was left behind to bring the final volume to 80 ml. The mass of fibrous crystals of the diol which separated on cooling was removed by filtration and dried to afford 7.6 g. (93%) of IV which softens to a clear gum at about 75° without sharp melting. An analytical sample was prepared by three recrystallizations from benzene followed by heating at 150° under high vacuum.

Anal. Calcd. for $C_{24}H_{22}O_2$: C, 83.2; H, 6.4. Found: C, 83.2; H, 6.5.

The bis-*p*-nitrobenzoate, prepared by heating 0.5 g. of the diol with an equal weight of *p*-nitrobenzoyl chloride in 1.5 ml. of pyridine, was recrystallized from benzene–ethanol to yield rod-like yellow crystals, m.p. 178.0–178.8° cor.

Anal. Calcd. for $C_{38}H_{22}O_8N_2$: C, 71.2; H, 4.4. Found: C, 71.3; H, 4.5.

3-[Di-(1-naphthyl)-methyl]-glutaric Acid (VI).—Methanesulfonyl chloride (7.6 g.) was added to an ice-cooled solution of 7.6 g. of IV in 75 ml. of pyridine. After one hour the reaction mixture, from which a mass of crystals of pyridine hydrochloride had separated, was poured into water to yield 16.6 g. (86%) of the solid mesyl ester, m.p. 145–150°.

This crude product was dissolved in 100 ml. of dimethylformamide (DMF) and the solution added to 7.6 g. of potassium cyanide and 0.2 g. of potassium iodide in 50 ml. of water. After heating for two hours at 85–90°, the reaction mixture was diluted to 400 ml. with water and worked up in the usual manner to afford the nitrile as a brown tar.

This tar was then refluxed for 1 hour with 10% sodium hydroxide in ethylene glycol. Ammonia was evolved copiously and a crystalline mass of the sodium salt separated, was collected by filtration and dissolved in water. The acid obtained on acidification was recrystallized from ethanol to yield 5.06 g. (54.9% from IV) of colorless needles, m.p. 217–221°. Three recrystallizations from aqueous ethanol afforded the analytical sample of VI, m.p. 224.2–225.0° cor.

Anal. Calcd. for $C_{26}H_{22}O_4$: C, 78.4; H, 5.6; neut. equiv., 199. Found: C, 78.2; H, 5.7; neut. equiv., 203.

This glutaric acid was also formed in poor yield by the bis-homologation of the malonic acid corresponding to III. The procedure was similar to that described for a similar bis-homologation.[3]

1,2,3,4-Tetrahydro-4-(1-naphthyl)-1-oxo-3-phenanthreneacetic Acid (VI).—To 30 g. of VI was added 120 ml. of liquid hydrogen fluoride. When all the liquid had evaporated the residue was washed with water and shaken with 3% aqueous potassium hydroxide and ether–benzene. The alkaline solution was acidified and the precipitate extracted with ether–benzene. Removal of the solvent yielded 19.1 g. (67%) of VII as granular crystals, m.p. 254–260°. A sample was recrystallized from aqueous ethanol to a constant m.p. of 263–267°.

Anal. Calcd. for $C_{26}H_{20}O_3$: C, 82.1; H, 5.6; neut. equiv., 380. Found: C, 81.5, 81.5; H, 5.6, 5.7; neut. equiv., 387.

1,2,3,4-Tetrahydro-4-(1-naphthyl)-3-phenanthreneacetic Acid (VIII).—A solution of 19.1 g. (0.051 mole) of the acid VII in 48 ml. of hydrazine hydrate, 9.6 g. of potassium hydroxide and 200 ml. of diethylene glycol was brought to reflux. At the end of one hour sufficient water was removed by distillation to bring the temperature of the solution to 210°. The evolution of nitrogen started immediately, and at the end of one hour the theoretical volume (1.14 l.) had been collected. The resulting solution was then allowed to cool, poured onto ice-water and extracted well with ether. The precipitate produced by acidification of the alkaline solution was taken up in ether. When the ethereal solution was evaporated to dryness 15.8 g. (87%) of the pentacyclic acid VIII was obtained as colorless granular crystals, m.p. 236–240°.

A portion of this was recrystallized from ethanol to a constant m.p. of 237.0–238.0° cor. On analysis carbon was low in several samples.

Anal. Calcd. for $C_{26}H_{22}O_2$: C, 85.2; H. 6.1; neut. equiv., 366. Found: C, 84.2, 84.2; H, 6.2, 6.1; neut. equiv., 352.

7,8,8a,9,10,16c-Hexahydro-7-oxohexahelicene (IX).—A suspension of 3.80 g. of VIII and 2.20 g. of phosphorus pentachloride in 40 ml. of purified *o*-dichlorobenzene was warmed on a steam-bath for one hour. After cooling in ice and adding 3.40 g. of stannic chloride to the yellow solution, the reaction mixture was warmed for one hour on a steam-bath. The now dark green solution was poured onto ice and dilute hydrochloric acid. The reaction mixture was worked up in the usual manner.

Acidification of the alkaline washes yielded 0.30 g. of crude starting acid, m.p. 195–230°. The neutral extracts, after steam distillation, yielded a solid which on recrystallization from benzene–ethanol afforded 3.56 g. (56% based on acid consumed) of the ketone IX as yellow flakes, m.p. 219–221°. Colorless flaky crystals, m.p. 221.4–221.8° cor., were obtained by repeated recrystallization.

Anal. Calcd. for $C_{26}H_{20}O$: C, 89.6; H, 5.8. Found: C, 89.4; H, 6.0.

7,8,9,10,16c-Hexahydro-7-hydroxyhexahelicene (XII) was prepared by adding a solution of 1.5 g. of IX in 50 ml. of benzene and 25 ml. of ether to a well-stirred suspension of 0.20 g. of lithium aluminum hydride in 15 ml. of ether over 5 minutes. After refluxing for one-half hour, the reaction mixture was treated with 15 ml. of water and 30 ml. of 10% hydrochloric acid. The resulting two phased mixture was worked up in the usual manner and the extracts concentrated to a volume of 15 ml. The heavy white fibrous mass which came out of solution on cooling was separated by filtration to yield 1.25 g. (83%) of XII, m.p. 210–215°. A portion of this was recrystallized to a constant m.p. of 213–215° from benzene.

Anal. Calcd. for $C_{26}H_{22}O$: C, 89.1; H, 6.3. Found: C, 89.2; H, 6.3.

7,8,8a,16c-Tetrahydrohexahelicene (XIII).—The alcohol XII (0.20 g.) in the presence of a small amount of iodine was placed in a sublimation apparatus; when this was immersed in a salt-bath at 210° melting accompanied by evolution of water was noted. The temperature was then slowly raised to 240° (5 minutes) under a pressure of 0.1 mm. The light yellow oil which distilled onto the cold finger crystallized (m.p. 175–185°) on cooling. One recrystallization from benzene–ethanol afforded XIII (0.15 g., 79%) as colorless needles, m.p. 192.5–195°. The analytical sample m.p. 191.8–192.4° cor. was obtained by repeated recrystallization from benzene–ethanol.

Anal. Calcd. for $C_{26}H_{20}$: C, 93.9; H, 6.1. Found: C, 93.9; H, 6.1.

The yield was appreciably lower when this reaction was run with more than 0.40 g. of XII.

7,8,8a,9,10,16c-Hexahydrohexahelicene (X).—A suspension of 5.0 g. of the monoketone IX and 2.5 g. of potassium hydroxide in 12.5 ml. of hydrazine hydrate and 50 ml. of diethylene glycol was maintained at reflux for one hour. The temperature of the reaction was then brought to 210° by distilling water. The evolution of nitrogen which commenced at 200° was complete (310 ml.) after 40 minutes. The hot solution was poured onto ice-water and worked up in the usual manner to yield a crystalline solid, m.p. 150–158°, sintering at 100°, which was recrystallized from benzene–ethanol to yield 4.26 g. (88.7%) of slightly yellow flakes of X, m.p. 162–165°. A portion of this was recrystallized (benzene–ethanol) to a constant m.p. of 168.0–168.6° cor.

Anal. Calcd. for $C_{26}H_{22}$: C, 93.4; H, 6.6. Found: C, 93.5; H, 6.5.

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(19) All melting points are uncorrected unless otherwise specified.

(20) Mr. H. R. Flanagan performed these experiments.

Dihydrohexahelicene (XIV). (a) **From XIII.**—A solution of 100 mg. (0.3 mmole) of XIII and 140 mg. (0.61 mmole) of DDQ[10] in 5 ml. of xylene was heated at reflux for 24 hours. Once cool, the brown solution was decanted from the solid which had come out of solution, and the latter washed with benzene. The combined mother liquor and washes were passed through an alumina column and, on evaporation, left behind a crystalline solid, m.p. 165–185°. One recrystallization of this from benzene–ethanol afforded 80 mg. (80%) of yellowish needle-like plates, m.p. 186–188°; mixed m.p. with XIII, 168–180°.

Further recrystallization from the same solvent afforded a sample of XIV, m.p. 185.0–185.5° cor.

Anal. Calcd. for $C_{26}H_{18}$: C, 94.5; H, 5.5. Found: C, 94.4; H, 5.6.

(b) **From X.**—A solution of 200 mg. (0.6 mmole) of X and 0.41 g. of DDQ[10] in 10 ml. of xylene was refluxed for 9 hours. The reaction mixture was worked up in the same manner as above to yield 0.14 g. (70%) of XIV m.p. 182–186°. A mixed m.p. of this with pure XIV (m.p. 186–188°) was 180–184°. The infrared spectra were almost identical.

Helihexacene (I). (a) **From the Tetrahydro Compound XIII.**—(1) An intimate mixture of 96 mg. of the olefin and 30 mg. of sulfur was heated at 250–260°. When the rate of evolution of hydrogen sulfide began to subside (20 minutes) a few granules of zinc were added to the melt, and after an additional five minutes, the system was evacuated. The glassy yellow solid which distilled onto the cold finger was chromatographed on an alumina column. The solid obtained from the fraction which on the column showed a bluish-purple fluorescence was recrystallized from benzene–ethanol to a constant m.p. of 231–233°.

Anal. Calcd. for $C_{26}H_{16}$: C, 95.1; H, 4.9. Found[21]: C, 95.3, 95.4; H, 5.1, 5.1.

(b) Following the procedure of Adkins,[22] a solution of 0.2 g. of XIII in 4 ml. of thiophene-free benzene was treated for 11 hours (with rocking) at 300° in the presence of 10% palladium-on-charcoal in a bomb first flushed with nitrogen. The catalyst was removed by filtration and the solution evaporated to dryness to leave behind a yellow solid, m.p. 115–200°. One pass through an alumina column, followed by four recrystallizations from benzene–ethanol, afforded a small amount of some yellowish crystals, m.p. 217–227°. This was judged by its ultraviolet spectrum to be impure I.

(2) A solution of 1.16 g. of the tetrahydro compound XIII in 16 ml. of thiophene-free benzene and 0.58 g. of 5% rhodium-on-alumina were placed in a hydrogenation bomb. The system was flushed with nitrogen and then heated at 300° (rocking) for ten hours. The catalyst was removed by filtration and washed with chloroform. The filtrates were boiled down to a volume of 10 ml. and ethanol added so that the hydrocarbon was just soluble. On cooling compound I was obtained (0.83 g., 73%) as pale yellow hexagonal plates m.p. 223–228°. A sample of this was recrystallized from benzene–ethanol to a constant m.p. of 230.4–230.9° cor.

Anal. Calcd. for $C_{26}H_{16}$: C, 95.1; H, 4.9. Found: C, 95.3, 94.9; H, 5.1, 4.8.

The ultraviolet spectrum of this product was identical to that of the hydrocarbon produced by dehydrogenation with sulfur.

(b) **From the Dihydro Compound XIV.**—A melt of 80 mg. of XIV and 30 mg. of sulfur was heated for 20 minutes at 255°. A few granules of zinc were added. Vacuum sublimation afforded 53 mg. of I, m.p. 222–231°.

(c) **From the Hexahydro Compound X.**—A solution of 4.26 g. (0.013 mole) of the hydroaromatic compound X in 45 ml. of benzene, in the presence of 2.13 g. of 5% rhodium-on-alumina was treated as in 3 above for 10 hours. In a similar work-up there was isolated 2.70 g. of I, m.p. 231.0–232.5°; mixed m.p. with pure I, 231–232.5°.

The 2,4,5,7-tetranitrofluorenone derivative of I was prepared by dissolving 0.12 g. of the hydrocarbon and 0.10 g. of the nitro compound in 2 ml. of boiling acetic acid. The short black needles which came out on cooling were recrystallized (acetic acid) to a constant m.p. of 229.4–230.4° cor.

Anal. Calcd. for $C_{39}H_{20}N_4O_9$: C, 68.0; H, 3.0. Found: C, 67.9; H, 3.2.

Resolution of I.—One-half equivalent,[23] 1.47 g., of (−)-TAPA,[24] $[\alpha]^{24}\text{D}$ −95.3° (*c* 0.57, dioxane), was added to a solution of 2.27 g. of I in 18 ml. of boiling benzene. The hydrocarbon was obtained on cooling as the characteristic yellow plates after 20 ml. of ethanol was added to the burgundy colored solution. Three repetitions of this treatment followed by percolation of a benzene solution through a short alumina column, afforded 0.49 g. of partially resolved I, $[\alpha]^{27}\text{D}$ −123° (*c* 0.56, chloroform). Eight recrystallizations of this sample yielded 11.9 mg. of the hydrocarbon, m.p. 263.5–267°, $[\alpha]^{22}\text{D}$ −3570° (*c* 0.24, chloroform). This was recrystallized once again from benzene–ethanol to yield 4.92 mg. of I, m.p. 265–267°, remelting 234–250°: $[\alpha]^{24}\text{D}$ −3640 ± 10°, $[\alpha]^{24}_{546}$ −4820 ± 15° (*c* 0.098, chloroform). Alternately 0.72 g. of I and 2.5 g. of (+)-TAPA were dissolved in 20 ml. of hot benzene. Judicious additions of alcohol and concentration by allowing slow evaporation of solvent from an open Erlenmeyer flask covered with a 250-ml. inverted beaker afforded 0.18 g. of I. This was redissolved in benzene containing 0.5 g. of (+)-TAPA and, after careful slow concentration and alcohol addition as above a few large well developed crystals (15 mg.) separated. Recrystallization afforded 4.1 mg. of (+)-I, $[\alpha]^{25}\text{D}$ 3707 ± 12° (4.1 mg. in 5 ml. of chloroform, 2-dm. tube).

7,8,8a,9,10,16b-Hexahydro-7,10-dioxonaphtho-[1′,8′,3,-4,5]cyclohepta[1,2-*c*]phenanthrene (XV).—A suspension of the keto acid VII (1.0 g. 0.0026 mole) was warmed with 20 ml. of thionyl chloride on a steam-bath until a homogeneous solution was obtained. A yellowish-green crystalline solid remained when the excess reagent was evaporated under reduced pressure. This was dissolved in 10 ml. of *sym*-tetrachloroethane and 0.80 g. (0.006 mole) of aluminum chloride added to the ice-cooled solution. After heating for one-half hour on a steam-bath the dark green solution was cooled, treated with dilute hydrochloric acid and the solvent removed by steam distillation. The residual solid was recrystallized from ethanol to yield 0.57 g. (58%) of the diketone as yellowish granular crystals, m.p. 211–214° The same product was obtained when *o*-dichlorobenzene was used as the solvent. A sample was recrystallized from aqueous ethanol to a constant m.p. of 213.8–215.0° cor.

Anal. Calcd. for $C_{26}H_{18}O_2$: C, 86.2; H, 5.0. Found: C, 86.4; H, 5.0.

7,8,8a,9,10,16b-Hexahydro-7,10-dihydroxynaphtho[1′,8′,-3,4,5]cyclohepta-[1,2-*c*]phenanthrene (XVII).—A solution of 1.0 g. of the diketone in 20 ml. of ether and 30 ml. of benzene was added to a vigorously stirred suspension of 0.24 g. of lithium aluminum hydride in 5 ml. of ether. The reaction mixture was heated at reflux for one-half hour, and after cooling treated with 10 ml. of water, followed by 50 ml. of cold 20% hydrochloric acid. The usual work-up afforded the diol (0.84 g., 83%) as yellow granules, m.p. 185–194° dec. The analytical sample was recrystallized thrice from aqueous ethanol.

Anal. Calcd. for $C_{26}H_{22}O_2$: C, 85.2; H, 6.1. Found: C, 84.3, 84.4; H, 6.1, 6.3.

The diacetate of XVII was prepared by briefly heating 0.20 g. of the diol with 2 ml. each of pyridine and acetic anhydride. The white solid (0.90 g.), obtained on adding the reaction solution to ice-water, was recrystallized from benzene–ethanol to a constant m.p. of 254.5–255.5° dec.

Anal. Calcd. for $C_{30}H_{26}O_4$: C, 80.0; H, 5.8. Found: C, 80.1; H, 5.9.

7,7,8a,9,10,16c-Hexahydronaphtho[1′,8′,3,4,5]cyclohepta[1,2-*c*]phenanthrene (XVI).—A mixture of 1.0 g. of the diketone, 1 g. of potassium hydroxide and 5 ml. of hydrazine hydrate in 20 ml. of diethylene glycol was heated at reflux for 15 minutes. The temperature was brought up to 210° by distilling off water. Within 30 minutes of reaching that temperature, the theoretical volume (120 ml.) of nitrogen had been collected. At this point the reaction mixture was diluted with water and worked up in the usual manner to yield a viscous yellow oil. This was crystallized from benzene–ethanol to yield 0.69 g. (73%) of glassy yellow granules, which softened at 107° but did not melt sharply. A

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[21] Analysis performed by Clark Microanalytical Laboratories, Urbana, Ill.

[22] H. Adkins, L. M. Richards and J. W. Davis, THIS JOURNAL, **63**, 1320 (1941).

[23] It has subsequently been found that the resolution is rendered more efficient by the use of a higher TAPA:hydrocarbon ratio.

[24] 2-(2,4,5,7-Tetranitro-9-fluorenylideneaminoöxy)-propionic acid (TAPA); a sample of this was kindly supplied by Dr. Wilson B. Lutz.[14]

sample of this was recrystallized twice from benzene–ethanol and then distilled at 0.1 mm. (bath temp. 200°).

Anal. Calcd. for $C_{26}H_{22}$: C, 93.4; H, 6.6. Found: C, 93.2, 93.3; H, 6.9, 6.8.

Attempted Preparation of an Aromatic Compound from Derivatives of XV. (a).—Treatment of the hexahydro compound XVI with DDQ for nine hours in refluxing toluene afforded only an intractable gum. (b) Attempts to proceed from the diol XVII *via* iodine catalyzed dehydration, pyrolysis of the acetate or replacement of the hydroxyl by chlorine and subsequent dehydrohalogenation all failed. In no case could anything but gums and glasses be isolated. (c) An intimate mixture of 1.0 g. of the diol XVII and 0.1 g. of sulfur was heated for 30 minutes at 185°, and then to 240° over a period of 1.5 hours. Vigorous initial decomposition followed by slow evolution of hydrogen sulfide was noted. The product was then chromatographed over alumina. The first zone which showed a strong blue fluorescence was eluted, and again passed through an alumina column. The solid obtained on removal of solvent was recrystallized from benzene–ethanol to yield 110 mg. of yellow leaves, m.p. 177–182°. This was recrystallized to a constant m.p. of 183–184°.

Anal. Calcd. for $C_{26}H_{20}$: C, 93.9; H, 6.1. Found: C, 93.7, 93.6; H, 5.7, 5.7.

COLUMBUS 10, OHIO

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

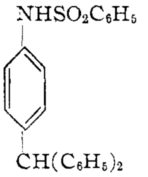
Quinol Imide Acetates. II. 2,4,6-Trimethyl-*o*-quinolbenzenesulfonimide Acetate and 2,4-Dimethyl-*o*-quinolbenzenesulfonimide Acetate

BY ROGER ADAMS AND K. R. BROWER

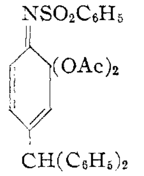
RECEIVED APRIL 16, 1956

The action of lead tetraacetate on N-benzenesulfonyl-2,4,6-trimethylaniline and N-benzenesulfonyl-2,4-dimethylaniline produces 2,4,6-trimethyl- and 2,4-dimethyl-*o*-quinolbenzenesulfonimide acetate, respectively. The quinol imide acetates add a variety of active hydrogen compounds with simultaneous aromatization by loss of acetic acid to form 5-substituted derivatives of the starting materials. This reaction provides an easy means of synthesis for a variety of aromatic compounds, many of which would be very difficultly accessible by known procedures.

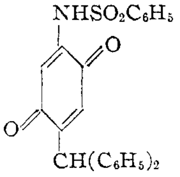
In a recent paper[1] it was reported that the lead tetraacetate oxidation of 4-benzenesulfonamidotriphenylmethane (I) forms 4-benzhydryl-*o*-quinone diacetate-1-benzenesulfonimide (II) and a by-product, 2-benzenesulfonamide-5-benzhydryl-*p*-benzoquinone (III). A similar reaction has been reported by Wessely and co-workers[2] who oxidized various alkylphenols to quinol acetates with the same reagent and also with acetyl peroxide. The study has now been extended to the alkyl derivatives of benzenesulfonanilide.



I

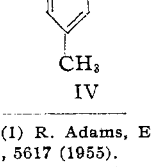


II

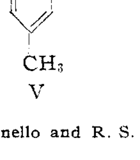


III

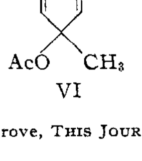
This communication describes the oxidation of the benzenesulfonyl derivatives of mesidine and 2,4-xylidine to form 2,4,6-trimethyl-*o*-quinolbenzenesulfonimide acetate (IV) and 2,4-dimethyl-*o*-quinolbenzenesulfonimide acetate (V), respectively. The properties of IV and V resemble those of the quinone diimides in that they add active hydrogen compounds to produce substituted alkyl benzenesulfonanilides. They are oxidizing agents of sufficient strength to release iodine from hydriodic acid and bromine from hydrobromic acid, but they are unaffected by sulfurous acid. Catalytic reduction converts them to the original sulfonamides.



IV



V



VI

The assignment of the *o*-quinol configuration to IV and V, although not proved chemically, is strongly supported by the relationship of the ultraviolet and infrared spectra to those of 4-methyl-*p*-quinolbenzenesulfonimide acetate (VI)[3] and Wessely's *o*- and *p*-quinol acetates. The relevant maxima are listed in Table I. It is to be expected *a priori* that the crossed-conjugation of the *p*-quinol derivatives should lead to a hypsochromic displacement of the ultraviolet absorption relative to that of the linearly conjugated *o*-quinol derivatives, and in the unequivocal cases this is seen to be so. In the infrared region the shift toward higher wave numbers in the absorption of the C=N bond in the putative *o*-quinol imide acetates is consistent with the expectation of lower bond order in the crossed-conjugated system VI.

TABLE I

Compound	First absorption maximum in u. v. λ_{max}, mμ	log ϵ	C=N absorption in i.r. λ_{max}, cm.$^{-1}$
IV	355	3.7	1575
V	350	3.8	1575
VI	270	4.3	1540
o-Quinol acetates	320–290	3.4–3.6	
p-Quinol acetates	240	3.7–4.1	

The quinol imide acetates IV and V are prepared by oxidation of the appropriate benzenesulfonanilides with lead tetraacetate in chloroform solution at room temperature. An effort to produce IV by oxidation in acetic acid solution was unsuccessful

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(1) R. Adams, E. J. Agnello and R. S. Colgrove, THIS JOURNAL, **77**, 5617 (1955).

(2) F. Wessely, *et al.*, *Monatsh. Chem.*, **81**, 811 (1950); **81**, 1055 (1950); **83**, 902 (1952); **84**, 291 (1953); **85**, 69 (1954).

(3) The preparation and properties of this compound will be more fully described in a forthcoming publication.