[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

A Synthesis of Dibenzocycloheptadiene[1]

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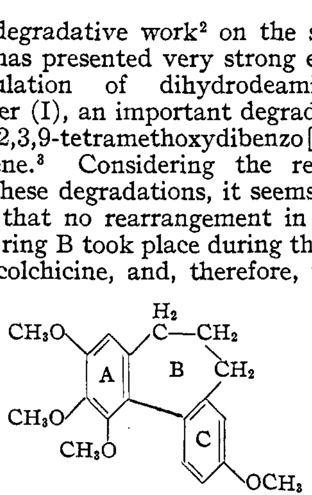
Recent degradative work[2] on the structure of colchicine has presented very strong evidence for the formulation of dihydrodeaminocolchinol methyl ether (I), an important degradation product, as 1,2,3,9-tetramethoxydibenzo[a,c][1,3]cycloheptadiene.[3] Considering the reactions involved in these degradations, it seems reasonable to assume that no rearrangement in the carbon skeleton of ring B took place during the formation of I from colchicine, and, therefore, that colchicine similarly contains a seven-membered central ring. The importance of colchicine, because of its mitosis-arresting action, in the general problem of cell growth[4] makes the establishment of its structure and the synthesis of related compounds exceedingly desirable.



I

The objective of the present work has been to develop a synthesis of the parent dibenzocycloheptadiene ring system that might be sufficiently general to extend to the synthesis of its various derivatives, including I. Relatively little is known about the synthesis of this type of compound, and the few reported methods[5] do not appear very attractive from the standpoint of adaptability to the synthesis of analogs.

With the above in mind, a synthesis of the dibenzocycloheptadiene system has been developed employing phenanthrenequinone as starting material as outlined in the formula diagram. Proceeding by a series of well-known reactions, the desired products were obtained in over-all yields of 20 to 30%. In view of the several excellent syntheses of substituted phenanthrenes[6] and the ready conversion of the latter to quinones, this synthetic sequence may also possibly serve for the synthesis of substituted dibenzocycloheptadienes.

The first step in the procedure was the facile preparation of the biphenyl cyanoacid IV by Beckmann rearrangement of phenanthrenequinonemonoxime.[7] Two methods were then examined for extending the carbon chain by two atoms: *viz.*, the Willgerodt reaction and the condensation of an aldehyde with malonic acid.

The requisite ethyl ketone VI for carrying out the Willgerodt reaction was prepared from the acid chloride V using diethylcadmium.[8] However, attempts to convert this to the propionic acid derivative using the various modified procedures[9] all failed. In view of the fact that no report could be found of a successful Willgerodt reaction with a molecule containing a cyano group whereas many ethyl ketones are known to react normally,[9a] the reaction was repeated after the cyano group had been first hydrolyzed to the carboxyl. This latter compound was converted to the desired dibasic acid VII but in extremely poor yield (8%).

The second path investigated required the aldehyde IX, and this was prepared in excellent yield from the acid chloride V by Rosenmund reduction. It is interesting to note that the presence of a cyano group caused no difficulty in this reaction.[10] In both the preparation of the acid chloride and the aldehyde a small amount of 4-cyanofluorenone was isolated, and probably the presence of a *m*-orienting group in the second ring prevented this side reaction from taking place to a larger extent.[11]

From the aldehyde IX, the propionic acid side chain was easily formed by condensation with malonic acid[12] followed by decarboxylation and reduction. The final saturated dibasic acid VII was obtained by either (a) hydrolysis of the cyanocinnamic acid X and hydrogenation of the hydrolysis product XI, or (b) hydrogenation to the saturated cyanoacid XII and hydrolysis of the latter to VII. Both routes gave about 80% over-

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(1) This work was supported in part by a grant from the Cancer Research Fund, University of California.

(2) (a) Buchanan, Cook and Loudon, *J. Chem. Soc.*, 325 (1944); (b) Barton, Cook and Loudon, *ibid.*, 176 (1945); (c) Tarbell, Frank and Fanta, THIS JOURNAL, **68**, 502 (1946).

(3) Various other numbering sequences have been used in the prior literature for this ring system, but we believe the method used above and recommended by *Chemical Abstracts* provides the most logical and extensible system.

(4) (a) Krythe and Wellensiek, *Bibliogr. genet.*, **14**, 1 (1942); (b) Levine, *Botan. Rev.*, **11**, 145 (1945); (c) Ludford, *J. Natl. Cancer Inst.*, **6**, 89 (1945).

(5) (a) Kenner and Turner, *J. Chem. Soc.*, **99**, 2101 (1911); (b) Kenner, *ibid.*, **103**, 613 (1913); (c) Weitzenböck, *Monatsh.*, **34**, 199 (1913); (d) Borsche and Herbet, *Ann.*, **546**, 293 (1941); (e) Buchanan, Cook, Loudon and MacMillan, *Nature*, **162**, 692 (1948), in a preliminary communication that appeared after this work was completed, have described a method for synthesizing this ring system that holds promise of general applicability.

(6) Fieser, "The Chemistry of Natural Products Related to Phenanthrene," Reinhold Publishing Corp., New York, N. Y., 1937.

(7) Werner and Piguet, *Ber.*, **37**, 4311 (1904).

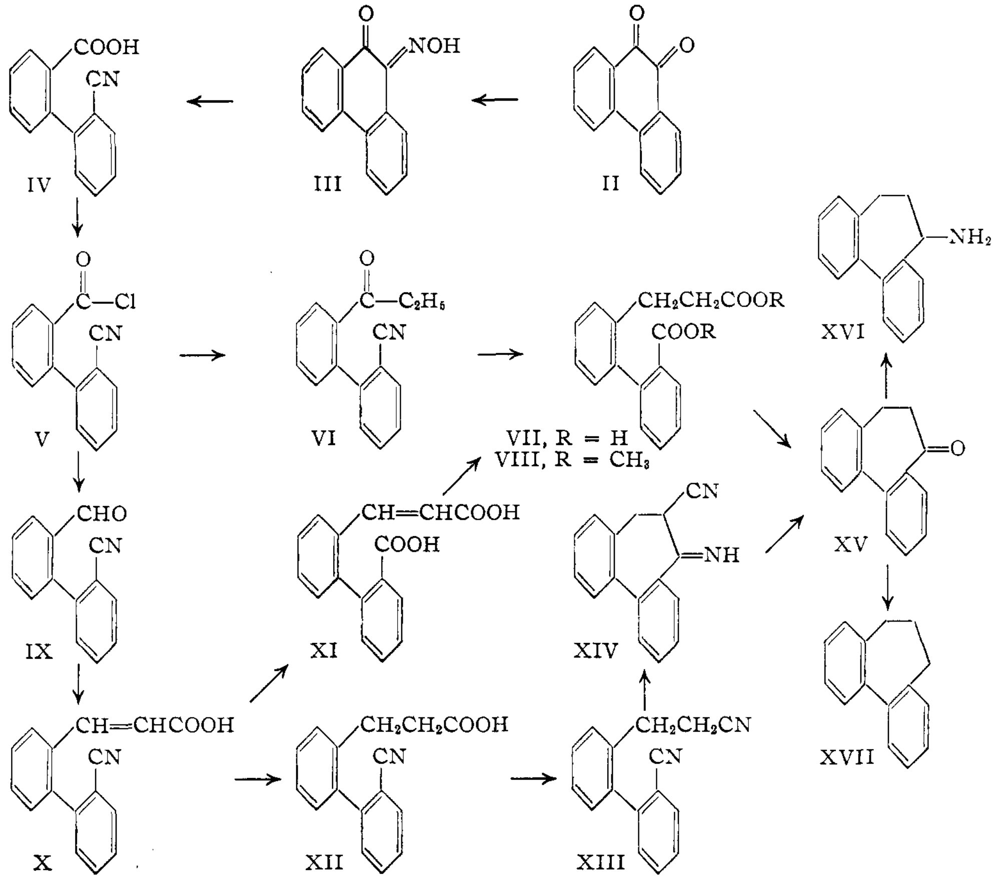
(8) Cason, *Chem. Rev.*, **40**, 15 (1947).

(9) (a) Carmack and Spielman, "Organic Reactions," Vol. III, John Wiley and Sons, New York, N. Y., 1946, p. 83; (b) De Tar and Carmack, THIS JOURNAL, **68**, 2025 (1946).

(10) No previous report of the application of the Rosenmund reaction to a cyanoacid chloride could be found; see Mosettig and Mozingo, "Organic Reactions," Vol. IV, John Wiley and Sons, New York, N. Y., 1948, p. 362.

(11) See Frank, Fanta and Tarbell, THIS JOURNAL, **70**, 2314 (1948), for a similar case in which fluorenone formation was the predominant reaction.

(12) (a) Livshits and co-workers, *J. Gen. Chem.* (*U. S. S. R.*), **17**, 1671 (1947); (b) Phillips, THIS JOURNAL, **70**, 452 (1948).



all yields from aldehyde IX to dibasic acid VII. Hydrogenation of the cyanocinnamic acid X to the cyanopropionic acid XII required some study, but conditions were found using palladium-on-carbon in carbonate solution for selectively reducing the double bond and obtaining XII with the cyano group intact.

Cyclization of the dibasic acid VII to the ketone XV was effected directly by pyrolysis of the thorium salt[13] and by the Dieckmann method followed by saponification and decarboxylation of the intermediate β-ketoester. The ketone thus obtained was a colorless solid melting at 85–86°[14]; however, the yields in both processes were only about 50%.

As an alternative procedure, the elegant Ziegler cyclization method[15] was applied to the dinitrile XIII, and excellent yields of the ketone XV resulted after hydrolysis of the cyano-imine XIV. The dinitrile was readily prepared from the acid XII by way of the acid chloride, amide, and dehydration of the amide with phosphorus oxychloride.[16] Thus, this became the best of the three routes for converting the cyanocinnamic acid X to the cycloheptadienone XV.

The amino compound XVI, which would correspond to colchinol methyl ether, was then prepared from the ketone by reductive amination[17] and also by the Leuckart reaction,[18] the latter proving to be superior.

Reduction of the ketone XV by the Wolff–Kishner method as modified by Huang-Minlon[19] gave a good yield of the desired parent hydrocarbon, dibenzo[a,c][1,3]cycloheptadiene which was found to exist in dimorphic forms, m. p. 40° and m. p. 54.5–55°.[20] The low-melting form is obtainable only by cooling the liquid hydrocarbon; on standing it is converted to the high-melting form which is also obtained directly by steam-distillation or crystallization from a solvent. In order to eliminate any possibility that the Wolff–Kishner reduction of XV caused a rearrangement,

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(13) Ruzicka and co-workers, *Helv. Chim. Acta*, **9**, 499 (1926).

(14) Cook, Dickson and Loudon, *J. Chem. Soc.*, 746 (1947), have recently reported this ketone as yellow prisms, m. p. 85–86°, prepared by the method of Kenner (ref. 5a and b).

(15) Ziegler, Eberle and Ohlinger, *Ann.*, **504**, 94 (1933).

(16) (a) Zemplén and Kiss, *Ber.*, **60**, 165 (1927); (b) Ladenburg, Tishler, Wellman and Babson, THIS JOURNAL, **66**, 1217 (1944).

(17) (a) Haskelberg, *ibid.*, **70**, 2811 (1948); (b) Emerson, "Organic Reactions," Vol. IV, John Wiley and Sons, New York, N. Y., 1948, p. 174.

(18) Ingersoll, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, New York, N. Y., 1943, p. 503.

(19) Huang-Minlon, THIS JOURNAL, **68**, 2487 (1946).

(20) This hydrocarbon has been reported twice in the recent literature. Cook, Dickson and Loudon (ref. 14) report what is presumably this compound as an oil. Lettré, *Angew. Chem.*, **59**, 218 (1947), reports it as melting at 52° and refers to Wichmann, *Angew. Chem.*, **59**, 180 (1947); neither reference provides any experimental details. Both groups used the method of Kenner (ref. 5a and b).

which seems highly improbable, the isomeric 9-methyl-9,10-dihydrophenanthrene was synthesized and found to differ considerably from the dibenzo[a,c][1,3]cycloheptadiene.

Work is continuing on the application of the above method to the synthesis of colchicine degradation products.

Experimental[21]

Phenanthrenequinonemonoxime (III).—The monoxime of phenanthrenequinone was prepared in 87% yield by the method of Pschorr.[22]

2-(2′-Cyanophenyl)-benzoic Acid (IV).—This compound was prepared by the following modifications of the method of Werner and Piquet.[7] To 10 g. (0.045 mole) of phenanthrenequinonemonoxime dissolved in 40 ml. of pyridine (dried over potassium hydroxide), 8.4 g. (0.046 mole) of benzenesulfonyl chloride was added with stirring during one-half hour while the solution was heated under reflux, and the boiling was continued for an additional half hour. After cooling, the pyridine solution was slowly poured into 300 ml. of 3.5 *N* hydrochloric acid, whereupon a brown amorphous solid precipitated. This was filtered after the solution had been allowed to stand for an hour in the cold, washed well with water, and digested with 150 ml. of 1 *N* potassium carbonate. The carbonate solution was concentrated to 100 ml., cooled, and filtered to remove any unreacted oxime, and the filtrate was acidified cautiously with concentrated hydrochloric acid. The precipitated 2-(2′-cyanophenyl)-benzoic acid (IV) was filtered, washed well with water, dried, and crystallized from benzene to give 8.8 g., 88% yield, of colorless prisms melting at 170–172° (reported[7] m. p. 170–172°).

2-(2′-Cyanophenyl)-benzoyl Chloride (V).—A mixture of 10 g. (0.045 mole) of the cyanoacid (IV), 50 ml. of dry benzene, and 10.6 g. (0.09 mole) of thionyl chloride was heated under reflux for one hour. At the end of this period, the solution was concentrated to 20 ml., 50 ml. of benzene was added, and the solution again concentrated to 20 ml. This procedure was repeated two times, and hexane was then added to the hot 20 ml. of final solution until it became turbid. On cooling the crystalline acid chloride was obtained in a 95% yield, 10.3 g., m. p. 80–81°.

In experiments where the acid chloride was isolated by distillation (b. p. 193–195° at 4–5 mm.), 4-cyanofluorenone, yellow needles melting at 244° (reported[23] m. p. 244°) was obtained as a side product in yields as high as 10%.

2-(2′-Cyanophenyl)-propiophenone (VI).[24]—To 0.083 mole of ethylmagnesium bromide in 100 ml. of ether, cooled in an ice-bath, was added 8.1 g. of cadmium chloride (anhydrous) during five minutes after which the mixture was stirred and heated under reflux until a negative Gilman test was obtained. The ether was then distilled from a steam-bath, 27 ml. of benzene was added and an additional 10 ml. of the solution distilled. To the residual solution was added 50 ml. of benzene, the solution was heated to boiling with stirring, and, after removal of the external heat, 10 g. (0.0415 mole) of the acid chloride (V) in 12 ml. of benzene was added during fifteen minutes. After an additional thirty minutes of boiling and stirring the reaction mixture was cooled, decomposed with 80 g. of ice, and acidified to congo red with 6 *N* sulfuric acid. The aqueous layer, after separating the oily material, was extracted with one half its volume of benzene in two portions and the combined oil and benzene extracts were washed twice with one-third volume portions of 5% sodium carbonate solution, then with water, and finally with saturated sodium chloride solution. Acidification of the carbonate washings gave 0.7 g. of recovered acid (IV). The ketone (VI) was obtained as residue after distilling the benzene, and crystallization from ethanol gave 5.6 g. (58% yield) of needles melting at 72–73°.

Anal. Calcd. for $C_{16}H_{13}NO$: C, 81.68; H, 5.57; N, 5.95. Found: C, 81.65; H, 5.72; N, 6.10.

The **semicarbazone** of VI was crystallized from ethanol-water and melted at 157–158°.

Anal. Calcd. for $C_{17}H_{16}N_4O$: C, 69.84; H, 5.52; N, 19.17. Found: C, 70.19; H, 5.57; N, 18.87.

2-(2′-Cyanophenyl)-benzaldehyde (IX).—The general procedure of Hershberg and Cason[25] for the preparation of α-naphthaldehyde was followed. Using 113 g. (0.47 mole) of the cyanoacid chloride (V), 550 ml. of xylene, 11 g. of 10% palladium-on-barium sulfate catalyst, and 1.1 g. of sulfur-quinoline poison, 98% of the theoretical quantity of hydrogen chloride was evolved during six hours, after which evolution came to an abrupt halt. The hot xylene solution was then treated with decolorizing carbon, filtered, and concentrated to one-fourth its original volume. Cooling gave a precipitate which was digested with six 100-ml. portions of 20% aqueous sodium bisulfite, leaving as an insoluble residue a small amount of 4-cyanofluorenone, m.p. 244°[23] after crystallization from ethanol. The bisulfite addition product was decomposed with potassium carbonate solution and the resulting solid further purified by crystallization from benzene, giving 88 g. (91% yield) of cyanoaldehyde (IX) melting at 118–119°. For analysis a sample was sublimed under reduced pressure.

Anal Calcd. for $C_{14}H_9NO$: C, 81.14; H, 4.38; N, 6.76. Found: C, 81.18; H, 4.29; N, 6.62.

The **semicarbazone** of IX, prepared in the usual manner, was crystallized from ethanol and melted at 203°.

Anal. Calcd. for: $C_{15}H_{12}N_4O$: C, 68.16; H, 4.58; N, 21.20. Found: C, 68.00; H, 4.53; N, 21.60.

The **2,4-dinitrophenylhydrazone** of IX was prepared by heating under reflux with 2,4-dinitrophenylhydrazine hydrochloride in ethanol containing 1% concentrated hydrochloric acid. Crystallization from ethanol, ethyl acetate, and finally chloroform gave soft orange needles melting at 249° with decomposition.

Anal. Calcd. for $C_{20}H_{13}N_5O_4$: C, 62.01; H, 3.38; N, 18.08. Found: C, 61.72; H, 3.36; N, 17.82.

2-(2′-Cyanophenyl)-cinnamic Acid (X).—A mixture of 30 g. (0.145 mole) of the cyanoaldehyde (IX), 22.6 g. (0.22 mole) of malonic acid, 115 ml. of pyridine, and 2.5 ml. of piperidine was heated for one-half hour at 80° and two hours at 100°, and then boiled gently for one-half hour. The solution was poured into 850 ml. of 3.5 *N* hydrochloric acid and the resulting precipitate was filtered, washed well with water, and digested with one liter of 1 *N* potassium carbonate solution until solution was practically complete. Concentration to 700 ml. and cooling followed by filtration gave 4.0 g. of recovered cyanoaldehyde (IX). The filtrate was carefully acidified to give a finely divided solid which, after crystallization from ethanol, melted at 224–225°. The yield of 29.9 g. of the cyanocinnamic acid (X) was 83% of theoretical based on starting aldehyde or 96% allowing for recovered aldehyde.

Anal. Calcd. for $C_{16}H_{12}NO_2$: C, 77.09; H, 4.45; N, 5.62. Found: C, 77.20; H, 4.45; N, 5.60.

The ***p*-nitrobenzyl ester** of X was prepared in the usual way and crystallized from an ethanol–water mixture; m.p. 150–151°.

Anal. Calcd. for $C_{23}H_{16}N_2O_4$: C, 71.86; H, 4.20; N, 7.29. Found: C, 72.07; H, 4.13; N, 7.44.

2-(2′-Carboxyphenyl)-cinnamic Acid (XI).—Hydrolysis was effected by heating 5 g. (0.02 mole) of the cyanocinnamic acid (X) and 100 ml. of 5 *N* potassium hydroxide in ethylene glycol at 200–205° for twenty-five hours after which the solution was diluted with 100 ml. of water, treated with decolorizing carbon, and filtered. Upon

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[21] All melting points are corrected; microanalyses were performed by C. W. Koch and V. H. Tashinian of these laboratories.

[22] Pschorr, *Ber.*, **35**, 2729 (1902).

[23] Graebe and Schestakow, *Ann.*, **284**, 314 (1895).

[24] Prepared by Donald E. Green.

[25] Hershberg and Cason, "Organic Syntheses," Vol. 21, John Wiley and Sons, New York, N. Y., 1941, p. 84.

acidification of the filtrate and crystallization from ethanol-water, 4.5 g. (84%) of the unsaturated dibasic acid (XI) was obtained; m.p. 230–231°.

Anal. Calcd. for $C_{16}H_{12}O_4$: C, 71.63; H, 4.51; eq. wt., 134. Found: C, 71.42; H, 4.64; eq. wt., 134.

β-[2-(2′-Cyanophenyl)]-phenylpropionic Acid (XII).—Hydrogenation of 10 g. (0.04 mole) of the unsaturated cyanoacid (X) in 100 ml. of 1 *N* potassium carbonate solution with 1 g. of a 5% palladium-on-carbon catalyst was interrupted after 1.07 moles of hydrogen were absorbed in twenty minutes at room temperature and twenty pounds pressure. Filtration and acidification gave 8.4 g., an 84% yield, of the saturated cyanoacid (XII) which melted at 117–118° after crystallization from a benzene–hexane mixture.

Anal. Calcd. for $C_{16}H_{13}NO_2$: C, 76.48; H, 5.21; N, 5.57. Found: C, 76.32; H, 5.26; N, 5.64.

The ***p*-nitrobenzyl ester** of XII was crystallized from ethanol–water and melted at 99–101°.

Anal. Calcd. for $C_{23}H_{18}N_2O_4$: C, 71.49; H, 4.69; N, 7.25. Found: C, 71.47; H, 4.86; N, 7.18.

β-[2-(2′-Carboxyphenyl)]-phenylpropionic Acid (VII). A. By Hydrogenation of XI.—The unsaturated dibasic acid (XI) was hydrogenated as described above. After absorption of one mole of hydrogen, hydrogenation ceased, and the solution was filtered, the filtrate acidified, and the precipitate crystallized from ethanol–water. From 21.9 g. (0.082 mole) of XI there was obtained a 98% yield, 21.6 g., of saturated dibasic acid (VII), m.p. 171–173°.

Anal. Calcd. for $C_{16}H_{14}O_4$: C, 71.12; H, 5.22; eq. wt., 135. Found: C, 71.42; H, 5.24; eq. wt., 135.

B. By Hydrolysis of XII.—Hydrolysis of the saturated cyanoacid (XII) was carried out as described above for the unsaturated cyanoacid (X). Heating was discontinued when the ammonia evolution ceased after five hours, and from 1.0 g. of XII a 94% yield (1.0 g.) of VII resulted, m.p. 171–173°.

C. By the Willgerodt Reaction.—To 3 g. of potassium hydroxide dissolved in 20 ml. of ethanol, 3.5 g. (0.015 mole) of the cyanoketone (VI) was added and the solution heated under reflux for twenty-four hours during which 92% of the theoretical amount of ammonia was evolved. Water (30 ml.) was added, the mixture was distilled until all the alcohol had been removed, and the solution was acidified. The **2-(2′-carboxyphenyl)-propiophenone** separated as an oil which resisted all efforts toward crystallization, and therefore the crude acid was treated directly with 1.8 g. of morpholine and 0.7 g. of sulfur. To this mixture, after heating under reflux for six hours, was added 9 ml. of glacial acetic acid, 1.3 ml. of concentrated sulfuric acid, and 2 ml. of water, and the mixture was boiled for another six hours. Dilution to 100 ml. with water gave a tarry precipitate which was filtered and digested with potassium carbonate solution. The carbonate solution was decolorized with carbon and acidified, yielding 0.4 g. of an amorphous solid. By fractional extraction of this material dissolved in benzene with 0.05 *N* potassium carbonate solution, 0.3 g. (8%) of the saturated dibasic acid (VII) was obtained which melted at 171–173° after crystallization from ethanol. A mixed melting point determination with the compound prepared in procedures A and B showed no depression.

Methyl β-[2-(2′-Carbomethoxyphenyl)]-phenylpropionate (VIII).—A solution of 10 g. (0.037 mole) of the saturated dibasic acid (VII) and 3 ml. of concentrated sulfuric acid in 60 ml. of methanol was heated under reflux overnight, after which it was poured into five volumes of water and extracted with benzene. The organic layer was washed twice with water, once with carbonate solution, and again with water. Acidification of the last two washings gave an oil from which 1 g. of the original acid (VII) was obtained by boiling with 3 *N* aqueous potassium hydroxide. The benzene was evaporated and the dimethyl ester (VIII) was distilled at a bath temperature of 210–230° at 3 mm. as a colorless oil; yield, 9.5 g., 86% based on total acid taken or 96% allowing for recovered material.

2-[2′-(Cyanophenyl)]-phenylpropionamide.—From 39.3 g. (0.157 mole) of the saturated cyanoacid (XII), 60 g. (0.5 mole) of thionyl chloride, and 400 ml. of benzene, the crude acid chloride was prepared by the procedure used above for compound V. Evaporation of the final benzene solution and treatment of the residue with concentrated aqueous ammonia gave 37.5 g. (96%) of the amide as an oil which solidified on standing. Repeated crystallization from benzene–hexane gave material melting at 100–102°.

Anal. Calcd. for $C_{16}H_{14}N_2O$: C, 76.77; H, 5.64. Found: C, 76.82; H, 5.75.

β-[2-(2′-Cyanophenyl)]-phenylpropionitrile (XIII).—A solution of 37.5 g. (0.15 mole) of the amide prepared above and 67.5 g. (0.44 mole) of phosphorus oxychloride was heated at 80° for one half hour after which the excess phosphorus oxychloride was distilled at reduced pressure. The residue was dissolved in 100 ml. of chloroform and the solution was slowly dropped into 200 ml. of ice. After washing with water and carbonate solution, the chloroform was evaporated and the dinitrile (XIII) was distilled, b.p. 184–194° at 1–2 mm. The distillate, 29 g., 83% yield, slowly set to a solid, m.p. 55–56°.

Anal. Calcd. for $C_{16}H_{12}N_2$: C, 82.73; H, 5.21; N, 12.06. Found: C, 82.88; H, 5.16; N, 12.52.

Dibenzo[a,c][1,3]cycloheptadien-5-one (XV). A. By Pyrolysis of the Thorium Salt.—A solution of 10 g. (0.037 mole) of the dibasic acid VII in 20 ml. of ethanol was neutralized with 1 *N* sodium hydroxide and to it a warm solution of 16.9 g. (0.031 mole) of thorium nitrate ($\cdot 4H_2O$) in 20 ml. of water was added slowly, giving a finely divided precipitate of the thorium salt of VII. This salt was dried to constant weight at 150° and pyrolyzed at 350–380° and 5–11 mm. The resulting 3.9 g., 51% yield, of yellow oil gave colorless crystals from methanol–water melting at 85–86°.[14]

Anal. Calcd. for $C_{15}H_{12}O$: C, 86.51; H, 5.95. Found: C, 86.30; H, 5.75.

The **semicarbazone** of XV was prepared by refluxing the ketone in ethanol with pyridine and semicarbazide hydrochloride for one hour. It formed colorless platelets from ethanol, m.p. 219–221° (evac. tube) after drying in vacuum at 130° overnight.

Anal. Calcd. for $C_{16}H_{16}N_3O$: C, 72.73; H, 5.65; N, 15.67. Found: C, 72.43; H, 5.70; N, 15.84.

The **2,4-dinitrophenylhydrazone** of XV was obtained as orange needles from chloroform, m.p. 238–239° with decomposition (reported[14] m.p. 240° with decomposition).

B. By Dieckmann Cyclization.—A mixture of 3.03 g. (0.13 mole) of powdered sodium in 50 ml. of xylene was heated to 115° and with stirring, five drops of methanol was added followed by 9.5 g. (0.032 mole) of the dimethyl ester (VIII) in 10 ml. of xylene during one and one-half hours. After addition of the ester was completed, the heating was continued for an additional half hour, and the solution was then poured into 100 ml. of water. The organic layer was washed with water, the xylene was removed under reduced pressure, and the residual crude keto-ester was dissolved in 100 ml. of 0.5 *N* ethanolic potassium hydroxide and allowed to stand at room temperature overnight. After the ethanol was distilled at reduced pressure, the solution was acidified with 1 *N* sulfuric acid to *p*H 3, heated under reflux until carbon dioxide evolution ceased, and extracted with three 30-ml. portions of benzene. The benzene solution, after washing with water, carbonate solution, and again with water, was dried over sodium sulfate and concentrated to a yellow oil which was crystallized from methanol–water to give 2.9 g., 44% yield, of pure ketone (XV) melting at 85–86°. On acidification of the carbonate and water washes of the benzene extract, 1.1 g. of the dibasic acid (VII) was recovered.

C. By Ziegler Cyclization. 6-Cyanodibenzo[a,c][1,3]-cycloheptadien-5-imine (XIV).—Phenyllithium was prepared by adding 62.8 g. (0.4 mole) of bromobenzene during four hours to 6.0 g. (0.86 mole) of lithium ($^1/_8$ inch diameter wire cut into 2.5 mm. lengths) in 450 ml. of boiling ether in a nitrogen atmosphere; yield, 97%.

To 230 ml. of 0.087 *N* phenyllithium (0.2 mole) in ether was added 42.8 g. (0.4 mole) of methylaniline and the solution was heated under reflux for one hour. After cooling, 28 g. (0.12 mole) of the dinitrile (XIII) in 200 ml. of ether was added during ten hours, and the ether solution was then washed with water, dilute hydrochloric acid, and again with water. Drying and concentrating the ether solution precipitated the cyano-imine (XIV) which was crystallized from chloroform; yield, 27.5 g., 98%, of material melting at 160–161°.

Anal. Calcd. for $C_{16}H_{12}N_2$: C, 82.73; H, 5.21; N, 12.06. Found: C, 82.81; H, 5.32; N, 11.55.

Hydrolysis to the Ketone (XV).—The cyano-imine (XIV) was hydrolyzed by boiling 26.5 g. (0.114 mole) with 100 ml. of 18 *N* sulfuric acid until carbon dioxide evolution ceased. The ketone was obtained by extraction with chloroform, evaporation of the chloroform extract, and crystallization of the residue from methanol–water; yield, 18.1 g., 76%, m.p. 85–86°.

5-Aminodibenzo[a,c][1,3]cycloheptadiene (XVI). A. By the Leuckart Reaction.—A mixture of 4 g. (0.0192 mole) of the ketone (XV) and 7.25 g. (0.115 mole) of ammonium formate was slowly heated to 160° and maintained at 160–170° overnight. After diluting with 10 ml. of water and decanting the aqueous layer, the residue was heated under reflux for six hours with 15 ml. of concentrated hydrochloric acid. The solution was filtered and the insoluble material was digested with six 20-ml. portions of water. Concentration of the combined aqueous digests until solid began to form and cooling gave 2.5 g. **amine hydrochloride**; an additional 0.6 g. was obtained from the mother liquors. The total yield was 3.1 g., 66%, m.p. 312–313° (sealed tube) with decomposition.

Anal. Calcd. for $C_{15}H_{16}ClN$: C, 73.30; H, 6.56; N, 5.70. Found: C, 73.59; H, 6.79; N, 6.16.

N-Acetyl-5-aminodibenzo[a,c][1,3]cycloheptadiene was prepared by treating an aqueous solution of the amine hydrochloride with acetic anhydride and sodium acetate. It was crystallized from ethanol, m.p. 234–235°.

Anal. Calcd. for $C_{17}H_{17}NO$: C, 81.24; H, 6.82; N, 5.57. Found: C, 81.08; H, 6.88; H, 5.48.

B. **By Reductive Amination.**—A solution of 0.5 g. (0.0024 mole) of the ketone (XV) in 10 ml. of methanol saturated with ammonia was hydrogenated at room temperature and atmospheric pressure using 0.1 g. of 5% palladium-on-carbon catalyst. After seventy-two hours the hydrogenation was stopped, the catalyst removed, and the methanol evaporated. The residue was treated with 20 ml. of 1 *N* hydrochloric acid and extracted with two 10-ml. portions of benzene. From the benzene extracts 0.2 g. (40%) of recovered ketone was obtained while the acid solution on concentration to 5 ml. yielded 0.18 g. (31%) of the amine hydrochloride.

Dibenzo[a,c][1,3]cycloheptadiene (XVII).—A mixture of 5 g. (0.024 mole) of the ketone (XV), 5.5 g. of potassium hydroxide, 35 ml. of ethylene glycol, and 3.5 ml. of 85% hydrazine hydrate was heated according to the general procedure of Huang-Minlon.[19] After cooling, the reaction mixture was diluted with 100 ml. of water and extracted with three 30-ml. portions of benzene. The residue after drying and evaporating the benzene was fractionated through a one meter Podbielniak column to give 2.78 g., 60% yield, of dibenzo[a,c][1,3]cycloheptadiene as a colorless liquid, b.p. 99–100° at 0.3 mm.; $n^{18}D$ 1.6229, $n^{25}D$ 1.6194. On cooling, this liquid slowly solidifies and melts at 40°. However, on standing at room temperature several days, the solid material is converted to a dimorphic form melting at 54.5–55° (previously reported as an oil and as melting at 52°[20]). Crystallization from glacial acetic acid or ethanol–water also gives the high-melting form.

Anal. Calcd. for $C_{15}H_{14}$: C, 92.74; H, 7.26. Found: C, 92.84; H, 7.34.

As a derivative of this hydrocarbon (XVII) the acetamido compound was prepared by first nitrating as directed by Krueger and Mosettig[26] for 9,10-dihydrophenanthrene and then reducing and acetylating according to the general procedure of Ipatieff and Schmerling.[27] After crystallization from ethanol–water, it melted at 175–177°.

Anal. Calcd. for $C_{17}H_{17}NO$: N, 5.57. Found: N, 5.34.

The above product is assigned the structure **N-acetyl-3-aminodibenzo[a,c][1,3]cycloheptadiene** by analogy with the product obtained on nitrating 9,10-dihydrophenanthrene.[26]

With alcoholic picric acid, the hydrocarbon (XVII) failed to form a picrate.

9-Methyl-9,10-dihydrophenanthrene.—9-Methylphenanthrene was prepared from 9-bromophenanthrene[28] by the method of Bachmann[29] and was hydrogenated as directed for the preparation of 9,10-dihydrophenanthrene.[30] Fractionation of the hydrogenation mixture from 15 g. (0.077 mole) of 9-methylphenanthrene through a one meter Podbielniak column gave 7 g., 46% yield, of 9-methyl-9,-10-dihydrophenanthrene, b.p. 158–160° at 9 mm., $n^{15}D$ 1.6320, $n^{25}D$ 1.6270 and 5 g. of recovered 9-methylphenanthrene, b.p. 184–186° at 9 mm. (m.p. 91–92°[29]; picrate, m.p. 151–152°[31]). The dihydro compound could not be induced to crystallize and failed to form a picrate with alcoholic picric acid.

Anal. Calcd. for $C_{15}H_{14}$: C, 92.74; H, 7.26. Found: C, 92.85; H, 7.26.

Oxidation of 9-methyl-9,10-dihydrophenanthrene with chromic anhydride in acetic acid gave phenanthrenequinone, m.p. 204–207°.

Summary

Phenanthrenequinone has been converted to dibenzo[a,c][1,3]cycloheptadien-5-one in 32% overall yield.

From this ketone, 5-aminodibenzo[a,c][1,3]cycloheptadiene and dibenzo[a,c][1,3]cycloheptadiene have been prepared.

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[29] Bachmann, THIS JOURNAL, **56**, 1363 (1934).

[30] Durland and Adkins, *ibid.*, **59**, 135 (1937).

[31] Windaus, Jensen and Schramme, *Ber.*, **57**, 1875 (1924).