acid and subsequent cyclization to yield 5,6,7,8-tetramethyl-1-tetralone. Clemmensen reduction of the cyclic ketone and subsequent dehydrogenation of the tetramethyltetralin then yielded the desired hydrocarbon.

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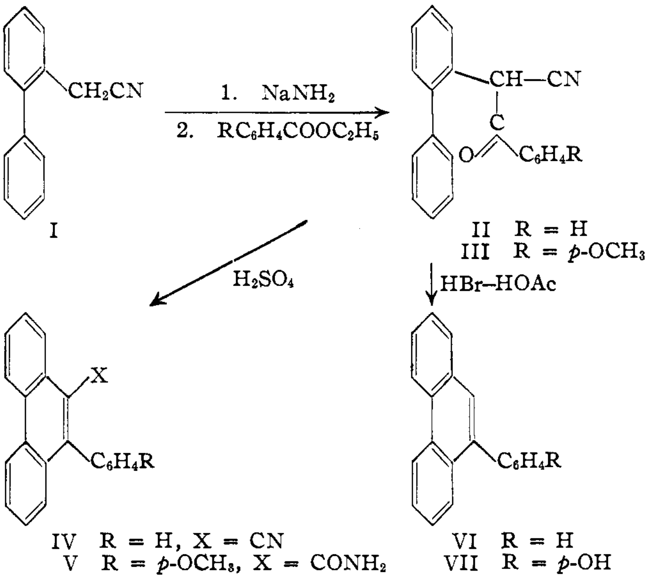
[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF DUKE UNIVERSITY]

Aromatic Cyclodehydration. XXIII.[1] Phenanthrene Derivatives by the Cyclization of Keto Nitriles

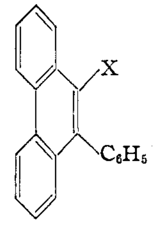
BY CHARLES K. BRADSHER* AND RICHARD S. KITTILA[2]

The present work was undertaken to determine whether *o*-phenylbenzyl cyanide (I) could be acylated and whether the resulting ketonitriles (II and III) would undergo typical aromatic cyclodehydration reactions to yield phenanthrene derivatives.[3]

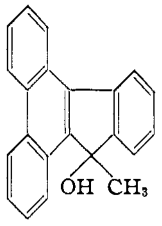
The method which we used in the preparation of *o*-phenylbenzyl cyanide (I) was essentially that of von Braun and Manz,[4] except that the required *o*-phenylbenzyl alcohol was prepared more conveniently from 2-biphenylylmagnesium iodide by the action of paraformaldehyde. Benzoylation of the nitrile was accomplished in 82% yield by treating it first with two moles of sodium amide and then with ethyl benzoate.[5] The resulting keto nitrile (II) when refluxed with a mixture of hydrobromic and acetic acids afforded 9-phenylphenanthrene (VI) in 46% yield. It is reasonable to assume that hydrolysis of the nitrile group, followed by decarboxylation of the resulting keto acid has preceded cyclization.



When the keto nitrile (II) was treated with cold concentrated sulfuric acid, 9-cyano-10-phenylphenanthrene (IV) was obtained. The structure of IV was established by comparison with the nitrile obtained from 9-bromo-10-phenylphenanthrene[6] (VIII) by the Rosenmund–von Braun method. The nitrile (IV) on treatment with methylmagnesium iodide afforded the expected imine (IX) which, probably as a result of steric hindrance, proved difficult to hydrolyze. With boiling dilute hydrochloric acid, the insoluble imine hydrochloride was recovered, but when the imine was dissolved in boiling dilute acetic acid and refluxed for sixteen hours, a product having the composition expected for 9-aceto-10-phenylphenanthrene (X) was obtained. In view of the failure of the product to undergo reaction with hydroxylamine or phenylhydrazine or to undergo reduction, it may be that the product is the isomeric 9-methyl-1,2,3,4-dibenzofluorenol-9 (XA). The acylation of *o*-phenylbenzyl cyanide (I) with ethyl anisate was accomplished in 55% yield. The product (III), on refluxing with hydrobromic and acetic acids, afforded the new 9-(*p*-hydroxyphenyl)-phenanthrene (VII) in a yield of 96%. The structure of this phenol (VII) was demonstrated by the synthesis of the corresponding methyl ether (XII) by a method studied previously.[7] The addition of *p*-anisylmagnesium bromide to 2-(ω-methoxy)-acetobiphenyl (XI), followed by cyclization of the crude carbinol, afforded a sample of 9-(*p*-methoxy-



VIII X = Br
IX X = (C = NH)CH$_3$
X X = COCH$_3$



XA

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* Harvard University Ph.D. 1937.

(1) For the preceding communication of this series see THIS JOURNAL, **71**, 1434 (1949).

(2) Public Health Service Fellow 1948–1949.

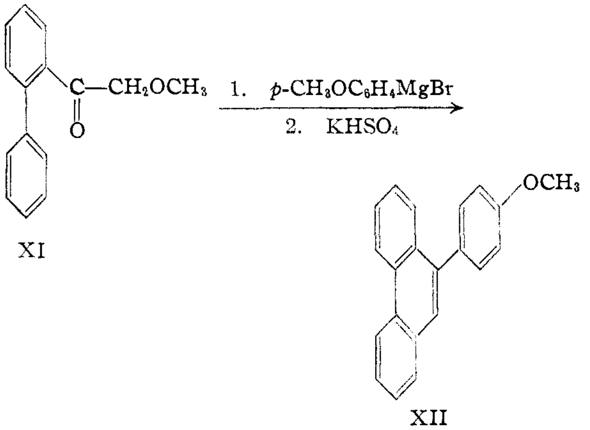
(3) Schönberg and Warren, *J. Chem. Soc.*, 1838 (1939), and Geissman and Tess, THIS JOURNAL, **62**, 514 (1940), have reported the cyclization of a related keto ester.

(4) von Braun and Manz, *Ann.*, **468**, 258 (1929).

(5) Hauser and Levine, THIS JOURNAL, **68**, 760 (1946).

(6) Koelsch, *ibid.*, **56**, 480 (1934).

(7) Bradsher and Schneider, *ibid.*, **60**, 2960 (1938).



phenyl)-phenanthrene (XII) similar to that obtained by methylation of the phenol (VII).

An interesting reaction occurred when the methoxy keto nitrile (III) was treated with cold concentrated sulfuric acid. The product is not a nitrile as would be expected from the behavior of the analogous phenyl keto nitrile (II), but appears to be 9-(*p*-methoxyphenyl)-10-phenanthramide[8] (V). On treatment with nitrous acid in acetic acid, the compound (V) yields a nitrogen-free product which is not the expected 9-(*p*-methoxyphenyl)-10-phenanthroic acid, but a neutral compound, corresponding in composition to the loss of one molecule of water from the acid. The nature of this substance will be studied further.

It will be seen in Fig. 1 that the ultraviolet absorption spectra of 9-(*p*-methoxyphenyl)-10-phenanthramide (V) and 9-(*p*-methoxyphenyl)-phenanthrene (XII) show marked qualitative similarity to each other and to that of 9-phenylphenanthrene.[9]

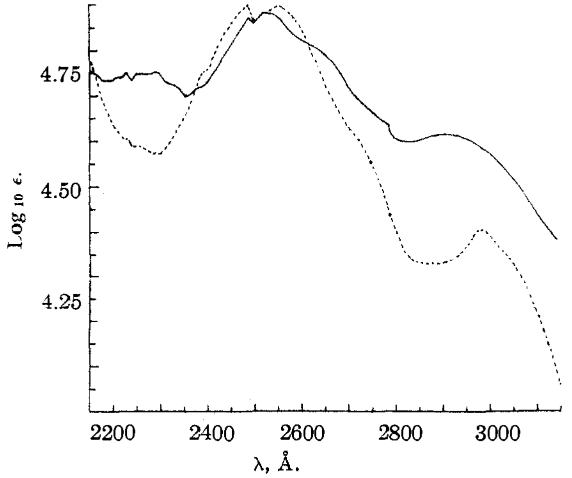


Fig. 1.—9-(*p*-Methoxyphenyl)-phenanthrene, - - -; 9-(*p*-methoxyphenyl)-10-phenanthramide,———.

Experimental

Absorption Spectra.—The ultraviolet absorption spectra were measured in 95% ethanol using a Beckman model DU quartz spectrophotometer. One centimeter silica cells were used in all measurements.

o-Phenylbenzyl Alcohol[10] **(I).**—To a solution of *o*-biphenylylmagnesium iodide prepared from 168 g. of 2-iodobiphenyl, 27 g. of thoroughly dried paraformaldehyde was added all at once, and the mixture stirred for nineteen hours at room temperature. Hydrolysis was effected by adding 102 ml. of saturated ammonium chloride solution. The ethereal solution was decanted and concentrated, and the residue was distilled, yielding 72.7 g. (66%) of a yellow oil, b. p. 146–152° (4 mm.); (lit.[4] b. p. 174° (13 mm.)), n^{25}_{D} 1.6118. On standing, this material solidified, m. p. 42–50°.

Phenylphenanthrene Series

α-Benzoyl-o-phenylbenzyl Cyanide (II).—Sodium amide was prepared from 2.3 g. of sodium and 75 ml. of liquid ammonia.[5] The flask was heated on a steam-bath and the ammonia gradually replaced by 50 ml. of dry ether. The ether solution was cooled, and 9.6 g. of the *o*-phenylbenzyl cyanide[4] in 10 ml. of dry ether was added and the mixture refluxed for one-half hour. To the cooled reaction mixture, 15 g. of dry, freshly distilled, ethyl benzoate was added over a period of twenty minutes, care being taken to prevent the reaction from becoming too vigorous. After refluxing for four hours, the reaction mixture was poured on 100 g. of ice and acidified with hydrochloric acid. The mixture was extracted with ether and the extract was washed with water, dried and concentrated, and the residue was distilled under reduced pressure. After a fore-run which contained ethyl benzoate and benzoic acid, the product (12.2 g.) was obtained as a yellow viscous liquid. This was the material used in subsequent experiments, although it was found that on standing the product solidified, m. p. 81–86°. A small portion triturated with cyclohexane gave white crystals, m. p. 88.5–89.5°. The analytical sample was obtained by distillation, b. p. 235° (4 mm.), n^{25}_{D} 1.6235.

Anal.[11] Calcd. for $C_{21}H_{15}ON$: C, 84.82; H, 5.08. Found: C, 84.55; H, 5.07.

9-Phenylphenanthrene (VI).—A 2-g. portion of the keto nitrile above was dissolved in 20 ml. of acetic acid and added to 20 ml. of refluxing 48% hydrobromic acid. After seventeen hours of refluxing, the acid was decanted from the viscous oil which had separated. The oil was taken up in ether, washed with water, and the ether evaporated. Crystallization of the residue, once from alcohol and once from acetic acid, gave 0.5 g. (29%) of white crystals, m. p. 103–104°. These did not depress the melting point of an authentic sample of 9-phenylphenanthrene.[7]

9-Cyano-10-phenylphenanthrene (IV).—(a) From α-Benzoyl-*o*-phenylbenzyl Cyanide (II)—Two grams of the keto nitrile (II) was stirred with 20 ml. of cold concentrated sulfuric acid and kept in an ice-bath for sixteen hours. The reaction mixture was poured on crushed ice and the solid which formed was collected and washed with water. Two recrystallizations from ethanol gave 0.5 g. (27%) of orange crystals, m. p. 179–182°. An analytical sample was prepared by repeated recrystallization from ethanol as amber plates, m. p. 185–185.5°.

(b) From **9-Bromo-10-phenylphenanthrene (VIII).**—A 0.25-g. portion of 9-bromo-10-phenylphenanthrene,[6,12] 0.17 g. of cuprous cyanide, 2 drops of tolunitrile, a small quantity of anhydrous cupric sulfate and 2 ml. of pyridine, were heated for two and one-half hours at 200–225°, the pyridine being allowed to distil. The residue was distilled under reduced pressure, and once recrystallized from ethanol. The product was obtained as orange crystals,

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(8) We are indebted to the referee for the suggestion that the low yields obtained in the sulfuric acid cyclizations may be due in both cases to the concurrent formation of nitrile and amide.

(9) Bradsher and Wissow, This Journal, 68, 2149 (1946).

(10) This procedure is based upon an unpublished experiment by Dr. S. T. Amore.

(11) Analyses by Micro-Tech Laboratories.

(12) The authors are indebted to Miss Kay Dohm for the preparation of this sample.

m. p. 184–185.5°. This material produced no depression of melting point when mixed with the analytical sample obtained by procedure a.

Anal. Calcd. for $C_{21}H_{13}N$: N, 5.01. Found: N, 4.76.

9-Acetimido-10-phenylphenanthrene (IX).—Methylmagnesium iodide was prepared from 7.3 g. of methyl iodide, and 7.2 g. of 9-cyano-10-phenylphenanthrene (IV) added in 30 ml. of dry benzene. The mixture was refluxed for seven hours, the ether was removed, and the resulting benzene solution was refluxed for an additional eight hours. The reaction mixture was decomposed with ammonium chloride, and worked up in the usual way. After removing the organic solvents, the viscous liquid residue solidified to give 8.1 g. of oily crystals. Once recrystallized from methanol, 4.5 g., m. p. 143–147°, and a second crop, 0.6 g., m. p. 148–151° (total 75%) was obtained. An analytical sample was prepared by repeated crystallization from methanol, m. p. 152–153°.

Anal. Calcd. for $C_{22}H_{17}N$: C, 89.46; H, 5.80; N, 4.74. Found: C, 89.38; H, 5.70; N, 4.83.

Hydrolysis of 9-Acetimido-10-phenylphenanthrene IX.—A solution of 1.5 g. of the imine (IX) in 25 ml. of acetic acid and 20 ml. of water was refluxed for sixteen hours, cooled and collected. The white solid, 1.2 g. (80%), melted at 173–174° and recrystallization from ethanol gave small white feathery crystals, m. p. 175.5–176°.

Anal. Calcd. for $C_{22}H_{16}O$: C, 89.16; H, 5.44. Found: C, 89.12, 89.07; H, 5.50, 5.62.

This product failed to give an oxime or phenylhydrazone under the usual conditions. It was largely unaffected when treated in decalin solution with hydrogen for four hours at a pressure of 2100 lb./sq. in. and a temperature of 177–183°, in the presence of a copper–chromium oxide catalyst.[13]

(*p*-Hydroxyphenyl)-phenanthrene Series

α-(*p*-Anisoyl)-*o*-phenylbenzyl Cyanide (III).—Sodium amide was prepared from 2.5 g. of sodium, and 9.6 g. of *o*-phenylbenzyl cyanide in 10 ml. of dry ether was added and the mixture refluxed for thirty minutes. Ethyl anisate (18 g.) in dry ether (15 ml.) was added slowly, whereupon the gray solution turned yellow. After refluxing for five and one-half hours and stirring overnight at room temperature, the mixture was worked up as in the case of the phenyl analog (II). Upon evaporation of the ether solution, the product solidified and was collected and washed with ethanol. Once recrystallized from ethanol, 8.5 g. (52%) of the product was obtained, m. p. 106–109°. An analytical sample prepared by repeated crystallization from ethanol gave white diamond-shaped plates, m. p. 108.5–109.5°.

Anal. Calcd. for $C_{22}H_{17}O_2N$: C, 80.71; H, 5.24. Found: C, 80.45; H, 5.22.

9-(*p*-Hydroxyphenyl)-phenanthrene (VII).—One gram of the keto nitrile (III) was refluxed for eleven hours with a mixture containing 15 ml. of 48% hydrobromic acid and 25 ml. of acetic acid. During this time an oil separated, and on cooling, it crystallized to give 0.8 g. (96%) of a brown solid, m. p. 152–153.5°. Sodium fusion showed this material to be free of nitrogen and halogen. The product was soluble in strong alkali from which it could be precipitated by addition of acid. An analytical sample, recrystallized repeatedly from benzene–cyclohexane, consisted of large, transparent prisms with a slightly pink cast, m. p. 153.5–154°.

Anal. Calcd. for $C_{20}H_{14}O$: C, 88.86; H, 5.22. Found: C, 88.90; H, 5.32.

9-(*p*-Methoxyphenyl)-phenanthrene (XII). (a) **By Alkylation of the Phenol.**—A 0.5-g. portion of the phenol was dissolved in 5% sodium hydroxide and alkylated in the usual way with methyl sulfate. The product was crystallized from cyclohexane to give flat colorless needles, m. p. 155.5–156°.

(b) **From 2-(ω-Methoxyaceto)-biphenyl.**—A Grignard reagent was prepared from 7.3 g. of *p*-bromoanisole and to this was added 5.5 g. of 2-(ω-methoxyaceto)-biphenyl.[7] The mixture was refluxed for eighteen hours and hydrolyzed with ammonium chloride solution. Concentration of the ethereal solution and distillation of the residue under reduced pressure, gave an 87% yield of crude carbinol. The carbinol was not purified, but used directly in further reactions.

One gram of the crude carbinol was heated with 2 g. of potassium bisulfate[14] for one hour at 160° and the product extracted by use of benzene. The benzene solution was washed, decolorized with charcoal, concentrated, and cyclohexane added. Yellow crystals (0.3 g., 31% from ketone) were obtained, m. p. 146–152°. A single recrystallization and sublimation yielded white crystals, m. p. 153–154°, which did not depress the melting point of the product obtained by procedure a.

Anal. Calcd. for $C_{21}H_{16}O$: C, 88.70; H, 5.67. Found: C, 88.54; H, 5.51.

9-(*p*-Acetoxyphenyl)-phenanthrene was prepared by acetylation of the phenol (VII) with acetic anhydride in pyridine. Twice recrystallized from ethanol, it formed white elongated plates, m. p. 147.5–148.5°.

Anal. Calcd. for $C_{22}H_{16}O_2$: C, 84.59; H, 5.16. Found: C, 84.61; H, 5.17.

9-(*p*-Methoxyphenyl)-10-phenanthramide (V).—The keto nitrile above (2 g.) was added with stirring to 20 ml. of cold concentrated sulfuric acid. After the mixture had been kept cold for three hours, it was poured on ice and the mixture centrifuged. The yellow solid which separated was taken up in ether, washed and dried. Upon evaporation of the solvent, 0.7 g. of a yellow solid was obtained. Recrystallization of 0.6 g. of the crude product from chloroform gave 0.4 g. (23%), m. p. 164–166°. The analytical sample melted at 166–166.5°.

Anal. Calcd. for $C_{22}H_{17}O_2N$: C, 80.71; H, 5.24. Found: C, 80.80; H, 5.27.

The product could be distilled under reduced pressure without change.

Action of Nitrous Acid on 9-(*p*-Methoxyphenyl)-10-phenanthramide (V).—The amide (V, 0.16 g.) was dissolved in a mixture containing 10 ml. of acetic acid and 3 ml. of methyl ethyl ketone. The solution was cooled in an ice-bath and over the period of thirty minutes, 0.3 g. of solid sodium nitrite was added. The mixture was allowed to warm to room temperature and the solid which formed was collected and recrystallized from ethanol as colorless crystals, m. p. 208–214°. An analytical sample obtained by crystallizing twice from ethanol melted at 234–234.5°.

Anal. Calcd. for $C_{22}H_{14}O_2$: C, 85.14; H, 4.55. Found: C, 85.48; H, 4.78.

Summary

It has been shown that α-(2-biphenylyl)-β-keto nitriles undergo aromatic cyclodehydration to yield phenanthrene derivatives.

DURHAM, N. C. RECEIVED AUGUST 27, 1949

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[13] Under these conditions, we have found that 9-acetophenanthrene is reduced to 9-ethylphenanthrene in 58% yield; *cf.* Mosettig and Van de Kamp, THIS JOURNAL, **55**, 3442 (1937).

[14] Potassium bisulfate has been used previously in effecting an aromatic cyclodehydration (Bradsher and Amore, *ibid.*, **65**, 2016 (1943)).