Anal. Calcd. for $C_8H_7Cl_2NO_2$: C, 43.66; H, 3.21. Found: C, 43.45; H, 3.30.

9-Phenanthryl-(2-methoxy-3,5-dichlorophenyl)-carbinol (XIV).—The 9-phenanthryl-magnesium Grignard was prepared by the method of Bachmann[16] from 0.65 g. of magnesium, 0.645 g. of 9-bromophenanthrene,[17] a crystal of iodine and 15 cc. each of dry ether and dry benzene, and refluxed seven hours in a nitrogen atmosphere. To it was added gradually and with cooling a solution of 5 g. of 2-methoxy-3,5-dichlorobenzaldehyde (XIII) in 35 cc. of benzene. A milky white precipitate resulted; after standing overnight, the benzene–ether layer was decanted, and the precipitate decomposed with 40 cc. of 20% sulfuric acid and ice. The yellow oil which formed soon solidified, and was dissolved in benzene. The solution was treated with charcoal, and, on addition of a little petroleum ether, deposited 3.6 g. (37%) of white crystals, m. p. 178–179°.

Anal. Calcd. for $C_{22}H_{16}Cl_2O_2$: C, 68.81; H, 4.21. Found: C, 68.90; H, 4.24.

Reduction of XIV.—The carbinol XIV (1 g.) was refluxed with 1 g. of iodine, 1 g. of red phosphorus, and 2 cc. of water in 20 cc. of acetic acid for four hours. The solution was filtered hot, poured into water, and the white precipitate which formed, collected and recrystallized from benzene–petroleum ether. White granular crystals (0.16 g.), m. p. 139–143°, were obtained; the product was triturated with a few cc. of Claisen alkali, washed thoroughly with water, and recrystallized from benzene–petroleum ether. The product obtained (0.125 g., m. p. 145–146°) is the methyl ether of the desired compound III.

Anal. Calcd. for $C_{22}H_{16}Cl_2O$: C, 71.94; H, 4.39. Found: C, 71.96; H, 4.40.

The benzene–petroleum ether mother liquors from which the above compound was isolated were extracted with three 10-cc. portions of Claisen alkali; on allowing the extract to stand five hours after acidification, 0.22 g. of a buff-colored precipitate was obtained, m. p. 136–138°. After treatment with charcoal and recrystallization from ethanol, fluffy white needles of III, m. p. 137.5–138.5°, were obtained, which showed no depression on mixed m. p. with the product of Tarbell and Wystrach.[1]

Compound III was also obtained by demethylation of the above methyl ether, by refluxing it with acetic-hydrobromic acid for several hours.

Attempted Synthesis of 9-(2-methoxy-3,5-dichlorobenzoyl)-phenanthrene.—A Friedel–Crafts reaction between 2,4-dichloroanisole,[18] aluminum chloride and 9-phenanthroyl chloride[19] did not yield the desired ketone under several sets of conditions. Using a mixture of nitrobenzene and tetrachloroethane as solvents at 5° for two days, 9-phenanthroic acid and 2,4-dichloroanisole were the only products obtained. They were also obtained in other runs using carbon disulfide as solvent. In another run, in which the reaction mixture was warmed on the steam-bath for a day, the crude product was submitted to Clemmensen reduction. The only product isolated was 2,4-dichlorophenyl 9-phenanthroate,[1,20] m. p. and mixed m. p. 181.5–182.5°

Attempts to rearrange this ester with aluminum chloride at 150° and at 110° gave none of the desired phenanthroyldichlorophenol.

Summary

The product obtained by heating the 9-phenanthrylmethyl ether of 3,5-dichlorosalicylic acid has been shown by synthesis to be 2-(9-phenanthrylmethyl)-4,6-dichlorophenol. 2-(9-Methyl-10 phenanthryl)-4,6-dichlorophenol has been synthesized by Bradsher's phenoxyethylcarbinol method, while a fluorene derivative (9-ethyl-9-(2-hydroxy-3,5-dichlorophenyl)-fluorene) has been obtained from the olefin oxide synthesis. Numerous new intermediates are described.

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[16] W. E. Bachmann, This Journal, **56**, 1363 (1934).

[17] Austin, *J. Chem. Soc.*, **93**, 1760 (1908).

[18] Holleman, *Rec. trav. chim.*, **37**, 96 (1918).

[19] Shoppee, *J. Chem. Soc.*, 37 (1933); Mosettig and van de Kamp, This Journal, **55**, 2995 (1933).

[20] A compound which was obtained in the previous work,[1] m. p. 114.5–115°, and was believed to be ethyl 9-phenanthroate, has now been found by mixed m. p. to be methyl 9-phenanthroate. Shoppee[19] reports the same m. p. for the methyl ester. The percentage composition of the methyl and ethyl esters is very similar, and our previous account[1] of ethyl phenanthroate should be disregarded.

Rochester, New York Received February 11, 1946

[Contribution from the Chemical Laboratory of Duke University]

Aromatic Cyclodehydration. XVIII.[1] Phenanthrene Derivatives by the Cyclization of Ketones

By Charles K. Bradsher and Lennard J. Wissow[2]

Previous communications of this series have described the preparation of phenanthrene derivatives by the cyclization of biphenylyl glycols,[3] their monoethers,[4] olefin oxides,[5] and an amino alcohol.[4] Although the suggestion has been made repeatedly[5,6a,6b] that ketones or aldehydes are intermediates in such a cyclization, no instance of their isolation or synthesis has been reported.[7]

Both the isolation and synthesis of such an intermediate has now been accomplished. In an effort to synthesize 2-chloro-9,10-diphenylphenanthrene (VI, X = Cl) by the glycol ether method,[4b] the lithium reagent prepared from 2-iodo-4′-chlorobiphenyl (I, X = Cl) was treated with desyl phenyl ether, and the resulting crude carbinols refluxed with a mixture of hydrobromic and acetic acids. The reaction product, on analysis, was found to have the composition of (4′-chlorobiphenyl-2)-phenylbenzoylmethane (IV, X

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[1] For the preceding communication of this series see This Journal, **66**, 1281 (1944).

[2] Eli Lilly Fellow, 1943–1944.

[3] Bradsher and Wissow, This Journal, **65**, 2304 (1943).

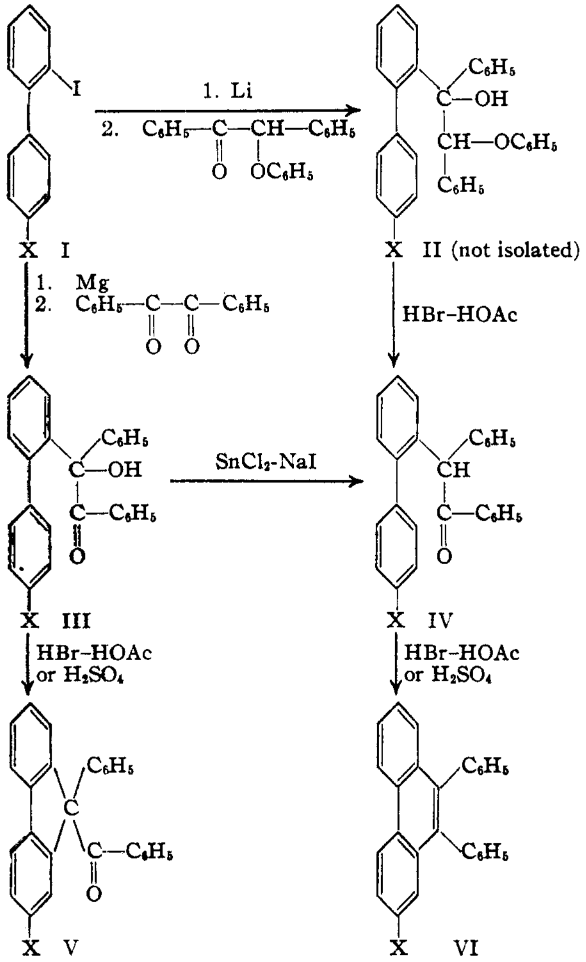
[4] (a) Bradsher and Tess, *ibid.*; **61**, 2184 (1939); (b) Bradsher and Rosher, *ibid.*, **61**, 1524 (1939).

[5] *E. g.*, Bradsher, *ibid.*, **61**, 3131 (1939).

[6] (a) Bradsher, *ibid.*, **62**, 486 (1940); (b) Bradsher and Wert, *ibid.*, **62**, 2806 (1940).

[7] The preparation and cyclization of a related keto-ester has been described by Schönberg and Warren (*J. Chem. Soc.*, 1838 (1939)), and by Geissmann and Tess (This Journal, **62**, 514 (1940)).

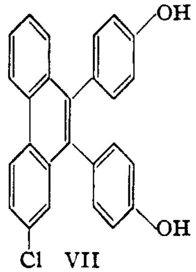
= Cl), while further refluxing in the acidic mixture yielded the expected chlorodiphenylphenanthrene (VI, X = Cl). The ketone (IV, X = Cl) was synthesized by the reaction of benzil with one mole of the Grignard reagent prepared from 2-iodo-4′-chlorobiphenyl (I, X = Cl), followed by reduction[8] of the hydroxyketone (III, X = Cl) thus obtained.



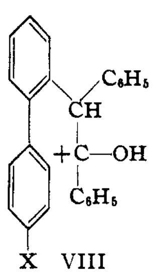
The chlorine-free ketone (IV, X = H) prepared in like manner starting from 2-iodobiphenyl (I, X = H) was found to cyclize more readily than its chlorine-containing counterpart (IV, X = Cl), an effect which might be predicted from the known deactivating influence of a halogen substituent on an aromatic nucleus,[9] as well as the previously observed difficulty in effecting cyclization *meta* to a chlorine atom.[10]

A similar effect was noted upon cyclization of the biphenylylbenzoins (III), the unsubstituted hydroxy ketone (III, X = H) yielding a fluorene derivative (V, X = H) more readily than its chlorine-containing analog (III, X = Cl). This cyclization affords a new and quite general method for the preparation of 9-phenyl-9-benzoylfluorene[11] (V, X = H) and its derivatives.

The glycol ether method was successfully applied to the synthesis of 2-chloro-9,10-*bis*-(*p*-hydroxyphenyl)-phenanthrene (VII) starting from iodochlorobiphenyl and anisoin methyl ether.



VII



VIII
(X = Cl or H)

In this case no ketonic intermediate was isolated.

The isolation of (4′-chlorobiphenylyl-2)-phenylbenzoylmethane[12] (IV, X = Cl) in the cyclization of 2-phenoxy-1,2-diphenyl-1-(4′-chlorobiphenylyl-2)-ethanol (II, X = Cl), is significant as it affords support to the conjecture[6a] that the phenanthrene cyclization is closely related to that yielding anthracene derivatives. The mechanism proposed for the anthracene cyclization[13,14,15] may be readily extended to the cyclization under discussion. The first step is undoubtedly the formation of the conjugate acid (VIII)[16] which cyclizes by the electrophilic attack of the positive carbon upon the *ortho* position of the adjacent benzene ring, followed by elimination of first a proton and then a molecule of water.

Experimental

Derivatives from 2-Iodo-4′-chlorobiphenyl

(4′-Chlorobiphenylyl-2)-benzoin (III, X = Cl).—To the Grignard reagent prepared from 18.9 g. of 2-iodo-4′-chlorobiphenyl[17] was added 10.5 g. of benzil in dry ether. The mixture was refluxed for three hours during which time an ether-insoluble red oil was formed. After decomposition of the mixture in the usual way with dilute sulfuric acid, the organic layer was washed, dried, concentrated, and the residue crystallized from ethanol. The product, 6.6 g. (33% calculated from benzil), was a white solid (m. p. 141–143°) pure enough for further reactions, but repeated recrystallization gave small white needles, m. p. 145.5–146.5°.

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[8] In this reduction, the stannous chloride solution used by Werner (*Ber.*, **39**, 1286 (1906)) for the reduction of phenylbenzoin was found to be less effective than the mixture of stannous chloride and sodium iodide recommended by Wanscheidt and Moldavski (*ibid.*, **64B**, 917 (1931)) for the reduction of triarylcarbinols.

[9] Price, *Chem. Rev.*, **29**, 37, 54 (1941).

[10] *E. g.*, Roberts and Turner, *J. Chem. Soc.*, 1832 (1927).

[11] Hanriot and St. Pierre, *Bull. soc. chim.*, [3] **1**, 774 (1889); Klinger and Lonnes, *Ber.*, **29**, 2152 (1896); Werner and Grob, *ibid.*, **37**, 2887 (1904).

[12] The isolation of an aldehyde or ketone would not be possible in every case, but is probably to be realized only when the rate of formation of the ketone significantly exceeds that of cyclization.

[13] Bradsher and Smith, Abstracts of Papers presented before the Division of Organic Chemistry at the 103rd meeting of the American Chemical Society in Memphis, Tenn., April, 1942.

[14] Berliner, THIS JOURNAL, **64**, 2894 (1942).

[15] Bradsher and Smith, *ibid.*, **65**, 854 (1943).

[16] Properly, the conjugate acid, rather than the ketone, should be considered as the true intermediate in the cyclization.

[17] Bradsher and Wissow, THIS JOURNAL, **68**, 404 (1946).

Anal. Calcd. for $C_{26}H_{19}O_2Cl$: C, 78.29; H, 4.80. Found:[18] C, 78.49; H, 4.94.

(4′-Chlorobiphenylyl-2)-phenylbenzoylmethane (IV, X = Cl).—(a) By reduction of (4′-chlorobiphenylyl-2)-benzoin: to a boiling solution containing 1.99 g. of the above benzoin (II, X = Cl) and 0.1 g. of sodium iodide in 15 ml. of acetic acid, a solution of 1.17 g. of stannous chloride in 3 ml. of concentrated hydrochloric acid was added cautiously. After refluxing for five minutes, the mixture was poured into a mixture of equal parts ice and hydrochloric acid. The tacky solid was recrystallized from ethanol with stirring to give 1.47 g. (77%) of a white powder, m. p. 125–127°, suitable for cyclization. An analytical sample obtained by recrystallization melted at 126.5–128°.

(b) From crude 1,2-diphenyl-1-(4′-chlorobiphenylyl-2)-2-phenoxyethanol: the lithium reagent was prepared in the usual way from 7.6 g. of 2-iodo-4′-chlorobiphenyl and to it was added a solution of 6.5 g. of desyl phenyl ether[4b] in dry benzene. The mixture was refluxed for three hours, decomposed with ice and water, and the organic layer separated and concentrated. To the residue was added 50 ml. each of acetic and 48% hydrobromic acid, and the mixture refluxed for two days. The product was taken up in benzene, the solution washed and concentrated and the residue distilled *in vacuo*. Crystallization of the distillate from ethanol gave 1.1 g. (13%) of ketone, m. p. 123–127°. Somewhat poorer results were obtained using the Grignard rather than the lithium reagent, an 8% yield (m. p. 120–122°) being obtained. On recrystallization, the ketone melted at 127–128° and showed no depression of melting point when mixed with the product obtained in (*a*).

Anal. Calcd. for $C_{26}H_{19}OCl$: C, 81.56; H, 4.96. Found:[19] C, 81.58; H, 5.02.

2-Chloro-9,10-diphenylphenanthrene (VI, X = Cl).—(a) Hydrobromic–acetic acid cyclization: a mixture of 0.25 g. of (4′-chlorobiphenylyl-2)-phenylbenzoylmethane, 5 ml. of acetic acid, and 5 ml. of 48% hydrobromic acid was refluxed for seventy-five hours, at which time the oily suspension had completely solidified. The product was collected and crystallized from acetic acid to yield 0.16 g. (68%) of small white needles, m. p. 204–205°.

(b) Sulfuric acid cyclization: a solution of 0.2 g. in 2.5 ml. of concentrated sulfuric acid was kept at room temperature for one hour and then poured on ice. The product was crystallized from acetic acid, m. p. 204–206°; yield 0.1 g. (53%). Repeated crystallization of the product gave white needles, m. p. 208–209°.

Anal. Calcd. for $C_{26}H_{17}Cl$: Cl, 9.71. Found[18]: Cl, 9.41.

2-Chloro-9-phenyl-9-benzoylfluorene (V, X = Cl).—(a) Sulfuric–acetic acid cyclization: to a boiling solution of 0.2 g. (4′-chlorobiphenylyl-2)-benzoin in 20 ml. of acetic acid, one drop of sulfuric acid was added and the solution refluxed for ten minutes. Upon standing, there precipitated 0.14 g. (73%) of white crystals, m. p. 161–162°.

(b) Hydrobromic–acetic acid cyclization: a mixture of 0.2 g. of the carbinol and 5 ml. each of acetic and hydrobromic acids was refluxed for twelve hours. The product was crystallized from acetic acid, m. p. 159–161°; yield 0.1 g. (52%). Recrystallization of a sample from acetic acid gave small well-defined cubes, m. p. 164–165°.

Anal. Calcd. for $C_{26}H_{17}OCl$: C, 81.99; H, 4.50. Found[18]: C, 81.74; H, 4.59.

2-Chloro-9,10-bis-(*p*-hydroxyphenyl)-phenanthrene (VII).—To the Grignard reagent prepared from 6.94 g. of 2-iodo-4′-chlorobiphenyl, a solution of 5.6 g. of anisoin methyl ether[20] in ether was added followed by a quantity of dry benzene to keep it all in solution, and the mixture was refluxed for fourteen hours. After decomposition with cold dilute hydrochloric acid, the benzene layer was washed and concentrated. The residue was dissolved in 50 ml. of acetic acid, 50 ml. of hydrobromic acid added and the whole refluxed for forty-eight hours. Attempts to isolate a crystalline intermediate at this point failed. Refluxing was continued with the exclusion of air (mercury seal) for an additional ninety-six hours. After cooling, the product was taken up in benzene and the benzene layer extracted with 10% sodium hydroxide solution. Acidification of the alkaline extract gave 1 g. (13%) of a solid product, m. p. 265–267°.

Repeated recrystallization from water–ethanol mixtures gave small matted white needles, m. p. 276–278°.

Anal. Calcd. for $C_{26}H_{17}O_2Cl$: C, 78.80; H, 4.28. Found[18]: C, 79.10; H, 4.57.

Derivatives from 2-Iodobiphenyl

2-(Biphenylyl)-benzoin (III, X = H) was prepared essentially as described for the preparation of the chloro derivative (III, X = Cl) except that the Grignard reagent from 16.8 g. of iodobiphenyl was refluxed with 10.5 g. of benzil for only thirty minutes. The crude yellow solid was pure enough for further reactions, m. p. 144–148°; yield 9.04 g. (50%).

Recrystallization from ethanol yielded flat white needles, m. p. 149.5–150°.

Anal. Calcd. for $C_{26}H_{20}O_2$: C, 85.69; H, 5.53. Found[18]: C, 85.25; H, 5.72.

(2-Biphenylyl)-phenylbenzoylmethane (IV, X = H).—Reduction of the hydroxy ketone above was effected as in the previous case (IV, X = Cl). The oily product, once crystallized from ethanol, gave 53.5% yield, m. p. 96–98°. An analytical sample prepared by recrystallization, was a white crystalline solid, m. p. 98–99°.

Anal. Calcd. for $C_{26}H_{20}O$: C, 89.62; H, 5.79. Found[19]: C, 89.96; H, 5.55.

Cyclization of (2-Biphenylyl)-phenylbenzoylmethane (IV, X = H).—Cyclization was effected with hydrobromic-acetic acid as in the previous case (IV, X = Cl) except that only fifteen hours refluxing was required for complete solidification of the oil. Crystallization from acetic acid gave 89% yield of 9,10-diphenylphenanthrene (VI, X = H), m. p. 234–236°, which gave no depression of melting point when mixed with an authentic[4b] sample.

Cyclization in concentrated sulfuric acid at room temperature for two hours gave a slightly poorer yield (48%) than did a mixture of acetic and sulfuric acids (53%). The yields with hot concentrated sulfuric acid were quite low, evidently due to sulfonation.

Cyclization of 2-Biphenylylbenzoin (III, X = H).—When 2 g. of the benzoin (III, X = H) was refluxed for one hour in the acetic–hydrobromic acid mixture and the resulting solid recrystallized from acetic acid, 1.2 g. (63%) of white crystals, m. p. 169–170° (lit.[11] 172°) was obtained.

Summary

It has now been demonstrated by isolation and synthesis that aromatic cyclodehydration of the phenanthrene type may involve a ketone intermediate.

A new route to 9-aryl-9-aroylfluorenes has been found.

DURHAM, N. C. RECEIVED MARCH 15, 1946

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[18] Analysis by Arlington Laboratories.

[19] Analysis by Dr. T. S. Ma, University of Chicago.

[20] Irvine and Moodie, *J. Chem. Soc.*, 536 (1907).