Poly-*p*-cyclohexylstyrene: mol. wt.[15] about 28,000; softening point 186–230°. *Anal.* Calcd. for $(C_{14}H_{18})_x$: C, 90.26; H, 9.73. Found: C, 89.97; H, 9.67.

Summary

1. The preparations of *m*-*t*-butylstyrene, *m*-*s*-butylstyrene and *p*-cyclohexylstyrene are described.

2. The polymers of these monomers have been prepared and characterized.

URBANA, ILL.

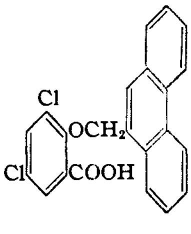
RECEIVED FEBRUARY 20, 1946

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

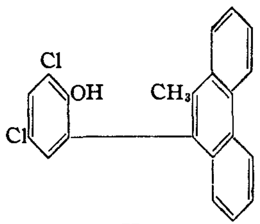
The Synthesis of 9-Phenanthrylmethyldichlorophenol and Related Compounds

BY D. S. TARBELL AND YOSHIO SATO

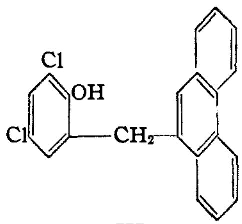
In a study of the effect of heat on benzyl, β-naphthylmethyl and 9-phenanthrylmethyl ethers of dichlorosalicylic acid,[1] it was found that the phenanthrene derivative I differed from the other two in its behavior. When heated at 230°, it evolved carbon dioxide in 75% yield and formed a phenolic rearrangement product of the composition corresponding to 2-(9-methyl-10-phenanthryl)-4,6-dichlorophenol (II) or 2-(9-phenanthrylmethyl)-4,6-dichlorophenol (III). The structure of the rearrangement product was not established by Wystrach, but it is shown in the present paper to be III, by the synthesis of both II and III.



I



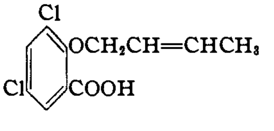
II



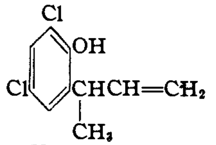
III

It was considered at the outset that the most likely structure for the product was II, since this corresponds to a rearrangement with attachment of the γ-carbon atom (inversion) of the pseudo-allyl group in I. It was shown previously[2] that the rearrangement of O-crotyl-3,5-dichlorosalicylic acid (IV) led to V, by inversion, and I can be regarded as a γ-substituted allyl ether similar to IV.

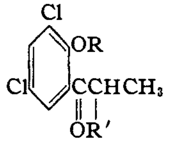
The absorption spectrum of the rearrangement product did not point unambiguously to either structure II or III. The most direct method of synthesis of II is the method of Bradsher and Schneider,[3] in which a 2-xenylphenylphenoxyethylcarbinol is cyclized to a 9-arylphenanthrene. The intermediates we employed for the synthesis are indicated below and the reactions proceeded well, following the general procedures of Bradsher and co-workers. The phenoxypropiophenone IX yielded the carbinol X when treated with 2-xenylmagnesium iodide, and this was cyclized to a compound, m. p. 128–129°, not, however, identical with the rearrangement product, which melts at 137.5–138.5°. The cyclization product was shown to be II by the similarity of its absorption curve to that of 9-methyl-10-phenylphenanthrene (Fig. 1). Further, on vigorous oxidation with chromic acid, it yielded what was probably phenanthrenequinone, although the small amount available prevented complete identification.[4]



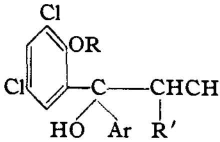
IV



V



VI, R = H, R' = H
VII, R = CH_3, R' = H
VIII, R = CH_3, R' = Br
IX, R = CH_3, R' = OC_6H_5



X, R = CH_3,
R' = OC_6H_5,
Ar = 2-xenyl

As an alternative synthesis of II, the olefin oxide method[5] was investigated at the same time. The carbinol X was prepared by the action of 2-

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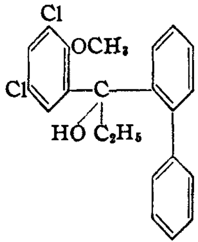
[1] Tarbell and Wystrach, THIS JOURNAL, **65**, 2149 (1943).

[2] Tarbell and Wilson, *ibid.*, **64**, 607 (1942).

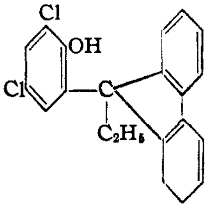
[3] Bradsher and Schneider, *ibid.*, **60**, 2960 (1938).

[4] One point in the synthesis of II may be mentioned. The bromination of the acylphenol VI to give the α-bromoketone was slow and unsatisfactory, whereas bromination of the methyl ether VII went smoothly, yielding VIII. A somewhat analogous situation was observed by Shriner and Witte (THIS JOURNAL, **61**, 2328 (1939)). The reason for the slow rate of substitution of the α-hydrogens in the o-acylphenol VI is probably the hydrogen bonding between the carbonyl group and the phenolic hydroxyl. This suggests that some interesting information might be gained by comparing rates of bromination of o-acylphenols and the amount of hydrogen bond formation as shown by infrared studies.

[5] Bradsher, THIS JOURNAL, **61**, 3131 (1939), and later papers.



XI



XII

xenylmagnesium iodide on the propiophenone VI, followed by methylation; the carbinol was then heated with potassium acid sulfate to dehydrate it, treated with perphthalic acid to form the oxide, and the product refluxed with hydrobromic–acetic acid. The compound obtained melted at 99–100°, and was shown to be 9-ethyl-9-(2-hydroxy-3,5-dichlorophenyl)-fluorene XII. The compound XII was oxidized by chromic acid to fluorenone; furthermore its absorption spectrum (Fig. 1) is very similar to that of 9-phenylfluorene.[6] The formation of the fluorene XII instead of the phenanthrene II by this synthesis may be due to a direct dehydration of the carbinol XI by the potassium acid sulfate; another possibility is that the olefin was actually formed from the carbinol, but was not completely oxidized to the oxide, and was cyclized to the fluorene by the hydrobromic acid treatment.[7]

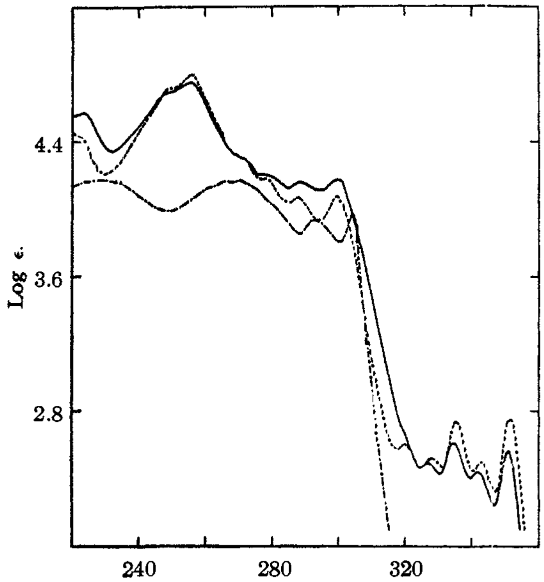
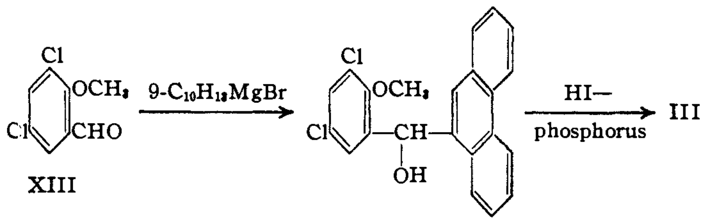


Fig. 1.—Absorption spectra: ——, 2-(9-methyl-10-phenanthryl)-4, 6-dichlorphenol; ------, 9-methyl-10-phenylphenanthrene; —·—·—, 9-ethyl-9-(2-hydroxy-3,5-dichlorophenyl)-fluorene.

Since the rearrangement product was thus shown not to be II, the synthesis of III was carried out. The obvious method of acylating 2,4-dichloroanisole with 9-phenanthroyl chloride, followed by Clemmensen reduction and demethylation, was unsuccessful; the only product isolated was 2,4-dichlorophenyl 9-phenanthroate (*cf.* 1). Two trials of a Fries reaction of 2,4-dichlorophenyl 9-phenanthroate failed to yield the desired acylphenol. III was finally obtained by the scheme



XIII XIV

Demethylation occurred during the reduction, and the product was shown to be identical with the original rearrangement product.

The reason why I rearranges without inversion to give III instead of II is not clear. It may be that the 9,10-phenanthrene double bond is not sufficiently aliphatic in character to imitate the behavior of γ-substituted allyl compounds. Another possibility which seems more plausible, is that the formation of the cyclic activated complex, which is undoubtedly a prerequisite to rearrangement with inversion, is prevented by steric interference from the bulky phenanthrene ring, especially the number 1 carbon.

Experimental[8]

2-Hydroxy-3,5-dichloropropiophenone (VI).—This product was prepared in 90% yield by Fries rearrangement at 155° of 2,4-dichlorophenyl propionate,[9] following Hartung's procedure[10]; the compound melted after crystallization from petroleum ether (90–100°), at 116.5–117.5°. Chien and Yin report the m. p. as 115–116°.

2-Methoxy-3,5-dichloropropiophenone (VII).—The hydroxypropiophenone VI (2 g.) was transformed with aqueous alkali into the yellow insoluble sodium salt, which was dried, dissolved in acetone and warmed gently with an excess of dimethyl sulfate, enough aqueous alkali being added to keep the solution alkaline. The excess dimethyl sulfate was decomposed by heating with alkali, and the reaction mixture allowed to evaporate at room temperature for several days. The methyl ether crystallized as long white needles (1.6 g., 80%), m. p. 35.5–37.5°, which was raised to 37–38° by recrystallization from dilute methanol.

Anal. Calcd. for $C_{10}H_{10}Cl_2O_2$: C, 51.53; H, 4.32. Found: C, 51.47; H, 4.43.

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[6] Jones, This Journal, **67**, 2021 (1945).

[7] 9,9-Dialkylxenylcarbinols are known to be cyclized to fluorenes by sulfuric acid (Bradsher and Amore, *ibid.*, **65**, 2016 (1943); Anchell and Blatt, *ibid.*, **63**, 1948 (1941); McPhee and Ball, *ibid.*, **66**, 1636 (1944)), but cyclization by potassium acid sulfate does not seem to have been observed.

[8] All melting points corrected; analyses by Mr. Carl Claus and Dr. Carl Tiedcke. Absorption curves were taken in alcohol solution, using a Beckmann spectrophotometer. We are indebted to Dr. C. K. Bradsher for a sample of 9-methyl-10-phenylphenanthrene.

[9] Obtained as a liquid, b. p. 136–138° (18 mm.), n^{24}D 1.5265; Chien and Yin, *J. Chinese Chem. Soc.*, **7**, 40 (1939) (*C. A.*, **34**, 1979 (1940)), report a b. p. of 148° (14 mm.).

[10] Hartung, Munch, Miller and Crossley, This Journal, **53**, 4149 (1931).

α-Bromo-2-methoxy-3,5-dichloropropiophenone (VIII).—The methoxy compound VII (11.7 g.) dissolved in 23 cc. of chloroform was treated dropwise with 8 g. of bromine; the mixture was heated at 40–50° for one half hour after addition was complete to discharge the bromine color. Air was blown over the surface to remove the hydrogen bromide, the solution was washed with dilute bisulfite, then with water and the chloroform removed. The residue, after being dissolved in methanol and decolorized with charcoal, crystallized as thin white plates (10.4 g., 67%) m. p. 74–75.5°, essentially unchanged by another crystallization from methanol.

Anal. Calcd. for $C_{10}H_9BrCl_2O_2$: C, 38.49; H, 2.91. Found: C, 38.35; H, 2.84.

α-Phenoxy-2-methoxy-3,5-dichloropropiophenone (IX).—This product, prepared by the method of Bradsher and Rosher[11] from the bromopropiophenone VIII, was obtained in 57% yield, m. p. 45.5–46.5° after two crystallizations from alcohol.

Anal. Calcd. for $C_{16}H_{14}Cl_2O_3$: C, 58.96; H, 4.34. Found: C, 59.04, H. 4.45.

α-Phenoxyethyl-(2-methoxy-3,5-dichlorophenyl)-2-xenylcarbinol (X).—To a solution of the Grignard prepared from 0.3 g. of magnesium, 3.5 g. of 2-iodobiphenyl and 20 cc. of ether was added 3.25 g. of the phenoxypropiophenone (IX) in 20 cc. of dry benzene. The ether was then removed and the mixture warmed on the steam-bath for ninety minutes. The product was decomposed with ammonium chloride solution, the mixture extracted with ether and dried, and, on evaporation of the ether, 0.4 g. of product, m. p. 194–202°, precipitated. Recrystallization from benzene yielded white granular crystals, (0.2 g.), m. p. 205.5–207°. Concentration of the combined mother liquors yielded 1.15 g. of additional product, m. p. 199–206.5°.

Anal. Calcd. for $C_{28}H_{24}O_3Cl_2$: C, 70.15; H, 5.05. Found: C, 69.93; H, 5.06.

2-(9-Methyl-10-phenanthryl)-4,6-dichlorophenol (III)—The crude carbinol (1.55 g.) was dissolved in a hot mixture of 20 cc. of acetic acid, 3 cc. of acetic anhydride and 18 cc. of propionic acid. To this was added gradually 26 cc. of 40% hydrobromic acid and the mixture was refluxed for forty-six hours. After standing several days in the refrigerator, about 1 cc. of oil on the surface was separated and dissolved in benzene. The remaining acid solution was neutralized with sodium hydroxide, and extracted with a total of 125 cc. of warm benzene, which was then washed with dilute sodium hydroxide to remove any free phenol. The combined benzene solutions were extracted with Claisen alkali; acidification yielded a grayish white precipitate, which was purified by vacuum sublimation, followed by crystallization from dilute alcohol. White granular crystals (0.12 g.), m. p. 128–129°, were obtained, which gave a depression on mixed m. p. with the rearrangement product.

Anal. Calcd. for $C_{21}H_{14}Cl_2O$: C, 71.40; H, 4.00. Found: C, 71.60; H, 4.09.

When 30 mg. of III was oxidized by the procedure described below for XII, about 1–2 mg. of a yellow-orange solid was obtained, which after recrystallization from dilute alcohol, melted at 200–202° (uncor.) on the heated stage. Phenanthrenequinone melts at 205–206°.

Ethyl-(2-hydroxy-3,5-dichlorophenyl)-2-xenylcarbinol.—This carbinol was made by the method previously described from 2.18 g. of magnesium, 2 cc. of 2-iodobiphenyl and 7.82 g. of 2-hydroxy-3,5-dichloropropiophenone (VI). The product was washed with cold petroleum ether to remove biphenyl, and after crystallization from benzene–petroleum ether (90–100°), yielded 6.5 g. (49%) of crystals, m. p. 114.5–115.5°.

Anal. Calcd. for $C_{21}H_{18}Cl_2O_2$: C, 67.57; H, 4.86. Found: C, 67,49; H, 4.76.

Ethyl-(2-methoxy-3,5-dichlorophenyl)-2-xenylcarbinol (XI).—The sodium salt of the carbinol described above (prepared from 3.7 g. of the carbinol and 2 g. of sodium hydroxide in a little water) was treated with 2 cc. of dimethyl sulfate and the mixture gently warmed on the steam-bath for a short time. The sticky white oil which formed was removed and dissolved in petroleum ether (60–70°); white crystals (2.4 g.) were obtained, whose m. p., 83–84°, was unchanged by recrystallization from the same solvent.

Anal. Calcd. for $C_{22}H_{20}Cl_2O_2$: C, 68.22; H, 5.21. Found: C, 68.22; H, 5.31.

9-Ethyl-9-(2-hydroxy-3,5-dichlorophenyl)-fluorene (XII).—The carbinol XI (2.4 g.) was intimately mixed[12] with 7.2 g. of freshly fused potassium acid sulfate and heated to 160° for ninety minutes in an oil-bath. The product was extracted with 75 cc. of benzene, washed with bicarbonate, dried and the benzene removed under reduced pressure. To the colorless viscous oil was added 100 cc. of 70% monoperthalic acid[13] and the mixture kept in the refrigerator for one day and at room temperature for four hours. The ethereal solution was washed with bicarbonate, dried, the solvent removed under diminished pressure, and the residual oil dissolved in 15 cc. acetic acid and dropped into 10 cc. of boiling hydrobromic acid (41%). Since the product did not dissolve completely, 10 cc. more of acetic acid and 5 cc. of acetic anhydride were added; the mixture was refluxed for forty-five hours, during which 7 cc. of acetic anhydride and 2.5 cc. of hydrobromic acid were added. After the cyclization mixture had stood in the refrigerator, 0.34 g. of white plates were obtained, whose m. p., 98–100°, was raised to 99–100° by crystallization from dilute alcohol.

Anal. Calcd. for $C_{21}H_{16}Cl_2O$: C, 71.00; H, 4.54. Found: C, 71.16; H, 4.31.

The **acetyl derivative** was prepared by refluxing 40 mg. of XII with 1.3 cc. of acetic anhydride for eight hours, and melted, after two recrystallizations from dilute acetic acid, at 143–144°.

Anal. Calcd. for $C_{23}H_{18}Cl_2O_2$: C, 69.53; H, 4.57. Found: C, 69.65; H, 4.62.

Hydrolysis of the acetyl derivative with methanolic potash yielded XII, as shown by a mixed m. p.

Oxidation to Fluorenone.—Thirty mg. of XII was refluxed with 0.25 g. of sodium dichromate[14] in 5 cc. of acetic acid for eighteen hours. About one-half of the acid was then evaporated, and 10 cc. of water containing four drops of concentrated sulfuric acid was added. The precipitate was collected, washed with a little 10% sodium hydroxide, with water and then vacuum-sublimed twice. The product (about 4 mg.) was recrystallized from dilute alcohol, and was shown to be fluorenone, m. p. 83–83.5°, by a mixed m. p. with an authentic sample.

2-Methoxy-3,5-dichlorobenzaldehyde (XIII).—The methylation of 3,5-dichlorosalicylaldehyde[15] caused a great deal of difficulty, due to the insolubility of the sodium salt. To 24 g. of 3,5-dichlorosalicylaldehyde, was added 7 g. of potassium hydroxide in 60 cc. of water. An insoluble deep yellow precipitate formed, and dimethyl sulfate was added with stirring to the above mixture. When the solution became colorless, more potassium hydroxide was added; when the yellow color reappeared, more dimethyl sulfate was added. This process was repeated about fifteen times during seven to eight hours, the mixture being maintained at 30–40°. At last, the excess dimethyl sulfate was decomposed by heating the alkaline solution, and the mixture when cooled deposited an oil which crystallized, giving 8.2 g. (32%) of long white needles, m. p. 86–88°. Recrystallization from alcohol with charcoal treatment yielded 6.2 g., m. p. 87–88°.

Anal. Calcd. for $C_8H_6Cl_2O_2$: C, 46.86; H, 2.95. Found: C, 46.91; H, 3.21.

The oxime, prepared in pyridine–alcohol, crystallized from alcohol as white cottony needles, m. p. 112.5–113.5°.

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(11) Bradsher and Rosher, THIS JOURNAL, **61**, 1525 (1939).

(12) *Cf.* Bradsher and Wert, *ibid.*, **62**, 2806 (1940); Bradsher and Burhams, *ibid.*, **62**, 3140 (1940).

(13) "Organic Syntheses," **20**, 70 (1940).

(14) *Cf.* France, Tucker and Forrest, *J. Chem. Soc.*, 7 (1945).

(15) Blitz and Stepf, *Ber.*, **37**, 4027 (1904).

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)).