[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

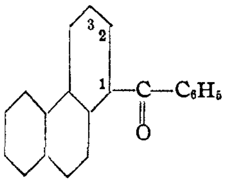
Synthesis of Phenanthrene Derivatives. II.[1] Benzoylphenanthrenes and Derivatives

BY W. E. BACHMANN

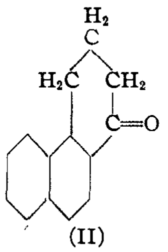
Willgerodt and Albert[2] reported that benzoyl chloride reacts with phenanthrene in carbon disulfide solution in presence of aluminum chloride and gives 9-benzoylphenanthrene having a melting point of 127°. Recently[1] we synthesized 9-benzoylphenanthrene and found it to have a melting point of 89.5–90°; another form which we have just obtained melts at 80–81°. In an attempt to determine the nature of Willgerodt and Albert's product, we have studied the reaction between benzoyl chloride and phenanthrene.

From the reaction between phenanthrene and benzoyl chloride in carbon disulfide we obtained a compound which melted at 148.5–149.5° which was proved to be 1-benzoylphenanthrene (I); this compound was easily isolated when the Perrier modification of the Friedel and Crafts reaction was employed. By running the reaction in nitrobenzene the three isomers, 1-benzoylphenanthrene, 2-benzoylphenanthrene and 3-benzoylphenanthrene were obtained. The compound reported by Willgerodt and Albert was not found.

The structures of the three new benzoylphenanthrenes were proved by synthesis. The 2- and 3-benzoylphenanthrenes were synthesized by the Grignard reaction from the corresponding cyanophenanthrenes and phenylmagnesium bromide. 1-Benzoylphenanthrene was obtained from 1-keto-1,2,3,4-tetrahydrophenanthrene (II) by the following reactions: treatment of the ketone with benzylmagnesium chloride gave 1-benzyl-1-hydroxy-1,2,3,4-tetrahydrophenanthrene (III); dehydration of this carbinol yielded 1-benzyl-3,4-dihydrophenanthrene (IV), which by dehydrogenation of the ring by selenium and oxidation of the methylene group in the side chain passed into 1-benzoylphenanthrene. When sulfur was used for dehydrogenation, the benzyl-3,4-dihydrophenanthrene was converted to 1-benzylphenanthrene (V) which was identical with the product obtained by reduction of the ketone from the Friedel and Crafts reaction. Further proof of the structure of 1-benzoylphenanthrene was obtained by cleavage of the ketone by potassium hydroxide; this reaction gave a small amount of 1-phenanthroic acid; that this acid was derived from the ketone and not from some impurity was proved by resynthesizing the ketone from the acid through the steps: 1-phenanthroic acid ⟶ 1-phenanthroyl chloride ⟶ 1-phenanthroic acid amide ⟶ 1-cyanophenanthrene ⟶ 1-benzoylphenanthrene.



(I)



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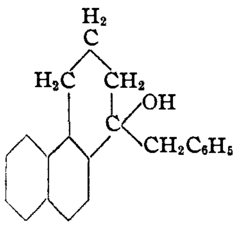

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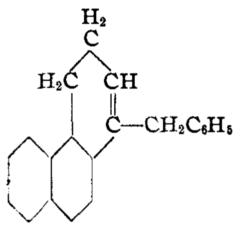

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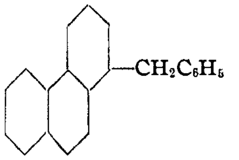

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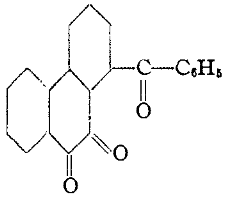

(VI)

In Table I is given a comparison of the properties of the four isomeric benzoylphenanthrenes. In three cases, two forms of the same ketone were obtained which possessed different crystalline shapes and different melting points. A mixture of the two forms usually melted near the melting point of the higher form; the solid obtained by cooling melted sharply at the value of the higher form. Other investigators also have observed that the phenanthrene derivatives seem to be particularly prone to possess this property of polymorphism.

Phenanthrylphenylcarbinols.—Reduction of the 1-, 2- and 3-benzoylphenanthrenes by sodium

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(1) For I, see Bachmann, THIS JOURNAL, **56**, 1363 (1934).

(2) Willgerodt and Albert, *J. prakt. Chem.*, [2] **84**, 383 (1911).

TABLE I

All of the compounds are colorless except the benzoylphenanthrenequinones

Position of group	Recryst. solvents	Cryst. form	M. p., °C.	Color with H_2SO_4	Analyses, %			
					Calcd.		Found	
Benzoylphenanthrenes, $C_{14}H_9COC_6H_5$								
1	AcMe	Prisms	148.5–149.5	Red-orange	89.4	5.0	89.8	5.0
1	Bz + alc.	Plates	148.5–149.5					
2	AcMe	Needles	117–118	Red-orange	89.4	5.0	89.0	5.0
2	Alc.	Plates	108–109					
3	AcMe	Stout prisms	111–112	Orange	89.4	5.0	89.0	5.0
3	Alc.	Long needles	107–108					
9	Bz + lig.	Needles[1]	89.5–90	Orange				
9	AcMe + alc.	Plates	80–81					
Phenanthrylphenylcarbinols, $C_{14}H_9CH(OH)C_6H_5$								
1	Alc.	Needles	125–126	Blue	88.7	5.6	88.9	5.5
2	AcMe + alc.	Needles	110–111	Violet-red	88.7	5.6	88.7	5.9
3	AcMe + alc.	Needles	128–129	Blue	88.7	5.6	88.7	5.7
Benzylphenanthrenes, $C_{14}H_9CH_2C_6H_5$								
1	AcOH	Needles	105–106	None	94.0	6.0	94.0	5.9
2	AcOH	Plates	107–108	None	94.6	6.0	94.0	5.9
2	AcMe + alc.	Plates	95–96					
3	AcOH	Needles	79–80	None	94.0	6.0	94.3	6.1
9	AcOH	Prisms[1]	153–154	None				
Benzoyl-9,10-phenanthrenequinones, $C_{14}H_7O_2COC_6H_5$								
1	Chlorobz.	Rhomboid plates	268–269	Brown	80.8	3.8	81.2	3.8
2	Chlorobz.	Needles	218–218.5	Brown	80.8	3.8	80.4	4.0
3[a]	Chlorobz.	Plates	209–210	Brown				
Phenanthryldiphenylcarbinols, $C_{14}H_9COH(C_6H_5)_2$								
2	Bz + MeOH	Stout needles	175–175.5	Red	90.0	5.6	90.0	5.9
3	Bz + MeOH	Broad needles	143.5–144.5	Blue	90.0	5.6	89.8	5.4
Phenanthryldiphenylbromomethanes, $C_{14}H_9CBr(C_6H_5)_2$								
2	Bz + lig.	Prisms	148–149		Br: 18.9		18.1	
3	Bz + lig.	Prisms	155–156		Br: 18.9		18.9	
Phenanthryldiphenylmethyl Peroxides, $C_{14}H_9(C_6H_5)_2COOC(C_6H_5)_2C_{14}H_9$								
2	Toluene	Rhomboid plates	190–191		90.2	5.3	90.5	5.6
3	Toluene	Rhomboid plates	195–196		90.2	5.3	90.1	5.5

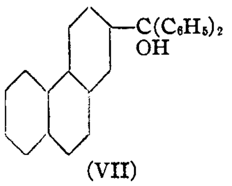
[a] Fieser, THIS JOURNAL, **51**, 3101 (1929), obtained this compound (m. p. 205–206°) by oxidation of the uncrystallizable product resulting from the action of phenylmagnesium bromide on 3-phenanthroyl chloride.

amalgam and alcohol gave the corresponding hydrols. The 2- and 3-phenanthrylphenylcarbinols were synthesized by the action of phenylmagnesium bromide on 2-phenanthraldehyde and 3-phenanthraldehyde, respectively; these products were identical with the hydrols obtained by reduction of the ketones. The hydrols give intense colors with concentrated sulfuric acid.

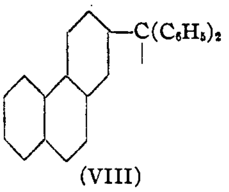
Benzylphenanthrenes.—The hydrols were reduced to benzylphenanthrenes by the action of phosphorus and hydriodic acid. None of these benzylphenanthrenes (Table I) corresponds to the "9-benzylphenanthrene" (m. p. 91–92°) reported by Willgerodt and Albert, although one form (m. p. 95–96°) of 2-benzylphenanthrene melts near their value.

Benzoyl-9,10-phenanthrenequinones (VI).—1-, 2- and 3-benzoyl-9,10-phenanthrenequinones were obtained by oxidation of the benzoylphenanthrenes by chromic acid in acetic acid; by recrystallization they were obtained in the form of golden-yellow crystals.

Phenanthryldiphenylmethyl Radicals.—Phenylmagnesium bromide reacted with 2-benzoylphenanthrene and gave 2-phenanthryldiphenylcarbinol (VII); 3-phenanthryldiphenylcarbinol was obtained in a similar manner from 3-benzoylphenanthrene. Both carbinols give intense colors with concentrated sulfuric acid. By reaction with acetyl bromide the carbinols were converted to the corresponding carbinol bromides. Molecular silver abstracted the halogen from the bromides and gave the free radicals, 2-phenanthryldiphenylmethyl (VIII) and 3-phenanthryldiphenylmethyl.



(VII)



(VIII)

These are the first examples of triarylmethyl radicals containing a phenanthryl group. A benzene solution of 2-phenanthryldiphenylmethyl is cherry-red in color; a solution of 3-phenanthryldiphenylmethyl is dark red. Exposure of the solutions to air results in a gradual loss of the red color with accompanying deposition of colorless crystals of the phenanthryldiphenylmethyl peroxides. The molecular state of the free radicals has not yet been determined.

The author is grateful to W. S. Struve for the analyses and for carrying out some of the reactions.

Experimental

Purification of Phenanthrene.—A kilo of technical 90% phenanthrene was heated with six liters of denatured alcohol; the hot solution was decanted from the insoluble material and cooled. One kilo of this recrystallized product was dissolved in 2200 cc. of hot glacial acetic acid; to the boiling solution was added gradually 72 cc. of an aqueous solution containing 60 g. of chromic anhydride; 30 cc. of concentrated sulfuric acid was then added slowly and the solution was refluxed for fifteen minutes more. After dilution with an equal volume of water and cooling, the mixture was filtered and the product was washed well with water. The product after distillation and recrystallization from alcohol was nearly colorless; after a second recrystallization the phenanthrene melted at 98.7–99.5°; yield, 750–800 g.[3]

Reaction of Benzoyl Chloride with Phenanthrene. (A) In Carbon Disulfide.—The reaction was carried out exactly as described by Willgerodt and Albert, including the isolation and purification of the product; by recrystallization from alcohol gleaming colorless needles were obtained which melted at 146–148°; after purification from acetone this 1-benzoylphenanthrene melted at 148.5–149.5°. In another run the crude product obtained from the reaction with 20 g. of phenanthrene was distilled under reduced pressure (b. p. 250–260° at 2 mm.) and the distillate was dissolved in a mixture of acetone and alcohol; after a few days in a refrigerator 2.35 g. of crystals (m. p. 140–144°) was filtered off; recrystallization from acetone raised the melting point to 148–149°.

(B) Perrier Method.—A mixture of 114 cc. of benzoyl chloride and 150 g. of aluminum chloride was heated in a 3-liter flask over a flame until a clear solution resulted. The cooled mixture was dissolved in 840 cc. of warm carbon disulfide and to this solution was added 204 g. of phenanthrene; hydrogen chloride was evolved but no heat. The solution was cooled to 0° and the solid which had precipitated was filtered off and hydrolyzed. The product obtained by distillation under reduced pressure was dissolved in ether; this solution deposited 30 g. of colorless crystals (m. p. 140–143°); the filtrate after concentration deposited a mixture of compounds which were not investigated. Treatment with hot acetone dissolved the 1-benzoylphenanthrene and left a few grams of insoluble high-melting material. The hot acetone solution was allowed to cool slowly undisturbed in order to get large prisms of the ketone; the large crystals were freed mechanically of the fine crystals of impurity adhering to them and then crystallized again from acetone; yield, 25 g.

(C) In Nitrobenzene.—To a solution of 160 g. of aluminum chloride in 750 cc. of nitrobenzene was added a solution of 100 g. of phenanthrene in 250 cc. of nitrobenzene; to the clear solution, which was kept below 0° throughout the reaction, was added gradually 70 cc. of benzoyl chloride. After being kept cold for two hours, the mixture was allowed to stand at room temperature for twelve hours and then hydrolyzed. The product which remained after the nitrobenzene was removed by steam distillation was dissolved in benzene; the dried benzene solution was distilled under reduced pressure (240–260° at 2 mm.). The distillate was dissolved in a mixture of acetone and alcohol and the solution kept at 0°. After several days 53 g. of benzoylphenanthrenes was filtered off; during the course of a month an additional 17 g. of crystals was obtained.

The mixture of ketones was dissolved in hot acetone and the solution was filtered from 2 g. of insoluble material; the hot acetone solution was allowed to cool slowly undisturbed; under these conditions the 3-benzoylphenanthrene crystallized in large stout prisms, the 1- and 2-isomers in fine needles. The mixture of needles and prisms was separated mechanically by sieving the needles through a fine wire gauze which retained the prisms; this procedure of slow crystallization from acetone followed by mechanical separation was repeated until the prisms were entirely free of fine crystals. The same procedure was frequently used in order to free the 2- and 1-isomers from small amounts of the 3-derivative.

The 1-benzoylphenanthrene present in the mixture of fine needles was isolated by recrystallization from acetone; the 1-isomer is less soluble than the 2-derivative and comes out first; an additional quantity of 1-benzoylphenanthrene was obtained by recrystallizing from alcohol the product obtained by evaporating the acetone filtrate. The 2-benzoylphenanthrene was most difficult to obtain pure; only after numerous recrystallizations from acetone and from alcohol was an appreciable amount of the pure substance isolated, although there seemed to be a considerable amount of this ketone in the mixture. From 100 g. of phenanthrene we isolated 32 g. (20%) of 3-benzoylphenanthrene, 5 g. (3%) of 2-benzoylphenanthrene and 10 g. (6%) of 1-benzoylphenanthrene.

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[3] Cohen and Cormier, THIS JOURNAL, **52**, 4363 (1930), used nitric acid in alcoholic solution to oxidize preferentially the anthracene in the mixture. We employed chromic acid in order to eliminate all possibility of explosion which Cohen and Cormier mention is possible if the final distillation of their product is carried too far.

2-Cyanophenanthrene and 3-Cyanophenanthrene.—Werner and co-workers[4] prepared these compounds from the phenanthrenesulfonic acids. We have found it convenient to make them from the phenanthroic acids, which are easily obtainable according to the directions of Mosettig and van de Kamp.[5] A mixture of 20 g. of 2-phenanthroic acid and 24 g. of phosphorus pentachloride was heated in a 250-cc. Claisen flask on a steam-bath for one-half hour; after five minutes a clear solution was obtained. After removal of the phosphorus oxychloride under reduced pressure at 120°, the phenanthroyl chloride was dissolved in 150 cc. of warm acetone; this solution was added to 400 cc. of ice-cold ammonium hydroxide in the course of five minutes. After ten minutes the phenanthroic acid amide was filtered and washed with water and methyl alcohol; yield, 20 g.

To prepare the cyanophenanthrene, an intimate mixture of 20 g. of 2-phenanthroic acid amide and 20 g. of phosphorus pentoxide was heated in a 20-cm. test-tube in an oil-bath at 140° for one hour; during this period the mixture was frequently pushed down and stirred about; after one-half hour the mixture was dark throughout and the volume had decreased to a small bulk. The liquid cyanophenanthrene was decanted and the residue was warmed with several portions of benzene; the test-tube was broken and the powdered residue was digested with benzene and filtered. The residue was then mixed with water; the acid amide which was recovered was treated again with phosphorus pentoxide. After recrystallization from alcohol, the 2-cyanophenanthrene melted at 108–109.5°, yield, 14 g. (77%). It is not unlikely that our high-melting product is a different form from that of Werner who reported 105°.

The 3-cyanophenanthrene was prepared in a similar manner from 3-phenanthroic acid; the yield of acid amide was nearly quantitative; from 20 g. of the acid amide 11.2 g. (62%) of 3-cyanophenanthrene was obtained; m. p. 102°.

Synthesis of 2- and 3-Benzoylphenanthrenes.—To the Grignard reagent which had been prepared from 7 cc. of bromobenzene in 25 cc. of ether was added 25 cc. of benzene and then 6 g. of 2-cyanophenanthrene. After being refluxed for four hours, the solution was hydrolyzed with ice and dilute acetic acid. The ether–benzene solution was separated and treated with concentrated hydrochloric acid which precipitated the imine-hydrochloride in crystalline form. Hydrolysis of the imine gave 2-benzoylphenanthrene; after recrystallization the product weighed 7 g. (85%). The ketone melted completely when placed in a bath heated to 108–109°; the melt solidified and remelted when heated to 117–118°. Sometimes recrystallization gave the form which melted only at 117–118°. When the bath containing the low-melting form was heated slowly from room temperature, the observed melting point was usually about 113–116°; after solidification of the melt, the melting point was 117–118°.

3-Benzoylphenanthrene was synthesized in like manner from 3-cyanophenanthrene; the imine-hydrochloride precipitated as an insoluble oil which crystallized after a few minutes; the yield of ketone was 60%. The 3-benzoylphenanthrene crystallized from absolute alcohol in long needles which melted at 107–108°; when the mixture of crystals and solution was allowed to stand for several days, the long needles gradually disappeared and stout rectangular prisms took their place; these prisms melted at 111–112° and were identical with those obtained by benzoylation of phenanthrene. Recrystallization of the higher-melting form usually gave back the same form; when, however, the hot alcoholic solution was rapidly cooled and seeded with a crystal of the low-melting crystals, only the long needles of the low-melting form were obtained.

Degradation and Re-synthesis of 1-Benzoylphenanthrene.—Five grams of 1-benzoylphenanthrene and 2 g. of potassium hydroxide were heated in a large Pyrex test-tube with shaking; after a time a violent exothermic reaction took place; the product was heated with 100 cc. of water, cooled and filtered; the aqueous solution was acidified and filtered while near the boiling point in order to keep benzoic acid in solution; this procedure left 0.2 g. of 1-phenanthroic acid.[6] Addition of the acid chloride made from 0.2 g. of acid and 0.24 g. of phosphorus pentachloride, to ammonium hydroxide gave 0.2 g. of 1-phenanthroic acid amide. By heating an intimate mixture of 0.2 g. of the acid amide and 0.2 g. of phosphorus pentoxide at 140° for one hour, followed by extraction of the nitrile by benzene and recrystallization from alcohol, 0.12 g. of 1-cyanophenanthrene was obtained. By refluxing a mixture of 0.1 g. of the nitrile and phenylmagnesium bromide from 0.3 cc. of bromobenzene in 2 cc. of ether and 1 cc. of benzene, followed by hydrolysis of the ketone-imine, 0.08 g. (58%) of 1-benzoylphenanthrene was obtained; the crystals melted at 147–148° alone and when mixed with the original ketone.

Total Synthesis of 1-Benzoylphenanthrene.—Two grams of 1-keto-1,2,3,4-tetrahydrophenanthrene (II), prepared from naphthalene,[7] was added to the Grignard reagent from 3 g. of benzyl chloride in 10 cc. of ether; after being refluxed for one hour, the solution was hydrolyzed. The crude 1-benzyl-1-hydroxyl-1,2,3,4-tetrahydrophenanthrene (III), which was isolated, was heated with 20 cc. of formic acid for one hour on a steam-bath in order to dehydrate the carbinol. The mixture was steam distilled in order to remove bibenzyl and the residue, presumably 1-benzyl-3,4-dihydrophenanthrene (IV), which weighed 3 g., was heated with 3.5 g. of powdered selenium at 300° for twelve hours. The crude product was pulverized and digested with hot benzene; the benzene solution was heated with charcoal, filtered and evaporated to dryness; the residue was dissolved in hot acetone, the solution was heated with charcoal, filtered and evaporated; the residue was finally taken up in absolute alcohol and treated with charcoal; the nearly colorless filtrate after concentration deposited

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[4] Werner and co-workers, *Ann.*, **321**, 248 (1902).

[5] Mosettig and van de Kamp, THIS JOURNAL, **52**, 3704 (1930).

[6] Fieser, *ibid.*, **54**, 4110 (1932), who first prepared this acid, reports the following melting points: acid, 232–233°; methyl ester, 57°; acid amide, 284°; nitrile, 128°; our values were 228°, 55.5–56°, 274° and 129–130°, respectively. Dr. Fieser kindly made a mixed melting-point determination of the two samples of methyl ester and found the esters to be identical; he also furnished a sample of the nitrile which we found to be the same as our product. The 1-cyanophenanthrene exists in two forms; one melts at 125.5°, the other at 130–130.2°; the low-melting form is frequently changed to the high-melting form by melting and can always be changed over by seeding the melt with a crystal of the high-melting form.

[7] Haworth, *J. Chem. Soc.*, 1128 (1932).

0.1 g. of 1-benzoylphenanthrene which melted at 147–148°.

In another run, the 1-benzyl-3,4-dihydrophenanthrene obtained from 1.6 g. of 1-keto-1,2,3,4-tetrahydrophenanthrene was dehydrogenated by heating it with an equal weight of sulfur at 250° for one hour; from the mixture by the method given above 0.4 g. of 1-benzylphenanthrene was isolated.

Reduction of Benzoylphenanthrenes to Hydrols.—The ketones were reduced by sodium amalgam and alcohol according to the procedure of Bachmann[8] except that more alcohol was employed. Four grams of benzoylphenanthrene was added to 60 g. of 1.5% sodium amalgam contained in a 50-cc. cylinder; 20 cc. of benzene, 10 cc. of ether and 20 cc. of absolute alcohol were added and the mixture was shaken vigorously for fifteen minutes; reduction seemed to be complete in about five minutes. In agreement with our previous results on aromatic ketones, reduction proceeded through the intermediate formation of sodium compounds; the sodium derivative from 1- and 3-benzoylphenanthrene was olive-green in color, that from 2-benzoylphenanthrene was intense green. The solutions were poured into water in a separatory funnel, the mercury and aqueous solution were drawn off (a water-soluble by-product was formed from 1-benzoylphenanthrene), the ether–benzene solution was acidified with dilute acid, separated and concentrated. The yields were: 1-phenanthrylphenylcarbinol, 70%; 2-phenanthrylphenylcarbinol, 80%; 3-phenanthrylphenylcarbinol, 90%.

2-Phenanthroic Acid Anilide and 3-Phenanthroic Acid Anilide.—The acid chloride obtained from 20 g. of 2-phenanthroic acid was dissolved in 100 cc. of warm acetone; the solution was cooled and treated with 25 cc. of aniline in the course of five minutes; after one hour, 100 cc. of water and 15 cc. of concentrated hydrochloric acid were added and the acid anilide was filtered, washed with water and then with alcohol; weight, 26 g. 2-Phenanthroic acid anilide crystallizes from chlorobenzene in colorless needles; m. p. 217–218°.

Anal. Calcd. for $C_{21}H_{15}ON$: N, 4.71. Found: N, 4.66.

3-Phenanthroic acid anilide was likewise obtained in nearly quantitative yield; it crystallizes from acetone in colorless needles; m. p. 216–217°.

Anal. Calcd. for $C_{21}H_{15}ON$: N, 4.71. Found: N, 4.67.

2-Phenanthraldehyde and 3-Phenanthraldehyde.—Mosettig and van de Kamp[9] obtained these aldehydes in excellent yield by catalytic reduction of the acid chlorides. We have prepared the aldehydes from the acid anilides, the method employed by Shoppee[10] for making 9-phenanthraldehyde. The yield of 2-phenanthraldehyde and also of 3-phenanthraldehyde was 58%; the properties of the aldehydes agreed with those reported by Mosettig and van de Kamp.

Synthesis of 2-Phenanthrylphenylcarbinol and 3-Phenanthrylphenylcarbinol.—By the action of phenylmagnesium bromide on 0.5 g. of 2-phenanthraldehyde, 0.55 g. (80%) of 2-phenanthrylphenylcarbinol (m. p. 110–111°) was obtained. Similarly, a 64% yield of 3-phenanthrylphenylcarbinol (m. p. 128–129°) was obtained from 3-phenanthraldehyde.

Oxidation of Benzoylphenanthrenes.—A solution of 0.5 g. of benzoylphenanthrene, 0.4 g. of chromic anhydride, 0.1 cc. of water and 10 cc. of acetic acid was heated at the boiling point for five minutes; water was added and the benzoyl-9,10-phenanthrenequinone was filtered off, washed, dried and recrystallized from acetic acid and then from chlorobenzene. The yield in each case was 0.3 g. (41%).

Reduction of Hydrols to Benzylphenanthrenes.—To a solution of hydriodic acid prepared from 0.5 g. of red phosphorus, 0.5 g. of iodine, 1 cc. of water and 10 cc. of acetic acid was added 0.5 g. of hydrol; after being refluxed for two hours the hot solution was filtered from the phosphorus into water containing sodium bisulfite. The yields after recrystallization were: 1-benzylphenanthrene, 68%; 2-benzylphenanthrene, 65%; 3-benzylphenanthrene, 73%.

Phenanthryldiphenylcarbinols.—A solution of 2.82 g. of 2-benzoylphenanthrene in 10 cc. of warm benzene was added to the Grignard reagent from 4 g. of bromobenzene in 10 cc. of ether. After being refluxed for one hour the mixture was hydrolyzed; the 2-phenanthryldiphenylcarbinol crystallized when it was stirred with methyl alcohol; yield, 1.9 g. (53%). In like manner 3.2 g. (89%) of 3-phenanthryldiphenylcarbinol was prepared from 3-benzoylphenanthrene.

Phenanthryldiphenylmethyl Radicals.—One gram of 2-phenanthryldiphenylcarbinol dissolved in 2 cc. of benzene was treated with 0.5 cc. of acetyl bromide; after the mixture had been warmed for twenty minutes most of the solvent was removed and the bromide was precipitated by addition of ligroin. The 2-phenanthryldiphenylbromomethane was filtered off and recrystallized; yield, 0.8 g. (69%). Similarly, a 70% yield of 3-phenanthryldiphenylbromomethane was obtained. The carbinol bromides are very soluble in warm benzene but are nearly insoluble in ligroin. Solutions of the free radicals were prepared by shaking a mixture of 0.5 g. of carbinol bromide and 1 g. of molecular silver in 10 cc. of benzene for twelve hours.

Summary

A study has been made of the action of benzoyl chloride on phenanthrene in the presence of aluminum chloride. In nitrobenzene solution 1-, 2- and 3-benzoylphenanthrenes are formed.

A number of derivatives have been prepared from the benzoylphenanthrenes: the hydrols, benzylphenanthrenes, benzoyl-9,10-phenanthrenequinones and phenanthryldiphenylcarbinols.

Two free triarylmethyl radicals containing the phenanthryl group have been prepared in solution.

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[8] Bachmann, THIS JOURNAL, **55**, 770 (1933).

[9] Mosettig and van de Kamp, *ibid.*, **55**, 2995 (1933).

[10] Shoppee, *J. Chem. Soc.*, 37 (1933).