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

Phenanthrene Derivatives. V. The Beckmann Rearrangement of the Oximes of Acetylphenanthrenes and Benzoylphenanthrenes

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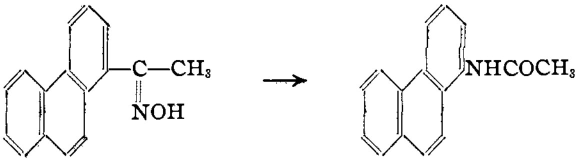
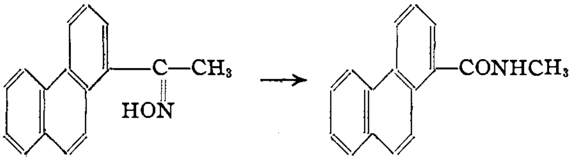
We have investigated the Beckmann rearrangement of the oximes of acetylphenanthrenes and benzoylphenanthrenes for two reasons. First, we wished to know how various phenanthryl groups were oriented with respect to the hydroxyl group in the two series of oximes. Secondly, the rearrangement appeared to offer a method for the practical preparation of certain phenanthrene derivatives. Accordingly we have prepared the oximes of 1-, 2-, 3- and 9-acetylphenanthrene and of 1-, 2-, 3- and 9-benzoylphenanthrene, and have submitted them to rearrangement by the action of phosphorus pentachloride. A preliminary communication was reported a year ago and one more recently.[2]

All eight ketones containing the phenanthryl group give mixtures of stereoisomeric oximes, *cis* and *trans*.[3] Although it would be difficult or even impossible to separate these mixtures quantitatively into the two components in order to determine the relative proportions of the two forms, this is not the case with the products obtained on rearrangement of the oximes. Thus, an acetylphenanthrene oxime would rearrange to give either an acetylaminophenanthrene (as I) or a N-methyl-phenanthroic acid amide (as II). Hydrolysis of these products would yield an aminophenanthrene and a phenanthroic acid, respectively, and these can be separated easily and quantitatively through their water-soluble salts. If we assume that each oxime gives rise to a single rearrangement product—and the work of most investigators indicates that this is the case—then the proportions of aminophenanthrene and phenanthroic acid would be a measure of the relative amounts of the *cis* and *trans* oximes in the original mixture. We have therefore rearranged the *mixture* of stereoisomeric oximes which was obtained in each case, and have determined the relative proportions of the two isomers by this procedure. The results obtained from the oximes of 1-, 2-, 3- and 9-acetylphenanthrene are presented in Table I.



trans oxime (I)



cis oxime (II)

The yields of the products do not total 100% because a certain amount of decomposition occurred during the rearrangement. On the basis of Meisenheimer's proof of the interchange of the hydroxyl group and the *trans* group[4] our results show that in the acetylphenanthrene oximes the 1-, 2-, 3- and 9-phenanthryl groups orient themselves for the most part *trans* with respect to the hydroxyl group.

TABLE I

REARRANGEMENT OF ACETYLPHENANTHRENE OXIMES

Isomer	Rearrangement products $C_{14}H_9NHCOCH_3$, %	$C_{14}H_9CONHCH_3$, %
1-	71	1
2-	81	1
3-	87	2
9-	50	6

Inasmuch as the 1-, 2-, 3- and 9-aminophenanthrenes can be obtained in yields of 50–87% from the ketones, the Beckmann rearrangement constitutes the most practical method of preparing these aminophenanthrenes, and by this procedure we have prepared several hundred grams of the amines. Although the 1-acetylphenanthrene is not obtained as easily as its isomers, nevertheless this method is the only one available for preparing the new 1-aminophenanthrene. Of interest in this connection is the work of Adelson and Bogert[5] who recently obtained 6-aminoretene by hydrolysis of the rearrangement product from 6-acetylretene oxime.

The mixtures of the stereoisomeric oximes ob-

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[1] From part of the Ph.D. dissertation of Charlotte H. Boatner.

[2] Bachmann, THIS JOURNAL, **57**, 1381 (1935); Bachmann and Boatner, *ibid.*, **58**, 857 (1936); see also Mosettig and Krueger, *ibid.*, **58**, 1311 (1936).

[3] We have used these terms to designate the relative positions of the phenanthryl and hydroxyl groups with respect to each other.

[4] Meisenheimer, *Ber.*, **54**, 3206 (1921); Meisenheimer, Theilacker and Beisswenger, *Ann.*, **495**, 249 (1932).

[5] Adelson and Bogert, THIS JOURNAL, **58**, 653 (1936).

tained from 1-, 2-, 3- and 9-benzoylphenanthrene are rearranged quantitatively without decomposition to mixtures of benzoylaminophenanthrene $C_{14}H_9NHCOC_6H_5$ and phenanthroic acid anilide $C_{14}H_9CONHC_6H_5$. The proportions of these products obtained from the various isomeric ketones are shown in Table II. From these results it is apparent that in the benzoylphenanthrene oximes the phenanthryl group is oriented chiefly *cis* with respect to the hydroxyl group. Apparently the size of the groups has little effect on the orientation of the groups in the oximes. From the results obtained with the two classes of oximes the various groups may be arranged in the following order of decreasing tendency toward *trans* orientation with respect to the hydroxyl group: phenyl, 2-phenanthryl, 3-phenanthryl, 1-phenanthryl, 9-phenanthryl, methyl.

TABLE II

REARRANGEMENT OF BENZOYLPHENANTHRENE OXIMES

	Rearrangement products	
	$C_{14}H_9NHCOC_6H_5$, %	$C_{14}H_9CONHC_6H_5$, %
1-	18	82
2-	44	56
3-	37	63
9-	4	96

The products obtained by rearrangement of the stereoisomeric oximes of 1-benzoylphenanthrene proved particularly valuable, for on hydrolysis there are produced 1-phenanthroic acid (hitherto rare) and the new 1-aminophenanthrene. Moreover, by reduction of the 1-phenanthroic acid anilide the new 1-phenanthraldehyde can be prepared in excellent yield. As a result the way is now open for the preparation of 1-phenanthrene derivatives.

Experimental Part

1-Acetylphenanthrene was prepared in two ways: (A) by oxidation of 1-phenanthrylmethylcarbinol and (B) by interaction of 1-cyanophenanthrene and methylmagnesium iodide.

(A) **1-Phenanthrylmethylcarbinol.**—To the Grignard reagent which had been prepared from 1.5 cc. of methyl iodide in 10 cc. of ether was added 10 cc. of benzene, followed by 2.6 g. of 1-phenanthraldehyde (preparation described later). After being refluxed for fifteen minutes the solution was hydrolyzed by ice-cold ammonium chloride solution; evaporation of the solvents gave the carbinol in crystalline form. By recrystallization from benzene 1-phenanthrylmethylcarbinol was obtained in the form of colorless plates: yield 2.5 g. (90%); m. p. 108–110°.

Anal. Calcd. for $C_{16}H_{14}O$: C, 86.5; H, 6.3. Found: C, 86.3; H, 6.6.

1-Acetylphenanthrene.—A solution of 1.5 g. of 1-phenanthrylmethylcarbinol in 25 cc. of glacial acetic acid was treated with a solution of 0.5 g. of chromic acid anhydride in 0.5 cc. of water and 10 cc. of acetic acid; throughout the reaction the temperature was kept at 20°. After standing for twelve hours the solution was poured into water and the ketone was extracted with benzene. The benzene solution, after being heated with charcoal and filtered, was evaporated and the residue was recrystallized from alcohol, yielding 1-acetylphenanthrene as large colorless diamond-shaped plates; weight 0.80 g. (53%); m. p. 112–113°.

Anal. Calcd. for $C_{16}H_{12}O$: C, 87.2; H, 5.5. Found: C, 87.0; H, 5.7.

(B) 1-Cyanophenanthrene was prepared from 1-phenanthroic acid amide which was obtained from the acid through the acid chloride.[6] A mixture of 5 g. of 1-phenanthroic acid amide and 5 g. of phosphorus pentoxide was heated at 140° for fifteen minutes; throughout the reaction the mixture was stirred and pressed with a glass rod. Most of the nitrile was obtained by decantation; the remainder was secured after extracting the phosphoric acid by water. The 1-cyanophenanthrene was then recrystallized from benzene–methyl alcohol; yield 4.3 g. (96%).

To the Grignard reagent prepared from 3 cc. of methyl iodide in 15 cc. of ether was added 25 cc. of benzene and then 4.3 g. of 1-cyanophenanthrene. After being refluxed for five hours the clear solution was cooled, whereupon the addition product crystallized; this solid was filtered off, washed with benzene and hydrolyzed to 1-acetylphenanthrene by refluxing it with dilute hydrochloric acid for four hours. The ketone which crystallized on cooling was obtained pure by distillation under reduced pressure, followed by recrystallization from alcohol; yield 4.0 g. (85%). The product was identical with the ketone prepared by method (A).

9-Acetylphenanthrene.—We prepared this ketone by the Grignard reaction from 9-cyanophenanthrene. The latter compound was made by heating 9-bromo-phenanthrene and cuprous cyanide[7] in a Claisen flask; when the reaction was at an end the nitrile was distilled from the flask under reduced pressure, b. p. 190–200° (3 mm.). This procedure avoids the long extraction otherwise required to separate the nitrile and cuprous salts.

To the Grignard reagent prepared from 7 cc. of methyl iodide in 30 cc. of ether was added 25 cc. of benzene and then 15 g. of 9-cyanophenanthrene. After being refluxed for three hours, the mixture was cooled and hydrolyzed with ice-cold ammonium chloride solution. The ether–benzene layer was shaken with ice-cold dilute hydrochloric acid and the aqueous solution which now contained the ketone-imine hydrochloride was heated for an hour in order to hydrolyze the product to the ketone. The latter, which precipitated as an insoluble oil, was purified by distillation under reduced pressure, followed by recrystallization from alcohol; yield 9.5 g. (57%); m. p. 73–74°. Mosettig and van de Kamp,[8] who prepared the ketone by a different method, reported a melting point of 74.5°.

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[6] Bachmann, This Journal, **57**, 555 (1935).

[7] Mosettig and van de Kamp, *ibid.*, **54**, 3328 (1932).

[8] Mosettig and van de Kamp, *ibid.*, **55**, 3442 (1933).

2- and 3-acetylphenanthrene were prepared according to the procedure of Mosettig and van de Kamp[9] with the modification that the mixture of crude ketones was distilled under reduced pressure, b. p. 180–214° (4 mm.). By digestion of the distillate with ether most of the 3-isomer was dissolved; the residue of the 2-isomer was obtained pure by two recrystallizations from benzene, the 3-isomer by recrystallization from methyl alcohol.

Oximation of Acetylphenanthrenes.—The preparation of oximes of ketones with large hydrocarbon radicals has often been found difficult and sometimes impossible. The use of pyridine by Bryant and Smith[10] in the hydroxylamine method for the titration of ketones and aldehydes suggested its use for the preparation of the oximes whose rearrangement we wished to study. With the modification of leaving out the water entirely we found that quantitative oximation of 1-, 2-, 3- and 9-acetylphenanthrene could be accomplished by heating a mixture of the ketone and hydroxylamine hydrochloride in a solution of absolute alcohol and pyridine for three hours on a steam-bath. The advantages of this procedure have been pointed out by one of us;[11] by this method it is possible to prepare oximes which do not form readily under the usual conditions.[12]

A mixture of 20 g. of 3-acetylphenanthrene (similarly for the 1- or 9-isomer) and 16 g. of hydroxylamine hydrochloride in 75 cc. of absolute alcohol and 28 cc. of pyridine was refluxed for three hours. A practically quantitative yield of the oxime was obtained by removing most of the solvent and pouring the residue into water. For the preparation of the 2-acetylphenanthrene oxime we refluxed a mixture of 2 g. of the ketone with 1.6 g. of hydroxylamine hydrochloride in 4 cc. of absolute alcohol and 12 cc. of pyridine on a steam-bath for three hours; a 97% yield of oximes (m. p. 187–190°) was obtained. By recrystallization from methyl alcohol the pure *trans*-2-acetylphenanthrene oxime was obtained as colorless needles; m. p. 196–197°.

Anal. Calcd. for $C_{16}H_{13}ON$: N, 6.0. Found: N, 6.2.

The properties of the 3- and 9-acetylphenanthrene oximes were similar to those prepared by the usual method.[9] Mosettig and Krueger[2] reported a melting point of 196–198° for the 2-acetylphenanthrene oxime which they prepared recently by the pyridine method.

1-Acetylphenanthrene Oxime.—The *trans* form of this oxime crystallizes from methyl alcohol in colorless plates; m. p. 174–176°.

Anal. Calcd. for $C_{16}H_{13}ON$: N, 6.0. Found: N, 6.0.

Rearrangement of the Acetylphenanthrene Oximes.—Anhydrous ether is generally employed as the solvent in the Beckmann rearrangement and at first we employed this solvent. We found, however, that the cheaper solvent benzene could be substituted and, indeed, in several cases we obtained better results; moreover, smaller volumes of this solvent suffice. The mixture of *cis* and *trans* oximes prepared from 5 g. of 3-acetylphenanthrene (or 1- or 9-isomer) was suspended in 80 cc. of dry benzene and treated with 5 g. of powdered phosphorus pentachloride. After the mixture had been refluxed for fifteen minutes, the mixture was cooled and hydrolyzed. In the rearrangement of the 2-acetylphenanthrene oximes 20 cc. of benzene was used for each gram of oxime and the solution was refluxed for a period of three hours. Using these procedures we have rearranged quantities of 50–100 g. of oxime at one time.

The mixture of acetylaminophenanthrene and N-methylphenanthroic acid amide obtained on rearrangement of the oximes from 5 g. of ketone was refluxed with 200 cc. of alcohol and 7 cc. of concentrated hydrochloric acid for twenty-four hours. After the alcohol had been removed by distillation the residue was digested with 300 cc. of boiling water and filtered. Addition of ammonium hydroxide to the aqueous filtrate precipitated the free aminophenanthrene (3.12 g. of 1-, 3.58 g. of 2-, 3.83 g. of 3- and 2.21 g. of 9-amine). The residue was then heated with a solution of 7 cc. of hydrochloric acid in 200 cc. of alcohol in order to hydrolyze the acid amide, and the phenanthroic acid was isolated through its water-soluble sodium salt (after hydrolysis by potassium hydroxide of any ester formed in the previous reaction). The acid amide was also hydrolyzed by a mixture of acetic acid and hydrochloric acid in a sealed tube at 200° for six hours.

The amines as obtained were usually practically colorless and pure. Further purification can be best accomplished by distillation under reduced pressure. The melting points of the 2- and 3-amines and their acetyl derivatives were in agreement with the values reported by Werner[13] for the products obtained from the corresponding phenanthrene sulfonic acids. Although Werner obtained 2-aminophenanthrene as yellow crystals we were able to isolate it in a colorless state.

1-Aminophenanthrene.—This amine, obtained in 72% yield (based on the ketone) in the manner described, crystallizes from a mixture of benzene and petroleum ether in broad, colorless glistening needles; m. p. 145–146°. The amine is insoluble in water, slightly soluble in cold petroleum ether and benzene and soluble in hot benzene.

Anal. Calcd. for $C_{14}H_{11}N$: N, 7.2. Found: N, 7.0.

The hydrochloride of this amine crystallizes from alcohol in the form of fine colorless needles; m. p. 253–255° with previous decomposition. The salt is soluble in water but not very soluble in cold alcohol.

1-Acetylaminophenanthrene.—This substance is the principal product of the rearrangement of 1-acetylphenanthrene oxime. A 90% yield of this compound was obtained by refluxing a mixture of 0.1 g. of 1-aminophenanthrene and 2 cc. of acetic anhydride for ten minutes, adding 3 cc. of water and cooling the solution. 1-Acetylaminophenanthrene crystallizes from acetic acid in broad colorless needles or plates; m. p. 219–220.5°.

Anal. Calcd. for $C_{16}H_{13}ON$: N, 6.0. Found: N, 6.2.

1-Benzoylaminophenanthrene.—A 99% yield of this derivative was obtained by treating a solution of 0.1 g. of 1-aminophenanthrene in 1 cc. of pyridine with 0.2 cc. of

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

[10] Bryant and Smith, *ibid.*, **57**, 57 (1935).

[11] "Annual Survey of American Chemistry," Reinhold Publishing Co., New York, Vol. X, 1935, p. 188.

[12] See for example Cook, Hewett and Lawrence, *J. Chem. Soc.*, 79 (1936).

[13] Werner, *Ann.*, **321**, 312 (1902).

benzoyl chloride and heating the mixture for five minutes. 1-Benzoylaminophenanthrene crystallizes from acetic acid in broad colorless needles; m. p. 224–226°.

Anal. Calcd. for $C_{21}H_{15}ON$: N, 4.7. Found: N, 4.9.

1-Aminophenanthrene Picrate.—The picrate, prepared by mixing hot benzene solutions of the amine and picric acid, crystallizes from *n*-propyl alcohol in fine pale-yellow needles; m. p. 203–204° with decomposition. The picrate is nearly insoluble in cold benzene, chloroform and alcohol.

Anal. Calcd. for $C_{14}H_{11}N \cdot C_6H_3O_7N_3$: N, 13.3. Found: N, 13.7.

1-Phenanthrylurethan.—A solution of 0.1 g. of 1-aminophenanthrene in 5 cc. of benzene was treated with 0.1 cc. of ethyl chlorocarbonate and 0.1 cc. of pyridine. After being warmed for a few minutes the mixture was allowed to stand at room temperature for three hours. 1-Phenanthrylurethan crystallizes from alcohol in colorless transparent plates; yield, quantitative; m. p. 153.5–154°.

Anal. Calcd. for $C_{17}H_{15}O_2N$: N, 5.3. Found: N, 5.3.

N-Phenyl-N′-(1-phenanthryl)-urea.—A solution of 0.2 g. of 1-aminophenanthrene and 0.15 g. of phenyl isocyanate in 5 cc. of benzene was warmed on a steam-bath for fifteen minutes and then allowed to stand at room temperature twelve hours. N-Phenyl-N′-(1-phenanthryl)-urea crystallizes from a mixture of chloroform and alcohol in fine colorless needles; m. p. 323–325° with decomposition; yield, quantitative. The compound is nearly insoluble in alcohol and in benzene but is soluble in hot chloroform.

Anal. Calcd. for $C_{21}H_{16}ON_2$: N, 9.0. Found: N, 8.8.

Synthesis of N-Methylphenanthroic Acid Amides.—These compounds, formed to a slight extent in the rearrangement of the acetylphenanthrene oximes, were synthesized from the acids. The acid chloride[6] from 1 g. of phenanthroic acid (1-, 2-, 3- or 9-isomer) was dissolved in 10 cc. of acetone and the resulting solution was poured into an ice-cold 33% aqueous solution of methylamine. The amide which precipitated immediately was filtered off, washed with water, dried and recrystallized from a mixture of benzene and methyl alcohol; yields 90–95%.

The properties of the N-methylphenanthroic acid amide (calcd. for $C_{16}H_{13}ON$: N, 6.0) are: 1-isomer, plates, m. p. 204–205.5° (N, 5.7); 2-isomer, needles, m. p. 201–202° (N, 6.2); 3-isomer, needles, m. p. 207–207.5° (N, 5.9); 9-isomer, needles, m. p. 191–192° (N, 6.3).

Benzoylphenanthrene Oximes.—1-Benzoylphenanthrene was prepared by the Perrier modification of the Friedel and Crafts reaction and the other ketones were prepared from the corresponding cyanophenanthrenes by means of the Grignard reaction.[6] Oximation was carried out according to the procedure described for the acetylphenanthrenes though usually twelve to twenty-four hours were allowed for heating. The yields of oximes were nearly quantitative. Thus, by heating a mixture of 70 g. of 1-benzoylphenanthrene and 68 g. of hydroxylamine hydrochloride in 500 cc. of absolute alcohol and 100 cc. of pyridine for twelve hours 67 g. of the oximes was obtained.

All of the oximes crystallized from methyl alcohol as colorless needles. The properties of the benzoylphenanthrene oximes (Calcd. for $C_{21}H_{15}ON$: N, 4.7) are: 1-isomer, m. p. 185–186° (N, 4.4); 2-isomer, m. p. 182–183° (N, 4.5); 3-isomer, m. p. 201–203° (N, 4.9); 9-isomer, m. p. 218–220 (N, 4.9).

The benzoylphenanthrene oximes were rearranged in the same manner as the acetylphenanthrene oximes. Thus, a mixture of 20 g. of the oximes in 100 cc. of ether (or benzene) was treated with 15 g. of phosphorus pentachloride. After being warmed for fifteen minutes the solution was carefully hydrolyzed; 19 g. of rearrangement products was obtained. When the mixture was heated with alcoholic hydrochloric acid for three weeks on a steam-bath, the benzoylaminophenanthrene was hydrolyzed to aminophenanthrene while the phenanthroic acid anilide was only slightly affected. The weight of aminophenanthrene (2.45 g. 1-aminophenanthrene from 20 g. of 1-benzoylphenanthrene, for example) indicated the proportion of *trans*-benzoylphenanthrene oxime in the original mixture.

1-Phenanthroic Acid Anilide.—This compound was obtained in a pure state by recrystallization of the rearrangement products obtained from the 1-benzoylphenanthrene oximes. For identification it was synthesized from 1-phenanthroic acid. The acid chloride, prepared from 0.15 g. of 1-phenanthroic acid by means of phosphorus pentachloride, was dissolved in warm acetone and treated with 1 cc. of aniline. After five minutes the mixture was digested with dilute hydrochloric acid and the precipitate of the anilide was filtered off. 1-Phenanthroic acid anilide crystallizes from acetone in colorless plates; m. p. 248–249°; yield, quantitative.

Anal. Calcd. for $C_{21}H_{15}ON$: N, 4.7. Found: N, 4.4.

1-Phenanthraldehyde.—This new aldehyde was prepared from the rearrangement product of 1-benzoylphenanthrene oximes which contained 82% of 1-phenanthroic acid anilide. An intimate mixture of 36 g. of the rearrangement product and 25 g. of phosphorus pentachloride in 40 cc. of anhydrous ether was heated on a steam-bath for fifteen minutes. The ether and phosphorus oxychloride were removed under reduced pressure at 140° (temperature of oil-bath), the imide chloride was dissolved in 50 cc. of ethylene dibromide and added to a solution of 94 g. of anhydrous stannous chloride in 340 cc. of anhydrous ether saturated with dry hydrogen chloride. After the mixture had stood at 0° for twenty hours, the precipitate was filtered off, washed with benzene and hydrolyzed by hot dilute hydrochloric acid. The crude aldehyde was digested with carbon tetrachloride and the filtered solution was evaporated to dryness. The residue was dissolved in a mixture of chloroform and ether and the solution was shaken with a saturated aqueous solution of sodium bisulfite for thirty-six hours; the addition product was filtered off and the filtrate was shaken with a fresh solution of sodium bisulfite for four days. The aldehyde obtained by hydrolysis of the addition compound with dilute hydrochloric acid was purified by distillation under reduced pressure and recrystallization; yield 16 g. (75%). 1-Phenanthraldehyde crystallizes from benzene and petroleum ether in colorless needles; m. p. 110.5–111.5°.

Anal. Calcd. for $C_{15}H_{10}O$: C, 87.3; H, 4.9. Found: C, 87.2; H, 5.1.

1-Phenanthraldehyde oxime crystallizes from benzene in colorless needles; m. p. 187–189°.

Anal. Calcd. for $C_{15}H_{11}ON$: N, 6.3. Found: N, 6.0.

1-Phenanthroic Acid.—1-Phenanthroic-acid-anilide hydrolyzes with difficulty; it is practically unaffected by a boiling alcoholic solution of hydrochloric acid or potassium hydroxide. Small amounts can be hydrolyzed readily in a sealed tube. A mixture of 2.0 g. of the product which was obtained by rearrangement of the oximes (containing 82% of 1-phenanthroic-acid-anilide), 10 cc. of concentrated hydrochloric acid and 50 cc. of glacial acetic acid was heated in a sealed tube at 200° for eight hours. The liquids were evaporated and the residue was digested with hot water in order to remove the 1-aminophenanthrene (0.17 g.). The 1-phenanthroic acid which remained was purified through its ammonium salt; yield 0.95 g. (77%).

For making larger amounts of 1-phenanthroic acid it was found more practical to carry out the following reactions: $C_{14}H_9CONHC_6H_5 \longrightarrow C_{14}H_9C(Cl){=}NC_6H_5 \longrightarrow C_{14}H_9COOH$. The imide chloride prepared from 20 g. of the rearrangement products as described above was added to a solution of sodium methylate which had been prepared from 5 g. of metallic sodium, 20 cc. of methyl alcohol and 20 cc. of ether. After the mixture had been refluxed for an hour, the solvents were distilled off, and the inorganic material was removed by extraction with water. The methoxyl derivatives of the imides were then hydrolyzed by heating them with a mixture of 50 cc. of concentrated hydrochloric acid and 200 cc. of methyl alcohol for two days. After removal of the solvents, the residue was heated with 100 cc. of a 25% solution of potassium hydroxide in methyl alcohol for twelve hours in order to hydrolyze the methyl ester of 1-phenanthroic acid which had formed in the preceding treatment. The solvent was removed, and the potassium salt of 1-phenanthroic acid was extracted from the residue by 1 liter of boiling water; yield of 1-phenanthroic acid, 7.2 g. From the undissolved residue 2.45 g. of 1-aminophenanthrene was extracted by hot dilute hydrochloric acid. The remainder of the product was unchanged 1-phenanthroic-acid-anilide which could be used over again.

Summary

The orientation of the 1-, 2-, 3- and 9-phenanthryl groups with respect to the methyl and the phenyl group in the oximes of the acetylphenanthrenes and benzoylphenanthrenes has been determined.

The Beckmann rearrangement has been developed as a practical method for the preparation of 1-, 2-, 3- and 9-aminophenanthrene.

A number of new 1-phenanthrene derivatives have been synthesized.

ANN ARBOR, MICHIGAN RECEIVED AUGUST 17, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HARVARD UNIVERSITY AND SWARTHMORE COLLEGE]

The Effect of Various Catalysts on the Phenanthrene–Bromine Reaction

BY CHARLES C. PRICE

The reasons for undertaking an investigation of the influence of catalysts on the reaction of phenanthrene with bromine have been presented in a previous paper.[1]

Since dioxane, one of the few available non-polar solvents unattacked by bromine at room temperature, has been found useless as a solvent for the rate determinations due to its phenanthrene-induced bromination,[1] carbon tetrachloride was used, although it was by no means ideal for the purpose. The slight solubility of hydrogen bromide in this solvent makes it difficult to determine accurately the rate of formation of this product, even when ground-glass-stoppered reaction flasks are used. In a blank test at the maximum concentration of hydrogen bromide of the experiments, the sodium hydroxide titer decreased about 25% in ten hours. The bromine, carbon tetrachloride and phenanthrene were purified as described in the previous paper. The iodine was resublimed.

All the rate measurements were made at 25°. Samples of the reaction mixture were pipetted into dilute potassium iodide, the liberated iodine then being titrated with sodium thiosulfate and the acid with carbonate-free sodium hydroxide. The disappearance of the iodine color was taken as the end-point of the first titration while phenolphthalein was the indicator in the second. The thiosulfate titer is a measure of the course of both addition and substitution, while the acid is produced by substitution alone.

The bromination catalysts investigated included aluminum chloride, antimony pentachloride, iodine, phosphorus trichloride, phosphorus pentachloride and stannic chloride. When one-tenth equivalent of catalyst was added to an equimolecular solution of bromine and phenanthrene, all of these compounds, especially iodine, catalyzed the formation of hydrogen bromide in appreciable quantities within an hour or two, although without the catalyst there was none formed after several days. Since iodine gave the

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(1) Price, THIS JOURNAL, **58**, 1834 (1936).