Summary

Two phenanthrene hydrocarbons, 9-phenyl- and 9-*p*-tolylphenanthrene, have been prepared from 2-iodobiphenyl by a synthesis involving a new type of ring closure.

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[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

Studies in the Phenanthrene Series. XXII. Derivatives of Dibenzisoquinoline and Naphthisoquinoline[1]

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In previous communications from this Laboratory we described the synthesis of a number of hydrogenated and N-methylated benzofuroquinolines[3] and naphthoquinolines,[4] which we hoped might exhibit an analgesic effect because of their superficial structural similarity to morphine. These compounds, however, proved to be either very weak analgesics or were entirely ineffective.[5] Since morphine may be interpreted as an isoquinoline derivative, a higher analgesic effectiveness—within the series of tetracyclic compounds consisting of three isocyclic rings and one nitrogen-containing ring—may be expected of phenanthrene derivatives in which the nitrogen is located in β-position to one of the benzene nuclei, *i. e.*, of compounds that include in their structure the isoquinoline system.

Apparently, the most practicable methods for preparing isoquinoline derivatives are those in which compounds of the general type R—C—C—N— are employed as starting materials. In various attempts to prepare compounds of this type we found that the phenanthrene derivatives $C_{14}H_9$-$CHOCH_3CH_2NH_2$ (IV, V) were relatively easily accessible by the method of Rosenmund,[6] which was later somewhat modified by Mannich and coworkers.[7] We employed in the second step of this preparation—the reduction of the corresponding nitro ether—platinum oxide as catalyst successfully, and alcohol as solvent. Attempts to cyclize the formyl derivatives of IV and V and the benzoyl derivative of V, according to Mannich and coworkers,[7] in order to obtain isoquinoline derivatives, by simultaneous loss of water and methanol, were unsuccessful, in spite of manifold experimental variations in respect to solvent and condensing agent. The resulting reaction mixtures consisted of colored, tarry, or partly charred products.

Equally unsuccessful were the attempts to cyclize the formyl derivatives of the β-phenanthryl ethyl amines VII and VIII to dihydroisoquinoline derivatives by the Bischler–Napieralski method. Also in this series of experiments we employed many variations such as those devised by Pictet, by Decker, and by Späth.[8] After several practically unsuccessful attempts to prepare the ethylamine derivatives (VI, VII, VIII) by the Hofmann or Curtius degradation of β-phenanthrylpropionic acids,[9] we finally obtained these amines, according to the method of Slotta and Szyszka,[10] by electrolytic reduction of the corresponding nitrostyrene derivatives (I, II, III). The 3-derivative (VII) was also prepared by chlorination of 3-(2-amino-1-hydroxyethyl)-phenanthrene and subsequent catalytic dechlorination.

By cyclizing the formaldehyde condensation products of VI and VIII with dilute aqueous hydrochloric acid according to the method of Decker and Becker,[11] we obtained the expected tetrahydroisoquinoline derivatives (IX, X)[12] in satisfactory yields. The cyclization apparently proceeded in both series (2 and 9) only in one di-

(1) The work reported in this paper is part of a unification of effort by a number of agencies having responsibility for the solution of the problem of drug addiction. The organizations taking part are: The Rockefeller Foundation, the National Research Council, the U. S. Public Health Service, the U. S. Bureau of Narcotics, the University of Virginia, and the University of Michigan. Paper XXI, THIS JOURNAL, **60**, 2464 (1938).

(2) Mallinckrodt Research Fellow, 1937–1938, E. R. Squibb and Sons Research Fellow, 1938–.

(3) Mosettig and Robinson, THIS JOURNAL, **57**, 902 (1935).

(4) (a) Mosettig and Krueger, *ibid.*, **58**, 1311 (1936); (b) Continued in "Studies in the Phenanthrene Series, XIX," Mosettig and Krueger, *J. Org. Chem.*, in press.

(5) Eddy, *J. Pharmacol.*, **58**, 159 (1936), and unpublished results.

(6) Rosenmund, *Ber.*, **46**, 1034 (1913).

(7) Mannich and Walther, *Arch. Pharm.*, **265**, 1 (1927); Mannich and Falber, *ibid.*, **267**, 601 (1929).

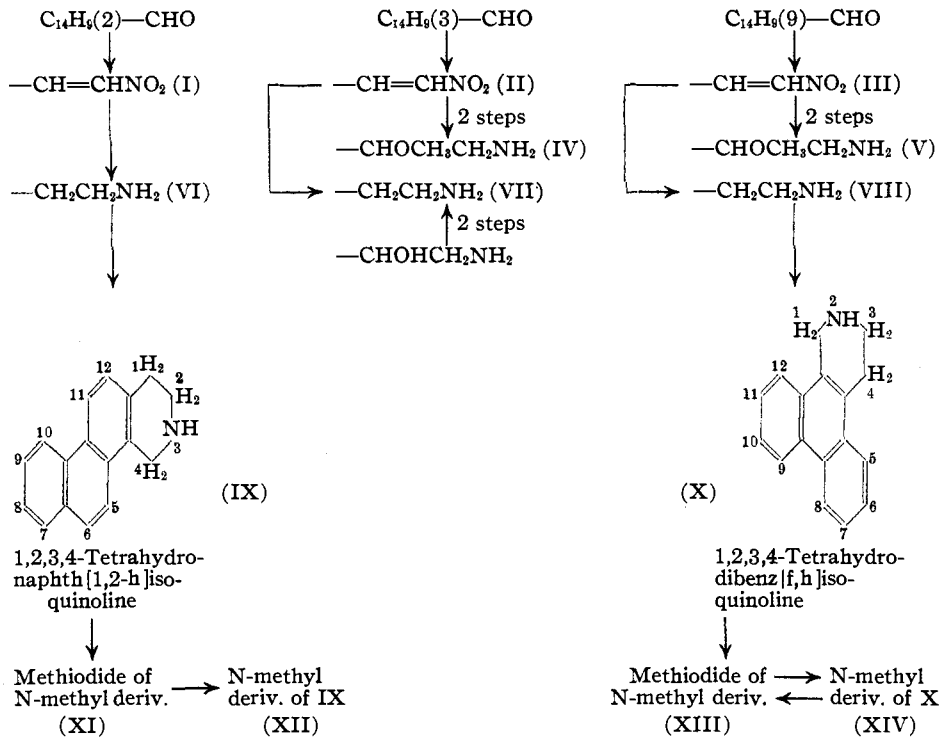
(8) Bischler and Napieralski, *Ber.*, **26**, 1903 (1893); Pictet and Kay, *ibid.*, **42**, 1973 (1909); Decker, Kropp, Hayer and Becker, *Ann.*, **395**, 299 (1913); Späth, Berger and Kuntara, *Ber.*, **63**, 134 (1930).

(9) See van de Kamp, Burger and Mosettig, THIS JOURNAL, **60**, 1321 (1938).

(10) Slotta and Szyszka, *J. prakt. Chem.*, [2] **137**, 339 (1933).

(11) Decker and Becker, *Ann.*, **395**, 342 (1913).

(12) The orientation, numbering, and names of the heterocyclic compounds included in this paper have been recommended to us by Dr. Capell through the kindness of Dr. Crane. *Cf.* Patterson, THIS JOURNAL, **50**, 3083 (1928).



rection. No tetrahydroisoquinoline ring closure could be accomplished in the 3-series, with the formaldehyde condensation product of VII. Under the conditions employed in the 2- and 9-series only hydrolysis took place, the whole starting material, the β-phenanthrylethylamine VII, being recovered unchanged. Forcing the reaction (concentrated hydrochloric acid, longer reaction time) led to amorphous hydrochlorides of a brown, muddy color which resisted all attempts of purification. 3-Methyl-1,2,3,4-tetrahydronaphth-[1,2-h]isoquinoline (XII) and 2-methyl-1,2,3,4-tetrahydrodibenz[f,h]isoquinoline (XIV) were prepared readily and in good yields by converting IX and X to the quaternary methiodides XI and XIII and subsequently decomposing the latter by heating in a vacuum.

There hardly can be any doubt concerning the structure of X, since the alternative ring closure from position 9 to position 8 of phenanthrene would necessarily result in a seven-membered nitrogen-containing ring. For the isoquinoline derivative, obtained from the formaldehyde condensation product of VI, we advance for reasons of analogy the structural formula IX, since, to our knowledge, all cyclizations of side chains as —C—C—C, —C—C—C—C, and —N—C—C—C— attached to position 2 of phenanthrene take place in position 1.[4b]

We also attempted to cyclize the formaldehyde condensation products of the amino ethers IV and V, respectively, according to the method of Decker and Becker,[11] but no cyclization took place and IV and V were recovered unchanged from the reaction mixture.

Because of present lack of material only 2-methyl-1,2,3,4-tetrahydrodibenz[f,h]isoquinoline XIV was investigated pharmacologically by Dr. Eddy at the University of Michigan.[13] Noteworthy, besides the marked analgesic effect of this substance (M. E. D. 20 mg./kg. cat), is its great hypnotic effect (M. E. D. 5 mg./kg. cat) which unfortunately is accompanied by an equally marked emetic effect when the substance is administered orally.

Experimental

3-(2-Nitrovinyl)-phenanthrene[14] (II).—To a solution of 10 g. of 3-phenanthrene aldehyde[15] in 375 cc. of alcohol was added 6.3 g. of nitromethane. The mixture was cooled (0–5°) and an ice cold solution of 5 g. of potassium hydroxide in 100 cc. of alcohol was dropped in with mechanical stirring during half an hour (the temperature was not allowed to rise above 15°). The precipitate (potassium salt of the condensation product) was brought into solution with ice water, and the nearly clear solution was poured slowly into 200 cc. of 10% hydrochloric acid which had

(13) Eddy, unpublished results.

(14) See Rosenmund, *Ber.*, **43**, 3412 (1910); Lange and Hambourger, THIS JOURNAL, **53**, 3865 (1931).

(15) Mosettig and van de Kamp, *ibid.*, **55**, 2995 (1933).

been cooled previously to 10°. The yellow, finely divided crystalline solid was collected, washed with water, and recrystallized from benzene; yellow needles, m. p. 180–180.5° (corr.), yield 90%.

Anal. Calcd. for $C_{16}H_{11}O_2N$: C, 77.10; H, 4.45. Found: C, 77.19; H, 4.06.

2-(2-Nitrovinyl)-phenanthrene (I).—This compound was prepared like the 3-isomer, but, owing to the lesser solubility of the phenanthrene-2-aldehyde, more solvent was necessary (5 g. of aldehyde in 350 cc. of alcohol). It showed a tendency to precipitate at first, in an amorphous state, when poured into the hydrochloric acid. It is decidedly more soluble in benzene than the 3-isomer and was purified by crystallization from benzene–petroleum ether as yellow needles, m. p. 134.5–137° (corr.), yield 80%.

Anal. Calcd. for $C_{16}H_{11}O_2N$: C, 77.10; H, 4.45. Found: C, 76.80; H, 4.18.

9-(2-Nitrovinyl)-phenanthrene (III).—The preparation was carried out as above, but more solvent was required (5 g. of aldehyde in 420 cc. of alcohol). The nitrostyrene derivative was recrystallized from benzene–petroleum ether: yellow needles, m. p. 173–173.5° (corr.), yield 95%.

Anal. Calcd. for $C_{16}H_{11}O_2N$: C, 77.10; H, 4.45. Found: C, 77.50; H, 4.66.

This compound has been prepared recently in essentially the same manner by Reichert and Wegner,[16] who report the m. p. 173°.

9-(1-Methoxy-2-nitroethyl)-phenanthrene.—To an ice cold (0–5°) suspension of 5.0 g. of finely divided III in 125 cc. of methanol was added, under mechanical stirring, 33 cc. of a sodium methoxide solution prepared from 4.5 g. of sodium and 100 cc. of methanol. A clear solution was obtained in about one-half hour. It was decanted from a small amount of unchanged starting material and acidified with 5 cc. of glacial acetic acid. The solution was evaporated in a water-pump vacuum to dryness at a temperature as low as possible, 500 cc. of water was added to the residue, and the resulting pale yellow precipitate was filtered, washed with water, and recrystallized from ethyl alcohol: pale yellow plates, m. p. 134–134.5° (corr.), yield nearly quantitative.

Anal. Calcd. for $C_{17}H_{15}O_3N$: OCH_3, 11.02. Found: OCH_3, 10.59.

3-(1-Methoxy-2-nitroethyl)-phenanthrene.—This compound was prepared like the 9-isomer, except that the reaction mixture was kept at 0 to −5° for two hours. The purification of the final precipitate (from water) offered some difficulties. It was dissolved in warm alcohol and gradually cooled to room temperature, whereby some oily material was deposited. The solution was decanted, and on further cooling more oil precipitated. The solution was again decanted until finally a clear solution resulted, from which, on standing overnight, pale yellow crystals separated. They were recrystallized from alcohol: pale yellow circular plates, m. p. 102–104° (corr.), yield 55%.

Anal. Calcd. for $C_{17}H_{15}O_3N$: OCH_3, 11.02. Found: OCH_3, 10.67.

3-(1-Methoxy-2-aminoethyl)-phenanthrene (IV).—Four grams of the corresponding nitro ether and 0.15 g. of platinum oxide suspended in 200 cc. of alcohol absorbed the required amount of hydrogen in twenty to thirty hours. The resulting clear, colorless solution was filtered from the catalyst and evaporated to dryness in a vacuum. The oily base was dissolved in alcoholic hydrogen chloride and the hydrochloride was precipitated with ether. It crystallized from alcohol–ether in short colorless needles of m. p. 232–233° (dec.), yield 85%.

Anal. Calcd. for $C_{17}H_{18}ONCl$: Cl, 12.32. Found: Cl, 12.03.

9-(1-Methoxy-2-aminoethyl)-phenanthrene (V).—This compound was prepared like the 3-isomer. Its hydrochloride crystallized from alcohol–ether in colorless needles, m. p. 252–253° (dec.), yield 95%.

Anal. Calcd. for $C_{17}H_{18}ONCl$: Cl, 12.32. Found: Cl, 12.09.

Picrate, m. p. 215–217° (dec.).

Anal. Calcd. for $C_{23}H_{20}O_8N_4$: N, 11.66. Found: N, 11.73.

Formyl Derivative.—To an ethereal solution of V (prepared from 3 g. of hydrochloride) was added 0.6 g. of anhydrous formic acid. The crystalline formate was filtered and heated in a metal bath at 150° for about thirty minutes. The resulting brown oil turned to a crystalline brittle mass on cooling. It was dissolved in a little benzene and precipitated with petroleum ether; colorless leaflets, m. p. 138–140° (corr.), yield 70%.

Anal. Calcd for $C_{18}H_{17}O_2N$: N, 5.01. Found: N, 4.90.

Benzoyl Derivative.—A mixture of V (prepared from 1 g. of hydrochloride), 0.6 g. of benzoyl chloride, and 4 cc. of 0.5 *N* sodium hydroxide solution was cooled and shaken. The crystalline mass that formed within a few minutes was filtered and washed with water. It crystallized from methanol–water in white leaflets of m. p. 147.5–148.5° (corr.), yield 80%.

Anal. Calcd. for $C_{24}H_{21}O_2N$: C, 81.09; H, 5.96. Found: C, 80.72; H, 5.92.

3-(2-Aminoethyl)-phenanthrene (VII).—The electrolytic reduction was carried out in an apparatus which was essentially the same as that described by Slotta and Szyszka.[10] A suspension of 7 g. of very pure 3-(2-nitrovinyl)-phenanthrene in a mixture of 50 cc. of alcohol, 80 cc. of glacial acetic acid, and 12 cc. of concentrated hydrochloric acid was introduced into the cathode compartment containing a prepared lead electrode of 60 sq. cm., while the anode compartment, containing a cooling spiral, was filled to the same level with 20% sulfuric acid. The current was kept at 3.5 amperes for three hours, at 4.5 amperes for two hours, and at 5 amperes for about five hours, temperature between 50 and 60°. The resulting clear solution at the cathode was decanted and evaporated nearly to dryness in a vacuum. The brown oily residue was dissolved in water and the solution was made alkaline and extracted with ether. The oil obtained from the ethereal solution was distilled slowly at 120–130° at a pressure of about 0.1 mm. The oily distillate was dissolved in a small volume of ether and allowed to stand in the cold for a few hours. A small amount of crystalline material (probably of higher molecular weight) precipitated and was filtered off. By addition of alcoholic hydrogen chloride to the filtrate, the

(16) Reichert and Wegner, *Ber.*, **71**, 1254 (1938).

amine hydrochloride precipitated in crystalline form. It crystallized from alcohol–ether in white, short matted needles, m. p. 254–256°, yield 50%.

Anal. Calcd. for $C_{16}H_{16}NCl$: C, 74.55; H, 6.26. Found: C, 74.50; H, 5.97.

Formyl Derivative.—This compound was prepared like the corresponding derivative of V. It crystallized from benzene–petroleum ether in small white leaflets, m. p. 122–124° (corr.), yield 61%.

Anal. Calcd. for $C_{17}H_{15}ON$: N, 5.62. Found: N, 5.84.

9-(2-Aminoethyl)-phenanthrene (VIII).—This compound was prepared like its 3-isomer. Its hydrochloride crystallized from alcohol–ether in colorless needles, m. p. 307–309° (dec.), yield 57%.

Anal. Calcd. for $C_{16}H_{16}NCl$: C, 74.55; H, 6.26. Found: C, 74.78; H, 6.13.

Formyl Derivative.—Small, white leaflets, m. p. 111–112°, yield 70%.

Anal. Calcd. for $C_{17}H_{15}ON$: N, 5.62. Found: N, 5.56.

2-(2-Aminoethyl)-phenanthrene (VI).—This compound was obtained by electrolytic reduction, like the 3- and 9-isomers, but under somewhat different conditions. Three grams of 2-(2-nitrovinyl)-phenanthrene was suspended in a mixture of 40 cc. of alcohol, 75 cc. of glacial acetic acid, and 8 cc. of concentrated hydrochloric acid. The temperature was kept at 25–30° for the first two hours and at 30–40° for the remainder of the time (nine hours). A current of 3.1 amperes was maintained throughout the whole reaction. No clear solution was obtained, varying amounts of a brown fluffy solid always remaining in the cathode compartment. The amine hydrochloride crystallized from alcohol–ether in colorless leaflets, m. p. 317–318°; average yield 35–40%.

Anal. Calcd. for $C_{16}H_{16}NCl$: C, 74.55; H, 6.26; Cl, 13.76. Found: C, 74.67; H, 6.18; Cl, 13.79.

The picrate crystallized from alcohol in large yellow needles, m. p. 225–226°.

Anal. Calcd. for $C_{22}H_{18}O_7N_4$: N, 12.44. Found: N, 12.09.

3-(2-Amino-1-chloroethyl)-phenanthrene Hydrochloride.—Five grams of finely powdered 3-(2-amino-1-hydroxyethyl)-phenanthrene[9] was added in small amounts to a suspension of 6 g. of phosphorus pentachloride in 50 cc. of dry chloroform (vigorous mechanical stirring is necessary). The amino alcohol dissolved immediately and the hydrochloride of the chloro compound began to precipitate. The stirring was continued for another half hour and ether was added to the suspension in order to facilitate the filtration of the hydrochloride. It was recrystallized from alcohol–ether as colorless square plates, m. p. 219–220° (dec.), (the melt resolidifies at 225° and melts then gradually in the wide range of 226–295°); yield 73%.

Anal. Calcd. for $C_{16}H_{15}NCl_2$: Cl, 24.27. Found: Cl, 24.20.

Conversion to 3-(2-Aminoethyl)-phenanthrene, VII.—After varying the catalyst (palladium, palladium on charcoal or calcium carbonate, platinum oxide) and the concentration of the alcohol (100, 95, 90, 75, 50%) in the catalytic dechlorination, the phenanthrylethylamine (VII) finally was obtained in a satisfactory yield (approximately 75%) by employing 0.02 g. of platinum oxide and 25 cc. of 70% alcohol per gram of hydrochloride of the chloro compound. After the hydrogen absorption came to a standstill the resulting clear solution was filtered from the catalyst and evaporated to dryness. The crystalline residue was dissolved in water and the solution made alkaline and extracted with ether. The ether residue was distilled slowly in an oil-pump vacuum at 120°. The oily distillate was dissolved in a very small amount of ether in order to remove the by-product, which crystallized gradually from this solution. The hydrochloride of the 3-(2-aminoethyl)-phenanthrene was prepared and purified as described above and was identical in every respect with the compound prepared from 3-(2-nitrovinyl)-phenanthrene. The crystalline by-product was shown by melting point, mixture melting point with an authentic sample, and analysis to be 3-(2-amino-1-hydroxyethyl)-phenanthrene.

1,2,3,4-Tetrahydrodibenz[f,h]isoquinoline (X).—In the preparation of the tetrahydroisoquinoline derivatives we followed partly Buck's[17] directions developed for the preparation of various tetrahydroisoquinoline derivatives substituted in the benzene nucleus with O-alkyl groups.

A mixture of VIII prepared freshly from 8.5 g. of the hydrochloride, and 3.4 cc. of 40% formaldehyde solution, was heated on the steam-bath for one-half hour. The reaction mixture was evaporated in a vacuum to dryness. To the condensation product was added 12 cc. of 23% hydrochloric acid and the mixture was heated for one-half hour on the steam-bath. The hydrochloride of the tetrahydroisoquinoline compound precipitated almost at the start of heating as a white and voluminous mass. The reaction mixture was diluted with water, made alkaline, and extracted with benzene. The residue from the benzene solution was treated with alcoholic hydrogen chloride and ether. The hydrochloride was recrystallized from alcohol–ether, m. p. 304–306° (dec.), average yield 65%.

Anal. Calcd. for $C_{17}H_{16}NCl$: C, 75.69; H, 5.98. Found: C, 75.96; H, 5.96.

The free base may be obtained with loss by evaporating the benzene extract to a small volume and allowing it to stand in the cold. It consists of white needles, m. p. 223–225°.

Methiodide of 2-Methyl-1,2,3,4-tetrahydrodibenz[f,h]-isoquinoline (XIII).—To a solution of X, prepared from 0.6 g. of the hydrochloride, in 5 cc. of acetone was added 0.8 cc. of methyl iodide and 0.35 g. of potassium hydroxide. The quaternary salt began to precipitate immediately. After four hours 0.2 cc. of methyl iodide was added and the reaction mixture was allowed to stand for ten hours. The methiodide was filtered off, recrystallized first from water containing some potassium iodide, and finally from alcohol: colorless, square plates, m. p. 268–270° (dec.), yield 86%.

Anal. Calcd. for $C_{19}H_{20}NI$: I, 32.60. Found: I, 32.96.

This methiodide was also formed by merely mixing XIV (below) and methyl iodide in acetone solution.

2-Methyl-1,2,3,4-tetrahydrodibenz[f,h]isoquinoline (XIV).—One and five-tenths grams of the methiodide described above was heated in an oil-pump vacuum at 200–220°, whereby the N-methyl derivative distilled very

(17) Buck, THIS JOURNAL, **56**, 1769 (1934).

slowly and practically no residue was left in the distillation bulb. The crystalline distillate was washed with water and taken up in ether. The ether residue sublimed in colorless needles, m. p. 113.5–114° (corr.), yield nearly quantitative.

Anal. Calcd. for $C_{18}H_{17}N$: N, 5.67. Found: N, 5.47.

The hydrochloride was prepared in the usual manner. It crystallizes from alcohol–ether in colorless lozenges.

Anal. Calcd. for $C_{18}H_{18}NCl$: C, 76.18; H, 6.39. Found: C, 75.80; H, 6.36.

1,2,3,4 - Tetrahydronaphth[1,2 - h]isoquinoline? (IX).—The free base VI obtained by liberation with alkali from 1.8 g. of the hydrochloride was condensed with formaldehyde and the condensation product was cyclized as described above in the "9-series." The resulting hydrochloride was converted to the base, which was extracted with benzene. The benzene solution left on evaporation a semi-solid base which was not very stable and was, therefore, transformed with alcoholic hydrogen chloride to the hydrochloride. This hydrochloride appeared to be not homogeneous and apparently contained a small amount of starting material, the phenanthrylethylamine hydrochloride. The difference in solubility of the hydrochlorides and picrates of the two bases was not marked enough for a practical separation. Therefore the crude hydrochloride was converted via the methiodide XI to the N-methyl compound which could be purified readily. The crude hydrochloride was obtained in a yield of 70% and melted at 270–290°. For analytical purposes a small sample was recrystallized repeatedly from alcohol-ether: white plates, m. p. 313–315° (dec.).

Anal. Calcd. for $C_{17}H_{16}NCl$: C, 75.69; H, 5.98. Found: C, 75.57; H, 6.28.

The mixture melting point with the hydrochloride of VI of m. p. 317–318° was indefinite, 275–314°.

Methiodide of 3-Methyl-1,2,3,4-tetrahydronaphth[1,2-h]isoquinoline (XI).—Eight-tenths gram of crude hydrochloride of m. p. 270–290° (see above) was converted to the quaternary methiodide as described in the preparation of XIII. After one crystallization from water, 0.7 g. of methiodide of m. p. 227–233° was obtained. For analysis it was recrystallized twice from alcohol as white plates, m. p. 244.5–246° (dec.).

Anal. Calcd. for $C_{19}H_{20}NI$: I, 32.60. Found: I, 32.41.

3 - Methyl - 1,2,3,4 - tetrahydronaphth[1,2 - h]isoquinoline (XII).—Five-tenths gram of an impure methiodide (m. p. 235–240°) was decomposed in an oil-pump vacuum at 200°. The oily distillate was taken up in ether and the ether residue was converted into the hydrochloride in the usual manner. This crude hydrochloride (0.25 g., m. p. 232–242°) was recrystallized first from a small volume of alcohol and then from alcohol–ether: white hexagonal crystals, m. p. 257–259° (dec.).

Anal. Calcd. for $C_{18}H_{18}NCl$: C, 76.18; H, 6.39. Found: C, 76.13; H, 6.38.

In some instances, particularly when a less pure methiodide was decomposed, it was possible to isolate from the mother liquors of the hydrochloride of XII, 2-(2-dimethylaminoethyl)-phenanthrene hydrochloride of m. p. 247–249°.

Anal. Calcd. for $C_{18}H_{20}NCl$: C, 75.62; H, 7.05. Found: C, 75.41; H, 6.91.

A compound in every respect identical with this hydrochloride (melting point and mixture melting point) was prepared by complete methylation of VI and subsequent heat decomposition of the resulting methiodide. The mixture melting point with the hydrochloride of XII was at 230–240°.

The above description of the preparation of IX and its derivatives is a typical average of twelve experiments each starting with from 1 to 3 g. of the 2-(2-aminoethyl)-phenanthrene (VI). In one instance, the tetrahydroisoquinoline derivative IX was obtained as the only reaction product in the cyclization of the formaldehyde condensation product. In another instance, when an impure phenanthrylethylamine was used, no cyclization took place and practically all of the starting material could be recovered.

Summary

The synthesis of phenanthrylethylamines $C_{14}H_9CH_2CH_2NH_2$ and phenanthrylethylamino ethers $C_{14}H_9CHOCH_3CH_2NH_2$ is described.

Cyclizations to isoquinoline derivatives were attempted according to the general methods of Bischler–Napieralski and of Decker and Becker. Only the method of Decker and Becker applied to the phenanthrylamines of the 2- and 9-series gave positive results.

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