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

STUDIES IN THE PHENANTHRENE SERIES. XX. NITRATION OF 9,10-DIHYDROPHENANTHRENE*

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The nitration of phenanthrene is known to be an unsatisfactory procedure for preparing nitrophenanthrenes, first, on account of the interference of the 9,10-double bond—formation of addition products with the nitrating agent—[1] and second, because of the tediousness involved in the separation of the isomeric nitro products.[2]

Our expectation that the nitration of 9,10-dihydrophenanthrene, which has no double bond of "olefinic character", would proceed quite normally was realized. This nitration gave an easily separable mixture of two mononitrophenanthrenes, the one being formed in a yield of 65 per cent., the other in a yield of 3–4 per cent. We have pointed out previously that 9,10-dihydrophenanthrene behaves like diphenyl rather than like phenanthrene.[3] Therefore we assumed that, in analogy to the nitration of diphenyl,[4] the main product(*A*) would be the 2-nitro-9, 10-dihydrophenanthrene (corresponding to *para*-nitrodiphenyl) and the by-product (*B*) the 4-nitro-9,10-dihydrophenanthrene (corresponding to *ortho*-nitrodiphenyl). This assumption was correct. *A* was reduced to an amino compound which was identical with 2-amino-9,10-dihydrophenanthrene prepared from 2-acetyl-9,10-dihydrophenanthrene.[5, 3b] *B*, also, was first reduced to an amino compound which by diazotization and subsequent methylation of the resulting hydroxy compound was converted to a methoxydihydrophenanthrene. We attempted to dehydrogenate this compound to one of the known methoxyphenanthrenes, but the only crystalline material that could be isolated from the dehydrogenation

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[1] SCHMIDT, *Ber.*, **33**, 3251 (1900); WIELAND AND RAHN, *ibid.*, **54**, 1770 (1921).

[2] (*a*) SCHMIDT, *ibid.*, **12**, 1153 (1879); (*b*) SCHMIDT AND HEINLE, *ibid.*, **44**, 1488 (1911).

[3] (*a*) BURGER AND MOSETTIG, *J. Am. Chem. Soc.*, **57**, 2731 (1935); (*b*) *ibid.*, **58**, 1857 (1936).

[4] JENKINS, MCCULLOUGH, AND BOOTH, *Ind. Eng. Chem.*, **22**, 31 (1930).

[5] BURGER AND MOSETTIG, *J. Am. Chem. Soc.*, **59**, 1302 (1937).

mixture was phenanthrene. The methoxyl group had been eliminated largely or entirely in this process. The ease of elimination of the methoxyl group was strongly suggestive of its location in position-4, since it is known that substituents so located in phenanthrene are relatively easily eliminated.[6]

The dehydrogenation of the diacetylaminodihydrophenanthrene (obtained from *B*) was more successful, and a monoacetylphenanthrene of m. p. 196–197° could be isolated in relatively good yields. It was hydrolyzed to an aminophenanthrene of m. p. 62.5–63.5° (benzoyl derivative of m. p. 216–218°) which on diazotization and subsequent methylation gave successively 4-hydroxy- and 4-methoxyphenanthrene, whose identities were established by direct comparison with authentic samples of these phenanthrene derivatives. Schmidt and Heinle[2b] described a 4-aminophenanthrene as melting at 104–105° (acetyl derivative, m. p. 190°, benzoyl derivative, m. p. 224°). Although these authors state that they did not observe two modifications of their 4-aminophenanthrene (in analogy with 3-aminophenanthrene[7] and 9-aminophenanthrene) we believe that the discrepancy in the melting points of these apparently different 4-aminophenanthrenes may be accounted for by the existence of this amine in two forms. (The hydrolysis of their 4-acetylaminophenanthrene was not described by Schmidt and Heinle.) Schmidt's structural proof for 4-aminophenanthrene rests upon the conversion of his 4-nitrophenanthrene to 4-nitro-9,10-phenanthrene quinone. Our attempts to oxidize 4-nitro-9,10-dihydrophenanthrene with chromic acid were unsuccessful, since it proved to be unexpectedly stable towards this reagent.

It seems worthy of mention, that we were not able, in various experiments, to obtain a naphthoquinoline by applying the Skraup method to 4-amino-9,10-dihydrophenanthrene. This failure, together with the empirical fact (see foregoing paper) that side-chains attached to position 2 of 9,10-dihydrophenanthrene cyclize entirely or largely in position 3, might indicate a fixed arrangement of double bonds in 9,10-dihydrophenanthrene (the double bond connecting positions 2 and 3, the single bond connecting 3 and 4) different from that in the terminal nuclei of phenanthrene. A more complete study of the empirical rule[†] mentioned above,

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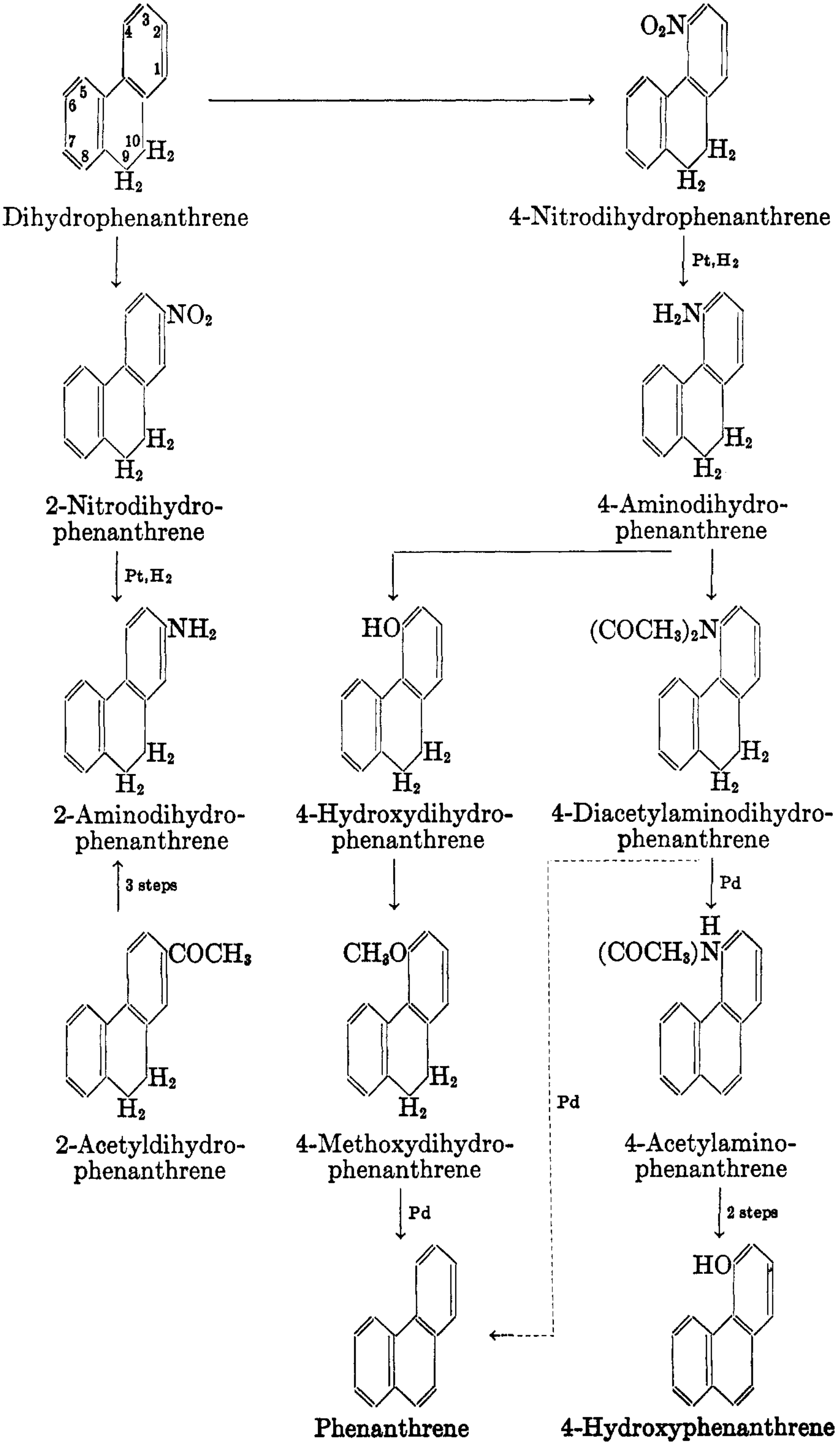
[6] Werner and Kunz, *Ber.*, **35**, 4419 (1902); Mosettig and Burger, *J. Am. Chem. Soc.*, **55**, 2981 (1933); Cook and Hewett, *J. Chem. Soc.*, **1933**, 403; Mosettig and Duvall, *J. Am. Chem. Soc.*, **59**, 368, footnote *m* (1937).

[7] Werner and Kunz, *Ber.*, **34**, 2524 (1901); Schmidt, *ibid.*, **34**, 3531 (1901).

[†] The ring closure of γ-[2-(9,10-dihydrophenanthryl)]-*n*-butyric acid resulted in only 30% yield of the benzanthracene derivative [Burger and Mosettig, *J. Am. Chem. Soc.*, **59**, 1302 (1937)] and the yield of dihydronaphtho[1,2-*g*]quinoline from 2-amino-9,10-dihydrophenanthrene was only 50% (see foregoing paper). But in both instances there was no indication of the formation of an isomeric compound.


O₂N
Dihydrophenanthrene
4-Nitrodihydrophenanthrene
Pt,H₂
NO₂
H₂N
2-Nitrodihydrophenanthrene
4-Aminodihydrophenanthrene
Pt,H₂
NH₂
HO
(COCH₃)₂N
2-Aminodihydrophenanthrene
4-Hydroxydihydrophenanthrene
4-Diacetylaminodihydrophenanthrene
3 steps
Pd
COCH₃
CH₃O
H (COCH₃)N
Pd
2-Acetyldihydrophenanthrene
4-Methoxydihydrophenanthrene
4-Acetylaminophenanthrene
Pd
2 steps
HO
Phenanthrene
4-Hydroxyphenanthrene

and the application of the Skraup synthesis to 4-aminophenanthrene, which is not available in sufficient quantity at present, appear necessary to substantiate such speculations.

EXPERIMENTAL

2-Nitro- and 4-nitro-9,10-dihydrophenanthrene.—To a mechanically stirred mixture of 20.5 g. of dihydrophenanthrene and 120 cc. of glacial acetic acid, 30 cc. of nitric acid (Merck Reagent "Acid Nitric Fuming" sp. gr. 1.5) was added during two hours, the temperature being kept between 29° and 33°. The red solution was poured into three liters of water, and the oily precipitate solidified overnight sufficiently to be separated by filtration (20 g., m. p. 70–75°). It was dissolved in acetone and carefully precipitated with alcohol, m. p. 77–81°, yield 63%. 2-Nitro-9,10-dihydrophenanthrene crystallized from ether in very small, pale pink prisms of m. p. 81–82°.

Anal. Calc'd for $C_{14}H_{11}NO_2$: N, 6.22. Found: N, 6.62.

The acetone-alcohol mother liquors from a series of reactions in which 200 g. of hydrocarbon had been nitrated and from which 147 g. of pure 2-nitro-9,10-dihydrophenanthrene had been obtained, were concentrated to a small volume and allowed to stand in a refrigerator for several days. Six grams of impure 2-nitro compound of m. p. 72–78° was filtered off. The remaining solvent was evaporated, and the oily residue was distilled in an oil-pump vacuum through a Vigreux column wrapped in asbestos paper (metal bath). The fraction distilling at 180°, approximately 20 g. of a yellow oil, was dissolved in ethyl acetate and yielded 8.7 g. of 4-nitro-9,10-dihydrophenanthrene of m. p. 82–94°. By another crystallization, 7 g. of well-defined, large yellow cubes, melting at 97–98° was obtained.

Anal. Calc'd for $C_{14}H_{11}NO_2$: C, 74.64; H, 4.93; N, 6.22.
Found: C, 74.74; H, 4.66; N, 6.03.

2-Amino-9,10-dihydrophenanthrene.—A suspension of 25 g. of 2-nitro-9,10-dihydrophenanthrene in 200 cc. of absolute alcohol with 0.05 g. of platinum oxide absorbed slightly more than the calculated amount of hydrogen in five hours. It was necessary to cool the reduction vessel from time to time in ice water and to work up the reaction mixture immediately after hydrogenation came to a standstill. The amine was isolated as hydrochloride by adding alcoholic hydrogen chloride to the solution filtered from the catalyst. The free base could be distilled readily in an oil-pump vacuum. To a suspension of the hydrochloride in water ammonia was added, and the mixture was extracted with ether. The ether solution was concentrated and cooled in an ice-salt mixture, whereby the amine (described by Burger and Mosettig[5] as an oil) crystallized out. The crystalline product liquified when allowed to stand at room temperature, but resolidified after some time and melted at 48–90°. Two days later the melting point had changed to 49–52°. The free amine prepared in exactly the same way from a hydrochloride obtained by Beckmann rearrangement (and subsequent hydrolysis) of the oxime of 2-acetyl-9,10-dihydrophenanthrene behaved in exactly the same way and melted finally at 49–52°. The mixture melting point of the two samples was at 49–52°. In later experiments only the melting point 49–52° was observed.

Anal. Calc'd for $C_{14}H_{13}N$: N, 7.18. Found: N, 7.62.

Diazotization of the amine (from the nitro compound) gave a hydroxy derivative identical with 2-hydroxy-9,10-dihydrophenanthrene described by Burger and Mosettig.[5]

4-Amino-9,10-dihydrophenanthrene.—The catalytic reduction of 4-nitro-9,10-

dihydrophenanthrene was carried out like that of the 2-isomer. The base crystallized from ethyl acetate in large, pale pink prisms of m. p. 53–54° (corr.).

Anal. Calc'd for $C_{14}H_{13}N$: C, 86.11; H, 6.71.
Found: C, 85.95; H, 6.94.

The hydrochloride crystallized from alcohol in white needles, m. p. 270–273° (corr., decomp.) in vacuo.

Anal. Calc'd for $C_{14}H_{14}ClN$: Cl, 15.31. Found: Cl, 15.27.

4-Diacetylamino-9,10-dihydrophenanthrene was obtained by boiling under reflux 3 parts of the amine in 10 parts of acetic anhydride for twenty minutes. It crystallized from acetone-water in small tablets of m. p. 100–103°.

Anal. Calc'd for $C_{18}H_{17}NO_2$: C, 77.38; H, 6.14.
Found: C, 77.60, 77.58; H, 6.25, 5.84.

4-Hydroxy-9,10-dihydrophenanthrene.—The diazotization of 4-amino-9,10-dihydrophenanthrene was carried out according to the method of de Milt and Van Zandt.[8] Four grams of the amine, dissolved in 20 cc. of pyridine, was added with stirring, during the course of one hour, to a solution of nitrosyl sulfuric acid cooled to −3° with ice and salt. The nitrosyl sulfuric acid solution was prepared by first adding 3 g. of sodium nitrite to an ice-cold mixture of 15 cc. of water and 30 cc. of concentrated sulfuric acid, and then carefully warming the mixture to 40° until a clear solution resulted. The stirring was continued at this temperature for one hour, and the reaction mixture was then diluted to 400 cc. with ice and water. A solution of 2 g. of urea in 50 cc. of water was added, and stirring was continued another hour. The solution of the diazonium sulfate was filtered and poured slowly into boiling water. A red oil precipitated, from which the aqueous solution was decanted. The oil was dissolved in a 1% potassium hydroxide solution and filtered. By acidification was obtained 1.7 g. of crystalline phenolic product, which distilled readily (at 130°) in an oil-pump vacuum. The distillate was recrystallized from benzene-petroleum ether; prisms, m. p. 72–74° (corr.)

Anal. Calc'd for $C_{14}H_{12}O$: C, 85.67; H, 6.17.
Found: C, 85.53, 85.26; H, 6.14, 6.01.

One and three-tenths grams of 4-hydroxy-9,10-dihydrophenanthrene was methylated in the usual manner with potassium hydroxide and dimethyl sulfate. The oily methoxy compound was dehydrogenated without further purification. It was heated in a nitrogen atmosphere with 0.1 g. of palladium black at 300° for one-half hour. By distillation of the reaction mixture in an oil-pump vacuum, 0.8 g. of crystalline material that melted from 42–76° was obtained. One crystallization from benzene-petroleum ether and three crystallizations from alcohol yielded 0.2 g. of phenanthrene melting at 99–101°, which showed no depression in melting point upon admixture with an authentic sample.

Conversion of 4-Diacetylamino-9,10-dihydrophenanthrene into 4-Hydroxyphenanthrene

4-Acetylaminophenanthrene.—One and eight-tenths grams of 4-diacetyl-amino-9,10-dihydrophenanthrene and 0.5 g. of palladium black were heated, in a nitrogen atmosphere, to 250° within fifteen minutes and kept for another fifteen minutes between 250° and 260°. (A violent gas evolution began at 230°.) A very slow distillation of the reaction mixture in an oil-pump vacuum (twelve hours at 120° and approximately one-half hour at 170°) gave as the first fraction a pasty crystalline

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[8] DE MILT AND VAN ZANDT, *J. Am. Chem. Soc.*, **58**, 2044 (1936). See also BACHMANN AND BOATNER, *ibid.*, **58**, 2194 (1936).

mass and then fine white needles. The latter were separated mechanically; they weighed 0.5 g. and melted at 190–192°. This material crystallized from alcohol as fine white needles of melting point 196–197°.

Anal. Calc'd for $C_{16}H_{13}NO$: C, 81.66; H, 5.57.
Found: C, 81.50; H, 5.91.

In another dehydrogenation experiment, 0.5 g. of the diacetylamino compound was heated at 250–280° for twelve minutes. The reaction mixture yielded by vacuum distillation and recrystallization 50 mg. of phenanthrene of m. p. 94–96° and 20 mg. of an impure 4-acetylaminophenanthrene that softened at 180° and melted at 192–194°.

4-Aminophenanthrene.—One gram of the acetylamino compound in 50 cc. of 15% alcoholic hydrogen chloride was boiled under reflux for eight hours. On cooling, 0.6 g. of amine hydrochloride separated, from which, by liberation with ammonia and extraction with ether, 0.4 g. of the base was obtained in white warts of m. p. 60.5–62°. Five cubic centimeters of concentrated hydrochloric acid was added to the alcoholic mother liquor from the first crop of amine hydrochloride, and the mixture was boiled for six hours. (A flocculent precipitate appeared after three hours boiling.) The hydrochloride was collected by filtration, and gave 0.35 g. of amine base melting at 60–62°. The 4-aminophenanthrene crystallized from petroleum ether in fine, white needles, m. p. 62.5–63.5° (corr.).

Anal. Calc'd for $C_{14}H_{11}N$: N, 7.25. Found: N, 7.32.

A mixture of 30 mg. of the amine in 3 cc. of ether, 3 cc. of 5% sodium hydroxide solution, and 0.1 cc. of benzoyl chloride was shaken at room temperature for three and one-half hours. Enough ether was added to dissolve the heavy white precipitate. The ether solution was evaporated to dryness, and the residue was heated in a watch glass on the steam bath in order to sublime off any benzoic acid. It crystallized from alcohol in fine white needles of m. p. 216–218° (corr.), yield 13 mg.

Anal. Calc'd for $C_{21}H_{15}NO$: N, 4.71. Found: N, 4.76.

A solution of 0.4 g. of 4-aminophenanthrene in 2 cc. of pyridine was added dropwise (forty-five minutes) with stirring to a cold solution (approximately $-5°$) of nitrosyl sulfuric acid, which was prepared as described above, from 0.3 g. of sodium nitrite, 1.6 cc. of water, and 3.2 cc. of concentrated sulfuric acid. The mixture was maintained at 0°, stirred forty-five minutes longer, and was then diluted to 40 cc. with ice and water. After addition of 0.2 g. of urea, stirring was continued at 0° for one hour. The diazonium sulfate solution was filtered and poured slowly into boiling water. The entire reaction mixture was extracted with ether, and the ether residue was treated with 10% potassium hydroxide solution. The filtered alkaline solution gave on acidification 135 mg. of pale yellow 4-hydroxyphenanthrene. After sublimation at 100° in an oil-pump vacuum, it melted at 112–113.5°. A mixture melting point determination with an authentic sample of 4-hydroxyphenanthrene of melting point 112–112.5°, showed the melting point 112–113°. In all the three melting point determinations a slight sintering at 109° was observed. The product, mixed with 3-hydroxyphenanthrene, melted below 85°.

A mixture of 20 mg. of sublimed 4-hydroxyphenanthrene (from the diazotization), 0.1 cc. of 5% sodium hydroxide solution, and 0.1 cc. of methyl iodide was allowed to stand at room temperature for one-half an hour. The reaction mixture was diluted with water, extracted with ether, and the ether residue was distilled in an oil-pump vacuum. The oily distillate (18 mg.) became crystalline when seeded with 4-methoxyphenanthrene, and melted at 64.5–66° (sintering at 60°). The mixture melting point with an authentic sample of 4-methoxyphenanthrene (of m. p. 64.5–66.5°, sintering at 63°) was at 64–65.5° (sintering at 60°). The mixture with 3-methoxyphenanthrene was liquid at room temperature.

SUMMARY

In the nitration of 9,10-dihydrophenanthrene, 2-nitro- and 4-nitro-9,10-dihydrophenanthrene are formed in yields of 65 per cent. and 4 per cent. respectively.

The structure of these nitro compounds has been proved by converting them into phenanthrene derivatives of well-established structure, namely 2-amino-9,10-dihydrophenanthrene, and 4-hydroxyphenanthrene.