crystallizing from acetone–ligroin it separated in blue iridescent crystals melting at 241–242°. The spectrum and color were identical with those of chlorin *a*.

Anal. Calcd. for $C_{35}H_{40}N_4O_6$: C, 68.62; H, 6.58; N, 9.15; OCH_3, 10.15. Found: C, 68.90, 68.61; H, 6.68, 6.46; N, 9.77, 10.14; OCH_3, 10.1, 10.3.

A dimethyl ester was also obtained when 200 mg. of trimethyl chlorin *a* was refluxed for thirty minutes in 1% methyl alcoholic potassium hydroxide. Only half of the product was alkali-soluble. On recrystallization from acetone–ligroin, minute greenish-black crystals separated, m. p. 208°.

Anal. Calcd. for $C_{35}H_{40}N_4O_6$: C, 68.62; H, 6.58; OCH_3, 10.15. Found: C, 68.05, 68.26; H, 6.43, 6.19; OCH_3, 10.8, 11.4.

Pyrolysis of each of these two dimethyl esters of chlorin *a* gave apparently different porphyrins in small yields but these were not positively identified.

An Unstable Chlorin *a*.[14]—A solution of 250 mg. of phaeopurpurin 18 in 15 cc. of pyridine was added to 1500 cc. of ether, the pyridine was removed with dilute acid and the phaeopurpurin was extracted into 500 cc. of 20% hydrochloric acid. After drawing air through this solution for forty hours the products obtained were a chlorin of acid number 3 and spectrum similar to that of chlorin *a*, and also a small amount of chlorin *a*. Methylation of the new chlorin gave a trimethyl ester of acid number 11 whose color and spectrum were identical with those of chlorin *a*. Dark blue iridescent crystals were obtained by recrystallizing from acetone–ligroin. These melted at 227–228° and gave no depression with known trimethyl chlorin *a*, melting at 228°.

Anal. Calcd. for $C_{36}H_{42}N_4O_6$: C, 69.01; H, 6.75; OCH_3, 14.8. Found: C, 69.16, 69.20; H, 6.54, 6.45; OCH_3, 14.8.

Summary

1. The transformation of the "unstable chlorins" to phaeopurpurin 18 has been shown to be an oxidation accompanied by loss of carbon dioxide.

2. Hydroxylamine derivatives characteristically formed by anhydrides have been obtained from phaeopurpurin 18 and rhodoporphyrin-γ-carboxylic anhydride. These facts substantiate the anhydride structure of phaeopurpurin 18.

3. Phaeopurpurin 7 is oxidized by potassium molybdicyanide to a monomethyl ester of chlorin *a* and carbon dioxide. This agrees with the α-ketonic acid structure previously postulated for this compound.

Cambridge, Mass. Received August 22, 1933

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[14] Compare Fischer's pseudo chlorin p. 6, *Ann.*, **498**, 222 (1932).

[Contribution from the Department of Chemistry, Washington University]

Preparation of 2-Iodophenanthrenequinone

By L. McMaster and R. S. Wobus

As a part of an investigation carried on in this Laboratory of some derivatives of phenanthrenequinone it was observed that the literature does not record any iodine derivatives. This paper describes the preparation of the 2-iodo derivative and work is in progress on the preparation of the 4-iodo compound.

Since iodine is not easily introduced by direct methods, the course of procedure that suggested itself was through the usual diazo reaction. Starting with phenanthrene, the synthesis involved the dichromate oxidation to the quinone, nitration of the quinone, and reduction of the 2-nitro compound to the amino quinone. The diazotized amine was then treated with potassium iodide. The phenanthrenequinone was prepared by the method of Anschütz and Schultz[1] and purified through the sodium bisulfite addition compound and subsequent crystallization from glacial acetic acid.

No method is described in the literature by which the 2- and 4-nitrophenanthrenequinones can be prepared separately by controlled nitration. We found the method of Schmidt and Austin[2] for the preparation of these compounds to be very unsatisfactory due apparently to the short time designated for the nitration. Also, we could not obtain the 2,7-dinitro derivative reported by them. Werner's[3] method, as given in detail by Schmidt and Spoun,[4] was finally used in a general way for the preparation and separation of the 2- and 4-nitro quinones. In the preparation of the amine our results differ somewhat from those described in the literature, particularly those of Brass and Ferber.[5]

Experimental

Preparation of 2-Aminophenanthrenequinone.—To 5 g. of the 2-nitro compound in 250 cc. of a 6% solution of

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[1] Anschütz and Schultz, *Ann.*, **196**, 38 (1879).

[2] Schmidt and Austin, *Ber.*, **36**, 3731 (1903).

[3] Werner, *Ann.*, **321**, 336 (1902); *Ber.*, **37**, 3086 (1904).

[4] Schmidt and Spoun, *ibid.*, **55**, 1194 (1922).

[5] Brass and Ferber, *ibid.*, **55**, 541 (1922).

sodium hydroxide, 16 g. of sodium hydrosulfite was added and the mixture warmed to 50° with stirring for fifteen minutes. The resulting dark green solution was diluted with 400 cc. of water and aerated for ten to fifteen minutes until a deep purple precipitate of the 2-amino quinone was formed. This, after washing and drying, was crystallized from alcohol; yield 4 g., 91% of the theoretical. Since the product did not have a definite melting point, it was identified by conversion into the monoacetyl derivative prepared by boiling in acetic acid with the addition of a small amount of acetic anhydride. The product, dark red-violet crystals, recrystallized from nitrobenzene, melted sharply at 324°, as recorded in the literature.

Sodium hydrosulfide was also used as the reducing agent, but the yield was only 63.6% of the theoretical.

Preparation of the 2-Iodophenanthrenequinone.—Six grams of the 2-amino compound was dissolved in 75 cc. of sulfuric acid (sp. gr. 1.84) and the solution kept at 0–5° with vigorous stirring. Two grams of sodium nitrite was added slowly and the stirring continued for two hours. The mixture was poured onto cracked ice and carefully diluted to 2 liters with water, and 6 g. of potassium iodide added. The cooled mixture, containing the diazonium salt in fine suspension, was stirred for three hours, then warmed on a water-bath for two hours, and sufficient sodium bisulfite solution added to remove the free iodine. The reddish-orange material was filtered off, washed with water, dried at 100° and crystallized several times from glacial acetic acid. Orange colored crystals were formed. They melted at 223–224° (corr.); yield 2.7 g., 30%.

Anal. Calcd. for $C_{14}H_7O_2I$: I, 38.0. Found: (micro) I, 37.84; 37.93.

The compound was stable at ordinary temperatures but decomposed with the liberation of iodine at temperatures well above its melting point. It sublimes, with slight decomposition, under reduced pressure to needle-shaped crystals of above melting point. It is only moderately soluble in benzene, toluene and alcohol. It dissolves in concentrated sulfuric acid, forming a dark green solution which turns to deep red when partly diluted. On continued dilution, the orange colored material is reprecipitated.

Summary

2-Iodophenanthrenequinone has been prepared from phenanthrene and some of its properties recorded.

ST. LOUIS, MO.

RECEIVED AUGUST 24, 1933

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OHIO STATE UNIVERSITY]

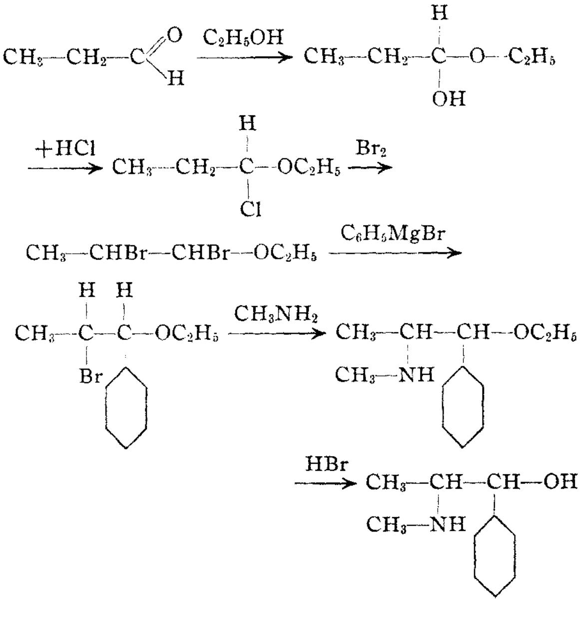
A Synthesis of Pseudoephedrine

BY ROY G. BOSSERT AND WALLACE R. BRODE

The synthesis of pseudoephedrine as described in this paper is based on the same methods as have been described previously for β-ethoxy amines[1] with the subsequent splitting of the ether to yield the amino alcohol.

Among the previously described syntheses of ephedrine and pseudoephedrine[2] the methods of Späth and Göhring, Späth and Koller, and Kanao and Nagai[3] approach to some extent the procedure used in the present synthesis. However, the variation in the order in which certain groups are introduced, with the possibility of inversion due to the existence of a second asymmetric atom in the molecule is important from the standpoint of the mechanism of the reactions. Since this method follows the Boord synthesis of olefins,[4] the known configuration of the final product in this pseudoephedrine synthesis should be of some assistance in the explanation of certain reactions and the formation of certain products in the olefin synthesis.

The reactions involved in this synthesis of *dl*-pseudoephedrine may be indicated as



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[1] Brode and Wernert, THIS JOURNAL, **54**, 4365 (1932); **55**, 1685 (1933).

[2] Chen and Schmidt, "Ephedrine and Related Substances," Williams and Wilkins Co., Baltimore, Md., 1930.

[3] (a) Späth and Koller, *Ber.*, **58**, 1268 (1925); (b) Späth and Göhring, *Monatsh.*, **41**, 319 (1920); (c) Nagai and Kanao, *Ann.*, **470**, 159 (1929).

[4] Boord *et al.*, THIS JOURNAL, **52**, 651, 3396 (1930); **53**, 1505, 2427 (1931); **54**, 751 (1932); **55**, 3293 (1933).