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

NOTE ON THE PURIFICATION OF PHENANTHRENE[1]

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Crude phenanthrene from anthracene oil is obtainable as a dark brown oily crystalline substance. It consists largely of phenanthrene, with varying amounts of anthracene, fluorene, carbazole and dark tarry substances. Of these, anthracene is the most persistent, and its complete removal offers considerable difficulty. By fractional crystallization from a number of solvents, a nearly white product can be obtained which, however, melts variously from 102 to 115°, and gives a brilliant red picrate (phenanthrene picrate is pure yellow, with no red tinge).

The toluene method of Wense[2] involves great losses of material, and does not give a sufficiently pure product, nor did Schmidt's procedure[3] give any better results; the method of Anschütz and Schultz[3,4] is difficult to carry out on large quantities of material. The alkali fusion method[5] is likewise poorly adapted to laboratory use. Purification over the picrate[6] also proved impracticable and too expensive on a large scale. The red picrate from the partially purified phenanthrene, when recrystallized many times and boiled with prepared charcoal, is obtained as yellow hair-like needles of m. p. 145°, but on decomposition with ammonia always gives phenanthrene melting at about 102 to 105°.

As emphasized by Anschütz,[4] phenanthrene is far easier to separate from anthraquinone than from anthracene itself; we therefore turned to a method used by Sandquist,[7] in which the novel feature was a controlled oxidation with concd. nitric acid. Under the conditions employed, anthracene is oxidized to anthraquinone almost completely, while the phenanthrene is nitrated only to a negligible extent. Sandquist made use of the picrate as well, which we have found to be time-consuming and expensive. Over forty kilograms of phenanthrene has been purified in this Laboratory by the method described below; it is rapid, economical, and can be applied to any reasonable quantity of material. The product is obtained in nacreous white flakes of m. p. 99–99.5°, and gives a pure yellow picrate (compare Limpricht, Ref. 6) of m. p. 145°.

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[2] Wense, *Ber.*, **19**, 761, note 3 (1886).

[3] Schmidt, *ibid.*, **12**, 1159 (1879).

[4] Anschütz and Schultz, *Ann.*, **196**, 32 (1879).

[5] Akt. Teer- u. Erd-Oel Ind., German Patent 130,679.

[6] Limpricht, *Ber.*, **6**, 532 (1873).

[7] Sandquist, "Studien über die Phenanthrensulfosäuren," Dissertation, Upsala, 1912.

Experimental

Five kg. of crude phenanthrene was refluxed with 12 liters of 95% alcohol until solution was complete. This was cooled to about 15° and filtered; the use of a basket centrifuge at this point proved to be of great advantage, both in the amount of solvent recovered and in increased purity of the product. From 4.0 to 4.3 kg. of gray crystalline material of m. p. 105–110° was obtained.[8] This crystallization removed the oily and wax-like impurities and most of the color. A small amount of phenanthrene goes with the mother liquor, but is so impure that its recovery is unprofitable.

The purified product so obtained is now further treated in smaller lots. One kilogram was dissolved in 6 liters of alcohol, 120 g. of concd. nitric acid added and the solution refluxed vigorously for one and a quarter to one and a half hours. If any considerable quantity of red product separates from the hot reaction mixture at this point, it should be filtered out of the nearly boiling solution (centrifuge). When cooled, the solution set to a mass of large red flakes, yield 800 to 900 g., m. p. 93–96°.

The substance was now distilled at atmospheric pressure, using about 500 g. in a liter distilling flask provided with a wide arm about 60 cm. in length to serve as an air condenser. The phenanthrene distilled as a pale yellow oil and dropped from the side arm into a large beaker of water which was stirred mechanically. The distillate solidified in thin yellow flakes or shells. Distillation was continued until the liquid began to come over somewhat darkened. Further heating results in a violent explosion; there is no danger of explosion if the distillation is interrupted at the point where the dark distillate begins to come over. Distillation at reduced pressure is impracticable because of clogging of the delivery tube with crystals.

The dried flakes of the distillate were recrystallized from alcohol (4 to 4.5 kg. in 12 liters), again centrifuging for best results. A second recrystallization may be necessary to obtain a pure white product. Crude phenanthrene varies greatly, and in two cases a second oxidation with nitric acid was found necessary. The yield of pure phenanthrene of m. p. 99–99.5° was from 30–45% of the weight of crude starting material. Over 80% of the solvent can be recovered when the centrifuge is used.

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[8] The presence of more than about 2% anthracene in phenanthrene raises the melting point, as may be shown by direct experiment.