Synthesis of Perylene

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Perylene, $C_{20}H_{12}$(I), is of interest in the field of organic and physical chemistry. It is possible to synthesize larger polycyclic aromatic compounds from this hydrocarbon; also, perylene forms molecular compounds with various kinds of electron donors and acceptors, all of which are typical organic semiconductors.

In 1910, perylene was first prepared by heating 1,1′-dinaphthyl or naphthalene with aluminum chloride.[1] However, the yield was extremely poor. Therefore, many studies concerning the synthesis of perylene and its derivatives have been carried out by a number of workers, as is described in Schemes A, B, and C.

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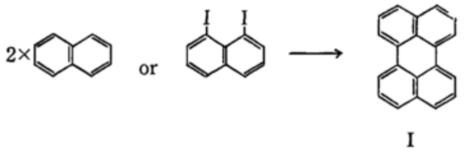
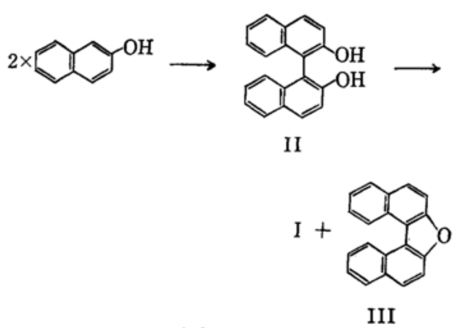
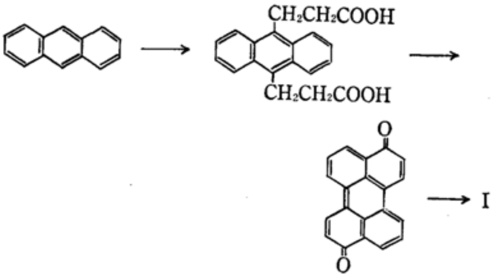
[1] R. Scholl and R. Weitzenböck, *Mh. Chem.*, **43**, 2202 (1910).



Scheme A



Scheme B

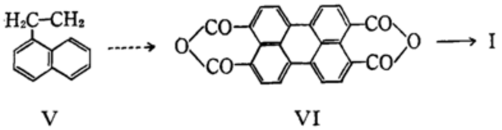


Scheme C

Of these methods, the A and C methods are very difficult to perform, and they yield only small percentages. The B method, in which the zinc-dust distillation is applied to β-dinaphthol (II), is a little easier to perform than the other two, but its yield is also low (3—7%) and purification is very difficult.

In this note, we will describe a method of preparing perylene which gives a good yield and a high purity. At first, we tried to improve the yields of perylene in the previous Schemes, A, B, and C, but we were unsuccessful. Secondly, we found that perylene is produced by the reduction of β-dinaphthylene oxide. This fact is interesting, but the yield is still low.

It has, however, also been found that perylene can readily be prepared by heating perylene tetracarboxylic acid anhydride (VI) with soda-lime in a vacuum. We denote this as Scheme D. This method gives a good yield of 80%, for the crude product has a high purity and purification can be readily carried out.



Scheme D

In addition, it has been reported that the decarboxylation of VI can also be carried out by heating it with 12% potassium hydroxide under pressure.[2] This method may also be considered a good method of preparing perylene, for it gives a considerable yield.

Experimental

The melting points are uncorrected.

Zinc-dust Fusion of β-Dinaphthylene Oxide (III). A mixture of 24 g of III, 16 g of zinc dust, 100 g of zinc chloride, and 20 g of sodium chloride was fused at 260°C for 20 min. After cooling, the mixture was dissolved in diluted hydrochloric acid. The insoluble part was collected, washed with water, and then dried. Fine, brownish-colored crystallites (2.0 g), extracted by hot xylene from this crude product, were sublimed *in vacuo* (10^{-3} Torr) and then recrystallized from xylene as yellow plates. The melting point of the crystal was 268—269°C (Ref. 1, 264—265°C). Yield, 1.5 g (6.6% of the theoretical amount).

Reduction of III by Martin's Method.[3] A mixture of 50 g of III, 125 g of zinc dust, 160 g of sodium hydroxide, 500 m*l* of xylene, and 2000 m*l* of water was refluxed for 20 hr. After the reaction mixture had cooled, the precipitate, containing zinc dust, was collected; this was then purified by a procedure similar to that described above. Yield, 3.6 g (7.7%) of fine, golden yellow plates; mp, 268—269°C.

Decarboxylation of Perylene Tetracarboxylic Anhydride (VI). A mixture of 1.00 g of VI[4] and 6 g of soda-lime was heated at 350°C for 1 hr; then, under a reducing pressure of 10^{-2} Torr, the temperature was raised to 440°C and kept there for 7hr. By the latter process, 0.60 g of fine, yellow crystals was obtained as a sublimate. This product was recrystallized from toluene, giving golden yellow plates. Yield, 0.51 g (80%); mp, 269.5°C (uncorr.), 280.3°C (corr.).

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2) N. Goto and Y. Koga, Presented at the 20th Annual Meeting of the Chemical Society of Japan, Tokyo, April 1, 1967; see also *D.R.P.* 486491 (1926).

3) E. L. Martin, *J. Am. Chem. Soc.*, **58**, 1441 (1936).

4) This material was prepared from acenaphthene (V) by the method reported by T. Maki *et al.* (*Kogyo Kwagaku Zasshi* (*J. Chem. Soc. Japan, Ind. Chem. Sect.*), **54**, 480, 544 (1951)).