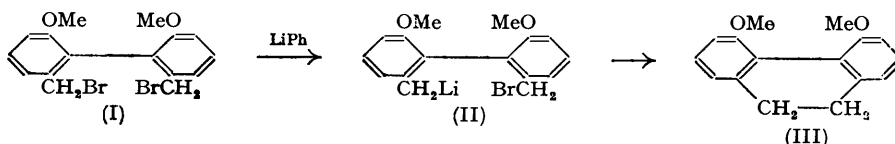


679. 9 : 10-Dihydrophenanthrenes. Part II.* 9 : 10-Dihydro-4 : 5-dimethoxyphenanthrene.

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9 : 10-Dihydro-4 : 5-dimethoxyphenanthrene is formed in low yield by the interaction of phenyl-lithium and 2 : 2'-bisbromomethyl-6 : 6'-dimethoxydiphenyl.

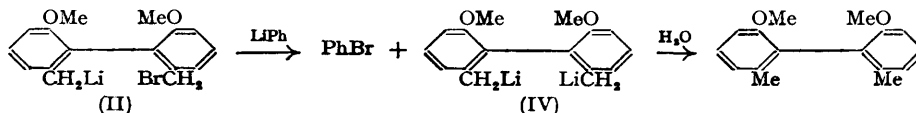
9 : 10-DIHYDROPHENANTHRENE can readily be obtained by the action of phenyl-lithium on 2 : 2'-bisbromomethyldiphenyl (Hall, Lesslie, and Turner, *J.*, 1950, 711). It was considered that the method might be generally applicable to the preparation of substituted 9 : 10-dihydrophenanthrenes and, in particular, to the preparation of 4 : 5-disubstituted dihydrophenanthrenes which would be of considerable stereochemical interest. In fact we find that the action of phenyl-lithium on 2 : 2'-bisbromomethyl-6 : 6'-dimethoxydiphenyl (I) gives only a poor yield of 9 : 10-dihydro-4 : 5-dimethoxyphenanthrene (III), isolated after tedious fractional crystallisation. The main product was a complex mixture, evidently more complex than dimeric material such as would have arisen from interaction at only one of the 2 : 2'-groups. It is probable that the presence of additional groups in the 6 : 6'-positions in the diphenyl prevents the sufficiently close approach of the methyl-lithium and the bromomethyl groups in the intermediate compound (II). The final product (III) must also be somewhat



strained since the normal twist of the dihydrophenanthrene system is insufficient to accommodate the two methoxyl groups without bringing into play their mutual repulsive forces.

By heating 9 : 10-dihydro-4 : 5-dimethoxyphenanthrene with sulphur we obtained a small amount of 4 : 5-dimethoxyphenanthrene, isolated as the picrate. The corresponding dihydrophenanthrene does not form a picrate and most of it was recovered unchanged from the attempted dehydrogenation (cf. Krueger and Mosettig, *J. Org. Chem.*, 1938, 3, 340, who were unable to dehydrogenate 9 : 10-dihydro-4-methoxyphenanthrene without removal of the methoxyl group).

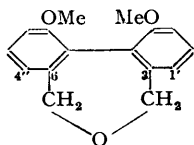
The possibility of an alternative course of reaction between the dibromide and phenyl-lithium, in which the dilithium compound (IV) might be formed, was considered.



This would be decomposed by water to give 6 : 6'-dimethoxy-2 : 2'-ditolyl (Me = 2), which might also be expected to undergo dehydrogenation with the formation of 4 : 5-dimethoxyphenanthrene when heated with sulphur.

* Part I, *J.*, 1950, 711.

For three reasons we consider the former course of reaction to be that followed: (1) The analytical values are much closer to those required for the dihydrophenanthrene than to those for the ditolyl. (2) The ultra-violet absorption spectrum corresponds more closely to a hindered dihydrophenanthrene than to a hindered ditolyl (unpublished work). (3) For given amounts of lithium and of dibromide the former reaction leads to more ionic bromide than the latter (since in the latter some remains as bromobenzene) and this larger amount was observed experimentally.



6 : 6'-Dimethoxydiphenic acid was prepared as described in the literature, with minor but significant modifications. Its dimethyl ester was reduced with excess of lithium aluminium hydride. The resulting diol could readily be converted into the cyclic ether, 2 : 7-dihydro-4' : 1''-dimethoxy-3 : 4-5 : 6-dibenzoxepine (inset), by warming it with 50% sulphuric acid. Treatment of the diol with an excess of phosphorus tribromide gave 2 : 2'-bisbromomethyl-6 : 6'-dimethoxydiphenyl.

The ultra-violet absorption spectra of 9 : 10-dihydro-4 : 5-dimethoxyphenanthrene and of 2 : 7-dihydro-4' : 1''-dimethoxy-3 : 4-5 : 6-dibenzoxepine are discussed in a later paper.

EXPERIMENTAL.

3-Methoxy-2-nitrotoluene.—2-Nitro-*m*-cresol was prepared by Gibson's method (*J.*, 1923, **123**, 1269) with the modification proposed by Kenner and Turner (*J.*, 1928, 2340). The crude product from steam-distillation was dissolved in xylene and dried over sodium sulphate before methylation by Haworth and Lapworth's method (*J.*, 1923, **123**, 2982). In later runs the volume of xylene used was increased by 33% and the methyl sulphate added in 3–4 lots with vigorous shaking. Under these conditions methylation appeared to be complete in less than an hour instead of the 18 hours recorded by Haworth and Lapworth. The overall yield based on *m*-cresol was 60%.

3-Methoxy-2-nitrobenzoic Acid.—Initially the 3-methoxy-2-nitrotoluene was oxidised in 5-g. batches with potassium permanganate (16 g. in 600 c.c. of water) in presence of hydrated magnesium sulphate (12 g.). Boiling under reflux was continued for 12 hours. Later, 15-g. batches were oxidised with 80 g. of permanganate in 2 l. of water in presence of 36 g. of hydrated magnesium sulphate, with 19 hours' boiling. In both series the permanganate solution was added at intervals during the oxidation. The acid was isolated by passing in sulphur dioxide, separated from a small quantity of non-acidic material by dissolution in aqueous sodium hydrogen carbonate, reprecipitated, and crystallised from aqueous alcohol. The yield was 60–65%, and the m. p. 255–256°.

6 : 6'-Dimethoxydiphenic Acid.—The nitro-acid was reduced by Pschorr's method (*Annalen*, 1912, **391**, 23), and the resulting 2-amino-3-methoxybenzoic acid (33.5 g., 1 mol.) diazotised as described by Wittig and Petri (*Annalen*, 1933, **505**, 17). The following catalyst gave a better yield more quickly. Copper sulphate (48.5 g.) was dissolved in water (275 c.c.) and ammonia (*d* 0.88; 55 c.c.), and sodium metabisulphite (110 g.) and ammonia (110 c.c.) were added just before final use. The catalyst solution was cooled to about 30° and the diazo-solution added with rapid stirring, followed by a solution of anhydrous ferric chloride (72 g.) in water (110 c.c.) and concentrated hydrochloric acid (360 c.c.). The precipitated 6 : 6'-dimethoxydiphenic acid (26 g., 87%), after dissolution in sodium hydrogen carbonate solution and reprecipitation, had m. p. 296–298°.

The dimethyl ester was obtained by heating the acid (30 g.) with methyl alcohol (400 c.c.) and concentrated sulphuric acid (30 g.) for 6 hours under reflux. The yield, after one crystallisation from methyl alcohol, was 30.5 g. (92%), and the m. p. 136.5–137.5.

2 : 2'-Bishydroxymethyl-6 : 6'-dimethoxydiphenyl.—The ester was very sparingly soluble in ether and was accordingly added to the lithium aluminium hydride (3.5 g., 2.5 mols.) in ether (250 c.c.) as a finely ground solid (12 g.), each lot being washed into the reaction flask with ether (300 c.c. altogether). The reaction was completed by ½ hour's boiling under reflux. Diluted sulphuric acid was added, the ether distilled off from the reaction vessel, and the solid filtered off. 2 : 2'-Bishydroxymethyl-6 : 6'-dimethoxydiphenyl crystallised from alcohol in rods (9 g., 90%), m. p. 158–159° (Found : C, 70.1; H, 6.7. C₁₈H₁₈O₄ requires C, 70.1; H, 6.6%). Warming this for a few minutes with an excess of 50% sulphuric acid gave 2 : 7-dihydro-4' : 1''-dimethoxy-3 : 4-5 : 6-dibenzoxepine, which crystallised from alcohol in needles, m. p. 136° (Found : C, 74.9; H, 6.7. C₁₈H₁₆O₃ requires C, 75.0; H, 6.3%).

2 : 2'-Bisbromomethyl-6 : 6'-dimethoxydiphenyl (I).—The finely ground diol (9 g., 1 mol.) was added gradually to phosphorus tribromide (54 g., 6 mols.) with ice-cooling. The vigorous reaction was completed by keeping the mixture at room temperature for ½ hour and finally warming it to ca. 30° for 15 minutes. The product was poured on crushed ice, and the sticky dibromide which separated was ground with water. It was dried in a vacuum-desiccator over sodium hydroxide and crystallised once from light petroleum (b. p. 80–100°) (yield 9.5 g., 71%; m. p. 111–113°). Rapid recrystallisation from methyl alcohol gave a product, m. p. 113–115°, but was accompanied by some loss. Repeated crystallisation from light petroleum or methyl alcohol raised the m. p. to 115° (Found : C, 48.7; H, 4.3; Br, 39.6. C₁₈H₁₆O₂Br₂ requires C, 48.0; H, 4.0; Br, 39.9%).

9 : 10-Dihydro-4 : 5-dimethoxyphenanthrene (III).—(1) Finely ground 2 : 2'-bisbromomethyl-6 : 6'-dimethoxydiphenyl (9 g.), in warm ether (300 c.c.), was added gradually to an ethereal solution of phenyl-lithium (from 0.42 g. of lithium and 4.5 g. of bromobenzene). Solid immediately separated. Water was added and the solid, which was insoluble in both water and ether, was filtered off (ca. 3.5 g.). It had an indefinite m. p. and after repeated attempts at crystallisation and purification it was discarded. The ethereal solution was dried and distilled under reduced pressure. The main fraction

(2.4 g.) had b. p. 210—240°/12 mm. and eventually solidified. Repeated crystallisations from methyl alcohol and from light petroleum (b. p. 60—80°), accompanied where possible by mechanical separation of two types of crystals, finally gave very small amounts of (a) the original dibromide (mixed m. p. not depressed) and (b) needles, m. p. 133—134°, which proved to be 9:10-dihydro-4:5-dimethoxyphenanthrene (Found: C, 80.2; H, 6.7. $C_{16}H_{16}O_2$ requires C, 80.0; H, 6.7. Calc. for 6:6'-dimethoxy-2:2'-ditolyl, $C_{16}H_{18}O_2$: C, 79.3; H, 7.5%).

(2) The experiment was repeated using a larger volume of ether (500 c.c. altogether), a larger excess of phenyl-lithium (from 0.70 g. of lithium and 7.9 g. of bromobenzene), with vigorous stirring during the slow addition of the dibromide. A negligible amount of the insoluble solid was obtained on addition of water. Ether was distilled off from the ethereal layer and the residue extracted repeatedly with light petroleum (b. p. 80—100°). The extracts deposited gums and some crystals; these were repeatedly extracted with various fractions of light petroleum and any crystalline products obtained repeatedly crystallised from light petroleum and from methyl alcohol. Finally, 0.6 g. (11%) of 9:10-dihydro-4:5-dimethoxyphenanthrene, m. p. 130—133°, was obtained (mixed m. p. with previous specimen not depressed). No unchanged dibromide was detected in the product. The total bromide in the combined aqueous solutions was precipitated as silver bromide (15.5 g.). For an initial weight of lithium of 0.70 g. the dihydrophenanthrene reaction requires 13.7 g. of silver bromide, and the ditolyl reaction 9.5 g. The amount found is consistent with the dihydrophenanthrene reaction and an initial lithium weight of 0.83 g., an amount within the experimental error in view of the difficulty of weighing the lithium as wire: for the ditolyl reaction the amount of silver bromide found would require an initial lithium weight of 1.22 g.

Dehydrogenation of 9:10-Dihydro-4:5-dimethoxyphenanthrene.—9:10-Dihydro-4:5-dimethoxyphenanthrene (0.1055 g., 1 mol.) and sulphur (0.0141 g., 1 atom) were heated in a metal-bath at about 220° for 4 hours. The residue was extracted with alcohol and boiled with charcoal, and the filtered solution concentrated to about 60 c.c. An excess of alcoholic picric acid was added and long scarlet needles of 4:5-dimethoxyphenanthrene picrate slowly separated (0.06 g.), m. p. 191—193° (Found: C, 56.2; H, 3.7; N, 9.2. $C_{22}H_{17}O_8N_3$ requires C, 56.5; H, 3.7; N, 9.0%). By washing of the filtrate with sodium hydroxide and extraction with ether, unchanged 9:10-dihydro-4:5-dimethoxyphenanthrene was recovered.

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