

308. The Nitration of 2-Methylindole.

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It is now established that trinitrostrychol is 3:5:7-trinitroindole-2-carboxylic acid (synthesis, Hill and Robinson, J., 1933, 486), and as we have obtained a different 3:?:?-trinitroindole-2-carboxylic acid by nitration of 2-methylindole, followed by oxidation, it is evident that the nitro-groups in the latter cannot occupy positions 5 and 7. This being so, it would appear that the aromatic nucleus is activated by the nitrogen atom through the double bond in position 2:3, and hence it is probable on theoretical grounds that one nitro-group occupies position 4; the third nitro-group may be in position 5, 6, or 7.

Nitration in the methyl group is excluded by the formation of a *trinitro-acid* on oxidation, and the alkali-solubility of the *trinitromethylindole* similarly excludes the 1-position.

EXPERIMENTAL.

Dinitro-2-methylindole (Walther and Clemen, *J. pr. Chem.*, 1900, 61, 249) is conveniently obtained by slowly heating a mixture of 2-methylindole (10 g.) and nitric acid (100 c.c., *d* 1.42) to about 50°, a vigorous reaction then setting in. After cooling, the solid is collected, rapidly dissolved in dilute aqueous potassium hydroxide, and expeditiously reprecipitated by means of nitric acid. Three recrystallisations from 50% alcohol afford 5.6 g., m. p. 265—267°, not depressed by admixture with an authentic specimen.

3:?:?-*Trinitro-2-methylindole*.—Working as above and with double quantities, we allowed the first vigorous reaction to proceed and subside. Heating on the steam-bath was then continued until a clear solution resulted (30 mins.) and, on cooling, the pure *trinitro*-derivative crystallised. Recrystallised from nitric acid, it formed long cream-coloured needles (8.2 g.), m. p. 254—256° (decomp.) with previous darkening (Found: C, 40.6, 40.9; H, 2.3, 2.3; N, 21.0. $C_9H_6O_6N_4$ requires C, 41.1; H, 2.5; N, 20.6%). The substance is moderately readily soluble in alcohol and very sparingly soluble in ether and benzene. It dissolves in aqueous sodium carbonate or sodium hydroxide to a yellow solution, from which a yellow crystalline salt separates; it is insoluble in aqueous sodium hydrogen carbonate. Picric acid was isolated from the mother-liquor of the preparation, but it cannot be obtained by oxidative nitration of the trinitromethylindole. The latter was also obtained from dinitro-2-methylindole by heating this with 10 times its weight of nitric acid (*d* 1.42).

Condensation with p-dimethylaminobenzaldehyde. A mixture of trinitro-2-methylindole (5 g.), *p*-dimethylaminobenzaldehyde (2.5 g.), piperidine (2 c.c.), and alcohol (100 c.c.) was refluxed for 2 hours and then concentrated. The separated *trinitro-2-p-dimethylaminostyrylindole* was very sparingly soluble in most solvents, but crystallised from pyridine as long, dark green needles, of which the decomposition point could not be observed yield, (80%) (Found: C, 54.5; H, 3.8; N, 17.2. $C_{18}H_{16}O_6N_5$ requires C, 54.4; H, 3.8; N, 17.6%). The formation of this substance shows that the methyl group in the 2-position is activated by an *o*-situated nitroxyl.

Trinitroindole-2-carboxylic Acid.—A solution of potassium permanganate (27 g.) in water (300 c.c.) was added to one of trinitro-2-methylindole in hot aqueous potassium hydroxide (200 c.c. of 5%). After 2 hours' heating on the steam-bath, a crude *acid* (5 g.) was isolated from the concentrated alkaline solution. It was purified by solution in, and recovery from, aqueous sodium hydrogen carbonate, and by crystallisation from nitric acid (*d* 1.42), forming small, intensely yellow needles (1.5 g.), m. p. 227—229° (Found: C, 36.2; H, 1.5; N, 18.4. $C_9H_3O_8N_4$ requires C, 36.5; H, 1.4; N, 18.9%). The acid is soluble in ether, acetone, and alcohol, and sparingly soluble in benzene and chloroform. The alkaline solutions are yellow and stable on heating (distinction from trinitrostrychol); the yellow crystalline sodium salt is rather sparingly soluble.

The *ethyl* ester (acid refluxed with alcoholic sulphuric acid for 7 hours) crystallised from 50% alcohol in long cream-coloured needles, m. p. 198—199° (Found: C, 40.9; H, 2.5. $C_{11}H_8O_8N_4$ requires C, 40.7; H, 2.7%). The methyl ester darkens at 195° and melts at 202—205°.