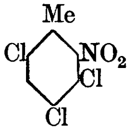
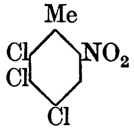
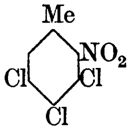
X.—*Chlorination of* o- *and* p-*Nitrotoluenes. 3 : 4 : 6-Trichloro-2-nitrotoluene and 2 : 6-Dichloro-4-nitrotoluene.*

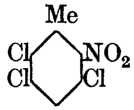
By LEOPOLD FERDINAND LEVY and HENRY STEPHEN.

DURING the course of an investigation for which 6-chloro-2-nitrotoluene was required, the action of chlorine on *o*-nitrotoluene in presence of antimony pentachloride was on one occasion carried beyond the stage of monochlorination. The nitrotoluene was saturated with chlorine, and next day there was a copious deposit of a trichloro-2-nitrotoluene, m. p. 93—94° after purification, for which the following structures are possible :


(I.)

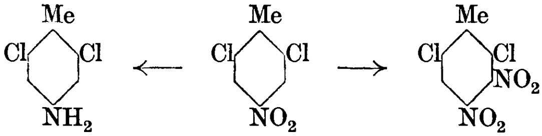

(II.)


(III.)


(IV.)

Of these four substances, (III), prepared by Cohen and Dakin (J., 1902, **81**, 1338), melts at 81—82°, and (IV) may be excluded from consideration since in the monochlorination of *o*-nitrotoluene chlorine enters position 4 or 6 (Janson, D.R.-P. 107505; Cohn, *Monatsh.*, 1902, **22**, 474). Hence trichlorination should result in a compound in which both positions are occupied, and this condition is fulfilled by (I) and (II). To decide which of these structures may be assigned to the trichloro-2-nitrotoluene above, the latter was nitrated, a trichlorodinitrotoluene, m. p. 226° (corr., 229·5°), being obtained. The trichlorodinitro-compounds corresponding to (I) and (II), namely, 3 : 4 : 6-trichloro-2 : 5-dinitrotoluene, m. p. 226°, and 4 : 5 : 6-trichloro-2 : 3-dinitrotoluene, m. p. 140—141°, have been described by Seelig (*Annalen*, 1887, **237**, 140). It follows, therefore, that the trichloro-compound obtained as described is 3 : 4 : 6-*trichloro-*2-*nitrotoluene* (I). On reduction it was converted into 3 : 4 : 6-*trichloro-*o-*toluidine*.

The investigation was now extended to include the chlorination of *p*-nitrotoluene. Antimony pentachloride in solution in the nitro-compound, saturated with chlorine, chlorinates very slowly after the stage of monochlorination, and only after three months was a crystalline deposit obtained. This proved to be a *dichloro-*4-*nitrotoluene*, m. p. 63—64°. Wachendorff (*Annalen*, 1877, **185**, 273; compare also Lellmann, *Ber.*, 1884, **17**, 534) obtained 2-chloro-4-nitrotoluene by the action of chlorine on a solution of antimony pentachloride in *p*-nitrotoluene, from which it may be concluded that the probable structure of the above dichloro-4-nitrotoluene is represented by (V).



(VII.) (V.) (VI.)

The nitro- and dinitro-derivatives of the six dichlorotoluenes have been studied by Cohen and Dakin (J., 1901, **79**, 1111), but an inspection of the properties of the mononitro-derivatives shows that none of these corresponds to (V), and this appears now to have been prepared for the first time.

Nitration of (V) gave 2 : 6-*dichloro-*3 : 4-*dinitrotoluene* (VI), which is also new since it does not correspond to any of the dinitro-compounds described by Cohen and Dakin (*loc. cit.*). On reduction (VI) gave the hydrochloride of the corresponding diamine, which showed the usual qualitative reactions characteristic of an *o*-diamine; there was insufficient of the latter for analysis and for the preparation of a benziminazole.

Further proof of the structure (V) was obtained by reducing it to a dichloro-*p*-toluidine, m. p. 55°. Of the four possible isomeric dichloro-*p*-toluidines, the 2 : 3- (m. p. 40—42°), 2 : 5- (m. p. 91—92°), and 3 : 5- (m. p. 60°) are described in the literature, from which it appears probable that the dichloro-compound (m. p. 55°) is the fourth isomeride, 2 : 6-*dichloro*-p-*toluidine* (VII). Its *acetyl* and *benzoyl* derivatives have been prepared, and these differ in melting point from the corresponding derivatives of the other isomerides.

An attempt was made to oxidise (I) and (V) by means of potassium permanganate to 3 : 4 : 6-trichloro-2-nitrobenzoic acid and 2 : 6-dichloro-4-nitrobenzoic acid respectively, but both compounds resisted oxidation after six days' continual heating on the water-bath.

EXPERIMENTAL.

3 : 4 : 6-*Trichloro*-2-*nitrotoluene*.—A solution of antimony pentachloride (5 g.) in *o*-nitrotoluene (27·4 g.) was saturated with chlorine. The crystalline deposit which separated over-night was removed by filtration and well pressed on a porous tile. The mother-liquor retained appreciable quantities of the nitro-compound, a further small amount being obtained by freezing. Yield, about 9 g. of pale yellow, elongated needles, m. p. 93—94° after crystallisation from alcohol. The *trichloronitro*-compound is soluble in the usual solvents with the exception of light petroleum (Found : Cl, 44·3. $C_7H_4O_2NCl_3$ requires Cl, 44·3%).

3 : 4 : 6-*Trichloro*-2 : 5-*dinitrotoluene*.—The above trichloronitro-compound (1 g.) was warmed at 60° with nitric acid (8 c.c., *d* 1·51) and sulphuric acid (5 c.c.) for 15 minutes. The mixture was cooled and poured into water; the precipitate obtained crystallised from alcohol–glacial acetic acid in shining flat needles, m. p. 226° (corr., 229·5°) (Found : Cl, 37·3. Calc. for $C_7H_3O_4N_2Cl_3$: Cl, 37·3%).

3 : 4 : 6-*Trichloro*-o-*toluidine*.—The mononitro-compound (4·8 g.), dissolved in alcohol, was boiled with hydrochloric acid (40 c.c.), crystalline stannous chloride (14 g.), and a trace of metallic tin for 10 minutes. When the mixture was poured into cold water, the *base* was obtained (the hydrochloride is completely hydrolysed in aqueous solution). It crystallised from alcohol in long colourless needles, m. p. 89°, was volatile in steam, and had the odour of a toluidine (Found : Cl, 50·7. $C_7H_6NCl_3$ requires Cl, 50·6%).

The *acetyl* derivative, prepared by heating the base with acetic anhydride and one drop of sulphuric acid, crystallised from dilute alcohol in colourless needles, m. p. 199° (Found : Cl, 42·1. $C_9H_8ONCl_3$ requires Cl, 42·8%). The *benzoyl* derivative, prepared by the usual Schotten–Baumann method, crystallised from alcohol in plates, m. p. 230° (Found : Cl, 33·8. $C_{14}H_{10}ONCl_3$ requires Cl, 33·9%).

2 : 6-*Dichloro*-4-*nitrotoluene*.—Chlorination of *p*-nitrotoluene was carried out as in the previous case. The crystalline deposit which separated after 3 months was recrystallised from alcohol, forming

long needles, m. p. 63—64° (Found : Cl, 35·2. $C_7H_5O_2NCl_2$ requires Cl, 35·5%).

2 : 6-*Dichloro*-3 : 4-*dinitrotoluene*.—The dichloronitro-compound above (1 g.) was warmed with nitric acid (5 c.c., *d* 1·51) and sulphuric acid (8 c.c.) on the water-bath. Crystals separated at first and afterwards melted to an oil. On cooling and dilution with water the *dinitro*-compound was precipitated; it crystallised from alcohol in needles, m. p. 130° (Found : Cl, 28·2. $C_7H_4O_4N_2Cl_2$ requires Cl, 28·3%).

2 : 6-*Dichloro*-p-*toluidine*.—2 : 6-Dichloro-4-nitrotoluene (2 g.) was reduced with stannous chloride (7·6 g.) and hydrochloric acid (40 c.c.). The *base* crystallised from dilute alcohol in needles, m. p. 55° (Found : Cl, 40·3. $C_7H_7NCl_2$ requires Cl, 40·3%).

The *acetyl* derivative, prepared from the base and acetic anhydride, crystallised from water in colourless needles, m. p. 215° (Found : Cl, 32·4. $C_9H_9ONCl_2$ requires Cl, 32·6%). The *benzoyl* derivative formed colourless needles, m. p. 179° (Found : Cl, 25·3. $C_{14}H_{11}ONCl_2$ requires Cl, 25·35%).

THE UNIVERSITY OF THE WITWATERSRAND,
JOHANNESBURG, SOUTH AFRICA.

[*Received, November* 17*th*, 1930.]