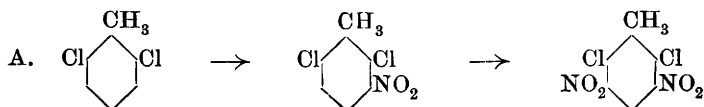


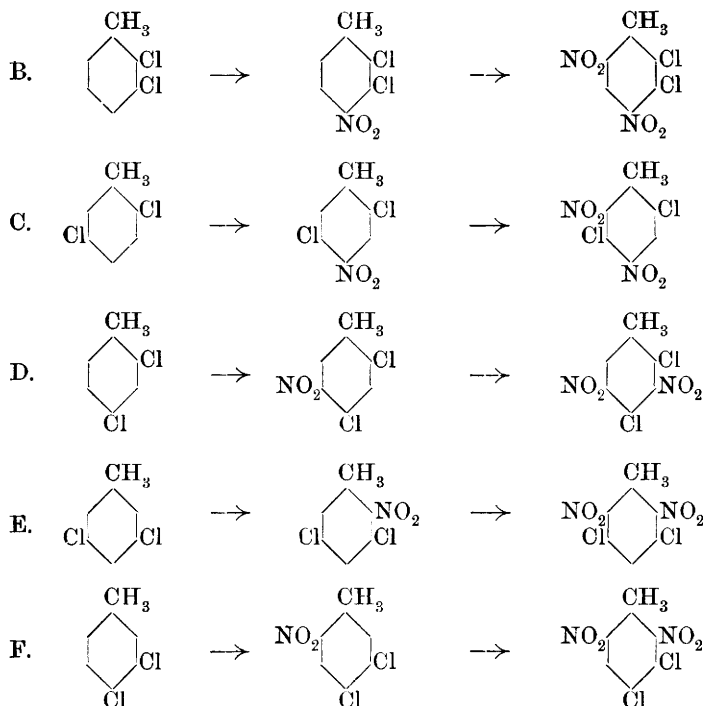
CXXXV.—*The Constitution of the Nitro- and Dinitro-derivatives of the Dichlorotoluenes.*

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THE nitro- and dinitro-derivatives of the six dichlorotoluenes have been previously described by us (Trans., 1901, 79, 1111) and have been made use of in identifying the products of chlorination of *o*- and *p*-chlorotoluene. It appeared to be of interest to ascertain the constitution of these substances in order to obtain evidence as to the laws of substitution which hold in the case of substances that are already highly substituted.

The following scheme represents the progressive nitration of the dichlorotoluenes :





Thus the nitro-group in the mononitro-compounds occupies the following positions with regard to the methyl group :

ortho-position in E, F.
 meta- ,, A, D.
 para- ,, B, C.

In regard to one of the chlorine atoms, the nitro-group stands in the following relations :

ortho-position in A, B, C, D, E.
 para- ,, A, C, D, E, F.
 meta- ,, B, C, F.

The chief directing influence clearly belongs to the chlorine atoms in relation to which the nitro-group enters the ortho- and para-positions.

The nitro-group also appears to avoid entering the nucleus between two other groups in the meta-position (C, D, F), which seems to be a case of space interference. When it is unavoidable, it selects the position between a chlorine atom and a methyl group.

In the case of the dinitro-compounds, the position of the first entering

nitro-group appears to be of primary importance in determining the position occupied by the second; for in all the six dichlorodinitrotoluenes, the nitro-groups are in the *meta*-position relatively to one another.

EXPERIMENTAL.

It was found that the nitro-derivatives of the dichlorotoluenes were, in many cases, most easily prepared by the action of cold fuming nitric acid at low temperatures, than by the methods previously described in which mixtures of sulphuric acid and small amounts of nitric acid, together with the substance to be nitrated, are heated together on the water-bath.

Nitro-derivatives of 2:6-Dichlorotoluene.

2:6-Dichloro-3-nitrotoluene.—Nitration in the cold was adopted in case of 2:6-dichlorotoluene. Ten grams of dichlorotoluene (b. p. 196—200°) were taken and 20 c.c. of fuming nitric acid added in small portions at a time. The mixture was thoroughly well shaken and cooled to the temperature of the air between each addition of acid. The addition of the last portions of nitric acid resulted in the production of a perfectly clear solution, from which the nitro-compound was precipitated by the addition of water. The crude product was pressed on a porous tile and then melted at 52—53°. By operating in the manner described, there appears to be no danger of the dinitro-compound being formed.

The nitro-compound was reduced by means of stannous chloride and hydrochloric acid and the base separated by addition of caustic soda followed by distillation in steam. A portion of the base was boiled with acetic anhydride and the acetyl derivative crystallised from alcohol. White, shining needles melting at 120—122° were obtained, identical with 2:6-dichloro-3-acetotoluidide. The remainder of the base was converted into trichlorotoluene by means of Sandmeyer's reaction, which after nitration gave 2:3:6-trichloro-4:5-dinitrotoluene, melting at 140°.

2:6-Dichloro-3:5-dinitrotoluene.—This substance was reduced by means of tin and hydrochloric acid, a little alcohol being added to assist in the solution of the dinitro-compound. After adding caustic soda, the solution was extracted with chloroform. On evaporation, a white, crystalline base was obtained, which gave a brilliant, orange-red coloration with a trace of nitrous acid. The base also gave the chrysoidine reaction for meta-diamines.

Nitro-derivatives of 2:3-Dichlorotoluene.

2:3-Dichloro-4-nitrotoluene.—Five grams of 2:3-dichlorotoluene were nitrated in the cold with 6 c.c. of fuming nitric acid. The nitro-compound was separated and purified in the usual way and was then reduced with tin and hydrochloric acid. After excess of caustic soda had been added, the base was separated by distillation in steam, and melted at 40—42°. It gave an acetyl derivative melting at 128—129°. On replacing the amino-group by chlorine, a trichlorotoluene (m. p. 40—41°) was obtained, which gave a dinitro-compound, melting at 140—141°, identical with 2:3:4-trichloro-5:6-dinitrotoluene.

2:3-Dichloro-4:6-dinitrochlorotoluene.—This substance was reduced with tin and hydrochloric acid and the resulting diamine extracted from the alkaline solution by means of chloroform. The base crystallised in leaflets from alcohol, in which it was readily soluble and slowly darkened on exposure to air. The substance readily responded to the nitrous acid and chrysoidine tests for meta-diamines. A negative result was obtained on testing the base with an acetic acid solution of phenanthraquinone.

Nitro-derivatives of 2:5-Dichlorotoluene.

2:5-Dichloro-4-nitrotoluene.—A mononitro-derivative of 2:5-dichlorotoluene in which the nitro-group was known to occupy position 3 has already been prepared (this vol., p. 1330) and as this substance is *not* identical with the product of nitration of 2:5-dichlorotoluene, it follows that the nitro-group in the latter substance must occupy either position 4 or 6. Since 2:5-dichloro-3-nitrotoluene, on further nitration, did not give the same dinitro-compound (m. p. 100—101°) as is produced by the nitration of 2:5-dichlorotoluene, but a substance melting at 69°, it appeared probable that position 3 was not substituted in either the mono- or dinitro-derivatives of 2:5-dichlorotoluene.

This supposition was confirmed in the following way:—2:5-Dichlorotoluene was nitrated with fuming nitric acid and the nitro-compound separated as usual. On reduction with tin and hydrochloric acid, a base was obtained which was readily volatile in steam and crystallised from alcohol in lustrous leaflets melting at 91—92°. This base was shown to be 2:5-dichloro-4-aminotoluene by converting it into 2:4:5-trichlorotoluene, which was obtained in the form of long, white, characteristic needles melting at 80—82°.

2:5-Dichloro-4:6-dinitrotoluene.—The second nitro-group in this substance was shown to occupy position 6, by reducing the dinitro-

compound to a base, which readily gave the nitrous acid and chrysoidine reactions for a meta-diamine. Negative results were obtained on applying tests for ortho- and para-diamines.

Nitro-derivatives of 2:4-Dichlorotoluene.

2:4-Dichloro-5-nitrotoluene.—The constitution of this substance was determined by two methods, (i) by synthesis, (ii) by conversion into 2:4-dichloro-5-acetotoluidide and subsequently into 2:4:5-trichlorotoluene.

(i) *p*-Nitro-*o*-toluidine was converted into 2-chloro-4-nitrotoluene, and this substance was then reduced by means of stannous chloride and hydrochloric acid to *o*-chloro-*p*-toluidine. The dry nitrate of this base was added to cold concentrated sulphuric acid and the resulting 2-chloro-5-nitro-4-aminotoluene purified by crystallisation from alcohol. The amino-group in this substance was replaced by chlorine by means of Sandmeyer's reaction and the 2:4-dichloro-5-nitrotoluene separated by distillation in steam. The product was found to be identical with the 2:4-dichloronitrotoluene prepared by the nitration of 2:4-dichlorotoluene.

(ii) The nitro-compound was reduced by means of stannous chloride and hydrochloric acid and the base separated by steam distillation of the alkaline solution. The substance melted at 87°, and was identical with 2:4-dichloro-5-aminotoluene. On heating with acetic anhydride, an acetyl derivative was formed which melted at 156—157°, agreeing with 2:4-dichloro-5-acetotoluidide, previously prepared by the chlorination of *m*-acetotoluidide. The amino-group in the base was replaced by chlorine, using Sandmeyer's reaction, and 2:4:5-trichlorotoluene obtained which melted at 80—82°, after crystallisation from alcohol.

2:4-Dichloro-3:5-dinitrotoluene.—The dinitro-derivative, on reduction, gave a base which responded to the nitrous acid and chrysoidine tests for meta-diamines.

An alcoholic solution of the base did not give a precipitate with phenanthraquinone dissolved in acetic acid.

Nitro-derivatives of 3:5-Dichlorotoluene.

3:5-Dichloro-2-nitrotoluene.—The constitution of the mononitro-derivative of 3:5-dichlorotoluene can only be represented by one of two possible formulæ. The nitro-compound was reduced by tin and hydrochloric acid, and the base, which does not readily form a hydrochloride, was extracted from the acid solution by means of chloroform. The crude base melted at 58—60°, and this melting point was unchanged by crystallisation from alcohol. The melting point agrees

with that of 3:5-dichloro-4-aminotoluene prepared by Lellmann and Klotz (*Annalen*, 1885, 231, 322), but the acetyl derivative melts at 185—187°, agreeing, therefore, with 3:5-dichloro-2-acetotoluidide. The trichlorotoluene obtained from the base, and its nitro- and dinitro-derivatives, corresponded in properties with the 2:3:5-compound and its nitro- and dinitro-derivatives. The melting point, therefore, of 3:5-dichloro-2-aminotoluene is 58—60°, and not 56° as usually given.

3:5-Dichloro-2:1-dinitrotoluene.—The constitution of this dinitro-compound can only be represented by two formulæ, namely, 3:5-dichloro-2:4-dinitrotoluene and 3:5-dichloro-2:6-dinitrotoluene. We have not yet succeeded in ascertaining which is the correct formula, as both substances yield meta-diamines on reduction.

Nitro-derivatives of 3:4-Dichlorotoluene.

3:4-Dichloro-6-nitrotoluene.—The constitution of this substance was determined by synthesis. 3-Chloro-4-aminotoluene was treated with dilute nitric acid and the dry crystalline nitrate added in small portions to cold strong sulphuric acid (Claus and Davidsen, *Annalen*, 1891, 265, 343). The resulting 3-chloro-6-nitro-4-aminotoluene was converted into 3:4-dichloro-6-nitrotoluene by means of Sandmeyer's reaction and the product purified by distillation in steam. The nitro-compound melted at 63—64° and was identical with the product of nitration of 3:4-dichlorotoluene.

3:4-Dichloro-2:6-dinitrotoluene.—3:4-Dichloro-5-nitrotoluene has been previously prepared from 3-chloro-5-nitro-4-acetotoluidide, and since this substance, on further nitration, gave a dinitro-compound melting at 80—81°, whilst the product of nitration of 3:4-dichloro-6-nitrotoluene melts at 91·5—92·5°, it was probable that the second nitro-group in the latter substance did not occupy position 5. This supposition was confirmed by the fact that the base obtained on reducing the dinitro-derivative with tin and hydrochloric acid gave both the nitrous acid and chrysoidine test for a meta-diamine, thus proving that the second nitro-group occupies position 2.

A negative result was obtained on testing the base with phenanthraquinone.

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