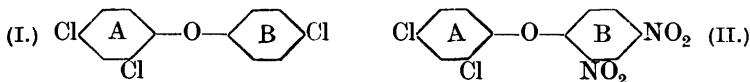


LXXVI.—*The Scission of Diaryl Ethers and Related Compounds by Means of Piperidine. Part II. The Nitration of 2:4:4'-Trichlorodiphenyl Ether, and of 2:4-Dichlorophenyl p-Toluenesulphonate and Benzoate.*

By LESLIE GEORGE GROVES, EUSTACE EBENEZER TURNER,
and (in part) GLADYS IRENE SHARP.

IF, as Flürscheim contends, residual affinity is a sufficiently descriptive name for the main origin of the factors controlling benzene substitution, then, since the phenoxy group is very weakly directing (Lea and Robinson, J., 1926, 411), 2:4:4'-trichlorodiphenyl ether (I) might be expected to undergo a certain, although not necessarily a large, amount of nitration in position 3' in nucleus B. For, according to Flürscheim's view, the effect of the chlorine atoms in positions 2 and 4 will be to release an extra amount of affinity in position 1, so that in effect the oxygen atom is much less unsaturated than it would be in diphenyl ether or in 4:4'-dichlorodiphenyl ether, and therefore, on the residual-affinity view, it is even more weakly directing than the oxygen atom in diphenyl ether itself, and approaches, in fact, the directive power of a chlorine atom. On the other hand, on Robinson's view of orientation effects, the conjugation of the oxygen atom will be decreased as a result of the presence of the two chlorine atoms in nucleus A, and further decreased owing to the presence of the 4'-chlorine atom. Its directive power should therefore be increased, and the trichloro-ether would not be expected to undergo nitration at all in position 3'. At the same time, however, the absence of 3'-nitration could not be put forward as necessarily invalidating Flürscheim's theory, owing to the complexity of the case in question.

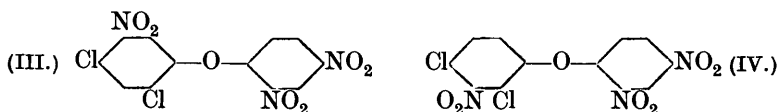


The trichloro-ether was readily obtained from 4:4'-dichloro-2-aminodiphenyl ether by the Sandmeyer reaction, which has otherwise (see Experimental) given unsatisfactory results in this series, as has also the Gattermann reaction. The amino-ether was obtained from 4:4'-dichloro-2-nitrodiphenyl ether.

2:4:4'-Trichlorodiphenyl ether was dinitrated with unexpectedly great readiness, but when, by control of the conditions, mononitration was effected, it took place quantitatively in the 2'-position, the constitution of the product following from its ready scission by means

of piperidine into 2:4-dichlorophenol and 4-chloro-2-nitrophenyl-piperidine (compare Le Fevre, Saunders, and Turner, J., 1927, 1168).

The dinitro-derivative, which was not accompanied by any isomerides, reacted with piperidine to give a mixture of products, amongst which 4-chloro-2-nitrophenylpiperidine and piperidine hydrochloride were recognised (see below), so the second nitro-group must have entered position 3 or 5 in nucleus A. This behaviour was sufficiently unexpected to merit further investigation, and we accordingly studied first the nitration of the more readily accessible 2:4-dichloro-2':4'-dinitrodiphenyl ether (II); this was readily mononitrated to give a dichlorotrinitro-ether, unaccompanied by isomerides, which was converted by boiling piperidine into 2:4-dinitrophenylpiperidine and a dichloronitrophenol, or by boiling aniline into the latter and 2:4-dinitrodiphenylamine. The phenol, although not identical with the known 2:4-dichloro-6-nitrophenol, and therefore containing a chlorine atom and a nitro-group ortho to each other, did not react with piperidine. The trinitro-ether was evidently (III) or (IV), and although (III) appeared the more probable, the complete absence of chlorine reactivity on



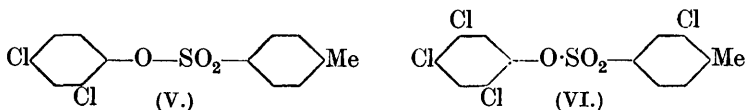
the part of the ether itself made it essential to prove the non-validity of (IV), in which the activating effect of the nitro-group would possibly be masked owing to steric influences. The proof, however, presented unexpected difficulties.

For example, it was anticipated that 2:4-dichloro-5-nitroaniline would be convertible by the diazo-method into 2:4-dichloro-5-nitrophenol, but we have been unable to effect this change. The base, previously obtained in small yield by Körner and Contardi (*Atti R. Accad. Lincei*, 1909, **18**, 93), is readily obtainable by hydrolysing its *phthalyl* derivative, which is formed in almost quantitative yield by nitrating N-2:4-dichlorophenylphthalimide (compare Brady, Quick, and Welling, J., 1925, **127**, 2264).

Again, it did not appear improbable that dichlorination of *m*-nitrophenol would give, as one product, 2:4-dichloro-5-nitrophenol. Actually, the main, if not the only, product was 2:4-dichloro-3-nitrophenol, identified as follows: its *p*-toluenesulphonyl derivative is reducible to an amino-compound, and replacement of the amino-group by a chlorine atom, followed by hydrolysis of the *p*-toluenesulphonyl group, gives 2:3:4-trichlorophenol. Holleman (*Rec. trav. chim.*, 1920, **39**, 740) obtained the benzoate (m. p. 141°) of this phenol, but not the substance itself. We have now found that

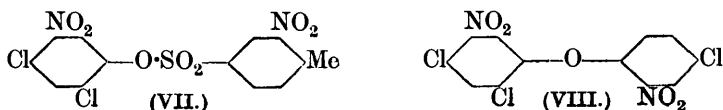
2 : 3 : 4-trichlorophenol is the chief product when 3 : 4-dichlorophenol is monochlorinated, a result of considerable interest. Again, the above result of chlorination of *m*-nitrophenol is somewhat unexpected in view of the fact that *m*-nitroaniline is dichlorinated in the 2 : 6- and the 2 : 4-positions (Körner and Contardi, *loc. cit.*). The constitution of the 2 : 3 : 4-trichlorophenol now described follows by exclusion (apart from the evidence of the m. p. of our benzoate, *viz.*, 143°), since the method used to produce it could only give 2 : 3 : 4-, 2 : 3 : 6-, or 2 : 4 : 5-trichlorophenol. Of these, the last was in our possession (see below) and the benzoate of the 2 : 3 : 6-compound melts at 90° (Holleman, *loc. cit.*).

The constitution of the above dichloronitrophenol had therefore to be proved by a less direct method. It was anticipated that since (II) was nitrated in the meta-position (nucleus A), 2 : 4-dichlorophenyl *p*-toluenesulphonate (V) would behave similarly. This was



found to be the case, for nitration of (V) gave a dinitro-compound, which was converted by boiling piperidine into the above dichloronitrophenol and 1-*o*-nitro-*p*-toluenesulphonylpiperidine, the constitution of which was proved by synthesis. Reduction of the dichlorodinitro-compound gave a diamino-compound which was converted in turn into a tetrachloro-compound. The latter, when boiled with piperidine, gave a trichlorophenol, the properties of which agreed with those recorded by Holleman for the 2 : 4 : 5-compound. In view of the method by which Holleman obtained this phenol (*loc. cit.*), it was thought desirable to seek independent evidence as to its properties. This has been done as follows : 2 : 5-dichlorophenol, which on monochlorination would be expected to give either 2 : 4 : 5- or 2 : 3 : 6-trichlorophenol, gives the same trichlorophenol as that just mentioned. Additional proof of the constitution was obtained by establishing the identity of the latter with the phenol resulting by the diazo-method from 2 : 4 : 5-trichloroaniline.

It follows from this that the tetrachloro-sulphonate was (VI) and that the dinitro-compound from which it was obtained was (VII), so that the dichloronitrophenol is 2 : 4-dichloro-5-nitrophenol, and the dichlorotrinitrodiphenyl ether is (III) and not (IV).



It would therefore appear probable that the dinitro-derivative of (I) is (VIII). This substance was readily reduced to the corresponding diamino-compound, but attempts to replace the amino-groups by chlorine atoms led to inseparable mixtures. Endeavours to synthesise the expected pentachloro-ether (for seeding purposes) were similarly unsuccessful. 4 : 5-Dichloro-1 : 2-dinitrobenzene was readily converted by potassium *p*-chlorophenoxide into 4 : 5 : 4'-trichloro-2-nitrodiphenyl ether, nitration of which gave 4 : 5 : 4'-trichloro-2 : 2'-dinitrodiphenyl ether, reducible to a diamino-compound, but the latter could not be converted into the desired pentachloro-ether. Similarly, interaction of the above dichloro-dinitrobenzene with potassium 2 : 4-dichlorophenoxide produced 4 : 5 : 2' : 4'-tetrachloro-2-nitrodiphenyl ether, also reducible to an amine, but the latter, again, did not react normally under the conditions of a Sandmeyer or Gattermann replacement.

The formation of piperidine hydrochloride when the dinitro-derivative of (I) was heated with piperidine, and the non-formation of this hydrochloride when (III) was so treated, could be explained by assuming that activation of the 4-chlorine atom (formula VIII) by the 5-nitro-group was of an order similar to the activation of the oxygen-C₁ linkage by the 2'-nitro-group, so that some scission and some replacement of chlorine by piperidine resulted. Introduction of a third nitro-group into (VIII) in position 6' should make scission much more rapid than replacement of chlorine. The dinitro-compound can be nitrated to give a trichlorotrinitrodiphenyl ether, which is very readily converted into 2 : 4-dichloro-5-nitrophenol, together with a chlorodinitrophenylpiperidine. The readiness of formation of the latter substance suggested that it is 4-chloro-2 : 6-dinitrophenylpiperidine, but this compound, prepared for the purpose by treating 4-chloro-2 : 6-dinitroanisole with piperidine, had entirely different properties, so that its isomeride must be either 4-chloro-2 : 5- or 4-chloro-2 : 3-dinitrophenylpiperidine. It seems extremely unlikely that the original nitration could have occurred in the position, *viz.*, 3' in (VIII), corresponding to the production of 4-chloro-2 : 3-dinitrophenylpiperidine, and also that the trichlorotrinitro-ether would have undergone scission prior to replacement of a nitro-group by piperidine. It therefore appears certain that the ether in question is 2 : 4 : 4'-trichloro-5 : 2' : 5'-trinitrodiphenyl ether, but in any case the formation of 2 : 4-dichloro-5-nitrophenol in the scission of the trinitro-ether shows that the dinitro-ether is (VIII). Further investigation of the action of piperidine on the latter showed that 76% of this substance undergoes replacement of chlorine by piperidine (it being assumed that only the 4-chlorine atom reacts), and

2 : 4-dichloro-5-nitrophenol was actually isolated from the scission mixture.

Finally, we have studied the nitration of 2 : 4-dichlorophenyl benzoate, and found that this substance, when dinitrated, gives 2 : 4-dichloro-5-nitrophenyl *m*-nitrobenzoate, accompanied apparently by traces of the *o*- and *p*-nitrobenzoates, but unaccompanied by the 3- or the 6-nitro-compound. For the benzoate of 2 : 4-dichloro-5-nitrophenol is nitrated to give a product of the same composition, and the main constituent of either nitration product is identical with the product of the *m*-nitrobenzoylation of 2 : 4-dichloro-5-nitrophenol, but distinct from 2 : 4-dichloro-6-nitrophenyl *m*-nitrobenzoate.

The monohalogenation of *m*-nitrophenol and the nitration of ethers analogous to those described above are under investigation.

EXPERIMENTAL.

Preparation of 2 : 4-Dichlorophenol.—We have found that this substance is most readily obtained from *p*-chlorophenol. Chlorine was passed into a cooled solution of 128.5 g. of the latter substance in 500 c.c. of glacial acetic acid, until the required increase in weight was obtained. The product was then distilled, and 129 g. of 2 : 4-dichlorophenol (b. p. 209—211°) were obtained (yield, 80%). *o*-Chlorophenol may be used instead of *p*-chlorophenol.

2 : 4-Dichlorophenyl *p*-toluenesulphonate is readily formed by the normal method, and crystallises from alcohol in rhombohedral prisms, m. p. 125° (Found : Cl, 22.4. $C_{13}H_{10}O_3Cl_2S$ requires Cl, 22.4%).

Nitration of 2 : 4-Dichlorophenyl p-Toluenesulphonate.—The sulphonate (30 g.) was added in small quantities to 300 c.c. of nitric acid (*d* 1.5), with water-cooling. After 30 minutes, the solution was poured on ice, and the resulting solid washed with boiling water. 2 : 4-Dichloro-5-nitrophenyl *o*-nitro-*p*-toluenesulphonate separates from alcohol in colourless prisms, m. p. 103° (Found : Cl, 17.3. $C_{13}H_8O_7N_2Cl_2S$ requires Cl, 18.0%).

2 : 4-Dichloro-5-aminophenyl *o*-Amino-*p*-toluenesulphonate.—The preceding dinitro-compound was reduced by iron powder, water, and a little acetic acid. The diamino-compound forms colourless tooth-shaped needles from alcohol-acetone, and has m. p. 159—161° (Found : Cl, 19.8. $C_{13}H_{12}O_3N_2Cl_2S$ requires Cl, 20.4%); it is diazotised readily, and the resulting solution couples normally with β -naphthol. The base does not condense with salicylaldehyde in boiling alcoholic solution, but does so at the b. p. of the aldehyde.

Isolation of 2 : 4 : 5-Trichlorophenol.—The diamino-compound was diazotised in dilute hydrochloric acid, the resulting solution being added to cuprous chloride-hydrochloric acid. After normal

procedure, the tetrachloro-sulphonate was obtained as a red gum, which was not further purified. It was heated under reflux for 3 hours with piperidine. The resulting solution was then rendered strongly acid, and distilled in a current of steam. The oil passing over solidified on cooling, and had m. p. 66—67° (Found : Cl, 54.2. Calc. : Cl, 54.0%). 2 : 4 : 5-Trichlorophenol forms a sparingly soluble potassium salt. The benzoate obtained from our specimen of the phenol melted at 91—92° (compare Holleman, *loc. cit.*).

Chlorination of 2 : 5-Dichlorophenol.—The phenol was dissolved in three times its weight of glacial acetic acid, in which the necessary amount of anhydrous sodium acetate had previously been dissolved. Chlorine was passed through the cooled solution until the required increase in weight was obtained, and water was then added. The precipitated 2 : 4 : 5-trichlorophenol was purified by sublimation, and then had m. p. 66—67°. The benzoate melted at 91—92°.

Preparation of 2 : 4 : 5-Trichlorophenol from 2 : 4 : 5-Trichloro-aniline.—This was satisfactorily effected by the method described by Noelting and Kopp (*Ber.*, 1905, **38**, 3506) for the conversion of 2 : 5-dichloroaniline into 2 : 5-dichlorophenol. The specimen of trichlorophenol obtained had m. p. 66—67° (benzoate, m. p. 91—92°). Mixtures of any two of the various preparations of trichlorophenol also melted at 66—67°.

1-p-Toluenesulphonylpiperidine and 1-o-Nitro-p-toluenesulphonylpiperidine.—Piperidine readily reacted with *p*-toluenesulphonyl chloride or with its *o*-nitro-derivative in aqueous alkaline suspension. 1-*p*-Toluenesulphonylpiperidine crystallises from alcohol in colourless needles, m. p. 103° (Found : S, 13.7. $C_{12}H_{17}O_2NS$ requires S, 13.4%). 1-*o*-Nitro-*p*-toluenesulphonylpiperidine separates from alcohol in pale greenish-yellow prisms, m. p. 112° (Found : S, 12.4. $C_{12}H_{16}O_4N_2S$ requires S, 12.1%).

Action of Piperidine on 2 : 4-Dichloro-5-nitrophenyl o-Nitro-p-toluenesulphonate.—The latter compound was heated with one-third of its weight of piperidine for 1.5 hours at 100°. No separation of piperidine hydrochloride occurred, showing that hydrolysis of the sulphonate group takes place much more rapidly than replacement of chlorine. The red solution was treated with dilute alkali, and the oil which separated soon became solid, and after crystallisation from alcohol had m. p. 112° either alone or when mixed with a specimen of synthetic 1-*o*-nitro-*p*-toluenesulphonylpiperidine. The alkaline mother-liquor was acidified, and the resulting precipitate recrystallised from water (Found : Cl, 34.1. $C_6H_3O_3NCl_2$ requires Cl, 34.1%). 2 : 4-Dichloro-5-nitrophenol forms almost colourless needles, m. p. 105—106°. The potassium salt is sparingly soluble.

N-2 : 4-*Dichlorophenylphthalimide*.—2 : 4-Dichloroaniline (132 g.) was treated with powdered phthalic anhydride (124 g.), and the mixture heated at 200° for an hour. The still molten material was poured into 300 c.c. of cold alcohol, and when the resulting solution cooled, the required *phthalimide* crystallised out. It was recrystallised from alcohol, and then formed colourless prisms, m. p. 155° (Found : Cl, 24·4. $C_{14}H_7O_2NCl_2$ requires Cl, 24·3%) (yield, 195 g.).

2 : 4-*Dichloro-5-nitroaniline*.—To a solution of 190 g. of the dichlorophenylphthalimide in 1 litre of concentrated sulphuric acid were slowly added 34·5 c.c. of nitric acid (*d* 1·5), the temperature being kept below 30°. The solution obtained was poured on ice, and the precipitate collected and washed (208 g.). N-2 : 4-*Dichloro-5-nitrophenylphthalimide* crystallises from *cyclohexanone* in pale yellow octahedra, m. p. 217—219° (Found : Cl, 20·8. $C_{14}H_6O_4N_2Cl_2$ requires Cl, 21·1%). The phthalimide (200 g.) was heated at 120° for 30 minutes with 1 litre of 90% sulphuric acid, the solution was cooled, poured into excess of ammonia containing ice, and the precipitated base collected. After purification it had the properties recorded by Körner and Contardi (*loc. cit.*) (Found : Cl, 34·3. Calc. : Cl, 34·3%). It was found impossible to prepare the base by nitrating 2 : 4-dichloroaniline in excess of concentrated sulphuric acid at -15°.

Diazo-solutions obtained from the base in either dilute or concentrated hydrochloric acid, or in dilute or moderately concentrated sulphuric acid, were heated under a variety of conditions. In two cases copper sulphate was added, but in no case could 2 : 4-dichloro-5-nitrophenol be isolated.

2 : 4-*Dichloro-2' : 4'-dinitrodiphenyl Ether*.—When 40 g. of 1-chloro-2 : 4-dinitrobenzene were added to a solution of 32 g. of 2 : 4-dichlorophenol in 11 g. of potassium hydroxide, previously dissolved hot in about 0·5 c.c. of water, rapid interaction occurred, and after the mixture had been kept at 100° for $\frac{1}{4}$ hour, water was added. The solid obtained was ground with dilute alkali solution and washed with water. It crystallised from glacial acetic acid in very pale greenish-yellow leaflets, m. p. 118—119° (Found : Cl, 21·6. $C_{12}H_6O_5N_2Cl_2$ requires Cl, 21·6%).

Nitration of 2 : 4-Dichloro-2' : 4'-dinitrodiphenyl Ether.—10 G. of the ether were added slowly to 100 c.c. of nitric acid (*d* 1·5), without cooling. After one hour, the clear solution was poured into excess of water. The resulting precipitate crystallised from 90% acetic acid in colourless rhombohedra, m. p. 128° (Found : Cl, 18·9. $C_{12}H_5O_7N_3Cl_2$ requires Cl, 19·1%).

Scission of 2 : 4-Dichloro-5 : 2' : 4'-trinitrodiphenyl Ether.—(a) *With piperidine*. A mixture of 18·5 g. of the trinitro-compound

with 22 g. of piperidine was heated at 100° for 2 hours. No piperidine hydrochloride separated. The solution was diluted and rendered strongly alkaline, and the precipitated 2 : 4-dinitrophenylpiperidine was collected and extracted with benzene until no more coloured product was removed. The aqueous solution was freed from benzene by heating at 100°, cooled, and slowly acidified. The almost colourless precipitate was dried, and crystallised from light petroleum (b. p. 80—100°). The resulting product melted at 105—106° either alone or when mixed with the 2 : 4-dichloro-5-nitrophenol obtained from the above toluenesulphonate.

When a chloroform solution of either 1 or 2 mols. of piperidine was added slowly to a boiling solution of the dichlorotrinitro-compound (1 mol.), scission was quantitatively effected.

(b) *With aniline.* A solution of 20 g. of the dichlorotrinitro-compound in 150 g. of aniline was heated for 4 hours at 100°. The solution was shaken with hydrochloric acid, and the resulting reddish precipitate filtered off; it was identical with a pure specimen of 2 : 4-dinitrodiphenylamine, and was obtained in theoretical yield. When the filtrate became cool, 2 : 4-dichloro-5-nitrophenol, containing a little dinitrodiphenylamine and considerable aniline hydrochloride, separated and was filtered off. After removal of aniline hydrochloride by washing with cold water, the phenol was purified by dissolution in dilute alkali, filtration, and precipitation with dilute acid.

4 : 4'-Dichloro-2-nitrodiphenyl Ether.—The following method was found much more satisfactory than existing methods, e.g., that of Raiford and Colbert (*J. Amer. Chem. Soc.*, 1926, **48**, 2652) : *p*-Dichlorobenzene (100 g.) was added within 15 minutes to 500 g. of nitric acid (*d* 1.5). After a further 15 minutes, the solution was poured into excess of cold water, and the precipitated solid air-dried. The whole was introduced into a solution obtained by adding 88 g. of *p*-chlorophenol to 37 g. of potassium hydroxide which had previously been heated to a clear melt in presence of 1—2 c.c. of water. The mixture was heated in a bath kept at 160—170° for 2 hours, cooled, and shaken with dilute alkali until the precipitated material (162 g.) was crystalline. After one crystallisation from alcohol, the nitro-compound was pure. Use of copper bronze does not increase the yield, and hampers manipulation; moreover, it apparently causes formation of some 4-chloro-4'-hydroxydiphenyl ether.

4 : 4'-Dichloro-2-aminodiphenyl Ether.—The nitro-compound was reduced at 100° by means of iron filings and excess of water in presence of a little acetic acid. The crude *base*, produced in 90% of the theoretical yield, crystallises from light petroleum (b. p. 80—100°)

in colourless needles, m. p. 67° (Found: Cl, 27.7. $C_{12}H_9ONCl_2$ requires Cl, 27.9%); it is readily diazotised in presence of excess of hydrochloric acid, and the resulting solution couples normally with sodium β -naphthoxide.

2 : 4 : 4'-Trichlorodiphenyl Ether.—The last-named amine (30 g.) was diazotised (70 c.c. of concentrated hydrochloric acid, 70 c.c. of water, and 9 g. of sodium nitrite in 20 c.c. of water) and poured into cuprous chloride-hydrochloric acid; normal decomposition took place, and the red oil produced was well washed with water and with alkali, and extracted with carbon tetrachloride. Removal of solvent, followed by vacuum distillation, gave 13 g. of *2 : 4 : 4'-trichlorodiphenyl ether*, b. p. $183^{\circ}/11$ mm. This became solid on cooling and, when crystallised from light petroleum (b. p. $40-60^{\circ}$), formed colourless needles, m. p. $54-55^{\circ}$ (Found: Cl, 39.2. $C_{12}H_7OCl_3$ requires Cl, 38.9%).

Nitration of 2 : 4 : 4'-Trichlorodiphenyl Ether.—(1) *Mononitration.* One g. of the trichloro-ether was added to a mixture of 10 c.c. of nitric acid (d 1.4) with 10 c.c. of glacial acetic acid. Nitric acid (d 1.5) and glacial acetic acid were added alternately until the whole of the solid passed into solution (in all, 30 c.c. of the fuming acid and 15 c.c. of acetic acid were added). After $\frac{1}{2}$ hour, the solution was slowly treated with water. The resulting precipitate was collected and dried, and then crystallised from light petroleum (b. p. $40-60^{\circ}$) in tough pads of almost colourless needles, m. p. $86-87^{\circ}$ (Found: Cl, 33.6. $C_{12}H_6O_3NCl_3$ requires Cl, 33.4%). When this *2 : 4 : 4'-trichloro-2'-nitrodiphenyl ether* was heated with piperidine, *2 : 4-dichlorophenol* and *4-chloro-2-nitrophenylpiperidine* were formed.

(2) *Dinitration.* The trichloro-ether was slowly added to 7 parts of nitric acid (d 1.5), without cooling, and the solution obtained allowed to stand for an hour. It was then poured into excess of cold water, and the precipitate formed was crystallised from alcohol. In an experiment carried out under quantitative conditions, there were obtained from 2.00 g. of initial ether, 2.00 g. of product of m. p. $103-104^{\circ}$ and 0.32 g. of material of m. p. $101-103^{\circ}$, showing that no appreciable quantity of by-products was formed. *2 : 4 : 4'-Trichloro-5 : 2'-dinitrodiphenyl ether* forms pale yellow prisms, m. p. $103-104^{\circ}$ (Found: Cl, 28.7; N, 8.1. $C_{12}H_5O_5N_2Cl_3$ requires Cl, 29.3; N, 7.7%).

The dinitro-derivative reacted readily with boiling piperidine to give piperidine hydrochloride and a reddish solution. The mixture was treated with alkali, and exhaustively extracted with benzene. From the benzene layer, nothing but *4-chloro-2-nitrophenylpiperidine* was obtained. The alkaline solution was acidified

and then extracted with ether. The extract yielded a reddish-brown solid, m. p. 102—103°, which, after being dissolved in alkali and reprecipitated with dilute acid, gave almost colourless leaflets, m. p. 104—105°, identical with 2 : 4-dichloro-5-nitrophenol obtained from other sources (above) (Found : Cl, 34.0. Calc. : Cl, 34.1%).

Reduction of the dinitro-compound by the iron-water-acetic acid method gave 2 : 4 : 4'-trichloro-5 : 2'-diaminodiphenyl ether, which crystallises from light petroleum (b. p. 80—100°) in rhombohedra, m. p. 93—94° (Found : Cl, 35.0. $C_{12}H_9ON_2Cl_3$ requires Cl, 35.1%).

(3) *Trinitration*. The trichloro-compound (or its dinitro-derivative) was dissolved in 50 parts of nitric acid (*d* 1.5), and 10 parts of fuming sulphuric acid (20% SO_3) were slowly added, the temperature being kept below 50°. When the mixture was poured on ice, 2 : 4 : 4'-trichloro-5 : 2' : 5'-trinitrodiphenyl ether was precipitated; this, after being crystallised from alcohol, formed yellowish-green leaflets, m. p. 155—157° (Found : Cl, 25.3. $C_{12}H_4O_7N_3Cl_3$ requires Cl, 26.1%). The trinitro-compound dissolved in cold piperidine to give a purple-red solution. After a few minutes' boiling the colour faded. Excess of alkali was then added, the whole was repeatedly extracted with benzene, and the alkaline solution acidified. A precipitate of 2 : 4-dichloro-5-nitrophenol was formed. The benzene solution was washed with dilute acid and then dried and evaporated; the 4-chloro-2 : 5-dinitrophenylpiperidine obtained crystallised from alcohol in red leaflets, m. p. 70—71° (Found : Cl, 12.9. $C_{11}H_{12}O_4N_3Cl$ requires Cl, 12.4%).

Action of Piperidine on 4-Chloro-2 : 6-dinitroanisole.—The latter compound, prepared by treating the dry or moist silver salt of 4-chloro-2 : 6-dinitrophenol with methyl iodide, reacted vigorously with piperidine to give 4-chloro-2 : 6-dinitrophenylpiperidine, which crystallised from alcohol in golden prisms, m. p. 165—166° (Found : Cl, 12.0. $C_{11}H_{12}O_4N_3Cl$ requires Cl, 12.4%).

Nitration of 2 : 4-Dichlorophenyl Benzoate.—The benzoate was added gradually to 10 parts of nitric acid (*d* 1.5), the temperature not being allowed to rise above 30°. After one hour, the solution was poured on ice, and the gummy solid so obtained heated with water until it became hard. It then crystallised from alcohol, in which it is very sparingly soluble, in colourless leaflets, m. p. 148° (Found : Cl, 20.0. $C_{13}H_6O_6N_2Cl_2$ requires Cl, 19.9%). This product is almost pure 2 : 4-dichloro-5-nitrophenyl *m*-nitrobenzoate (see below), but contains traces of *o*- and/or *p*-nitrobenzoate, not removed by recrystallisation. When mixed with the pure *m*-nitrobenzoate, it melted at 152—153°.

Benzoylation of 2 : 4-dichloro-5-nitrophenol gave a benzoate, which, after being crystallised from alcohol, had m. p. 111—112°.

This was nitrated as above, and gave a product identical in properties with that obtained from 2 : 4-dichlorophenyl benzoate.

The *m*-nitrobenzoate of 2 : 4-dichlorophenol crystallises from alcohol in hairy needles, m. p. 115—116° (Found : Cl, 23.3. $C_{13}H_7O_4NCl_2$ requires Cl, 22.8%). Nitration of this product gave pure 2 : 4-dichloro-5-nitrophenyl *m*-nitrobenzoate, m. p. 154°. An identical substance was obtained by condensing 2 : 4-dichloro-5-nitrophenol with *m*-nitrobenzoyl chloride in warm alkaline suspension.

2 : 4-Dichloro-6-nitrophenyl *m*-nitrobenzoate, prepared for comparison purposes from the product of dichlorinating *o*-nitrophenol (Tarugi, *Gazzetta*, 1891, **30**, 491), is very sparingly soluble in alcohol, from which it crystallises in colourless prisms, m. p. 149—150° (Found : Cl, 19.5%). A mixture of this substance with 2 : 4-dichloro-5-nitrophenyl *m*-nitrobenzoate melted at 128—129°.

Chlorination of m-Nitrophenol.—Chlorine was passed into 20 g. of *m*-nitrophenol, which was kept just liquid by heating. When the calculated increase in weight was obtained the 2 : 4-dichloro-3-nitrophenol (see below) was twice crystallised from light petroleum (b. p. 80—100°). It formed very pale yellowish-green needles, m. p. 70—72°, raised to 85—87° after drying in a vacuum over sulphuric acid (Found : Cl, 34.1. $C_6H_3O_3NCl_2$ requires Cl, 34.1%).

The *p*-toluenesulphonyl derivative crystallised from alcohol in leaflets, m. p. 122° (Found : Cl, 19.3; S, 9.5. $C_{13}H_9O_5NCl_2S$ requires Cl, 19.6; S, 8.8%); it was reduced by means of iron, water, and a little acetic acid to 2 : 4-dichloro-3-aminophenyl *p*-toluenesulphonate, which crystallised from light petroleum (b. p. 80—100°) in colourless plates, m. p. 113—114° (Found : Cl, 21.4; S, 9.5. $C_{13}H_{11}O_3NCl_2S$ requires Cl, 21.9; S, 9.6%).

The amino-compound is apparently unaffected by hot concentrated hydrochloric acid, the resulting suspension after being cooled not undergoing diazotisation to any appreciable extent. Replacement of the amino-group by chlorine was therefore effected as follows : A solution of 9 g. of the amino-compound in 30 c.c. of concentrated sulphuric acid was diazotised at 20° with a solution of 2 g. of sodium nitrite in 15 c.c. of concentrated sulphuric acid, prepared at -15°. The clear solution obtained by pouring on ice was added to cuprous chloride-hydrochloric acid, and the resulting mixture was distilled in steam. The crude solid which passed over was dissolved in excess of piperidine and the solution was boiled under reflux for an hour, then strongly acidified, and distilled in steam. Almost pure 2 : 3 : 4-trichlorophenol passed over. It was purified by dissolution in alkali, followed by acidification, and finally by sublimation. It forms colourless needles, m. p. 80—81° (Found : Cl, 54.8. $C_6H_3OCl_3$

requires Cl, 54.0%). The benzoate had m. p. 143° (compare Holleman, *loc. cit.*).

Chlorination of 3:4-Dichlorophenol.—This phenol was readily obtained by application of the method of Noeltling and Kopp (*loc. cit.*). Chlorination was carried out as in the case of 2:5-dichlorophenol (p. 517). The sample of 2:3:4-trichlorophenol was in no way different from that described above, and gave a benzoate of m. p. 143° (Found: Cl, 35.2. Calc.: Cl, 35.3%), unaltered on admixture with the benzoate described above.

Action of Phosphorus Pentachloride and of Thionyl Chloride on 2:4-Dichloro-5-nitrophenol.—In preliminary attempts to establish the identity of this phenol, it was heated with 2 parts (= 2 mols.) of phosphorus pentachloride at 150—160° for 1.5 hours. The cooled product was extracted with carbon tetrachloride, and the extract well washed with alkali. Removal of the solvent gave a product, b. p. 150—160°/15 mm., m. p. 80—89°, but insufficient was obtained for detailed examination.

The dichloronitrophenol crystallises unchanged from thionyl chloride even after prolonged boiling of the solution.

4:5-Dichloro-2-nitrodiphenyl Ether.—4:5-Dichloro-1:2-dinitrobenzene (1 mol.) was added to a solution of potassium phenoxide (1 mol.) in the minimum amount of water. A brown-red coloration appeared, and rapidly faded. Completion of the condensation was effected by heating at 100° for $\frac{1}{4}$ hour and the ether, after being washed with alkali, became solid, and then crystallised from alcohol in yellow prisms, m. p. 69—70° (Found: Cl, 24.8. $C_{12}H_7O_3NCl_2$ requires Cl, 25.0%).

4:5:4'-Trichloro-2-nitrodiphenyl ether was similarly obtained from potassium *p*-chlorophenoxide. It separates from alcohol in very pale yellow needles, m. p. 77° (Found: Cl, 32.8. $C_{12}H_6O_3NCl_3$ requires Cl, 33.4%). When the ether was dissolved in 20 parts of nitric acid (*d* 1.5), the temperature rose appreciably, and after 10 minutes crystallisation set in. The whole was poured on ice, and the precipitate was crystallised from alcohol. *4:5:4'-Trichloro-2:2'-dinitrodiphenyl ether* forms very pale yellow, hairy needles, m. p. 131—132° (Found: Cl, 29.0. $C_{12}H_5O_5N_2Cl_3$ requires Cl, 29.2%). Boiling piperidine converted this substance into a mixture, the alkali-insoluble portion being 4-chloro-2-nitrophenyl-piperidine. This establishes the constitution of the ether.

4:5:2':4'-Tetrachloro-2-nitrodiphenyl ether, obtained from 4:5-dichloro-1:2-dinitrobenzene and potassium 2:4-dichlorophenoxide, crystallises from alcohol in pale yellow leaflets, m. p. 125—126° (Found: Cl, 40.1. $C_{12}H_5O_3NCl_4$ requires Cl, 40.2%).

Reduction of the tetrachloronitro-ether by the iron method gave

4 : 5 : 2' : 4'-*tetrachloro-2-aminodiphenyl ether*, crystallising from light petroleum (b. p. 80—100°) in colourless needles, m. p. 97—98° (Found : Cl, 43.9. $C_{12}H_7ONCl_4$ requires Cl, 43.9%). Attempted replacement of the amino-group by chlorine proved unsuccessful.

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EAST LONDON COLLEGE,
UNIVERSITY OF LONDON.

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