

40. *Orientation Effects in the Diphenyl Series. Part X. The Quantitative Nitration of 4 : 4'-Dichloro- and 4 : 4'-Dibromo-diphenyl and of 4-Chloro-4'-bromodiphenyl.*

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SOME time ago it was stated (Groves and Turner, J., 1929, 509) that 4-chloro-4'-bromodiphenyl could not be caused to undergo straightforward dinitration under conditions which allowed of the ready dinitration of 4 : 4'-dichloro- and 4 : 4'-dibromo-diphenyl. In view of this unexpected result, we have effected the synthesis of the chlorobromo-compound by a different method, and have re-studied its nitration. The original specimen of this compound dissolved in fuming nitric acid to a purple solution, from which no clean product could be isolated, but the new preparation gives no appreciable colour under similar conditions, and it is possible to obtain a mixture which consists of dinitro-derivatives only. We cannot discover any reason for the original result and regard it merely as another anomaly in the series which has already produced so many.

Determination, by heating with piperidine, followed by routine analysis, of the proportion of labile chlorine to labile bromine in the

dinitration product from chlorobromodiphenyl led to a series of important observations. In the first place, it was found that either some of the 2 : 3'-type of dinitration product had failed to react with piperidine or there was present a new species of dinitro-compound of a non-reactive character. The fundamental point being an analytical one, namely, the quantitative nature of a piperidine analysis for labile halogen, we submitted specially purified *o*-bromonitrobenzene to such analysis and satisfied ourselves that it was entirely trustworthy in the benzene series, but preferred to apply the test also in the diphenyl series. As a substance hitherto regarded as of unimpeachable identity (Fittig, *Annalen*, 1864, **132**, 206; Schultz, *ibid.*, 1874, **174**, 218; Dennett and Turner, J., 1926, 476; Le Fèvre and Turner, J., 1926, 2041) we therefore took 4 : 4'-dibromo-2 : 3'-dinitrodiphenyl, prepared by the dinitration of dibromodiphenyl and having the accepted m. p. of 147—148° : we were surprised to obtain a result apparently showing that considerably less than 100% of the bromine present in the activated position had reacted with piperidine.

Similar determination of labile bromine in the *total* product of controlled dinitration of 4 : 4'-dibromodiphenyl showed that only $83.4 \pm 1.0\%$ of 4 : 4'-dibromo-2 : 3'-dinitrodiphenyl was present, the rest presumably being an isomeride unaffected by piperidine. Ordinary crystallisation of small quantities of such a mixture of dinitration products only effects partial removal of this isomeride, but careful slow fractional crystallisation of the product of dinitrating 50 g. of 4 : 4'-dibromodiphenyl showed that there were in fact two substances present. The main portion melted at 152—153° and was the pure 2 : 3'-dinitro-compound, whilst a second substance, m. p. 150°, easily distinguished from the former by its crystalline habit, was obtained. Ullmann (*Ber.*, 1901, **34**, 2181), who obtained 4 : 4'-dibromo-2 : 2'-dinitrodiphenyl by heating 2 : 5-dibromonitrobenzene with copper-bronze, gave its m. p. as 138°, and it therefore appeared that our second substance was a new compound. Repetition of Ullmann's experiments, employing improved technique, gave 4 : 4'-dibromo-2 : 2'-dinitrodiphenyl, m. p. 150°. In view of the marked discrepancy in the two m. p.'s we prepared the 2 : 2'-dinitro-compound from 2 : 2'-dinitrobenzidine by the diazoperbromide method and assured ourselves that it actually did possess m. p. 150°.

The pure 2 : 3'-dinitro-compound gave a normal result when its labile bromine content was determined by the piperidine method. The pure 2 : 2'-compound, under similar conditions, reacted with piperidine to a slight extent, and this necessitated correction of the results of all analyses of mixtures of these two dinitro-compounds.

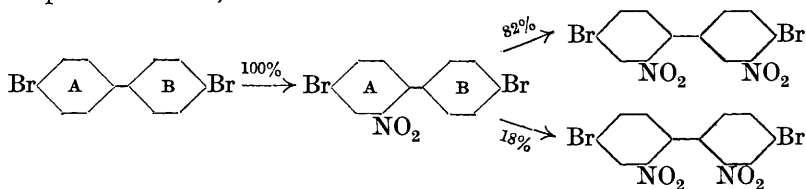
It is therefore definitely proved that dinitration of 4 : 4'-dibromodiphenyl gives only $83.4 \pm 1.0\%$ of the 2 : 3'-dinitro-compound, the

remainder consisting essentially, and as far as we know entirely, of the 2 : 2'-compound. An artificial mixture of these two substances in the stated proportion showed the same melting phenomena as the substance obtained by direct nitration.

On a previous occasion (J., 1926, 2044), comment was made on the indefinite appearance of 4 : 4'-dibromo-2-nitrodiphenyl, and since this substance is undoubtedly the intermediate stage in the dinitration of dibromodiphenyl, we have re-investigated its preparation. It has now been obtained by nitrating dibromodiphenyl either in glacial acetic acid or in nitrobenzene, by the Gattermann process from diazotised 2-nitrobenzidine, and by decomposing in boiling alcohol the bisdiazoperbromide from the latter base. All the products obtained had identical properties. When 4 : 4'-dibromo-2-nitrodiphenyl was nitrated under the conditions used for dinitrating 4 : 4'-dibromodiphenyl, 2 : 3'- and 2 : 2'-dinitro-compounds were obtained in the proportion 81.2% : 18.8%, which is in good agreement with the above figures.

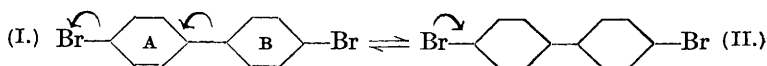
The trinitration of 4 : 4'-dibromodiphenyl, originally effected by Lellmann (*Ber.*, 1882, 15, 2838) and discussed on a previous occasion (J., 1927, 2332), has been found to occur rather more readily than had been supposed. Mononitration of the 2 : 3'-dinitro-compound gives a mixture of trinitro-compounds and trinitration of dibromodiphenyl itself gives a complex mixture, owing to the fact that further nitration of the 2 : 2'-compound proceeds in more than one direction.

The results of the dinitration of 4 : 4'-dibromodiphenyl and of the mononitration of 4 : 4'-dibromo-2-nitrodiphenyl, which may be represented thus,



afford in the first place a simple statement of the relative directive influences of a bromine atom and a 4-bromo-2-nitrophenyl group, but they also permit of a more detailed discussion of the whole problem than has hitherto been possible.

For purposes of considering the mononitration (nucleus A), 4 : 4'-dibromodiphenyl may be regarded as a mixture of (I) and (II) in mobile equilibrium :



In order to satisfy the demand of the bromine atom in nucleus A to approach more nearly a condition of ionisation, an electronic displacement can originate from nucleus B. As a result the equilibrium is displaced if necessary in the direction $\text{II} \rightarrow \text{I}$. For (I) permits the bromine atom in A to exert its normal tendencies, whereas (II) requires it to behave abnormally, say at the request of a reagent. In (I) the 3-positions are deactivated by the electron displacements desired by the bromine atom, and these also deactivate, though to a lesser extent, the 2-positions. This 2-deactivation is, however, diminished by the electronic displacements from nucleus B. Therefore, 2-nitration is the only result.

Although previous work in this series has shown qualitatively that 4:4'-dibromo-2-nitrodiphenyl is the sole product of mononitration, we have now worked out more satisfactory conditions for the mononitration and shown quantitatively that no 3-nitration occurs.

That nitration occurs in (A) in a *less deactivated* position rather than in a *more activated* one appears to follow from the fact that 4-bromo-4'-chlorodiphenyl (see below) undergoes mononitration less in the chlorophenyl than in the bromophenyl nucleus. The effect produced is thus meta-direction by a halogen atom. The well-known increase in nitration meta to the bromine atom as one passes from *p*-bromoaniline nitrated in excess of sulphuric acid through *p*-bromoacetanilide nitrated in sulphuric acid to *p*-bromoacetanilide nitrated with nitric acid, may be a further demonstration, in part, of the meta-directing effect of a halogen atom.

The nitration of 4:4'-dibromo-2-nitrodiphenyl [(III) \rightleftharpoons (IV)] is clearly controlled to a large extent by the nitro-group in nucleus (A), which will at least prevent electron displacements from (A) to (B), and may exert a small positive effect in the opposite sense. In so far as this means shifting of the equilibrium of the direction of (IV),



2'-nitration will be much less rapid than 3'-nitration. At the same time (III) is not entirely suppressed, and therefore some 2'-nitration also occurs.

Similar considerations suggest that dinitration of 4:4'-dichlorodiphenyl would also give 2:2'- as well as 2:3'-dinitro-derivatives. We find that the dinitration of 4:4'-dichlorodiphenyl gives 81.3% of the 2:3'- and 18.7% of the 2:2'-dinitro-compound. These figures are corrected for a slight reactivity of the 2:2'-compound towards piperidine. By carrying out the dinitration of dichlorodiphenyl on a moderately large scale, we have isolated pure specimens of 4:4'-

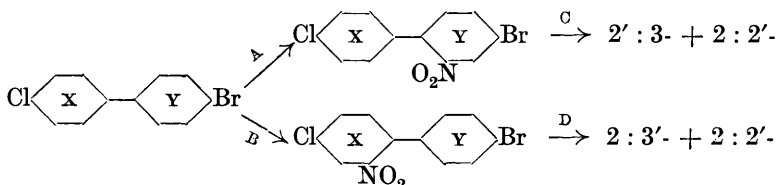
dichloro-2 : 3'-dinitrodiphenyl and of the 2 : 2'-isomeride. The latter was identical with a sample prepared by the Ullmann process from 2 : 5-dichloronitrobenzene. It appears that the product, m. p. 140°, hitherto regarded as the pure 2 : 3'-dinitro-compound, contained some 2 : 2'-isomeride, but less than is the case in the dibromo-series.

We have also made a quantitative study of the mononitration of 4 : 4'-dichloro-2-nitrodiphenyl. This gave $80.9 \pm 0.3\%$ of 2 : 3'- and 19.1% of the 2 : 2'-dinitro-compound. The method (J., 1926, 2045) previously used for the preparation of the 2-nitro-compound was only suitable for the preparation of very small quantities. We have devised a more suitable process for this purpose.

The very close agreement between the figures for the mononitration of 4 : 4'-dichloro-2-nitrodiphenyl and the dinitration of 4 : 4'-dichlorodiphenyl shows that there is little need to consider the possibility of any 3-nitro-compound being formed in the first stage of the second process. We have, however, effected the quantitative mononitration of 4 : 4'-dichlorodiphenyl and determined the labile chlorine present in the product. This showed that if any 3-nitro-compound had been formed, its amount did not exceed 1% of the total.

The further nitration of 4 : 4'-dichloro-2 : 3'-dinitrodiphenyl has not hitherto been effected. We find that the main product is 4 : 4'-dichloro-2 : 3' : 5'-trinitrodiphenyl; the constitution of this follows from the fact that piperidine readily displaces one chlorine atom to give 4-chloro-2 : 3' : 5'-trinitro-4'-piperidinodiphenyl.

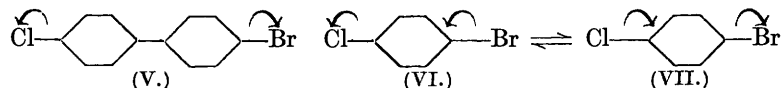
The fact that 2 : 2'-dinitration accompanies 2 : 3'-dinitration in both of the above instances suggests at first sight that results for the quantitative dinitration of 4-chloro-4'-bromodiphenyl would be incapable of satisfactory interpretation. Yet further consideration shows that in the scheme



stages (C) and (D) may, without serious error, be assumed to proceed to the extent of 80 to 85% in the direction of the 2 : 3'- and 2' : 3-compounds, so that the determination of total labile halogen, and then of the component labile chlorine and bromine in the nitration mixture, will in fact lead to figures for stages (A) and (B) accurate within the limits of experimental error. Concordant experimental observations have shown that 61.5% of mononitration occurs in

nucleus (Y) and 38.5% in nucleus (X). The product of dinitration contained 52.5% of 4-chloro-4'-bromo-2' : 3-dinitrodiphenyl, 32.8% of the 2 : 3'-compound, and 14.7% of the 2 : 2'-compound. Of the last, 9.1% was formed from 4-chloro-4'-bromo-2'-nitrodiphenyl and 5.6% from 4-chloro-4'-bromo-2-nitrodiphenyl.

These figures probably give a more accurate comparison of the relative directive effects of chlorine and bromine than can be deduced from the results (Holleman, *Rec. trav. chim.*, 1915, **34**, 216) of nitrating *p*-chlorobromobenzene, since in 4-chloro-4'-bromodiphenyl the (antagonistic) effect of one halogen on the other is, as it were, "buffered" by the two interposed aromatic nuclei, whilst in chlorobromobenzene the antagonistic effects will have free play. That is to say, it would be anticipated that, since both the chlorine and the bromine have a relatively large reserve of electronic systems to assist their ionising tendencies, each will exhibit the latter to the maximum extent (V) :



whilst in *p*-chlorobromobenzene the electron-attracting properties of one halogen atom can only be manifested to the extent permitted by the electron-sharing properties of the other halogen. For this reason alone it is not surprising to find that the ratio of nitration figures rises from 55 : 45 in the benzene compound to 62 : 38 in the diphenyl compound, that is, from 1.2 to 1.6.

EXPERIMENTAL.

Method employed in the Determination of Labile Halogen.—A mixture of about 1 g. of the halogenonitro-compound with 5 g. of pure piperidine was heated in a sealed glass tube by means of boiling water for 2 hours. One of the two methods, A and B, was then adopted.

Method A. The contents of the tube were washed out with water, and a little potassium hydroxide added. The mixture was extracted with ether until no more coloured material was removed, freed from ether by warming, and acidified with nitric acid. The halide present was then determined gravimetrically as silver chloride or bromide.

Method B. The contents of the tube were dissolved in alcohol, and the solution at once treated with silver nitrate in presence of a little nitric acid.

Check analysis using o-bromonitrobenzene. A specially purified specimen of this substance (1.024 g.), analysed by method B, gave 0.9510 g. AgBr, corresponding to 1.023 g. of *o*-bromonitrobenzene.

Isolation of Pure 4 : 4'-Dibromo-2 : 3'-dinitrodiphenyl and 4 : 4'-Dibromo-2 : 2'-dinitrodiphenyl from the Product of dinitrating 4 : 4'-Dibromodiphenyl.—4 : 4'-Dibromodiphenyl (50 g.) was slowly added to 600 c.c. of ice-cooled nitric acid (*d* 1.52). After 30 minutes, the solution was treated with ice and water, and the precipitate washed and dried (67 g., m. p. 134—138° with slight previous softening at 120°). Of this material, 50 g. were crystallised from 500 c.c. of glacial acetic acid. This gave 37 g. of needles (A), m. p. 142—144°, and, after long standing, a further 0.9 g. of prisms (B), m. p. 145°.

The mother-liquor was evaporated to 260 c.c. On cooling, octahedra separated (C) (4.2 g., m. p. 146—148°).

Crystallisation of (A) from 500 c.c. of glacial acetic acid gave 32 g. of needles, m. p. 150—151°. These, after two further crystallisations from glacial acetic acid, melted at 152—153° and were pure 4 : 4'-dibromo-2 : 3'-dinitrophenyl. The m. p. of "A.R." salicylic acid determined in the same apparatus was 158—159°.

Crops (B) and (C) were combined, and crystallised from butyl alcohol; pure 4 : 4'-dibromo-2 : 2'-dinitrophenyl was then obtained as octahedra, m. p. 150°.

Evaporation of the mother-liquor from (C) gave a mixture, m. p. 125—132°, of needles and octahedra, and a similar product was obtained by evaporating the mother-liquors from the crystallisation of (A).

In all, 49.5 g. of solid were recovered.

Piperidine Analysis of 4 : 4'-Dibromo-2 : 3'-dinitrodiphenyl.—By Method A, 1.000 g. of the pure dinitro-compound, m. p. 152—153°, gave 0.4628 g. AgBr; whence the 2 : 3'-dinitro-compound present was 99.0%. The crude 4-bromo-2 : 3'-dinitro-4'-piperidinodiphenyl formed in this process, and isolated from the ethereal extract, melted at 134—135°. The pure substance has m. p. 136—137°.

Preparation of 4 : 4'-Dibromo-2 : 2'-dinitrodiphenyl.—(1) 2 : 5-Dibromonitrobenzene (18 g.) was heated with copper-bronze (8 g.) at 240° as described by Ullmann (*Ber.*, 1901, **34**, 2181), but this author's method of extraction proved unsatisfactory. The still hot mixture was treated with *o*-dichlorobenzene (100 c.c.), the liquid filtered hot, and most of the solvent distilled off. The cool solution deposited 6 g. of crystalline material, which after being washed with light petroleum had m. p. 133°. After being crystallised first from glacial acetic acid and then from *n*-butyl alcohol, it formed pale yellow octahedra, m. p. 150°, and was unaffected by further crystallisation from ethyl alcohol (Found : Br, 39.4. Calc. : Br, 39.8%).

(2) 2 : 2'-Dinitrobenzidine (10 g.) was diazotised in a mixture of 40 c.c. of 47% hydrobromic acid and 120 c.c. of water with 5 g. of sodium nitrite in 10 c.c. of water. The solution was filtered, and

treated with a solution of bromine in hydrobromic acid, until no further precipitation occurred. The perbromide was filtered off, and heated in 50 c.c. of glacial acetic acid until no more bromine was disengaged. The solution was cooled, and gave 12 g. of crystalline material, m. p. 134—137°. Difficulty was experienced in removing traces of colloidal matter, but crystallisation from *n*-butyl alcohol gave octahedra, m. p. 149—150°. Recrystallisation from the same solvent raised the m. p. to 150°, and the product did not depress the m. p. of the dinitro-compound obtained by the Ullmann reaction or that of the 2:2'-dinitro-compound isolated from the nitration of 4:4'-dibromodiphenyl.

Control Piperidine Analysis of 4:4'-Dibromo-2:2'-dinitrodiphenyl.—0.9530 G. of the pure 2:2'-compound gave by Method A, 0.0385 g. AgBr. The figures given below for the results of piperidine analysis of all mixtures of 2:3'- and 2:2'-compounds are corrected to the extent required by this observation.

Artificial Mixture of 4:4'-Dibromo-2:3'- and -2:2'-dinitrodiphenyl.—A mixture of 0.8450 g. of the 2:3'- compound and 0.1550 g. of the 2:2'-compound was dissolved in 10 c.c. of nitric acid (*d* 1.52). Ice and water were added and the solid was collected, washed, and dried. It melted at 133—138° and in all respects resembled the crude product of nitrating 4:4'-dibromodiphenyl.

A mixture of 0.8048 g. of the 2:3'-compound and 0.1538 g. of the 2:2'-compound was analysed by Method A. Found: 2:3'-dinitro-compound, 0.8098 g. or, corrected for the effect of the 2:2'-compound, 0.7963 g.

Quantitative Dinitration of 4:4'-Dibromodiphenyl.—The dibromodiphenyl used had m. p. 167—168°.

Preliminary experiments carried out to determine the conditions suitable for dinitration showed that when solutions of dibromodiphenyl in 12 parts by weight of nitric acid (*d* 1.52) were heated at 100° for $\frac{1}{2}$ hour, considerable trinitration occurred.

When the acid (*d* 1.52) was replaced by acid of *d* 1.465, the dibromocompound (readily soluble in the stronger acid) did not dissolve in the cold and only slowly dissolved on warming. After $\frac{1}{2}$ hour at 100°, crystallisation set in and the main product was of the dinitro-species.

The following method was found to give consistent dinitration: The dibromodiphenyl was slowly stirred with 12 parts by weight of nitric acid (A.R. quality) (*d* 1.52) which was kept cool in ice. After 30 minutes, ice and water were gradually added and the precipitate was collected, washed, and dried in a vacuum over sulphuric acid and caustic potash. It melted indefinitely between 132° and 138°. Experiment I. 3.4 G. of dibromodiphenyl gave 4.4 g. of mixed

dinitro-compounds (Found : Br, 39.6. Dinitro-compounds require Br, 39.8%).

Piperidine analyses. (1) *Method A* : 0.9870 g. gave 0.3862 g. AgBr; 2 : 3'-compound present, 83.8% or, corrected, 82.4%. (2) *Method B* : 1.006 g. gave 0.4000 g. AgBr; 2 : 3'-compound present, 85.1% or, corrected, 84.0%. Experiment II. 10.0 G. of dibromodiphenyl gave 13.0 g. of mixed dinitro-compounds, m. p. 130—137° (Found : Br, 38.4%).

Piperidine analysis. Method A : 1.009 g. gave 0.3984 g. AgBr; 2 : 3'-compound present, 84.5% or, corrected, 83.8%.

Preparation of 4 : 4'-Dibromo-2-nitrodiphenyl.—(a) 2-Nitrobenzidine was diazotised in hydrobromic acid, and copper powder added. Normal working up gave 4 : 4'-dibromo-2-nitrodiphenyl, which crystallised from alcohol or from light petroleum (b. p. 80—100°) in indefinite crystals, m. p. 124°.

(b) 2-Nitrobenzidine was diazotised in hydrobromic acid, and the bis-diazonium perbromide precipitated in the usual manner. When it was decomposed in hot glacial acetic acid it gave the tribromo-compound previously described (J., 1926, 2043). When the perbromide from 10 g. of 2-nitrobenzidine was gradually added to 100 c.c. of absolute ethyl alcohol kept gently boiling, a clear solution was obtained, and, on cooling, an oil first separated and was followed by a solid precipitate (5 g., m. p. 110—112°). After two crystallisations from alcohol, this melted at 124° (Found : Br, 44.5. Calc. : Br, 44.8%).

(c) A solution of 6 g. of 4 : 4'-dibromodiphenyl in 100 g. of nitrobenzene was heated to 100°, and a solution of 6 c.c. of nitric acid (*d* 1.52) in 10 g. of nitrobenzene added. After 2 hours' heating, the nitrobenzene was removed in steam, and the residue heated for 1 hour with 20 c.c. of piperidine. The solution was poured into water, the precipitate dissolved in benzene, and the solution extracted with hydrochloric acid (1 : 1) until free from piperidine compounds derived from dinitro-compounds formed in the nitration. Evaporation of the benzene solution, followed by crystallisation from alcohol, gave

plates, but more frequently in pale yellow needles, matted together. The indefinite appearance of most specimens of the compound may be due to the presence of both forms.

Quantitative Mononitration of 4 : 4'-Dibromodiphenyl.—The dibromo-compound (2.0 g.) was nitrated in acetic acid under the conditions just described. The nitration mixture was poured into water and after filtration and drying, 2.2 g. were obtained. Of this quantity, 1.000 g. was submitted to routine piperidine analysis and gave an unweighable quantity of silver bromide, showing that no 3-nitro-compound was present.

Quantitative Mononitration of 4 : 4'-Dibromo-2-nitrodiphenyl.—(a) The nitro-compound (2 g.) obtained by the perbromide method was added to 15 c.c. of nitric acid (d 1.52), kept ice-cooled. After $\frac{1}{2}$ hour, ice-water was added until no further solid was precipitated. The precipitate was collected, washed, and dried, 2.2 g., m. p. 130—135° with softening at 120°, being obtained (Found : Br, 39.1. A mononitrated product requires Br, 39.8%).

Piperidine analyses by method A. (1) 0.8300 G. gave 0.3214 g. AgBr, whence 2 : 3'-dinitro-compound, 82.9% or, corrected for 2 : 2' reactivity, 81.4%. (2) 0.8172 G. gave 0.3172 g. AgBr, whence the corresponding figures are 83.1 and 81.6%.

(b) The nitro-compound (2.5 g.) obtained by the nitrobenzene method was similarly nitrated; 2.8 g., m. p. 130—135° with softening at 120°, resulted (Found : Br, 39.1%).

Piperidine analyses by method A. (1) 0.8120 G. gave 0.3146 g. AgBr, whence 2 : 3'-dinitro figures are 82.9 and 81.4%. (2) 0.8100 G. gave 0.3112 g. AgBr, whence the corresponding figures are 82.2 and 80.5%.

Nitration of 4 : 4'-Dibromo-2 : 2'-dinitrodiphenyl.—A solution of 2 g. of the dinitro-compound in 25 c.c. of nitric acid (d 1.5) was heated at 100° for 4 hours. Addition of water to the cooled solution precipitated a gummy solid, m. p. 70—90°, from which by crystallisation no definite products were isolated.

Nitration of 4 : 4'-Dibromo-2 : 3'-dinitrodiphenyl.—A solution of 10 g. of the pure 2 : 3'-dinitro-compound in 100 c.c. of nitric acid (d 1.52) was heated at 100° for 4 hours. The cooled solution was treated with water, and the precipitate collected, washed, and dried (11 g., m. p. 125—140°). Crystallisation from glacial acetic acid gave 4 g. of rectangular needles, m. p. 176—177°, recrystallisation from the same solvent raising this m. p. to 178—179°. The pure 4 : 4'-dibromo-2 : 3' : 5'-trinitrodiphenyl so obtained reacted with piperidine to give between 109% and 114% of the expected labile bromine under different conditions of heating, a result due no doubt to a "general effect" activation of the second bromine atom.

Preparation of 4 : 4'-Dichlorodiphenyl.—This substance is readily

prepared by passing chlorine through a gently boiling solution of 20 g. of diphenyl in 50 c.c. of glacial acetic acid for 2—3 hours. The use of much larger quantities leads to diminished yields. On cooling, about 12 g. of almost pure dichlorodiphenyl crystallises, and this is best recrystallised from toluene—light petroleum. This gives a product, m. p. 148—149°. It is unprofitable to attempt working up the original mother-liquor.

Isolation of 4 : 4'-Dichloro-2 : 3'- and -2 : 2'-dinitrodiphenyl from the Product of dinitrating 4 : 4'-Dichlorodiphenyl.—Dichlorodiphenyl (39 g.) was added gradually to 300 c.c. of well-stirred nitric acid (*d* 1.52) kept in an ice-bath. After 1 hour, ice and water were added until precipitation was complete, and the precipitate was collected, washed, and dried. Of this product (54 g., m. p. 120—126°), 40 g. were crystallised from 500 c.c. of glacial acetic acid. On cooling, 24 g. of cream-coloured needles separated, m. p. 139—141°. After three crystallisations from acetic acid the m. p. was 141—142°(A). Evaporation of the mother-liquor to 200 c.c. led to a second crop (7 g.), a mixture, m. p. 123—128°, of needles and octahedra, and further concentration gave a third crop (1.3 g. of octahedra), m. p. 110—135°. Crystallisation of the last from *n*-butyl alcohol gave only octahedra, m. p. 138—139°(B).

(A) was pure 4 : 4'-dichloro-2 : 3'-dinitrodiphenyl. (B) was pure 4 : 4'-dichloro-2 : 2'-dinitrodiphenyl and did not depress the m. p. of a sample prepared by the Ullmann process (*loc. cit.*) from 2 : 5-dichloronitrobenzene. Of the 40 g. used, 39.6 g. were accounted for either as (A) or (B) or as mixtures of the two.

Control Piperidine Analysis of 4 : 4'-Dichloro-2 : 2'-dinitrodiphenyl.—0.9000 G. gave 0.0350 g. AgCl. These figures are used below as required to correct results of analyses of mixtures of the 2 : 3'- and 2 : 2'- isomerides.

Quantitative Dinitration of 4 : 4'-Dichlorodiphenyl.—This substance (10 g.) was gradually stirred into 80 c.c. of nitric acid (*d* 1.52) kept at 0°. After $\frac{1}{2}$ hour, ice and water were added until no further precipitation occurred. The precipitate was collected, washed, and dried (14.0 g., m. p. 118—127°. Found : Cl, 22.5. A dinitrated product requires Cl, 22.7%).

Piperidine analyses by method A. (1) 1.0024 G. gave 0.3798 g. AgCl, whence the 2 : 3'-isomeride = 82.8% or, corrected for 2 : 2'-reactivity, 81.3%. (2) 1.0070 G. gave 0.3816 g. AgCl, whence the corresponding figures are 82.8 and 81.3%.

Mononitration of 4 : 4'-Dichlorodiphenyl.—(1) *In nitrobenzene.* A solution of 9 g. of dichlorodiphenyl in 150 g. of nitrobenzene was heated under reflux at 100°. A mixture of 18 c.c. of nitric acid (*d* 1.52) and 30 g. of nitrobenzene was added, and heating continued

for 2 hours. The mixture was treated with water, and the nitrobenzene removed in steam. The residue was collected when cold and dissolved in 20 c.c. of piperidine. The solution was boiled for an hour, cooled, and poured into water. The precipitate was collected and dissolved in benzene, and the solution extracted with (1 : 1) hydrochloric acid until the piperidine derivatives, derived from dinitro-compounds in the crude nitration product, were removed. The benzene solution, after being washed, was evaporated, and the residue was crystallised from alcohol, from carbon tetrachloride, and then again from alcohol. The product had m. p. 98—99°.

(2) *In glacial acetic acid.* Nitric acid (100 c.c. of *d* 1.46) was added to a solution of 10 g. of 4 : 4'-dichlorodiphenyl in 150 c.c. of glacial acetic acid. The solution was kept at 100° for $\frac{1}{2}$ hour and cooled and 20 c.c. of water were very carefully stirred in. The crystalline precipitate was collected and recrystallised from alcohol; the pure 2-nitro-compound was then obtained, m. p. 102°.

Quantitative Mononitration of 4 : 4'-Dichlorodiphenyl.—Nitration of 2 g. of dichlorodiphenyl under the conditions of the last preparation gave 2.25 g. of crude nitration product, m. p. 95—99°. When 1.000 g. was submitted to piperidine analysis, less than 0.005 g. of silver chloride was formed, representing less than 1% of 3-nitration.

Quantitative Nitration of 4 : 4'-Dichloro-2-nitrodiphenyl.—The material used was obtained by the last-mentioned nitration, and 5 g. were added gradually to 40 c.c. of ice-cooled nitric acid (*d* 1.52). After $\frac{1}{2}$ hour, ice and water were added and the precipitate was collected and dried (6 g., m. p. 119—128°) (Found : Cl, 22.5. A mononitrated product requires Cl, 22.7%).

Piperidine analyses by method A. (1) 0.8226 G. gave 0.3092 g. AgCl, whence 2 : 3'-compound, 82.1% or, corrected for 2 : 2'-reactivity, 80.6%. (2) 0.8000 G. gave 0.3026 g. AgCl, whence the corresponding figures are 82.6 and 81.2%.

4 : 4'-Dichloro-2 : 3' : 5'-trinitrodiphenyl.—A solution of 10 g. of 4 : 4'-dichlorodiphenyl in 100 c.c. of nitric acid (*d* 1.52) was heated at 100° for 2 hours and then poured into much water. The gummy precipitate slowly became hard, and was collected and crystallised from 100 c.c. of glacial acetic acid. Cream-coloured needles (7 g.) separated, m. p. 150—155°. Three further crystallisations from the same solvent raised the m. p. to 166—167° (Found : Cl, 19.9. $C_{12}H_5O_6N_3Cl_2$ requires Cl, 19.8%).

4-Chloro-2 : 3' : 5'-trinitro-4'-piperidinodiphenyl.—The trinitro-compound reacted vigorously with piperidine to give the 4'-piperidino-compound, which crystallised from glacial acetic acid in crimson prisms, m. p. 182° (Found : Cl, 8.7. $C_{17}H_{15}O_6N_4Cl$ requires Cl, 8.7%).

4-Chloro-4'-bromodiphenyl.—(a) 4-Aminodiphenyl, prepared from

specially purified 4-nitrodiphenyl, was diazotised in hydrochloric acid, and, by the Sandmeyer process, converted into 4-chlorodiphenyl, m. p. 75° (*lit.* 76°). A solution of 10 g. of the chlorodiphenyl in not more than 40 c.c. of glacial acetic acid was treated with 5 c.c. of bromine, and the whole heated at 100° under reflux for 4 hours. Dilution, followed by filtration, gave 11 g. of solid, m. p. $140-145^{\circ}$. This, after being crystallised several times from acetone, had m. p. $157-158^{\circ}$ (Found : Cl + Br, 42.2. Calc. : Cl + Br, 43.2%).

(b) The method used by Groves and Turner (*loc. cit.*) was repeated, and gave a product similar in all respects to the above (Found : *M* in freezing benzene, 236, 238. Calc. : *M*, 267).

The solution of either product in nitric acid was pale yellow.

Quantitative Dinitration of 4-Chloro-4'-bromodiphenyl.—(a) 4-Chloro-4'-bromodiphenyl (10 g.), obtained by brominating chlorodiphenyl, was nitrated by the method used for dibromodiphenyl. The crude product, 13.3 g., had m. p. $115-130^{\circ}$ (Found : Cl + Br, 31.7. A dinitrated product requires Cl + Br, 32.3%).

Piperidine analyses by method A. (1) 1.000 G. gave 0.3876 g. AgCl + AgBr. This, after being heated to constant weight in chlorine, gave 0.3456 g. AgCl, whence 4-chloro-4'-bromo-2' : 3-dinitrodiphenyl = 52.4% (corrected, 51.7%), 2 : 3'-derivative = 33.8% (corrected, 33.2%), and 2 : 2'-derivative = 13.8% (corrected, 15.1%). (2) 1.000 G. gave 0.3888 g. AgCl + AgBr, and subsequently, 0.3460 g. AgCl, whence the corresponding figures are 51.9 (51.2), 34.4 (33.9), and 13.7 (14.9)%.

(b) 4-Chloro-4'-bromodiphenyl (5 g.), obtained from 4-bromo-4'-aminodiphenyl, was dinitrated as before, and gave 6 g., m. p. $115-130^{\circ}$ (Found : Cl + Br, 31.3%).

Piperidine analyses by method A gave the following figures, corresponding in order with the above : (1) 1.000 G. gave 0.3864 g. AgCl + AgBr, and 0.3460 g. AgCl. 53.8 (53.0), 32.5 (32.0), and 13.7 (15.0)%. (2) 1.000 G. gave 0.3906 g. AgCl + AgBr, and 0.3500 g. AgCl. 54.7 (54.0), 32.6 (32.2), and 12.7 (13.8)%.

The mean composition of the two products of dinitration is therefore : 2' : 3-dinitro-compound, 52.5%; 2 : 3', 32.8%; 2 : 2', 14.7%, whence, assuming that both the mononitro-compounds are nitrated to give 2' : 3- (or 2 : 3'-) and 2 : 2'-compounds in the ratio 85.3 : 14.7, the 2'-nitro-compound in the first stage of nitration = 61.5% and the 2-nitro-compound = 38.5%.

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