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THESIS PRESENTED BY
ELIZABETH ESTHER JESSIE MARLER
FOR THE DEGREE OF MASTER OF SCIENCE
IN THE UNIVERSITY OF LONDON.
NOVEMBER 10th. 1930.



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ABSTRACT OF THESIS.

The nitration of halogeno-benzenes.

The formation of unsymmetrical dinitro-derivatives of symmetrical 4:4'-dihalogeno-diphenyls.

The nitration of 4-chloro:4'-fluoro-diphenyl and of 4-bromo:4'-fluoro-diphenyl. Reasons for expecting that more of the 2:3-dinitro-derivative than of the 2':3- compound would be formed. Details of the method of analysis.

4-Chloro:4'-fluoro-diphenyl underwent 71.6% of 2:3-dinitration and 28.4% of 2':3-dinitration. 4-Bromo:4'-fluoro-diphenyl underwent 85.8% of 2:3'- and 14.2% of 2':3-dinitration.

Experimental details of the preparation of the mixed dihalogeno-diphenyls:

Attempts to study the effect of 4:4'- halogen substituents on further halogen substitution in the diphenyl molecule. Small amounts of a tribromo- and a tetrabromo-diphenyl have been isolated.

STUDIES IN DIPHENYL CHEMISTRY.

The effect of halogen atoms on nitration in the benzene nucleus was studied by Ingold and Shaw (J., 1927, 2918.) In the mono-halogeno-benzenes substitution in each case was found to occur almost exclusively in the ortho and para positions.

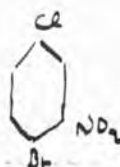
They nitrated, under standard conditions, binary mixtures of benzene with a halogeno-benzene, and by determining the proportions of nitrobenzene and nitro-halogeno-benzene in the product they were able to arrive at the velocity of nitration of the halogeno-benzene relatively to that of benzene. It was found that the "coefficient of activation" diminished in this order:- Iodine > Bromine > Chlorine > Fluorine; and that for all except Iodine it was fractional, i.e. these last three halogens diminished the velocity of substitution.

It had been shown by Holleman (Rec.Trav. Chim., 1915, 34, 216.) that the mono-nitration of p-bromo-chloro-benzene gave the following mixture of nitro-compounds:-



45%

and



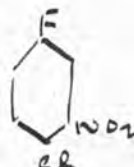
54%

and by Swarts (ibid. 1915, 34, 131.) that p-chloro-fluorobenzene gave:-



27.7%

and

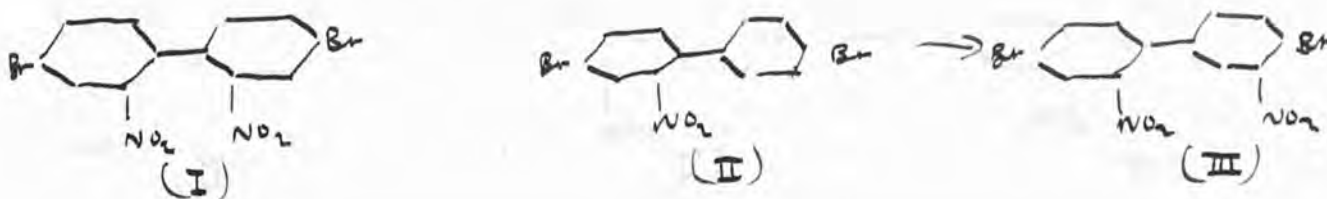


72.3%

Both these results are in agreement with the work of Ingold and Shaw.

A further comparison of the activating effects of halogen atoms has been obtained by a study of mixed dihalogeno-diphenyls. Before this work is described, however, reference must be made to the investigation of the nitration products of the symmetrical 4:4'-dihalogeno-diphenyls.

The dinitration of 4:4'-dibromo-diphenyl was described by Fittig (Ann., 1864, 132, 206.) and Schultz (ibid., 1874, 174, 218.) By the action of fuming nitric acid on 4:4'-dibromo-diphenyl they obtained a dinitro-derivative melting at 148°. This was regarded by Beilstein as being probably identical with the 2:2'-dinitro-compound (I), melting at 138°, synthesised by Ullmann and Bielecki (Ber., 1901, 34, 2177.) from 2:5-dibromo-nitrobenzene. The work of Fittig and Schultz was repeated by Dennett and Turner (J., 1926, 476.), who found that the resulting dinitro-compound melting at 148° depressed the melting point of Ullmann and Bielecki's compound, and also that the corresponding diamine melting at 89° described by Schultz did not undergo condensations of the type then to be expected of a symmetrical diamine. This suggested that unsymmetrical nitration had occurred. In order to test this hypothesis they mononitrated 4:4'-dibromo-diphenyl by a modification of the method of Lellmann (Ber., 1882, 15, 2837.) and found the product to be identical with 4:4'-dibromo-2-nitro-diphenyl (II) prepared from 2-nitro-benzidine. Further

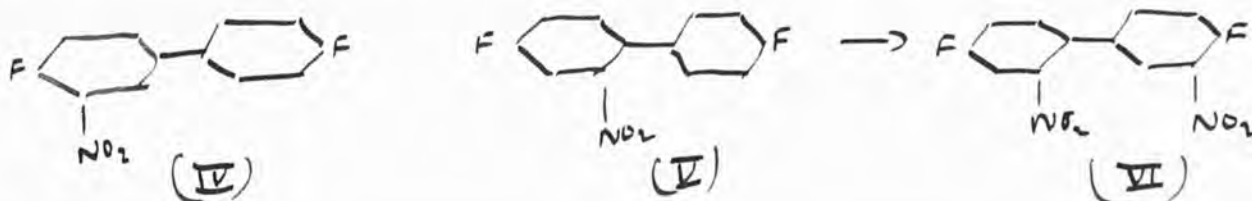


nitration of this substance gave a dinitro-compound which melted at 148° and did not affect the melting-point of, and was therefore identical with, the dinitro-dibromo-diphenyl of Fittig and Schultz. This compound must therefore have one nitro-group in the 2-position. It was then found to react vigorously with two molecules of piperidine, giving a bromopiperidinodinitrodiphenyl, i.e. one bromine atom was much more reactive than the other, indicating that it had a nitro-group adjacent to it. Since 4:4'-dibromo-2-nitro- and 4:4'-dibromo-2:2'-dinitro-diphenyl were unaffected by piperidine it followed that the dinitration product of 4:4'-dibromo-diphenyl must be 4:4'-dibromo-2:3'-dinitro-diphenyl (III).

In a similar manner Dennett and Turner showed that the first product of nitration of 4:4'-dichloro-diphenyl (Schmidt and Schultz Ann., 1881, 207, 340.) is 4:4'-dichloro-2-nitro-diphenyl, and that further nitration gives 4:4'-dichloro-2:3'-dinitro-diphenyl.

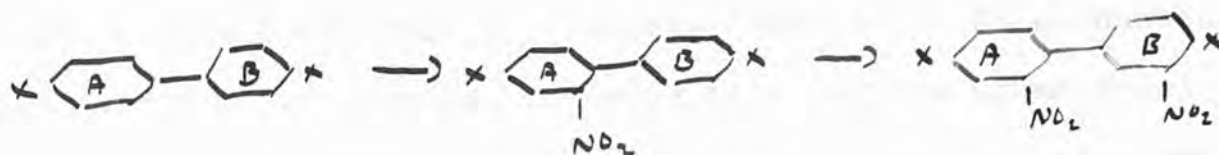
By the dinitration of 4:4'-diiodo-diphenyl Hodgson (J. 1926, 2384) obtained only the 2:3'-dinitro-derivative, which indicates that the first nitro-group had entered only the 2-position.

It had been stated by Schiemann and Bolstad (Ber., 1928, 61, 1403.) that the nitration of 4:4'-difluoro-diphenyl gave only a 3-monoditro-derivative (IV), but their evidence was unconvincing, and since by analogy with the cases already mentioned such a result seemed unlikely, Le Fevre and Turner (J., 1930, 1158.) undertook the reinvestigation of the problem. 4:4'-Difluoro-



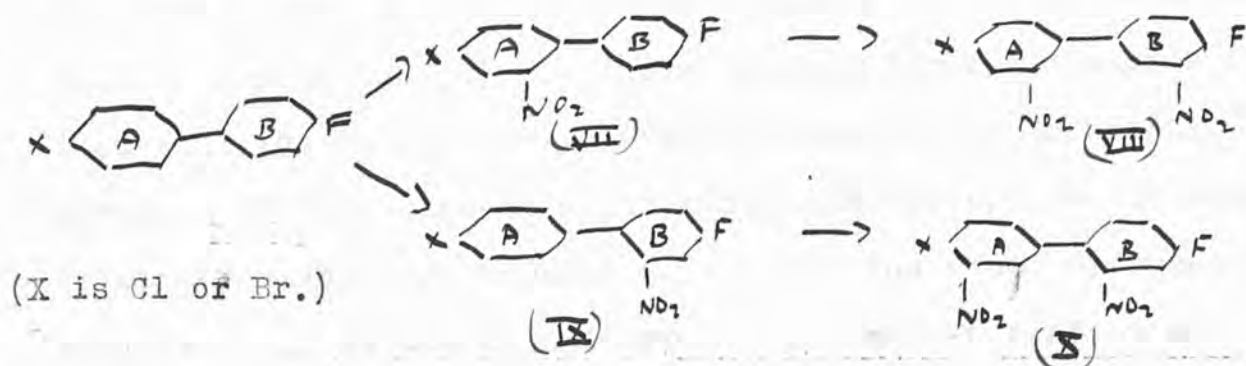
diphenyl and the mononitro-derivative melting at 94-95°, described by Schiemann and Bolstad were found not to react with boiling-piperidine, and the nitro-compound was found to be identical with 4:4'-difluoro-2-nitro-diphenyl (V), prepared synthetically from 2-nitro-benzidine. As in the previous cases both the synthetic mononitro-derivative and that obtained by nitrating difluoro-diphenyl were further nitrated and found to give the same dinitro-derivative which reacted vigorously with two molecules of piperidine to give ^amonopiperidino-derivative, and was therefore 4:4'-difluoro-2:3'-dinitro-diphenyl (VI).

It has thus been established that the symmetrical 4:4'-dihalogeno-diphenyls nitrate quantitatively according to the scheme:-



The explanation advanced by Dennett and Turner is that in the entrance of the nitro-group into the nucleus A the directive influence of the group $\text{---}(\text{B})\text{---}$ is greater than that of the halogen atom in A, so that the nitro-group enters the ortho-position to the group B, i.e. position 2. The group A has now lost its directive power on the entrance of the nitro-group, and nitration in B takes place, according to the ordinary theories of substitution, in position 3', i.e. in the ortho-position to the halogen atom.

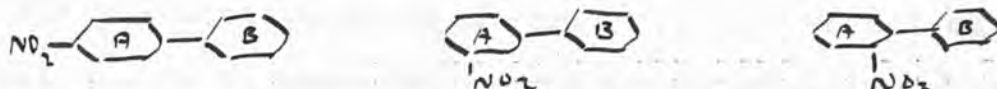
The present investigation has been concerned with the nitration of the mixed dihalogeno-diphenyls, 4-chloro:4'-fluoro- and 4-bromo:4'-fluoro-diphenyls. The nitration of 4-bromo:4'-chloro-diphenyl had already been attempted by Groves and Turner (J., 1929, 509.) but without success, the substance undergoing degradation.



In the nitration of 4-chloro:4'-fluoro-diphenyl the following considerations led to the expectation that a 2-nitro-derivative (VII) would initially be formed. Dennett and Turner had accounted for the formation of 2-mononitro-derivatives of the symmetrical dihalogeno-diphenyls by suggesting that the ortho-directive power of the halogeno-phenyl nucleus was greater than that of the halogen atom, i.e. that its deactivating effect was less than that of the halogen. In the case under consideration however we have different halogen atoms of which one, fluorine, has a much greater deactivating effect than the other. It might therefore be possible that the fluorine atom in the nucleus B would so reduce the directive power of the latter as to make it less than that of the chlorine atom in A, in which case 3-nitration in A would occur. On the other hand, the

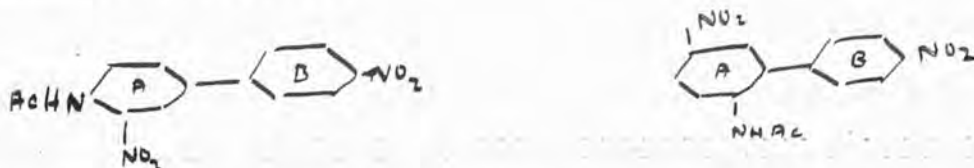
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fact that the symmetrical dihalogeno-diphenyls have been found to nitrate almost exclusively in the 2-position indicates that the directive influence of the halogeno-phenyl nucleus is large in comparison with that of the halogen atom, and it appears possible that the directive influence of such a group, whichever halogen it contains is sufficiently large to predominate over that of any halogen atom. There is considerable evidence to show that the phenyl-group, whether substituted or not, has always a strong ortho-para directing influence, i.e. it acts as an "electron source", resembling in this the other hydrocarbon radicals such as the methyl group. The mono-nitration of diphenyl is known to give only ortho and para derivatives; the three mono-nitro-diphenyls are all substituted in ring B in

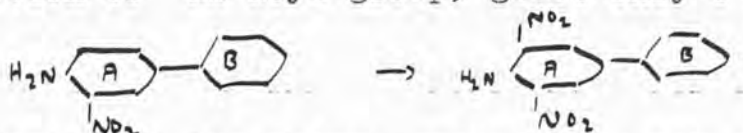


the ortho and para positions to the ring A, i.e. in positions 2' and 4', although A now contains the strongly deactivating nitro-group; the symmetrical 4',4'-dihalogeno-diphenyls already mentioned, and phthalyl-benzidine (Le Fevre and Turner J., 1928, 245.) all give rise exclusively to 2-mononitro-derivatives. The nitration of 4-acetamido-diphenyl however gives a 3;4'-dinitro-derivative (Scarborough and Waters. J., 1927, 1132.). Presumably the o-p.directive power of the phenyl-group is not sufficient to outweigh that of the NHAc group and nitration therefore occurs at position 3; the nucleus A is deactivated by the nitro-group, so that further nitration occurs in B and is governed by A, a

4' derivative resulting. Similarly 2-acetamido-diphenyl gives a 4:5 dinitro derivative



4-Amino-diphenyl, containing the strongly ortho-para directing amino-group, whose effect in this case is not diminished by the introduction of an acyl group, gives only 3 and 3:5 derivatives,



the influence of the phenyl group being now completely outweighed. It would appear therefore that the phenyl group has an ortho-para directive influence much greater than that of the halogens, and of the phthalyl-substituted amino-group, and less than that of the acetyl-substituted amino-group. The effect of the halogens except iodine is known to be one of deactivation, that of the phenyl-group may either be one of much less deactivation or, as seems more probable, of considerable activation. Diphenyl is readily nitrated in glacial acetic acid at 70 by the addition of **fuming** nitric acid, whilst benzene is not nitrated when subjected to these conditions, although diphenyl has ten possible positions of attack and benzene only six, so that the probability of substitution in any one position should be greater in the case of benzene. This suggests that the phenyl nucleus has an activating effect. A comparison of the velocities of nitration of toluene and benzene with that of diphenyl should be of interest in this connection.

Returning to the nitration of 4-chloro-4'-fluoro-diphenyl, it will be seen that according to the above reasoning nitration might equally well occur in either nucleus, resulting in a 2- or a 2'-derivative or a mixture of the two. It might be expected that it would occur mainly in the position ortho to the nucleus containing the less deactivating substituent, chlorine, i.e. that it would occur in nucleus B giving a 2'-nitro-derivative (V); but if, as has already been suggested, the directive effect of the phenyl nucleus is so large that it makes little difference which halogen it contains then the proportions of 2- and 2' substitution will be governed by the relative deactivating effects of the halogen atoms, each on its own phenyl group. The case thus becomes one of substitution in the meta-position to a halogen atom. Since the meta-position is deactivated even more than the ortho, and the effect of fluorine is the stronger, nitration will take place mainly in the nucleus A, giving a 2-nitro derivative (VI). The same argument as that used in the case of the symmetrical compounds can be applied to the introduction of a second nitro-group. A now contains a substituent with a polar linking, the nitro-group $-\overset{+}{\text{N}}(\text{O})_2-\overset{-}{\text{O}}$, this attracts electrons, thus tending to deactivate the whole molecule, but particularly to reduce the "electron source" character of the phenyl group A to such an extent that its ortho-para directive influence becomes less than that of the fluorine atom in B, and therefore further nitration gives a 2:3'-dinitro derivative (VII). At the same time a certain

amount of the 2'-mononitro-compound(IX) must be formed, and this will give on further nitration the 2':3-dinitro-compound(X)

The product of the dinitration of 4-chloro:4'-fluoro-diphenyl should therefore be a mixture of (VIII) and (X), containing considerably more of (VIII) than of (X).

An exactly similar argument can be applied to 4-bromo:4'-fluoro-diphenyl, but in this case the amount of 2':3-dinitro-derivative formed should be even less, as bromine has less deactivating effect than chlorine.

The mononitration of 4-chloro:4'-fluoro- and of 4-bromo:4'-fluoro-diphenyl (the preparation of which is described later) was first attempted, but it was found impossible to isolate any pure substances from the resulting mixtures. Crystallisation of the dinitration product also failed to give one individual, but it was found possible, by carrying out the nitration under standard conditions and treating the whole of the product with piperidine, to determine the proportions of 2':3-dinitro-compound present; since the action of piperidine on this compound resulted in the

quantitative formation of piperidine hydrochloride (or hydrobromide) which was estimated as potassium halide. The results obtained were in accordance with expectations.

From the crude mixture of piperidino-derivatives obtained by treating dinitro-bromo-fluoro-diphenyl with piperidine an almost pure specimen of 4-bromo-2:3'-dinitro-4'-piperidino-diphenyl was isolated, identical with that obtained from 4:4'-dibromo-2:3'-dinitro diphenyl.

The method used was as follows:-

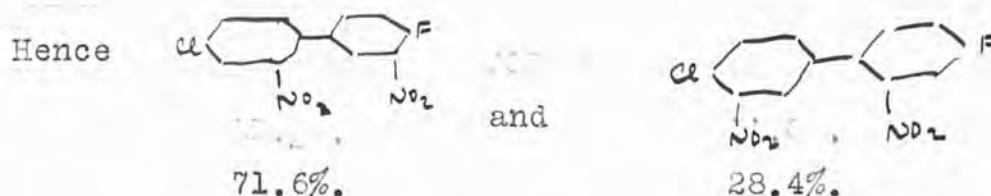
A weighed amount (about 0.01 gm. molecule) of the dihalogeno-diphenyl was slowly stirred into 30 c.c. of fuming nitric acid at room temperature, the solution was heated for five minutes on the water bath and allowed to cool. Distilled water was added until precipitation was complete, care being taken to add the water ^{addition} slowly as too rapid ^{addition} caused the nitro-compound to come out as an oil. The precipitate was filtered off and placed with the filter paper over sulphuric acid in a vacuum desiccator where it was left overnight. When dry it was removed as completely as possible from the filter paper and weighed. This precaution was taken to ensure that the dinitro-substance used in the experiment was as nearly as possible of the same composition as the precipitated mixture of dinitro-compounds, for since the substance tended to become somewhat gummy, there was a danger that owing to a difference

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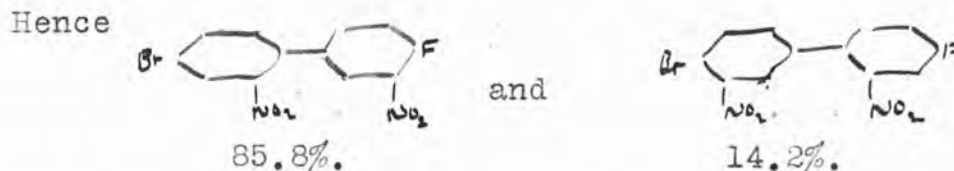
between the melting points more of one isomer than of the other, might be lost during filtration etc. The yield of dinitro-compounds however was found in each case to be nearly theoretical. The weighed dinitro-body was placed in a small flask and covered with piperidine; the mixture was heated on the water-bath for half an hour, 25 c.c. of caustic potash solution (10%) were then added to decompose the piperidine halides, forming potassium fluoride and chloride (or bromide). The mixture of piperidino-compounds and excess of ^{piperidine} ~~benzene~~ was removed by extraction with benzene. The aqueous solution of potassium salts was boiled until free from the smell of piperidine and benzene and made up to 250 c.c. with distilled water. 25 c.c. of this solution were acidified with nitric acid and 10 c.c. approximately decinormal silver nitrate added; the chloride (or bromide) was thus precipitated, while the silver-fluoride remained in solution. The solution was boiled until the precipitated silver halide coagulated and could be filtered off. The filtrate and washings were placed in a dish, a few drops of ferric sulphate solution added, and approximately decinormal ammonium thiocyanate solution, previously standardised against the silver nitrate, added from a burette until the red colour of ferric thiocyanate appeared. The amount of thiocyanate required corresponded to the excess of silver nitrate in the solution. The difference between the original quantity of silver nitrate (10 c.c.) and this excess was the amount equivalent to the chloride (or bromide) in 25 c.c. of the aqueous extract. The total quantity of

chlorine or bromine, and thence the proportion of 2':3-nitration could be calculated, since the weight of dinitro-substance taken was known. The results thus obtained were of the type expected, the dinitro-substance in each case reacting immediately with piperidine in the cold and the numerical results being as follows:-

	<u>Dinitro-chloro-fluoro diphenyl.</u>	<u>Chlorine estimated as potassium chloride</u>	<u>%age of total chlorine</u>
Expt. (1)	0.4701 gm.	0.01617 gm.	28.7
(2)	0.4800 gm.	0.01620 gm.	28.1



	<u>Dinitro-bromo-fluoro diphenyl</u>	<u>Bromine estimated as potassium bromide</u>	<u>%age of total bromine.</u>
Expt. (1)	2.9905 gm.	0.1035 gm.	14.7
(2)	2.2370 gm.	0.0716 gm.	13.7



Analysis of dinitration product of bromo-fluoro-diphenyl

Found Br 23.9% $C_{12}H_6N_2O_4BrF$ requires 23.5%.

($C_{12}H_7N_2O_4BrF$ requires 27 %.)

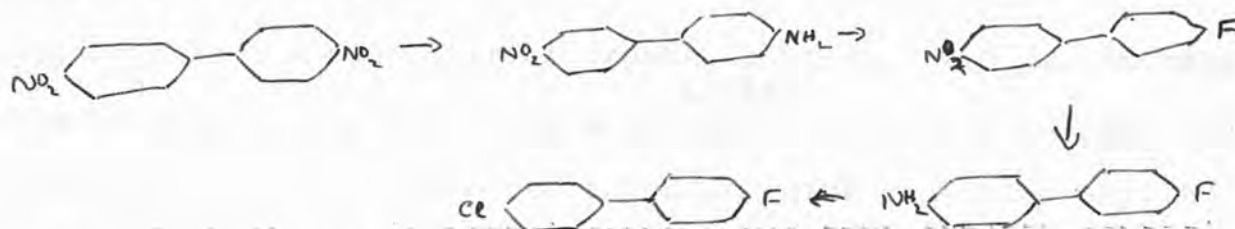
In the case of the chloro-fluoro-diphenyl, which was difficult to prepare, it was found necessary to work with a smaller amount than 0.01 gm. molecule. About 0.003 gm. molecule was used, it was dissolved in 10 c.c. fuming nitric acid, and the solution for analysis made up to 100 c.c. In every other respect the two sets of experiments were exactly similar.

A blank experiment was carried out to determine the amount of halide in the caustic potash solution, but this was found to be negligible.

The direct estimation of insoluble halide by means of silver nitrate with potassium chromate as indicator was first attempted, but was abandoned as the end point was insufficiently sharp to give a satisfactory result. The ammonium thiocyanate method which was employed was found to give an excellent end-point.

The Preparation of 4-Chloro:4'-Fluoro-Diphenyl.

This synthesis presented some difficulty, but was ultimately achieved as follows:-



The reduction of 4:4'-dinitro-diphenyl has been greatly simplified by the substitution of an aqueous solution of sodium ^{di}sulphide Na_2S_2 for an aqueous alcoholic solution of ammonium hydrogen sulphide, the reagent used by Willstätter and Kalb (Ber., 39 3749)

The method of replacing an amino-group by fluorine, described by Balz and Schiemann (Ber., 60, 1186.) and improved by Le Fevre and Turner J., 1930, 1161.) was still further simplified as it was found unnecessary to mix the diazonium borofluoride with sand preparatory to decomposing it by heat.

The above synthesis was found preferable to the scheme which involves the use of 4-chloro:4'-nitro-diphenyl, as the method of obtaining this compound by the direct chlorination of 4-nitrodiphenyl, previously described by Le Fevre and Turner (J., 1928, 245.) proved unsuitable for the preparation of large quantities. Attempts to prepare this substance from 4-nitro:4'-amino-diphenyl by the usual method for the replacement of an amino-group by a

chlorine atom also gave unsatisfactory results.

4-Nitro:4'-Amino-Diphenyl was prepared thus:-

165 Gm. sodium sulphide, $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ were heated until it dissolved in its own water of crystallisation. 14.0 gm. flowers of sulphur were added and the mixture ^{boiled} until all the sulphur had dissolved, giving a clear red solution which contained sodium disulphide, Na_2S_2 .

70 Gm. 4:4'-dinitro-diphenyl were ground to a paste with 300 c.c. of cold water, the solution of sodium disulphide was added to ~~this~~ and the mixture heated on the water-bath for five hours, during which time the colour gradually changed from yellow to a bright orange-red. The red solid was filtered and washed several times with boiling water to remove sulphur compounds and benzidine. It ~~was~~ was then extracted with successive small amounts of boiling dilute hydrochloric acid and decanted through a filter; any unchanged dinitro-compound, being insoluble in the acid, was thus removed. The filtrate was made alkaline with .880 ammonia and the precipitate ~~ated~~ base filtered and washed with hot water. Forty grams of red powder melting at 199° were obtained.

The amount of sodium sulphide used was about one-and-a-half-times the theoretical amount; when only the theoretical quantity was used a considerable amount of unchanged dinitro-compound was recovered, while the use of more than 50% excess tended to give benzidine. The advantage of this method over that of Willstätter

and Kalb is that, since the products of the reaction are the nitro-amino-compound and sodium thiosulphate, all the sulphur compounds present at the end of the reaction can be easily washed out of the solid residue with water, so that there is no precipitation of sulphur on the addition of acid and the process of extraction is therefore much simplified.

4-Nitro:4'-Fluoro-Diphenyl.

40 gm. of 4-nitro:4'-amino-diphenyl, mixed with 50c.c. of concentrated hydrochloric acid and 50 gm. ice, were diazotised in a freezing mixture of ice and salt by adding a strong solution of 14 gm. sodium nitrite. After urea had been added to decompose any excess of nitrous acid the solution was filtered and the solid residue washed with water until no more went into solution. The solution was then added slowly with stirring to a cold concentrated aqueous solution of sodium borofluoride which had previously been filtered. A thick cream coloured precipitate of 4-nitro diphenyl;4'-diazonium borofluoride at once separated. This was filtered and dried, first in the air and finally over sulphuric acid in a vacuum desiccator. Considerable difficulty was experienced in the drying as the precipitate was very finely divided and of the consistency of mud. The complete removal of moisture was essential before thermal decomposition could be attempted, as the effect ^{of heat} on a diazonium borofluoride in the presence of water is the

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the formation not of a fluoro compound but of a phenol.

After several days' drying the substance was placed in an open, long-necked flask and heated on a metal bath at 135°-140° when decomposition took place with evolution of white fumes of boron trifluoride. The decomposition temperature of a sample of the substance had previously been found by the method used for melting-points. The black, coke-like mass remaining in the flask after the evolution of white fumes had ceased was treated with caustic soda solution to dissolve any phenol and steam-distilled. After prolonged distillation 6 gm. of a substance which melted at 119°-121° were obtained. It crystallised from alcohol in long yellow needles melting at 120° - 121°.

Found: Nitrogen 6.85%. $C_{12}H_8O_2NF$ requires 6.45%.

4-Amino:4'-Fluoro-Diphenyl.

5 gm. 4-nitro:4'-fluoro-diphenyl were dissolved in boiling glacial acetic acid, 25 c.c. conc. hydrochloric acid and 26 gm. stannous chloride were added and heating continued for 15 minutes. The contents of the flask were cooled and treated with strong aqueous caustic potash until the liquid appeared grey. It was then extracted with ether, the ether was distilled off and the solid residue crystallised from alcohol: 4.5 gm. of a substance melting at 121° were obtained. It crystallised in small, pale-yellow, irregular leaflets.

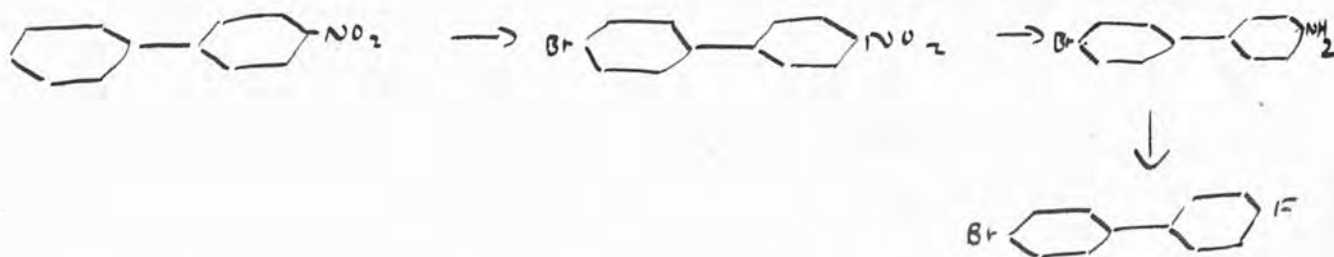
Found: N 7.84%. $C_{12}H_{10}NF$ requires 7.48%.

4-Chloro:4'-Fluoro-Diphenyl.

4 Gm. 4-amino:4'-fluoro-diphenyl, mixed with 5 c.c. concentrated hydrochloric acid and 5 gm. ice, were diazotised in a freezing mixture and treated in the usual manner with excess of cuprous chloride. After standing for some hours the solution was made alkaline and steam-distilled. 1.5 Gm. were obtained of a substance which crystallised from alcohol in colourless, fern-like groups of needles, melting at 87-88°.

Found: Cl 16.9%.

$C_{12}H_9ClF$ requires 17.2%.

The Preparation of 4-Bromo:4'-Fluoro-diphenyl.

4-Bromo:4'-nitro-diphenyl was obtained by the direct bromination of 4-nitro-diphenyl in glacial acetic acid at 100°, as described by Le Fevre and Turner (J., 1926, 2041.) It was reduced with stannous chloride and hydrochloric acid in precisely the same way

as the fluoro-nitro-diphenyl already described, giving
4-bromo:4'-amino-diphenyl.

4-Bromo:4'-Fluoro-Diphenyl was prepared from the above base by the method already described for the preparation of 4-nitro:4'-fluoro-diphenyl from 4-nitro:4'-amino-diphenyl. 24 Gm. base, 25 c.c. conc. hydrochloric acid with 25 gm. ice, and 7 gm. sodium nitrite were used for the diazotisation, and the diazo-solution was added to a solution of 50 gm. sodium borofluoride. 35 Gm. of diazonium borofluoride were obtained. The precipitate was of a pinkish colour, and was more crystalline, and therefore easier to dry than the chloro-compound already described. decomposition at 100° and steam distillation gave 13 gm. of a white substance which melted at 97°-99°. It crystallised from alcohol in colourless, fern-like groups of needles, similar to those of the chloro-compound. It melted at ~~100~~ 99°-100°.

Found: Br 32.0%.

$C_{12}H_8BrF$ requires 32.6%.

In the hope of obtaining further information about the orienting effect of 4:4'- halogen~~s~~ atoms in the diphenyl molecule an attempt was made to study the effect of such substituents on further halogen substitution. It was proposed to prepare from diphenyl by direct chlorination or bromination, derivatives containing more than two halogen atoms, and to compare them with synthetic polyhalogeno-diphenyls of known constitution.

It had been shown by Kramer (Ann., 189 , 142.) that direct chlorin-

ation of diphenyl in the presence of antimony pentachloride gave a mixture of the 2-chloro, 4-chloro, and 4:4'-dichloro-~~c~~ compounds. In addition to these substances only the hexachloro-compound had been obtained directly from diphenyl (Ruoff Ber., 9, 1491.), although Schmidt and Schultz (Ann., 207, 340) obtained a penta-chloro-diphenyl by the action of phosphorous pentachloride on 4:4'-dichloro-diphenyl;

Since the nitration of 4:4'-dichloro-diphenyl gives first the 2-nitro- and then the 2:3U-dinitro-derivatives (Dennett and Turner. loc.cit.) it is probable that the compound obtained by Schmidt and Schultz contains chlorine atoms in the positions 2-, 4-, 3'-, 4'-.

An attempt was made to prepare chloro-diphenyls by the method described by Silberrard (J., 1925, 2677.) which consists of the addition of sulphuryl chloride containing a trace of sulphur chloride to diphenyl mixed with anhydrous aluminium chloride, but only the 4:4'-dichloro-compound could be isolated in a pure condition.

It was found that 4:4'-dichloro-diphenyl could be easily prepared by passing chlorine into a solution of diphenyl in boiling glacial acetic acid until the evolution of hydrogen chloride ceased. On cooling, 25% of the theoretical yield of 4:4'-dichloro-diphenyl crystallised out in ^apractically pure

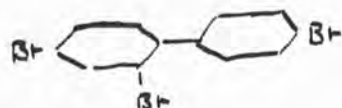
(2E)

condition. Addition of water to the mother-liquor gave an oil which could not be made to solidify by further treatment with chlorine in acetic acid.

Previous workers have described the bromination of diphenyl as giving first the 4-bromo-derivative (Schultz Ann., 174, 207) and then the 4:4'-dibromo-compound. A tribromo-diphenyl, melting at 90° was described by Carnelly and Thomson (J., 1885, 587.), who obtained it by brominating a mixture of diphenyl and 4-methyl-diphenyl. No other bromo-compounds had been obtained directly from the hydrocarbon.

The 4:4'-dibromination of diphenyl has been found to proceed very readily in boiling glacial acetic acid, the yield of pure dibromo-compound being about 85% of the theoretical amount. An attempt to introduce a third bromine atom under similar conditions yielded only the unchanged dibromo-compound.

It was found possible to effect further bromination of 4:4'-dibromo-diphenyl by heating it just above its melting-point 165° , and passing through it a current of carbon dioxide laden with bromine vapour; From the product a small amount of a tribromo diphenyl has been isolated. It was found impossible to free this from a trace of the dibromo-compound. There seems little doubt that the higher bromination product is 2:4:4'-tribromo-diphenyl,



and may be identical with the compound

obtained by Carnelly and Thomson (loc.cit.). It crystallised from alcohol in colourless needles, melting at 75° - 80° , and this melting point was found to be unaffected by further recrystallisation.

found: Br 59.94%

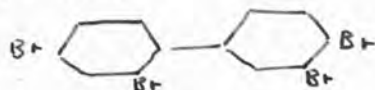
$C_{12}H_7Br_3$ requires 61.38%

Attempts to synthesise 2:4:4'-tribromo-diphenyl, with which the above compound is probably identical, were unsuccessful



as the Sandmeyer reaction gave a mixture of products from which no tribromo-diphenyl could be isolated.

Dibromination of 4:4'-dibromo-diphenyl under the same conditions as those just described was also attempted. From the product was obtained a small amount of a substance which melted at about the same temperature (165°) as the dibromo-diphenyl, but which depressed the melting-point of the latter compound by about thirty degrees. It crystallised from alcohol in small colourless needles, melting at 165° - 167° . It is probably 2:4:3':4'-tetrabromo-diphenyl.



Found: Br 69.32%

$C_{12}H_6Br_4$ requires 68.13%

An attempt was made to synthesise 2:4:2':4'-tetrabromo-diphenyl from 2:4-dibromo-iodobenzene, which was obtained from 2:4-dibromoacetanilide. The preparation of the latter compound has been

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considerably simplified, and has been accomplished by the rapid addition of bromine to a solution of p-bromo-acetanilide and sodium acetate in boiling glacial acetic acid. (cf. Chattaway and Orton. Ber., 32 3573)

When 2:4-dibromo-iodobenzene was heated with copper bronze a mixture of products was obtained from which no tetrabromo-diphenyl could be isolated.

The investigation of the products of direct bromination of diphenyl was abandoned at this point on account of the loss of bromo-diphenyls by sublimation which was always observed during the reaction. This meant that it was impossible to determine exactly by weighing when the desired amount of bromine had been introduced, and it was therefore very unlikely that pure products would be obtained.

For the same reason the further chlorination of 4:4'-dichloro-diphenyl was discontinued.

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E.E.J.M.