CLXXXIII.—2:2'-*Dibromodiphenyl* and 2:2'-*Dichlorodiphenyl*.

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IN the course of an investigation having for its object the preparation of diphenylene (this vol., p. 683), it was necessary to obtain 2:2'-*dibromodiphenyl*, a substance hitherto unknown. Treatment of the tetrazo-derivative of 2:2'-diaminodiphenyl with cuprous bromide, as in the ordinary Sandmeyer reaction, suggested itself as a convenient method of preparation. This procedure ultimately proved successful, but unexpected difficulties arose in the first experiments, and very little dibromodiphenyl was formed. With the object of ascertaining the most suitable conditions for the reaction, the behaviour of cuprous bromide towards diphenyltetrazonium bromide under various conditions was investigated. Täuber had found that potassium sulphide reacted with diphenyltetrazonium chloride solutions, yielding carbazole (*Ber.*, 1893, **26**, 1703). This same substance had been obtained by v. Niementowski (*Ber.*, 1901, **36**, 3329), who made use of copper powder in an attempt to prepare dichlorodiphenyl. Mascarelli had also noticed that the main product of the reaction between diphenyltetrazonium chloride and potassium iodide was carbazole (*Gazzetta*, 1908, **38**, ii, 619), the di-iododiphenyl which was his aim being formed in small amount only. It is clear, therefore, that cuprous chloride and certain other reducing substances act on diphenyltetrazonium solutions mainly to produce the very stable substance carbazole.

Cuprous bromide behaves in the same way as cuprous chloride, but at least two other products besides carbazole are formed simultaneously, namely, 2:2'-dibromodiphenyl and diphenyleneazone,

When a solution of cuprous bromide dissolved in hydrobromic acid is poured into a cold solution of diphenyltetrazonium bromide, diphenyleneazone is the main product of the reaction, very little carbazole or dibromodiphenyl being formed. If, on the other hand, diphenyltetrazonium bromide is poured into a hot solution of cuprous bromide, carbazole is formed to a much greater extent, and the amount of diphenyleneazone is diminished. In this case also, very little dibromodiphenyl is produced. A much better yield of the latter substance with a little diphenyleneazone and a con-

siderable proportion of carbazole is obtained when 2:2'-diaminodiphenyl is dissolved in a hot solution of cuprous bromide in concentrated hydrobromic acid, and treated with sodium nitrite. The amount of 2:2'-dibromodiphenyl isolated from the product of the reaction rarely, however, exceeds 8 to 10 per cent. of the theoretical quantity.

In a study of the Sandmeyer reaction as applied to the formation of *o*-chlorotoluene, Erdmann (*Annalen*, 1893, **272**, 141) drew the conclusion that Sandmeyer's method of dissolving the base in a solution of the cuprous salt and halogen acid, and then diazotising, leads to a diminished yield of the required halogen derivative as compared with the yield obtained when the diazonium solution is poured into the solution of the cuprous salt. In the present instance the reverse is the case; Sandmeyer's method gives an appreciable amount of dibromodiphenyl, whereas Erdmann's produces mainly carbazole and diphenyleneazone, with only traces of dibromodiphenyl. The reactions which take place between diphenyltetrazonium bromide and cuprous bromide under the various conditions referred to may be represented by the following scheme :

In an attempt to prepare dibromodiphenyl by the action of alcohol on diphenyltetrazonium perbromide, only traces of dibromodiphenyl were obtained, carbazole being the main product of the reaction.

2:2'-Dibromodiphenyl can also be obtained from 2:2'-dibromo-4:4'-diaminodiphenyl by elimination of the amino-groups, both methods giving a product melting at 81°. As already shown in our previous paper, 2:2'-dibromodiphenyl reacts slowly with sodium, yielding diphenylene; mixed with methylene dibromide and acted on by sodium, it yields fluorene.

In order to complete the series of diortho-halogen derivatives of diphenyl, 2:2'-dichlorodiphenyl was prepared by a method similar to that used in the preparation of 2:2'-dibromodiphenyl. The yield of this substance was smaller than that of the correspond-

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ing bromo-derivative, carbazole being again the main product. 2:2'-Dichlorodiphenyl crystallises from light petroleum in colourless prisms, melting at 59°. Both halogen derivatives are very stable towards oxidising agents, being scarcely, if at all, attacked, even by chromic acid mixture.

EXPERIMENTAL.

Formation of Diphenyleneazone.—2:2'-Diaminodiphenyl was dissolved in excess of hydrobromic acid, and diluted with water until the solution contained approximately 3 per cent. of the base. The solution was cooled to 0°, and diazotised with sodium nitrite. To the tetrazonium solution so formed, cuprous bromide, dissolved in hydrobromic acid (40 grams of Cu_2Br_2 to 50 c.c. of acid, D 1.49), was slowly added with stirring, the solution being kept cool by means of ice. Each addition of cuprous bromide was followed by a vigorous evolution of gas and formation of a bluish-black mass enclosing nitric oxide. The products of the reaction were heated on a water-bath for an hour, and the liquid then filtered from the solid matter (A). The filtrate was evaporated to small volume, and on treatment with excess of ammonia a large amount of almost pure diphenyleneazone was precipitated. The solid (A) was boiled with 15 per cent. hydrochloric acid, the acid liquid filtered from undissolved solid matter (B), and the filtrate treated with excess of ammonia, which precipitated a further quantity of slightly impure diphenyleneazone. After one crystallisation from alcohol, the diphenyleneazone was obtained pure in the form of long, greenish-yellow prisms, melting at 155°. The yield was good, 11 grams of pure material being obtained from 20 grams of 2:2'-diaminodiphenyl. The identity of this substance with the diphenyleneazone obtained by Täuber by the action of sodium amalgam on 2:2'-dinitrodiphenyl (*Ber.*, 1891, **24**, 3081), and by Ullmann and Dieterle from diphenyleneazone oxide (*Ber.*, 1904, **37**, 23), was proved by the melting point and by analysis of the base (Found, N=15.7. Calc., N=15.6 per cent.) and of the platinum salt. (Found, Pt=25.1. Calc., Pt=25.0 per cent.)

It is noteworthy that the formation of diphenyleneazone by the above process is accompanied by evolution of nitric oxide.

The solid (B) was found to contain carbazole, which was extracted by successive treatment with alcohol, ether, benzene, and carbon tetrachloride. These solutions were boiled with animal charcoal, and concentrated, when crystals were deposited, from which pure carbazole was ultimately obtained. The first crops of carbazole crystals were mixed with a very small quantity of dibromodiphenyl.

Attempts to increase the yields of dibromodiphenyl were next made by modifying the method described above in various directions. The diphenyltetrazonium bromide solution was poured into a hot solution of cuprous bromide dissolved in hydrobromic acid. The black, tarry solid which formed yielded a fair amount of carbazole and of diphenyleneazone, but only traces of dibromodiphenyl. By this method the amount of diphenyleneazone was diminished, and that of the carbazole increased.

Preparation of 2:2'-Dibromodiphenyl.—When 2:2'-diaminodiphenyl hydrobromide is diazotised in the presence of cuprous bromide, dibromodiphenyl is formed, together with other products. Thirty-six grams of cuprous bromide were dissolved in 90 c.c. of hydrobromic acid (D 1.49), and 20 grams of 2:2'-diaminodiphenyl added. The liquid was heated on a water-bath, and small quantities of hot water added from time to time until all the solid was dissolved. Sixteen grams of sodium nitrite in 50 c.c. of water were added to the hot solution of the base drop by drop, with vigorous stirring after the addition of each drop, the heating being continued during the addition of the nitrite solution. When all the nitrite had been added, the liquid was heated on a water-bath for an hour, cooled, and diluted with water. The dark soft solid which separated was collected, washed with water, and digested with ether several times. A considerable amount of solid matter containing carbazole remained undissolved in the ether. The undissolved matter also contained some copper compound, but this was not further investigated. A very small amount of diphenyleneazone was obtained from the aqueous filtrate from the soft solid. The ethereal solution, which contained almost all the dibromodiphenyl, was boiled with animal charcoal, filtered, and evaporated to a syrupy consistency. The syrupy residue was distilled in a current of steam, in which the dibromodiphenyl, together with a little carbazole, passed over. This method of separation is slow, but, so far, is the only one by which we have been able to obtain dibromodiphenyl free from coloured impurities. The distillate was extracted with ether, and the crystalline residue obtained by evaporation of the ethereal solution, dissolved in light petroleum (boiling below 60°), and allowed to crystallise. A small quantity of carbazole first separated, and was removed by filtration. Dibromodiphenyl crystallised from the filtrate in long, hard, colourless prisms or in feathery tufts of needles, which melted at 81° after recrystallisation from 90 per cent. alcohol. The yield is about 15 per cent. of the weight of the base employed.

2:2'-Dibromodiphenyl is readily soluble in the usual organic solvents. It is very stable towards oxidising agents; after heating

with a mixture of chromic acid and diluted sulphuric acid for five hours practically the whole of the substance was recovered unchanged. Advantage may be taken of this fact to remove traces of impurities:

0.1346 gave 0.2262 CO_2 and 0.0323 H_2O . $\text{C}=45.9$; $\text{H}=2.65$.

0.1226 „ 0.1482 AgBr . $\text{Br}=51.4$.

$\text{C}_{12}\text{H}_8\text{Br}_2$ requires $\text{C}=46.2$; $\text{H}=2.6$; $\text{Br}=51.3$ per cent.

The constitution of dibromodiphenyl follows from its preparation from 2 : 2'-diaminodiphenyl.

2 : 2'-Dibromodiphenyl can also be prepared from 2 : 2'-dibromo-4 : 4'-diaminodiphenyl (*mm'*-dibromobenzidine), a substance which was obtained by Gabriel from *m*-bromonitrobenzene (*Ber.*, 1876, **9**, 1405). For the preparation of dibromodiphenyl, the hydrochloride which is obtained from *mm'*-dibromohydrazobenzene may be used directly after drying. The amino-groups can be removed by means of ethyl nitrite and alcohol in the usual way. The resulting alcoholic solution is evaporated to dryness, and the residue distilled in steam, whereby an impure dibromodiphenyl is obtained. After purification, the substance prepared in this way melted at 81° , and no alteration in the melting point was observed when it was mixed with the dibromodiphenyl prepared from 2 : 2'-diaminodiphenyl. As regards yield, the preparation from *mm'*-dibromobenzidine offers no advantage over the first method, and the final product requires several recrystallisations involving considerable loss of material before it is obtained quite pure.

An attempt to prepare 2 : 2'-dibromodiphenyl through a perbromide was made. 2 : 2'-Diaminodiphenyl was diazotised, and to the tetrazo-solution a mixture of bromine in hydrobromic acid was added. A bulky, yellow precipitate of the perbromide formed at once. This was collected, and boiled with absolute alcohol, the solution changing in colour through green and blue to brown. After removal of the alcohol a fair amount of diphenyleneazone was obtained, but only traces of halogen derivative.

Preparation of 2 : 2' - Dichlorodiphenyl.—2 : 2'-Diaminodiphenyl was dissolved in hydrochloric acid containing the calculated quantity of cuprous chloride. The solution was then heated, and treated with sodium nitrite, as in the preparation of 2 : 2'-dibromodiphenyl. The subsequent treatment of the soft, black solid was also similar. A large amount of carbazole was isolated from the reaction products, and a small quantity of dichlorodiphenyl was found in the ethereal solutions. After distillation in a current of steam a mixture of dichlorodiphenyl with a little carbazole was obtained, from which the pure dichlorodiphenyl was isolated by recrystallisation from light petroleum, in which carbazole is but sparingly soluble.

2:2'-Dichlorodiphenyl crystallises from light petroleum in nodular masses of colourless prisms, melting at 59°. It dissolves in the usual organic solvents, and is stable towards oxidising agents:

0.1134 gave 0.1428 AgCl. Cl=31.2.

$C_{12}H_8Cl_2$ requires Cl=31.8 per cent.

An interesting synthesis of fluorene was effected by the action of sodium on a mixture of 2:2'-dibromodiphenyl and excess of methylene dibromide dissolved in ether. The crystalline residue remaining after evaporating off the ether contained unchanged dibromodiphenyl, which was removed by recrystallisation from alcohol and light petroleum. After recrystallisation several times from these solvents a small amount of almost pure fluorene was obtained, melting at 115°. The substance was further identified by the preparation of the characteristic brown picrate, melting at 80°.

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