VII.—*Diphenylene. Part II.*

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IN previous papers dealing with the preparation and properties of 2:2'-dibromodiphenyl it was shown that the action of sodium on this substance results in the formation of the hydrocarbon diphenylene, $C_{12}H_8$ (T., 1911, **99**, 683, 1617). In the experiments by which this substance was first obtained the sodium was employed in the form of thin slices. The reaction proceeded slowly, but gave only a small quantity of by-products. The amount of these was reduced by substituting light petroleum for ether, whereas it was increased by the use of benzene, probably because of the ready solubility of the by-products in this medium. By using finely-divided sodium the rate of the reaction was increased, but the yield of diphenylene was greatly reduced owing to the formation of compounds of high molecular weight. One of these was found by analysis and determination of the molecular weight to have the formula $C_{84}H_{56}Br_2$.

We have made numerous experiments in the hope of finding a more convenient method for the preparation of diphenylene, but so far without success. In one of these attempts *o*-di-iodobenzene was heated with copper powder, both in air and in closed exhausted tubes to 250°. Only resinous products were obtained, from which no diphenylene could be isolated, although there was reason to believe that a small quantity had been formed. Silver diphenate suggested itself as another possible starting point for the preparation of diphenylene. On subjecting this salt to dry distillation it was observed that at a particular temperature sudden decomposition set in, accompanied by much charring and a violent evolution of carbon dioxide. The distillate condensed to a mass of yellow crystals, which dissolved almost completely in light petroleum.

This solution deposited pale yellow crystals, which on recrystallisation melted at 92° . The crystals agreed in character with the lactone described by Graebe and Schestakov (*Annalen*, 1895, **284**, 316) under the name of "biphenylmethylid," $\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{O}$, and by Griess (*Ber.*, 1888, **21**, 981) and Richter. Bromination of the crystals resulted in the formation of the bromo-derivative melting at 194° prepared by Richter (*J. pr. Chem.*, 1883, [ii], **28**, 294). Their identity with the lactone derived from *o*-hydroxydiphenylcarboxylic acid is therefore established. The mother liquors from this substance were evaporated to dryness and distilled in a current of steam, when crystals of pure diphenyl were obtained. No trace of diphenylene was found in these operations.

To obtain a supply of material for the further examination of the reactions of diphenylene we were compelled to revert to the original method of preparation described in our first paper on the subject. We have been obliged in consequence to limit our investigation for the present to a few of the simpler derivatives. A *dinitrodiphenylene* was obtained by heating diphenylene with diluted nitric acid under pressure. By the action of the fuming acid a *tetranitro*-derivative was formed. Considerable loss of material occurred in both cases, resinous and waxy substances being formed, which were not sufficiently well defined for investigation. Bromine reacted with diphenylene with the formation of two products, namely, 2:2'-dibromodiphenyl and a *dibromodiphenylene*. By the oxidation of the latter, *p*-bromobenzoic acid was obtained, together with an acid which yielded a strongly fluorescent solution when condensed with resorcinol. The formation of *p*-bromobenzoic acid indicates that under the conditions described substitution takes place in the meta-position with respect to the middle ring.

The behaviour of diphenylene when heated with diluted nitric acid is of special interest. From the products of the reaction three definite substances were isolated, namely, (1) a dinitrodiphenylene, (2) diphenylene oxide, and (3) a nitrophthalic acid. In addition, a quantity of waxy matter of indefinite character was formed.

It is quite clear from the production of diphenylene oxide by the oxidation with dilute nitric acid, on the one hand,

and from the regeneration of 2:2'-dibromodiphenyl on the other, $\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4 \longrightarrow \text{C}_6\text{H}_4\text{Br}\cdot\text{C}_6\text{H}_4\text{Br}$, that the diphenylene molecule is rather unstable. It is probably owing to this instability that

diphenylene forms waxy substances so readily under the influence of various reagents, and that the formation of substitution derivatives is accompanied by so much loss of material.

EXPERIMENTAL.

Finely divided sodium was immersed in dry ether, and dried 2:2'-dibromodiphenyl was added. An immediate reaction resulted, the solution became deep brown, and a quantity of red, insoluble matter separated. The reaction was complete in a very short time. The ether and suspended solid matter were separated from unchanged sodium, and the ethereal liquid was filtered. When the insoluble matter was boiled with a little water to remove sodium bromide a yellow powder was left behind. This dissolved readily in cold benzene and chloroform, from the solution in which it could be precipitated by light petroleum or alcohol. The substance was readily purified by repeated treatment with a mixture of benzene and light petroleum, from which it separated as an amorphous, yellow powder, melting and decomposing at 306° :

0.1246 gave 0.3756 CO_2 and 0.0532 H_2O . $\text{C} = 82.2$; $\text{H} = 4.7$.

0.1036 „ 0.0312 AgBr . $\text{Br} = 12.8$.

0.2876 in 18.74 benzene gave $\text{E} = 0.037$. $\text{M.W.} = 1180$.

$\text{C}_{84}\text{H}_{56}\text{Br}_2$ requires $\text{C} = 82.3$; $\text{H} = 4.6$; $\text{Br} = 13.1$ per cent.

$\text{M.W.} = 1224$.

The formula of this substance may be written $(\text{C}_{12}\text{H}_8)_7\text{Br}_2$ when it is seen to be derived from the action of sodium on two molecules of 2:2'-dibromodiphenyl, the product of which then reacts with a third molecule, and so on until the compound having eighty-four carbon atoms is reached, which is insoluble in ether. The compound $\text{C}_{84}\text{H}_{56}\text{Br}_2$ is similar in character to the compound $\text{C}_{78}\text{H}_{52}\text{Br}_2$ described by Goldschmiedt (*Monatsh.*, 1886, 7, 40) and Hosaeus (*ibid.*, 1893, 14, 323), which results from the action of sodium on the various dibromobenzenes. The ethereal filtrate from the compound $\text{C}_{84}\text{H}_{56}\text{Br}_2$ contains the diphenylene formed in the reaction, together with other substances similar in character to $\text{C}_{84}\text{H}_{56}\text{Br}_2$, but soluble in ether. These may be readily separated from diphenylene by taking advantage of their insolubility in light petroleum or in cold alcohol.*

Bromination of Diphenylene.—The diphenylene to be operated on was covered with water, four times its weight of bromine was added a little at a time, and the whole mass ground up in a mortar. No perceptible rise of temperature resulted, and only a small amount of hydrogen bromide was evolved. The whole mass was

* The behaviour and properties of these substances are not described here, as they have no bearing on the derivatives of diphenylene.

treated with dilute aqueous sodium hydroxide solution until all the unchanged bromine was removed, the residual solid collected, washed with water and a little alcohol, and dissolved in benzene. Colourless needles separated, which did not melt sharply, but after a second crystallisation melted at 80° . This substance was identical with 2:2'-dibromodiphenyl formerly described by us (T., 1911, 99, 1618). The mother liquors on concentration deposited further crops of crystals, of which the first fractions, judging from the low melting point, contained more 2:2'-dibromodiphenyl. The last fractions consisted chiefly of a substance which melted after several crystallisations at 171° , and had the composition of *dibromodiphenylene*:

0.1330 gave 0.1624 AgBr. Br = 52.0.

$C_{12}H_6Br_2$ requires Br = 51.6 per cent.

The yield of pure substance was not more than 30 per cent., a large proportion of the diphenylene operated on having been converted into 2:2'-dibromodiphenyl and waxy substances of indefinite character containing halogen. Dibromodiphenylene dissolves fairly readily in benzene and alcohol, from which it separates in long, stout, colourless needles. When oxidised by chromic acid it yields a mixture of acids. One of these was recognised as a phthalic acid by the strongly fluorescent solution obtained by condensing it with resorcinol. The other was proved by its equivalent weight and melting point (248°) to be *p*-bromobenzoic acid.

Nitration of Diphenylene.—One part of diphenylene was dissolved in ten parts of concentrated sulphuric acid, and the mixture cooled with ice; four parts of nitric acid (D 1.5) were then added a little at a time, keeping the whole immersed in a freezing mixture. When the action, which at first was very violent, had moderated, the flask containing the mixture was heated on a water-bath for one hour. The contents of the flask after being allowed to cool were poured into ten times their volume of ice-water; the solid which separated was collected, washed with water and a little alcohol, and dried. The yield of crude solid was about 30 per cent. of the weight of the diphenylene taken. The dried precipitate was boiled with a large quantity of alcohol, from which it crystallised on cooling in fine, yellow needles, melting at 223° :

0.2372 gave 0.3768 CO_2 and 0.0304 H_2O . C = 43.3; H = 1.4.

0.1038 „ 15.1 c.c. N_2 at 19.5° and 768 mm. N = 17.1.

$C_{12}H_4O_8N_4$ requires C = 43.4; H = 1.2; N = 16.9.

The substance is therefore a *tetranitrodiphenylene*. It dissolves sparingly in alcohol and glacial acetic acid, but is almost insoluble in other organic solvents.

Action of Diluted Nitric Acid on Diphenylene.

Diphenylene was heated in a sealed tube for sixteen hours at 150° with twenty times its weight of diluted acid (D 1.2). Considerable decomposition resulted, and a yellow, semi-crystalline mass remained. This was washed with water, digested with ether, and finally with alcohol and benzene. The residue obtained after this treatment consisted of pale yellow needles, which dissolved sparingly in alcohol. It separated from its alcoholic solution in small needles melting at 204° . Analysis showed that the substance was a *dinitro-*

Oscillation frequencies. *Diphenylene oxide in alcohol.*

diphenylene. The yield was small. Dinitrodiphenylene is almost insoluble in ether, benzene, or carbon disulphide, but dissolves sparingly in alcohol, acetone, or glacial acetic acid:

0.1236 gave 0.2678 CO_2 and 0.0334 H_2O . $\text{C}=59.1$; $\text{H}=3.0$.

0.1314 „ 13.4 c.c. N_2 at 17° and 761 mm. $\text{N}=11.8$.

$\text{C}_{12}\text{H}_6\text{O}_4\text{N}_2$ requires $\text{C}=59.5$; $\text{H}=2.5$; $\text{N}=11.6$ per cent.

The ethereal solution was treated with aqueous sodium hydroxide, whereby a small amount of an acid was removed. On evaporating off the ether a waxy mass was left behind, which was redissolved

in alcohol. From the alcoholic solution small plates deposited. On redissolving these plates and treating with picric acid, a picrate separated out from the concentrated alcoholic solution, which on recrystallisation melted at 95° . By acting on the picrate with aqueous sodium hydroxide and extracting the resulting liquid with ether a crystalline solid was obtained melting at $78-79^{\circ}$, and possessing the properties of diphenylene oxide. Its identity with this substance was clearly established by its melting point, the melting point of its picrate, and by its absorption spectrum. The absorption spectrum of diphenylene oxide (see diagram) is strikingly characteristic. It possesses two bands; the head of the larger and more persistent band is at $1/\lambda 3530$, and of the small narrow band at $1/\lambda 4000$. The spectrum of the substance from diphenylene is identical with this.

The aqueous liquid remaining after the reaction contained an acid which was purified by means of its sodium salt. It corresponded in molecular weight and in the melting point of its methyl ester with 3-nitrophthalic acid (Ag salt: Found, $\text{Ag}=49.9$. Calc., $\text{Ag}=50.5$ per cent.).

We hope in a future paper to give a more particular account than has yet been possible of the physical properties of diphenylene.

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