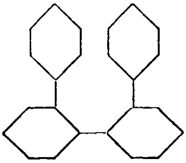
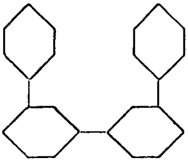
CXLII.—*Polyphenyls. Part I. The Symmetrical Diphenyldiphenyls.*

By Sydney Thomas Bowden.

The polyphenyls comprise a series of hydrocarbons of the general formula $C_nH_{n-2(N-1)}$, where n = number of carbon atoms and N = number of phenyl nuclei. As a result of the work of Pummerer and Bittner (*Ber.*, 1924, **57**, 84) and Gerngross and Dunkel (*ibid.*, p. 739) the series of linear hydrocarbons is now complete up to hexaphenyl, and the data available indicate that there is a general increase in thermal stability with increasing complexity of the ring system. The possibility of isomerism first occurs with 4-phenyldiphenyl, and 2- and 3-phenyldiphenyl have in fact been described, but the only isomeride of the fourth member of the series, 4 : 4′-diphenyldiphenyl, which has hitherto been prepared is 1 : 3 : 5-triphenylbenzene.

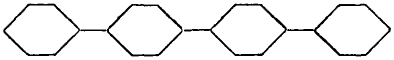
(I.)





(II.)

(III.)



4 : 4′-Diphenyldiphenyl (III) is conveniently prepared from 4-bromo- or 4-iodo-diphenyl, magnesium, and cupric chloride after the manner described by Krizewsky and Turner (J., 1919, **115**, 560) for the production of diphenyl from magnesium phenyl halide. It may also be obtained by treating the prepared Grignard compound with cupric chloride, and the mechanism of the reaction is thus essentially similar to that which obtains in the corresponding diphenyl synthesis. The reaction proceeds somewhat more smoothly with the bromo-derivative than with the corresponding iodo-compound.

The hydrocarbon may be readily prepared by heating 4-iododiphenyl with copper-bronze, but only a trace is formed by the similar treatment of 4-bromodiphenyl. Molecular silver may be used instead of copper, but is less efficacious.

4 : 4′-Diphenyldiphenyl may be obtained by the pyrolysis of diphenyl : the yield, however, is very low, there is considerable formation of carbon, and the product is contaminated with isomeric diphenyldiphenyls and possibly octaphenyl.

2 : 2′- and 3 : 3′-*Diphenyldiphenyl* (I and II), prepared from the corresponding iododiphenyls, are stable crystalline substances, much more fusible and more soluble than 4 : 4′-diphenyldiphenyl.

EXPERIMENTAL.

2-Iododiphenyl.—2-Nitrodiphenyl (Bell, Kenyon, and Robinson, J., 1926, 1239) was reduced by van Hove's method (*Bull. Soc. chim. Belg.*, 1923, **32**, 53) to the amino-derivative, which was converted, by treatment of the diazotised base with potassium iodide, into 2-iododiphenyl; this, after being extracted, washed (with sodium bisulphite and water), and dried in ether and fractionated under reduced pressure, was obtained as an oil, b. p. 189—192°/36 mm. (Found : I, 45·0. Calc. for $C_{12}H_9I$: I, 45·3%).

2 : 2′-*Diphenyldiphenyl.*—A mixture of 2-iododiphenyl (4 g.) and copper-bronze (4 g.) was heated in a long tube to about 255°; an exothermic reaction then began, the temperature rising rapidly to 310°. When this had subsided, the metal-bath temperature was held at 260° for 10 minutes. The cold melt was broken up and extracted with benzene, and the extract concentrated and cooled; 2 : 2′-*diphenyldiphenyl*, which separated in hard white crystals, was recrystallised from alcohol; m. p. 118—119° (Found : C, 93·8; H, 6·0; *M*, in camphor, 303. $C_{24}H_{18}$ requires C, 94·1; H, 5·9%; *M*, 306). The hydrocarbon is slightly soluble in cold alcohol, fairly readily soluble in light petroleum, glacial acetic acid, ether, and benzene, and readily soluble in acetone. It dissolves in liquid sulphur dioxide and gives no colour with concentrated sulphuric acid.

3-Iododiphenyl.—3-Aminodiphenyl, m. p. 33°, was prepared by reduction of 3-nitrodiphenyl with stannous chloride and hydrochloric acid (Fichter and Sulzberger, *Ber.*, 1904, **37**, 882), liberated from the stannichloride, and isolated by steam-distillation. Although the amine is not very volatile in steam, this process is more satisfactory than that involving extraction with ether. The base was converted in the usual way into 3-iododiphenyl, b. p. 188—189°/16 mm. (Found : I, 45·2%).

3 : 3′-*Diphenyldiphenyl.*—This was prepared (from 4 g. each of 3-iododiphenyl and copper-bronze) and isolated in the same way as the 2 : 2′-compound. The yellow oil obtained from the benzene extract was triturated with carbon disulphide and kept under alcohol until it solidified. It then crystallised from hot alcohol, on cooling, in aggregates of white needles, m. p. 83—84°, and 86° after recrystallisation (Found : C, 93·3; H, 6·0%; *M*, in camphor, 303). 3 : 3′-*Diphenyldiphenyl* is readily soluble in ether and benzene, somewhat less soluble in light petroleum and liquid sulphur dioxide, and slightly soluble in alcohol and glacial acetic acid. It gives no colour with concentrated sulphuric acid.

Action of Metals on 4-Halogenodiphenyls.—(a) 4-Bromodiphenyl (2 g.) and copper-bronze (2 g.) were heated together as previously described, the temperature being held at 295—300° for 20 minutes :

there was no evidence of an exothermic reaction. After cooling, the mass was extracted with several portions of hot alcohol and the combined extracts were concentrated to small bulk, 96% of the bromodiphenyl being thus recovered. The metallic residue, heated at 300°/15 mm., gave a trace of crude 4 : 4′-diphenyldiphenyl (m. p. 300°).

(b) 4-Iododiphenyl (2 g.) and copper-bronze (2 g.), heated together, began to react at 220° (compare Ullmann and Meyer, *Annalen*, 1904, **332**, 51). At 270° the exothermic character of the reaction became evident, the temperature rising rapidly to 285°. After further heating at 265—270° for 10 minutes, the product was cooled, pulverised, and heated under a pressure of 15 mm. A small amount of 4-iododiphenyl sublimed at about 150°, and at 330° 4 : 4′-diphenyldiphenyl was obtained as a colourless crystalline sublimate, m. p. 315°. (Owing to the low solubility of the hydrocarbon in benzene, the method of Ullmann and Meyer, *loc. cit.*, is less convenient than the present method.) Recrystallised from hot nitrobenzene, it was obtained in fine plates, m. p. 320° (Found : C, 93·6; H, 6·2%).

Preparation of 4 : 4′-*Diphenyldiphenyl from Magnesium* 4-*Diphenylyl Halides.*—(a) 4-Bromodiphenyl (Gomberg and Bachmann, "Organic Syntheses," 1928, **8**, 42) (5 g.) and strongly activated magnesium (0·75 g.) were heated together in anhydrous ether (20 c.c.) on the water-bath over-night, the solution of magnesium 4-diphenylyl bromide obtained was filtered into finely-powdered anhydrous cupric chloride (2·9 g.), and the mixture heated under reflux for 4 hours and then treated with ice and water. The separated ethereal layer gave on evaporation small amounts of diphenyl and 4-bromodiphenyl. The insoluble material which remained after treatment of the reaction mixture with water was triturated with small portions of concentrated hydrochloric acid and finally washed with ether. Sublimation of the residual solid at 290—300°/12 mm. gave 4 : 4′-diphenyldiphenyl in 52% yield.

(b) Strongly activated magnesium (1·6 g.), cupric chloride (8·7 g.), 4-bromodiphenyl (15 g.), and ether (50—55 c.c.) were heated on the water-bath for 8 hours. The diphenyldiphenyl early separated as a greyish solid and the mixture was frequently shaken to prevent caking. The mixture was treated with ice-water and sufficient concentrated hydrochloric acid to dissolve most of the precipitated cuprous chloride. From the insoluble material, by sublimation at 310—320°/50 mm., 4 : 4′-diphenyldiphenyl was obtained in 63% yield.

(c) The preparation of 4 : 4′-diphenyldiphenyl was also carried out from magnesium 4-diphenylyl iodide in accordance with the procedure described above. The yield was 53%. The ethereal solution obtained after decomposition of the reaction mixture gave, on evaporation, a mixture of diphenyl and iododiphenyl.

The Formation of 4 : 4′-*Diphenyldiphenyl in the Pyrolysis of Diphenyl.*—Meyer and Hoffmann (*Monatsh.*, 1916, **37**, 711) obtained 4 : 4′-diphenyldiphenyl (m. p. 308°) by passing the vapour of diphenyl through a red-hot tube, but gave no record of the yield.

In the author's preliminary experiments to test the suitability of the pyrolytic method, an apparatus was used which allowed the continuous circulation of diphenyl vapour over a heating element constructed from 40 cm. of 32 gauge nichrome wire (compare the preparation of diphenyl from benzene; Bell, Kenyon, and Robinson, J., 1926, 1242). When a current of 3 amps. was employed, a white mist was produced in the neighbourhood of the element. The current was reduced to 2·5 amps. and held at this value for 5 hours. After cooling, the unchanged diphenyl was recovered by steam-distillation. The black residue, heated at 310—320°/50 mm., gave a small amount of oily sublimate, which on trituration with alcohol was converted into a white solid melting below 200°. From 22 g. of diphenyl, 2·2 g. of residual carbonaceous material were obtained.

In another experiment (22 g. of diphenyl) a current of 2 amps. was passed for 20 hours. After the steam-distillation the residue gave about 0·2 g. of oily sublimate, which was converted into a colourless solid, m. p. below 200°, by successive trituration with alcohol and light petroleum. After two recrystallisations from nitrobenzene at 100°, the material was obtained in colourless plates, m. p. 308°, which did not depress appreciably the melting point of authentic 4 : 4′-diphenyldiphenyl.

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