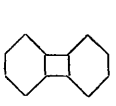
89. *Benzcyclooctatetraenes. Part III. Diphenylene and Tetraphenylene.*

By W. S. Rapson, R. G. Shuttleworth, and (in part †) J. N. van Niekerk.

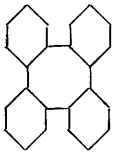
The action of cupric chloride on the Grignard reagent prepared from 2 : 2′-dibromodiphenyl has yielded a compound, $C_{12}H_8$, identical with that formulated as diphenylene (I) by Lothrop (*J. Amer. Chem. Soc.*, 1941, **63**, 1187), and a compound, $C_{24}H_{16}$, formulated as 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-*tetrabenz*-$\Delta^{1:3:5:7}$-cyclo*octatetraene* (*tetraphenylene*) (II). Crystallographic data are presented for the latter and the preparation of a *monobromo*- and a *tetranitro*-derivative is described.

The application of the Krizewsky–Turner reaction to 2 : 2′-dibromodiphenyl was stated (J., 1941, 488) to yield diphenyl and traces of a halogen-free, picrate-forming substance, m. p. 107°. Repetition of the work on a larger scale has shown the presence among the products of a hydrocarbon, $C_{24}H_{16}$, and also that the material mentioned above is a hydrocarbon, $C_{12}H_8$, identical in physical characteristics with that since described by Lothrop (*J. Amer. Chem. Soc.*, 1941, **63**, 1187) and formulated by him as being diphenylene (I) (compare, however, Baker, *Nature*, 1942, **150**, 210).

The compound $C_{24}H_{16}$ is almost certainly *tetraphenylene* (II). It is a colourless, high-melting, exceedingly stable compound, being recovered unchanged after treatment with potassium permanganate in boiling acetone. It failed to yield addition compounds with trinitrobenzene, picric acid, and styphnic acid, but crystallised from some solvents in rather stable, solvated forms. A *tetranitro*-derivative was prepared, and bromination to yield a *monobromo*-derivative occurred only in the presence of a catalyst. Crystallographic data for the hydrocarbon are presented and its full crystal structure is under investigation.



(I.)



(II.)

In some of our experiments widely varying quantities of diphenyl and 2 : 2′-diphenyldiphenyl accompanied diphenylene and tetraphenylene. Their formation was apparently due to reactions catalysed by traces of water, since neither could be isolated from the reaction mixture when moisture was rigorously excluded.

Experimental.

Action of Cupric Chloride on the Grignard Reagent from 2 : 2′-Dibromodiphenyl.—Reaction between 2 : 2′-dibromodiphenyl (78 g.; 1 mol.) and magnesium (7·3 g.; 1·2 mols.) in dry ether (500 c.c.) was initiated with the aid of iodine; after 48 hours' refluxing, a white precipitate formed. The heavy red oil which separated on the gradual addition, with ice-cooling and stirring, of dry cupric chloride (78 g.; 2·16 mols.) changed to a reddish-brown precipitate after 3—4 hours' refluxing. The ethereal solution was decanted, and the precipitate treated with ether and water, residual magnesium then reacting. The cuprous chloride was dissolved by the addition of hydrochloric acid, and the combined ethereal solutions filtered, washed with concentrated hydrochloric acid and with water, dried, and evaporated. The residue was separated into fractions (1) b. p. 105—130°/4 mm., (2) b. p. 130—170°/4 mm., and (3) b. p. 170—250°/4 mm., leaving a resinous residue. Fractions (1) and (2) were refractionated through a short column, fractions boiling at 105°/4 mm. (95°/0·2 mm.) and 150°/4 mm. (135°/0·2 mm.) respectively being collected. Fraction (1) was dissolved in its own volume of absolute alcohol; light yellow needles of diphenylene (1·0 g.) separated on ice-cooling, m. p. 111—112° after recrystallisation from alcohol (Lothrop, *loc. cit.*, gives m. p. 109—110°) (Found: C, 94·7; H, 5·4. Calc. for $C_{12}H_8$: C, 94·7; H, 5·3%). To the hot mother-liquor was added solid picric acid (1 g. per 10 c.c.), the solution cooled in ice, and the picrate filtered off. Further small portions of picric acid were introduced, and the above process repeated until picric acid itself separated. The picrate, recrystallised once from the minimum quantity (2 c.c. per g. of picrate) of absolute alcohol saturated with picric acid (ice-cooling) and once from absolute alcohol, formed red needles (1·4 g.), m. p. 121—122°, and on decomposition with dilute aqueous ammonia yielded a further 0·5 g. of diphenylene (total yield, 4%). Fraction (2) on recrystallisation from alcohol gave recovered 2 : 2′-dibromodiphenyl (7—10 g.). Fraction (3) on sublimation at 200°/0·2 mm. or on treatment with an equal volume of light petroleum (b. p. 80—90°) yielded almost pure tetraphenylene (6·0 g.; 16%), m. p. 230°, and 233° after recrystallisation.

If complete exclusion of moisture from the reactants had not been achieved, diphenyl and 2 : 2′-diphenyldiphenyl accompanied the other products. Thus in one experiment 6 g. of diphenyl and 0·4 g. of diphenylene were obtained from fraction (1), and 3·7 g. of tetraphenylene and 3·0 g. of 2 : 2′-diphenyldiphenyl from fraction (3). An attempt to bring about a chromatographic separation of diphenyl and diphenylene having failed, fraction (1) was in such cases treated with its own volume of absolute alcohol and cooled in ice; diphenyl separated and was filtered off. Treatment of the mother-liquor with picric acid in the manner detailed above then yielded diphenylene picrate. When 2 : 2′-diphenyldiphenyl accompanied tetraphenylene in fraction (3), the latter separated first on treatment of the distillate with light petroleum. Redistillation of the residue then yielded a fraction, b. p. 205—215°/1 mm., which deposited crystals on treatment with an equal volume of light petroleum, followed by ice-cooling. Purification from absolute alcohol gave large, colourless, brittle prisms, m. p. 118—119°, not depressed by authentic 2 : 2′-diphenyldiphenyl (Bowden, J., 1931, 1111).

† *Crystallography and Space Group of Tetraphenylene.*—The crystals used for the *X*-ray examination were transparent and colourless, with well-developed faces, making accurate goniometric measurements possible. The symmetry is monoclinic holohedral as judged from external form. Single crystal oscillation photographs made with Fe-$K\alpha$ radiation show that the structure may be based on a unit cell with $a = 16{\cdot}39$, $b = 13{\cdot}16$, $c = 15{\cdot}60$ A., $\beta = 100°\ 40'$. An inspection of the general *X*-ray reflections reveals that this cell is not primitive, but centred on the A face. The space group is determined uniquely as $C2h^6$, or A2/a in the Hermann–Maugin notation.

The density of the crystal, determined by the flotation method, lies between 1·20 and 1·25 g./c.c. The unit cell thus contains eight molecules of tetraphenylene, and the true density is 1·214 g./c.c.

The external form exhibited by the crystals is more conveniently described crystallographically in terms of axes with a monoclinic angle $\beta = 123°\ 56'$, and axial ratios $a : b : c = 1{\cdot}475 : 1 : 1{\cdot}185$. The eight faces of the form {111} referred to these axes are commonly developed, together with the (100) and (001) faces, and very rarely the (010) faces. Structurally, however, the unit cell based on these axes is less convenient than the one given above.

Tetraphenylene showed a relatively low solubility in most solvents. It crystallised without solvation from ethyl alcohol, *n*-butyl alcohol, acetic acid, ethyl acetate, methyl ethyl ketone, or nitrobenzene [Found : C, 94·5, 94·75; H, 5·25, 5·6; *M* (Rast), 300, 306. $C_{24}H_{16}$ requires C, 94·7; H, 5·3%; *M*, 304], but gave solvated forms in transparent rectangular prisms from the following solvents :

Solvent.	Analysis of solvate. C.	H.	Loss on heating.*	
C_6H_6	94·7, 94·5	5·5, 5·6	11·0% at 110°	$2C_{24}H_{16},C_6H_6$ requires C, 94·5; H, 5·5; loss, 11·1%.
CCl_4	77·2	4·4	—	$2C_{24}H_{16},CCl_4$ requires C, 77·2; H, 4·2%.
Dioxan	89·65	5·95	—	$2C_{24}H_{16},C_4H_8O_2$ requires C, 89·65; H, 5·75%.
C_5H_5N	—	—	11·5% at 150°	$2C_{24}H_{16},C_5H_5N$ requires loss, 11·5%.
$CHCl_3$	—	—	16·5% at 150°	$2C_{24}H_{16},CHCl_3$ requires loss, 16·4%.
$COMe_2$	—	—	8·65% at 150°	$2C_{24}H_{16},C_3H_6O$ requires loss, 8·7%.

* Blank estimations were made to allow for pronounced sublimation of tetraphenylene.

x-*Bromotetraphenylene*.—Tetraphenylene (0·6 g.) was mixed with carbon tetrachloride (20 c.c.), bromine (0·48 g.) in carbon tetrachloride (10 c.c.) added, together with a little powdered iron, and the mixture heated till bromine vapour had disappeared. After filtration and evaporation, the residue was boiled in ethyl acetate with active carbon, and the solution filtered and treated with absolute alcohol; a white powder (0·78 g.), m. p. 130—140°, separated. A long series of crystallisations from ethyl acetate–ethyl alcohol gave x-*bromotetraphenylene*, m. p. 182°, free from tetraphenylene (Found : C, 75·5; H, 4·1. $C_{24}H_{15}Br$ requires C, 75·2; H, 3·9%).

Tetranitrotetraphenylene.—When tetraphenylene (0·4 g.; 1 mol.), dissolved in cold carbon tetrachloride (10 c.c.), was shaken with nitric acid (*d* 1·5, 0·4 g.; 4 mols.) and concentrated sulphuric acid (0·8 g.) in a closed tube, a semi-solid product immediately formed. When this had solidified, a little water was added, and the solid (0·7 g.) collected. It liquefied in contact with most solvents except alcohol and carbon tetrachloride, in both of which it was only very slightly soluble. It was taken up in benzene and filtered, the solvent allowed to evaporate until the material showed signs of separating, and carbon tetrachloride then added drop by drop with stirring. Repetition of this process, followed by trituration with successive portions of carbon tetrachloride, gave minute, light yellow prisms of *tetranitrotetraphenylene* which contained carbon tetrachloride of crystallisation. On heating, evolution of carbon tetrachloride was complete at 185°, and a thick viscous liquid formed at 195—197°. This set, on cooling, to a glassy mass which did not contain halogen and was reconverted into the above crystalline condition on treatment with carbon tetrachloride (Found : C, 47·2; H, 2·1; loss at 180—190°, 24·7. $C_{24}H_{12}O_8N_4,CCl_4$ requires C, 47·0; H, 1·9; loss, 24·1%).

UNIVERSITY OF CAPE TOWN, SOUTH AFRICA.

[*Received, March 25th*, 1943.]