27. *Benz*cyclo*octatetraenes. Part IV.* 1 : 2 : 3 : 4 : 5 : 6-*Tribenz*-$\Delta^{1:3:5:7}$-cyclo*octatetraene.*

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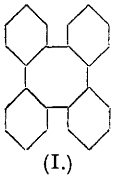
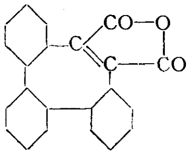
The oxidation of tetraphenylene (I) to 1 : 2 : 3 : 4 : 5 : 6-*tribenz*-$\Delta^{1:3:5:7}$-cyclo*octatetraene*-7 : 8-*dicarboxylic anhydride* (II) and the decarboxylation of this to yield 1 : 2 : 3 : 4 : 5 : 6-*tribenz*-$\Delta^{1:3:5:7}$-cyclo*octatetraene* (IV) are described. On further oxidation the anhydride yields o-*diphenylbenzene*-2′ : 2″-*dicarboxylic acid* (III), identical with a specimen prepared by the Ullmann reaction, the formulations of both tetraphenylene (I) and tribenz*cyclo*octatetraene (IV) thereby being established. The latter hydrocarbon, though stable to alkaline permanganate, adds bromine to yield 1 : 2 : 3 : 4 : 5 : 6-*tribenz*-$\Delta^{1:3:5:7}$-cyclo*octatetraene* 7 : 8-*dibromide*, and on catalytic hydrogenation gives the corresponding tribenz*cyclo*octatriene.

Evidence now available would seem to indicate that in the oxidative degradation of tetraphenylene (I) (Part III, J., 1943, 326) the benzene rings are more susceptible to attack than the exposed bonds of the eight-membered ring system. The hydrocarbon was stable to chromium trioxide in glacial acetic acid below 70°, and treatment with this reagent at higher temperatures yielded 1 : 2 : 3 : 4 : 5 : 6-*tribenz*-$\Delta^{1:3:5:7}$-cyclo*octatetraene*-7 : 8-*dicarboxylic anhydride* (II). The sodium salt of the acid was stable to permanganate. The anhydride itself was only oxidised by chromium trioxide in glacial acetic acid at temperatures near 100°, being converted into o-*diphenylbenzene*-2′ : 2″-*dicarboxylic acid* (III), identical with a specimen prepared in low yield by the action of copper on a mixture of ethyl 2-iododiphenyl-2′-carboxylate with a large excess of ethyl *o*-iodobenzoate.

The anhydride (II) was not decarboxylated when its quinoline solution was refluxed with copper bronze, but pyrolysis in the presence of barium hydroxide gave 1 : 2 : 3 : 4 : 5 : 6-*tribenz*-$\Delta^{1:3:5:7}$-cyclo*octatetraene* (IV), the overall yield from 2 : 2′-dibromodiphenyl being *ca.* 0·5%. Its formulation as (IV), and that of tetraphenylene as (I), follow from the isolation of the acid (III).


(I.)



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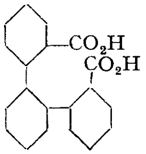

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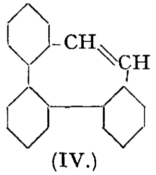

(IV.)

Tribenz*cyclo*octatetraene (IV), on treatment with bromine in boiling carbon tetrachloride, gave 1 : 2 : 3 : 4 : 5 : 6-*tribenz*-$\Delta^{1:3:5:7}$-cyclo*octatetraene* 7 : 8-*dibromide*. On hydrogenation in the presence of a reduced platinum oxide catalyst it yielded 1 : 2 : 3 : 4 : 5 : 6-tribenz-$\Delta^{1:3:5}$-*cyclo*octatriene.

An attempt to prepare 7-keto-1 : 2 : 3 : 4 : 5 : 6-tribenz-$\Delta^{1:3:5}$-*cyclo*octatriene was abandoned when it was found that ethyl *o*-iodophenylacetate, ethyl 2-iododiphenyl-2′-carboxylate, and copper gave only ethyl phenylacetate, phenylacetic acid (obtained also from *o*-iodophenylacetic ester alone) and 3 : 4-benzcoumarin.

Ethyl 2-iododiphenyl-2′-carboxylate was prepared by coupling *o*-di-iodobenzene with ethyl *o*-iodobenzoate by means of a restricted amount of copper, the yield being superior to that obtainable by oxidation of 2-iodo-2′-methyldiphenyl. An attempt to obtain the iodo-acid from the corresponding nitro-acid failed because the required amine was not obtainable by reduction.

α : o-*Di*-(o-*bromophenyl*)*cinnamic acid* was prepared by condensation of *o*-bromophenylacetic acid with 2-bromo-2′-aldehydodiphenyl by means of acetic anhydride, but its conversion into (IV) by cyclisation and decarboxylation was not attempted in view of the successful production of this hydrocarbon from tetraphenylene.

Experimental.

Action of Chromium Trioxide on Tetraphenylene.—The oxide (7·0 g.) in water (7 c.c.) and glacial acetic acid (50 c.c.) was added during 2 hours to a stirred solution of tetraphenylene (3·0 g.) in glacial acetic acid (200 c.c.) at 80—90°. After removal of most of the acetic acid by distillation, water was added, and the precipitated material collected and washed with water. Repeated extraction with hot 2N-sodium hydroxide left unchanged tetraphenylene (0·6 g.) On addition of concentrated hydrochloric acid to the alkaline extract, the white milky suspension first formed was rapidly converted into a crystalline mass. Recrystallisation from glacial acetic acid (charcoal) yielded deep yellow, plate-like prisms (0·6 g.) of 1 : 2 : 3 : 4 : 5 : 6-*tribenz*-$\Delta^{1:3:5:7}$-cyclo*octatraene*-7 : 8-*dicarboxylic anhydride* (II), m. p. 228—229° (Found : C, 81·4; H, 3·8; equiv., by solution in excess of aqueous alkali and back-titration, 165; equiv., by direct titration in alcohol, 280—300. $C_{22}H_{12}O_3$ requires C, 81·5; H, 3·7%; equiv., 162; *M*, 324). Fusion with resorcinol and phenol in the presence of concentrated sulphuric acid and subsequent addition of excess of aqueous alkali gave respectively a rose-red solution with a dull green fluorescence and a brown solution with a dull green fluorescence, changed to a greenish-yellow solution by addition of excess of acid. The anhydride was not attacked by boiling water, but reacted with boiling caustic alkali solution. The colourless sodium salt did not give a coloration with neutral ferric chloride, was insoluble in hot 5N-sodium hydroxide and in cold water, but dissolved in hot water and in hot 2N-sodium hydroxide solution. The anhydride was recovered unchanged both in quality and in quantity after its solution in water containing the minimum of sodium hydroxide had been refluxed for 6 hours with potassium permanganate (1·3 mols.).

The combined oxidation, precipitation, and recrystallisation mother-liquors from the isolation of the above anhydride, after standing for 2 months in an open container, had evaporated to about half their original bulk and a further quantity of material had separated. This was collected and extracted with hot 2N-sodium hydroxide, and the hot solution treated with excess of concentrated hydrochloric acid. Recrystallisation from glacial acetic acid (charcoal) gave colourless prisms (0·1 g.), m. p. 262·5—263·5°, of *o*-diphenylbenzene-2′ : 2″-dicarboxylic acid (III) containing acetic acid of crystallisation, identical (mixed m. p.) with the material prepared as described below. The same acid, contaminated with other acid materials, was obtained in low yield when the anhydride (II) was treated with chromium trioxide (2·7 mols.) in boiling glacial acetic acid, more than half the anhydride being recovered unchanged.

2-*Nitrodiphenyl*-2′-*carboxylic Acid*.—This was prepared by Sadler and Powell's method (*J. Amer. Chem. Soc.*, 1934, **56**, 2652) except that by using 1·6 mols. of *o*-iodonitrobenzene ethyl diphenate was not formed and the yield of 2-nitrodiphenyl-2′-carboxylic acid was increased to 68%. The reduction of the nitro-acid by means of ferrous sulphate and aqueous ammonia or barium hydroxide (cf. Pschorr, *Ber.*, 1906, **39**, 3109; Neber, *ibid.*, 1922, **55**, 834) did not yield an alkali-soluble product.

2′-*Nitro*-2-*methyldiphenyl*.—Sadler and Powell's method (*loc. cit.*) was improved by using 1·75 mols. of *o*-iodonitrobenzene, and fractionating the products through a short efficient column. Only 2′-nitro-2-methyldiphenyl (37%), b. p. 143°/4 mm., and 2 : 2′-dinitrodiphenyl, b. p. 194°/4 mm., were then produced.

2′-*Iodo*-2-*methyldiphenyl*.—The nitro-compound was reduced with tin and hydrochloric acid, and the amine, isolated by extraction with carbon tetrachloride, distilled. Yield 83%, b. p. 127—128°/4 mm. Diazotisation and reaction with potassium iodide gave 2′-iodo-2-methyldiphenyl (63%), b. p. 135—138°/4 mm. (cf. Mascarelli and Gatti, *Atti R. Accad. Lincei*, 1932, **15**, 89).

Oxidation of 2′-*Iodo*-2-*methyldiphenyl*.—This compound is apparently much less stable to either permanganate or chromium trioxide than either 4- or 2-bromo-4′-methyldiphenyl (Gomberg and Pernert, *J. Amer. Chem. Soc.*, 1926, **48**, 1378), since treatment with permanganate resulted in extensive oxidation of the nucleus, and chromium trioxide under the conditions described by the above authors gave only a 23% yield of 2-iododiphenyl-2′-carboxylic acid. It had m. p. 149—150° after crystallisation from petroleum (b. p. 120—130°) or glacial acetic acid, and was identical (mixed m. p.) with the material prepared as described below (Found : equiv., 322. $C_{13}H_9O_2I$ requires equiv., 324).

o-*Di-iodobenzene*.—Yields of not more than 100 g. of *o*-iodoaniline were obtainable from *o*-iodonitrobenzene when the quantities and conditions given by Baeyer (*Ber.*, 1905, **38**, 2761) were used. *o*-Iodoaniline (125 g.) was warmed with concentrated hydrochloric acid (150 c.c.) and water (200 c.c.), and the solution cooled rapidly and diazotised below 5° with sodium nitrite (46 g.) in water (100 c.c.). A layer of ether was added to the diazo-solution, and then cautiously at 0° a solution of potassium iodide (120 g.) in water (200 c.c.). In some experiments dangerous explosions occurred in the copious froth produced. After being warmed gradually to 60°, the product was separated, taken up in ether, and washed with alkali and thiosulphate. Distillation gave di-iodobenzene (134 g., 37%), b. p. 109°/3 mm., 143°/13 mm.

Ethyl 2-*Iododiphenyl*-2′-*carboxylate*.—*o*-Di-iodobenzene (50 g., 2 mols.) and ethyl *o*-iodobenzoate (20 g., 1 mol.) were heated in a metal-bath at 290—300°, and copper bronze (15 g.) added in portions with stirring during 15 minutes so that the internal temperature remained at 280—285° and the vigour of the reaction did not subside. After a further 15 minutes' heating, the mixture was cooled and extracted with organic solvents, and the material obtained by evaporating the solvents distilled in a vacuum. The condensation products, b. p. 160—175°/3 mm., were refluxed with potassium hydroxide (15 g.) in alcohol for 2 hours. After removal of the alcohol by distillation, neutral materials were extracted with ether, and 2-iododiphenyl-2′-carboxylic acid (8·5 g.) precipitated by addition of acetic acid. Recrystallisation (charcoal) from petroleum (b. p. 120—130°) or aqueous acetic acid gave small colourless prisms, m. p. 149—150°. Refluxing the acid for 4 hours with alcohol containing dry hydrogen chloride gave a 90% yield of ethyl 2-iododiphenyl-2′-carboxylate as a viscous oil, b. p. 168—169°/3 mm. Further acidification with mineral acid of the original mother-liquor from which the above acid had been obtained gave diphenic acid (7·5 g.), and evaporation of the above ethereal extract yielded 2 : 2′-di-iododiphenyl (3 g.), which crystallised from alcohol in colourless, flat prisms of hexagonal outline, m. p. 109°.

Reaction between Ethyl 2-*Iododiphenyl*-2′-*carboxylate, Ethyl* o-*Iodobenzoate, and Copper Bronze*.—Ethyl 2-iododiphenyl-2′-carboxylate (5 g., 1 mol.) and ethyl *o*-iodobenzoate (20 g., 5 mols.) were heated in a metal-bath at 280°, and copper bronze (10 g.) added in small portions with stirring. After being finally heated at 320° for 10 minutes, the mixture was cooled and extracted with benzene. Distillation through a short efficient column gave low-boiling materials (2 g.), ethyl diphenate (11·8 g.), b. p. 157°/0·5 mm., 173°/3 mm., and a viscous oil (1·8 g.), b. p. 180—200°/1 mm. The oil was refluxed for 3 hours with potassium hydroxide (2 g.) in alcohol. After removal of the alcohol, neutral materials were extracted with ether, and hydrochloric acid added. Recrystallisation from acetic acid of the material thus precipitated gave colourless prisms, containing acetic acid of crystallisation, of o-*diphenylbenzene*-2′ : 2″-*dicarboxylic acid* (III) (0·5 g.), m. p. 262·5—263·5°. Solvent of crystallisation was readily lost at 150°, the crystalline form changing to colourless needles (Found for material dried by suction : loss, 26·5. $C_{20}H_{14}O_4,2C_2H_4O_2$ requires loss, 27·4%. Found for material previously heated for 1 hour at 150° : C, 75·5; H, 4·6; equiv., 157. $C_{20}H_{14}O_4$ requires C, 75·4; H, 4·4%; equiv., 159). The acid readily sublimed above 200°. Its sodium salt was soluble in hot, but insoluble in cold, 2N-sodium hydroxide. Its barium salt formed colourless needles insoluble in alcohol.

1 : 2 : 3 : 4 : 5 : 6-*Tribenz*-$\Delta^{1:3:5:7}$-cyclo*octatetraene* (IV).—An intimate mixture of tribenz*cyclo*octatetraene-dicarboxylic anhydride (II) (0·5 g.), anhydrous barium hydroxide (1·5 g.), and copper bronze (1·5 g.) was heated (metal-bath) in a 3 c.c. distilling flask. Reaction began at about 300°, and as soon as it was complete, the pressure was reduced to 2 mm. 1 : 2 : 3 : 4 : 5 : 6-*Tribenz*-$\Delta^{1:3:5:7}$-cyclo*octatetraene*, which sublimed into the neck of the flask, was scraped out, taken up in the minimum quantity of ethyl acetate, and boiled with active charcoal, and the filtered solution diluted with alcohol. Further recrystallisation in this manner gave colourless elongated prisms (0·15 g.), m. p. 138·5—139° (Found : C, 94·45; H, 5·7. $C_{20}H_{14}$ requires C, 94·45; H, 5·55%). The hydrocarbon had a fairly high solubility in most organic solvents. It did not separate with solvent of crystallisation from benzene or carbon tetrachloride and did

not form a picrate. It (0·05 g.) was stable to potassium permanganate (0·09 g.) in acetone, being recovered unchanged in quantity and quality upon evaporation of the acetone after 5 hours' refluxing. No acidic material was produced.

*Action of Bromine on Tribenz*cyclo*octatetraene* (IV).—The hydrocarbon (0·03 g.) in carbon tetrachloride (1 c.c.) was treated with bromine (0·02 g., 1 mol.) in carbon tetrachloride (1 c.c.). Addition occurred rapidly at the b. p. of the mixture, and evaporation, followed by recrystallisation from alcohol, gave light yellow prisms (0·03 g.), m. p. 155—156°, of 1 : 2 : 3 : 4 : 5 : 6-*tribenz*-$\Delta^{1:3:5:7}$-cyclo*octatetraene* 7 : 8-*dibromide* (Found : C, 58·0; H, 3·4. $C_{20}H_{14}Br_2$ requires C, 58·0; H, 3·4%) (micro-analysis by courtesy of Dr. O. G. Backeberg).

*Catalytic Hydrogenation of Tribenz*cyclo*octatetraene* (IV).—An alcoholic solution of the hydrocarbon (0·0460 g.) was treated with hydrogen in the presence of a reduced platinum oxide catalyst. After a 3-minute induction period, reduction was complete in 50 minutes (Found : hydrogen absorbed, 4·4 c.c. Calc. for 1 mol., 4·3 c.c.). Filtration, and evaporation of the alcohol, followed by recrystallisation from the same solvent, gave colourless prisms of 1 : 2 : 3 : 4 : 5 : 6-tribenz-$\Delta^{1:3:5:7}$-*cyclo*octatriene, m. p. 111—113°.

Reaction between Ethyl 2-Iododiphenyl-2′-carboxylate, Ethyl o-*Iodophenylacetate, and Copper Bronze.*—Ethyl 2-iododiphenyl-2′-carboxylate (10 g., 1 mol.), ethyl *o*-iodophenylacetate (24 g., 3 mols.), and copper bronze (20 g.) were heated in a sealed tube for 3 hours at 290—295°, great pressure being developed. Extraction of the mixture with benzene or ether, followed by distillation, gave low-boiling materials (3 g.), phenylacetic acid (3·4 g.), a product (2·9 g.), b. p. 180—200°/3 mm., and a resinous residue which decomposed on further distillation. The material of b. p. 180—200°/3 mm. was refluxed for 2 hours with potassium hydroxide (3 g.) in alcohol. Removal of the alcohol by distillation, extraction of neutral materials with ether, and acidification of the alkaline solution gave 3 : 4-benzcoumarin (1·8 g.), m. p. 92·5° after crystallisation from aqueous alcohol (Graebe and Schestakow, *Annalen*, 1894, **284**, 317) (Found : C, 79·7; H, 4·1; equiv., by solution in excess of aqueous alkali and back-titration, 200. Calc. for $C_{13}H_8O_2$: C, 79·6; H, 4·1%; equiv., 196).

Ethyl o-*bromophenylacetate*, prepared from the acid, had b. p. 114°/4 mm. and m. p. 35—36° after crystallisation from aqueous acetic acid (Found : C, 49·6; H, 4·6. $C_{10}H_{11}O_2Br$ requires C, 49·4; H, 4·5%).

2-*Bromo-2′-aldehydodiphenyl* (cf. Smith and Nichols, *J. Org. Chem.*, 1941, **6**, 489).—2 : 2′-Dibromodiphenyl (7·8 g.), magnesium (0·85 g.), and ethyl bromide (0·75 c.c.) in ether (50 c.c.) were refluxed for 36 hours, ethyl orthoformate (redistilled, 5·8 c.c.) in ether (10 c.c.) then added dropwise at room temperature, and the mixture refluxed for 5 hours. After removal of the ether at 60° the residue was heated for a short time at 100°, and ice (30 g.) and concentrated hydrochloric acid (17 c.c.) added. After being heated for 30 minutes on the water-bath, the mixture was extracted with ether, this and propaldehyde removed by distillation, and the residue fractionated. 2-Bromo-2′-aldehydodiphenyl, contaminated with dibromodiphenyl, was collected at 152—157°/7 mm. (4 g.). Its 2 : 4-*dinitrophenylhydrazone* formed orange-yellow plates, m. p. 217° (sealed tube), from xylene (Found : C, 51·5; H, 3·1. $C_{19}H_{13}O_4N_4Br$ requires C, 51·7; H, 3·0%). The *semicarbazone* crystallised from alcohol in colourless plates, m. p. 198° (sealed tube) (Found : C, 52·9; H, 3·8. $C_{14}H_{12}ON_3Br$ requires C, 52·8; H, 3·8%). The impure aldehyde was used in the next stage, since its purification through the bisulphite compound involved loss.

α : o-*Di*-(o-*bromophenyl*)*cinnamic Acid.*—The impure aldehyde (10 g.), sodium *o*-bromophenylacetate (9·1 g.), and acetic anhydride (21·6 c.c.) were heated overnight in an oil-bath at 150—160°. After boiling with water, the mixture was extracted with ether. The dark oil obtained on washing the ethereal extract with sodium hydroxide gave, on treatment with hydrochloric acid, α : o-*di*-(o-*bromophenyl*)*cinnamic acid* (3 g.), which formed colourless prisms, m. p. 186°, from benzene–light petroleum (Found : C, 55·3; H, 3·2. $C_{21}H_{14}O_2Br_2$ requires C, 55·0; H, 3·1%).

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