84. *Benz*cyclo*octatetraenes. Part I.*

By W. S. Rapson and R. G. Shuttleworth.

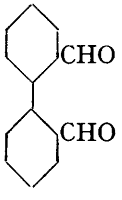
Preliminary attempts to prepare benz*cyclo*octatetraenes, in particular, 1 : 2 : 3 : 4-dibenz-$\Delta^{1:3:5:7}$-*cyclo*octatetraene (II) derivatives by direct synthesis, and 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-tetrabenz-$\Delta^{1:3:5:7}$-*cyclo*octatetraene or tetraphenylene, have not been successful, and it seems as if the preparation of (II) must be carried out from the corresponding dibenz*cyclo*octadiene. A beginning has been made along these lines.

The possibility has been discussed (Hurd and Drake, *J. Amer. Chem. Soc.*, 1939, **61**, 1943) that the *cyclo*octatetraene prepared by Willstätter and his co-workers (*Ber.*, 1913, **46**, 517; 1911, **44**, 3423, and earlier papers) was not $\Delta^{1:3:5:7}$-*cyclo*octatetraene, and there are indications (Vincent, Thompson, and Smith, *J. Org. Chem.*, 1939, **3**, 603; Kohler, Tishler, Potter, and Thompson, *J. Amer. Chem. Soc.*, 1939, **61**, 1057; Steadman, *ibid.*, 1940, **62**, 1606) that investigations are in progress which have as one of their aims its synthesis and re-examination.

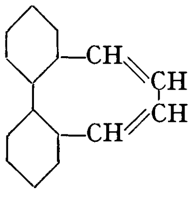
Our aim has been to synthesise benz-$\Delta^{1:3:5:7}$-*cyclo*octatetraenes, since these might be easier to produce and more stable than *cyclo*octatetraene itself. The publications of Wawzonek (*J. Amer. Chem. Soc.*, 1940, **62**, 745) and of Fry and Fieser (*ibid.*, p. 3489) lead us to record our as yet incomplete observations.

Because of the analogy between 2 : 2′-disubstituted diphenyls and *o*-disubstituted benzenes (Kenner, J., 1911, **99**, 2101; 1913, **103**, 613) our first experiments were attempts to prepare 1 : 2 : 3 : 4-dibenz-$\Delta^{1:3:5:7}$-*cyclo*octatetraene (II) by condensation of diphenyl-2 : 2′-dialdehyde (I) with succinic acid (cf. Kuhn and Winterstein, *Helv. Chim. Acta*, 1928,

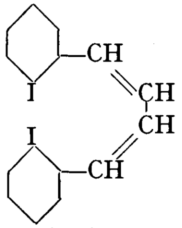
11, 87) or ethyl succinate (cf. Cordier, *Ann. Chim.*, 1931, **15**, 228). These experiments failed. *o*-Iodocinnamaldehyde was then condensed with *o*-iodophenylacetic acid by Kuhn and Winterstein's method (*loc. cit.*), 1 : 4-*bis*-o-*iodophenyl*-$\Delta^{1:3}$-*butadiene* (III) being obtained in two isomeric forms. The conversion of (III) into (II) has not, however, been effected. Reaction with copper-bronze alone or in high concentrations in quinoline gave intermolecular condensation products, and at lower concentrations in quinoline 1 : 4-diphenyl-$\Delta^{1:3}$-butadiene was the only product of low molecular weight isolated.



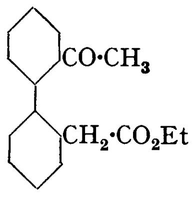
(I.)



(II.)



(III.)



(IV.)

Other experiments had as their objective the compound (IV), from which the desired ring system should be accessible. One attempt to produce (IV) failed because *o*-iodoacetophenone could not be condensed with ethyl *o*-iodophenylacetate by the Ullmann reaction, and another was abandoned when it was found that the arylation of ethyl phenylacetate by the Gomberg–Hey method was not feasible because of the reactivity of the methylene group.

The reaction of sodium with 2 : 2′-dibromodiphenyl has been described by Dobbie, Fox, and Gauge (J., 1911, **99**, 683; 1913, **103**, 36) as yielding diphenylene in almost quantitative yield. Like Schwechten (*Ber.*, 1932, **65**, 1606), and Mascarelli, Gatti, and Longo (*Gazzetta*, 1933, **63**, 661), we have been unable to reproduce this result; the only simple product we observed was diphenyl, the yield of which increased rapidly as the amount of diluent (ether) used in the reaction was increased. The coupling technique of Krizewsky and Turner (J., 1919, **115**, 560) has been applied to 2 : 2′-dibromodiphenyl without success. It led to a small amount of diphenyl, mixed with a trace of another steam-volatile halogen-free substance, m. p. 107°, which was separated as its picrate but was not identified.

EXPERIMENTAL.

2′-Iodobenzanilide.—*o*-Iodobenzoyl chloride (158 g.) in dry benzene (600 c.c.) was cooled in ice and treated slowly with aniline (120 g.) in carbon tetrachloride (250 c.c.). The precipitated *anilide* was filtered off (a further small quantity was obtained by evaporating the washed and dried mother-liquor), washed with dilute hydrochloric acid and water, and crystallised from aqueous alcohol or toluene, separating in colourless needles (185 g.), m. p. 142·5°, slightly soluble in ether (Found : C, 48·6; H, 3·0. $C_{13}H_{10}ONI$ requires C, 48·3; H, 3·1%).

o-*Iodobenzaldehyde.*—The above anilide (100 g.), suspended in dry toluene (100 c.c.), was heated with phosphorus pentachloride (65 g.) on the water-bath till hydrogen chloride was no longer evolved. The residue obtained by removal of the toluene and phosphorus oxychloride under reduced pressure on the water-bath was dissolved in the minimum quantity of ether and treated under reflux with anhydrous stannous chloride (120 g.) in dry ethereal hydrogen chloride (200 c.c.) with efficient ice-cooling (much heat was developed and resinous material formed if the reaction was not carefully controlled). After 2 hours' standing with intermittent shaking, the ether was decanted, and the orange-yellow crystals added slowly with stirring to water and ether. The aldehyde was removed in steam [resinous material and anilide (15 g.) remained in the flask], taken up in ether, washed with aqueous sodium carbonate and water, and recovered from the dried solution; it had b. p. 129°/14 mm. (55 g.) and solidified on cooling (cf. Stuart, J., 1888, **53**, 141; Willgerodt and Rieke, *Ber.*, 1905, **38**, 1479).

o-*Iodobenzaldehyde Diethylacetal.*—*o*-Iodobenzaldehyde (12 g.), orthoformic ester (8 g.), and absolute alcohol (10 c.c.) were treated with dry powdered ammonium chloride (0·1 g.) and refluxed for 1·5 hours. After removal of the alcohol by distillation, the product was extracted in ether and washed with water containing a few drops of aqueous ammonia. After drying over potassium carbonate, the ether was removed, and the diethylacetal (12 g.) obtained by distillation as a light yellow oil, b. p. 159°/23 mm., $n_D^{18°}$ 1·5428. When boiled with dilute hydrochloric acid, it was readily reconverted into the aldehyde. Treatment with copper-bronze in the Ullmann reaction did not give a homogeneous product, much resinification being apparent, so, in spite of the adverse experience of Mayer (*Ber.*, 1911, **44**, 2304), the direct reaction of *o*-iodobenzaldehyde with copper was explored.

Diphenyl-2 : 2'-dialdehyde.—Equal weights of *o*-iodobenzaldehyde and copper-bronze, in an inert atmosphere, were warmed slowly to 200—220°. A violent reaction set in and had to be controlled in order to avoid extensive resinification. Extraction of the reaction mass with ether, followed by distillation of the extracts, gave benzaldehyde (12%) (identified by the formation of its semicarbazone, and by its oxidation to benzoic acid), and diphenyl-2 : 2'-dialdehyde, b. p. 179°/2 mm., m. p. 63° (yield, 70%).

o-*Iodophenylacetic Acid.*—The conditions given by Raum (*Ber.*, 1894, **27**, 3233) for the preparation of *o*-iodobenzyl bromide required modification as follows: A flask filled almost completely with *o*-iodotoluene (153 g.) was heated at 220° in direct sunlight, and bromine (56 g., half the theoretical quantity) added at a constant rate (*ca.* 0·5 hour) on to the surface of the liquid. An efficient condenser was used. Distillation under reduced pressure gave *o*-iodotoluene (40 g. after purification) contaminated with iodine, and *o*-iodobenzyl bromide (67·5 g., 65%), b. p. 125°/4 mm., which solidified on cooling. This compound can be handled with reasonable facility if it is kept in closed flasks away from water vapour. An attempt to prepare the corresponding chloro-compound by the use of sulphuryl chloride failed, iodine being produced (cf. Kharasch and Brown, *J. Amer. Chem. Soc.*, 1939, **61**, 2142).

The bromide (112 g.), heated under reflux for 3 hours on the water-bath with potassium cyanide (75 g.) in alcohol, gave *o*-iodophenylacetonitrile (73·5 g., 80%), which was isolated by removal of the alcohol, ether extraction, and distillation, b. p. 140°/4 mm. The nitrile (72 g.) was heated for 2 hours at 170° with sulphuric acid (150 c.c.) and water (150 c.c.). Dilution with water and extraction with ether, followed by washing with alkali and addition of dilute hydrochloric acid, gave *o*-iodophenylacetic acid in 80% yield, m. p. 114° (Dippy and Lewis, J., 1936, 646). Refluxed for 12 hours with alcoholic sulphuric acid, it gave the *ethyl* ester, b. p. 128°/3 mm., which formed colourless needles, m. p. 42—43°, from dilute acetic acid (Found: C, 41·3; H, 3·7. $C_{10}H_{11}O_2I$ requires C, 41·4; H, 3·8%).

o-*Iodocinnamaldehyde.*—*o*-Iodobenzaldehyde (90 g.) in dry alcohol (100 c.c.) was added to a solution of acetaldehyde (33 g.; 2 mols.) in alcohol (150 c.c.). Dry diethylamine (1·5 c.c.) in alcohol (50 c.c.) was added to the ice-cold solution, and the whole left at room temperature (18°) for 3 days. After being just acidified with 2N-sulphuric acid, the solution was evaporated to about 125 c.c. and extracted with ether, and the extracts washed with water. The product was separated into two fractions boiling below and above 140°/3 mm. Redistillation of these fractions gave *o*-iodobenzaldehyde (50 g.), b. p. 102°/3 mm., and *o*-iodocinnamaldehyde (30 g.), b. p. 155°/3 mm., which crystallised from light petroleum in prisms, m. p. 78—79°. Oxidised with ammoniacal silver oxide, it gave *o*-iodocinnamic acid, m. p. 216—217° (Weitzenbock, *Monatsh.*, 1913, **34**, 193).

1 : 4-*Bis*-o-*iodophenyl*-$\Delta^{1:3}$-*butadiene* (III).—*o*-Iodophenylacetic acid (18·3 g.), *o*-iodocinnamaldehyde (18 g.), lead oxide (7·8 g.), and acetic anhydride (10 c.c.) were heated under reflux at 150—160° for 5 hours (cf. Kuhn and Winterstein, *loc. cit.*). The liquid was left overnight in a beaker, the almost solid mass then diluted with a little cold acetic acid, and the liquid filtered. The product (14 g.) was washed with acetic acid (5 c.c.) and extracted with boiling acetic acid (50 c.c.); the material which crystallised on cooling was removed, and the solvent used again, until four or five lots of crystals had been collected. The undissolved material (10 g.) separated as an oil from pyridine, but crystallisation from dioxan or a large volume of xylene gave small colourless rhombohedra, m. p. 249—250° (Found: C, 42·0; H, 2·6. $C_{16}H_{12}I_2$ requires C, 42·0; H, 2·6%). The material obtained from the acetic acid extractions was taken up in benzene, filtered, and caused to crystallise by the addition of about 20 c.c. of absolute alcohol, separating in yellow needles (2·5 g.), m. p. 180—181°, which, if left in contact with the mother-liquor, formed rhombohedra of the same m. p. It was much more soluble in organic solvents than the other product of the reaction and was isomeric with it (Found: C, 42·2; H, 2·6%).

Attempts to cyclise 1 : 4-*Bis*-o-*iodophenyl*-$\Delta^{1:3}$-*butadiene.*—(1) The isomer of m. p. 249—250° (3 g.) was dissolved in quinoline (5 c.c.) and heated until the latter was just refluxing. Copper bronze (3 g.) was then added in small portions, and the heating continued for 15 minutes. After thorough extraction with benzene, the quinoline was removed by washing with dilute hydrochloric acid, and the benzene evaporated. The product was mainly resinous, but repeated treatment with small quantities of benzene left a small amount of a crystalline *substance*, m. p. 200—202° (Found : C, 56·3; H, 2·9. $C_{32}H_{24}I_2$ requires C, 58·0; H, 3·6%).

(2) In the absence of quinoline and with a bath temperature of 280°, the same product was obtained, contaminated with a greater amount of resinous material.

(3) The use of 53 c.c. of quinoline led to a much milder reaction. From the viscous reddish product, light petroleum extracted *trans*-1 : 4-diphenyl-$\Delta^{1:3}$-butadiene, identified by m. p. and mixed m. p. (yield, 17%).

(4) With the isomer of lower m. p. reaction could not be initiated in quinoline solution. Treated with copper-bronze in an inert atmosphere at 300° for 15 minutes, however, this isomer yielded a viscous product, which could be partially purified by repeated precipitation from ethyl acetate with dry ethyl alcohol and was finally obtained with m. p. *ca.* 200° (Found : C, 69·0; H, 4·1. $C_{48}H_{36}I_2$ requires C, 66·5; H, 4·2%).

o-*Iodoacetophenone*.—Sodium (12·5 g.) was added slowly to a cooled solution of ethyl acetoacetate (76 g.) in dry ether (300 c.c.), followed after 12 hours by *o*-iodobenzoyl chloride (140 g.) in dry ether (150 c.c.); the mixture was refluxed for a short time. Filtration, followed by evaporation of the ether, left a dark brown condensation product. Hydrolysis of the product by dilute sulphuric acid (cf. Gevekoht, *Annalen*, 1883, **221**, 323) was not complete after 7 hours' heating, but yielded *o*-iodoacetophenone, b. p. 112°/4 mm., $n_D^{20°}$ 1·6180 (oxime, m. p. 130—132°; Auwers, Lechner, and Bundesmann, *Ber.*, 1925, **58**, 50), and ethyl *o*-iodobenzoate, b. p. 122°/4 mm., $n_D^{21°}$ 1·5850, in approximately equimolecular proportion (the formation of the latter is evidently due to the presence of an *O*-*o*-iodobenzoyl derivative in the condensation product). These substances could be separated either by conversion of the ester into *o*-iodobenzoic acid through saponification with dilute aqueous alcoholic alkali, or by treatment with hydroxylamine or semicarbazide and allowing sufficient time for complete formation to take place of the oxime or the *semicarbazone*, which separated from aqueous alcohol in colourless needles, m. p. 178·5—179·5° (Found : C, 35·9; H, 3·3. $C_9H_{10}ON_3I$ requires C, 35·7; H, 3·3%).

The Action of Sodium on 2 : 2′-*Dibromodiphenyl*.—(1) Sodium (1·5 g.) and 2 : 2′-dibromodiphenyl (3 g.) were heated for 5 hours (protected from moisture), sublimed material being periodically shaken back into the flask. From the dark mass, ether extracted a brown viscous product, from which the only homogeneous substance isolable was a trace of diphenyl, separated by steam-distillation.

(2) Sodium (15 g.) was sliced under xylene, washed several times with dry ether, and refluxed with dry ether (250 c.c.) for 24 hours. Dry 2 : 2′-dibromodiphenyl (10 g.) was then added, and the mixture refluxed for 10 days (protection from moisture). The ethereal solution was filtered from a high-melting substance containing halogen (cf. Dobbie, Fox, and Gauge, *loc. cit.*) and evaporated, and the residue (4·5 g.) steam-distilled. The product (2 g.) was identified as diphenyl.

(3) Similar experiments to the above, but with smaller amounts of ether as diluent, gave reduced yields of diphenyl, products of high molecular weight predominating.

(4) 2 : 2′-Dibromodiphenyl (6 g.) in dry benzene (30 c.c.), after being refluxed for 4 days with " molecular " sodium, was recovered unchanged.

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