395. *Derivatives of* 4-cyclo*Hexyldiphenyl. Part II.*

By F. Robert Basford.

Attempts to obtain a monobromo-derivative of 4-*cyclo*hexyldiphenyl by the action of one molecule of bromine on the hydrocarbon in carbon disulphide were without success, the substance being mainly unchanged. In presence of excess of the halogen, however, three atoms of bromine entered the *cyclo*hexyl nucleus and a fourth went into the 4'-position of the diphenylyl radical, producing *4'-bromo-4-(tribromo*cyclo*hexyl)diphenyl.* This compound slowly undergoes thermal decomposition above its melting point with loss of three molecules of hydrogen bromide, giving *p*'-bromo-1 : 4-diphenylbenzene (cf. Braun, Irmisch, and Nelles, *Ber.*, 1933, **66**, 1481). This reaction is parallel to the formation of 1 : 4-diphenylbenzene by the action of bromine at 160° on 1 : 4-di*cyclo*hexylbenzene (Braun, *Ber.*, 1927, **60**, 1180), the initial stage of which is presumed to be the introduction of three atoms of bromine into each of the *cyclo*hexyl nuclei, with their subsequent elimination in the form of hydrogen bromide. In this case, however, the isolation of an intermediate compound is not reported. Hydrogen bromide may also be removed from 4'-bromo-4-(tribromo*cyclo*hexyl)diphenyl with alcoholic potassium hydroxide.

Bromination of 4-*cyclo*hexyldiphenyl in acetic acid solution in presence of anhydrous sodium acetate gives *4'-bromo-4-*cyclo*hexyldiphenyl* in small yield, but the most convenient method for its preparation is the action of *cyclo*hexyl bromide on 4-bromodiphenyl in presence of aluminium chloride (cf. Mayes and Turner, J., 1929, 500). The bromo-derivative is oxidised by sodium dichromate and sulphuric acid to *p*-bromobenzoic acid. It is converted by bromine at 160° into *p*'-bromo-1 : 4-diphenylbenzene, but its dehydrogenation with selenium at 330° did not give this expected product; instead, bromine also was removed and 1 : 4-diphenylbenzene obtained. The bromo-derivative did not form a Grignard compound.

Bromination of 4'-bromo-4-*cyclo*hexyldiphenyl with an excess of bromine in carbon disulphide also gave 4'-bromo-4-(tribromo*cyclo*hexyl)diphenyl.

Experimental.

*4'-Bromo-4-*cyclo*hexyldiphenyl.*—(a) 4-*cyclo*Hexyldiphenyl (0·7 g.) in carbon disulphide (10 c.c.) was shaken with 5 c.c. of a solution of bromine (1 c.c.) in carbon disulphide (30 c.c.) and after 1 hour the solvent was distilled off. The residue, recrystallised from alcohol, gave unchanged 4-*cyclo*hexyldiphenyl, m. p. and mixed m. p. 74·5° (this vol., p. 1593).

(b) To a boiling solution of 4-*cyclo*hexyldiphenyl (1 g.) in acetic acid (8 c.c.) containing anhydrous sodium acetate (1 g.), bromine (0·8 g. in 2 c.c. of glacial acetic acid) was added, and the mixture was kept at 120° until the colour of the bromine had disappeared (10 minutes). The product, precipitated by water after recrystallisation from alcohol, gave some unchanged hydrocarbon and also about 0·25 g. of a substance, m. p. 154°, which was stable at 200°.

(c) 4-Bromodiphenyl (10 g.) (Schultz, *Annalen*, 1874, **174**, 201) and *cyclo*hexyl bromide (8 g.) were dissolved in carbon disulphide (20 c.c.) and anhydrous aluminium chloride (0·5 g.) was added to initiate the reaction, which was allowed to proceed at 18° during 6 hours and was completed during ¼ hour at 40°. The product, after decomposition with dilute hydrochloric acid, was steam-distilled to remove the solvent and the excess of *cyclo*hexyl bromide, and the residue (14 g.), which became solid on cooling, was filtered off, dried, and distilled at 7 mm. The fraction, b. p. 230—280°, gave, after repeated crystallisation from alcohol–acetone, 5 g. of pure *4'-bromo-4-*cyclo*hexyldiphenyl* in transparent plates having a faint odour of aniseed, m. p., alone or mixed with the product of (b), 154° (Found: Br, 25·9. $C_{18}H_{19}Br$ requires Br, 25·5%).

*Oxidation of 4'-Bromo-4-*cyclo*hexyldiphenyl to* p-*Bromobenzoic Acid.*—The bromo-derivative (1·5 g.) was stirred into a solution of sodium dichromate (10 g.) in water (20 c.c.) and glacial acetic acid (20 c.c.). Concentrated sulphuric acid (25 c.c.) was run in fairly rapidly until oxidation set in, and then more slowly so that the reaction proceeded smoothly. The oxidation was completed at 95° during 90 minutes and the acid was isolated and purified by precipitation with water, dissolution in aqueous sodium carbonate and reprecipitation with hydrochloric acid. Sublimation of the product gave crystalline plates, m. p. and mixed m. p. with authentic *p*-bromobenzoic acid (Hübner, Ohly, and Philipp, *Annalen*, 1867, **143**, 247) 248°.

*Dehydrogenation of 4′-Bromo-4-*cyclo*hexyldiphenyl.*—(a) To 4′-bromo-4-*cyclo*hexyldiphenyl (0 315 g; 1 mol.) at 160°, bromine (0·16 g.; 3 mols.) was added during ¼ hour; the temperature was kept at 200° during ¼ hour and the melt was then cooled, extracted with acetone, and recrystallised from alcohol, giving plates, m. p. 232° (corr.), of *p*′-bromo-1 : 4-diphenylbenzene, not depressed by an authentic specimen.

(b) 4′-Bromo-4-*cyclo*hexyldiphenyl (0·25 g.) and selenium (1 g.) were heated together at 330—360° during 30 minutes. The cooled melt was finely ground and extracted with chloroform; evaporation of the filtrate gave 0·18 g. of a crystalline product which, after recrystallisation from alcohol, had m. p. 213° (corr.), alone or mixed with 1 : 4-diphenylbenzene (Gerngross and Dunkel, *Ber.*, 1924, **57**, 739) (Found: C, 93·8; H, 6·2. Calc. for $C_{18}H_{14}$: C, 93·9; H, 6·1%).

*4′-Bromo-4-(tribromo*cyclo*hexyl)diphenyl.*—(a) 4-*cyclo*Hexyldiphenyl (1·5 g.) was dissolved in carbon disulphide (10 c.c.), and bromine added gradually at 18° during 24 hours until the solution was no longer decolorised. The excess of bromine was destroyed with dilute aqueous sodium carbonate and the product was extracted with ether; evaporation of the solvent left a residue (3·5 g.), which began to decompose on heating. It was therefore treated with hot acetone, from which crystals, m. p. 148°, were obtained on cooling (Found: Br, 56·0. $C_{18}H_{18}Br_4$ requires Br, 57·95%).

(b) To 4′-bromo-4-*cyclo*hexyldiphenyl (0·25 g.), dissolved in carbon disulphide (5 c.c.), were added 10 c.c. of a solution of bromine (1 g.) in carbon disulphide (20 c.c.): a small piece of iron wire was used as catalyst. The reaction was allowed to proceed during 2 hours in the cold and was completed at 50°. The product was extracted with ether in the presence of dilute aqueous sodium carbonate, and the ethereal solution was washed with water, dried with calcium chloride, and carefully evaporated, leaving a residue (0·5 g.), which separated from alcohol–acetone in crystals, m. p. and mixed m. p. with the product of (a) 148°.

*Decomposition of 4′-Bromo-4-(tribromo*cyclo*hexyl)diphenyl.*—(a) *Thermal decomposition.* When the tetrabromo-derivative was heated between watch glasses at 160—220°, evolution of hydrogen bromide gradually occurred, and the residue sublimed in feathery plates, m. p. 232° (corr.) (Found: Br, 25·8. Calc. for $C_{18}H_{13}Br$: Br, 25·9%), undepressed by authentic *p*′-bromo-1 : 4-diphenylbenzene (Olgiati, *Ber.*, 1894, **27**, 3394).

(b) *Alkali decomposition.* 4′-Bromo-4-(tribromo*cyclo*hexyl)diphenyl (0·1336 g.) was refluxed for several hours in an alcoholic solution of potassium hydroxide; crystals separated. The mixture was diluted with nitric acid and the residue was filtered off and recrystallised from alcohol, forming plates, m. p. 232°. The filtrate and washings were treated with silver nitrate in excess, and the excess was titrated with standard ammonium thiocyanate (Found: replaceable Br, 42·2. $C_{18}H_{16}Br_4$ requires replaceable Br, 43·5%).

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