297. *Derivatives of* 4-cyclo*Hexyldiphenyl. Part III.*

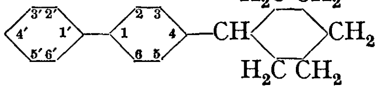
By F. Robert Basford.

Nitration of 4-*cyclo*hexyldiphenyl affords, according to the conditions used, either the 2- and the 4′-nitro-derivative, or a trinitro-compound. Both the mononitro-compounds give the corresponding amine on reduction, and the corresponding nitro-1 : 4-diphenylbenzene on dehydrogenation by means of bromine. 2-Nitro-1 : 4-diphenylbenzene has been reduced to the amine.

4 : 4′-Di*cyclo*hexyldiphenyl, on nitration in acetic acid solution, affords a dinitro-compound, which has been reduced to the corresponding diamine.

Among other compounds described are 4′-bromo- and 4′-*p*-nitrobenzoyl-4-*cyclo*hexyldiphenyl and 4-*cyclo*hexyldiphenyl-4′-carboxylyl chloride.

When 4-*cyclo*hexyldiphenyl (I) is nitrated in acetic acid solution, both homo- and heteronuclear nitration occur, just as in the case of 4-methyldiphenyl (Grieve and Hey, J., 1932, 1888). The 2- and the 4′-*nitro*-derivative are formed in the approximate ratio of 2 : 1, together with some 4-nitrodiphenyl and oily products. If the nitric acid is not diluted with acetic acid, a *trinitro*-derivative is formed.



(I.)

The constitution of the 2-nitro-4-*cyclo*hexyldiphenyl was proved by (a) oxidation with chromic acid to 2-nitrodiphenyl-4-carboxylic acid (Grieve and Hey, *loc. cit.*), (b) reduction with stannous chloride and hydrochloric acid or iron and hydrochloric acid to the corresponding *amine*, and (c) dehydrogenation with bromine at 180—200° to 2-*nitro*-1 : 4-*diphenylbenzene*. The 4′-nitro-derivative yielded a similar series of compounds, and in addition its constitution was proved by its conversion into 4′-bromo-4-*cyclo*hexyldiphenyl (J., 1936, 1780) through the *diazonium perbromide*, prepared from 4′-amino-4-*cyclo*hexyldiphenyl, characterised as its *hydrochloride*.

Nitration of 4 : 4′-di*cyclo*hexyldiphenyl in acetic acid solution gives a *dinitro*-compound, which is reduced with iron and hydrochloric acid to the corresponding *diamine*.

Other compounds obtained are mentioned in the foregoing summary.

EXPERIMENTAL.

2-*Nitro*-4-cyclo*hexyldiphenyl*.—4-*cyclo*Hexyldiphenyl (6 g.), dissolved in glacial acetic acid (12 c.c.), was nitrated with a mixture of 7 c.c. of nitric acid (*d* 1·488) and 3 c.c. of glacial acetic acid. The temperature, initially at 65°, rose rapidly when nitration set in, and cooling was necessary. The remaining acid was then run in, and the solution kept at 85° during 10 minutes; on cooling, 4·4 g. of crystalline material were deposited, m. p. 125—145°. Recrystallised from alcohol–acetone (6 : 1), this gave pale yellow needles (3 g.), m. p. 164·5° (sharp) (Found: N, 5·3. $C_{18}H_{19}O_2N$ requires N, 4·98%).

Oxidation of 2-*Nitro*-4-cyclo*hexyldiphenyl to* 2-*Nitrodiphenyl*-4-*carboxylic Acid*.—A solution of chromic anhydride (2·5 g.) in glacial acetic acid (25 c.c.) was added to 2-nitro-4-*cyclo*hexyldiphenyl (0·5 g.) dissolved in 15 c.c. of glacial acetic acid. The mixture was boiled during 1 hour and then diluted with water; the acid was extracted with ether and purified by dissolution in sodium carbonate solution and reprecipitation with hydrochloric acid. The product crystallised from alcohol in pale yellow needles, m. p. 191°, undepressed on admixture with authentic 2-nitrodiphenyl-4-carboxylic acid, kindly supplied by Dr. Hey, of Manchester University.

2-*Amino*-4-cyclo*hexyldiphenyl*.—(a) The nitro-compound was dissolved in hot alcohol, and the solution added to stannous chloride dissolved in concentrated hydrochloric acid. The stannichloride of the base separated, and the reaction was completed by warming the mixture until a clear solution resulted; this was treated with an excess of dilute alkali, and the free base extracted with ether. Evaporation of the ethereal solution left a product which recrystallised from aqueous alcohol in colourless plates, m. p. 102°.

(b) Iron filings and concentrated hydrochloric acid were added to a solution of the nitro-compound in alcohol. After the reaction was completed, most of the alcohol was distilled off, and the hydrochloride of the base separated from the cooled solution; it was filtered off, and washed with hydrochloric acid until free from all traces of ferric chloride. Colourless needles were obtained; the free *base*, liberated by suspending the hydrochloride in dilute ammonia, was recrystallised from aqueous alcohol; m. p. 102° (Found: N, 5·3. $C_{18}H_{21}N$ requires N, 5·58%).

The *acetyl* derivative was prepared by refluxing a toluene solution of the amine with acetic anhydride for 8 hours; the toluene was removed by steam-distillation, the solid product separated, and crystallised from dilute alcohol; colourless rhombohedral crystals were obtained, m. p. 116° (Found: N, 4·9. $C_{20}H_{23}ON$ requires N, 4·78%). The *benzoyl* derivative, prepared by the Schotten–Baumann method, crystallised from alcohol; m. p. 158° (Found: N, 3·9. $C_{25}H_{25}ON$ requires N, 3·94%).

2-*Nitro*-1 : 4-*diphenylbenzene*.—2-Nitro-4-*cyclo*hexyldiphenyl was melted at 165°, and bromine added during 15 minutes. The temperature was raised to 180° and maintained thereat during 15 minutes, and the reaction was completed by warming for a short time at 200°. The product was extracted with acetone, most of the material remaining undissolved; this crystallised from alcohol in almost colourless plates, m. p. 125° (Found: N, 5·1. $C_{18}H_{13}O_2N$ requires N, 5·09%).

2-*Amino*-1 : 4-*diphenylbenzene*.—A solution of the nitro-compound in alcohol was added gradually to stannous chloride dissolved in hydrochloric acid. The mixture was warmed until it formed a clear solution; dilute sodium hydroxide was added, and the base extracted with ether. Evaporation of the ethereal extract left a product which crystallised from alcohol as colourless plates, m. p. 169° (Found: N, 6·0. $C_{18}H_{15}N$ requires N, 5·71%). The *benzoyl* derivative, prepared in the usual way, crystallised from alcohol as colourless needles, m. p. 144° (Found: N, 4·1. $C_{18}H_{19}ON$ requires N, 4·11%).

*4′-Nitro-*4-cyclo*hexyldiphenyl.*—The mother-liquors from the crystallisation of the product obtained by the nitration of the parent hydrocarbon were evaporated, and on cooling, pale yellow, long, narrow plates were deposited, m. p. 124° (Found : N, 5·0. $C_{18}H_{19}O_2N$ requires N, 4·98%).

*Oxidation of 4′-Nitro-*4-cyclo*hexyldiphenyl to 4-Nitrodiphenyl-4′-carboxylic Acid.*—A suspension of the nitro-derivative in a solution of sodium dichromate in water and acetic acid was treated with concentrated sulphuric acid. Oxidation was not very ready, and the mixture was boiled for 1 hour; water was added, and a precipitate separated. This was stirred into dilute aqueous sodium hydroxide and filtered from some unchanged nitro-compound; the filtrate, treated with hydrochloric acid, gave an organic acid which sublimed in white plates, m. p. 340°, not depressed by admixture with authentic 4-nitrodiphenyl-4′-carboxylic acid.

*4′-Amino-*4-cyclo*hexyldiphenyl.*—The nitro-compound was reduced by the same methods as were employed for the preparation of the 2-amino-isomer; the free base separated from aqueous alcohol in an amorphous form. It was analysed as the *hydrochloride,* which melted to a cloudy liquid at 90° and became clear at 110° (Found : N, 4·7. $C_{18}H_{21}N,HCl$ requires N, 4·87%).

The *acetyl* derivative was prepared by refluxing a suspension of the amine in a mixture of water, acetic acid, and acetic anhydride during 3 hours; the solid was filtered off, dried, and crystallised from methyl alcohol; colourless plates, m. p. 225° (Found: N, 4·9. $C_{20}H_{23}ON$ requires N, 4·78%). The *benzoyl* derivative, prepared by the Schotten–Baumann reaction, crystallised from alcohol in colourless plates, m. p. 240° (Found : N, 3·8. $C_{25}H_{25}ON$ requires N, 3·94%).

*4′-Nitro-*1 : *4-diphenylbenzene.*—Bromine was dropped into 4′-nitro-4-*cyclo*hexyldiphenyl at 150° during 15 minutes; the product was then cooled, shaken with warm acetone, and filtered. The filtrate was boiled with charcoal, and the filtered solution deposited pale yellowish-brown plates, which, from alcohol–acetone, had m. p. 211° (Found: N, 5·0. $C_{18}H_{13}O_2N$ requires N, 5·09%).

4-cyclo*Hexyldiphenyl-4′-diazonium Perbromide.*—4′-Amino-4-*cyclo*hexyldiphenyl was suspended in 10% hydrochloric acid and diazotised by addition of solid sodium nitrite. The diazonium solution was filtered, and poured into a saturated solution of potassium bromide; the resulting yellow precipitate was separated, washed, and dried. Crystallisation from benzene–light petroleum afforded yellow needles, m. p. 105° (decomp.) (Found: Br, 48·0. $C_{18}H_{19}N_2Br_3$ requires Br, 47·72%).

*4′-Bromo-*4-cyclo*hexyldiphenyl.*—The diazonium perbromide was added to alcohol at 78°, and evaporation of the solution left a crystalline residue which recrystallised from alcohol in colourless plates, m. p. and mixed m. p. with authentic 4′-bromo-4-*cyclo*hexyldiphenyl, 154°.

*Trinitro-*4-cyclo*hexyldiphenyl.*—4-*cyclo*Hexyldiphenyl (2 g.) was added during ½ hour to 20 c.c. of concentrated nitric acid at 20°. The mixture was thoroughly stirred so that the hydrocarbon dissolved continuously, and the temperature rose to 35°. The *trinitro*-derivative separated on cooling (0·4 g.), and crystallised from alcohol–acetone in long needles, m. p. 235° (Found : N, 11·1. $C_{18}H_{17}O_6N_3$ requires N, 11·32%).

*4′-(*p*-Nitrobenzoyl)-*4-cyclo*hexyldiphenyl.*—(a) 4-*cyclo*Hexyldiphenyl and *p*-nitrobenzoyl chloride were dissolved in carbon disulphide; reaction was initiated by addition of aluminium chloride, and completed after 2 hours by warming at 50° during ½ hour. The product was decomposed with dilute acid, and the solvent removed by evaporation; the solid residue was extracted with three successive portions of dilute caustic alkali, and the nitro-compound filtered off. This was washed with water, dried, and recrystallised from benzene–light petroleum, forming a yellow, micro-crystalline powder (1·6 g.), m. p. 175°.

(b) 4′-Benzoyl-4-*cyclo*hexyldiphenyl was stirred into concentrated nitric acid at 0° during ½ hour; the temperature was then allowed to rise to 18°, and was maintained thereat for 1 hour. The product was separated by the addition of water, dried, and recrystallised as above, affording small crystals, m. p. and mixed m. p. with the previous preparation, 175° (Found: N, 3·8. $C_{25}H_{23}O_3N$ requires N, 3·66%).

4-cyclo*Hexyldiphenyl-4′-carboxylyl Chloride.*—4-*cyclo*Hexyl-4′-carboxylic acid was refluxed with thionyl chloride during 2 hours; the excess thionyl chloride was then removed by distillation, and the residue, a light-brown, crystalline mass, was recrystallised from light petroleum, from which pale yellow needles were obtained, m. p. 109° (Found: Cl, 12·3. $C_{19}H_{19}OCl$ requires Cl, 11·9%).

*Dinitro-*4 : *4′-di*cyclo*hexyldiphenyl.*—(a) 4 : 4′-Di*cyclo*hexyldiphenyl (1 g.) was stirred into 15 c.c. of concentrated nitric acid at 18°; the nitration was completed by heating at 40° until a clear solution was obtained (5 mins.). Water precipitated the *nitro-compound,* which was separated, washed, and dried (1·25 g.); after two recrystallisations from alcohol, yellow needles, m. p. 182°, were obtained.

(b) The hydrocarbon (0·5 g.), dissolved in acetic acid (40 c.c.) at 70°, was nitrated by addition of a mixture of 10 c.c. each of fuming nitric acid and glacial acetic acid. The solution was diluted, and the filtered nitro-compound recrystallised from alcohol; yellow needles were deposited; m. p. and mixed m. p. with the product obtained in (a), 182° (Found: C, 70·0, H, 6·9. $C_{24}H_{28}O_4N_2$ requires C, 70·59, H, 6·86%).

Diamino-4 : 4′-*di*cyclo*hexyldiphenyl*.—The nitro-derivative was reduced in alcoholic solution with iron and hydrochloric acid; the solvent was distilled off, and the hydrochloride of the base separated from the cooled solution. This was extracted with ether in the presence of ammonia, and evaporation of the ethereal extract left the *diamine*, which crystallised from alcohol in pale buff-coloured needles, m. p. 225° (Found: N, 8·1. $C_{24}H_{32}N_2$ requires N, 8·05%).

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