

350. Derivatives of 4-cycloHexyldiphenyl. Part I.

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DIPHENYL combines with *cyclohexene* in the presence of aluminium chloride to give, amongst other products, two crystalline derivatives, *cyclohexyl*- and *dicyclohexyl*-diphenyl (Bodroux, *Ann. Chim.*, 1928, **11**, 511). The same compounds have now been prepared from diphenyl and *cyclohexyl* bromide in the presence of the same catalyst and they have been identified as the 4- and the 4 : 4'-derivative respectively. Under suitable conditions, a yield of 35% of the 4-compound can be obtained.

Selenium dehydrogenation of both hydrocarbons gives respectively 1 : 4-diphenylbenzene and 4 : 4''-bisdiphenyl; and 4-*cyclohexyl*diphenyl reacts with acetyl chloride and benzoyl chloride in the presence of aluminium chloride to give the corresponding *ketones*.

EXPERIMENTAL.

4-cycloHexyldiphenyl.—To a solution of diphenyl (50 g.; $\frac{1}{3}$ mol.) and *cyclohexyl* bromide (27 g.; $\frac{1}{3}$ mol.) in carbon disulphide (35 c.c.), anhydrous aluminium chloride (1 g.) was added; after 5 hours, the reaction was completed at 45° in $\frac{1}{2}$ hour. The solvent and the excess of diphenyl were removed in steam and the non-volatile residue was extracted with benzene; after evaporation the remaining oil was distilled under reduced pressure. The fraction, b. p. 210—230°/7 mm., partly solidified at 0°; the crystalline material was collected and recrystallised, giving fine colourless needles (11 g.), m. p. 74·5° (Found : C, 91·4; H, 8·4. Calc. for C₁₈H₂₆ : C, 91·5; H, 8·5%).

With quantities of aluminium chloride greater than that used above, the percentage of isomeric oils increases considerably.

Oxidation of 4-cycloHexyldiphenyl to Terephthalic Acid.—The hydrocarbon (2 g.) was suspended in a solution of sodium dichromate (12 g.) in water (35 c.c.), and concentrated sulphuric acid (27 c.c.) added with constant stirring; the mixture was finally heated at 100° during 1 hour. The precipitate obtained by dilution was purified by dissolution in alkali and reprecipitation with hydrochloric acid; the product did not melt at 360° but sublimed, and its methyl ester, m. p. 139°, was identified by a mixed m. p. as methyl terephthalate (Noelting, *Ber.*, 1875, **8**, 1113).

Dehydrogenation of 4-cycloHexyldiphenyl to 1 : 4-Diphenylbenzene.—4-*cycloHexyl*diphenyl (1 g.) was heated during 8 hours with selenium (3 g.) at 330°. The cooled melt was extracted

with hot benzene, from which plates, m. p. (and mixed m. p.) 213°, were obtained (Gerngross and Dunkel, *Ber.*, 1924, 57, 739).

4 : 4'-Dicyclohexyldiphenyl.—This was obtained either (a) from the higher-boiling fractions formed during the preparation of the mono-derivative or (b) by the action of cyclohexyl bromide on 4-cyclohexyldiphenyl.

(a) The fraction, b. p. 230—280°/7 mm., became solid when cooled, and on agitation with cold acetone crystalline plates remained undissolved; m. p. (from acetone) 205° (corr.); yield, 1.5 g. (Found : C, 90.4; H, 9.5. Calc. for $C_{24}H_{30}$: C, 90.6; H, 9.4%).

(b) 4-cycloHexyldiphenyl (3 g.) was dissolved in a mixture of cyclohexyl bromide (2 g.) and carbon disulphide (10 c.c.), and the reaction initiated by the addition of aluminium chloride (0.25 g.). After 2 hours the carbon disulphide and the excess of cyclohexyl bromide were removed by steam-distillation; the residual oil was extracted with benzene and after evaporation of the solvent the product was treated with cold acetone, crystals, m. p. (from acetone) 205°, being obtained; yield, 0.65 g. or 16%.

Dehydrogenation of 4 : 4'-Dicyclohexyldiphenyl to 4 : 4''-Bisdiphenyl.—4 : 4'-Dicyclohexyldiphenyl (0.5 g.) was heated during 2 hours at 340° with selenium (2 g.); the melt was cooled, pulverised, and extracted with hot xylene; the plates deposited from the cold solution melted at 320° and did not depress the m. p. of authentic 4 : 4''-bisdiphenyl (*p*-bisdiphenyl; 4 : 4'-diphenylbiphenyl; Noyes and Ellis, *Amer. Chem. J.*, 1895, 17, 620).

4'-Acetyl-4-cyclohexyldiphenyl.—4-cycloHexyldiphenyl (2.5 g.) was dissolved in a mixture of acetyl chloride (3 g.) and carbon disulphide (10 c.c.), and anhydrous aluminium chloride (4 g.) added in small portions. The reaction was completed at 50° during $\frac{1}{4}$ hour, the product decomposed with dilute hydrochloric acid, the ketone extracted in ethyl acetate, and the solvent evaporated. The product (3 g.) after two recrystallisations from alcohol-acetone gave transparent plates, m. p. 158°; yield, 1.75 g. or 60% (Found : C, 86.7; H, 7.8. $C_{20}H_{22}O$ requires C, 86.3; H, 7.9%). Crystallised from alcohol, the phenylhydrazone formed yellow plates, m. p. 172° (Found : N, 7.8. $C_{26}H_{28}N_2$ requires N, 7.6%), the semicarbazone, needles, m. p. 270° (Found : N, 12.6. $C_{21}H_{25}ON_3$ requires N, 12.5%), and the oxime, plates, m. p. 196° (Found : N, 4.9. $C_{20}H_{22}ON$ requires N, 4.8%).

4-cycloHexyldiphenyl-4'-carboxylic Acid.—(a) 4'-Acetyl-4-cyclohexyldiphenyl (0.5 g.) was refluxed during 36 hours with a dilute solution of sodium hypochlorite or hypobromite. The solid sodium salt floating at the surface of the liquid was separated and boiled with hydrochloric acid; the organic acid obtained crystallised from alcohol in fine needles, m. p. 288° (Found : C, 81.75; H, 7.6. $C_{18}H_{20}O_2$ requires C, 81.5; H, 7.1%). The methyl ester was prepared by refluxing a mixture of the acid, methyl alcohol, and phosphorus pentachloride for 2 hours; it was precipitated by water and crystallised from methyl alcohol; m. p. 152°.

(b) 4'-Benzoyl-4-cyclohexyldiphenyl (see below) (0.5 g.) was added gradually to potash-lime (15 g.) in a nickel crucible, the temperature being kept at 300° during 1½ hours. The cooled melt was finely ground and extracted with dilute hydrochloric acid; the residue on treatment with caustic alkali gave an insoluble sodium salt, which was therefore decomposed with hot hydrochloric acid. The dried precipitate was extracted with alcohol, from which needles were obtained, m. p. 288° alone or mixed with specimen (a). The methyl ester had m. p. 152°.

Oxidation of 4'-Acetyl-4-cyclohexyldiphenyl to Diphenyl-4 : 4'-dicarboxylic Acid.—The ketone was stable to both acid and alkaline permanganate, even after 24 hours' refluxing. It (0.35 g.) was dissolved in glacial acetic (15 c.c.), a solution of sodium dichromate (2.5 g.) in water (20 c.c.) added, and concentrated sulphuric acid (20 c.c.) run in with vigorous stirring. As oxidation did not set in at 80°, the mixture was boiled during 2 hours. It was then diluted and the precipitate was dissolved in sodium carbonate solution, reprecipitated with hydrochloric acid, and dried. The acid sublimed and decomposed above 300° [Found : equiv., from the silver salt, 128. Calc. for $C_{12}H_8(CO_2H)_2$: equiv., 121]. The methyl ester, prepared according to Weiler (*Ber.*, 1899, 32, 1061, Anm.), melted at 214° (corr.) and did not depress the m. p. of an authentic specimen (Weiler, *loc. cit.*).

4'-Benzoyl-4-cyclohexyldiphenyl.—4-cycloHexyldiphenyl (2.36 g.), dissolved in benzoyl chloride (2.5 g.) and carbon disulphide (15 c.c.), was treated with anhydrous aluminium chloride (2.5 g.) in small portions during 2 hours, the reaction being completed by warming during 15 minutes on a water-bath. The product was decomposed with dilute hydrochloric acid and extracted with ethyl acetate; after distillation of the solvent there were left 4 g. of semi-solid matter, which gave colourless plates, m. p. 123°, from alcohol-acetone (2 : 3); yield, 2 g. or 60% (Found : C, 88.9; H, 6.75. $C_{25}H_{24}O$ requires C, 88.25; H, 7.05%). The ketone formed an oxime, m. p. 188° (Found : N, 4.1. $C_{25}H_{25}ON$ requires N, 3.9%), and a semicarbazone, m. p.

240° (Found : N, 10·8. $C_{26}H_{27}ON_3$ requires N, 10·6%), both of which crystallised from alcohol in needles.

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