

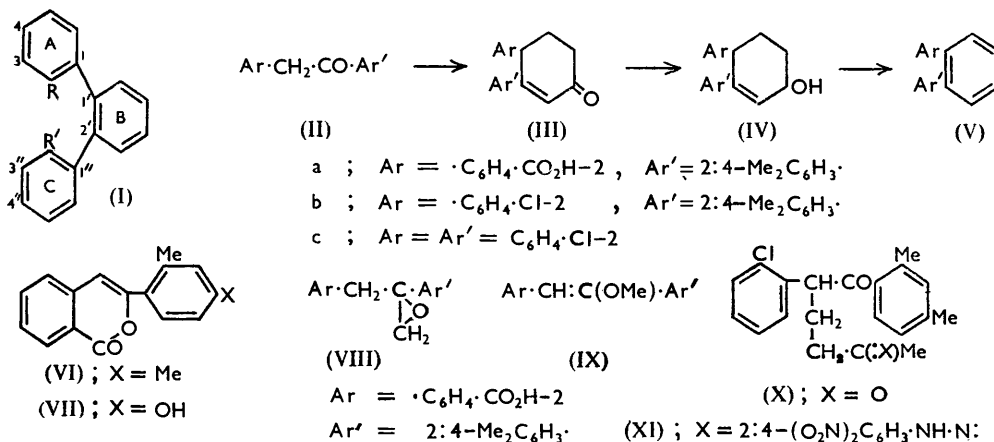
188. *Synthetical Experiments in the o-Terphenyl Series. Part II.*¹

By R. L. HUANG and KHENG-HOON LEE.

Of attempted syntheses of the *o*-terphenyls (V) via the cyclohexenones (III), the first two broke down at intermediate stages, while the third yielded a glass, probably (Vc). Preparative methods have been worked out for the intermediate deoxybenzoin and some of their properties are reported.

In a 2 : 2''-disubstituted *o*-terphenyl (I), the non-planarity of the benzene rings^{2,3} could give rise to geometrical isomers in which substituents R and R' are *cis* or *trans* to each other with respect to the central ring. An attempt to substantiate this postulate was made by synthesis¹ of the *o*-terphenyl (I; R = R' = OMe), but only one form could be isolated. This failure could be due to either (a) the existence of a preferred form, or (b) insufficient restriction of rotation as a result of the relatively small size of the methoxyl group. This paper now reports attempts to synthesise *o*-terphenyls with bulkier *ortho*-substituents such as chloro-, carboxy-, and methyl groups.

Estimates suggest that for the 2 : 2''-dichloro-derivative (I; R = R' = Cl), for instance, in the rotation of ring A about the pivot bond, interference is considerable between a chlorine atom at C₍₂₎ and the hydrogen atom at C₍₆₎, when rings A and B becomes co-planar (interatomic distance 1.59 Å; sum of van der Waals radii 2.80 Å), normal bond angles and bond



lengths³⁻⁵ being assumed. Similarly, the interference between the same chlorine atom and ring c, even when at a minimum (which is the case when ring c is at right angles to B) is still considerable (1.25 Å and 3.59 Å, respectively). Thus, it appears probable that, unless large distortion of bond angles can occur, the geometrical isomers of 2 : 2''-dichloro-*o*-terphenyl should be stable entities.

Relatively few methods are available for the synthesis of *ortho*-substituted *o*-terphenyls. The Ullmann reaction gives low yields,⁶ and moreover the high reaction temperature appears unsuitable for synthesis of isomers which might be thermally labile. The route via a 2-arylcyclohexanone did not give promising results,¹ while the approach involving

¹ Huang, J., 1954, 3655, is considered as Part I of this series.

² See Pickett, Walter, and France, *J. Amer. Chem. Soc.*, 1936, **58**, 2296; Clews and Lonsdale, *Proc. Roy. Soc.*, 1937, *A*, **161**, 493; Merkel and Wiegand, *Z. Naturforsch.*, 1948, **3b**, 93.

³ Brockway and Karle, *J. Amer. Chem. Soc.*, 1944, **66**, 1974.

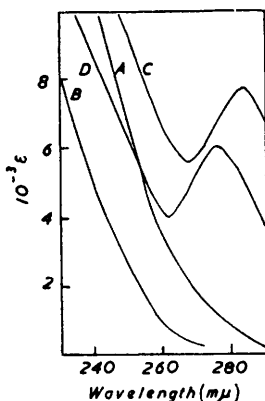
⁴ Adams and Yuan, *Chem. Rev.*, 1933, **12**, 261.

⁵ Brockway and Robertson, *J.*, 1939, 1329; Robertson, *Sci. Progress*, 1939, **33**, 666; Robertson, "Organic Crystals and Molecules," Cornell Univ. Press, Ithaca, N.Y., 1953, p. 227.

⁶ Sadler and Powell, *J. Amer. Chem. Soc.*, 1934, **56**, 2650; Shuttleworth, Rapson, and Stewart, *J.*, 1944, **71**; cf. Bachmann and Clark, *J. Amer. Chem. Soc.*, 1927, **49**, 2089.

homolytic arylation ⁷ by a substituted *o*-diphenyl radical has yet to be investigated. A method which has achieved considerable success ⁸ and was used in the synthesis of the dimethoxy-derivative ¹ makes use of a modified Robinson–Mannich synthesis from a deoxybenzoin (II) to give the diarylcyclohexenone (III). This is reduced to the alcohol (IV), then dehydrated and dehydrogenated to the terphenyl (V). This scheme, when used for the terphenyls (Va) and (Vb), broke down at intermediate stages, although practical preparative methods have been developed for the intermediates (IIa) and (IIb). In the case of the 2 : 2''-dichloro-compound, (Vc), the synthesis was carried through, but the product could not be obtained crystalline.

m-Xylene was acylated by homophthalic anhydride in the presence of aluminium chloride to the deoxybenzoin (IIa) in good yield. The presence of the *p*-methyl group, though of no steric significance in the ultimate product (Va), served here to ensure unambiguity in the course of acylation. Before use of the Robinson–Mannich reaction, the carboxyl group had to be esterified. However, ethanol and sulphuric acid converted the deoxybenzoin into the lactone (VI), while ethereal diazomethane produced a mixture of the same lactone and an acid, probably (VIII) or (IX). Since infrared absorption of the deoxybenzoin (in Nujol) showed an inflected peak at 5.9 μ (carbonyl absorption, ketone



A, 2 : 2''-Dichloro-*o*-terphenyl (?).
 B, 2 : 2''-Dichlorodiphenyl.
 C, 2 : 2''-Dimethoxy-*o*-terphenyl.
 D, 2 : 2''-Dimethoxydiphenyl.

and acid mixed) but no hydroxy-band in the 3 μ region, it probably exists in the solid state in the ketonic, rather than the enolic form, so that enolisation had occurred by acid catalysis, and by the action of diazomethane, and this was followed by lactonisation. An analogy for the acid catalysis is found in the direct synthesis of the isocoumarin (VII) from homophthalic anhydride and *m*-cresol in the presence of stannic chloride.⁹

The deoxybenzoin (IIb) was prepared from *m*-xylene and *o*-chlorophenylacetyl chloride, a modification of Perrier's method ¹⁰ being adopted. The preparation of *o*-chlorophenylacetic acid through *o*-chlorobenzaldehyde cyanohydrin ¹¹ did not prove promising, but the route *via* the oxazolone and *o*-chlorophenylpyruvic acid gave satisfactory results.¹² The pyruvic acid was unstable, decomposing readily into *o*-chlorobenzaldehyde.

Condensation of the above ketone with 4-diethylaminobutan-2-one in the presence of sodium ethoxide gave, not the expected cyclohexenone (IIIb), but the open-chain diketone (X) isolated as a mono-2 : 4-dinitrophenylhydrazone. To this the ketonic structure (XI) is assigned since its infrared spectrum (in Nujol) exhibits the peak at 6.0 μ characteristic of an aryl ketone, and no hydroxyl peak in the 3 μ region. As variation of conditions

⁷ E.g., see Cadogan, Hey, and Williams, *J.*, 1954, 3352.

⁸ Dodds, Huang, Lawson, and Robinson, *Proc. Roy. Soc.*, 1953, B, 140, 470.

⁹ Buu Hoi, *Bull. Soc. chim. France*, 1944, 11, 338.

¹⁰ Perrier, *Ber.*, 1900, 33, 815.

¹¹ Levine, Eble, and Fishbach, *J. Amer. Chem. Soc.*, 1948, 70, 1930.

¹² Cf. *Org. Synth.*, Col. Vol. II, p. 55; Adams, "Organic Reactions," Vol. III, pp. 209, 225.

in the Robinson–Mannich reaction did not bring about cyclisation, and as attempts to cyclise the open-chain ketone (X) with potassium *tert.*-butoxide and with hydrogen bromide in acetic acid⁸ were unsuccessful, the synthesis of the terphenyl (IIb) was not pursued.

The preparation of 2 : 2'-dichlorodeoxybenzoin by reaction of an excess of *o*-chlorophenylmagnesium bromide with *o*-chlorobenzamide, reported by Jenkins and Richardson¹³ to give a 70% yield, afforded only 34% of the product accompanied by considerable quantities of 2 : 2'-dichlorodibenzyl, despite variations of conditions. An alternative route, *via* the benzoin condensation^{14,15} of *o*-chlorobenzaldehyde followed by reduction, was next examined. An adaptation of Lutz and Murphey's method¹⁶ gave a higher yield of the benzoin, which was directly oxidised to the benzil (49% overall). This on reduction with hydriodic acid gave not the deoxybenzoin as would be expected by analogy with benzil and certain substituted benzils,¹⁷ but 2 : 2'-dichlorobenzoin (69%). Reduction with tin–copper couple¹⁸ gave the required deoxybenzoin in 83% yield, and in a much purer form than that obtained by Jenkins and Richardson's method. Reduction by the same method of the product from the above benzoin condensation gave an inseparable mixture probably of 2 : 2'-dichloro-hydrobenzoin and -deoxybenzoin, which gave the benzil by oxidation with nitric acid.

The 2 : 2'-dichlorodeoxybenzoin condensed with methyl vinyl ketone (Robinson–Mannich synthesis) to furnish the cyclohexenone (IIIc). Ponderff reduction of this ketone gave the cyclohexenol (IVc), or an isomer thereof, dehydration occurring readily with potassium hydrogen sulphate in boiling cumene (though sluggishly in refluxing benzene). The diene so obtained was directly dehydrogenated with palladised charcoal to a glass, probably 2 : 2''-dichloro-*o*-terphenyl, which could not be induced to crystallise. This tendency to supercool has been noted in *o*-terphenyl itself¹⁹ and is attributed to interlocking of molecules in the crystal. The ultraviolet absorption of the product, measured in hexane, possesses characteristics very similar to that of 2 : 2'-dichlorodiphenyl^{20,21} (see Figure), a resemblance also shown between 2 : 2''-dimethoxy-*o*-terphenyl¹ and 2 : 2'-dimethoxydiphenyl.²⁰

EXPERIMENTAL

2'-Carboxy-2 : 4-dimethyldeoxybenzoin.—*m*-Xylene (14 g.) in tetrachloroethane (*ca.* 25 c.c.) was added during 15 min. to a well-stirred mixture of homophthalic anhydride²² (10.5 g.) and powdered aluminium chloride (20 g.) in the same solvent (150 c.c.). The mixture was stirred for 24 hr., poured on chipped ice, and after addition of concentrated hydrochloric acid (30 c.c.) was heated to 70° for 30 min. The organic layer was separated, the aqueous layer extracted with ether, and the combined organic solution washed with water, and extracted 3 times with 10% aqueous sodium hydroxide. The alkaline extract, after being washed with ether, was acidified with dilute hydrochloric acid, and the precipitate taken up in ether. Removal of the solvent then gave the required *deoxybenzoin* (9.5 g., 54% yield), m. p. 135–136° after crystallisation from benzene–cyclohexane (Found: C, 76.2; H, 6.2. C₁₇H₁₆O₃ requires C, 76.1; H, 6.0%). It dissolved readily in 10% aqueous sodium hydrogen carbonate.

Attempted Esterification.—(a) The *deoxybenzoin* (7.5 g.) was refluxed with ethanol (80 c.c.) containing sulphuric acid (5.6 g.) for 12 hr. Most of the alcohol was removed under reduced pressure, and the residue poured on ice containing sodium hydrogen carbonate just sufficient to neutralise the sulphuric acid. The organic matter was taken up in ether, washed with water,

¹³ Jenkins and Richardson, *J. Amer. Chem. Soc.*, 1933, **55**, 1618.

¹⁴ Hodgson and Rosenberg, *J.*, 1930, **14**; Weissberger, Strasser, Mainz, and Schwarz, *Annalen*, 1930, **478**, 112; Gilman and Broadbent, *J. Amer. Chem. Soc.*, 1948, **70**, 2619.

¹⁵ Cf. *Org. Synth.*, Col. Vol. I, p. 87.

¹⁶ Lutz and Murphey, *J. Amer. Chem. Soc.*, 1949, **71**, 478.

¹⁷ Japp and Klingemann, *J.*, 1893, **63**, 770; Fuson, Armstrong, Chadwick, Kneisky, Rowland Shank, and Soper, *J. Amer. Chem. Soc.*, 1945, **67**, 386; Fuson and Hoch, *ibid.*, 1949, **71**, 1585.

¹⁸ Allen and Buck, *J. Amer. Chem. Soc.*, 1930, **52**, 310.

¹⁹ Andrews and Ubbelohde, *Proc. Roy. Soc.*, 1955, *A*, **228**, 435.

²⁰ Williamson and Rodebush, *J. Amer. Chem. Soc.*, 1941, **63**, 3018.

²¹ Bastiansen, *Acta Chem. Scand.*, 1950, **4**, 926.

²² *Org. Synth.*, Col. Vol. II, p. 449.

dried, and concentrated. The crystalline residue was crystallised from ethanol, giving 3-(3 : 4-dimethylphenyl)isocoumarin as long needles (3.7 g.), m. p. 120.5—121.5° after several recrystallisations (Found: C, 81.6; H, 5.8. $C_{17}H_{14}O_2$ requires C, 81.6; H, 5.6%).

(b) An ice-cold solution of diazomethane in dry ether (prepared from 10.3 g. of methyl-nitrosourea) was added portionwise to a solution of the deoxybenzoin (15.0 g.) in dry ether (ca. 250 c.c.) at 20°. Next day, the solution was extracted twice with 10% aqueous sodium hydrogen carbonate and the aqueous and ethereal solutions were worked up separately as follows. (i) The aqueous solution was acidified, and precipitated organic matter isolated by ether extraction, giving a crystalline compound (4.7 g.), hexagonal prisms, m. p. 129—130° after crystallisation from light petroleum-benzene (Found: C, 76.3; H, 6.1. $C_{18}H_{18}O_3$ requires C, 76.6; H, 6.4%). It did not react with 2 : 4-dinitrophenylhydrazine. (ii) The ethereal solution was washed with water, dried, and concentrated, and the residue (10.8 g.) distilled to give a viscous orange liquid, b. p. 186—192°/0.8 mm. (7.6 g.), which partially crystallised, giving the isocoumarin obtained previously, m. p. and mixed m. p. 120—121° (Found: C, 81.6; H, 5.6%).

o-Chlorophenylacetic Acid.—The oxazolone (75 g.; m. p. 158—159°) prepared from *o*-chlorobenzaldehyde and hippuric acid by Mauthner's method²³ was boiled with 10% aqueous sodium hydroxide (1200 c.c.) for 5 hr. under nitrogen. The solution was cooled in ice and vigorously stirred while 10% hydrogen peroxide (380 c.c.) was added during $\frac{1}{2}$ hr. Next day, 6*N*-hydrochloric acid was added, and the precipitate filtered off. Benzoic acid was removed by prolonged steam-distillation, and the *o*-chlorophenylacetic acid, which remained in the residue, crystallised repeatedly from light petroleum (b. p. 60—80°), m. p. 93—94° (12.1 g., 27%). Campbell and McKail²⁴ report m. p. 93—95°. An attempt to isolate *o*-chlorophenylpyruvic acid from the hydrolysis products of the oxazolone, Perkin's sulphur dioxide method being used,²⁵ yielded only *o*-chlorobenzoic acid (odour of aldehyde).

2'-Chloro-2 : 4-dimethyldeoxybenzoin.—Crude *o*-chlorophenylacetyl chloride [from the acid (12.0 g.)] was added to a stirred mixture of powdered aluminium chloride (10.0 g.) and *sym*-tetrachloroethane (75 c.c.). When all the aluminium chloride had dissolved (ca. 20 min.), *m*-xylene (12.5 c.c.) in the same solvent (25 c.c.) was added during 1 hr., the mixture being kept at room temp. (28°). Stirring was continued for 2 hr. more, and the mixture then poured on ice. Next day, concentrated hydrochloric acid (20 c.c.) was added, the organic layer was separated, and the aqueous layer extracted with tetrachloroethane. The combined organic solution was washed with water, aqueous sodium hydrogen carbonate, and water, and dried. On removal of the solvent under reduced pressure the deoxybenzoin (16.5 g.) separated. It crystallised from methanol in needles, m. p. 90—90.5° (Found: C, 74.4; H, 5.9; Cl, 14.2. $C_{16}H_{15}OCl$ requires C, 74.3; H, 5.8; Cl, 13.7%). The 2 : 4-dinitrophenylhydrazone, orange-coloured leaflets from ethanol-ethyl acetate, had m. p. 234—235° (Found: N, 12.5. $C_{22}H_{19}O_4N_4Cl$ requires N, 12.7%).

Robinson-Mannich Reaction.—The above deoxybenzoin (4.0 g.) in dry benzene (30 c.c.) was added at 5—10° to the methiodide prepared from methyl iodide (2.4 g.) and 4-diethylamino-butan-2-one²⁶ (2.4 g.), under nitrogen. Sodium ethoxide [from sodium (0.8 g.)] in ethanol (30 c.c.) was then added in two equal portions, the first during 30 min. and the second during 10 min. The mixture was kept at ca. 10° for 1 hr., then heated slowly, and finally refluxed gently for 15 min. It was poured on chipped ice containing a slight excess of sulphuric acid, and the organic matter isolated with ether. The extract, after being washed with aqueous solutions of sodium hydrogen sulphite and of sodium hydrogen carbonate, and with water, was dried, concentrated, and distilled with benzene until the ethanol was completely removed. The residue was then adsorbed on alumina and eluted with benzene. When distilled under nitrogen it gave a pale yellow oil, b. p. 176—185°/0.5 mm. (ca. 3.6 g.), which failed to crystallise. With Brady's reagent it gave 2-*o*-chlorophenyl-1-(2 : 4-dimethylphenyl)hexane-1 : 5-dione mono-2 : 4-dinitrophenylhydrazone, m. p. 147—148° after crystallisation from ethanol-ethyl acetate (Found: C, 61.1; H, 5.0. $C_{26}H_{25}O_5N_4Cl$ requires C, 61.3; H, 4.95%). A portion of the distillate slowly crystallised, and proved to be unchanged deoxybenzoin. However, further distillation failed to give the diketone pure. Variation of conditions by (a) using potassium ethoxide or *tert*-butoxide instead of sodium ethoxide, and (b) increasing the period of reflux (1—2 hr.), did not improve the results.

²³ Mauthner, *J. prakt. Chem.*, 1917, **95**, 55.

²⁴ Campbell and McKail, *J.*, 1948, 1251.

²⁵ Haworth, Perkin, and Rankin, *J.*, 1924, **125**, 1686.

²⁶ Wild and Shunk, *J. Amer. Chem. Soc.*, 1943, **65**, 469.

2 : 2'-Dichlorodeoxybenzoin.—(a) *Jenkins and Richardson's method*.¹³ Finely powdered *o*-chlorobenzamide (39 g.) was added in 1.5 hr. with stirring to a Grignard solution [from *o*-chlorobenzyl chloride (161 g.) and magnesium (24.3 g.)] in ether (ca. 500 c.c.) under nitrogen. The stirred mixture was heated under reflux for 50 hr., then poured on ice containing dilute sulphuric acid, and the product was extracted into ether, and worked up in the usual way. Distillation through a 15-cm. Vigreux column under nitrogen gave fractions: (i) *o*-chlorotoluene (51 g.); (ii) 2 : 2'-dichlorodibenzyl (23.4 g.), b. p. 115—124°/0.2 mm., m. p. 62—62.5° (from methanol) (Found: C, 67.1; H, 5.0. Calc. for C₁₄H₁₂Cl₂: C, 66.9; H, 4.9%) (lit.²⁷ m. p. 65°); (iii) material (9.3 g.), b. p. 124—134°/0.2 mm., which was mostly 2 : 2'-dichlorodibenzyl; and (iv) a yellow liquid which when refractionated gave the benzoin (16.0 g.), b. p. 138—144°/0.2 mm., *n*_D²⁰ 1.6023 (Found: Cl, 27.1. Calc. for C₁₄H₁₀OCl₂: Cl, 26.7%). Jenkins and Richardson¹³ record b. p. 195—210°/6 mm. The 2 : 4-dinitrophenylhydrazone formed plates, m. p. 171—172° (from ethanol-ethyl acetate) (Found: N, 11.7. C₂₀H₁₄O₄N₄Cl₂.C₂H₆O requires N, 11.4%).

Use of benzyl bromide instead of the chloride reduced the yield of ketone to only 34%.

(b) Crystalline 2 : 2'-dichlorobenzoin (12.8 g.; see below) was heated with granulated tin (25 g.), saturated aqueous copper sulphate (3 c.c.), and ethanol (125 c.c.) for 2.5 hr., during which time concentrated hydrochloric acid (100 c.c.) containing the same copper sulphate solution (7.5 c.c.) was added in small portions. The deoxybenzoin was then isolated by benzene extraction, and distilled; it had b. p. 154—156°/0.5 mm. (10.0 g.), *n*_D²³ 1.5983.

2 : 2'-Dichloro-benzoin and -benzil.—(a) A saturated aqueous solution of potassium cyanide (1.8 g.; "AnalaR") was slowly added to a boiling solution of freshly distilled *o*-chlorobenzaldehyde (177 g.) in methanol (110 c.c.), and the mixture boiled for a further 30 min. Methanol was removed, and the residue, dissolved in benzene, was repeatedly extracted with 20% aqueous sodium hydrogen sulphite, then washed with 10% aqueous sodium hydrogen carbonate, and water, dried, and concentrated. The crude dichlorobenzoin (144 g.) could not be induced to crystallise. A portion (4.0 g.) was oxidised by copper sulphate in pyridine¹⁵ to give 2 : 2'-dichlorobenzil, m. p. 133—134° (2.4 g.) (lit.,²⁸ m. p. 133—134°). Reduction of the crude dichlorobenzoin by a tin-copper couple (Allen and Buck's method¹⁸) gave a mixture, apparently of isomeric hydrobenzoin, which on oxidation with nitric acid (5 hr. at 100°) also gave the benzil (71% yield).

(b) 2 : 2'-Dichlorobenzil (31 g.), 55% hydriodic acid (250 c.c.), and acetic acid (400 c.c.) were stirred at the boiling point for 2 hr. Water was added, and the product taken up in benzene, washed with aqueous sodium hydrogen sulphite and sodium hydrogen carbonate, and water, then dried, and concentrated under reduced pressure. On distillation under nitrogen 2 : 2'-dichlorobenzoin (25.5 g.) was obtained, b. p. 160—170°/0.9 mm., needles, m. p. 62—63° [from benzene-petroleum (b. p. 60—80°)] (Found: C, 59.7; H, 3.6. Calc. for C₁₄H₁₀O₂Cl₂: C, 59.8; H, 3.6%) (lit.,¹⁴ m. p. 63—64°). It was stable in air.

3 : 4-Di-*o*-chlorophenylcyclohex-2-en-1-one.—The above deoxybenzoin (6.0 g.) was subjected to the Robinson-Mannich reaction as previously described. The mixture, after 3.5 hr. at room temperature, was finally refluxed gently for 0.5 hr., and the product was isolated and chromatographed on alumina. The oil (5.1 g.) failed to crystallise and was distilled, giving (i) material, b. p. 158—168°/0.2 mm. (1.4 g., of which 0.9 g. separated as a solid), and (ii) the required cyclohexenone (1.7 g.), b. p. 171—180°/0.2 mm., m. p. 117—118° (from light petroleum) (Found: C, 68.1; H, 4.6; Cl, 22.7. C₁₈H₁₄OCl₂ requires C, 68.1; H, 4.4; Cl, 22.3%). It gave a 2 : 4-dinitrophenylhydrazone, orange needles, m. p. 223.5—224° from ethanol-ethyl acetate (Found: N, 11.5. C₂₄H₁₈O₄N₄Cl₂ requires N, 11.3%). The solid which separated from fraction (i) was the same cyclohexenone (total yield 2.6 g., 35%).

3 : 4-Di-*o*-chlorophenylcyclohex-2-en-1-ol.—The cyclohexenone (2.4 g.) was heated with aluminium isopropoxide (10 g.) and dry isopropyl alcohol (50 c.c.) for 24 hr. under a fractionating column at such a rate that the acetone produced slowly distilled off. The mixture was then poured on ice and dilute hydrochloric acid, and the organic matter taken up in benzene, washed in turn with dilute hydrochloric acid, water, aqueous sodium hydrogen carbonate, and dried, and the solvent removed. The oil which remained did not react with 2 : 4-dinitrophenylhydrazine, and was absorbed on alumina and eluted first with benzene and then with benzene containing 5% of acetone, to give the cyclohexenol (ca. 2.1 g.) which formed fine needles, m. p.

²⁷ Thiele and Holzinger, *Annalen*, 1899, **305**, 100.

²⁸ Deliwala and Rajagopalan, *Proc. Indian Acad. Sci.*, 1950, **31**, A, 110; cf. Gilman and Broadbent, ref. 14.

83—85° (from petroleum) (Found: C, 68.1; H, 5.3; Cl, 22.3. $C_{18}H_{16}OCl_2$ requires C, 67.75; H, 5.0; Cl, 22.2%).

Dehydration. The cyclohexenol (1.9 g.) in cumene (15 c.c.) was heated under reflux (bath temp. 170—175°) with freshly fused potassium hydrogen sulphate (1 g.) for 22 hr. under nitrogen, additional sulphate (1 g.) being introduced after the first 6 hr. Water was introduced, and the product extracted into benzene, washed with water and aqueous sodium carbonate, dried, and concentrated. Chromatography on alumina with benzene as eluent gave an oil (1.0 g.) which absorbed bromine readily; it did not crystallise and was dehydrogenated as such. Some unchanged cyclohexenol was recovered in the later fractions in the chromatography.

Dehydrogenation. The crude dehydration product (0.85 g.) was boiled in cumene (15 c.c.) with 10% palladised charcoal (0.3 g.) under nitrogen for 22 hr. Benzene was added, and after filtration the solvents were completely removed under reduced pressure. The residue, in benzene, was adsorbed on alumina and eluted with the same solvent. The first 80 c.c. gave a viscous oil (0.74 g.) whilst later fractions affording negligible quantities of material. Attempts to induce the oil to crystallise failing, it was repeatedly distilled to give a glass, probably 2 : 2'-dichloro-o-terphenyl (ca. 0.4 g.), b. p. 144—147° (bath)/0.2 mm. (Found: C, 72.3; H, 4.1; Cl, 23.4. $C_{18}H_{14}Cl_2$ requires C, 72.2; H, 4.0; Cl, 23.7%). All attempts to induce crystallisation were unsuccessful. Dehydrogenation was repeated, in boiling ethylbenzene for 43 hr., to give material which after chromatography and distillation similarly would not crystallise.

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UNIVERSITY OF MALAYA, SINGAPORE 10.

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