

### 372. Hydrogenation of Diphenylene Oxide and 2 : 2'-Dihydroxydiphenyl.

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The products obtained by pressure hydrogenation of diphenylene oxide and 2 : 2'-dihydroxydiphenyl over Raney nickel are described. The existence of a hexahydrodiphenylene oxide of unknown stereochemical configuration has been confirmed. The ultra-violet absorption spectra of diphenylene oxide, tetra- and hexa-hydrodiphenylene oxide, coumarone, and coumaran have been measured and are compared.

A SURVEY of the literature showed that some confusion existed over the preparation and homogeneity of the hydrogenation products of diphenylene oxide and 2 : 2'-dihydroxydiphenyl, and that the independent existence of one of these products, namely hexahydrodiphenylene oxide, was doubtful. The present work has sought to clarify the position by a re-examination of the preparative methods given in the literature and by the preparation of pure samples of some of the materials involved and characterisation of them by means of their ultra-violet absorption spectra.

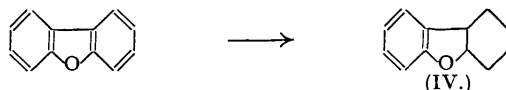
Cullinane and Padfield (*J.*, 1935, 1131), for example, claim to have prepared tetrahydrodiphenylene oxide by controlled hydrogenation of diphenylene oxide over platinum black, but give no proof of the homogeneity of their product. Again Fieser *et al.* (*J. Amer. Chem. Soc.*, 1940, **62**, 2966) state that hexahydrodiphenylene oxide has been prepared as an intermediate, by reduction of 2 : 2'-dihydroxydiphenyl (von Braun, *Ber.*, 1922, **55**, 3763), but Gilman, Smith, and Chaney (*J. Amer. Chem. Soc.*, 1935, **57**, 2095) had shown earlier that the derivatives obtained by von Braun (*loc. cit.*) from the reduction products, and regarded by him as derived from hexahydrodiphenylene oxide, corresponded to the tetrahydrodiphenylene oxide derivatives. Gilman *et al.* (*loc. cit.*) were also unable to confirm the claim of Ebel (*Helv. Chim. Acta*, 1929, **12**, 11) to have reduced the tetra- to the hexa-hydrodiphenylene oxide. Stenger (G.P. 566,782/1930) obtained perhydrodiphenylene oxide by hydrogenation of diphenylene oxide over a nickel catalyst but did not mention any other products of the reaction. On the other hand, Hall and Cawley (*J. Soc. Chem. Ind.*, 1939, **58**, 7), by hydrogenation-cracking of diphenylene oxide over molybdenum oxide and sulphide catalysts at high temperatures, obtained as an initial product *o*-cyclohexylphenol, which became further hydrogenated and broken down to yield a number of products, amongst which was dicyclohexyl.

In the present work diphenylene oxide has been subjected to both exhaustive and controlled hydrogenation over Raney nickel at a high temperature and pressure. In the former instance perhydrodiphenylene oxide (I) was obtained as the main product; cleavage of the furan ring



also occurred to give dicyclohexyl (III) and the *cis*- and *trans*-isomers of 2-cyclohexylcyclohexanol (II). Identification of the last-named isomers was confirmed by preparation of their phthalates and phenylurethane derivatives; and in both cases chromic acid oxidation of the isomers yielded *cyclohexylcyclohexanone* which was directly compared with a synthetic specimen. The identity of the dicyclohexyl obtained during hydrogenolysis was confirmed by comparing its infra-red absorption spectrum with that of an authentic sample of dicyclohexyl obtained by dehydration of *cis*-cyclohexylcyclohexanol followed by hydrogenation. These spectra were substantially identical. Various Sachse-Mohr stereoisomers of dicyclohexyl are mentioned in the literature. Hückel and Neunhoeffer (*Annalen*, 1930, **477**, 106), however, were unable to confirm the preparation of three forms of this compound by dehydration of *cis*- and *trans*-cyclohexylcyclohexanols and hydrogenation of the products (Schrauth and Görig, *Ber.*, 1923, **56**, 1900), and concluded that such isomers do not exist. The *trans-trans*-isomer of Levina *et al.* (*J. Gen. Chem., Russia*, 1937, **7**, 341) was found by Orchin and Feldman (*J. Amer.*

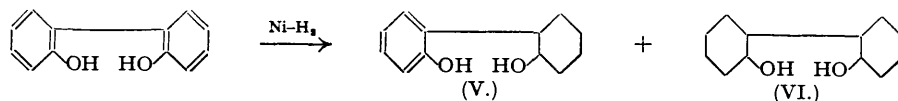
*Chem. Soc.*, 1946, **68**, 2737) to be a mixture containing, *inter alia*, 2 : 2'-dimethyldicyclopentyl and 1-cyclohexyl-2-methylcyclopentane. The physical constants of the product now obtained are close to those reported for the more normal form (cf. Zelinsky *et al.*, *Chem. Zentr.*, 1933, II, 1673).



Controlled hydrogenation of diphenylene oxide so that three moles of hydrogen were absorbed yielded hexahydrodiphenylene oxide (IV) as the chief product. This material could be readily dehydrogenated to diphenylene oxide by heating it in contact with platinised charcoal, and gave on oxidation with chromic acid at room temperature  $\delta$ -*o*-hydroxybenzoylvaleric acid. The same acid was also obtained by chromic acid oxidation of tetrahydrodiphenylene oxide and it is likely that the hexahydrodiphenylene oxide used by Fieser *et al.* (*loc. cit.*) for the preparation of this acid was a mixture of both the tetra- and the hexahydro-oxides.

The methods reported by Ebel and by von Braun (*loc. cit.*) for the preparation of hexahydrodiphenylene oxide were investigated. Tetrahydrodiphenylene oxide took up one mole of hydrogen slowly in alcoholic solution, and much more rapidly in glacial acetic acid, in the presence of platinum or palladium black at room temperature, to give a product which chemical analysis indicated to be hexahydrodiphenylene oxide. The ultra-violet absorption spectrum of this product, however, showed it to be a mixture of approximately 75% of tetra- and 25% of per-hydrodiphenylene oxide only. No break in the rate of hydrogenation curve was observed in these experiments and it would appear that, under the conditions mentioned, hydrogenation of both rings occurred before the molecule was desorbed from the catalyst. Smith *et al.* (*J. Amer. Chem. Soc.*, 1949, **71**, 3772) have shown that for dinuclear compounds, such as diphenyl, hydrogenation of one ring initially occurred, followed by desorption of the molecule from the catalyst, and in such cases, when the hydrogenation was halted at a half-way stage, the bulk of the product existed as the hexahydro-compound. On the other hand, addition of three moles of hydrogen to diphenylene oxide under similar conditions gave a mixture of perhydro- and unchanged diphenylene oxide (Smith and Fuzek, *J. Amer. Chem. Soc.*, 1949, **71**, 415) and it is probable that the tetrahydrodiphenylene oxide prepared by Cullinane and Padfield (*loc. cit.*) was chiefly unchanged diphenylene oxide.

When 2 : 2'-dihydroxydiphenyl was hydrogenated over Raney nickel so that between two and three moles of hydrogen were absorbed, and the products were carefully fractionated through a Stedman-type column, two main liquid products together with 60% of solid residue were obtained. Ultra-violet absorption analysis of the lower-boiling fraction showed it to be a crude specimen of hexahydrodiphenylene oxide admixed with some tetra- and per-hydrodiphenylene oxides. The higher-boiling fraction was identified as tetrahydrodiphenylene oxide by means of its picrate and physical constants. From the solid residue *o*-2-hydroxycyclohexylphenol (V) and 2 : 2'-dihydroxydicyclohexyl (VI) were isolated by fractional crystallisation. Neither of the two compounds appears to have been previously characterised. The "dodecahydro-*o*-*o'*-diphenol" mentioned by Schwenk and Priewe (G.P. 602,837/1934) has a much lower melting point (143—145°) than the compound isolated by us; it may be an impure sample of the same compound or is possibly another stereoisomer. The perhydrodiphenol readily formed a bisphenylurethane and a bis-3 : 5-dinitrobenzoate, and from its mode of formation is most likely to be (VI). The *o*-2-hydroxycyclohexylphenol would only yield a mono-phenylurethane when treated with phenyl isocyanate under the normal reaction conditions; this derivative still possessed a free phenolic group and could be readily coupled with a diazonium salt. Dehydration of the hexahydro-phenol by means of fused potassium hydrogen sulphate removed the alcoholic hydroxyl group, giving one of the isomeric cyclohexenylphenols. The hexahydro-phenol most probably corresponds to the half-hydrogenated form of 2 : 2'-dihydroxydiphenyl (V).

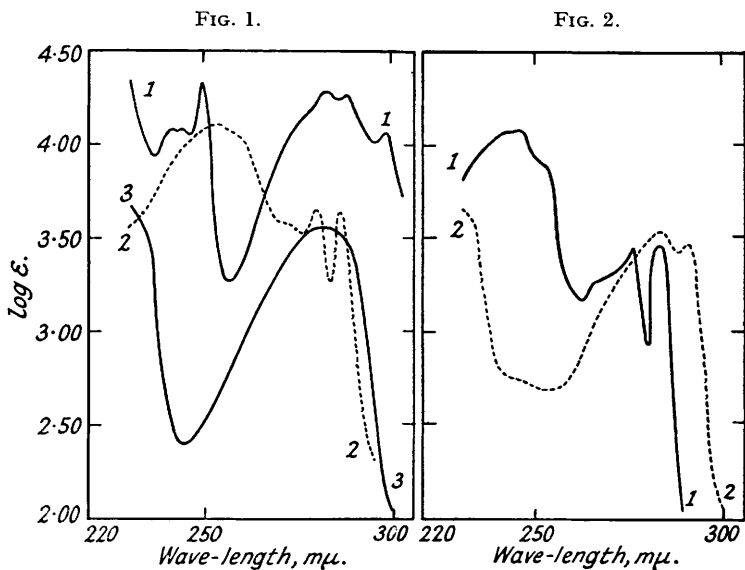


Investigation of the stereochemical configuration of these two compounds was not carried out, but it is interesting that quantitative hydrogenation of 2 : 2'-dihydroxydiphenyl over

Adams's catalyst at room temperature yields a mixture of perhydrodiphenylene oxide and the 2 : 2'-dihydroxydicyclohexyl already mentioned.

An independent synthesis of hexahydrodiphenylene oxide was also attempted by preparation of 1 : 4 : 10 : 11-tetrahydrodiphenylene oxide, followed by reduction of the 2 : 3-double bond. It was hoped to prepare 1 : 4 : 10 : 11-tetrahydrodiphenylene oxide by condensation of butadiene with coumarone or with coumarilic acid. A number of experiments at various temperatures and with various times of heating failed, however, to lead to any of the desired product.

It was considered useful to confirm the homogeneity and structure of the hexahydrodiphenylene oxide, obtained by partial reduction of diphenylene oxide, by measurement of its ultra-violet absorption spectrum. Some of the material was therefore purified by adsorption on to a dry column of alumina, followed by desorption with absolute alcohol (cf. *Analyt. Chem.*, 1947, 19, 992), giving 60% of a pure material of constant refractive index. The ultra-violet absorption spectrum of this material (Fig. 1, curve 3) was closely similar to that of the starting material which lent some support to its homogeneity. For comparison the ultra-violet absorption spectra of pure samples of diphenylene oxide, tetrahydrodiphenylene oxide (Fig. 1,



Absorption spectra, in cyclohexane.

FIG. 1.—1, Diphenylene oxide. 2, Tetrahydrodiphenylene oxide. 3, Hexahydrodiphenylene oxide.  
FIG. 2.—1, Coumarone. 2, Coumaran.

curves 1 and 2 respectively), coumarone, and coumaran (Fig. 2, curves 1 and 2 respectively) were also measured. F. Williams (*Nature*, 1948, 162, 925) has shown that the melting point of diphenylene oxide is no criterion of its purity and, in view of the difficulty of obtaining, from coal tar, a pure specimen suitable for spectroscopic work, preparation by a synthetic route was obviously desirable. This was accomplished by dehydrogenating tetrahydrodiphenylene oxide, synthesised by Ebel's method (*loc. cit.*), by means of *N*-bromosuccinimide (cf. Barnes, *J. Amer. Chem. Soc.*, 1948, 70, 145). The diphenylene oxide so obtained was then purified by crystallisation followed by chromatography and sublimation. Pure coumarone was prepared by decarboxylation of coumarilic acid; and coumaran by hydrogenation of coumarone over Adams's catalyst at room temperature.

In comparison with the spectra of diphenyl (O'Shaughnessy and Rodebush, *ibid.*, 1940, 62, 2906) and diphenyl ether (Mayer-Pitsch *et al.*, *Z. Elektrochem.*, 1943, 49, 368), the spectrum of diphenylene oxide (Fig. 1, curve 1) shows much more fine structure. This can be attributed to the strain set up in the molecule by the bonding in the *ortho*-positions, and similar enhancement of fine structure has been observed in the case of other bridged nuclear compounds (cf. diphenyl and fluorene; diphenyl and carbazole; *o*-xylene and indane). The curve shown here for diphenylene oxide in *cyclohexane* agrees very closely with that recently published by the U.S. Bureau of Mines (Tech. Paper 708) for a synthetic sample in 95% ethanol.

Some of the fine structure is eliminated, however, when hydrogen is added at the 1 : 2 : 3 : 4-positions of diphenylene oxide (Fig. 1, curve 2), and the bands at 242, 245, and 250  $\mu$ . are replaced by a broad band having a maximum at 253  $\mu$ . At the same time the 282-, 287-, and 298- $\mu$ . bands are shifted towards the shorter wave-band of the spectrum, as might be expected for a system containing a smaller number of conjugated double bands (Hausser and Kuhn, *Z. physikal. Chem.*, 1935, **29**, B, 363). Comparison of the diphenylene oxide spectrum with the ultra-violet absorption spectrum of coumarone (Fig. 2, curve 1) shows both the curves to be very similar in general shape and position of absorption maxima. Both molecules resemble indene in containing the  $C_6H_5 \cdot C:C$  chromophore, and it is interesting that the positions of the absorption bands are in agreement with Morton and de Gouveia's suggestion (*J.*, 1934, 915) that the  $C_6H_5 \cdot$  part of such a chromophore would give rise to bands in the 270—290- $\mu$ . wave-length region and the ethylenic bond to a band about 250  $\mu$ . This is shown in the table below.

## Maximum absorption bands.

Diphenylene oxide.		Tetrahydrodiphenylene oxide.		Coumarone.		Indene.*		Hexahydrodiphenylene oxide.		Coumaran.		Indane.*	
$\lambda$ (max.), $\mu$ .	log $\epsilon$	$\lambda$ (max.), $\mu$ .	log $\epsilon$	$\lambda$ (max.), $\mu$ .	log $\epsilon$	$\lambda$ (max.), $\mu$ .	log $\epsilon$	$\lambda$ (max.), $\mu$ .	log $\epsilon$	$\lambda$ (max.), $\mu$ .	log $\epsilon$	$\lambda$ (max.), $\mu$ .	log $\epsilon$
242	4.09	—	—	—	—	—	—	—	—	—	—	—	—
245	4.09	253	4.11	245	4.08	246	4.00	—	—	—	—	—	—
249.5	4.32	—	—	—	—	—	—	—	—	—	—	—	—
281.5	4.29	272	3.58	—	—	273	2.94	—	—	—	—	260	3.00
287	4.28	279	3.66	275	3.45	280	2.90	280	3.56	282	3.52	267	3.16
298	4.06	286	3.65	282	3.48	288	2.73	—	—	289	3.48	274	3.25
—	—	—	—	—	—	291.5	2.21	—	—	—	—	—	—

\* Values taken from Morton and de Gouveia, *J.*, 1934, 915.

Addition of hydrogen to the 10 : 11-positions to give hexahydrodiphenylene oxide (IV) causes elimination of the 253- $\mu$ . band of tetrahydrodiphenylene oxide and replaces the three peaks between 270—290  $\mu$ . by a broad band with a maximum at 280  $\mu$ . It might be expected that saturation of the 10 : 11-double bond would cause a much greater shift of  $\lambda_{\max}$ . away from the visible region, but comparison of the spectra of coumarone and coumaran, where a similar saturation of the 2 : 3-double bond has been carried out, shows that for this type of molecule a shift of the maxima occurs towards the visible region of the spectrum. This anomalous shift appears to be associated with the presence of a cyclic oxygen atom in the molecule. Examination of the spectra of indene and indane (*J.*, 1934, 915) shows that saturation of the 1 : 2-double bond in this case causes the more usual shift of the absorption bands away from the visible, and a similar effect is observable on comparison of the spectra of 1 : 2 : 3 : 4-tetrahydrophenanthrene and 1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydrophenanthrene (Askew, *J.*, 1935, 512).

The close similarity of the spectra of coumaran and hexahydrodiphenylene oxide strongly supports the structure (IV) already suggested from dehydrogenation and oxidation experiments, and there can be little doubt that hexahydrodiphenylene oxide definitely exists as a stable chemical entity. The stereochemical configuration of the material prepared by us has, however, not been investigated, but it would appear to differ from that of the hexahydrodiphenylene oxide described by Cornforth, Hughes, and Lions (*J. Proc. Roy. Soc. New South Wales*, 1938, **71**, 323) who obtained it by pyrolysis of phenyl cyclohexenyl ether.

## EXPERIMENTAL.

*Exhaustive Hydrogenation of Diphenylene Oxide.*—Diphenylene oxide (1 kg.) in absolute alcohol (750 ml.) was exhaustively hydrogenated over Raney nickel (60 g.) in a 2-litre stainless-steel autoclave at 190°/200 atm. during 23 hours. The liquid products (1078 g.) were fractionated through a Stedman column (equivalent to 50 theoretical plates), at 20 mm., giving four main fractions :

Fraction 1 (34 g.), b. p. 116—118°/20 mm.,  $n_D^{20}$  1.4800, m. p. 4.5° (Found : C, 86.65; H, 13.3. Calc. for  $C_{12}H_{22}$  : C, 86.7; H, 13.3%), was shown to be dicyclohexyl by comparison of its infra-red absorption spectrum with that of dicyclohexyl prepared by dehydration of *cis*-cyclohexylcyclohexanol, followed by hydrogenation over palladium black in acetic acid solution at room temperature.

Fraction 2 (365 g.), b. p. 134—137°/20 mm.,  $n_D^{20}$  1.5000 (Found : C, 80.2; H, 11.0. Calc. for  $C_{12}H_{20}O$  : C, 80.0; H, 11.1%), agreed in its physical and chemical properties with perhydrodiphenylene oxide. Gilman *et al.* (*J. Amer. Chem. Soc.*, 1935, **57**, 2095) give b. p. 258—259°/740 mm.,  $n_D^{20}$  1.5023. Smith and Fuzek (*ibid.*, 1949, **71**, 415) give b. p. 162°/45 mm.,  $n_D^{20}$  1.4990.

Fraction 3 (205 g.), b. p. 149—151°/20 mm., solidified when kept and on recrystallisation from light petroleum had m. p. 61° (Found : C, 79.05; H, 11.8. Calc. for  $C_{12}H_{22}O$  : C, 79.05; H, 12.2%). This

material readily formed a phthalate, m. p. 115°, and a phenylurethane, m. p. 153°. Hüchel *et al.* (*Annalen*, 1930, **477**, 99) give *cis-o-cyclohexylcyclohexanol*, m. p. 63° (phenylurethane, m. p. 153°). Vavon (*Bull. Soc. chim.*, 1926, **39**, 1138) reports two forms of the phthalate, *viz.*, m. p. 112—113° and 126—127°.

Fraction 4 (272 g.), b. p. 151—153°/20 mm., also solidified after distillation. Repeated recrystallisation from light petroleum gave a material, m. p. 52—53° (Found : C, 79.1; H, 11.9. Calc. for  $C_{12}H_{22}O$  : C, 79.05; H, 12.2%). The derived phenylurethane, after repeated recrystallisation from light petroleum (b. p. 80—100°), had m. p. 133—134° alone and admixed with the phenylurethane (m. p. 133—134°) of authentic *trans-o-cyclohexylcyclohexanol* (prepared by reduction of *cyclohexylcyclohexanone*; Hüchel *et al.*, *loc. cit.*). Vavon (*loc. cit.*) gives phenylurethane, m. p. 132°; Hüchel *et al.* (*loc. cit.*) give 136°.

Chromic acid oxidation of the last two fractions at room temperature yielded the same *o-cyclohexylcyclohexanone*. Authentic *o-cyclohexylcyclohexanone*, prepared according to Hüchel *et al.* (*loc. cit.*), gave two products on treatment with alcoholic 2 : 4-dinitrophenylhydrazine : one, m. p. 120—121°, as orange flakes, easily soluble in alcohol, and a second, m. p. 176.5—177°, as orange needles (from alcohol-chloroform), sparingly soluble in alcohol. These two derivatives presumably correspond to the *syn*- and *anti*-forms. For ease in purification, the less soluble derivative melting at 176.5—177° was used, and admixture with the corresponding 2 : 4-dinitrophenylhydrazones prepared from the chromic acid oxidation products (both melting at 176—177°) led to no depression in melting point.

*Partial Hydrogenation of Diphenylene Oxide.*—Diphenylene oxide (1 kg.) in alcohol (750 ml.) was hydrogenated over Raney nickel at 200°/200 atm. until approximately 3 moles of hydrogen had been taken up. The crude product was steam-distilled, and the liquid products (483 g.) were fractionated through a Stedman-type column at 20 mm., yielding 50% of unchanged diphenylene oxide in the still and a main liquid fraction (36%), b. p. 140—142°/20 mm.,  $n_D^{20}$  1.5491, namely, *hexahydrodiphenylene oxide*, a colourless mobile liquid, with a pleasant aromatic smell, which did not yield a picrate (Found : C, 82.8; H, 7.9.  $C_{12}H_{14}O$  requires C, 82.7; H, 8.1%). A small fraction, b. p. 134—136°/20 mm., collected in the above distillation was also examined (see below).

*Purification of the hexahydrodiphenylene oxide.* 4 ml. of the fraction, b. p. 140—142°/20 mm., were adsorbed on a column of dry activated alumina (33' × ½'' at top, tapering to ¼'' at base) and subsequently desorbed with 20 ml. of absolute alcohol under slight air pressure at the top of the column (1—2 lbs./sq. in.), 0.2-ml. fractions being collected. The middle fractions (corresponding to 60% of the starting material) had a constant  $n_D^{20} = 1.5515$ .

*Dehydrogenation of hexahydrodiphenylene oxide.* The fraction, b. p. 140—142°/20 mm. (2.0 g.), was heated at 270—290° for 5 hours with platinised charcoal (0.2 g.). A quantitative yield of a white solid, m. p. 74—76° after one crystallisation from hot alcohol, was obtained, infra-red absorption analysis of this material showing it to be substantially pure diphenylene oxide. Repeated recrystallisation from alcohol gave m. p. 81.0—82.0° undepressed when mixed with authentic diphenylene oxide (m. p. 82—83°). Likewise a mixed m. p. of the derived picrate with the same derivative of diphenylene oxide (m. p. 96—97°) showed no depression.

*Chromic acid oxidation of tetra- and hexa-hydrodiphenylene oxide.* 5.0-G. quantities of both the hexahydrodiphenylene oxide and the synthetic tetrahydrodiphenylene oxide (see below) were separately oxidised by keeping them in contact with chromic acid at room temperature for 24 hours. Both compounds yielded the same  $\delta$ -*o*-hydroxybenzoylvaleric acid, m. p. 93—94° (Found : C, 64.7; H, 6.25. Calc. for  $C_{12}H_{14}O_4$  : C, 64.85; H, 6.35%).

*Examination of the fraction, b. p. 134—136°/20 mm.* Dehydrogenation of this fraction over platinised charcoal yielded a mixture of diphenylene oxide and fluorene. Infra-red absorption analysis of the diphenylene oxide used in these experiments showed it to contain a small amount of fluorene. Hydrogenation followed by fractionation had obviously concentrated the fluorene, in a hydrogenated form, in the 134—136°/20 mm. fraction. No further examination of the fraction was carried out.

*Partial Hydrogenation of 2 : 2'-Dihydroxydiphenyl.*—2 : 2'-Dihydroxydiphenyl (200 g.) in alcohol was hydrogenated over Raney nickel (20 g.) at 200°/120 atm. until approx. 2 moles of hydrogen had been absorbed. The dark brown, rather viscous product (193 g.) was distilled through a Stedman-type column, yielding two main liquid fractions, b. p. 142—146°/20 mm.,  $n_D^{20}$  1.5461 (Found : C, 82.8; H, 8.45. Calc. for  $C_{12}H_{14}O$  : C, 82.7; H, 8.1%) (8% yield), and 154—158°/20 mm.,  $n_D^{20}$  1.5695 (23% yield), and leaving a solid residue (60%) in the still.

Attempted purification of the lower-boiling fraction by adsorption on a column of dry alumina was not completely successful, since, although the refractive index of the material was raised considerably, the ultra-violet absorption spectrum indicated that this purified material contained only 80% of hexahydrodiphenylene oxide, the other 20% apparently being a mixture of tetra- and per-hydrodiphenylene oxides.

The higher-boiling fraction readily yielded a picrate, m. p. 98° (from alcohol), which gave no depression on admixture with the picrate of authentic tetrahydrodiphenylene oxide (m. p. 98°).

*Investigation of the solid residue.* In another experiment the total reaction product was steam-distilled, and the non-volatile portion worked up in the usual manner and finally distilled at 9 mm. pressure. After a small mobile fore-fraction, the bulk distilled as a viscous syrup, b. p. 194—200°/9 mm., which solidified on cooling and on fractional crystallisation from light petroleum (b. p. 60—80°) yielded a small amount of colourless hexagonal prisms, m. p. 180—181° (Found : C, 72.4; H, 11.2.  $C_{12}H_{22}O_2$  requires C, 72.7; H, 11.2%) and a much larger quantity of material as colourless plates, m. p. 115—116° (Found : C, 74.9; H, 8.5.  $C_{12}H_{18}O_2$  requires C, 75.0; H, 8.4%).

The former compound, 2 : 2'-*dihydroxydicyclohexyl*, m. p. 180—181°, readily formed a *bisphenylurethane*, m. p. 273° (from alcohol) (Found : C, 71.2; H, 7.4; N, 6.4.  $C_{24}H_{32}O_2N_2$  requires C, 71.55; H, 7.4; N, 6.4%), and a *bis*-3 : 5-*dinitrobenzoate*, m. p. 292° (crystallised from benzene-nitrobenzene) (Found : C, 53.5; H, 4.7; N, 10.0.  $C_{26}H_{28}O_{12}N_4$  requires C, 53.2; H, 4.5; N, 9.6%).

The latter compound, *o*-2-*hydroxycyclohexylphenol*, m. p. 115—116°, gave an olive-green colour in aqueous-alcoholic solution with neutral ferric chloride, and readily coupled with diazotised *p*-nitroaniline.

It yielded a *mono-phenylurethane*, m. p. 172° (Found : C, 73.3; H, 6.8; N, 4.5.  $C_{15}H_{11}O_2N$  requires C, 73.3; H, 7.0; N, 4.5%), by reaction with the alcoholic hydroxyl group. A *O*-carboxymethyl derivative, m. p. 132° (prepared as described by Koelsch, *J. Amer. Chem. Soc.*, 1931, **53**, 304), was also obtained.

*Hydrogenation of 2 : 2'-dihydroxydiphenyl over platinum.* 2 : 2'-Dihydroxydiphenyl, m. p. 109—111° (1.0 g.), in glacial acetic acid (25 ml.), was hydrogenated at room temperature and pressure over Adams's catalyst (0.2 g.). (Hydrogen absorption = 780 c.c. Theor. for complete saturation = 780 c.c.) The hydrogenated product was treated with dilute sodium hydroxide, and the insoluble oil removed by ether-extraction and subsequently distilled at reduced pressure (some decomposition occurring), to yield a small amount of a colourless liquid,  $n_D^{20}$  1.4989 (Found : C, 79.8; H, 11.3. Calc. for  $C_{12}H_{10}O$  : C, 79.9; H, 11.2%), considered to be perhydrodiphenylene oxide. The residue left in the flask treated with phenyl isocyanate yielded white feathery crystals (from alcohol), m. p. 272—273° (alone or admixed with the bisphenylurethane of 2 : 2'-dihydroxydicyclohexyl described above).

*Hydrogenation of tetrahydrodiphenylene oxide over platinum.* Pure tetrahydrodiphenylene oxide (0.3 g.), prepared as described below, was quantitatively hydrogenated at room temperature and pressure in the presence of glacial acetic acid and Adams's catalyst (0.1 g.), in an apparatus similar to that described by Jackson and Jones (*J.*, 1936, 895) until 42.5 c.c. of hydrogen had been absorbed (theor. for conversion into hexahydrodiphenylene oxide = 41.9 c.c.). Absorption took place rapidly during 20 minutes, but no break in the rate of absorption was observed at the end of this time. Measurement of the ultra-violet absorption spectrum of the recovered product,  $n_D^{20}$  1.5568 (Found : C, 82.7; H, 8.3. Calc. for  $C_{12}H_{14}O$  : C, 82.7; H, 8.1%), showed it to contain approximately 75% of unchanged tetrahydrodiphenylene oxide and 25% of perhydrodiphenylene oxide.

*Preparation of Pure Tetrahydrodiphenylene Oxide.*—Tetrahydrodiphenylene oxide, synthesised by Ebel's method (*Helv. Chim. Acta*, 1929, **12**, 11), was purified by regeneration from its picrate, m. p. 98°, and possessed the following physical constants : b. p. 154—156°/20 mm.,  $n_D^{20}$  1.5787 (Found : C, 83.6; H, 7.2. Calc. for  $C_{12}H_{12}O$  : C, 83.7; H, 7.0%).

*Preparation of Pure Diphenylene Oxide.*—To tetrahydrodiphenylene oxide (2.5 g.) in dry carbon tetrachloride (35 ml.) were added *N*-bromosuccinimide (5.2 g.) and benzoyl peroxide (0.1 g.), and the mixture was gently refluxed for 1½ hours. Sodium acetate (5 g.) and glacial acetic acid (2 ml.) were then added and the whole was refluxed for a further half hour. The reaction mixture was poured on ice-sodium hydroxide (solid). The product, isolated in ether, was distilled at 2 mm., giving 1.8 g. (72%) of a slightly yellow solid of m. p. about 79°. After 2 recrystallisations from alcohol, chromatography [in light petroleum (b. p. 40—60°)] on alumina, recrystallisation from alcohol, and sublimation under reduced pressure, the diphenylene oxide was obtained as lustrous white flakes, m. p. 82.0—83.0° (Found : C, 85.5; H, 4.65. Calc. for  $C_{12}H_8O$  : C, 85.7; H, 4.8%) (F. Williams, *loc. cit.*, gives the m. p. of pure diphenylene oxide as 82.8—83.0°).

*Preparation of Pure Coumarone.*—Recrystallised coumarilic acid (*Org. Synth.*, **24**, 33), m. p. 192°, was dry distilled with soda-lime. Ether-extraction of the oil-water distillate, followed by distillation of the dried product, yielded coumarone,  $n_D^{20}$  1.5666 (*J. Inst. Physics*, 1947, **33**, 687 :  $n_D^{20}$  1.5663).

*Preparation of Pure Coumaran.*—Coumarone, b. p. 171°, in glacial acetic acid was hydrogenated over Adams's catalyst at room temperature and pressure until 1 g.-mol. of hydrogen had been absorbed. The recovered product, purified by conversion into the picrate, had constant m. p. 75—76° (pre-heated bath) after 3 recrystallisations from alcohol. Regeneration from the picrate followed by distillation yielded coumaran,  $n_D^{25}$  1.5479 (Found : C, 79.7; H, 6.6. Calc. for  $C_8H_8O$  : C, 80.0; H, 6.7%) (Rindfus, *J. Amer. Chem. Soc.*, 1919, 669, gives  $n_D^{20}$  = 1.543).

From the higher refractive index and the slight inflexion in the ultra-violet absorption curve at 245 m $\mu$ . it would appear that the sample still contained a small amount of coumarone. Owing to the small amount available further purification was not undertaken.

*Measurement of Ultra-violet Absorption Spectra.*—The ultra-violet absorption spectra were measured with a Beckman Quartz Spectrophotometer, using approx. 10<sup>-4</sup>M-solutions in cyclohexane.

Analyses were carried out by Dr. Weiler and Dr. Strauss, Oxford.

In the temporary absence of the senior author (J. I. J.), Dr. N. J. Cartwright supervised the concluding stages of the work and we are also indebted to him for valuable assistance in the preparation of the manuscript. We thank Mr. W. Kynaston for measuring the ultra-violet absorption spectra and Dr. E. F. G. Herington for many helpful discussions on their interpretation. Mr. J. Hales kindly performed the infra-red absorption analyses.

The work described above has been carried out as part of the research programme of the Chemical Research Laboratory, Department of Scientific and Industrial Research, and this paper is published by permission of the Director of the Laboratory.