635. *Experiments in the* cyclo*Butane Series. Part III.* Attempts to obtain Optically Active Substituted* 1 : 2-*Dimethylene*cyclo*butanes.*

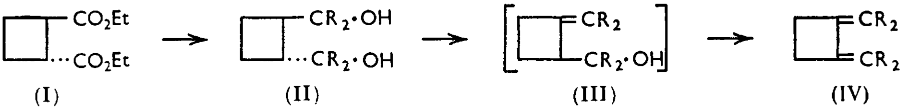
By F. B. Kipping and J. J. Wren.

Optically active derivatives of *cyclo*butane (IV; R = Ph) could not be obtained by chromatography on (+)-lactose or (IV; R = Ph and *p*-C_6H_4Me) by dehydration from an active diol (II). Attempts to make derivatives of the compound (IV; R = Ph) with acidic groups substituted in the phenyl radicals are described. Unusual difficulties were encountered in the preparation of Grignard reagents from benzyloxyhalogenobenzenes.

A study of the ultraviolet spectrum of 1 : 2-bisdiphenylmethylene*cyclo*butane (IV; R = Ph),[1] together with those of homologues (R = *p*-tolyl, *p*-*iso*propylphenyl, and *p*-*tert.*-butylphenyl), strongly favoured a non-planar configuration for such a system [2] and molecular models served to confirm this. Attempts have now been made to demonstrate optical activity in compounds of this type.

The hydrocarbon (IV; R = Ph) crystallises from various solvents as tufts of large needles, but the crystals show no evidence of being a conglomerate; chromatography on activated (+)-lactose [3, 4] failed to effect resolution.

The synthesis of these dienes is indicated (I ⟶ II ⟶ IV) and it was thought that an optically active diene might be obtained by starting with (+)- or (—)-ester (I) : loss of one molecule of water from the diol (II) should give an active olefinic alcohol (III), which by stereospecific dehydration might yield an optically active hydrocarbon (IV).



Accordingly, (±)-*trans*-*cyclo*butane-1 : 2-dicarboxylic acid was resolved by Goldsworthy's method,[5] and the esterified (—)-acid treated with phenylmagnesium bromide to give the (—)-diol (II; R = Ph), which was then treated with a variety of dehydrating agents. No appreciable dehydration occurred in boiling acetic anhydride, with boiling 6% aqueous oxalic acid, or in light petroleum saturated with toluene-*p*-sulphonic acid at 60°. Reagents which effected dehydration, namely, hydrochloric acid in glacial acetic acid, iodine in xylene, toluene-*p*-sulphonic acid in toluene, and even (—)-camphor-10-sulphonic acid in toluene,[6] all yielded optically inactive diene. Use of any of these

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* Part II, *J.*, 1957, 1733.

[1] Alberman and Kipping, *J.*, 1951, 779.

[2] Alberman, Haszeldine, and Kipping, *J.*, 1952, 3287.

[3] Henderson and Rule, *Nature*, 1938, **141**, 917; *J.*, 1939, 1568; Lecoq, *Bull. Soc. roy. Sci. Liège*, 1943, **12**, 316.

[4] Prelog and Wieland, *Helv. Chim. Acta*, 1944, **27**, 1127.

[5] Goldsworthy, *J.*, 1924, 2012.

[6] Wuyts, *Bull. Soc. chim. Belg.*, 1921, **30**, 30; Maitland and Mills, *J.*, 1936, 987.

reagents is open to serious objection, since they might promote *cis-trans*-isomerisation of the phenyl groups in (IV), and this would cause racemisation (the dimethylamino-derivatives to be described in a future communication isomerised very rapidly in presence of acid). Thermal dehydration, on the other hand, appeared more suitable, but this also yielded optically inactive dienes (IV; R = Ph and R = *p*-tolyl).

Attempts were next made to prepare a diene containing acidic groups in the *para*-positions in the benzene rings by using, instead of phenylmagnesium bromide, Grignard reagents from *p*-benzyloxyhalogenobenzenes (V; X = halogen) or *p*-methoxymethoxyhalogenobenzenes (VI; X = halogen). It was proposed to remove the benzyl groups by hydrogenolysis, or the methoxymethyl groups by hydrolysis, and then to convert the hydroxyl groups into $O{\cdot}CH_2{\cdot}CO_2H$, thus giving finally (IV; R = p-$HO_2C{\cdot}CH_2{\cdot}O{\cdot}C_6H_4$). Although Grignard reagents have been prepared from *p*-bromoanisole and *p*-bromophenetole[7] in very good yield, neither the chloride (V; X = Cl) nor the bromide (V; X = Br) reacted with magnesium: this was demonstrated by recovery of the pure halides and by the sensitive colour test for Grignard reagents.[8] The iodide (V; X = I) reacted sluggishly with activated magnesium,[9] but although the reaction was repeated frequently in attempts to improve the yield of Grignard reagent [which was measured by the yield of *p*-benzyloxybenzoic acid (V; X = CO_2H) isolated after carboxylation and hydrolysis], satisfactory results could not be obtained.

p-$Ph{\cdot}CH_2{\cdot}O{\cdot}C_6H_4X$	$MeO{\cdot}CH_2{\cdot}O{\cdot}C_6H_4X$$p$-	(p-$Ph{\cdot}CH_2{\cdot}O{\cdot}C_6H_4)_2CMe{\cdot}OH$
(V)	(VI)	(VII)

The use of activated magnesium–copper alloy[10] with the iodide (V; X = I) was next investigated: a fairly vigorous reaction occurred at first, but it died down as a sticky oil was deposited from the solution. Addition of benzene to the ether largely prevented this deposition and improved the yield by about 20%. Despite the recovery of large amounts of unchanged iodide, further additions of activated magnesium or alloy had virtually no effect upon the yield of Grignard reagent, which was diminished when shorter or longer reaction periods were employed. The best yield of carboxylation product obtained was 46%.

Lithium reacted very sluggishly with the bromide (V; X = Br) in boiling ether, and only 1% of carboxylation product was obtained after thirty hours' stirring under nitrogen; a considerable amount of phenol was isolated from the product. In view of the known lability of benzyl ethers towards lithium aryls[11] the reaction was not investigated further. For comparative purposes, a Grignard reaction was attempted on benzyl *m*-iodophenyl ether under the conditions which were best for the *p*-isomer: after starting vigorously the reaction yielded only 36% of carboxylation product.

After a preliminary experiment, in which the Grignard reagent (V; X = MgI) reacted with ethyl acetate to yield the expected product, 1 : 1-di-*p*-benzyloxyphenylethanol (VII), it was then treated with the *cyclo*butane diester (I): this yielded a small amount of an unidentified colourless substance (see Experimental section) but none of the expected diol (II; R = p-$Ph{\cdot}CH_2{\cdot}O{\cdot}C_6H_4$) which had in fact already undergone dehydration to the yellow diene (IV; R = p-$Ph{\cdot}CH_2{\cdot}O{\cdot}C_6H_4$). This illustrates that the ease of dehydration of the diols (II) depends upon the electron-releasing power of the groups R: the diol in which R = *p*-tolyl is dehydrated more readily than those in which R = Ph, p-$Pr^iC_6H_4$, and p-$Bu^tC_6H_4$ (see ref. 1 and Experimental section), and less readily than that in which R = p-$Ph{\cdot}CH_2{\cdot}O{\cdot}C_6H_4$.

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[7] Gilman, Zoellner, Selby, and Boatner, *Rec. Trav. chim.*, 1935, **54**, 584.

[8] Gilman and Schulz, *J. Amer. Chem. Soc.*, 1925, **47**, 2002.

[9] Holliman and Mann, *J.*, 1942, 737.

[10] Gilman, Peterson, and Schulze, *Rec. Trav. chim.*, 1928, **47**, 19; Gilman and Heck, *Bull. Soc. chim. France*, 1929, **45**, 250.

[11] Luttringhaus and Sääf, *Angew. Chem.*, 1938, **51**, 915; Wittig and Löhmann, *Annalen*, 1942, **550**, 260.

Treatment of the diene (IV; R = *p*-$Ph{\cdot}CH_2{\cdot}O{\cdot}C_6H_4$) in benzene solution with hydrogen at atmospheric temperature and pressure, with palladium–charcoal as catalyst, failed to reduce the diene system (possibly owing to steric hindrance), but neither did it hydrogenolyse the benzyl ether groupings. (Successful hydrogenolysis of benzyl *p*-chlorophenyl ether (V; X = Cl) confirmed the activity of the catalyst used.) Hydrogenation at elevated temperature and pressure was precluded, since it had been shown to reduce the diene system of the parent hydrocarbon (IV; R = Ph).[12] Hydrochloric acid at 100° [13, 14] also failed to debenzylate the molecule. In view of the wide variety of benzyl ethers which have been successfully hydrogenolysed,[15] these findings may be attributed to conjugation of the lone electron pairs of the oxygen atom with the diene system.

The bromide (VI; X = Br) and the iodide (VI; X = I) proved to be unstable in alkaline as well as in acidic media and both failed to yield Grignard reagents, probably because of this lability, since traces of formaldehyde, methanol, or phenol would inhibit the Grignard reaction.

EXPERIMENTAL

M. p.s are corrected, b. p.s uncorrected. Infrared spectra were examined in Nujol mull, and ultraviolet spectra were measured on Unicam SP 500 spectrophotometers.

Chromatography of 1 : 2-*Bisdiphenylmethylene*cyclo*butane* (IV; R = Ph) *on* (+)-*Lactose*.—The diene (0·50 g.) in light petroleum (previously shaken with concentrated sulphuric acid and distilled; b. p. 40—60°) was chromatographed on lactose (700 g.; column diameter 55 mm.), activated according to Prelog and Wieland [4] but without the final 250-mesh sifting. The diene was eluted in eighteen fractions: several of these were examined polarimetrically in 4 dm. tubes, but all were optically inactive. The first six fractions were combined and evaporated at room temperature, and the residue dissolved in benzene: no optical activity was detected in the resulting solution, or in a solution similarly obtained from the last six fractions.

(±)-trans-cyclo*Butane*-1 : 2-*dicarboxylic Acid*.—The *cis*-anhydride was prepared in 30% overall yield from adipic acid [16] *via* the diethyl αδ-dibromoadipates,[17] and converted into the (±)-*trans*-acid by Perkin's method.[18] The resulting dark solution in concentrated hydrochloric acid was boiled with charcoal, filtered, and evaporated, and the residue crystallised from 20 : 1 benzene–dioxan. The yield was 69% and the m. p. 130·5—131°. Its infrared spectrum showed bands at 2630 (OH str.), 1693 (C:O str.), and 917 cm.$^{-1}$ (*cyclo*butane ?).

(−)-trans-cyclo*Butane*-1 : 2-*dicarboxylic Acid*.—Goldsworthy's resolution [5] was repeated. The diquinine salt of the (−)-acid, recrystallised from water and dried *in vacuo* at 120°, gave $[\alpha]_D^{17\cdot5}$ −174°, $[\alpha]_D^{29\cdot5}$ −168° (*c* 0·5), $[\alpha]_D^{29}$ −171° (*c* 1 in EtOH); it decomposed before melting (Found: C, 69·4; H, 7·3; N, 6·95. Calc. for $C_{46}H_{56}O_8N_4$: C, 69·7; H, 7·1; N, 7·1%). These values were not appreciably changed by further recrystallisation or by liberating the acid and reconverting it into the salt, and they differ considerably from Goldsworthy's, $[\alpha]_D$ −192·9° (concentration and temperature not stated). The discrepancy between our result and Goldsworthy's clearly cannot be accounted for by the differences of temperature and concentration, and it seems that it may be due mainly to the presence of water in the alcohol used by Goldsworthy, as shown:

Ethanol	Anhydrous	+10% water	+19% water
$[\alpha]_D^{19\cdot5}$ ……………………	−171°	−188°	−198°
$[\alpha]_D^{29}$ ……………………	−167	−182	−192

Excess of ammonia was added to a solution of the salt in hot water, the precipitated quinine removed by filtration, and the filtrate acidified with hydrochloric acid and evaporated under reduced pressure; after thorough drying, the residual solid was extracted with anhydrous ether, and the extract evaporated to give the (−)-acid, recrystallising from benzene [in which it is more soluble than the (±)-acid] as prisms, m. p. 116—117°, $[\alpha]_D^{18\cdot5}$ −158°, $[\alpha]_D^{29}$ −157°

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[12] K. B. Alberman, Ph.D. Thesis, Cambridge, 1951.

[13] Sintenis, *Annalen*, 1872, **161**, 329.

[14] Baker, Nodzu, and Robinson, *J.*, 1929, 74.

[15] Hartung and Simonoff, " Organic Reactions," Vol. VII, 1953, pp. 295—301.

[16] Buchman, Reims, Skei, and Schlatter, *J. Amer. Chem. Soc.*, 1942, **64**, 2696.

[17] *Org. Synth.*, 1946, **26**, 57.

[18] Perkin, *J.*, 1894, 572.

(*c* 0·75 in H_2O) (Found: C, 50·1; H, 5·7. Calc. for $C_6H_8O_4$: C, 50·0; H, 5·6%). Goldsworthy reported m. p. 105°, $[\alpha]_D^{30}$ $-124{\cdot}3°$ (*c* 0·85 in H_2O); the possibility that his specimen had been partially racemised by recrystallisation from concentrated hydrochloric acid was eliminated, since (−)-acid recovered after 2 hr. in boiling concentrated hydrochloric acid had $[\alpha]_D^{22}$ $-151°$. Changes of concentration and temperature had virtually no effect on the rotation of the (−)-acid.

The mother-liquor from the original crystallisation of the diquinine salt yielded acid having $[\alpha]_D^{29}$ $+86°$ (from benzene): treatment of this with the theoretical amount of quinine for (−)-acid present, with care that the salt separated as crystals and not as an oil, yielded acid, after removal of the salt, having $[\alpha]_D^{22}$ $+107°$, which was then fractionally crystallised from a large volume of benzene. Ultimately a small quantity of material, $[\alpha]_D^{21}$ $+150°$, was obtained; thus, the (+)-acid was not isolated in a pure state. One of the crops from benzene had m. p. 105—108°, $[\alpha]_D^{21}$ $+123{\cdot}8°$ {cf. Goldsworthy's values for the (+)-acid, m. p. 105°, $[\alpha]_D^{30}$ $+123{\cdot}3°$}.

Diethyl (−)-trans-cyclo*Butane*-1 : 2-*dicarboxylate* (I).—(−)-Acid (3·1 g.) and 10% ethanolic sulphuric acid (22 ml.) were refluxed during 2½ hr., cooled, and poured into water, and the resulting mixture was extracted three times with carbon tetrachloride. The combined extracts were washed with dilute aqueous sodium carbonate, then with water, dried ($CaCl_2$), and distilled, giving 3·3 g. (78%) of the (−)-*diester*, b. p. 80·3°/1·0 mm., n_D^{22} 1·4372, $[\alpha]_D^{15{\cdot}5}$ $-124°$, $[\alpha]_D^{29}$ $-122°$ (*c* 0·5 in acetone) (Found: C, 59·8; H, 8·2. $C_{10}H_{16}O_4$ requires C, 60·0; H, 8·0%). The rotations do not agree with Goldsworthy's for the (+)-diester, $[\alpha]_D^{30}$ $+77{\cdot}9°$ (in acetone).

(−)-trans-1 : 2-*Di*-(α-*hydroxydiphenylmethyl*)cyclo*butane* (II; R = Ph).—Prepared from the (−)-diester (1·5 g.) exactly as was the (±)-compound from the (±)-diester,[1] the diol (2·8 g., 89%), crystallised from light petroleum (b. p. 100—120°), had m. p. 158—161° and $[\alpha]_D^{29}$ $-56{\cdot}4°$ (*c* 0·5 in acetone). Recrystallisation from aqueous ethanol gave needles, m. p. 174—175·5°, $[\alpha]_D^{14}$ $-53°$, $[\alpha]_D^{29}$ $-59{\cdot}0°$ (*c* 0·5 in acetone) (Found: C, 85·5; H, 7·0. $C_{30}H_{28}O_2$ requires C, 85·7; H, 6·7%).

Thermal dehydration of the diol (II; R = Ph). (−)-Diol (0·65 g.) was heated at 200—210° during 2¼ hr. in a stream of dry, acid-free nitrogen. The yellow glass which formed on cooling was extracted with boiling light petroleum (b. p. 60—80°), and the extract decanted from a small residue of unchanged diol. The extract, which had $[\alpha]_D$ *ca.* $+22°$, was run on to an alumina column (25 g.; diameter 10 mm.) which was then developed with light petroleum: a large, pale yellow zone of the diene was eluted first, giving an optically inactive solution which yielded rods of the (±)-diene, m. p. 182·5—183·5°. A pale orange band was eluted next, which gave an optically inactive solution and yielded a few orange-brown crystals on evaporation. Two coloured bands then remained on the column, one small and dark at the top, and the other sharp and yellow; elution of these with acetone gave a strongly dextrorotatory solution, which gave a little viscous yellow oil on evaporation, and this could not be crystallised.

Tetra-p-*tolyl Diene* (IV; R = p-C_6H_4Me).—Use of the (−)-diester in place of the (±)-diester employed previously[2] gave a Grignard product consisting of both diol (II; R = p-C_6H_4Me) and diene (IV; R = p-C_6H_4Me), and neither could be crystallised from ethanol (contrast the earlier experiment). The strongly lævorotatory product was therefore heated slowly to 170° in a stream of dry, acid-free nitrogen; dehydration was proceeding rapidly at 140°, and no diol was found in the product, chromatography of which gave results closely parallel to those described above for the tetraphenyldiene.

Benzyl p-*Chlorophenyl Ether* (V; X = Cl).—*p*-Chlorophenol (25 g.), benzyl chloride (26 g.), and potassium carbonate (28 g.) were heated under reflux in acetone (50 ml.) during 7 hr., with intermittent shaking to break the solid mass of inorganic material.[19] After removal of the acetone under reduced pressure the residue was shaken with water and ether, and the ether layer washed with alkali and water and dried ($CaCl_2$). The ether was then distilled, residual benzyl chloride removed *in vacuo*, and the product crystallised from methanol (31·2 g., 73%; m. p. 71—72°; lit.,[20] 71°).

Benzyl *p*-bromophenyl ether (V; X = Br), prepared as above (yield 61%), had m. p. 62—63·5° (lit.,[13, 21] 59—59·5°, 64—65°).

Benzyl *p*-iodophenyl ether (V; X = I), prepared as above, except that refluxing was for 74 hr. (yield 85%), had m. p. 62—63° (lit.,[22] 62—63°).

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[19] Claisen, *Annalen*, 1919, **418**, 69; Powell and Adams, *J. Amer. Chem. Soc.*, 1920, **42**, 646.

[20] Baw, *Quart. J. Indian Chem. Soc.*, 1926, **3**, 101.

[21] Auwers, *Annalen*, 1907, **357**, 85.

[22] Matheson and McCombie, *J.*, 1931, 1103.

Benzyl *m*-iodophenyl ether, prepared as was the *p*-isomer, crystallised from light petroleum (b. p. 40—60°) and separated by centrifugation, had m. p. 51·5—52·5° (lit.,[23] 52°).

Grignard Reagent from Benzyl p-*Iodophenyl Ether.*—Active magnesium–copper alloy[10] (0·45 g.) was reactivated and a solution of the iodide (4·0 g.) in dry ether (20 ml.) and dry benzene (4 ml.) added during ¾ hr. with refluxing. After a further 2¼ hours' refluxing, freshly ground solid carbon dioxide was added, and the mixture treated with ice and sulphuric acid and extracted with ether. The ether layer was then extracted twice with large volumes of 10% aqueous sodium carbonate (the sodium salt is only sparingly soluble), which was then acidified and extracted with ether. After being washed with water the ether layer was evaporated, giving 1·35 g. (46%) of crude *p*-benzyloxybenzoic acid (V; X = CO_2H) : recrystallisation from aqueous ethanol (charcoal) and vacuum-sublimation at 120° yielded colourless plates, m. p. 193·5—194·5° (lit.,[24] 188°) (Found : C, 73·4; H, 5·1. Calc. for $C_{14}H_{12}O_3$: C, 73·7; H, 5·3%).

Extraction of the ethereal layer, after the sodium carbonate extraction, with aqueous sodium hydroxide gave no phenolic material but benzyl *p*-iodophenyl ether (1·9 g., 48%) was recovered from it.

The yield of acid obtained as above but without the addition of benzene was 24%, and on use of benzene but activated magnesium instead of the alloy was 37%.

1 : 1-*Di*-p-*benzyloxyphenylethanol* (VII).—Pure ethyl acetate (0·227 g.) in ether (5 ml.) was added to a Grignard solution prepared as above. After hydrolysis with ice and ammonium chloride the product was worked up and crystallised from benzene, giving 0·556 g. of the *alcohol*, m. p. 182—184°. Recrystallisation from acetic acid gave plates, m. p. 187—188° (Found : C, 82·2; H, 6·7. $C_{28}H_{26}O_3$ requires C, 81·9; H, 6·4%).

1 : 2-*Bisdi*-p-*benzyloxyphenylmethylene*cyclo*butane* (IV; R = p-Ph·CH_2·O·C_6H_4).—(±)-*trans*-Diester (I) (0·58 g.) in ether (15 ml.) was added during ½ hr. to the refluxing Grignard solution prepared as above, and refluxing maintained during a further 1½ hr. The resulting yellow solution was poured on ice and ammonium chloride, and the ethereal layer evaporated to give a viscous, yellow-brown oil (5·8 g.) which was then dissolved in hot benzene. The filtered solution was evaporated to 15 ml. and cooled; it then yielded crystals of an unidentified colourless substance (70 mg.), m. p. 213—216° (decomp.), from aqueous ethanol (see below). After removal of these crystals the benzene was evaporated and the residual oil extracted with a large volume of *cyclo*hexane : the resulting solution was run on to an alumina column (250 g.; diameter 35 mm.). Unchanged iodide was eluted in *cyclo*hexane; the *diene*, which formed a sharp yellow band near the top of the column, was then eluted in benzene, giving yellow needles from acetone (0·48 g., 21%), m. p. 179—180°, which fluoresced intensely pale green in ultraviolet light (Found : C, 86·1; H, 6·1. $C_{58}H_{48}O_4$ requires C, 86·1; H, 6·0%). The ultraviolet absorption maxima of this compound, $\lambda_{max.}$ (in EtOH) 372 mμ (ε 25,300) and 272 mμ (ε 39,600), show bathochromic and hyperchromic displacements compared with those of the parent hydrocarbon (IV; R = Ph).

Unidentified Colourless Substance (see above).—After chromatography (benzene–chloroform on alumina) and vacuum-sublimation at 205° it had m. p. 220·5—221° [Found : C, 83·1; H, 6·6%; *M* (Rast), 219], $\lambda_{max.}$ (in EtOH) 266 mμ (ε 14,500 for mol. wt. 219). The infrared spectrum had strong bands at 3370 (OH str.), 1616, 1603, 1504, 1248, 816, 747, and 700 cm.$^{-1}$, and a band of medium strength at 918 cm.$^{-1}$ which might indicate the presence of a *cyclo*butane ring :[25] the spectra of most of the 1 : 2-disubstituted *cyclo*butanes studied in the present work showed such bands (918—911 cm.$^{-1}$). The substance was unaffected by hydrochloric acid in boiling glacial acetic acid, was insoluble in boiling aqueous sodium hydroxide, and gave no oxime, and its ethanolic solution gave no colour with ferric chloride; it did not fluoresce in ultraviolet light. Its m. p. is high compared with those of most possible products of the reaction, but is similar to that (215°, not sharp) recorded for 4 : 4′-dibenzyloxydiphenyl;[26] this compound is excluded by the analysis and infrared spectrum.

Grignard Reagent from Benzyl m-*Iodophenyl Ether.*—*m*-Benzyloxybenzoic acid (36%) was obtained in the same way as the *p*-isomer, and recovery of the iodide was 22%. The acid, crystallised from acetic acid, had m. p. 135·5—136° (lit.,[27] 134°).

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[23] Buchan and McCombie, *J.*, 1932, 2857.
[24] Cavallito and Buck, *J. Amer. Chem. Soc.*, 1943, **65**, 2140.
[25] Bellamy, " The Infrared Spectra of Complex Molecules," Methuen, London, 1954, pp. 28—29.
[26] Van Alphen, *Rec. Trav. chim.*, 1931, **50**, 415.
[27] Jones, *J.*, 1943, 430.

Hydrogenolysis of Benzyl p-*Chlorophenyl Ether* (V; X = Cl).—The ether (1·02 g.), 5% palladium–charcoal (60 mg.), and " AnalaR " acetic acid (15 ml.), were shaken under hydrogen at atmospheric temperature and pressure: hydrogen uptake was 95% in 35 hr., and pure *p*-chlorophenol (83%) was isolated.

p-*Iodo-methoxymethoxybenzene* (VI; X = I).—Chloromethyl methyl ether (7·32 g.) was added slowly to *p*-iodophenol (20·0 g.) and sodium (2·00 g.) in ethanol (70 ml.), in a flask fitted with an efficient reflux condenser: a vigorous reaction took place and sodium chloride was deposited from the solution. Water (400 ml.) was then added, the organic layer washed with aqueous sodium hydroxide, then with water, ether was added, and the solution dried (K_2CO_3). Filtration and distillation then yielded 7·06 g. (29%) of the *acetal* (VI; X = I), b. p. 89—92°/0·6 mm.: this was redistilled and the middle fraction taken (Found: C, 36·4; H, 3·6. $C_8H_9O_2I$ requires C, 36·4; H, 3·4%). Left with water overnight, the crude reaction product yielded only *p*-iodophenol; the purified acetal decomposed over pellets of potassium hydroxide.

p-*Bromo-methoxymethoxybenzene* (VI; X = Br).—Prepared as above, this had b. p. 72°/0·5 mm. Redistillation always left appreciable white residues, m. p. >150° (product of decomposition + condensation?). It decomposed in one week in ether over anhydrous potassium carbonate; no satisfactory analysis was obtained (Found: C, 43·7; H, 3·7. Calc. for $C_8H_9O_2Br$: C, 44·3; H, 4·2%).

Attempted Preparation of Grignard Reagents from p-*Halogeno-methoxymethoxybenzenes* (VI).—Activated magnesium–copper alloy gave exothermic reactions with ethereal solutions of the bromide and the iodide, but the colour test was negative: these reactions appeared to be formation of the phenoxides, since *p*-iodophenol in ether also reacted vigorously with the alloy. Moreover, no carboxylic acid was isolable after carboxylation of the products.

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