212. *Reduction by Dissolving Metals. Part II.*

By Arthur J. Birch.

The reduction of a number of substituted vinyl carbinols by means of sodium and alcohol in liquid ammonia has been investigated. The following transformations were observed with compounds in which the vinyl double bond is aliphatic: sabinol (III) $\longrightarrow$ α-thujene (IV); 1-vinyl*cyclo*hexanol (VI) $\longrightarrow$ ethylidene*cyclo*hexane (VII); 3-hydroxy-1-phenyl-Δ^1-butene (X, R = H) $\longrightarrow$ 1-phenyl-Δ^2-butene (XI; R, R′ = H) and a trace of 3-hydroxy-1-phenylbutane (XII, R = H); 3-hydroxy-1-phenyl-3-methyl-Δ^1-butene (X, R = CH_3) $\longrightarrow$ 1-phenyl-3-methyl-Δ^2-butene (XI; R = H, R′ = CH_3) and 2-hydroxy-4-phenyl-2-methylbutane (XII, R = CH_3). 4-Hydroxy-Δ^2-octene (IX) was mainly unchanged but gave a trace of Δ^2- or Δ^3-octene; and carveol (V) and 1-Δ^1-*heptenyl*cyclo*hexanol* (VIII) were not reduced. The products obtained with compounds where the double bond forms part of an aromatic system are tabulated.

All of these results are consistent with the hypothesis that a mesomeric anion is formed in the transition state.

In Part I (J., 1944, 430) the view was expressed that the hydrogenolysis by means of sodium and alcohol in liquid ammonia of vinyl carbinols such as geraniol (I, R = OH) takes place by way of the anion such as (II) because of the frequent rearrangement of the double bond in the process. The structural requirements

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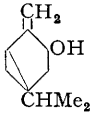
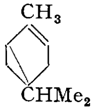
* The details given by Heilbron (*op. cit.*, Vol. III, p. 210, last line) are erroneous, and presumably refer to its *N*-β-naphthyl derivative (Ris, *Ber.*, 1887, **20**, 2625).

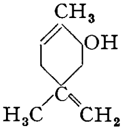
for hydrogenolysis, and the relation between structure and the position of the double bond in the products, have now been investigated.

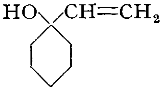
$CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CH_2R$
(I.)

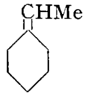
$CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}\overbrace{CMe{=}CH{=}CH_2}$
(II.)

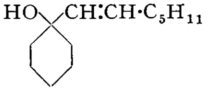

(III.)


(IV.)


(V.)


(VI.)


(VII.)

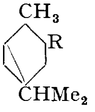

(VIII.)

$CHMe{:}CH{\cdot}CH(OH){\cdot}C_4H_9$
(IX.)

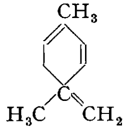
$CHPh{:}CH{\cdot}CR(OH){\cdot}CH_3$
(X.)

$CHPhR{\cdot}CH{:}CR'{\cdot}CH_3$
(XI.)

$CH_2Ph{\cdot}CH_2{\cdot}CR(OH){\cdot}CH_3$
(XII.)


(XIII.)

$CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe(OH){\cdot}CH{:}CH_2$
(XV.)


(XIV.)

In the following table the reductions were carried out as nearly as possible under the same conditions. Since all the carbinols are readily soluble in liquid ammonia, the relative yields of hydrogenolysis product give a rough indication of the relative ease of reduction. In the case of furfuryl alcohol the 2-methylfuran is so volatile in boiling ammonia that the method had to be modified, but the amount of unchanged material was the same with the original or the modified process.

Compound reduced.	Product.
Benzyl alcohol	Toluene (unchanged negligible).
Phenylmethylcarbinol	Ethylbenzene (unchanged negligible).
Phenyldimethylcarbinol	*iso*Propylbenzene (unchanged negligible).
Phenylbutylcarbinol	*n*-Amylbenzene (unchanged negligible).
p-Methoxyphenylcarbinol	*p*-Tolyl methyl ether (29%). Dihydro-*p*-tolyl methyl ether (7%). Unhydrogenolysed (containing some nuclear hydrogenated product) (59%).
Furfuryl alcohol	2-Methylfuran (20%), unchanged (38%).
Furfurylbutylcarbinol	2-*Amylfuran* (3·5%), unchanged (82%).

The reduction of *d*-sabinol (III) to *d*-thujyl alcohol (XIII, R = OH) by means of sodium and amyl alcohol (Semmler, *Ber.*, 1900, **33**, 1461) may at first appear to be a direct reduction of the double bond made possible by conjugation with the *cyclo*propane ring. However, it seems probable, from the fact observed by Schmidt (*Ber.*, 1929, **62**, 103) that sabinol is readily isomerised by alkaline reagents to thujone (XIII, R = :O), that formation of the latter precedes reduction. No thujyl alcohol was produced by reaction with sodium and alcohol in liquid ammonia, the product being *l*-α-thujene, recognised by oxidation to *d*-α-thujaketonic acid. It gives a crystalline *nitrolpiperidine* which may be useful for identification in essential oils.

Since the triple bond is readily reduced to a double bond by sodium in liquid ammonia, the carbinols (VI) and (VIII) were prepared from the corresponding acetylenes by this reagent (cf. Campbell and Eby, *J. Amer. Chem. Soc.*, 1941, **63**, 2683). The hydrocarbon formed by further reduction of (VI) was shown to be ethylidene*cyclo*hexane (VII) since it gave in good yield a characteristic nitrosochloride, convertible into derivatives of acetyl*cyclo*hexene. Examination of its infra-red absorption spectrum by Dr. H. W. Thompson and Mr. Torkington (Oxford) showed the bands expected for this type of double bond and indicated that the alternative vinyl*cyclo*hexane could not be present to any appreciable extent.

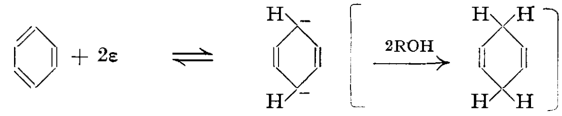
d-Carveol was not reduced, and distillation of both the treated and the untreated substance with a trace of iodine gave water and a hydrocarbon (XIV) characterised by its crystalline maleic anhydride *adduct*.

Reduction of the benzenoid compounds may be complicated by the addition of hydrogen atoms to the ring (Part I, *loc. cit.*), but this was negligible except in the case of *p*-methoxyphenylcarbinol, where hydrogenolysis was difficult. It is noteworthy that none of the furan derivatives showed any appreciable reduction of the ring, probably because of the unshared electrons on the oxygen atom. With (X, R = H) and (X, R = CH_3) there is some reduction of the vinyl double bond made possible by conjugation with the aromatic ring.

On the assumption that the anion forms part of the transition state, its ease of formation, which must be greater the greater the stability of the negative charge in the mesomeric system, probably decides whether or not hydrogenolysis can occur. From the known electrical effects of the groups and from the relative basicities of carbanions (cf. Morton, *Chem. Reviews*, 1944, **35**, 8) it is clear that the stability of a negative charge is greater the lower the degree of alkylation and the higher the degree of arylation of the carbon atom on which it resides. From the results now obtained and those of Chablay (*Ann. Chim.*, 1917, **8**, 192) it can be seen that the only purely aliphatic alcohols which are readily reduced contain a CH_2 in the allylic system (sabinol, 1-vinyl*cyclo*hexanol, geraniol, and linalol). The assisting effect of a phenyl group (which can stabilise an adjacent charge) is seen by comparing carveol (V), 1-Δ^1-*heptenyl*cyclo*hexanol* (VIII), and 4-hydroxy-Δ^2-octene (IX) with 3-hydroxy-1-phenyl-Δ^1-butene (X, R = H), 3-hydroxy-1-phenyl-3-methyl-Δ^1-butene (X, R = CH_3) and 1-hydroxy-1-phenyl-Δ^2-butene (XI, R = OH, R′ = H). Since the ion in the transition state is mesomeric, it does not matter to a first approximation whether the hydroxyl group is directly attached to the CH_2 or CPh or not; *e.g.*, geraniol (I, R = OH) and linalol (XV) give the same hydrocarbon (I, R = H) (Chablay, *loc. cit.*; Dupont, Dulou, and Desreux, *Bull. Soc. chim.*, 1939, **6**, 83) by way of the same ion (II), and (X, R = H) and (XI; R = OH, R′ = H) give the same hydrocarbon (XI; R, R′ = H).

Similarly, hydrogenolysis of the arylcarbinols can be assumed to depend on the ability of the aryl group to stabilise the adjacent negative charge in the transition state. This effect must be large with a benzene ring, since substitution of two methyl groups (phenyldimethylcarbinol) or a butyl group (phenylbutylcarbinol) in the carbinol is not sufficient to cause a significant drop in hydrogenolysis. However, the presence of an oxygen atom with unshared electrons (*p*-methoxyphenylcarbinol and furfuryl alcohol) does so, and when added to the effect of an alkyl group (furfurylbutylcarbinol) the drop is marked. Klages (*Ber.*, 1906, **39**, 2589), using the less powerful reagent sodium and alcohol, was able to reduce benzyl alcohol but not phenyldimethylcarbinol, and a competitive reduction of these substances in liquid ammonia also demonstrated the relative ease of reduction of the former. The same effect of alkylation can be seen by comparing (X, R = H) with (X, R = CH_3), where hydrogenolysis is in competition with reduction of the double bond. The latter reaction should be little affected by the extra methyl group in (X, R = CH_3) so the lower proportion of hydrogenolysis in this case must be traced to the effect of this group on the stability of the intermediate anion.

The constitutions of the hydrocarbons obtained show that the mesomeric anions react with a proton donor at the end where the charge is most stable. The full significance of this will be discussed in a later communication, but the result, in conjunction with the observation of Ziegler and Wollschitt (*Annalen*, 1930, **479**, 131) that addition of sodium to compounds like anthracene is readily reversible, makes possible an explanation of the rôle of a proton donor in the reduction of the benzene ring (Part I) other than assumption of the intervention of atomic hydrogen. This is to assume that in a solution of a metal and an aromatic compound in liquid ammonia the following equilibrium is present but is far to the left unless there is present in the molecule some group such as carboxyl (*e.g.*, benzoic acid) or another benzene ring (*e.g.*, naphthalene or diphenyl) which is capable of stabilising the charges to some extent, thereby lowering the energy of formation of the anion. However, if a ready proton donor such as alcohol be present which reacts with such anions in a transition state at a rate comparable to its reaction with the metal electrons to give hydrogen, significant reduction should occur. It may be noted that the reaction of sodium with alcohol in liquid ammonia occurs at quite a moderate speed.



On this theory the points of addition of the two hydrogen atoms should correspond to the positions of maximum stability of the charges, since the system is a doubled allylic ion of the type considered above. The charges would tend to separate, thus giving αδ-reduction, and also tend to avoid alkyl groups and groups such as methoxyl having unshared electrons, thus leading to the rule already found from experiment (Part I). It seems significant also that the presence of a hetero-atom such as oxygen whose electrons contribute to the aromatic resonance should tend to prevent reduction of the ring.

EXPERIMENTAL.

Reduction of d-*Sabinol.*—A mixture of *d*-sabinol (14 g.) [α_D (1 dcm.) + 5·6°, purified as the *p*-nitrobenzoate by the method of Read and Storey (J., 1939, 1040)] and ethyl alcohol (10 g.) was added dropwise to a stirred solution of sodium (10 g.) in liquid ammonia (200 c.c.). Further alcohol (8 g.) was then added, and after the blue colour had disappeared the solution was cautiously decomposed with water (200 c.c.). The oil was taken up in ether and fractionated through a column : (i) b. p. 154—156° (9·8 g.), α_D (1 dcm.) − 22°; (ii) b. p. 156—158° (1·5 g.), α_D (1 dcm.) −4·5°. Redistillation of (i) over sodium gave a pleasant-smelling mobile oil, b. p. 155—156° (8·2 g.), $n_D^{19^\circ}$ 1·4555, $d_{4^\circ}^{19^\circ}$ 0·8332, $[\alpha]_D$ −29·7° (Found : C, 88·0; H, 11·8. Calc. for $C_{10}H_{16}$: C, 88·2; H, 11·8%). This was identified as α-thujene by permanganate oxidation, using the procedure of Birch and Earl (*J. Proc. Roy. Soc. N.S.W.*, 1938, **72**, 59). A 58% yield of *d*-α-thujaketonic acid, m. p. 74—75° (semicarbazone, m. p. 197—198°), was obtained, convertible by heating to 130° into optically inactive β-thujaketonic acid, m. p. 78—79° (semicarbazone, m. p. 202°), the last two m. p.'s undepressed by authentic specimens. Birch (*ibid.*, 1938, **71**, 330) obtained a crystalline nitrosochloride corresponding to the *dl*-α-thujene, but the above hydrocarbon gave by the same procedure a blue solution but no precipitate. On addition of excess of piperidine and warming on the steam-bath, the colour disappeared, and on pouring into water a solid was obtained. This crystallised from alcohol or ethyl acetate as large, colourless, elongated prisms, m. p. 180°, $[\alpha]_D$ −120·9° (6% solution in pyridine) (Found : C, 72·0; H, 10·4. $C_{15}H_{26}ON_2$ requires C, 72·0; H, 10·4%). It was therefore 1-α-*thujene nitrolpiperidine*.

Attempted Reduction of d-*Carveol.*—*d*-Carveol [α_D (1 dcm.) +98°; Johnston and Read (J., 1934, 233)] was treated in the same manner as sabinol. There was no lower-boiling fraction in the product corresponding to hydrocarbon, and the physical constants were practically unaltered (Found : C, 78·7; H, 10·7. Calc. for $C_{10}H_{16}O$: C, 79·0; H, 10·4%). Distillation with a trace of iodine gave water and a substance, b. p. 177—180°, which must contain

$\Delta^{1:5:8(9)}$-*p*-menthatriene since it gave a maleic anhydride *adduct* in acetone solution as colourless laths (from aqueous alcohol), m. p. 84—87° (Found : C, 72·1; H, 6·6. $C_{14}H_{16}O_3$ requires C, 72·4; H, 6·8%).

1-*Vinyl*cyclo*hexanol.*—To ethynyl*cyclo*hexanol (34 g.) (prepared by treatment of *cyclo*hexanone with sodium acetylide in liquid ammonia) and ethyl alcohol (28 g.) in liquid ammonia (300 c.c.) was slowly added sodium (14 g.) in small pieces with stirring. Most of the ammonia was evaporated, water (150 c.c.) cautiously added, and the product extracted with ether and distilled. Some lower-boiling product was discarded and 1-vinyl*cyclo*hexanol obtained as a colourless oil with a pleasant camphor-like odour, b. p. 75°/15 mm. (24 g.) (Found : C, 75·9; H, 11·3. Calc. for $C_8H_{14}O$: C, 76·2; H, 11·1%). It gave no precipitate with ammoniacal cuprous chloride or silver nitrate, indicating the absence of unchanged acetylene.

*Ethylidene*cyclo*hexane.*—A solution of the above carbinol (24 g.) and ethyl alcohol (10 g.) in ether (50 c.c.) was added dropwise to a solution of sodium (10 g.) in liquid ammonia (250 c.c.) with stirring. A further 10 g. of ethyl alcohol was then added. Cautious addition of water (250 c.c.), ether extraction, and distillation through a column gave a fraction, b. p. 134—140°. Redistilled over sodium, it had b. p. 135—136° (10·5 g.), $n_{\mathrm{D}}^{19^\circ}$ 1·4622 (Found : C, 86·9; H, 13·0. Calc. for C_8H_{14} : C, 87·3; H, 12·7%). It gave a colourless nitrosochloride, m. p. 131—132° (from benzene), and a nitrolpiperidine, m. p. 107—108° (colourless prisms from alcohol) (Found : C, 69·5; H, 10·5. Calc. for $C_{13}H_{24}ON_2$: C, 69·6; H, 10·6%). Godchot and Cauquil (*Compt. rend.*, 1928, **186**, 377) give for ethylidene*cyclo*hexane, b. p. 135—136°, n_{D}^{19} 1·4577, nitrosochloride, m. p. 130°, and nitrolpiperidine, m. p. 108—109°; Wallach and Evans (*Annalen*, 1908, **360**, 45) give b. p. 137—138°, $n_{\mathrm{D}}^{18^\circ}$ 1·4631, and nitrolpiperidine, m. p. 116—117°. Owing to the discrepancy in the last m. p. the constitution was further proved as follows. The nitrosochloride (2 g.) was heated on the steam-bath with pyridine (3 c.c.) and after the vigorous reaction the mixture was added to dilute hydrochloric acid and extracted with ether. The oil so obtained was heated on the steam-bath with a solution of 2 : 4-dinitrophenylhydrazine in alcoholic sulphuric acid, and the product recrystallised from benzene–alcohol as bright red elongated prisms, m. p. 203°, undepressed by an authentic specimen of 1-acetyl-Δ^1-*cyclo*hexene 2 : 4-dinitrophenylhydrazone.

Ethylidene*cyclo*hexane was also produced in one step from 1-ethynyl*cyclo*hexanol by reduction as above, using sodium (4·4 equivs.) and alcohol (4·4 equivs.) in ammonia.

1-Δ^1-*Heptynyl*cyclo*hexanol.*—To the Grignard solution from magnesium (4 g.) and ethyl iodide (30 g.) was added heptyn-1 (12 g.) and after refluxing for 2½ hours the solution was cooled in ice and *cyclo*hexanone (17 g.) added. Worked up in the usual manner, the product was a colourless, rather viscous oil with a pleasant odour (14 g.), b. p. 133—134°/11 mm. (Found : C, 80·1; H, 11·1. $C_{13}H_{22}O$ requires C, 80·4; H, 11·3%).

1-Δ^1-*Heptenyl*cyclo*hexanol.*—A solution of the above *compound* (14 g.) and alcohol (15 g.) in ether (30 c.c.) was added dropwise to a solution of sodium (6 g.) in ammonia (150 c.c.). Worked up as usual, the product (12 g.) had b. p. 131°/11 mm., so no appreciable hydrogenolysis had occurred. This was confirmed by repeating the process using sodium (10 g.), alcohol (20 g.), and liquid ammonia (250 c.c.). The *product* (10 g.), b. p. 130°/11 mm., was a colourless, rather viscous oil with a rose odour (Found : C, 79·8; H, 12·1. $C_{13}H_{24}O$ requires C, 79·6; H, 12·25%).

4-*Hydroxy*-Δ^2-*octene.*—This carbinol (12 g.) (Leven and Haller, *J. Biol. Chem.*, 1929, **83**, 583) and alcohol (10 g.) were dissolved in ammonia (150 c.c.), and sodium (5 g.) added in small pieces with stirring during 30 minutes. Worked up as usual, the product was distilled at 20 mm., with the receiver cooled in a freezing mixture. The fraction, b. p. <60°, was redistilled over sodium; b. p. 122—124°/755 mm., $n_{\mathrm{D}}^{18^\circ}$ 1·4150 (0·8 g.) (Found : C, 85·4; H, 14·5. Calc. for C_8H_{16} : C, 85·7; H, 14·3%). It was therefore Δ^2- or Δ^3-octene, or a mixture of the two. The higher-boiling fraction (b. p. 80°/12 mm.) (8 g.) was starting material (Found : C, 74·8; H, 12·6. Calc. for $C_8H_{16}O$: C, 75·0; H, 12·5%).

Reduction of 3-*Hydroxy*-1-*phenyl*-Δ^1-*butene.*—This carbinol (14 g.) (Klages, *Ber.*, 1902, **35**, 2649) and ethyl alcohol (10 g.) were dissolved in liquid ammonia (250 c.c.), and sodium (5 g.) added in small pieces during 30 minutes with stirring. Worked up as usual, two fractions were obtained : (i) b. p. 77°/12 mm.; (ii) b. p. 120—124°/10 mm. Fraction (i) was redistilled over sodium and obtained as a colourless oil (8 g.), b. p. 183—184°, $n_{\mathrm{D}}^{20^\circ}$ 1·5102 (Found : C, 90·6; H, 9·3. Calc. for $C_{10}H_{12}$: C, 90·9; H, 9·1%). It gave a liquid dibromide, and was not reduced by sodium in liquid ammonia, and was therefore 1-phenyl-Δ^2-butene (cf. Klages, *Ber.*, 1906, **39**, 2591). Fraction (ii) was shaken with powdered potassium permanganate in acetone to remove starting material and redistilled; b. p. 123°/10 mm. (0·9 g.) (Found : C, 79·8; H, 9·2. Calc. for $C_{10}H_{14}O$: C, 80·0; H, 9·3%). It gave a phenylurethane, m. p. 115° (needles from alcohol). Klages (*Ber.*, 1904, **37**, 2313) gives m. p. 113° for the phenylurethane of 3-hydroxy-1-phenylbutane.

Reduction of 3-*Hydroxy*-1-*phenyl*-3-*methyl*-Δ^1-*butene.*—This carbinol (23·5 g.) (Kohler and Heritage, *Amer. Chem. J.*, 1905, **33**, 28) was reduced as above, using sodium (7·5 g.), alcohol (15 g.), and ammonia (350 c.c.). The product gave two fractions : (i) b. p. 95°/18 mm. (9·7 g.) and (ii) b. p. 125—128°/13 mm. (9 g.). Fraction (i) was redistilled over sodium, b. p. 202—204°, $n_{\mathrm{D}}^{17^\circ}$ 1·5158 (Found : C, 89·9; H, 9·9. Calc. for $C_{11}H_{14}$: C, 90·3; H, 9·6%). It gave a colourless dibromide (plates from alcohol), m. p. 62—63° (Found : C, 43·3; H, 4·7. Calc. for $C_{11}H_{14}Br_2$: C, 43·7; H, 4·8%), and a nitrosochloride (flat colourless needles from benzene), m. p. 154°. Klages (*Ber.*, 1904, **37**, 2315) gives m. p. 66° for the dibromide and 146—147° for the nitrosochloride of 1-phenyl-3-methyl-Δ^2-butene. Claisen (*J. pr. Chem.*, gives m. p. 63—65° for the dibromide. However, there is no doubt that (i) was this butene, since it was not reduced by sodium in liquid ammonia, and the dibromide of the alternative 1-phenyl-3-methyl-Δ^1-butene has m. p. 128° (Klages, *Ber.*, 1904, **37**, 2316).

Fraction (ii) was shaken with powdered potassium permanganate in acetone and redistilled. A colourless, rather viscous oil with a pleasant rose odour was obtained, b. p. 125—126°/15 mm. (Found : C, 80·4; H, 9·6. Calc. for $C_{11}H_{16}O$: C, 80·4; H, 9·75%). It gave a phenylurethane, m. p. 138—139° (Found : C, 76·25; H, 7·4. Calc. for $C_{18}H_{21}O_2N$: C, 76·3; H, 7·4%). Klages (*loc. cit.*) gives m. p. 144° for the phenylurethane of 3-hydroxy-1-phenyl-3-methylbutane.

Reduction of 1-*Hydroxy*-1-*phenyl*-Δ^2-*butene.*—This substance (14 g.) (Burton, J., 1929, 456) was reduced as above by using sodium (5 g.) and alcohol (10 g.) in ammonia (250 c.c.). The product was a colourless oil, b. p. 183—184°, $n_{\mathrm{D}}^{20^\circ}$ 1·5108 (Found : C, 90·7; H, 9·2. Calc. for $C_{10}H_{12}$: C, 90·9; H, 9·1%). Since it was not further reduced by sodium in liquid ammonia, and took up 1·12 mols. of bromine in acetic acid to give an oily dibromide, it must be 1-phenyl-Δ^2-butene.

Reduction of the Compounds in the Table.—The benzyl alcohol, anisyl alcohol, and furfuryl alcohol were from stock, the others were prepared in the standard manner by the action of the appropriate Grignard reagent on the requisite aldehyde or ketone.

The carbinol (0·2 mol.) and ethyl alcohol (0·44 mol.) were dissolved in ammonia (about 30 times the volume of the alcohol), and sodium (0·44 mol.) added in small pieces with stirring during 45 minutes. After all the sodium had disappeared most of the ammonia was evaporated, and the residue cautiously decomposed by the addition of crushed ice. The product was extracted with ether and fractionated through a column.

Benzyl alcohol. Carbinol (22 g.) gave 14 g. of product, b. p. 109—111°, and 1·4 g., b. p. 190—205°. The former fraction was redistilled over sodium (13·5 g.); b. p. 109—110°, $n_{\mathrm{D}}^{17^\circ}$ 1·4998. Nitration gave 2 : 4-dinitrotoluene, m. p. 71°.

Phenylmethylcarbinol. Carbinol (24·2 g.) gave 15·8 g., b. p. 134—135°, and 1·3 g. of residue. The former fraction was redistilled over sodium; b. p. 134—135°, $n_{\mathrm{D}}^{17^\circ}$ 1·4972 (Found: C, 90·3; H, 9·5. Calc. for C_8H_{10}: C, 90·6; H, 9·4%).

Phenyldimethylcarbinol. Carbinol (27 g.) gave 18·1 g., b. p. 149—150°, and residue (0·72 g.). Redistilled over sodium, the former had b. p. 149—150°, $n_{\mathrm{D}}^{17^\circ}$ 1·4944 (Found: C, 89·5; H, 9·8. Calc. for C_9H_{12}: C, 90·0; H, 10·0%).

Phenylbutylcarbinol. Carbinol (33 g.) gave 24 g., b. p. 87—90°/15 mm., and 2·1 g. of residue. Redistilled over sodium, the former had b. p. 199—201°, $n_{\mathrm{D}}^{18^\circ}$ 1·4913. *n*-Amylbenzene has b. p. 200—201°, $n_{\mathrm{D}}^{20^\circ}$ 1·4943.

Anisyl alcohol. Carbinol (28 g.) gave: (i) b. p. 75—78°/15 mm. (9·0 g.), and (ii), b. p. 143—146°/12 mm. (15·1 g.). Fraction (i) was refluxed with 10% aqueous sulphuric acid for 45 minutes, and the product extracted with ether and heated with excess of aqueous-alcoholic semicarbazide acetate on the steam-bath. The solution was diluted with water, and light petroleum (b. p. 40—60°) added. The solid semicarbazone was filtered off, and recrystallised from alcohol as colourless needles (2·4 g.), m. p. 188—189°, undepressed by a sample of the semicarbazone prepared from the reduction product of *p*-tolyl methyl ether (Part I). This corresponds to a 7% yield of dihydro-*p*-tolyl methyl ether. The petroleum solution was distilled, giving *p*-tolyl methyl ether (7·5 g.), b. p. 175—177°. Fraction (ii) gave a *p*-nitrobenzoate, m. p. 83—86°, undepressed by an authentic specimen of *anisyl* p-*nitrobenzoate*, m. p. 92—93° (pale yellow needles from alcohol) (Found: N, 5·1. $C_{15}H_{13}O_5N$ requires N, 4·9%). A specimen of the fraction which had been left in air for a week gave a *p*-nitrobenzoate, m. p. 91—92°, and it seems very probable that it contains mostly starting material with a trace of nuclear hydrogenated product.

Furfuryl alcohol. Reduced as above; 42% of unchanged material was recovered; p-*nitrobenzoate*, m. p. 75° (Found: N, 6·1. $C_{12}H_9O_5N$ requires N, 5·8%). No lower-boiling material could be recovered, so the method was modified as follows. A mixture of furfuryl alcohol (17 g.) and ethyl alcohol (8 g.) was dropped into a solution of sodium (8 g.) in ammonia (200 c.c.), the evaporating ammonia being led through two wash-bottles each containing tetralin (100 c.c.). Finally, a further 4 g. of ethyl alcohol was added and all the ammonia evaporated through the tetralin, with final warming on the steam-bath. The tetralin was distilled from sodium wire, the fraction, b. p. $<$ 100°, being collected, and this was again distilled over sodium. The product was a colourless oil, b. p. 63—65° (2·9 g.), $n_{\mathrm{D}}^{17^\circ}$ 1·4362 (Found: C, 73·0; H, 7·0. Calc. for C_5H_6O: C, 73·2; H, 7·3%). 2-Methylfuran has b. p. 65°, n_{D} 1·4344.

Furfurylbutylcarbinol. The *carbinol* was obtained in 72% yield by the action of butylmagnesium bromide on furfuraldehyde in the standard manner; b. p. 105°/15 mm. (Found: C, 70·4; H, 9·3. $C_9H_{14}O_2$ requires C, 70·1; H, 9·1%). This substance (19 g.) gave on reduction (i), b. p. *ca.* 60°/15 mm., and (ii), b. p. 105°/16 mm. (15·5 g.). Fraction (ii) consisted of unchanged material (Found: C, 70·1; H, 9·2%). Fraction (i) was redistilled over sodium and obtained as a colourless oil, b. p. 162° (0·6 g.) (Found: C, 78·1; H, 10·1. $C_9H_{14}O$ requires C, 78·2; H, 10·1%). It was therefore 2-*amylfuran*.

Competitive Reduction of Benzyl Alcohol and Phenyldimethylcarbinol.—Benzyl alcohol (9·5 g.) and phenyldimethylcarbinol (11 g.) were added to a solution of ethyl alcohol (8 g.) in ammonia (200 c.c.), followed by sodium (4·0 g.) in small pieces during 30 minutes, with stirring. The product was worked up as usual and gave the fractions: (i), b. p. 110—113° (4·0 g.); (ii), b. p. 113—145° (0·3 g.); and (iii), b. p. 145—150° (0·4 g.), with residue (11 g.). Fraction (i) was redistilled over sodium and found to be toluene, b. p. 110°, $n_{\mathrm{D}}^{17^\circ}$ 1·5002, 2 : 4-dinitro-derivative, m. p. 71°. Fraction (iii) was redistilled over sodium, b. p. 145—150° (0·3 g.), $n_{\mathrm{D}}^{17^\circ}$ 1·4980, and is probably impure *iso*propylbenzene.

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