The Reduction of Some Methyl Phenyl Ketones, the Corresponding Carbinols, and 2-Methyl-2-phenyl-1 : 3-dioxolans with Sodium or Potassium and Alcohols in Liquid Ammonia.

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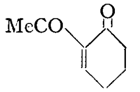
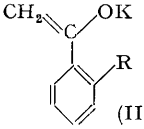
The action of potassium *tert.*-butoxide in liquid ammonia on acetophenone and *o*-methoxyacetophenone gives the corresponding enolates, which are not reduced by the further action of potassium and *tert.*-butanol in liquid ammonia. The factors involved in the protection against hydrogenolysis of the hydroxyl group of alcohols of α-methylbenzyl alcohol type are discussed. Reduction with sodium and methanol in liquid ammonia of 2-methyl-2-phenyl-1 : 3-dioxolan and the *o*-, *m*-, and *p*-methoxy-derivatives gives ethylbenzene and the corresponding ethylanisoles, which can undergo further reduction in the aromatic nucleus. The mechanism of these reductions is discussed. The same reagent completely hydrogenolyses 2-methyl-2-phenyl-1 : 3-oxathiolan.

PRELIMINARY attempts to obtain 2-acetyl*cyclo*hex-2-enone (I), an important intermediate in steroid synthesis, have already been described (Smith, *J.*, 1953, 803). It has been suggested (unpublished observations by Birch and Robinson) that (I) might be obtained by reduction by Birch's method (*J.*, 1944, 430, and later papers) of a suitable aromatic precursor, and the present investigation is essentially an exploration of this idea.

Clearly the most suitable compound for reduction is *o*-methoxyacetophenone, possessing the correct side-chain and an oxygen function *ortho* to it, provided that the carbonyl group can be protected against the sodium–liquid ammonia–alcohol reagent. Birch (*Quart. Reviews*, 1950, 4, 93) has indicated that the enol salts of certain unsaturated ketones are stable enough for this purpose, and so we investigated first the reduction of the potassium enolates (II; R = H) and (II; R = OMe) of acetophenone and *o*-methoxyacetophenone, respectively. Birch (*J.*, 1950, 1551) has postulated that the hydrogenation of an aromatic system by a dissolving metal proceeds by electron and proton addition in either successive or simultaneous stages depending on the conditions, the rate- or potential-determining stage being the addition of the first electron. In the reduction of benzene rings containing a carboxyl group the 1 : 4-addition of hydrogen occurs at positions which include the substituted one (Birch, *J.*, 1950, 1551; Birch, Murray, and Smith, *J.*, 1951, 1945), and this effect has been ascribed to the ability of the alkali-metal carboxylate group to stabilise a negative charge on an adjacent nuclear carbon atom by the resonance $\underbrace{>\overset{\ominus}{\text{C}}\text{–C(ONa)=O} \quad >\text{C=(ONa)–}\overset{\ominus}{\text{O}}}$ (cf. Birch, *Quart. Reviews*, 1950, 4, 88). A similar resonance is clearly possible in the formally analogous potassium enolate group, and although the charge-stabilising effect of the latter would not be expected to be as powerful as that of the alkali-metal carboxylate group, owing to the lower electron-affinity of the methylene group compared with oxygen, it was considered that the effect might operate sufficiently strongly to direct the addition of hydrogen to positions 1 and 4 of (II; R = H) and (II; R = OMe) to give (III; R = H) and (III; R = OMe), respectively. Acid hydrolysis of the latter, followed by double-bond shift would then give the desired (I).



(I)



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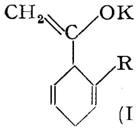


(III)

The enol form of acetophenone has been estimated to have a p*K* value of 10 (McEwen, *J. Amer. Chem. Soc.*, 1936, **58**, 1124), and therefore should be a strong acid in liquid ammonia (p*K* about 34; Makishima, *J. Fac. Eng. Tokyo Imp. Univ.*, 1938, **21**, 115). Also, it should be possible to prepare the potassium enolate by a simple metathesis in liquid ammonia between acetophenone and the potassium salt of a sufficiently weak acid. *tert.*-Butanol is such an acid (p*K* 19; McEwen, *loc. cit.*) and is especially suitable since it can be used as a proton source in the subsequent reduction with potassium. This type of reduction of the potassium enolate of acetophenone was first investigated by Birch and Smith (unpublished work), who observed the presence of unchanged acetophenone in the product. No evidence for the presence of 3-acetyl*cyclo*hexa-1 : 4-diene (capable of forming an addition compound with sodium hydrogen sulphite) was obtained. This reaction has now been examined in detail. We have found about 10% of unchanged acetophenone in the product when the reduction is started within several minutes of the addition of acetophenone to a solution of potassium *tert.*-butoxide in liquid ammonia. The remainder of the product consists of ethylbenzene or 1-ethyl*cyclo*hexa-1 : 4-diene, depending upon the amount of reducing agent used. When the reduction is started three hours after the addition of acetophenone to a solution of potassium *tert.*-butoxide in liquid ammonia, no reduction product is obtained, acetophenone being recovered. Under similar conditions, without preliminary treatment with potassium *tert.*-butoxide, acetophenone is completely transformed into ethylbenzene or its nuclear reduction product. This is not surprising, since it would first be converted into α-methylbenzyl alcohol (cf. Birch, *Quart. Reviews*, **1950**, **4**, 88), which is known to be hydrogenolysed completely (*idem, J. Proc. Roy. Soc. N.S.W.*, 1950, **83**, 245). The most reasonable interpretation of these data is that the potassium enolate of acetophenone is unaffected by the potassium–*tert.*-butanol–liquid ammonia reagent, and that the following equilibria :

$$\mathrm{Ph{\cdot}CO{\cdot}CH_3 \rightleftharpoons Ph{\cdot}C(OH){:}CH_2 + Bu^tOK \rightleftharpoons Ph{\cdot}C(OK){:}CH_2 + Bu^tOH}$$

which are involved in the formation of the potassium enolate from acetophenone and potassium *tert.*-butoxide in liquid ammonia, are relatively slow to be established under the conditions we used. Thus, if the reduction is started before the establishment of equilibrium, the enolate present is unattacked whilst the unchanged acetophenone is reduced in the usual way. The metathesis between a strong acid and the salt of a strong base and a weaker acid in a highly ionising solvent in general requires a low activation energy and so equilibrium is established rapidly. Hence it would appear that the initial enolisation is comparatively slow and thus is the rate-determining stage in the formation of the potassium enolate of acetophenone by the above process. Similar results were obtained in the case of *o*-methoxyacetophenone. Reduction of the simple ketone resulted in complete hydrogenolysis of the side-chain oxygen and nuclear reduction to give 6-ethyl*cyclo*hex-2-enone, and reduction within several minutes of the addition of the ketone to a solution of potassium *tert.*-butoxide in liquid ammonia gave about 15% of the unchanged ketone, together with 25% of 6-ethyl*cyclo*hex-2-enone and 33% of a syrupy, involatile material, probably derived from a self-condensation product of *o*-methoxyacetophenone. The effect of leaving the mixture of ketone and potassium *tert.*-butoxide in solution in liquid ammonia for several hours was obscured by extensive formation of this involatile product.

We next considered the possibility of achieving nuclear reduction in α-methylbenzyl alcohol and *o*-methoxy-α-methylbenzyl alcohol whilst protecting the side-chain hydroxyl group against hydrogenolysis. The reductive fission of allyl or benzyl alcohols by sodium and liquid ammonia can be prevented by inducing a negative charge on the oxygen atom through salt formation (Birch, *Quart. Reviews*, **1950**, **4**, 69), but we would point out that when a proton donor is required to achieve nuclear reduction, the effectiveness of the method will depend on the relative acid strengths of the alcohol to be reduced and that used as proton source, since the equilibrium between the salt of the former and the latter would be established before appreciable reduction could occur. Conant and Wheland (*J. Amer. Chem. Soc.*, 1932, **54**, 1212) have examined a number of metatheses of the type :

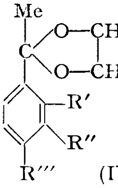
$$\mathrm{R_1OH + R_2OM \rightleftharpoons R_1OM + R_2OH,}$$

where R_1OH and R_2OH can be alcohols and M an alkali metal, and, making a number of reasonable assumptions, have derived for equilibrium the (corrected) expression :

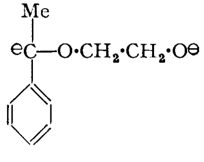
$$pK_1 - pK_2 = \log \frac{[R_2OM]}{[R_2OH]} - \log \frac{[R_1OM]}{[R_1OH]}.$$

From this expression it may be deduced that if at equilibrium R_2OM is to be decomposed to the extent of only 10% by a three-fold excess of R_1OH, then R_2OH must be a stronger acid than R_1OH by approximately 2·6 pK units, and that if R_1OM, acting upon R_2OH in the presence of a three-fold excess of R_1OH, is to give at equilibrium 90% of R_2OM, then R_2OH must be a stronger acid than R_1OH by 2·5 pK units. Hence if α-methylbenzyl and *o*-methoxy-α-methylbenzyl alcohols are to be protected against hydrogenolysis when *tert.*-butanol is used as proton source during reduction by Birch's method they are required to have pKs of the order of 16—17. No data are available for these carbinols, but it is known that the pK of benzyl alcohol is 18, and, owing to the electron-repelling effect of the methyl group, the value for α-methylbenzyl alcohol must be greater than this. If the effect of the additional methyl group is of the same order as that found in passing from methanol (pK 16) to ethanol (pK 18), then the pK of α-methylbenzyl alcohol would be expected to be about 20. A comparison of the acid strengths of benzoic and *o*-methoxybenzoic acid (Dippy, *Chem. Reviews*, 1939, **25**, 206; Jones and Speakman, *J.*, 1944, 19) indicates that *o*-methoxy-α-methylbenzyl alcohol should be only a very slightly stronger acid than the unsubstituted carbinol. It would appear therefore that both carbinols are not sufficiently acidic to be protected conveniently against hydrogenolysis, and in confirmation of this view we have observed that both, after preliminary treatment with one equivalent of potassium *tert.*-butoxide, gave reduction products almost identical with those obtained without such preliminary treatment. These results indicate that the equilibrium, $Ph{\cdot}CHMe{\cdot}OH + Bu^tOK \rightleftharpoons Ph{\cdot}CHMe{\cdot}OK + Bu^tOH$, lies to the left almost completely.

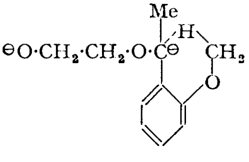
We next studied the formation of cyclic ethylene ketals (dioxolans) as a means of protecting the carbonyl group in various acetophenones. This means has been used for the protection of the 3-oxo-group of various steroids during reduction by Birch's method of another portion of the molecule (Sarett *et al.*, *J. Amer. Chem. Soc.*, 1952, **74**, 4974; Bernstein, Littell, and Williams, *ibid.*, 1953, **75**, 1481), and we have confirmed that the cyclic ethylene ketal of *cyclo*hexanone is unattacked under the conditions we used. The cyclic ketals (dioxolans) from acetophenone and its *o*-, *m*-, and *p*-methoxy-derivatives were obtained by Salmi's general method (*Ber.*, 1938, **71**, 725), that from *p*-methoxyacetophenone being the least readily formed, in accord with observations by Birch, Quartey, and Smith (*J.*, 1952, 1768) that 6-methoxy-1-oxotetralin failed to give derivatives of this type. Reduction of the dioxolans in liquid ammonia with 6—10 atoms of sodium, with methanol as proton source, resulted in each case in complete hydrogenolysis of the ketal grouping, which could be accompanied by further nuclear reduction of the intermediate ethylbenzene or ethylanisole. Evidence has been presented (cf. Birch, *Quart. Reviews*, 1950, **4**, 72) that the transition state for the reductive fission of various ethers and



(IV)



(V)



(VI)

alcohols by sodium in liquid ammonia involves anions rather than radicals, and there seems no reason to doubt that the hydrogenolysis of our dioxolans entails similar anionic intermediates. We envisage the hydrogenolysis of, *e.g.*, the dioxolan (IV; R′ = R″ = R‴ = H), to proceed first by the addition of two electrons to give (V), a process which would be facilitated both by the ability of the aromatic nucleus to stabilise a negative charge, and by the high affinity for electrons of the oxygen atoms present in the dioxolan ring. Addition of two protons gives 1-2′-hydroxyethoxyethylbenzene, and this, like other benzyl ethers, is hydrogenolysed to ethylbenzene by the addition of two more electrons and protons. A two-stage mechanism of this type is more feasible than one involving the addition of four electrons in one stage, since this would necessitate the development of two negative charges on the carbon atom adjoining the nucleus, and the energy of activation for the process is likely to be prohibitively high. If a two-stage mechanism is in fact involved, then the second stage must be the easier (this would not be surprising in view of the fact that benzyl ethers are split by sodium and ammonia even in the absence of alcohols), since reduction of (IV; $R' = R'' = R''' = H$) with only two atoms of sodium and methanol gave ethylbenzene together with unchanged dioxolan, but no 1-2′-hydroxyethoxyethylbenzene. The hydrogenolysis of the methoxyphenyldioxolans would be expected to proceed by similar mechanisms. The *o*-methoxy-group could facilitate the process by virtue of its ability to stabilise, by the cyclic hyperconjugation mechanism illustrated in (VI), the negative charge on the carbon atom adjoining the benzene nucleus (cf. Birch, *J. Proc. Roy. Soc., N.S.W.*, and *Quart. Reviews, locc. cit.*); the effect of the *m*-methoxy-group would, in any case, be small, but it might be expected that the *p*-methoxy-group by exerting its normal electron-repelling influence would tend to inhibit hydrogenolysis by destabilising a negative charge on the carbon atom involved in the hydrogenolysis. This effect has been observed with *p*-methoxy-α-methylbenzyl alcohol, which with two atoms of sodium is reduced preferentially in the benzene ring (Birch, *J. Proc. Roy. Soc., N.S.W., loc. cit.*), and with 6-methoxy-1-oxotetralin (Birch, Quartey, and Smith, *loc. cit.*), but no evidence of its operation could be detected in the reduction of 2-*p*-methoxyphenyl-2-methyldioxolan, which with two atoms of sodium and proton donor gave *p*-ethylanisole and the unchanged dioxolan. It has been reported that the carbonyl group of anisaldehyde can be protected as the acetal during reduction of the benzene ring (Birch, Quartey, and Smith, *loc. cit.*), and so it would appear that the strain energy of the five-membered dioxolan ring, even if comparatively low, can assist the reductive fission sufficiently to nullify the effect of the *p*-methoxy-group.

Since dialkyl sulphides, unlike dialkyl ethers, are reduced readily with sodium in ammonia (Williams and Gebauer-Füllnegg, *J. Amer. Chem. Soc.*, 1931, **53**, 532) replacement of oxygen by sulphur in the dioxolan ring should increase the ease of reductive fission. We have observed that the normal reduction process converts 2-methyl-2-phenyl-1 : 3-oxathiolan into ethylbenzene and 1-ethyl*cyclo*hexa-1 : 4-diene.

EXPERIMENTAL

All spectral measurements are by Dr. F. B. Strauss, with the technical assistance of Mr. F. Hastings. Ultra-violet absorption spectra were determined in methanol except where stated otherwise.

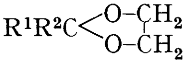
o-*Methoxyacetophenone.*—*o*-Hydroxyacetophenone (Freudenberg and Orthner, *Ber.*, 1922, **55**, 1749) was methylated with an excess of methyl sulphate and alkali as described by von Auwers (*Annalen*, 1915, **408**, 246). The product, in ethereal solution, was washed with dilute sodium hydroxide solution until no more phenolic matter was extracted. The ketone n_D^{16} 1·380 (yield 75%), distilled at 116°/11 mm.; infra-red absorption: bands at 5·95 (carbonyl), 7·76, 8·04, and 9·80 (aromatic ether), and 8·90 and 13·27 μ (*o*-disubstituted benzene ring). The 2 : 4-*dinitrophenylhydrazone* separated from ethyl acetate in glistening, red rhombs, m. p. 185° (Found: C, 54·5; H, 4·4. $C_{15}H_{14}O_5N_4$ requires C, 54·5; H, 4·2%); ultra-violet absorption in chloroform: max. at 225 (ε = 11,300), 250 (ε = 14,200), and 370 mμ (ε = 29,000).

o-*Methoxy-α-methylbenzyl Alcohol.*—*o*-Methoxyacetophenone (5 g.) in methanol (30 c.c.) was added to a solution of sodium borohydride (2·6 g.) in methanol (100 c.c.), and the mixture heated on the water-bath for 45 min. Most of the methanol was removed under reduced pressure, and ether (250 c.c.) was added; the crystalline deposit dissolved on the addition of water (25 c.c.). The ethereal solution was washed with 1% aqueous acetic acid (2 × 50 c.c.), 5% sodium hydroxide solution (50 c.c.), and water (50 c.c.), and dried (potassium carbonate). Distillation gave the carbinol (4·6 g.), b. p. 124°/13 mm., n_D^{20} 1·539 (Klages, *Ber.*, 1903, **36**, 3588, gives b. p. 119—120°/11 mm., n_D 1·5379). The infra-red absorption spectrum showed a hydroxyl band at 2·9—3·0 μ, but no trace of a carbonyl band in the 6 μ region.

α-Methylbenzyl Alcohol.—Acetophenone (10 g.) in dry ether (50 c.c.) was reduced with lithium aluminium hydride (1·5 g.) in ether (50 c.c.) as described by Larsson (*Trans. Chalmers*

Univ. Technol., 1950, No. 94, 15; *Chem. Abs.*, 1951, **45**, 1494). The carbinol (9·9 g.) distilled at 97°/17 mm. (Klages and Keil, *Ber.*, 1903, **36**, 1632, give b. p. 94°/12 mm.). Infra-red absorption: hydroxyl band at 3·0 μ; no carbonyl band in the 6 μ region.

1 : 3-*Dioxolans.*—The following general method was used for the preparation of the 1 : 3-dioxolans (ethylene ketals). The ketone (5—10 g.), ethylene glycol (1—5 mols.), and toluene-*p*-sulphonic acid (10—20 mg.) in benzene (40 c.c.) were refluxed in a Dean and Stark apparatus until the elimination of water was complete (16—48 hr.). The cooled solution was diluted with ether, washed with sodium hydrogen carbonate solution and water, and dried, and the solvents evaporated under reduced pressure (Salmi *et al.*, *Ber.*, 1938, **71**, 1803; 1939, **72**, 600; see also Sarett *et al.*, *J. Amer. Chem. Soc.*, 1953, **75**, 422, 1716). The results are summarised in the table.

1 : 3-*Dioxolans*, 

$R^1R^2C{<}\begin{matrix}O{-}CH_2\\ |\\ O{-}CH_2\end{matrix}$

R_1	R_2	Glycols, mol.	Time, hr.	Yield, %	M. p.	Formula	Found, %, C	Found, %, H	Reqd., %, C	Reqd., %, H
Me	Ph	1·07	48	95	60—61°	$C_{10}H_{12}O_2$	72·9	7·5	73·2	7·3 [b]
Me	*o*-C_6H_4OMe	1·06	16	90	124—125/11 mm. [a]	$C_{11}H_{14}O_3$	68·1	7·1	68·0	7·2 [c]
Me	*m*-C_6H_4OMe	3·85	24	70	47—48	$C_{11}H_{14}O_3$	68·1	7·1	68·0	7·2 [d]
Me	*p*-C_6H_4OMe	5·0	48	70	35—36	$C_{11}H_{14}O_3$	67·8	7·2	68·0	7·2 [e]

[a] B. p. [b] Large hexagonal prisms from light petroleum (b. p. 40—60°). [c] n_D^{16} 1·527. [d] Long needles from light petroleum (b. p. 60—80°). Ultra-violet absorption: max. at 275 mμ (ε = 2400) and 285 mμ (ε = 2400). [e] B. p. 136°/13 mm.

2-*Methyl*-2-*phenyl*-1 : 3-*oxathiolan.*—Acetophenone (8 g.) and 2-mercaptoethanol (10·4 g.) in dioxan (20 c.c.) were treated with freshly fused zinc chloride (10 g.) and freshly ignited anhydrous sodium sulphate (10 g.), and the mixture kept at room temperature for 24 hr. with occasional shaking (compare Djerassi, Romo, and Rosenkranz, *J. Amer. Chem. Soc.*, 1951, **73**, 4961). Water (200 c.c.) was added and the product extracted with ether. The ethereal extract was washed with water several times, and dried (sodium sulphate), and the ether evaporated. The residual oil was distilled through a 15-cm. Vigreux column, the fraction of b. p. 132—133°/16 mm., n_D^{17} 1·610 (7·1 g.) (Found: C, 66·95; H, 7·0. $C_{10}H_{12}OS$ requires C, 66·7; H, 6·7%), being the *oxathiolan*. A small fore-run, b. p. <130°/17 mm. (3·2 g.), consisted chiefly of unchanged acetophenone. Infra-red absorption: bands at 6·26 and 6·73 (benzene ring), 13·17 and 14·35 μ (monosubstituted aromatic ring); ether and thioether bands at 7·93, 8·25, and 8·9 μ.

Reductions with Sodium or Potassium and Alcohols in Liquid Ammonia.—The following general procedure was adopted (cf. Birch, *locc. cit.*). To a mechanically stirred solution of the compound (5—10 g.), the alcohol (*ca.* 100 c.c.), and ether (50 c.c.) in liquid ammonia (500 c.c.) was added, in small portions at a time during 1 hr., sodium or potassium metal (2—10 g.-atoms), the blue colour being allowed to disappear between additions. The vigorously stirred solution was treated with ether (200 c.c.), followed by water (100 c.c.), the organic layer was separated, the aqueous layer extracted with more ether (3 × 100 c.c.), and the combined extracts washed with a little water and dried (Na_2SO_4). Evaporation of the ether in a stream of nitrogen gave the product. Hydrolysis of the reduction products of anisole derivatives was effected by refluxing them for 1 hr. with 10% sulphuric acid (100 c.c.) in an atmosphere of nitrogen, the product being isolated with ether. Reduction products were in all cases purified by fractionation through a 15-cm. Vigreux column.

Acetophenone. (*a*) A solution of potassium (2·6 g.; 1 g.-atom) in *tert.*-butanol (100 c.c.) was added to liquid ammonia (400 c.c.) with stirring, followed by acetophenone (8 g.). Reduction with potassium (16 g.; 6·2 g.-atoms) gave ethylbenzene (5·5 g.), b. p. 136—137°, n_D^{20} 1·487, and unchanged acetophenone (1·0 g.), b. p. 202° (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 247—248°).

(*b*) A solution of potassium (3·25 g.; 1 g.-atom) in *tert.*-butanol (175 c.c.) was added to liquid ammonia (500 c.c.) followed by acetophenone (10 g.), and the solution left for 3 hr. Further treatment with potassium (20 g.) had no observable effect, acetophenone (5·5 g.), b. p. 204°, being recovered (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 247—248°).

α-*Methylbenzyl alcohol.* A solution of potassium (3·17 g.; 1 g.-atom) in *tert.*-butanol (75 c.c.) was added to liquid ammonia (500 c.c.) with stirring, followed by the carbinol (9·9 g.). Reduction with potassium (25·4 g.; 8·1 atoms) gave 1-*ethyl*cyclo*hexa*-1 : 4-*diene* (7·3 g.), b. p. 139—141°/755 mm., n_D^{18} 1·770 (Found: C, 89·1; H, 11·0. C_8H_{12} requires C, 88·9; H, 11·1%). The infra-red absorption spectrum, with medium bands at 6·25 and 6·70 μ, suggested that the product contained a small proportion of ethylbenzene. Bands in the 6 μ region indicate the presence of the ·CH:CH· system. When the product (1·0 g.) was shaken for several minutes with bromine water (200 c.c.), 1 : 2 : 4 : 5-*tetrabromo*-1-*ethyl*cyclo*hexane* was obtained, forming glistening plates (3·8 g.) (from methanol), m. p. 146° (Found : C, 22·65; H, 3·1. $C_8H_{12}Br_4$ requires C, 22·4; H, 2·8%).

2-*Methyl*-2-*phenyl*-1 : 3-*dioxolan* (IV; R′ = R″ = R‴ = H). (*a*) The dioxolan (7·3 g.), methanol (60 c.c.), and ether (70 c.c.) in liquid ammonia (400 c.c.), reduced with sodium (7 g.; 6·85 g.-atoms), gave ethylbenzene (5·0 g.), b. p. 135—138° (mainly 137°), n_{D}^{20} 1·486 (Found : C, 90·3; H, 9·5. Calc. for C_8H_{10} : C, 90·6; H, 9·4%). The appearance of a turbidity when the product was kept overnight, and the slight reaction towards bromine water suggested that the product contained a little 1-ethyl*cyclo*hexa-1 : 4-diene.

(*b*) The dioxolan (9·4 g.), reduced with sodium (2·65 g.; 2 g.-atoms) and methanol (30 c.c.) in liquid ammonia (400 c.c.) and ether (50 c.c.), gave ethylbenzene (2·4 g.), b. p. 44°/19 mm., n_{D}^{22} 1·495, and unchanged dioxolan (6·6 g.), b. p. 100—102°/19 mm., m. p. and mixed m. p. 60—61°.

2-*Methyl*-2-*phenyl*-1 : 3-*oxathiolan*. The thioketal (7 g.) in liquid ammonia (400 c.c.) and ether (50 c.c.), reduced with sodium (7 g.; 7·8 g.-atoms) and methanol (50 c.c.) gave ethylbenzene (4·0 g.), b. p. 139—140°/768 mm., n_{D}^{20} 1·490. The product contained some 1-ethylcyclo*hexa*-1 : 4-*diene*, as shown by the reaction towards bromine water, and the appearance of a turbidity when the product was kept for some hours.

o-*Methoxyacetophenone*. (*a*) The ketone (7·5 g.), reduced in liquid ammonia (400 c.c.) and ether (50 c.c.) with methanol (75 c.c.) and sodium (15 g.; 13 g.-atoms), gave after hydrolysis 6-*ethyl*cyclo*hex*-2-*enone* (3·5 g.), b. p. 85—86°/14—15 mm., n_{D}^{18} 1·479 (Found : C, 77·5; H, 10·0. $C_8H_{12}O$ requires C, 77·4; H, 9·7%). Ultra-violet absorption : max. at 225 mμ (ε = 7700). Infra-red absorption : bands at 5·96 (αβ-unsaturated carbonyl); slight evidence of saturated carbonyl band at 5·85 and of hydroxyl band at 2·87 μ. The ketone gave two 2 : 4-*dinitrophenylhydrazones*, which were separated by fractional crystallisation from ethanol. The more insoluble separated from ethyl acetate in deep-red, glistening plates or needles, m. p. 226° (Found : C, 55·4; H, 5·4; N, 18·5. $C_{14}H_{16}O_4N_4$ requires C, 55·3; H, 5·3; N, 18·4%); ultra-violet absorption (chloroform) : principal max. at 380 mμ (ε = 23,800). The more soluble form crystallised from ethanol in orange-red needles, m. p. 137—138° (Found : C, 55·6; H, 5·6; N, 18·1%); ultra-violet absorption (chloroform) : principal max. at 380 mμ (ε = 22,800). In view of the identity of the two curves, we consider it very likely that the two compounds are geometrical isomers. Birch (*J. Proc. Roy. Soc., N.S.W.*, 1949, **83**, 245) obtained a 2 : 4-dinitrophenylhydrazone, m. p. 225°, from the reduction product of *o*-methoxy-α-methylbenzyl alcohol, stated to be that of 2-ethyl*cyclo*hex-2-enone. It is almost certain that this derivative is identical with ours of m. p. 226°, and must in fact be derived from 6-ethyl*cyclo*hex-2-enone, which is the ketone to be expected after acid treatment of an initial dihydro-derivative formed in accordance with Birch's rules (*J.*, 1944, 430). This structure is confirmed by the ultra-violet absorption spectrum (see above). Birch also reports the separation of a second 2 : 4-dinitrophenylhydrazone, m. p. 118—119°, which he considered to be derived from 6-ethyl*cyclo*hex-2-enone; it is possible that this product was impure and corresponds with ours of m. p. 137—138°.

The *semicarbazone* separated from aqueous methanol in clusters of irregular prisms, m. p. 175—176° (Found : C, 59·7; H, 8·3. $C_9H_{15}ON_3$ requires C, 59·7; H, 8·3%); ultra-violet absorption : max. at 265 mμ (ε = 13,400), which is consistent with the assigned structure for the ketone (cf. Evans and Gillam, *J.*, 1943, 565).

(*b*) A solution of potassium (2·0 g.; 1 g.-atom) in *tert.*-butanol (60 c.c.) was added to liquid ammonia (600 c.c.) with stirring, followed by the ketone (7·5 g.; 1 mol.). Reduction with *tert.*-butanol (40 c.c.) and potassium (20 g.; 10 g.-atoms) gave after hydrolysis two fractions, (i) b. p. 84—90°/17·5 mm., n_{D}^{18} 1·513 (1·8 g.), and (ii) b. p. 100—130° (mainly 115—120°)/16·5 mm., n_{D}^{18} 1·379 (1·2 g.), together with an involatile syrup (2·5 g.). Fraction (i) showed bands in the infra-red at 5·97 (αβ-unsaturated carbonyl), 6·25, 6·70, and 13·31 (*o*-disubstituted benzene ring) and 7·78 and 8·07 μ (aromatic ether). It gave two 2 : 4-dinitrophenylhydrazones, m. p. 225—226° and 137—138° alone or mixed with the respective derivatives of 6-ethyl*cyclo*hex-2-enone (see above). Fraction (i) is therefore a mixture of the latter ketone and *o*-ethylanisole. Fraction (ii) gave an infra-red absorption curve almost identical with that of *o*-methoxyacetophenone. It formed a 2 : 4-dinitrophenylhydrazone, orange-brown needles (from pyridine), m. p. 240° (Found : C, 54·8; H, 4·1. Calc. for $C_{15}H_{14}O_5N_4$: C, 54·5; H, 4·2%), which appeared to be a polymorphic form of *o*-methoxyacetophenone 2 : 4-dinitrophenylhydrazone, m. p. 184—185° (see above), since the mixture had m. p. 184—185° and the ultra-violet absorption curves (chloroform) were identical. The syrupy residue crystallised partially on storage.

(*c*) Experiment (*b*) above was duplicated, with the modification that the solution of the ketone and potassium *tert.*-butoxide in liquid ammonia was kept for 4 hr. before reduction, during which time the solution darkened. The product (1·5 g.) distilled at 86—100°/19—20 mm. and had n_D^{19} 1·514; it was found to be 6-ethyl*cyclo*hex-2-enone, containing a little *o*-ethylanisole (comparison of 2 : 4-dinitrophenylhydrazones, and infra-red absorption spectra). An involatile syrup (3·0 g.) was obtained, which crystallised to a small extent when cool. With the aid of a little ether, the crystals, irregular prisms, m. p. 189—190° (Found : C, 62·0; H, 6·4%; *M*, 231), were collected. The substance was phenolic, and insoluble in ether, methanol, or ethanol. It afforded a brownish-red ferric test. Infra-red absorption : no hydroxyl band in 3 μ region, and no carbonyl band in 6 μ region. Ultra-violet absorption (acetic acid) : maxima at 245 mμ ($\varepsilon = 4000$) and 280 mμ ($\varepsilon = 10,000$).

o-Methoxy-α-methylbenzyl alcohol. A solution of potassium (1·2 g.; 1 g.-atom) in *tert.*-butanol (100 c.c.) was added to liquid ammonia (300 c.c.) with stirring, followed by the carbinol (3·6 g.). Reduction with potassium (9·7 g.; 10 g.-atoms) gave an oil (2·4 g.), b. p. 68°/13 mm. (Found : C, 79·2; H, 9·4. Calc. for $C_9H_{12}O$: C, 79·4; H, 8·8%), which appeared to be mainly *o*-ethylanisole (Birch, *Proc. Roy. Soc., N. S. W., loc. cit.*, gives b. p. 80°/14 mm.). Ultra-violet absorption : max. at 270 mμ ($\varepsilon = 1100$); infra-red absorption : bands at 6·25 and 6·70 (*o*-disubstituted benzene), 8·07 (aromatic ether) and 5·87 and 5·93 μ (both weak; ketones derived from the 1 : 4-addition of hydrogen to the aromatic nucleus). The product gave two 2 : 4-dinitrophenylhydrazones, in poor yield, identical with the two derivatives of 6-ethyl*cyclo*hex-2-enone, m. p. and mixed m. p. 226° and 137—138°.

2-o-*Methoxyphenyl*-2-*methyl*-1 : 3-*dioxolan* (IV; R′ = OMe, R″ = R‴ = H). The dioxolan (4·9 g.) in liquid ammonia (300 c.c.) and ether (50 c.c.) was reduced with sodium (5 g.; 8·7 g.-atoms) and methanol (30 c.c.). Hydrolysis and distillation gave an oil (2·7 g.), b. p. 72—73°/12 mm., n_D^{20} 1·512 (Found : C, 79·1; H, 8·8. Calc. for $C_9H_{12}O$: C, 79·4; H, 8·8%). The infra-red absorption spectrum, with bands at 7·80 and 8·10 (aromatic ether) and 8·90 and 13·35 μ (*o*-disubstituted benzene), and no carbonyl band in the 6 μ region, confirmed that the product was *o*-ethylanisole (b. p. 70—71°/11 mm.).

2-m-*Methoxyphenyl*-2-*methyl*-1 : 3-*dioxolan* (IV; R′ = R‴ = H, R″ = OMe). Reduction of the dioxolan in liquid ammonia (300 c.c.) with sodium (6·1 g.; 10 g.-atoms) and methanol (30 c.c.) gave an oil (3·2 g.), b. p. 74—77°/14 mm., n_D^{20} 1·490 (Found : C, 77·9; H, 10·0. $C_9H_{14}O$ requires C, 78·3; H, 10·1%), which appeared to be mainly 3-*ethyl*-2 : 5-*dihydroanisole*. The ultra-violet absorption spectrum showed only a weak max. at 270 mμ ($\varepsilon = 600$), indicating the presence of a small quantity of a *cyclo*hexadiene with conjugated double bonds. Hydrolysis gave an oil (1·3 g.), b. p. 88—92°/14 mm., n_D^{17} 1·485 (Found : C, 77·4; H, 9·2. Calc. for $C_8H_{12}O$: C, 77·5; H, 9·7%), which was evidently 3-ethyl*cyclo*hex-2-enone. Blaise and Maire (*Bull. Soc. chim.*, 1908, **4**, 419), give b. p. 83°/8 mm. The infra-red absorption indicated that some aromatic material was present in the product (bands at 6·25, 6·75, and 8·0 μ), probably 3-ethylanisole. The ultra-violet absorption spectrum showed a max. at 230 mμ ($\varepsilon = 11,400$), a rather low wave-length for the structure [compare 3-methyl*cyclo*hex-2-enone (R. M. Acheson, unpublished work), max. at 240 mμ ($\varepsilon = 12,000$)]. The 2 : 4-dinitrophenylhydrazone separated from ethanol in orange-red needles, m. p. 163—164° (Found : C, 55·5; H, 5·1; N, 18·3. Calc. for $C_{14}H_{16}O_4N_4$: C, 55·3; H, 5·3; N, 18·4%), undepressed in m. p. on admixture with a specimen of the same derivative (m. p. 159—160°) of 3-ethyl*cyclo*hex-2-enone prepared by the unambiguous method of Woods and co-workers (*J. Amer. Chem. Soc.*, 1949, **71**, 2028) (specimen kindly supplied by Professor G. F. Woods, University of Maryland).

2-p-*Methoxyphenyl*-2-*methyl*-1 : 3-*dioxolan* (IV; R′ = R″ = H, R‴ = OMe). (*a*) The dioxolan (6·7 g.), reduced with sodium (1·67 g.; 2 g.-atoms) in liquid ammonia (300 c.c.) and ether (5 c.c.) and methanol (9 c.c.), gave two fractions : (i) (1·6 g.), b. p. 82—84°/17 mm., n_D^{20} 1·509 (for *p*-ethylanisole, Klages, *Ber.*, 1903, **36**, 3593, gives b. p. 83—84°/16 mm., n_D 1·509), and (ii) (3·8 g.) b. p. 154—160°/17 mm., infra-red examination of which indicated that it was chiefly unchanged dioxolan.

(*b*) The dioxolan (9·4 g.), reduced in liquid ammonia (500 c.c.), ether (50 c.c.) and methanol (50 c.c.) with sodium (8·0 g.; 7·2 g.-atoms), gave after hydrolysis an oil (4·5 g.), b. p. 88—93°/14·5 mm. (Found : C, 77·6; H, 9·7. $C_8H_{12}O$ requires C, 77·4; H, 9·7%), together with a little residue (0·8 g.). The product was chiefly 4-*ethyl*cyclo*hex*-2-*enone*; ultra-violet absorption : max. at 225 mμ ($\varepsilon = 10,000$), with a subsidiary max. at 285 mμ ($\varepsilon = 3650$). Infra-red absorption : bands at 5·84 (medium intensity, saturated carbonyl), 5·97 (high intensity, αβ-unsaturated carbonyl), 6·35 and 6·62 (aromatic ring), and 6·12 (double bond) and an inflexion at 6·20 μ (conjugated diene). The band at 285 mμ indicates the presence of an impurity containing a conjugated dienone system (Evans and Gillam, *J.*, 1945, 432), and that at 5·84 μ reveals the presence of material containing a saturated or βγ-unsaturated carbonyl group (probably 4-ethyl*cyclo*hex-3-enone). The latter possibility is considered the more likely in view of the failure of certain 4-alkyl*cyclo*hex-3-enones to be isomerised to the corresponding *cyclo*hex-2-enones on treatment with mineral acids (Birch and Mukherji, *J.*, 1949, 2531).

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