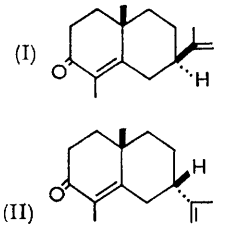
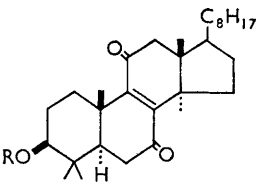
581. *Mechanisms of Catalytic Hydrogenation. Part I. An Examination of the Rôle of Alkali and of Acid.*

By F. J. McQuillin and W. O. Ord.

The observation [1] that alkaline conditions retard hydrogenation of the 11,12-olefinic bond in (+)-α-cyperone (I) and its $C_{(7)}$-epimer (II) in comparison with the 4,5-bond of the enone system has been extended to further examples of enones, dienones, olefins, and acetylenic compounds. The hydrogenation of the enones examined is generally unaffected by alkali or, in some cases, accelerated, whilst most of the acetylenes and olefins show retardation of reduction. Alkali promotes reduction of butyne-1,4-diol to *trans*-but-2-ene-1,4-diol. Possible reasons for these results are discussed as well as for the catalytic effect of acid.

In examining the catalytic hydrogenation of (+)-α-cyperone (I) and its $C_{(7)}$-epimer (II) in alcohol in the presence of alkali, reduction of the 11,12-olefinic bond was found to be retarded relative to that of the 4,5-bond.[1] Such differential reduction had already been noted.[2] Acid is known to catalyse and in many cases influence the steric course of hydrogenation of olefins, ketones,[3] and aromatic substances.[4]





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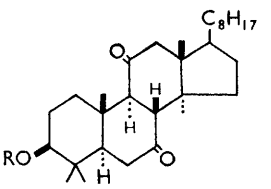


(IV)

Hydrogenations were carried out as far as possible under standardised conditions, a neutral palladised charcoal catalyst being used,[5] in a differential apparatus [6] with compensating solvent vessel. The solvent was usually ethanol or ethanolic potassium hydroxide. The ratio, rate in alkaline ethanol : rate in ethanol, was determined from the ratio of the slopes of the hydrogenation curves, which under these conditions are essentially linear for a large part of the reaction.

The rate of hydrogenation of a range of αβ-unsaturated ketones was relatively unaffected or increased by alkali, whilst the olefins examined, except styrene, showed considerable retardation, most marked with guaiazulene. Alkali catalysis of hydrogenation of the conjugated enone system is known [7] but more examples are important to show that alkali is not a catalyst poison. The lanost-8-ene-7,11-dione examples, which showed the largest alkali catalysis, were included as apparent exceptions to *cis*-hydrogen addition.[8] 7,11-Dioxolanost-8-en-3β-yl acetate (III; R = Ac) is hydrogenated directly [9] to 7,11-dioxolanostan-3β-yl acetate (IV; R = Ac).

7,11-Dioxolanost-8-en-3β-ol (III; R = H) and its acetate were reduced extremely slowly in neutral solvent, but alkali (0·5%) was strongly catalytic. In the same solvent,

[1] Howe and McQuillin, *J.*, 1958, 1194.
[2] Cf. Johnson, Bannister, Pappo, and Pike, *J. Amer. Chem. Soc.*, 1956, **78**, 6354, who give earlier references.
[3] Cf. Brewster, *ibid.*, 1954, **76**, 6361.
[4] Brown, Durand, and Marvel, *ibid.*, 1936, **58**, 1594; cf. Keenan, Giesemann, and Smith, *ibid.*, 1954, **76**, 229.
[5] Linstead and Thomas, *J.*, 1940, 1127.
[6] Jackson, *Chem. and Ind.*, 1938, **57**, 1076.
[7] Wilds, Johnson, and Sutton, *J. Amer. Chem. Soc.*, 1950, **72**, 5524; Anliker, Heusser, and Jeger, *Helv. Chim. Acta*, 1952, **35**, 838.
[8] Cf. Linstead, Doering, Davis, Levine, and Whetstone, *J. Amer. Chem. Soc.*, 1942, **64**, 1985.
[9] Dorée, McGhie, and Kurzer, *J.*, 1948, 988.

hydrogenation of the sterol and its acetate was greatly accelerated by small amounts of perchloric or acetic acid. The effect of alkali is clearly not generally catalytic (see Tables), and it appears unlikely that acid and alkali should influence the catalyst work function [10] in the same sense.

Analogous 7-oxo-8,9-olefinic steroids of the cholestane series are hydrogenated to the 8β,9α(*H*)-derivative,[11,12] whilst corresponding 11-oxo-8,9-olefinic steroids yield the 8α,9α(*H*)-derivative but much more slowly.[12] 8,9-Olefinic steroids lacking the conjugated

Relative rate : rate in alkaline ethanol/rate in ethanol.

(a) *αβ-Unsaturated ketones*

Cholest-4-en-3-one	0·9	10-Ethoxycarbonyl-2-oxo-$\Delta^{1,9}$-octalin ...	1·0
(+)-Carvone	0·8	α-Ionone	2·2
(+)-Carvotanacetone	0·7	7,11-Dioxolanost-8-en-3β-ol *	v. large
Mesityl oxide	0·8	7,11-Dioxolanost-8-en-3β-yl acetate *	v. large
10-Methyl-2-oxo-$\Delta^{1,9}$-octalin	1·3	Sodium anthraquinone-2-sulphonate † ...	1·0

(b) *Acetylenes*

Propargyl alcohol	0·3	1-Ethynylcyclohexan-1-ol	1
Butyne-1,4-diol	0·2	Phenylacetylene	0·7
Pent-2-yne-1,4-diol	0·2	Potassium acetylenedicarboxylate †	0·4

(c) *Olefins*

Allyl alcohol ‡	0·12	Styrene ‡	0·6
Butene-1,4-diol ‡	0·07	(−)-Dihydrocarvone	0·14
Pent-2-ene-1,4-diol ‡	0·07	Hexa-2,4-diene-1-ol	0·18
1-Vinylcyclohexan-1-ol ‡	0·11	Guaiazulene	0

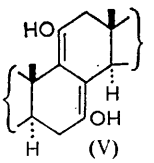
(d) *More conjugated ketones*

Benzylideneacetone	0·5	3,4-Methylenedioxybenzylideneacetone...	0·13
p-Dimethylaminobenzylideneacetone	0·3	*p*-Hydroxybenzylideneacetone	0·2
p-Chlorobenzylideneacetone	0·3	(+)-β-Cyperone	0·2
p-Methoxybenzylideneacetone	0·2	β-Ionone	0·2

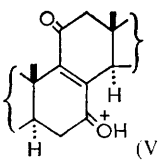
* In dioxan–ethanol (3 : 1). † In water.

‡ These figures represent the rate of the second stage of reduction of the corresponding acetylene of table (*b*).

carbonyl group are resistant to hydrogenation.[9,13] 8α,9α-Hydrogen addition leads to chair ⟶ boat compression of the molecule.[11] Isolation of the 8β,9α(*H*)-dihydro-derivative in the 7-oxo-series has been ascribed to enolisation inversion following reduction,[11] or to reduction *via* an enol.[12] Inversion following hydrogenation will not relieve compression at the reduction stage associated with 8α,9α-hydrogen addition, and alkali stabilisation of the dienol (V) or dienolate ion offers a more reasonable explanation of alkali



(V)



(VI)

catalysis in the present case. The formal analogy [14] led us to include sodium anthraquinonesulphonate in Table (a). Similarly the acid catalysis is consistent [3] with reduction *via* the conjugate acid, *e.g.* (VI).

Hydrogen-ion catalysis appeared also to be implicated in the behaviour of the benzylidene derivatives in Table (d). Those in alcohol absorbed up to 1·5 mols. of hydrogen to give mixed products showing hydroxyl absorption in the infrared region, but in presence of

[10] Cf. Dowden, *J.*, 1951, 242.
[11] Bladon, Henbest, Jones, Lovell, Wood, Woods, Elks, Evans, Hathway, Oughton, and Thomas, *J.*, 1953, 2921.
[12] Djerassi, Fricke, Rosenkranz, and Sondheimer, *J. Amer. Chem. Soc.*, 1953, **75**, 2496.
[13] Cf. Barton and Cox, *J.*, 1949, 214.
[14] Cf. Michaelis and Schubert, *Chem. Rev.*, 1938, **22**, 437.

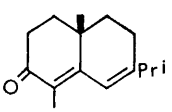
alkali absorption of hydrogen stopped at 1 mol. to give the benzyl ketones. The catalyst rather than the solvent appeared to be the proton source since *p*-dimethylaminobenzylideneacetone was reduced at palladised charcoal in ethyl acetate to the same mixed product (*i.e.*, VIII, IX) as was obtained in alcohol. The hydrogenation of benzylideneacetone was accelerated by addition of acid. These observations are most simply related to carbonyl reduction *via* the conjugate acid (VII), formed at the catalyst surface. This view was supported by quantitative reduction of *p*-hydroxybenzylideneacetone and piperonylideneacetone at palladium on strontium carbonate to the benzyl ketones.

$$\underset{\text{(VIII)}}{ArCH_2{\cdot}CH_2{\cdot}COMe} \longleftarrow ArCH{:}CH{\cdot}COMe \xrightarrow{H^+} \underset{\text{(VII)}}{ArCH{:}CH{\cdot}CMe{:}\overset{+}{O}H} \longrightarrow \underset{\text{(IX)}}{ArCH_2{\cdot}CH_2{\cdot}CHMe{\cdot}OH}$$

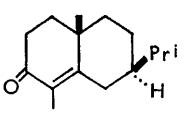
The product of absorption of 1 mole of hydrogen by (+)-β-cyperone (X) in alkaline ethanol was found by ultraviolet analysis to be ~20% recovered β-cyperone, 60% of a conjugated ketone ($\lambda_{max.}$ 249 mμ), and 20% of the tetrahydro-derivative. This composition is similar to that of the reduction of β-cyperone at a lead-poisoned catalyst in benzene,[15] and on this basis the conjugated ketone is clearly (XI). Woodward and his co-workers [16] refer to the importance of an aprotic medium for partial (4,5) hydrogenation of a dienone; use of alkali may sometimes offer a useful alternative.

β-Ionone was reduced in alkali to the expected mixture of conjugated and unconjugated dihydro-ionones, after absorption of one mole of hydrogen.[17] In α-ionone the olefinic bond is known to be the less readily hydrogenated; [18] the presence of alkali increased this contrast.

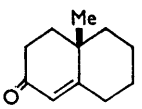
Alkaline conditions sometimes favour reduction to the *cis*- rather than to the *trans*-decalone of compounds of general type (XIII) in the steroid [7,19] and sesquiterpene field.[1] The octalones (XII) and (XIII) were examined since the ethoxycarbonyl derivative (XIII) yields [20] exclusively the *trans*-, and the methyl analogue (XII) mainly the *cis*-decalone [21] on hydrogenation in alcohol. We obtained the same products and at closely the same rate in alcohol and in alkali.



(X)



(XI)



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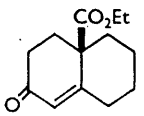

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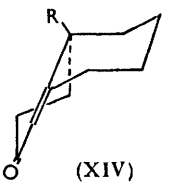

(XIV)

The conformation (XIV) shows a molecule predisposed to absorption on the upper face, *i.e.*, to reduction to the *cis*-decalone provided the group R is not too large, *e.g.*, Me, with reduction to the *trans*-decalone as a more difficult, competing process which becomes important when the group R, *e.g.*, CO_2Et, offers serious hindrance to absorption. The behaviour of examples (XII) and (XIII) shows that alkali does not here alter fundamentally the mode of absorption or the process of hydrogen transfer.

Although a minor proportion of *trans*-olefin is frequently formed, semi-hydrogenation of acetylenes is the most convenient route to *cis*-olefins. On reduction at palladium,[22]

[15] Howe and McQuillin, *J.*, 1956, 2670.
[16] Woodward, Sondheimer, Taub, Heusler, and MacLamore, *J. Amer. Chem. Soc.*, 1952, **74**, 4223.
[17] Naves and Aridizio, *Helv. Chim. Acta*, 1949, **32**, 206.
[18] Naves, *ibid.*, 1947, **30**, 769.
[19] Cf. Slomp, Shealy, Johnson, Donia, Johnson, Holysz, Pederson, Jensen, and Ott, *J. Amer. Chem. Soc.*, 1955, **77**, 1216, and for earlier references.
[20] Dauben, Tweit, and MacLean, *ibid.*, p. 48.
[21] Dauben, Rogan, and Blanz, *ibid.*, 1954, **76**, 6384; du Feu, McQuillin, and Robinson, *J.*, 1937, 53; Linstead, Millidge, and Walpole, *J.*, 1937, 1140.
[22] Johnson, *J.*, 1946, 1014; Raphael, *J.*, 1952, 401.

and in most instances at Raney nickel,[23] butyne-1,4-diol gives *cis*-but-2-ene-1,4-diol. We obtained *cis*-but-2-ene-1,4-diol in alcohol, but in presence of alkali, the product contained a high proportion of the *trans*-isomer. *cis*-But-2-ene-1,4-diol was not inverted in alcoholic alkali with palladised charcoal in nitrogen. The *trans*-isomer is therefore a primary reduction product. Salkind[24] found the corresponding *cis*- and *trans*-1,4-dimethylhex-2-ene-1,4-diols similarly resistant to inversion by contact with catalyst in alcohol.

Hydrogen adds to acetylenedicarboxylic acid and its ester predominantly *trans* under some conditions.[25] From monopotassium acetylenedicarboxylate we obtained fumarate by reduction in water or aqueous alkali.

Hydrogen addition to acetylenes is generally predominantly *cis* at a zinc–copper couple,[26] but acetylenedicarboxylic[26] and phenylpropiolic acid[27] are again exceptional. The rôle of the carboxyl group in promoting inversion suggests an intermediate in reduction of butyne-1,4-diol which is of longer life in presence of alkali.

For the compounds in the Table, of which each group contains varied examples, sensitiveness to alkali retardation of hydrogenation is apparently associated with the chemical type of unsaturated centre present; in the earlier examples[1,2,7] the differential effect of alkali was observed for different centres in the same molecule. Such a correlation could be fortuitous; by being rapidly reduced, or very strongly absorbed, a substance could be especially sensitive to access of hydrogen to the catalyst with which alkali might physically interfere. The measured rates of hydrogen uptake (in absence of alkali) were, however, of the same order, with in each group an appreciable range, *viz.* (*a*) 0·06—5, (*b*) 1·3—6, (*c*) 0·1—10, and (*d*) 0·8—4 c.c./min. Acetylenes are very strongly absorbed, and commonly more strongly than the related olefin. The acetylenes appear, however, to be less sensitive to alkali retardation than the olefin. These reasons, the altered steric result of reduction of butyne-1,4-diol, and the instances of alkali catalysis suggested that the influence of alkali may be at the stage of hydrogen transfer.

The hydrogenation of guaiazulene was strongly inhibited by alkali but accelerated in alcohol by addition of a little, but not further by larger amounts of perchloric acid. This azulene was included as a basic type of hydrocarbon known to be reversibly protonated in acid solution. Protonation at the catalyst surface would therefore merit consideration as a step in olefin reduction.

Experimental

$[\alpha]_D$ and $\lambda_{max.}$ refer to solutions in chloroform and ethyl alcohol, respectively, and infrared data to liquid film (0·01 mm.) or potassium bromide disc as appropriate.

Method.—The compound was introduced in a glass bucket which could be dropped into the contents of the vessel after the catalyst had been saturated with hydrogen at atmospheric pressure. The less soluble compounds were dissolved in a small volume of the solvent being used. The catalyst, prepared after Linstead and Thomas[5] from palladous chloride (1·8 g.) and activated charcoal (2·2 g.) by reduction with alkaline formaldehyde, was washed with acetic acid and then with water to neutrality.

Results.—Details are given in parentheses following the name of the compound in the following order: amount of compound hydrogenated (g.), amount of catalyst used (g.), temperature, rate of uptake in 30 c.c. of alcohol (c.c./min.), rate of uptake in 30 c.c. of 2% alcoholic potassium hydroxide (c.c./min.).

Cholest-4-en-3-one (0·199, 0·04, 23°, 0·8, 0·73). The product, isolated in each case by chromatography, afforded coprostan-3-one, m. p. 62°, from ethanol.

(+)-*Carvone* (0·531, 0·106, 18°, 5·7, 4·9). The product from reduction in alcohol had b. p. 120°/14 mm., n_D^{20} 1·4881, $[\alpha]_D$ −2·76° (*c* 5·17), showed infrared bands at 1704 (>C=O) and 1661 cm.$^{-1}$ (>C=C–C–C=O), and was clearly a mixture. The material from reduction in alkali

[23] Marvel and Young, *J. Amer. Chem. Soc.*, 1951, **73**, 1066; Romanet, *Compt. rend.*, 1953, **236**, 1044, 1176; Valette, *Ann. Chim.*, 1948, **3**, 644.
[24] Salkind, *Ber.*, 1923, **56**, 187.
[25] Ott and Schroter, *Ber.*, 1927, **60**, 624.
[26] Clark and Crombie, *Chem. and Ind.*, 1957, 143.
[27] Barth and Glemser, *Ber.*, 1934, **67**, 1669.

had b. p. 120°/14 mm., and showed only saturated carbonyl absorption at 1709 cm.$^{-1}$, n_D^{20} 1·4701, $[\alpha]_D$ −13·5° (*c* 4·7), in agreement with (−)-dihydrocarvone [28] (n_D^{20} 1·4716, $[\alpha]_D$ −16° liquid); the 2,4-dinitrophenylhydrazone had m. p. and mixed m. p. 146°.

(+)-*Carvotanacetone* (0·533, 0·10, 20°, 3·9, 2·6). The product from reduction in alcohol had b. p. 90°/11 mm., n_D^{20} 1·4606, and showed infrared absorption at 3408 cm.$^{-1}$ (OH). The material from reduction in alkali had b. p. 90°/11 mm., n_D^{20} 1·4551, $[\alpha]_D$ −11·7° (*c* 5·3), values agreeing closely with those for (−)-tetrahydrocarvone [29] (n_D^{30} 1·4531, $[\alpha]_D^{30}$ −9·3°, liquid). The 2,4-dinitrophenylhydrazone had m. p. and mixed m. p. 150°.

Mesityl oxide (0·348, 0·07, 20°, 6·5, 4·3). The product, after completion of reduction, in each case gave isobutyl methyl ketone semicarbazone, m. p. 132—133° (Wieland [30] gives m. p. 130°).

2,3,4,5,6,7,8,10-*Octahydro*-10-*methyl*-2-*oxonaphthalene* (0·49 0·07, 17·5°, 2·1, 2·7). The products, b. p. 60°/0·1 mm., n_D^{20} 1·4918 and 1·4940, respectively gave the same infrared spectra and when seeded gave *cis*-10-methyl-2-decalone, m. p. 37° (cf. du Feu, McQuillin, and Robinson, and Dauben, Rogan, and Blanz [21]).

10-*Ethoxycarbonyl*-2,3,4,5,6,7,8,10-*octahydro*-2-*oxonaphthalene* (0·08, 0·015, 16°, 0·35, 0·35, 3 c.c. of solution being used in each case). 10-Ethoxycarbonyl-2-decalone isolated from both experiments gave identical infrared spectra and the semicarbazone, m. p. 194°, of the pure *trans*-ketone, from aqueous ethanol (Dauben, Tweit, and MacLean [20] give n_D^{25} 1·4790; semicarbazone, m. p. 193—194°).

α-*Ionone* (0·349, 0·05, 19°, 0·9, 1·7). The product from alkaline reduction showed only saturated carbonyl absorption (1715 cm.$^{-1}$), and at 3031 and 813 cm.$^{-1}$ bands corresponding to the group >C=CH−; the 2,4-dinitrophenylhydrazone had m. p. 101° (cf. Naves and Lecomte [31]).

7,11-*Dioxolanost*-8-*en*-3β-*ol* (0·165, 0·032, 19°). In dioxan–alcohol (3 : 1; 50 c.c.) there was negligible absorption of hydrogen (0·2 c.c. in 15 min.). After addition of 60% perchloric acid (4 drops) hydrogen was absorbed at 1·3 c.c./min. In dioxan–alcohol (3·1; 50 c.c.) containing potassium hydroxide (0·5%) the uptake was initially 0·17 c.c./min. A product, m. p. 186°, $[\alpha]_D$ +26·9° (*c* 5·21), was isolated directly from the alkaline reduction and from reduction in acid after chromatography. Dorée, McGhie, and Kurzer [9] give m. p. 184°, $[\alpha]_D$ +25·7° for 7,11-dioxolanostan-3β-ol.

7,11-*Dioxolanost*-8-*en*-3β-*yl acetate* (0·494, 0·051, 24°). (*a*) In dioxan–alcohol (3 : 1; 50 c.c.) hydrogen uptake was very slow (3·1 c.c. in 49 min.); after addition of acetic acid (1 c.c.) the initial rate was 0·7 c.c./min. (*b*) In dioxan–alcohol (3 : 1; 50 c.c.) with 60% perchloric acid (0·1 c.c.) the uptake was 0·6 c.c./min. (*c*) In dioxan–alcohol (3 : 1; 50 c.c.) containing potassium hydroxide (0·5%) the initial uptake was 0·25 c.c./min. The products from reduction in acid solution isolated by chromatography gave 7,11-dioxolanostan-3β-yl acetate, m. p. 224°, $[\alpha]_D$ +56·3° (*c* 4·8) (Dorée, McGhie, and Kurzer [9] give m. p. 222—224°, $[\alpha]_D$ +54·6°). Hydrolysis of the product of reduction in alkali gave 7,11-dioxolanostan-3β-ol, m. p. 186° (cf. Dorée, McGhie, and Kurzer [9]).

Sodium anthraquinone-2-*sulphonate* (0·285, 0·057, 21°). In water (50 c.c.) and in sodium hydroxide (2%; 50 c.c.), hydrogen uptake was 1·45 c.c./min.

Propargyl alcohol (0·09 g., 0·019, 17°). In alcohol hydrogen uptake for the first step was 1·5 c.c./min. and for the second 7 c.c./min.; in alkali for the first step 0·5, and for the second 1·8 c.c./min.

Butyne-1,4-*diol* (0·147, 0·03, 18°, 4·0 + 3·0, 0·8 + 0·5). The product, b. p. 130°/20 mm., n_D^{20} 1·4710, of semireduction of butyne-1,4-diol (0·29 g.) in alcohol gave *cis*-but-2-ene-1,4-diol dibenzoate, m. p. 67°, in 91% yield (Clarke and Crombie [30] give m. p. 67°).

cis-But-2-en-1,4-diol (0·29 g.), prepared in this way, was shaken in alcoholic sodium hydroxide (2%, 50 c.c.) with palladised charcoal (0·32 g.) in nitrogen for some hours; it gave the same dibenzoate, m. p. 67°, in excellent yield.

The product of semireduction of butyne-1,4-diol (1·5 g.) in alcoholic sodium hydroxide (0·1%; 40 c.c.) had b. p. 127°/20 mm., n_D 1·4680. Its dibenzoate, m. p. 101° [from petroleum (b. p. 100—120°) and then methanol], was formed in substantial yield. For *trans*-but-2-ene-1,4-diol dibenzoate Prévost and Lutz [32] give m. p. 101°.

[28] Semmler and Feldstein, *Ber.*, 1914, **47**, 384.
[29] Simonsen and Rau, *J.*, 1922, 876.
[30] Wieland, *Ber.*, 1925, **58**, 2016.
[31] Naves and Lecomte, *Bull. Soc. chim. France*, 1953, 112.
[32] Prévost and Lutz, *Compt. rend.*, 1934, **198**, 2264.

Complete hydrogenation in alcohol gave butane-1,4-diol (dibenzoate, m. p. 81° cf. Hamonet [33])].

Pent-2-yne-1,4-diol (0·178, 0·035, 20°, 6 + 7·5, 1·4 + 1·1).

1-*Ethynylcyclohexan*-1-*ol* (0·221, 0·043, 18°, 6·5 + 10, 6·5 + 1·6).

The products, b. p. 63°/13 mm., n_D^{20} 1·4618, from alcohol reduction, and n_D^{20} 1·4620, from reduction in alkali (Found: C, 74·8; H, 12·6; and C, 75·0; H, 12·5; respectively. Calc. for $C_8H_{16}O$: C, 75·0; H, 12·5%) gave the same infrared spectra. Wallach [34] gives n_D^{20} 1·4638 for 1-ethylcyclohexan-1-ol.

Phenylacetylene (0·182, 0·038, 19°, 4·0 + 5·6, 2·6 + 3·7).

Potassium acetylenedicarboxylate (0·369, 0·074 g, 19·5°, 2·5, 1·05). The product from both experiments, isolated and recrystallised from water, was fumaric acid, sublimed ~200°, identical with an authentic specimen.

(−)-*Dihydrocarvone* (0·536, 0·096, 17°, 3·2, 0·42). The products, b. p. 125°/14 mm., n_D^{20} 1·4579, $[\alpha]_D$ −11·3° (*c* 5·18), from reduction in alcohol, and n_D^{20} 1·4579, $[\alpha]_D$ −13·3° (*c* 5·03), from alkali both gave a 2,4-dinitrophenylhydrazone, m. p. 149°, in agreement with that of (−)-tetrahydrocarvone.[29]

Hexa-2,4-dien-1-ol (0·173, 0·034, 24°, 10·1, 1·8). After absorption of 2 mols. of hydrogen in alcohol hexan-1-ol, b. p. 90°/34 mm., n_D^{20} 1·3964, was isolated (Behal [35] gives n_D^{20} 1·4133). After absorption of 1 mol. of hydrogen in alkaline alcohol hexenol was isolated, b. p. 95°/32 mm., n_D^{20} 1·4280; it showed strong bands at 972 and 1698 cm.$^{-1}$ (*trans*-CH=CH–).

Guaiazulene (0·101, 0·025, 19°).

Initial rates of reduction (*a*) in alcohol (30 c.c.), and in the same solvent containing (*b*) 0·1 c.c. and (*c*) 1·0 c.c. of 60% perchloric acid were 0·1, 0·27, and 0·28 c.c./min. respectively.

In alcoholic potassium hydroxide (0·1%, 30 c.c.) there was no uptake of hydrogen. Complete reduction in alcohol took 50 c.c. of hydrogen (theory for 4 double bonds, 49 c.c.).

Benzylideneacetone (0·141, 0·029, 19°). Hydrogen uptake in (*a*) alcohol (40 c.c.), (*b*) alcoholic potassium hydroxide (2%, 40 c.c.), and (*c*) alcohol (40 c.c.) with hydrochloric acid (2 drops) was 1·6, 0·8, and 2·9 c.c./min.

The products isolated from experiments (*a*) and (*b*) had b. p. 110—115°/12 mm., n_D^{20} 1·5095 and n_D^{20} 1·5090 respectively, and gave a semicarbazone, m. p. 142° (Klages [36] gives m. p. 142° for the semicarbazone of benzylacetone).

p-*Dimethylaminobenzylideneacetone* (0·141, 0·03, 19°). Hydrogen uptake in (*a*) alcohol (40 c.c.), (*b*) alcoholic potassium hydroxide (2%; 40 c.c.), and (*c*) ethyl acetate (40 c.c.) was 1·3, 0·35, and 0·55 c.c./min.

The product from experiment (*b*) was *p*-dimethylaminobenzylacetone, b. p. 70°/0·1 mm., m. p. 49° (from aqueous alcohol) (Rupe, Collin, and Schmiderer [37] give m. p. 50·5°). The products from (*a*) and (*c*), respectively n_D^{20} 1·5450 and 1·5439, failed to crystallise. The infrared spectra showed bands at 3425 cm.$^{-1}$ (OH, strong), 1712 and 1621 cm.$^{-1}$ (>CO and Ar·C=C·CO), and 947 cm.$^{-1}$ (·CH=CH·).

p-*Chlorobenzylideneacetone* (0·136, 0·029, 21°, 2·2, 0·7; 40 c.c. were used in each experiment). The product of reduction in alcohol had b. p. 110°/0·3 mm., n_D^{20} 1·5502 and showed strong infrared absorption at 3474 (OH), 1605 (ArCH=CH·CO), and 978 cm.$^{-1}$ (·CH=CH·). The product from reduction in alkali had n_D^{20} 1·5250 and showed strong carbonyl absorption at 1715 cm.$^{-1}$. It was clearly *p*-chlorobenzylacetone, giving a *semicarbazone*, m. p. 153—154° (from ethanol) which was phototropic (Found: C, 54·6; H, 6·0. $C_{11}H_{14}ON_3Cl$ requires C, 55·0; H, 5·8%).

p-*Methoxybenzylideneacetone* (0·132, 0·027, 20°, 2·4, 0·48; 40 c.c. were used in each experiment). The product, b. p. 105°/0·3 mm., n_D^{20} 1·5462, from reduction in alcohol showed strong absorption at 3435 (OH) and 1607 cm.$^{-1}$ (ArCH=CH·CO·). The product, n_D^{20} 1·5179, from alkali showed strong carbonyl absorption at 1712 cm.$^{-1}$ and was characterised as the semicarbazone, m. p. 169° (from alcohol). Strauss and Grindel [38] give m. p. 169—170° for *p*-methoxybenzylacetone semicarbazone.

3,4-*Methylenedioxybenzylideneacetone* (0·1, 0·021, 18°, 1·2, 0·16; 40 c.c. were used in each

[33] Hamonet, *Bull. Soc. chim. France*, 1905, **33**, 523.
[34] Wallach, *Annalen*, 1908, **360**, 26.
[35] Behal, *Bull. Soc. chim. France*, 1919, **25**, 473.
[36] Klages, *Ber.*, 1904, **37**, 2301.
[37] Rupe, Collin, and Schmiderer, *Helv. Chim. Acta*, 1931, **14**, 1340.
[38] Straus and Grindel, *Annalen*, 1924, **439**, 276.

experiment). From reduction in alkali 3,4-methylenedioxybenzylacetone was isolated, m. p. 50°; it was also obtained with some difficulty from reduction in alcohol. It was more conveniently obtained by reduction in ethyl acetate using a palladised strontium carbonate catalyst; it then had m. p. 51° without purification (Vavon and Faillebin [39] give m. p. 50—51° for 3,4-methylenedioxybenzylacetone).

p-*Hydroxybenzylideneacetone* (0·122, 0·025, 18°, 0·8, 0·17; 40 c.c. were used in each experiment). *p*-Hydroxybenzylacetone, m. p. 82—83°, was obtained in each case; reduction in alkali gave much the purer product. The use of palladised strontium carbonate and ethyl acetate gave a pure product directly. For *p*-hydroxybenzylacetone Mannich and Merz [40] give m. p. 83—84°.

(+)-β-*Cyperone* (0·22, 0·035, 17·5°, 1·6, 0·35). The product from absorption of 1 equivalent of hydrogen in alkali had n_D^{20} 1·5164, $\lambda_{max.}$ 249 and 298 mμ (ε 9499 and 5129).

β-*Ionone* (0·354, 0·05, 22°, 3·2, 0·6). Hydrogenation was complete in alcohol to give a tetrahydroionone, b. p. 90°/0·2 mm., n_D^{20} 1·4695. In alkaline solution reduction was only a little over half complete; the product had n_D^{20} 1·4808, $\lambda_{max.}$ 229 mμ, ε 6022.

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[39] Vavon and Faillebin, *Compt. rend.*, 1919, **169**, 65.
[40] Mannich and Merz, *Arch. Pharm.*, 1927, **265**, 22.