

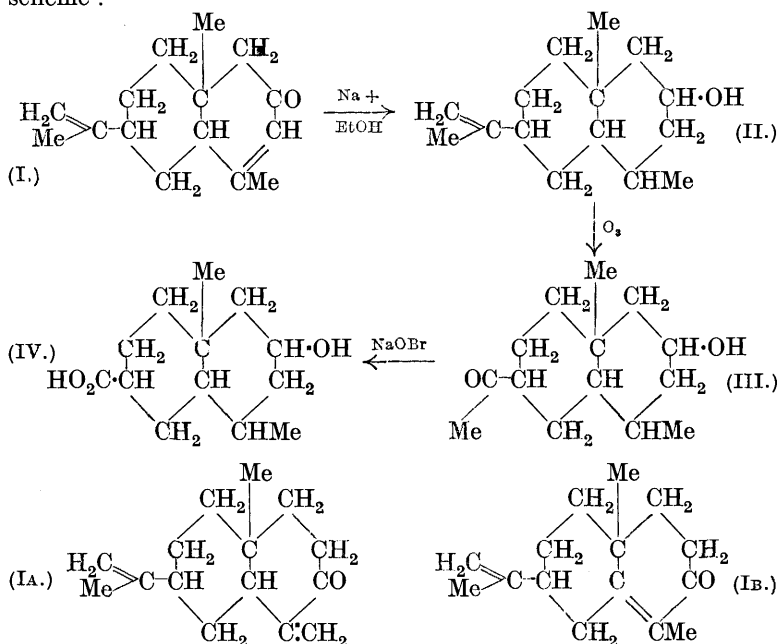
414. *The Constitution of Eremophilone and of Two Related Hydroxy-ketones from the Wood Oil of Eremophila Mitchellii.*

By A. E. BRADFIELD, A. R. PENFOLD, and J. L. SIMONSEN.

IN view of the somewhat wide distribution of the simpler terpene ketones, it is rather remarkable that, with the exception of the acyclic ketone, dorenone, isolated by Semmler, Jonas, and Roenisch (*Ber.*, 1917, 50, 1828) from the oil of ammoniacum, no sesquiterpene ketone has been described hitherto. During the investigation of the constituents of the oil from the wood of *Eremophila Mitchellii*, details of which will be published elsewhere, we separated a crystalline ketone,  $C_{15}H_{22}O$ , m. p. 41—42°, for which we propose the name *eremophilone*, and two hydroxy-ketones, *2-hydroxyeremophilone*,  $C_{15}H_{22}O_2$ , m. p. 66—67°, and *2-hydroxy-1 : 2-dihydroeremophilone*,  $C_{15}H_{24}O_2$ , m. p. 102—103°. As the outcome of the experiments to be described, we have been able to determine the constitutions of these substances.

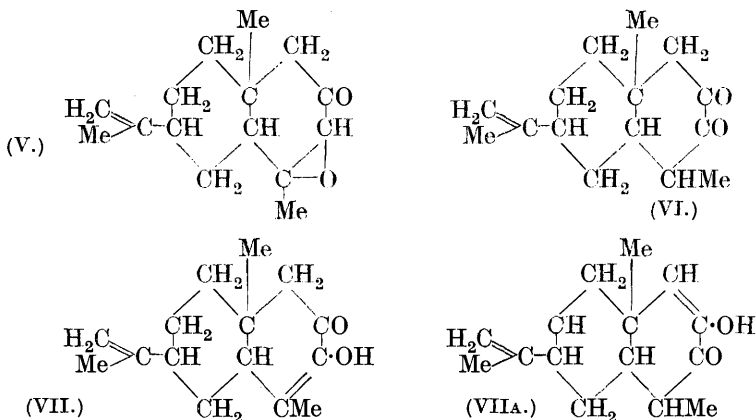
Eremophilone has been found to be a derivative of the naphthalene hydrocarbon eudalene, since dihydroeremophilol (p. 2753) on dehydrogenation with selenium yields this substance. It contains two ethylenic linkages, and can be reduced catalytically to *tetrahydroeremophilone*,  $C_{15}H_{26}O$ . The group  $\cdot CH_2 \cdot CO \cdot CH \cdot CH \cdot$  is present, since it yields a crystalline *hydroxymethylene* derivative, m. p. 105°, and on oxidation with hydrogen peroxide in alkaline solution an oxide, *eremophilone oxide*, m. p. 63—64°, is obtained. The latter reaction is known to be characteristic of ketones containing the ethylenic linkage in the  $\alpha\beta$ -position to the carbonyl group (compare Weitz and Scheffer, *Ber.*, 1921, 54, 2327), and confirmatory evidence of the presence of this group was afforded by the preparation of an unstable crystalline compound with hydrogen sulphide. Reduction of eremophilone with sodium in alcoholic solution yields a liquid unsaturated alcohol, *dihydroeremophilol*,  $C_{15}H_{26}O$ , characterised by the preparation of a crystalline 3 : 5-dinitrobenzoate, m. p. 119—121°, and this alcohol on oxidation with ozone gives formaldehyde and a

hydroxy-ketone,  $C_{14}H_{24}O_2$ . The latter was not obtained pure, but its composition was proved by analysis of its 2:4-dinitrophenylhydrazone, m. p. 146—149°. When the hydroxy-ketone was oxidised with sodium hypobromite in methyl-alcoholic solution, bromoform and an acid,  $C_{13}H_{22}O_3$ , m. p. 155°, were formed and it follows, therefore, that dihydroeremophilol must contain an isopropenyl side chain. The reduction of eremophilone to dihydroeremophilol makes it improbable that the carbonyl group is situated in the same ring as the isopropenyl side chain and (I), (IA), and (IB) are therefore possible formulæ for eremophilone. Of these, (I) is the most probable, and the reactions discussed above can be represented by the scheme :

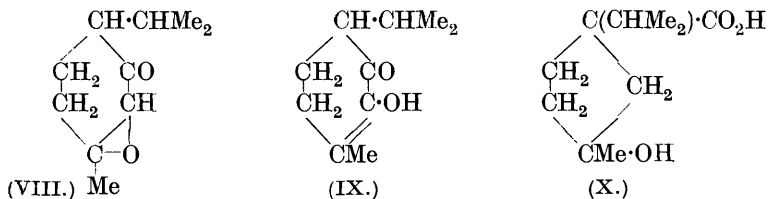


To distinguish between these three formulæ for eremophilone, a study of the crystalline oxide referred to above appeared to us to offer a suitable avenue of approach. We attempted first to oxidise dihydroeremophilone oxide, m. p. 53—54°, prepared by the catalytic hydrogenation of eremophilone oxide, with ozone in the manner used successfully by Wedekind and Tettweiler (*Ber.*, 1931, **64**, 1801) in the case of  $\alpha$ -dihydro- $\alpha$ -santenone oxide. We found, however, that dihydroeremophilone oxide was not attacked by ozone in carbon tetrachloride solution. The reactions of keto-ethylene oxides having an open-chain structure have been studied recently in great

detail by Baker and Robinson (this vol., p. 1798), and on the assumption that cyclic oxides would react in a similar manner it was anticipated that the oxide (V), derived from (I), would yield either with acetic acid and sodium acetate or with an alcoholic solution of sodium hydroxide the diketone (VI) or one of its enolic forms (VII) or (VIIA), whereas the oxides derived from (IA) and (IB) might be expected to behave in a more complicated manner.



Inspection of formulæ (V) and (VII) shows that they resemble in structure piperitone oxide (VIII) and diosphenol (IX), respectively, and it seemed to us desirable, in the first instance, to determine

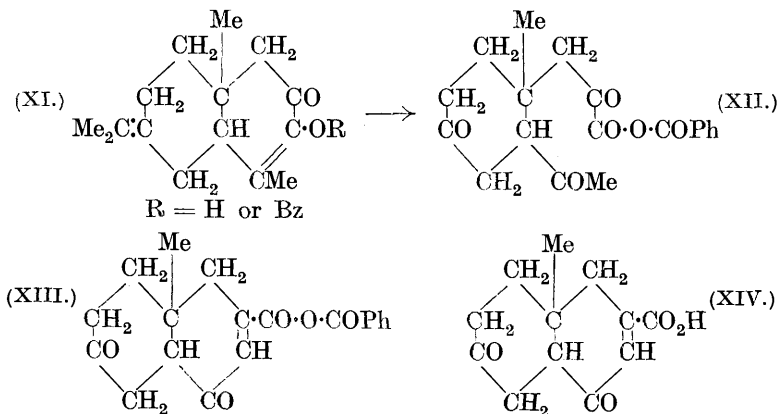


whether piperitone oxide (Kötz and Hoffmann, *J. pr. Chem.*, 1925, 110, 101) would yield diosphenol. We find that when the oxide is warmed with an alcoholic solution of sodium hydroxide for a short time on the water-bath, diosphenol is formed in a small yield, the main product being the hydroxy-acid (X) described by Treibs (*Ber.*, 1931, 64, 2548).

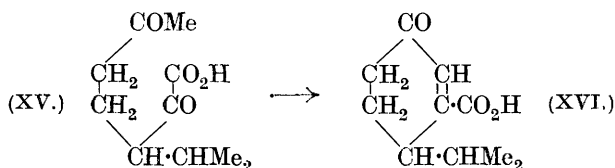
Eremophilone oxide is very much more stable than piperitone oxide and it is not attacked by alcoholic sodium hydroxide; if, however, the oxide is digested with acetic acid and sodium acetate an oil is obtained which on treatment with alkali (see p. 2754) yields an oil giving an intense blue-black coloration with ferric chloride. This oil was not purified, but was benzoylated and a crystalline

*benzoyl* derivative,  $C_{22}H_{26}O_3$ , m. p. 119—120°, obtained. The formation of this benzoate, which would be a derivative of the alcohol (VII) or (VIIA), supported the assumption that eremophilone has the structure (I), hence dihydroeremophilol would be (II) and its oxidation products 6-*acetyl*-4 : 9-*dimethyl*-2-*decalol* (III) and 4 : 9-*dimethyl*-2-*decalol*-6-*carboxylic acid* (IV).

Confirmation of the structure assigned to these substances was furnished by a study of the reactions of another constituent of the oil, 2-hydroxyeremophilone, since this alcohol gave on benzoylation a benzoyl derivative identical both in melting point and in rotatory power with that prepared from eremophilone oxide. 2-Hydroxyeremophilone is readily oxidised in the air to a brown resin, and it shows many properties resembling those of diosphenol. It is a strong reducing agent, gives an intense blue-black coloration with ferric chloride, but, unlike diosphenol, it is insoluble in alkalis. Oxidation of 2-hydroxyeremophilone benzoate with ozone yields acetone and a trace of formaldehyde, together with a neutral crystalline substance  $C_{19}H_{18}O_5$ , m. p. 186—188°. The formation of acetone shows that the benzoate must contain mainly an *isopropylidene* and not, like eremophilone, an *isopropenyl* side chain. In eremophilone and 2-hydroxyeremophilone we have, therefore, another instance of the isomerism shown in the simpler terpene derivatives, such as geraniol and citral. The substance  $C_{19}H_{18}O_5$  was found to be a mixed *anhydride*, since on hydrolysis with alcoholic potassium hydroxide it gave benzoic acid and a ketonic acid, which analysis of the *monosemicarbazone*, decomp. 215—216°, showed to have the composition  $C_{12}H_{14}O_4$ . There can be little doubt that the anhydride has the formula (XIII), being formed from the primary product of the oxidation (XII) by loss of water, the acid obtained on its hydrolysis being 9-methyl- $\Delta^2$ -decalene-4 : 6-dione-2-carboxylic acid (XIV).

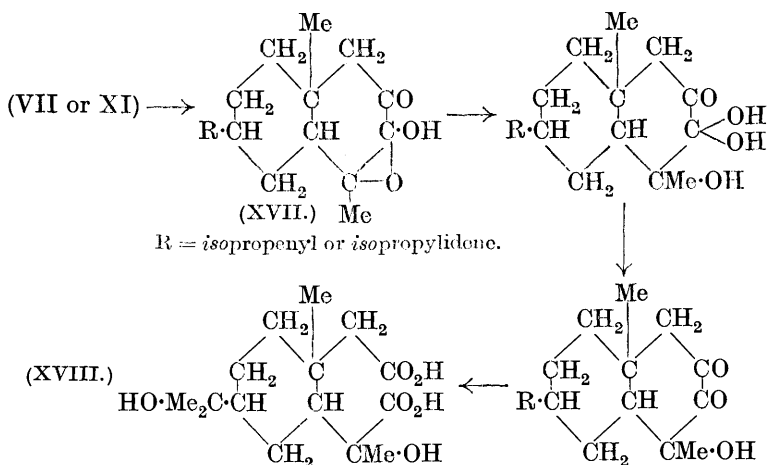


The cyclisation of this anhydride is analogous to the formation of 2-*isopropyl*- $\Delta^6$ -*cyclohexen*-5-one-1-carboxylic acid (XVI) from the acid (XV) (Semmler and McKenzie, *Ber.*, 1906, **39**, 1160). It follows, therefore, that 2-hydroxyeremophilone benzoate must have



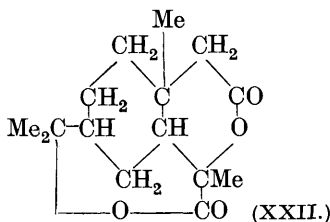
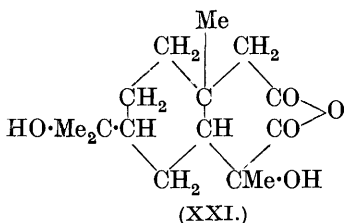
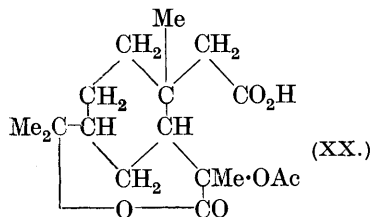
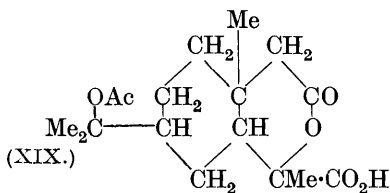
the structure (XI) corresponding to the enol (VII) (p. 2746) and that it cannot be derived from the isomeric enol (VIIA), which must yield an acid on oxidation.

Results of considerable interest have accrued from a study of the oxidation of 2-hydroxyeremophilone with hydrogen peroxide in alkaline solution. The main products of the reaction were (a) a substance,  $\text{C}_{15}\text{H}_{22}\text{O}_3$ , m. p. 150—151°, showing strong phenolic properties, and (b) two isomeric acids,  $\text{C}_{15}\text{H}_{26}\text{O}_6$ , m. p. 167—168° and 198°, respectively. There can be little doubt that the phenol, which gives an *acetyl* derivative, m. p. 122—123°, is 2-*hydroxyeremophilone oxide* (XVII); the two acids are probably stereoisomerides having the structure (XVIII), the mechanism of their formation being shown in the scheme :



The two acids were not obtained in sufficient quantity for a detailed study of their reactions. However, they show a notable difference in their reaction with acetyl chloride; the  $\alpha$ -acid, m. p. 167°, gives with this reagent a substance,  $\text{C}_{17}\text{H}_{26}\text{O}_6$ , m. p. 192°,

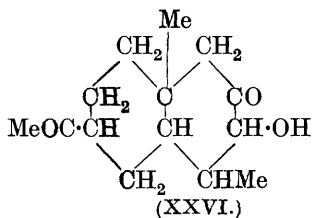
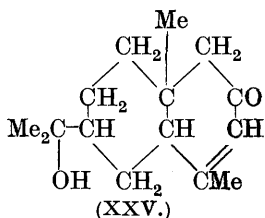
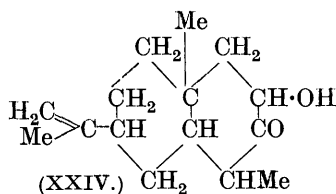
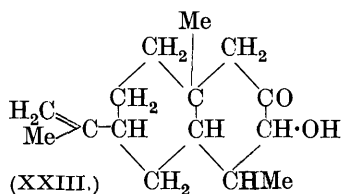
which is soluble in alkali and is probably the *acetyl* derivative of a *lactic acid* (XIX or XX), whereas under similar conditions the  $\beta$ -acid, m. p. 198°, gives a substance which is insoluble in alkali. This substance could not be prepared in a state of purity, but it is probably the anhydride (XXI) (or its acetyl derivative) or the dilactone (XXII).



We regard these experiments as leaving no doubt that eremophilone has the structure (I) and 2-hydroxyeremophilone (XI), although both these substances are undoubtedly mixtures in that they contain *isopropenyl* and *isopropylidene* side chains in varying proportions. We have obtained no evidence that 2-hydroxyeremophilone can exist in the isomeric form (VIIA), but it is not improbable that in solution the diketonic form (VI) exists, since, although the crystalline solid is colourless, it yields a yellow melt and dissolves in methyl alcohol to give a yellow solution. An attempt to prepare a quinoxaline derivative from it was unsuccessful. The structure assigned to the alcohol is supported by its physical constants, the molecular refraction showing a very marked exaltation (3.19). This is notably higher than the exaltation (0.92) shown by diosphenol, but too much weight must not be attached to the figures for 2-hydroxyeremophilone, since the rapidity with which this substance undergoes oxidation may have impaired the measurements of the physical constants.

It will now be shown that the third crystalline constituent of the oil, m. p. 102—103°, is 2-hydroxy-1:2-dihydroeremophilone (XXIII). It forms a 2:4-*dinitrophenylhydrazone*, decomp. 239—241°, a *dinitrobenzoate*, m. p. 145—146°, and with acetic anhydride, a *diacetate*, m. p. 69—70°. On catalytic reduction it takes up one

molecule of hydrogen, giving 2-hydroxytetrahydroeremophilone ( $\alpha$ -form), m. p. 84—85°, and dehydrogenation by selenium of the oil obtained by reduction with sodium and alcohol yields eudalene. The substance is, therefore, an unsaturated hydroxy-ketone with the same carbon skeleton as eremophilone, the diacetate being formed from the enolic form of the ketone. The next clue to the constitution of the hydroxy-ketone was the observation that on oxidation with hydrogen peroxide in alkaline solution it yields 1-methyl-4-( $\alpha$ -hydroxyisopropyl)cyclohexane-1-acetic-2- $\alpha$ -lactic acid ( $\alpha$ -form) (XXVIII), m. p. 167—168°, identical with one of the isomeric acids obtained by the similar oxidation of 2-hydroxyeremophilone. This product might be expected to arise from one of the following (XXIII to XXV) :



The formation of a dibasic acid,  $\text{C}_{15}\text{H}_{24}\text{O}_4$ , on oxidation of 2-hydroxytetrahydroeremophilone with hydrogen peroxide excludes (XXV). A decision between the remaining alternatives in favour of (XXIII) was readily obtained, since reduction of 2-hydroxytetrahydroeremophilone with sodium amalgam under the conditions used for the reduction of hydroxycamphor to camphor (Bredt and Bredt-Savelsberg, *Ber.*, 1929, **62**, 2214) yields tetrahydroeremophilone, thus fixing the position of the keto-group.

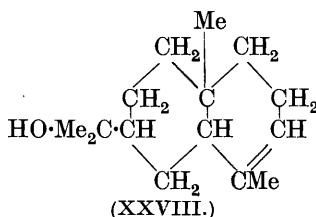
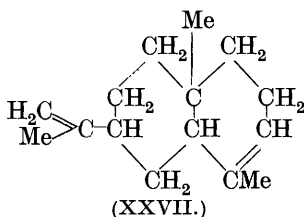
2-Hydroxy-1 : 2-dihydroeremophilone resembles eremophilone rather than 2-hydroxyeremophilone in that on oxidation with ozone it gives formaldehyde, with only a trace of acetone. The  $\text{C}_3$  side chain is, therefore, present mainly as the isopropenyl group, as shown (XXIII). The other product of the oxidation is an oil, the semicarbazone of which, decomp. 214—216°, is undoubtedly the semicarbazone of 6-acetyl-4 : 9-dimethyldecal-2-one-3-ol (XXVI).

The 2-hydroxytetrahydroeremophilone prepared by the hydrogenation of 2-hydroxy-1 : 2-dihydroeremophilone crystallises with great

facility and yields a number of characteristic derivatives, the oxime melting at  $154^{\circ}$ . An isomeride has been prepared, however, by the catalytic hydrogenation of 2-hydroxyeremophilone benzoate, which is an oil, and from which an *oxime*, m. p.  $146^{\circ}$ , was obtained. The relationship of these two alcohols, which are possibly *cis-trans* isomerides, has not been determined, and in the absence of any evidence regarding their configurations the crystalline alcohol has been designated  $\alpha$ -2-hydroxytetrahydroeremophilone, and that from the benzoyl derivative is designated  $\beta$ -.

An alcohol, m. p.  $101-103^{\circ}$ , having the same composition as 2-hydroxy-1 : 2-dihydroeremophilone and yielding an acetyl derivative, m. p.  $68.5-69.5^{\circ}$ , has been separated from the oil prepared from the wood of *Santalum Preissianum* (Schimmel's Rep., April, 1891, 49; Oct., 1891, 34; Berkenheim, *J. Russ. Phys. Chem. Soc.*, 1892, 24, 688). This is probably identical with 2-hydroxy-1 : 2-dihydroeremophilone, the diacetyl derivative of which, as mentioned above, melts at  $69-70^{\circ}$ . We propose to investigate the constituents of this oil.

The occurrence in one oil of these three closely related ketones appears to us to be of more than usual interest. It is obvious that eremophilone bears the same relationship to  $\alpha$ -selinene (XXVII) as verbenone does to  $\alpha$ -pinene. So far as we are aware,  $\alpha$ -selinene has not been found in nature and it is possible also that the ketone is derived from  $\alpha$ -eudesmol (XXVIII).



2-Hydroxyeremophilone might then be formed from eremophilone through eremophilone oxide (V). It is our intention to investigate the auto-oxidation products of  $\alpha$ -selinene and  $\alpha$ -eudesmol.

#### EXPERIMENTAL.

##### *Eremophilone* (I).

The ketone, regenerated from the semicarbazone by oxalic acid, was a colourless mobile oil with a faint and somewhat unpleasant odour. It solidified when cooled in a freezing mixture or inoculated, and then crystallised from MeOH in long prismatic needles, m. p.  $41-42^{\circ}$ , b. p.  $171^{\circ}/15$  mm.,  $d_{25}^{25}$  0.9994,  $n_D^{25}$  1.5182,  $[\alpha]_{5461}^{25} - 207^{\circ}$  (in MeOH,  $c = 2.46$ ),\*  $[R_L]_D 66.12$  (calc. for  $C_{16}H_{22}O$ , 66.15). *Eremophilone* is somewhat readily oxidised and if kept in

\* All rotatory powers were determined in a 1 dm. tube.



a corked tube for a month slowly changes to a yellow oil. For this reason, or owing to the presence of some impurity, it does not give good figures on analysis, both the freshly distilled oil and the recryst. solid yielding identical results either by macro- or micro-methods (Found : C, 81.6, 81.5, 81.8; H, 10.2, 10.2, 10.1.  $C_{15}H_{22}O$  requires C, 82.6; H, 10.1%). In EtOH eremophilone gave no colour with  $FeCl_3$ , nor did it reduce Fehling's solution; in  $CHCl_3$  solution, at  $0^\circ$ , Br was rapidly absorbed, but after the addition of 2 mols. evolution of HBr occurred and evaporation of the solvent left a viscid green oil. When  $H_2S$  was passed into an EtOH- $NH_3$  solution of the ketone in salt-ice, an addition compound crystallised in pale yellow leaflets: it decomposed, however, when separated. The ketone was sol. in hot  $NaHSO_3$  aq., and could be regenerated by treatment with alkali. With piperonal and *m*-nitrobenzaldehyde the ketone condensed in the presence of  $NaOEt$ , but the products were amorphous and could not be purified. The *semicarbazone* crystallised from MeOH in clusters of radiating needles, decomp.  $202-203^\circ$ ,  $[\alpha]_{5461} - 293^\circ$  (in MeOH,  $c = 2.35$ ) (Found : C, 69.7; H, 9.1.  $C_{16}H_{22}ON_3$  requires C, 69.8; H, 9.1%).

*Hydroxymethylene-eremophilone*.—To a suspension of finely divided Na (0.7 g.) in  $Et_2O$  (50 c.c.) and eremophilone (6 g.) cooled in salt-ice, amyl formate (3.6 g.) was gradually added. A deep brown solution resulted, the Na slowly dissolving. After 12 hr., ice was added, and the alkaline solution separated, extracted with  $Et_2O$ , and made just acid with AcOH. The oil which separated was isolated and dried ( $MgSO_4$ ) in  $Et_2O$  and recovered as a brown oil which crystallised on keeping; the crystals were drained and recrystallised twice from MeOH, *hydroxymethylene-eremophilone* forming faintly yellow, long, prismatic needles, m. p.  $105^\circ$ , which gave an intense purple-red colour with alc.  $FeCl_3$  (Found : C, 78.4; H, 9.0.  $C_{16}H_{22}O_2$  requires C, 78.1; H, 8.9%).

*Reduction of Eremophilone*.—(i) *Catalytic*. The ketone (2.05 g.) in EtOH (25 c.c.) was, after the addition of Pd-norite (1 g.; Pd 10%), shaken in H: rapid absorption of gas occurred and ceased after 443 c.c. H (2.1 mols.) had been absorbed. *Tetrahydroeremophilone*,\* isolated in the usual manner, was a colourless mobile oil, b. p.  $165^\circ/17$  mm.,  $d_{20}^{25} 0.9641$ ,  $n_D^{25} 1.4909$ ,  $[\alpha]_{5461} + 12.5^\circ$  (in MeOH,  $c = 4.08$ ),  $[R_L]_D 66.71$  (calc. for  $C_{15}H_{26}O$ , 67.08) (Found : C, 81.3; H, 11.4.  $C_{15}H_{26}O$  requires C, 81.1; H, 11.7%). Tetrahydroeremophilone reacts with amyl nitrite and HCl in salt-ice to yield a crystalline nitroso-derivative, decomp.  $139^\circ$ , and with Na and amyl formate a liquid hydroxymethylene derivative was obtained. In both cases the yield was too small to permit of purification. Cryst. derivatives could not be obtained by condensation with either piperonal or *m*-nitrobenzaldehyde. The *semicarbazone*, which formed very readily, crystallised from MeOH, in which it was sparingly sol., in needles, decomp.  $213-214^\circ$  (Found : C, 68.8; H, 10.5; N, 14.7.  $C_{16}H_{29}ON_3$  requires C, 68.8; H, 10.4; N, 15.1%). The *oxime*, prepared by refluxing the ketone with  $NH_2OH$ , HCl and  $K_2CO_3$  in EtOH, crystallised from EtOH in clusters of needles, m. p.  $126-127.5^\circ$ , a trace not melting below  $134^\circ$ . The m. p. was not improved by repeated cryst., and it is possible that the oxime was a mixture of isomerides,  $[\alpha]_{5461} + 17.2^\circ$  (in  $CHCl_3$ ,  $c = 4.19$ )

\* For the prepn. of tetrahydroeremophilone in quantity it was found convenient to reduce the crude essential oil and to purify the ketone so obtained through its semicarbazone. It was regenerated from this by hydrolysis with oxalic acid and steam distillation.

(Found: C, 75.8; H, 11.5.  $C_{15}H_{27}ON$  requires C, 76.0; H, 11.4%). The 2 : 4-dinitrophenylhydrazone crystallised from EtOH, in which it was sparingly soluble, in soft orange needles, m. p. 178—179° (Found: N, 14.1.  $C_{21}H_{30}O_4N_4$  requires N, 13.9%).

(ii) With Na and EtOH. To a solution of eremophilone (9 g.) in EtOH (400 c.c.), Na (42 g.) was added as rapidly as possible, the mixture being heated on the water-bath. The EtOH was removed in steam, and the residual oil dissolved and dried ( $K_2CO_3$ ) in  $Et_2O$  and recovered. Dihydroeremophilol (II), b. p. 168—170°/14 mm.,  $n_D^{20}$  1.5089,  $[\alpha]_{5461} + 68.8^\circ$  (in MeOH,  $c = 5.66$ ), was a colourless, extremely viscid oil (Found: C, 81.0; H, 11.9.  $C_{15}H_{26}O$  requires C, 81.1; H, 11.7%). The 3 : 5-dinitrobenzoate, prepared by treating the alcohol with 3 : 5-dinitrobenzoyl chloride in pyridine solution, crystallised from MeOH in leaflets, m. p. 119—121° (Found: C, 63.8; H, 6.6.  $C_{22}H_{28}O_6N_2$  requires C, 63.5; H, 6.7%). Dihydroeremophilol was readily oxidised by  $CrO_3$  in AcOH solution to the corresponding ketone, dihydroeremophilone, the semicarbazone of which crystallised in needles, decomp. 214—215° (Found: C, 69.5; H, 9.7.  $C_{16}H_{27}ON_3$  requires C, 69.3; H, 9.7%).

*Dehydrogenation of Dihydroeremophilol.*—A suspension of Se (7 g.) in the alcohol (4 g.) was heated at 270—300° for 40 hr.; much  $H_2Se$  was then evolved. The cooled residue was dissolved in  $Et_2O$ , the solution filtered, and after removal of the  $Et_2O$  the oil was distilled, the fraction b. p. up to 155°/11 mm. being collected separately. This gave a picrate, m. p. 90—91.5° both alone and after admixture with authentic eudalene picrate, for which we are indebted to Professor L. Ruzicka.

*Oxidation of Dihydroeremophilone with Ozone.*— $O_3$  was passed through a cooled solution of the alcohol (4 g., regenerated from the dinitrobenzoyl derivative) in pure dry  $CCl_4$  (20 c.c.), the issuing gases, which smelt strongly of formaldehyde, being passed through  $H_2O$ . The presence of formaldehyde in the wash  $H_2O$  was proved by the prepn. of its dimedone derivative, m. p. 187—188°, both alone and in admixture with an authentic specimen. The  $CCl_4$  was removed under diminished press., and the viscid residue decomposed with steam: a mobile oil (0.4 g.) which passed over in small quantity did not yield a cryst. derivative with 2 : 4-dinitrophenylhydrazine, and on treatment with  $NaOBr$  gave  $CHBr_3$  and an acid (0.1 g., prisms) in quantity too small for investigation. The residue in the distilling flask was made alkaline, and the oil dissolved and dried in  $Et_2O$  and recovered (2.4 g.). A portion of this oil was treated with 2 : 4-dinitrophenylhydrazine sulphate, a flocculent ppt. separating. This was repeatedly crystallised from EtOH; a small quantity of a red resinous impurity rendered purification difficult, but ultimately 6-acetyl-4 : 9-dimethyl-2-decalol-2 : 4-dinitrophenylhydrazone was obtained as minute orange needles, m. p. 146—149° (Found: C, 59.6; H, 7.3.  $C_{20}H_{28}O_5N_4$  requires C, 59.4; H, 6.9%). The remainder of the ketone was suspended in dilute MeOH and treated with an excess of  $NaOBr$  aq.; after 1 hr., addition of  $H_2O$  pptd.  $CHBr_3$ . The excess of hypobromite was removed with  $SO_2$ , and the MeOH and  $CHBr_3$  by evaporation on the water-bath, the cooled solution acidified and extracted with  $Et_2O$ , the ethereal solution dried, and the solvent evaporated. The colourless viscid oil obtained partly crystallised on keeping and the solid was purified with considerable difficulty by crystn. from dil. MeOH, 4 : 9-dimethyl-2-decalol-6-carboxylic acid (IV) being obtained in small plates, m. p. about 155° (Found: C, 68.6; H, 9.2.  $C_{13}H_{22}O_3$  requires C, 69.0; H, 9.7%).

*Oxidation of Eremophilone with Hydrogen Peroxide.* *Eremophilone Oxide* (V).—To a solution of the ketone (5 g.) in MeOH (50 c.c.) cooled to  $-1^{\circ}$ , a mixture of NaOH (4*N*, 5.7 c.c.) and  $H_2O_2$  (15%, 11 c.c.) was gradually added, care being taken that the temp. did not rise above  $2^{\circ}$ . A faint red colour developed first, but this faded and a pale yellow solution was obtained, an oil being deposited which gradually redissolved. After remaining in salt-ice for 1.5 hr. and at  $22^{\circ}$  for 2 hr., the mixture was poured on ice- $H_2O$  (200 c.c.), a cryst. solid separating. The solid from two such oxidations was collected, washed with  $H_2O$ , and drained on porous porcelain to remove a trace of adhering oil (yield, 7.4 g.). The milky filtrate was extracted with  $Et_2O$ , and the extract dried with  $K_2CO_3$ ; evaporation then gave an oil (1.8 g.) which partly crystallised and from which a further quantity of the oxide could be obtained. Acidification of the alkaline solution and extraction with  $Et_2O$  gave a gummy acid (1 g.). *Eremophilone oxide* crystallised from ligroin (b.p.  $40-60^{\circ}$ ) in prismatic needles, m. p.  $63-64^{\circ}$ ,  $[\alpha]_{5461} - 208^{\circ}$  (in MeOH,  $c = 1.94$ ). It was very readily sol. in the ordinary org. solvents (Found : C, 76.8; H, 9.9.  $C_{15}H_{22}O_2$  requires C, 76.9; H, 9.4%). The oxide gave an amorphous semicarbazone, and the nitrosochloride was an oil.

*Dihydroeremophilone oxide* was obtained when eremophilone oxide (4 g.) in EtOH (30 c.c.) containing Pd-norite (1 g., Pd 10%) was shaken in H. It crystallised from dil. MeOH in needles, m. p.  $53-54^{\circ}$ ,  $[\alpha]_{5461} - 205^{\circ}$  (in MeOH,  $c = 2.07$ ) (Found : C, 76.3; H, 10.4.  $C_{15}H_{24}O_2$  requires C, 76.3; H, 10.2%).

*Conversion of Eremophilone Oxide into 2-Hydroxyeremophilone* (VII).—A mixture of the oxide (5 g.), AcOH (25 c.c.), and anhyd. AcONa (5 g.) was boiled under reflux for 2 hr. The colourless solution gradually became yellow, then brown, and finally bright green. Addition of  $H_2O$  to the cooled solution separated a yellow oil, which was dissolved in  $Et_2O$ , washed with  $Na_2CO_3$  aq. (which removed AcOH and a small quantity of a liquid acid), dried, and recovered. The oil, which gave no colour with  $FeCl_3$ , was dissolved in EtOH (30 c.c.) and, after the addition of KOH (4 g.) in  $H_2O$ , heated on the water-bath for 5 min. The oil pptd. by the addition of  $H_2O$  and acidification was dissolved in  $Et_2O$ , washed with  $H_2O$  until free from EtOH, dried ( $CaCl_2$ ), and recovered. The brown oil (5 g.) so obtained, which gave an intense bluish-black coloration with  $FeCl_3$ , was dissolved in pyridine (20 c.c.) and to the mixture, cooled in salt-ice, benzoyl chloride (2.2 g.) was slowly added. After remaining overnight, the solution was poured on ice, a viscid reddish-brown oil separating. This was dissolved in  $Et_2O$ , washed successively with dil.  $H_2SO_4$ ,  $Na_2CO_3$  aq. and  $H_2O$ , dried over  $CaCl_2$ , recovered, and distilled (2 mm.), the fraction, b. p.  $200-240^{\circ}$ , being collected separately. This fraction (2.5 g.), which was a viscid gel, was dissolved in an equal vol. of MeOH and kept at  $0^{\circ}$  for 24 hr. The solid which had separated crystallised from MeOH in prisms, m. p.  $119-120^{\circ}$ , both alone and after admixture with benzoyl-2-hydroxyeremophilone prepared from the natural alcohol (p. 2755) (Found : C, 78.1; H, 7.8.  $C_{22}H_{26}O_3$  requires C, 78.1; H, 7.7%).  $[\alpha]_{5461} + 166^{\circ}$  (in AcOEt,  $c = 1.02$ ).

#### *2-Hydroxyeremophilone.*

*2-Hydroxyeremophilone*, obtained by the hydrolysis of the cryst. benzoyl derivative (see below) with methyl-alc. KOH, was a pale yellow, very viscid oil, b. p.  $189-190^{\circ}/22$  mm., with a characteristic smell somewhat reminiscent of ionone. It solidified on keeping and then crystallised from MeOH in colourless prisms, m. p.  $66-67^{\circ}$ . The supercooled oil had  $d_{25}^{25} 1.0620$ ,  $n_D^{25}$

1-5564,  $[\alpha]_{5461} + 153^\circ$  (in MeOH,  $c = 2.51$ ),  $[R_L]_D 70.85$  (calc. for  $C_{15}H_{22}O_2$ )<sub>2</sub>, 67-67). The hydroxy-ketone oxidised with extreme rapidity on exposure to the air, the crystals passing into a brown resin. This is reflected in the analytical figures, although the substance was analysed as soon as possible after recrystn. (Found : C, 76.3; H, 9.2.  $C_{15}H_{22}O_2$  requires C, 76.9; H, 9.4%). The hydroxy-ketone was insol. in alkali, although it gave a yellow colour to aq. NaOH; in EtOH it immediately reduced Fehling's and silver solutions and with  $FeCl_3$  it gave an intense bluish-black coloration. Like eremophilone, 2-hydroxyeremophilone is sol. in  $NaHSO_3$  aq. and can be recovered by means of alkali.

The facility with which the hydroxy-ketone resinified in air, especially in the presence of alkali, rendered special precautions necessary in the prepn. of derivatives. The benzoyl derivative, prepared by the benzoyl chloride-pyridine method at  $0^\circ$ , crystallised from MeOH in stout prisms, frequently twinned; m. p.  $119-120^\circ$ ,  $[\alpha]_{5461} + 162^\circ$  (in AcOEt,  $c = 2.01$ ) (Found : C, 78.0; H, 7.8.  $C_{22}H_{26}O_3$  requires C, 78.1; H, 7.7%). In an attempt to prepare the oxime,  $NH_2OH \cdot HCl$  (0.7 g.) in EtOH (15 c.c.) and KOH (1 g.) in  $H_2O$  (3 c.c.) were added to a solution of the hydroxy-ketone (1 g.) after the air in the apparatus had been replaced by N, and the mixture was heated under reflux for 6 hr. After addition of  $H_2O$  the N was replaced by  $CO_2$ , and the solution cooled. The solid was collected, an oily impurity removed by washing with ligroin (b. p.  $40-60^\circ$ ), and the residue crystallised from 50% MeOH, from which it separated in leaflets, m. p.  $157-158^\circ$  after sintering at  $148^\circ$ . Analysis (Found : C, 69.7, 69.9; H, 9.1, 9.1.  $C_{15}H_{23}O_2N$  requires C, 72.3; H, 9.2%) indicates that this was not the simple oxime.

*Oxidation of 2-Hydroxyeremophilone.*—(i) *With ozone.* A solution of the benzoyloxy-ketone (3 g.) in pure dry  $CCl_4$  (25 c.c.) was treated with  $O_3$ , the issuing gases being passed through  $H_2O$  (A). The  $CCl_4$  was removed in vac., and the residual gum refluxed with  $H_2O$ , a trap containing *p*-nitrophenylhydrazine in dil. AcOH being attached to the condenser. The cryst. ppt. which separated in the trap had m. p.  $147-148^\circ$ , both alone and after admixture with acetone-*p*-nitrophenylhydrazine. The aq. solution (A) contained a trace of HCHO (dimedone test). After the ozonide had been boiled for 1 hr., the cooled solution contained a cryst. solid; this was collected and a portion recrystallised from EtOH, in which it was very sparingly sol., and with which it slowly reacted on prolonged boiling. The anhydride (XIII) crystallised in short needles, m. p.  $186-188^\circ$  (Found : C, 70.1; H, 5.7.  $C_{19}H_{18}O_5$  requires C, 69.9; H, 5.5%). The mother-liquor of the anhydride was made alkaline with KOH and warmed on the water-bath for a short time. After removal of the EtOH, when the cooled solution was acidified, benzoic acid (m. p. and mixed m. p.) and an oily acid were obtained. The latter was prepared more conveniently by keeping the anhydride in cold dil. MeOH containing slightly more than the calc. quantity of NaOH for 12 hr., the solution being then saturated with  $CO_2$ , the MeOH removed on the water-bath in a current of  $CO_2$ , the solution acidified, the pptd. acids extracted with  $Et_2O$ , the benzoic acid removed in steam, and the residual liquid saturated with  $Am_2SO_4$  and extracted with  $Et_2O$ . Evaporation of the solvent left an oil. This was mixed with aq. semicarbazide acetate and kept over-night; a cryst. solid, mixed with some oil, had then separated. The oil dissolved on warming, the hot solution was filtered, and the semicarbazone of 9-methyl- $\Delta^2$ -decalene-4 : 6-dione-2-carboxylic acid crystallised from EtOH, in which it was sparingly sol., in rhombohedra,

decomp. 215—216° if introduced into a bath preheated to 195°. The decomp. point was much lower if taken in the usual manner. The substance, which is sol. in  $\text{Na}_2\text{CO}_3$  aq., crystallised with 2 EtOH, which were not removed at 100° under low press. Two distinct specimens were analysed (Found : C, 54.9, 55.1; H, 7.9, 8.1.  $\text{C}_{13}\text{H}_{17}\text{O}_4\text{N}_3, 2\text{C}_2\text{H}_6\text{O}$  requires C, 55.0; H, 7.8%).

(ii) *With hydrogen peroxide.* To a solution of the hydroxy-ketone (8 g.) in MeOH (40 c.c.), a mixture of 4*N*-NaOH (14 c.c.) and  $\text{H}_2\text{O}_2$  (28 c.c., 15%) was added. A deep reddish-brown colour developed, which became lighter on standing, but very little heat was generated. After 12 hr., the mixture was poured into  $\text{H}_2\text{O}$ , the neutral oil (4 g.) removed with  $\text{Et}_2\text{O}$ , the alkaline solution acidified and extracted with  $\text{Et}_2\text{O}$  (3 times), and the extract washed successively with  $\text{NaHCO}_3$  aq. (A),  $\text{Na}_2\text{CO}_3$  aq. (B), and NaOH aq. (C). The NaOH solution (C), which was deep red, was saturated with  $\text{CO}_2$ ; an oil (0.9 g.) then separated and in time partly crystallised. The oily solid was dissolved in  $\text{Et}_2\text{O}$  and after removal of the solvent redissolved in NaOH aq. and reprecipitated by  $\text{CO}_2$ . After isolation by  $\text{Et}_2\text{O}$ , the solid was drained and purified by crystallisation from MeOH, 2-hydroxyeremophilone oxide (XVII) separating in large prisms, m. p. 150—151°,  $[\alpha]_{5461} + 196^\circ$  (in MeOH,  $c = 2.07$ ) (Found : C, 72.0; H, 8.3.  $\text{C}_{16}\text{H}_{22}\text{O}_3$  requires C, 72.0; H, 8.8%). In EtOH the oxide gave with  $\text{FeCl}_3$  a bluish-purple coloration and it reduced Fehling's and silver solutions. The acetyl derivative, obtained when the oxide was heated with  $\text{Ac}_2\text{O}$  containing a drop of pyridine on the water-bath for 1 hr., crystallised from either dil. MeOH or ligroin (b. p. 40—60°) in slender prisms, m. p. 122—123° (Found : C, 69.8; H, 7.9.  $\text{C}_{17}\text{H}_{24}\text{O}_4$  requires C, 69.9; H, 8.2%). The  $\text{NaHCO}_3$  solution (A) was acidified, the liquid mixture of acids extracted with  $\text{Et}_2\text{O}$ , the oil (3.2 g.) left on evaporation of the solvent dissolved in  $\text{NH}_3$  aq., an amorphous Ca salt precipitated from the faintly alkaline solution by an excess of  $\text{CaCl}_2$ , and the filtrate acidified; the oil which separated partly crystallised when scratched. On extraction with  $\text{Et}_2\text{O}$ , a white solid (X) remained, which was collected; the extract was dried, and the solvent evaporated. After being kept for several days in vac., the residual oil partly crystallised when rubbed with a little dry  $\text{Et}_2\text{O}$ . The solid (Y) was separated, and after draining on porous porcelain was dissolved in hot dry  $\text{Et}_2\text{O}$ : the crystalline solid which separated after some days was added to (X). This acid, 1-methyl-4-( $\alpha$ -hydroxyisopropyl)cyclohexane-1-acetic-2- $\alpha$ -lactic acid ( $\alpha$ -form) (XVIII), readily crystallised from AcOEt in thin plates with very sharp edges, decomp. 167—168° after sintering at 140° (Found : C, 59.6; H, 8.6;  $M$ , 302.  $\text{C}_{16}\text{H}_{26}\text{O}_6$  requires C, 59.6; H, 8.6%;  $M$ , 302). The hydroxy-acid was stable to  $\text{KMnO}_4$  in alkaline solution and was only slowly attacked in acid solution; its alcoholic solution gave no colour with  $\text{FeCl}_3$ . When the acid was digested with acetyl chloride, the acetyl derivative of the lactic acid (XIX or XX) was obtained, which crystallised from dil. MeOH in prismatic needles, decomp. 192—193° (Found : C, 62.6; H, 8.0;  $M$ , 327.  $\text{C}_{17}\text{H}_{26}\text{O}_6$  requires C, 62.6; H, 8.0%;  $M$ , 326). The ethereal solution of the acid (Y) from which the sparingly soluble  $\alpha$ -acid had been separated was evaporated, and the residue repeatedly recrystallised from dil. MeOH, 1-methyl-4-( $\alpha$ -hydroxyisopropyl)cyclohexane-1-acetic-2- $\alpha$ -lactic acid ( $\beta$ -form) (XVIII) being obtained in long prismatic needles, decomp. 198° (Found : C, 59.9; H, 8.6;  $M$ , 298). When this acid was digested with acetyl chloride, an anhydride or dilactone, m. p. about 172°, was obtained which was insoluble in NaOH aq.: the quantity was insufficient for purification. The  $\text{Na}_2\text{CO}_3$  solution (B) gave a liquid acid (0.6 g.) which on keeping developed a green

colour; it was not further examined. The original Et<sub>2</sub>O extract (see above) which had been washed with NaOH gave, on evaporation, a further small quantity of the oxide.

*Reduction of Benzoyl-2-hydroxyeremophilone.*—A solution of the benzoyl derivative (5 g.) in AcOEt (60 c.c.) was shaken with H<sub>2</sub>, after the addition of Pd-norite (1 g.; Pd 10%). The absorption of gas was very slow and ceased after the addition of 617 c.c. (1.86 mols.). The filtered solution gave, on removal of the solvent, a viscid oil which did not crystallise and was therefore hydrolysed to the hydroxy-ketone with methyl-alc. KOH (5 g. KOH). The hydroxy-ketone was a pale yellow oil which slowly reduced Fehling's solution. It was digested for 6 hr. with an excess of NH<sub>2</sub>OH, HCl and KOH in MeOH solution, H<sub>2</sub>O added, and the pptd. *2-hydroxytetrahydroeremophilone oxime* ( $\beta$ -form) crystallised from MeOH, forming prisms with hexagonal ends, m. p. 146° after sintering at 143° (Found: C, 71.7; H, 10.8. C<sub>15</sub>H<sub>27</sub>O<sub>2</sub>N requires C, 71.2; H, 10.7%). The oxime gave no colour with alc. FeCl<sub>3</sub>.

*2-Hydroxy-1 : 2-dihydroeremophilone (XXIII).*

The hydroxy-ketone was purified by repeated crystn. from MeOH, from which it separated in long slender prisms, m. p. 102—103°,  $[\alpha]_{5461} + 94^\circ$  (in MeOH,  $c = 2.02$ ) (Found: C, 76.3; H, 10.5. C<sub>15</sub>H<sub>24</sub>O<sub>2</sub> requires C, 76.3; H, 10.2%). It is insol. in H<sub>2</sub>O, sparingly sol. in MeOH and EtOH, and somewhat readily sol. in the other org. solvents. Its alc. solution gave no colour with FeCl<sub>3</sub>, but readily reduced Fehling's solution. The 2 : 4-dinitrophenylhydrazone, which formed slowly, crystallised from EtOH, in which it was sparingly sol., in golden-yellow needles, decomp. 239—241° (Found: C, 61.1; H, 7.0. C<sub>21</sub>H<sub>28</sub>O<sub>5</sub>N<sub>4</sub> requires C, 60.6; H, 6.7%). The diacetate, prepared by digesting the alcohol with Ac<sub>2</sub>O and a drop of pyridine for 1 hr., crystallises from MeOH in prisms, m. p. 69—70° (Found: C, 71.4, 71.1; H, 8.8, 9.1. C<sub>19</sub>H<sub>28</sub>O<sub>4</sub> requires C, 71.2; H, 8.7%). The 3 : 5-dinitrobenzoate, prepared from the hydroxy-ketone and 3 : 5-dinitrobenzoyl chloride in pyridine, the mixture being finally heated on the water-bath for 3 hr., crystallised from MeOH in soft needles, m. p. 145—146° after sintering at 139—140° (Found: C, 61.6; H, 6.4. C<sub>22</sub>H<sub>26</sub>O<sub>7</sub>N<sub>2</sub> requires C, 61.4; H, 6.0%). The hydroxy-ketone did not react with phthalic anhydride at 110—120°. In the presence of NaOEt it reacted with *m*-nitrobenzaldehyde to give an amorph. brown solid which could not be purified. When the hydroxy-ketone was digested with formic acid, an oil distilling at 165—180°/15 mm. was obtained, which in EtOH gave an intense blue colour with FeCl<sub>3</sub> and with 2 : 4-dinitrophenylhydrazine yielded an amorph. red ppt. Sufficient material was not available for further investigation of this reaction. The alcohol was readily oxidised by CrO<sub>3</sub> in AcOH. If sufficient of this was used to oxidise the secondary alcohol group, much of the keto-alcohol was recovered unchanged, but an alc. solution of the product gave a deep blue-black colour with FeCl<sub>3</sub>, indicating that some 2-hydroxyeremophilone had been formed. The main products of the reaction were acidic and were not further investigated.

*Reduction of 2-Hydroxy-1 : 2-dihydroeremophilone.*—(i) *Catalytic.* The hydroxy-ketone (4 g.) in EtOH (100 c.c.) was shaken with Pd-norite (1 g., Pd 10%) in H<sub>2</sub> and 373 c.c. (0.98 mol.) were absorbed. Addition of H<sub>2</sub>O to the filtered solution pptd. *2-hydroxytetrahydroeremophilone* ( $\alpha$ -form), which crystallised from MeOH in cubes, m. p. 84—85°,  $[\alpha]_{5461} + 84.2^\circ$  (in MeOH,  $c = 2.07$ ) (Found: C, 75.7; H, 11.1. C<sub>15</sub>H<sub>26</sub>O<sub>2</sub> requires C, 75.6; H, 10.9% In

EtOH the hydroxy-ketone reduced Fehling's solution, but it gave no colour with  $\text{FeCl}_3$ . The *oxime* crystallised from dil. MeOH in fine needles, m. p. 158—160° after sintering at 154° (Found: C, 71.2; H, 10.6.  $\text{C}_{15}\text{H}_{27}\text{O}_2\text{N}$  requires C, 71.2; H, 10.7%), and the 2:4-dinitrophenylhydrazone from EtOH in orange needles melting, after three crystns., at 210—220° (Found: C, 60.6; H, 7.1.  $\text{C}_{21}\text{H}_{30}\text{O}_6\text{N}_4$  requires C, 60.3; H, 7.2%).

(ii) *With sodium and alcohol.* To a solution of the hydroxy-ketone (4 g.) in EtOH (200 c.c.), Na (15 g.) was added as rapidly as possible, the mixture being heated on the water-bath. The EtOH was removed in steam, the oil which remained dissolved in  $\text{Et}_2\text{O}$ , the  $\text{Et}_2\text{O}$  solution dried over  $\text{K}_2\text{CO}_3$ , and the solvent removed. The glycol remained as a viscid yellow oil, which could not be crystallised. Its 3:5-dinitrobenzoyl derivative was an oil which solidified below 0°, but liquefied at room temp. Without further purification the glycol was heated with Se at 300° for 48 hr., and the product distilled. From the oil, b. p. below 160°/18 mm., eudalene picrate was obtained, m. p. 91°, both alone and after admixture with an authentic specimen.

*Oxidation of 2-Hydroxy-1:2-dihydroeremophilone.*—(i) *With ozone.*  $\text{O}_3$  was passed through a solution of the hydroxy-ketone (1.05 g.) in  $\text{CCl}_4$  cooled in salt-ice and the issuing gases were passed through  $\text{H}_2\text{O}$ . The  $\text{H}_2\text{O}$  solution smelt strongly of formaldehyde and the presence of this was confirmed as described previously. The  $\text{CCl}_4$  was removed in vac., the ozonide decomposed by digestion with  $\text{H}_2\text{O}$ , and the solution made alkaline with  $\text{Na}_2\text{CO}_3$  and extracted with  $\text{Et}_2\text{O}$ ; the  $\text{Et}_2\text{O}$  solution was washed with NaOH aq. to remove traces of a weak acid and dried, and the solvent evaporated, leaving an oil (0.45 g.). In  $\text{H}_2\text{O}$  suspension this gave an immediate ppt. of  $\text{CHBr}_3$  with NaOBr and the filtered solution deposited a liquid acid on acidification. The ketone was mixed with semicarbazide acetate in dil. EtOH and after some days the semicarbazone was pptd. with  $\text{H}_2\text{O}$ , washed with  $\text{Et}_2\text{O}$  to remove a resinous impurity, and crystallised, 6-acetyl-4:9-dimethyldecal-2-one-3-ol semicarbazone being obtained in minute plates, decomp. 216—219° (Found: C, 61.3, 61.1; H, 8.2, 8.0.  $\text{C}_{15}\text{H}_{25}\text{O}_3\text{N}_3$  requires C, 61.1; H, 8.5%).

(ii) *With hydrogen peroxide.* To a solution of the hydroxy-ketone (4.2 g.) in MeOH (40 c.c.), a mixture of  $\text{H}_2\text{O}_2$  (30%; 7 c.c.) and 4N-NaOH (7 c.c.) was added. A yellow colour appeared and some heat was developed. After 12 hr., the reaction mixture, which had deposited some solid, was poured into  $\text{H}_2\text{O}$ . The pptd. solid (2.5 g.) was identified as unchanged hydroxy-ketone, m. p. 103°. After extraction with  $\text{Et}_2\text{O}$  to remove neutral products, the alkaline solution was saturated with  $\text{CO}_2$ . A colourless oil separated which, after solution in  $\text{Et}_2\text{O}$  and evaporation of the solvent, partly crystallised, but the quantity (0.1 g.) was insufficient for purification. Its EtOH solution gave with  $\text{FeCl}_3$  a dirty brown, almost black, colour. The  $\text{NaHCO}_3$  solution was acidified, the viscid oil which separated dissolved in  $\text{Et}_2\text{O}$ , and the solution dried and evaporated. The residual oil partly crystallised on keeping and the solid, after draining on porous porcelain, crystallised from  $\text{Et}_2\text{O}$  in thin plates, decomp. 167—168°, both alone and after admixture with 1-methyl-4-( $\alpha$ -hydroxyisopropyl)cyclohexane-1-acetic-2- $\alpha$ -lactic acid ( $\alpha$ -form) (p. 2756).

*Reduction of 2-Hydroxytetrahydroeremophilone with Sodium Amalgam.*—To a mechanically stirred solution of 2-hydroxytetrahydroeremophilone (5 g.) in EtOH (300 c.c., 50%), Na-Hg (100 g., 4%) was added gradually, the temp. being maintained at 40—50° for 5 hr., and EtOH added from time to time to replace that lost by evaporation. After 12 hr., the solution was decanted from

the Hg and distilled in steam; after removal of the EtOH, an oil passed over. This was separated with Et<sub>2</sub>O and distilled (18 mm.); b. p. 165—175°. The colourless viscid oil so obtained was identified as tetrahydroeremophilone by the prepn. of the 2 : 4-dinitrophenylhydrazone and the semicarbazone, which melted and decomposed, respectively, at 177—178° and 213—214°, both alone and in admixture with authentic specimens.

*Oxidation of 2-Hydroxytetrahydroeremophilone.*—(i) *With hydrogen peroxide.* To a solution of the hydroxy-ketone (1 g.) in MeOH (15 c.c.), 4*N*-NaOH (1.14 c.c.) and H<sub>2</sub>O<sub>2</sub> (15%, 2.2 c.c.) were added: no heat was generated and the hydroxy-ketone separated. The mixture was therefore warmed at 50—60° for 15 min. and kept over-night. Addition of H<sub>2</sub>O pptd. unchanged hydroxy-ketone (0.6 g.), which was separated; the alkaline solution was acidified and extracted with Et<sub>2</sub>O, and the extract washed with Na<sub>2</sub>CO<sub>3</sub> aq., dried, and evaporated, leaving a trace of an oil which gave a greenish-black colour with FeCl<sub>3</sub>. The Na<sub>2</sub>CO<sub>3</sub> solution was acidified and the liquid acid which separated was extracted and dried in Et<sub>2</sub>O and recovered as a very viscid oil (0.4 g.), which was kept in vac. over H<sub>2</sub>SO<sub>4</sub> for some days (Found: C, 66.8; H, 10.2. C<sub>15</sub>H<sub>26</sub>O<sub>4</sub> requires C, 66.7; H, 9.6%).

(ii) *With chromic acid.* To a solution of the hydroxy-ketone (0.7 g.) in AcOH (3 c.c.), CrO<sub>3</sub> (0.2 g.) in AcOH was slowly added. The oxidation proceeded rapidly and was completed by warming on the water-bath for 15 min. After the addition of H<sub>2</sub>O, the pptd. oil was dissolved in Et<sub>2</sub>O, washed with Na<sub>2</sub>CO<sub>3</sub> aq. to remove AcOH and a trace of a liquid acid, dried, and recovered as a yellow oil which gave a green colour with alc. FeCl<sub>3</sub>. It was insol. in NaOH. 2-Hydroxy- $\omega$ -dihydroeremophilone-2 : 4-dinitrophenylhydrazone separated at once on addition of 2 : 4-dinitrophenylhydrazine sulphate to an EtOH solution of the ketone and crystallised from EtOH, in which it was very sparingly sol., in pale sulphur-yellow needles, m. p. 158—160° (Found: C, 60.7; H, 6.6. C<sub>21</sub>H<sub>28</sub>O<sub>5</sub>N<sub>4</sub> requires C, 60.6; H, 6.7%).

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