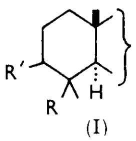
# **887.** *Terpene Synthesis. Part I. Alkylation with Benzyloxymethyl Chloride as a Method of Introducing a Hydroxymethyl Group.*

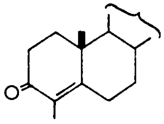
By C. L. GRAHAM and F. J. MCQUILLIN.

Alkylation with benzyloxymethyl chloride $[\mathrm{O{:}\underset{|}{C}{\cdot}CMe{:}\underset{|}{C}{\cdot}\underset{|}{C}H_2} \longrightarrow (a)$ $\mathrm{O{:}\underset{|}{C}{\cdot}CMeR{\cdot}\underset{|}{C}{:}\underset{|}{C}H}$ and $(b)$ $\mathrm{RO{\cdot}\underset{|}{C}{:}CMe{\cdot}\underset{|}{C}{:}\underset{|}{C}H}$, where $\mathrm{R = Ph{\cdot}CH_2{\cdot}O{\cdot}CH_2}]$ has been developed as a route to hydroxymethyl $[\mathrm{O{:}\underset{|}{C}{\cdot}CMe(CH_2{\cdot}OH){\cdot}\underset{|}{C}{=}\underset{|}{C}H}]$ and other derivatives of interest for terpene synthesis. The relative proportion of alkylation on carbon (*a*) and on oxygen (*b*) is influenced by the solvent used; the *C*-benzyloxymethyl derivative (*a*) may be made the principal product of reaction by use of a medium of low polarity. This alkylation shows a high degree of stereoselectivity; the configuration of the main product has been determined and its chemistry has been examined.

ELABORATION of the structural unit (I; $R = CH_2{\cdot}OH$, CHO, or $CO_2H$, $R' = H$ or OH), characteristic of a number of di-, tri-, and sesqui-terpenes, has been explored by various routes.[1] Stork and Schulenberg,[1a] by alkylation of the type (II) $\longrightarrow$ (III) ($R = \alpha\text{-}CH_2{\cdot}CO_2H$) * obtained a product which could be degraded to give the carboxylic acid (III; $R = \alpha\text{-}CO_2H$). The same stereochemical result has been realised by methylation, as in (IV) $\longrightarrow$ (V) ($R = CO_2H$ [1b] or CN [1c]), although it may be noted that in these instances the alkyl group enters from the β-side of the molecule. Further interesting work leading into the deoxy-series of terpenes (I; $R' = H$) has also been described.[2]



(I)



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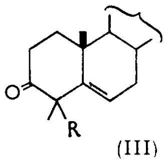

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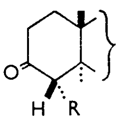

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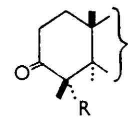

(V)

The Robinson annelation synthesis of substances of type (II), and alkylation [3] in the sense of (II) $\longrightarrow$ (III), are reactions of some generality. We have sought to extend the scope of these procedures by examining the use of benzyloxymethyl chloride for alkylation of substances of type (II).

Benzyloxymethyl chloride has previously been used to alkylate malonic ester,[4] as a route to barbiturates. It is, however, intrinsically more reactive [5] than, *e.g.*, methyl iodide or ethyl chloroacetate, and it would be expected to react preferentially by solvolysis, $Ph{\cdot}CH_2{\cdot}O{\cdot}CH_2Cl \longrightarrow Ph{\cdot}CH_2{\cdot}O^+{=}CH_2\ Cl^-$, rather than by direct substitution.[6] Simonsen and Storey,[7] using an analogous reagent, methoxymethyl chloride, with ethyl acetoacetate, obtained only the *O*-methoxymethyl ether; *O*- rather than *C*-alkylation predominates with other very reactive halides [8] such as $Me_2N{\cdot}CH_2{\cdot}CH_2Cl$. In preliminary

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* In referring to the relative orientation of substituent groups we use the steroid nomenclature. The compounds studied by us were, however, all racemic forms and α,β have only relative significance in this paper.

[1] (*a*) Stork and Schulenberg, *J. Amer. Chem. Soc.*, 1962, **84**, 284; (*b*) Wenkert and Tahara, *ibid.*, 1960, **82**, 3229; (*c*) Kuehne, *ibid.*, 1961, **83**, 1492.

[2] Saha, Ganguly, and Dutta, *J. Amer. Chem. Soc.*, 1959, **81**, 3670; Ghatak, Datta, and Ray, *ibid.* 1960, **82**, 1728, Barltrop and Day, *Tetrahedron*, 1961, **14**, 310.

[3] Conia, *Bull. Soc. chim. France*, 1954, 690; Conia and Nevot, *ibid.*, 1959, 493; Conia and Le Craz, *ibid.*, 1960, 1929, 1934; Barton, Ives, Kelly, Woodward, and Patchett, *J.*, 1957, 1131.

[4] Hill and Keach, *J. Amer. Chem. Soc.*, 1926, **48**, 257.

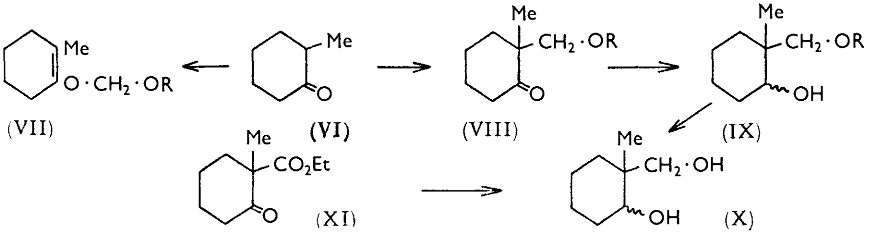
[5] Conant, Kirner, and Hussey, *J. Amer. Chem. Soc.*, 1925, **47**, 488.

[6] Ballinger, de la Mare, Kohnstam, and Prestt, *J.*, 1955, 3641.

[7] Simonsen and Storey, *J.*, 1909, **95**, 2106.

[8] Rhoads, Reynolds, and Rawlins, *J. Amer. Chem. Soc.*, 1952, **74**, 2889.

experiments with the sodium enolate of 2-methyl cyclohexanone, benzyloxymethyl chloride was found to give a product containing both the *O*- and *C*-benzyloxymethyl derivatives (VII and VIII; R = Ph·$CH_2$). The proportion of the former could, however, as we expected, be reduced by suitable choice of solvent. The *C*-benzyloxymethyl derivative was shown to have the constitution (VIII; R = Ph·$CH_2$) by comparison of its reduction product (X) with material made as indicated from ethyl 1-methyl-2-oxocyclohexanecarboxylate (XI).



The dimethyloctalone (XII) was then shown to give, in a similar reaction, a product from which a benzyloxymethyl derivative, m. p. 69°, later shown to be (XV), was isolated as the major constituent. With the precedent of phenol alkylation [9] in mind, we examined more fully in this case the influence of solvent on the proportions of *O*-alkylated (XXVI) and *C*-alkylated products (XV) and (XXV) formed. The results (see Table) confirmed the expectation that *O*-alkylation could be minimised by use of solvents of low polarity. We have found dioxan most generally useful; in a hydrocarbon solvent, formation of the sodium enolate is retarded by its low solubility.

| Solvent | Yield (%) | *O*/*C*-Alkyl |
|---|---|---|
| 1-Methylpyrrolidone | 47 | 68 : 32 |
| Tetrahydrofuran | 45 | 15 : 85 |
| Dioxan | 60 | 17 : 83 |
| Light petroleum | 38 | 5 : 95 |

Accompanying the crystalline benzyloxymethyl ketone which forms the major product of alkylation of the ketone (XII) was a non-crystalline material from which an isomeric ketone was isolated as the semicarbazone. Evidence that the crystalline product has the α-configuration (XV) was obtained from an examination of the pair of derived diols (XVIII) and (XIX).

Sodium borohydride reduced the ketone (XV) to a product from which isomeric 3,5-dinitrobenzoates, m. p. 160° and 144°, were obtained in a ratio of 40 : 1. Precedent [10] indicates that the major product should correspond with the β-alcohol (XVII). Similarly [11] Ponndorf–Meerwein reduction should give a higher proportion of the α-alcohol (XVI), and the experimental product gave the isomeric 3,5-dinitrobenzoates in nearly equal amounts. The alcohols regenerated from these esters were debenzylated by sodium–ammonia to the respective diols (XVIII) and (XIX). Both diols gave isopropylidene derivatives (XX and XXI, respectively) in good yield. Formation of such isopropylidene derivatives is known to be sensitive to the relative orientation of the hydroxyl groups,[12] and it would be possible with an α-OH,β-$CH_2$·OH diol structure such as (XXIV) only if the diol-containing ring took up the boat conformation.

An inversion of this type is not impossible,[13] and in assessing the significance of the

[9] Claisen, Kremers, Roth, and Tietze, *Annalen*, 1925, **442**, 210; Claisen and Tietze, *ibid.*, 1926, **449**, 81; cf. Ingold, *Ann. Reports*, 1926, **23**, 112; Curtin, Crawford, and Wilhelm, *J. Amer. Chem. Soc.*, 1958, **80**, 1391; Kornblum and Lurie, *ibid.*, 1959, **81**, 2705.

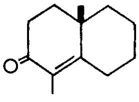
[10] Barton, *J.*, 1953, 1027; cf. Halsall, Hodges, and Jones, *ibid.*, p. 3109; Halsall, Meakins, and Swayne, *ibid.*, p. 4139.

[11] (*a*) Bancroft, Haddad, and Summers, *J.*, 1961, 3295; (*b*) Shoppee and Johnston, *J.*, 1962, 2684.

[12] Angyal and Macdonald, *J.*, 1952, 686.

[13] Barton, Lewis, and McGhie, *J.*, 1957, 2907; Banerji, Barton, and Cookson, *ibid.*, p. 5041.

formation of an isopropylidene derivative by both diols (XVIII) and (XIX) we reasoned as follows. Ketal formation is reversible; the conditions used were mild and unlikely to force a conformational inversion unless this is extremely easily achieved. A known 3α-OH,4β-$CH_2$·OH diol failed to give an isopropylidene derivative;[14a] 3β-OH,4β-$CH_2$·OH and 3β-OH,4α-$CH_2$·OH diols form derivatives of this type.[14] The conformational distortion indicated by the Cotton effect of 4,4-dimethyl-3-oxo-steroids and of simple analogues[15]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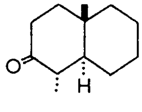
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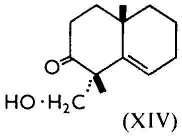
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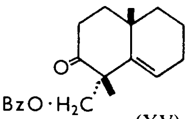
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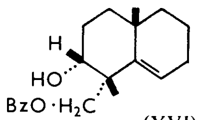
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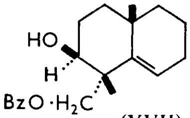
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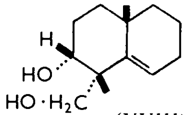
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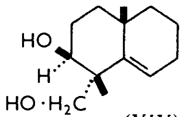
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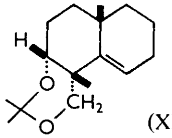
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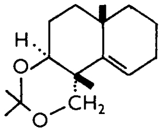
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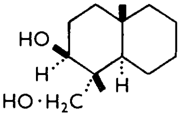
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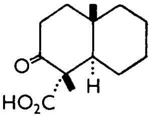
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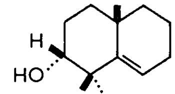
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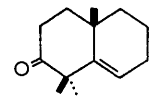
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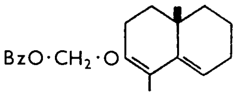
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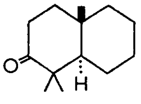
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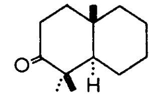
(XXVIII)

such as (XXVII) appears to amount[16a] to some twisting of the molecule and falls far short of chair ⟶ boat inversion.[16b] Rearrangements of 4,4-dimethyl-3α- and -3β-tosyloxy-steroids[17a] and the relative rates of hydrolysis of esters of diterpene 4α- and 4β-carboxylic acids[17b] become difficult to interpret if the 4,4-disubstituted ring has a boat conformation. Although our diols (XVIII) and (XIX) lack the 5α,6β-substituents of their steroid and triterpene analogues, formation of an isopropylidene derivative by diol (XVIII) appeared on the balance of evidence to be a reasonable indication of an α-oriented $CH_2$·OH group. Since this conclusion is supported by independent evidence discussed below, we regard our products as belonging to the α-oriented series, as in the previous alkylation experiments of Stork and Schulenberg.[1a]

Debenzylation of the ketone (XV) at palladised charcoal in alcohol was found to be rapid in comparison with hydrogenation of the double bond. The crude product, presumably (XIV), showed some absorption at 248 mμ due to the presence of the unsaturated ketone (XII) arising by elimination of formaldehyde. When this product was kept the 248 mμ absorption increased, slowly in alcohol solution and more rapidly in the presence of acid or of alkali. The parent ketone (XII), re-formed in this way, was characterised as the 2,4-dinitrophenylhydrazone and semicarbazone. On further hydrogenation of the ether (XV) a crystalline saturated hydroxymethyl ketone was

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[14] (*a*) Beton, Halsall, and Jones, *J.*, 1956, 2904; (*b*) Djerassi and Rittel, *J. Amer. Chem. Soc.*, 1957, **79**, 3528; (*c*) Jacobs, *J. Biol. Chem.*, 1925, **63**, 631.

[15] Djerassi, "Optical Rotatory Dispersion," McGraw-Hill Co., New York, 1960, pp. 76, 90, 94.

[16] (*a*) Allinger and Da Rooge, *Tetrahedron Letters*, 1961, 676; Lehn, Levisalles, and Ourisson, *ibid.*, p. 682; (*b*) Holker and Whalley, *Proc. Chem. Soc.*, 1961, 464.

[17] (*a*) Shoppee and Johnston, *J.*, 1961, 3261; 1962, 2684; Bancroft, Haddad, and Summers, *J.*, 1961, 3295; (*b*) Campbell and Todd, *J. Amer. Chem. Soc.*, 1942, **64**, 928; King, Godson, and King, *J.*, 1955, 1117.

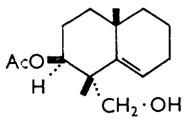
obtained, that is represented as (XXVIII) since, under the action of cold methanolic alkali, it generated the dimethyldecalone (XIII) by loss of formaldehyde. This reference ketone was prepared by reduction of the unsaturated ketone (XII) with sodium in liquid ammonia.

The steric course of reduction of the $\Delta^{8,9}$-bond was examined also by using the β-alcohol (XVII). This, on debenzylation and hydrogenation, gave in high yield a crystalline diol shown to be (XXII) since chromic acid converted it into the ketone (XIII) as end product, by decarboxylation of an intermediate (XXIII) which was not isolated. Formation of principally the *trans*-decalin derivative has been observed [18] in the hydrogenation of other substances analogous to (XVII). The diol (XXII) gave an isopropylidene derivative; the hydroxyl and hydroxymethyl groups are therefore proximate.

The acetate of the β-alcohol (XVII) on catalytic debenzylation, gave a crystalline monoacetate of the diol (XIX). This crystalline product, however, on contact with aqueous acetic acid, was converted into a non-crystalline mixture of this and an isomeric acetate; from this mixture the diol (XIX) was re-formed on hydrolysis. The evident isomerisation is most easily understood as an acetyl migration, (XXIX) ⟶ (XXX).

From the ketone (XV) it was possible to obtain, in good yield, the deoxy-derivative (XXXI; R = $Ph{\cdot}CH_2$) by Wolff–Kishner reduction (we used the method of Barton, Ives, and Thomas [19]). Debenzylation, catalytically, or by treatment with lithium-ammonia, then gave the alcohol (XXXI; R = H). The latter was converted through the 8,9-oxide into the triol (XXXIII; R = H), which was also obtained by hydrogenation of the 1-benzyl ether (XXXIII; R = $Ph{\cdot}CH_2$), similarly derived from its unsaturated relative (XXXI; R = $Ph{\cdot}CH_2$). The triol (XXXIII; R = H) did not form an isopropylidene derivative.

The unsaturated alcohol (XXXI; R = H) was rather sensitive to oxidation by chromium trioxide in acetic acid in the allylic position; the rather complex product had ν 1667 cm.$^{-1}$ and λ 230 mμ. Use of chromium trioxide in pyridine, however, gave the aldehyde (XXXII) as the major product. This aldehyde (which was characterised as a 2,4-dinitrophenylhydrazone) was reactive towards Schiff's and Tollens' reagents, but with silver oxide on a preparative scale gave an almost entirely neutral oxidation product, with only a trace of acidic material. This behaviour we attribute to the highly substituted and allylic environment of the aldehyde group. Pivalaldehyde, which is oxidised [20] by silver oxide to pivalic acid in fair yield, is also known to be rather easily decomposed: [20] $Me_3C{\cdot}CHO \longrightarrow Me_3CH + CO$. The neutral oxidation product from our aldehyde (XXXII) had $\lambda_{max.}$ 202 mμ (in hexane), and in alcoholic perchloric acid developed absorption at $\lambda_{max.}$ 239 mμ, with shoulders at 235 and 247 mμ (in alcohol). The parent alcohol (XXXI;



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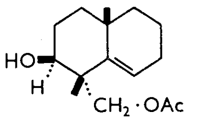

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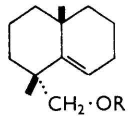

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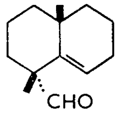

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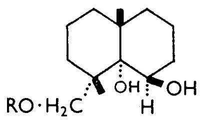

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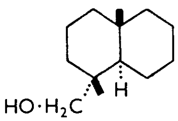

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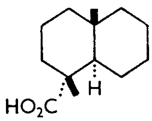

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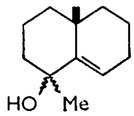

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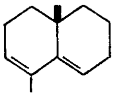
(XXXVII)

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[18] Kalvoda and Loffel, *Helv. Chim. Acta*, 1957, **40**, 2340; Sondheimer and Elad, *J. Amer. Chem. Soc.*, 1957, **79**, 5452; 1958, **80**, 1967; Gaspert, Halsall, and Willis, *J.*, 1958, 624; Halsall, Rodwall, and Willis, *Proc. Chem. Soc.*, 1958, 231; Haynes and Timmons, *Proc. Chem. Soc.*, 1958, 345; Mukherji and Dutta, *Proc. Chem. Soc.*, 1958, 351.

[19] Barton, Ives, and Thomas, *J.*, 1955, 2056.

[20] Conant, Webb, and Mendum, *J. Amer. Chem. Soc.*, 1929, **51**, 1246; Payne and Lemon, *ibid.*, 1941, **63**, 226.

R = H) has $\lambda_{max.}$ 203 mμ (in hexane) but is stable in acid. This behaviour of the oxidation product is consistent with the presence of the tertiary allylic alcohol (XXXVI) which in contact with acid should form the diene (XXXVII). This diene, prepared by reduction of the ketone (XII) with sodium borohydride, followed by acid dehydration, gave an ultraviolet absorption curve similar in detail to that of the material obtained on acid treatment of the product of silver oxide oxidation.

The silver oxide oxidation of the aldehyde (XXXII) is similar to the silver-catalysed oxidation of certain acids by persulphate.[21] The amount of silver oxide consumed was, however, quite insufficient to account for over-oxidation of a first-formed acid in this way.

The saturated alcohol corresponding to (XXXI; R = H) was oxidised without difficulty. This substance, obtained by hydrogenation, was converted by chromic acid into an acidic product in high yield. These products we regard (cf. ref. 18) as mainly the *trans*-decalin alcohol (XXXIV) and the corresponding *trans*-decalincarboxylic acid (XXXV).

The total acidic product from oxidation of the saturated alcohol (XXXIV) gave a methyl ester, which was hydrolysed by alcoholic alkali at a rate closely similar to that of hydrolysis of methyl abietate. Under the same conditions methyl *O*-methylpodocarpate was relatively unaffected. This behaviour lends strong support (cf. ref. 17*b*) to the α-configuration which we have assigned to our products.

An acid formulated as (XXXV) has previously been described [22] (m. p. 120°) cf., however, ref. 23. Through the kindness of Professor Dutta we have been able to compare this with an acid, m. p. 103° from our product, which is different.

## EXPERIMENTAL

Benzyloxymethylchloride, b. p. 105—109°/11 mm., $n_D^{20}$ 1·5192, made by Hill and Keach's method,[4] was obtained in best yield by saturating a stirred mixture of benzyl alcohol and aqueous formaldehyde, cooled in ice–salt, rapidly with hydrogen chloride. Carefully purified, it could be stored without decomposition, but it was always redistilled immediately before use. It had $\nu_{max.}$ 3084, 3061, 3030, 743, 697 (benzyl), and 1124 cm.$^{-1}$ (ether).

*Benzyloxymethylation of* 2-*Methylcyclohexanone*.—2-Methylcyclohexanone with 0·5 mol. of sodium hydride was converted into the enolate in various solvents by refluxing and stirring under nitrogen. Benzyl chloromethyl ether (0·5 mol.) was then added with ice-coling and stirring. The alkylated product was collected as a fraction, b. p. 115—125°/0·2 mm. The results are tabulated.

| Solvent | Ketone [1] (g.) | NaH [2] (g.) | Time [3] (hr.) | Ketone recovered (g.) | Product (g.) | $n_D^{20}$ |
|---|---|---|---|---|---|---|
| Ether .................. | 17·2 | 1·82 | 12 | 11·1 | 4·3 [4] | 1·5220 |
| Benzene ............... | 15·7 | 1·72 | 5 | 8·0 | 5·8 | 1·5160 |
| Dioxan ............... | 15·7 | 1·72 | 5 | 8·3 | 6·5 | 1·5210 |
| Dioxan–ether ......... | 20·0 | 3·42 | 5 | 10·2 | 11·8 | 1·5221 |

[1] 2-Methylcyclohexanone. [2] We used initially granular sodium hydride which was later replaced by the sodium hydride–mineral oil dispersion. With the latter, the oil was first removed by washing with dry ether. The remaining sodium hydride powder gave some 90% of the theoretical hydrogen evolution when dropped into isopropyl alcohol. [3] Time of refluxing to form the sodium enolate, [4] This product was redistilled to give material b. p. 128°/0·5 mm., $n_D^{20}$ 1·5235 (Found: C, 77·7; H. 8·8. Calc. for $C_{15}H_{20}O_2$: C, 77·6; H, 8·7%).

2-*Benzyloxymethyl*-2-*methylcyclohexanone* (VIII; R = Ph·CH$_2$).—The benzyloxymethylation product from dioxan (11 g.), hydrolysed for 1 hr. with warm N-hydrochloric acid (5 c.c.) in dioxan (90 c.c.), gave 2-*benzyloxymethyl*-2-*methylcyclohexanone*, (5·5 g.), b. p. 125°/0·5 mm., $n_D^{20}$ 1·5190, $\nu_{max.}$ 3079, 3059, 3026, 732, and 695 (benzyl), 1703 (saturated ketone), and 1099 cm.$^{-1}$ (ether) (Found: C, 77·8; H, 9·0. $C_{15}H_{20}O_2$ requires C, 77·6; H, 8·7%) [2,4-*dinitrophenylhydrazone*, m. p. 113° (from methyl alcohol) (Found: C, 61·0; H, 5·8. $C_{21}H_{24}N_4O_5$ requires C, 61·1; H, 5·8%)].

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[21] Bacon and Bott, *Chem. and Ind.*, 1953, 1285.
[22] Ghatak, Saha, and Dutta, *J. Amer. Chem. Soc.*, 1957, **79**, 4487.
[23] Sondheimer and Rosenthal, *J. Amer. Chem. Soc.*, 1958, **80**, 3995.

*2-Benzyloxymethyl-2-methylcyclohexanol* (IX; R = $Ph{\cdot}CH_2$).—The above ketone (1 g.) was reduced with sodium borohydride (0·5 g.) in 80% ethanol to *2-benzyloxymethyl-2-methylcyclohexanol*, b. p. 120—125/0·5 mm., $n_D^{20}$ 1·5222 (Found: C, 76·7; H, 9·2. $C_{15}H_{22}O_2$ requires C, 76·9; H, 9·4%).

*2-Hydroxymethyl-2-methylcyclohexanol* (X).—(*a*) 2-Benzyloxymethyl-2-methylcyclohexanol (0·356 g.), hydrogenated in alcohol with palladised charcoal (0·2 g.), gave 2-hydroxymethyl-2-methylcyclohexanol, b. p. 80—83°/0·3 mm., $n_D^{20}$ 1·4860, which formed prisms, m. p. 89°, from light petroleum.

(*b*) Ethyl 1-methyl-2-oxocyclohexanecarboxylate (5 g.), reduced with lithium aluminium hydride (4·65 g.) in ether (300 c.c.), gave 2-hydroxymethyl-2-methylcyclohexanol (3·3 g.), b. p. 84°/0·3 mm., $n_D^{20}$ 1·4850, m. p. 89°, identical with the material made as in (*a*) (Found: C, 66·6; H, 11·2. $C_{10}H_{16}O_2$ requires C, 66·6; H, 11·1%).

*Benzyloxymethylation of 1,10-Dimethyl-*$\Delta^{1,9}$*-2-octalone*.—(*a*) 1,10-dimethyl-$\Delta^{1,9}$-2-octalone was converted into the sodium enolate by treatment under reflux with sodium hydride in the solvents tabulated below with stirring in nitrogen. Benzyloxymethyl chloride (1 equiv.) was then added with cooling and continued stirring, and the product was isolated after the mixture had been kept overnight. Formation of the sodium enolate was faster in the more polar solvents, in which the enolate is more soluble.

| | | | Product | | |
|---|---|---|---|---|---|
| Solvent | Yield (%) | B. p./0·1 mm. | $n_D^{20}$ | $\lambda_{max.}$ | log $\varepsilon_{max.}$ |
| Dioxan | 55 | 145—155° | 1·5362 | 244 | 3·57 |
| 1-Methylpyrrolidone | 38 | 142—152 | 1·5457 | 245 | 4·14 |
| Tetrahydrofuran | 36 | 148—158 | 1·5380 | 244 | 3·52 |
| Light petroleum | 31 | 144—156 | 1·5362 | 248 | 3·00 |
| Tetrahydrofuran–light petroleum | 50 | 150—160 | 1·5375 | 245 | 3·65 |

(*b*) Hydrolysis of the benzyloxymethyl ether in the various products of alkylation listed in (*a*) was effected by warming for 20 min. on the steam-bath with 2·5% sulphuric acid in dioxan–water (8 : 1). Distillation of the hydrolysis product gave benzyl alcohol and regenerated 1,10-dimethyl-$\Delta^{1,9}$-2-octalone, followed by a fraction, b. p. 140—150°/0·1 mm., $n_D^{20}$ 1·5380, which crystallised to give *1α-benzyloxymethyl-1β,10β-dimethyl-*$\Delta^{8,9}$*-2-octalone* as prisms, m. p. 69°, $\nu_{max.}$ 3077, 3060, 3018, 739, 696 (benzyl), 1709 (saturated ketone), and 1099 cm.$^{-1}$ (ether) (Found: C, 81·0; H, 9·0. $C_{20}H_{26}O_2$ requires C, 80·7; H, 8·7%). The *semicarbazone* formed flat prisms, m. p. 168° (from ethyl alcohol), $\lambda_{max.}$ 230 (ε 13,800) and 211 mμ (ε 20,800) (Found: C, 70·6; H, 8·3. $C_{21}H_{29}N_3O_2$ requires C, 71·0; H, 8·2%). The oil remaining after removal of the crystalline ketone was eluted from alumina with light petroleum as a series of fractions, from the first of which further crystalline material was obtained. The remaining material, after rechromatography, gave a product, b. p. 140°/0·05 mm., $n_D^{20}$ 1·5390 (Found: C, 80·4; H, 8·9%). The non-crystalline material could alternatively be separated through the semicarbazone, which from alumina gave, first, fractions, m. p. 160—166°, by elution with benzene–chloroform (20 : 1), and then fractions, m. p. *ca.* 170°, eluted by benzene–chloroform (5 : 1). The former fractions were recrystallised to give the semicarbazone, m. p. 168° noted above; the latter fractions gave a *semicarbazone*, m. p. 174°, $\lambda_{max.}$ 231 (ε 14,800), 211 mμ (ε 20,400) (Found: C, 70·8; H, 7·9%), corresponding with the derivative of the isomeric 1β-benzyloxymethyl-1α,10β-dimethyl-$\Delta^{8,9}$-2-octalone.

*1α-Benzyloxymethyl-1β,10β-dimethyl-*$\Delta^{8,9}$*-2β-octalol* (XVII).—1β,10β-Dimethyl-1α-benzyloxymethyl-$\Delta^{8,9}$-2-octalone (0·5 g.) in alcohol (5 c.c.) with an excess of sodium borohydride (0·26 g.) was kept overnight, warmed briefly, and then carefully neutralised with acetic acid. Removal of the solvent and extraction of the residue with chloroform gave, in excellent yield, substantially pure *1α-benzyloxymethyl-1β,10β-dimethyl-*$\Delta^{8,9}$*-2β-octalol*, b. p. 130°/0·02 mm., $n_D^{20}$ 1·5444 (Found: C, 79·9; H, 9·6. $C_{20}H_{28}O_2$ requires C, 80·0; H, 9·3%). This gave a *3,5-dinitrobenzoate*, m. p. 162°, from benzene–light petroleum (Found: C, 65·7; H, 6·3. $C_{27}H_{30}N_2O_3$ requires C, 65·7; H, 6·1%), together with 2—3% of a second 3,5-dinitrobenzoate, m. p. 142°, from light petroleum. The 3,5-dinitrobenzoate of m. p. 162° was hydrolysed by 1% alcoholic potassium hydroxide to give the pure 2β-alcohol, b. p. 130°/0·02 mm., $n_D^{20}$ 1·5438, indistinguishable in its infrared absorption from the borohydride reduction product.

*1α-Benzyloxymethyl-1β,10β-dimethyl-*$\Delta^{8,9}$*-2α-octalol* (XVI).—1α-Benzyloxymethyl-1β,10β-dimethyl-$\Delta^{8,9}$-2-octalone (3 g.) in isopropyl alcohol (150 c.c.) with aluminium isopropoxide (3 g.)

was heated during 6 hr., whilst acetone was being removed; further isopropyl alcohol was added as necessary. The reduction product, b. p. 135—140°/0·02 mm., $n_D^{20}$ 1·5440, gave a mixed 3,5-dinitrobenzoate, m. p. *ca.* 127°, which was separated on silica gel into two 3,5-dinitrobenzoates, m. p. 144° (1·03 g.) (eluted with 1 : 9 benzene–light petroleum) and m. p. 162° (0·86 g.) (eluted with benzene). The latter proved to be identical with the 3,5-dinitrobenzoate of the 2β-alcohol described above. The 3,5-*dinitrobenzoate* of m. p. 144° (Found: C, 66·0; H, 6·2%), on hydrolysis with methanolic potassium hydroxide, gave 1α-*benzyloxymethyl*-1β,10β-*dimethyl*-$\Delta^{8,9}$-2α-*octalol*, b. p. 140°/0·1 mm., $n_D^{20}$ 1·5446 (Found: C, 80·4; H, 9·3%).

1α-*Hydroxymethyl*-1β,10β-*dimethyl*-$\Delta^{8,9}$-2α- *and* -2β-*Octalol* (XVIII and XIX) *and their Isopropylidene Derivatives* (XX and XXI).—(*a*) Debenzylation was carried out by adding small pieces of sodium to the benzyloxymethyl derivatives in a little dry alcohol with liquid ammonia until a blue colour persisted. The product was released by addition of water, after evaporation of ammonia. 1α-*Hydroxymethyl*-1β,10β-*dimethyl*-$\Delta^{8,9}$-2β-*octalol* (XIX) was an oil, b. p. 135°/0·15 mm., $n_D^{20}$ 1·5315 (Found: C, 74·0; H, 10·3. $C_{13}H_{22}O_2$ requires C, 74·3; H, 10·5%). The *bis*-3,5-*dinitrobenzoate* formed prisms, m. p. 195°, from benzene–light petroleum (Found: C, 54·5; H, 4·4. $C_{27}H_{26}O_{12}N_4$ requires C, 54·2; H, 4·4%).

1α-*Hydroxymethyl*-1β,10β-*dimethyl*-$\Delta^{8,9}$-2α-*octalol* (XVIII), similarly obtained, had b. p. 135°/0·02 mm., $n_D^{20}$ 1·5297, m. p. 77° (from light petroleum) (Found: C, 74·3; H, 10·3%).

(*b*) The isopropylidene derivatives were made by shaking a solution of the respective diol in dry acetone with anhydrous copper sulphate for 4—5 days. The 2β-hydroxy-1α-hydroxymethyl compound gave an *isopropylidene derivative*, b. p. 80°/0·05 mm., $n_D^{20}$ 1·5053 (Found: C, 76·9; H, 10·2. $C_{16}H_{26}O_2$ requires C, 76·8; H, 10·4%). The 2α-hydroxy-1α-hydroxymethyl compound gave an *isopropylidene derivative*, b. p. 90°/0·1 mm., $n_D^{20}$ 1·4986 (Found: C, 76·4; H, 10·4%).

1α-*Hydroxymethyl*-1β,10β-*dimethyl*-9αH-2β-*decalol* (XXII).—1α-Benzyloxymethyl-1β,10β-dimethyl-$\Delta^{8,9}$-2β-octaol (0·96 g.) in alcohol (45 c.c.) with palladised charcoal (0·45 g.) absorbed 2 mol. equivalents of hydrogen, the first rapidly. The product (0·6 g.), b. p. 120°/0·05 mm., $n_D^{20}$ 1·5180, crystallised to give prisms (0·45 g.), m. p. 107°, from light petroleum of 1α-*hydroxymethyl*-1β,10β-*dimethyl*-9αH-2β-*decalol* (Found: C, 73·2; H, 11·6. $C_{13}H_{24}O_2$ requires C, 73·6; 11·3%); the non-crystalline residue formed an oil, b. p. 120°/0·15 mm., $n_D^{20}$ 1·5150 (Found: C, 73·9; H, 10·9%). The former gave an *isopropylidene derivative* (by use of acetone and anhydrous copper sulphate), prisms, m. p. 97° (from methyl alcohol) (Found: C, 76·4; H, 11·0. $C_{16}H_{28}O_2$ requires C, 76·2; H, 11·1%), and a *bis*-3,4-*dinitrobenzoate*, m. p. 222° (from benzene–light petroleum (Found: C, 53·4; H, 4·3. $C_{27}H_{29}O_{12}N_4$ requires C, 53·4; H, 4·6%).

A solution of this diol (0·155 g.) in 90% acetic acid (3 c.c.) with chromium trioxide (0·164 g.) was kept overnight and then treated with water and a little sulphur dioxide. The bulk of the acetic acid was removed *in vacuo* and the residue saturated with ammonium sulphate and extracted with chloroform. Removal of the solvent gave a residue (0·11 g.) showing infrared absorption at 1729 and 1703 cm.$^{-1}$, and in the 3 μ region broad absorption typical of a carboxylic acid. This material, on decarboxylation by heat, gave a product (0·05 g.), b. p. 90—100°/0·6 mm., $n_D^{20}$ 1·4830, which formed a 2,4-dinitrophenylhydrazone, m. p. 187°, identical with the derivative of 1α,10β-dimethyl-9α*H*-2-decalone prepared as described below.

1α,10β-*Dimethyl*-9αH-2-*decalone* (XIII).—1,10-Dimethyl-$\Delta^{1,9}$-2-octalone (1·2 g.) in ether (20 c.c.) was added to a stirred solution of lithium (0·8 g.) in liquid ammonia (200 c.c.). After 0·5 hr. ammonium chloride was added. The product, isolated after evaporation of ammonia, gave indications (infrared) of appreciable reduction to the alcohol. It was therefore re-oxidised with chromic acid in acetic acid. Recovery then gave 1α,10β-dimethyl-9αH-2-decalone (1 g.), b. p. 85°/0·6 mm., $n_D^{20}$ 1·4900, $\nu_{\text{max.}}$ 1706 cm.$^{-1}$ (Found: C, 80·4; H, 10·8. Calc. for $C_{12}H_{20}O$: C, 80·0; H, 11·1%). The semicarbazone formed prisms, m. p. 188°, from alcohol (Found: C, 65·9; H, 9·8. Calc. for $C_{13}H_{28}N_3O$: C, 65·9; H, 9·7%). The 2,4-dinitrophenylhydrazone formed yellow prisms, m. p. 187°, from alcohol–ethyl acetate (Found: C, 59·7; H, 6·8. Calc. for $C_{18}H_{24}N_4O_4$: C, 60·0; H, 6·7%). By catalytic hydrogenation of 1,10-dimethyl-$\Delta^{1,9}$-2-octalone, Gunstone and Heggie [24] obtained a dimethyldecalone which gave a semicarbazone, m. p. 189°, and a 2,4-dinitrophenyl hydrazone, m. p. 186°. This product, to which these authors erroneously assign a *cis*-decalone structure, is the material described above.

*Oxidation of* 1α-*Benzyloxymethyl*-1β,10β-*dimethyl*-$\Delta^{8,9}$-2β-*octalol by Chromium Trioxide.*—The

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[24] Gunstone and Heggie, *J.*, 1952, 1437.

alcohol (0·4 g.) in pyridine (2 c.c.) was added to chromium trioxide (0·54 g.) in pyridine (5 c.c.) and kept for 24 hr. The product, isolated after addition of water and sulphur dioxide and acidification with sulphuric acid, was an oil, b. p. 145°/0·2 mm., $n_D^{20}$ 1·5378, which on being seeded afforded 1α-benzyloxymethyl-1β,10β-dimethyl-$\Delta^{8,9}$-2-octalone (0·17 g.), m. p. 69°.

*Decomposition of* 1α-*Hydroxymethyl*-1β,10β-*dimethyl*-$\Delta^{8,9}$-2-*octalone* (XIV).—The ketone (XV) (0·047 g.) was debenzylated by rapid hydrogenation with palladised charcoal (0·09 g.) in alcohol (5 c.c.). The catalyst was filtered off and the solvent removed *in vacuo* without heating. The residue showed ultraviolet absorption as tabulated. 1,10-Dimethyl-$\Delta^{1,9}$-2-octalone shows [24,25] $\lambda_{max.}$ 248 mμ (ε 13,800).

| Alcohol | | N-HCl in 50% aq. EtOH | | N-KOH in 50% aq. EtOH | |
|---|---|---|---|---|---|
| $\lambda_{max.}$ 245 mμ | | $\lambda_{max.}$ 251 mμ | | $\lambda_{max.}$ 251 mμ | |
| Hr. | $10^{-3}\varepsilon$ | Hr. | $10^{-3}\varepsilon$ | Hr. | $10^{-3}\varepsilon$ |
| 0 | 1·37 | | | | |
| 1 | 1·73 | 1 | 1·96 | 0·25 | 9·65 |
| 4·5 | 2·49 | 3 | 3·04 | 0·75 | 9·65 |
| 16 | 3·7 | 21 | 7·05 | | |
| 24 | 4·6 | 51 | 9·07 | | |
| 42 | 6·6 | 120 | 9·67 | | |
| 72 | 7·6 | | | | |

1α-*Hydroxymethyl*-1β,10β-*dimethyl*-2-*decalone* (XXVIII).—1α-Benzyloxymethyl-1β,10β-dimethyl-$\Delta^{8,9}$-2-octalone (0·15 g.) in ethanol (25 c.c.) with palladised charcoal (0·32 g.) absorbed >2 mol. of hydrogen in ~20 hr. The ethanol was removed *in vacuo* with a minimum of heating. The residue, on extraction with pentane, gave a *solid*, m. p. 60° (from pentane) (Found: C, 73·8; H, 10·5. $C_{13}H_{22}O_2$ requires C, 74·2; H, 10·5%). The same *product* was isolated more readily when hexane was used as solvent for hydrogenation. This material, when kept in 1 : 4 aqueous-methanol containing 4% of potassium hydroxide, gave 1α,10β-dimethyl-9αH-2-decalone (semicarbazone, m. p. 188°).

2β-*Acetoxy*-1α-*benzyloxymethyl*-1β,10β-*dimethyl*-$\Delta^{8,9}$-*octalin*.—The corresponding 2β-octalol (0·7 g.) was heated in acetic anhydride (4·5 c.c.) with dry pyridine (4 c.c.) for 4 hr. The product (0·7 g.), 2β-*acetoxy*-1α-*benzyloxymethyl*-1β,10β-*dimethyl*-$\Delta^{8,9}$-*octalin*, had b. p. 148—156°/0·05 mm. $n_D^{20}$ 1·5265 (Found: C, 76·9; H, 8·8. $C_{22}H_{30}O_3$ requires C, 77·2; H, 8·8%).

*Debenzylation of* 2β-*Acetoxy*-1α-*benzyloxymethyl*-1β,10β-*dimethyl*-$\Delta^{8,9}$-*octalin*.—The acetate (1·2 g.) in ethyl alcohol (25 c.c.) with palladised charcoal (0·58 g.) absorbed one mol. of hydrogen. The product crystallised as prisms (0·43 g.), m. p. 99° (from pentane), $\nu_{max.}$ 3521 (OH), 1717, 1258 cm.$^{-1}$ (OAc) (Found: C, 71·2; H, 9·2. $C_{15}H_{24}O_3$ requires C, 71·1; H, 9·5%), and an oil (0·27 g.), b. p. 90—100°/0·1 mm., $n_D^{20}$ 1·5075, ν 3448 (OH), 1730, 1721, 1258, 1245 cm.$^{-1}$ (acetate (Found: C, 70·75; H, 9·4%). The acetate, m. p. 99°, which we regard as 2β-*acetoxy*-1β,10β-*dimethyl*-1α-*hydroxymethyl*-$\Delta^{8,9}$-*octalin* (XXIX), when kept for 26 hr. in 90% acetic acid, was converted to a non-crystalline mixture of acetates, b. p. 90—100°/0·1 mm. (Found: C, 71·1; H, 9·7%). This had $\nu_{max.}$ 3448 (OH), 1730, 1721, 1258, 1245 cm.$^{-1}$ (OAc) in a spectrum very similar to that of the above non-crystalline material. The non-crystalline acetate, hydrolysed with methanolic potassium hydroxide under nitrogen, gave an oil, b. p. 130°/0·25 mm., $n_D^{20}$ 1·5315 (Found: C, 74·0; H, 10·7. Calc. for $C_{13}H_{22}O_2$: C, 74·3; H, 10·5%), with the infrared spectrum of 1α-hydroxymethyl-1β,10β-dimethyl-$\Delta^{8,9}$-2β-octalol and giving a bis-3,5-dinitrobenzoate, m. p. 193°, identical with that described above.

1α-*Benzyloxymethyl*-1β,10β-*dimethyl*-$\Delta^{8,9}$-*octalin* (XXXI).—1α-Benzyloxymethyl-1β,10β-dimethyl-$\Delta^{8,9}$-2-octalone (0·76 g.) was added to a solution from sodium (0·23 g.) in diethylene glycol (10 c.c.) containing anhydrous hydrazine (1 c.c.). The mixture was heated under reflux (180°) for 3 hr., kept overnight, and then, during distillation of hydrazine, the temperature was raised to 210° and kept thereat for 2 hr. The product, obtained by addition of water, dilute acid, and ether, gave 1α-*benzyloxymethyl*-1β,10β-*dimethyl*-$\Delta^{8,9}$-*octalin* (0·45 g.), b. p. 152°/0·2 mm., $n_D^{20}$ 1·5365 (Found: C, 84·0; H, 9·7. $C_{20}H_{28}O$ requires C, 84·2; H, 9·8%).

1α-*Hydroxymethyl*-1β,10β-*dimethyl*-$\Delta^{8,9}$-*octalin* (XXXI; R = H).—(i) 1α-Benzyloxymethyl-1β,10β-dimethyl-$\Delta^{8,9}$-octalin (0·292 g.) in ethyl alcohol (25 c.c.) with palladised charcoal (0·112 g.) absorbed 25 c.c. of hydrogen in 48 hr. The product, 1α-*hydroxymethyl*-1β,10β-*dimethyl*-$\Delta^{8,9}$-*octalin*, was an oil, b. p. 90°/0·1 mm., $n_D^{20}$ 1·5180, $\lambda_{max.}$ 202 mμ (log ε 3·65 in hexane) (Found: C, 80·1; H, 11·2. $C_{13}H_{22}O$ requires C, 80·3; H, 11·3%). The 3,5-*dinitrobenzoate*

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[25] McQuillin, *J.*, 1955, 528.

formed prisms, m. p. 68°, from methyl alcohol (Found: C, 61·7; H, 6·4. $C_{20}H_{24}N_4O_6$ requires C, 61·7; H, 6·4%).

(ii) 1α-Benzyloxymethyl-1β,10β-dimethyl-$\Delta^{8,9}$-octalin (3·4 g.) in dry ether (35 c.c.) was added with stirring to a solution of lithium (1·67 g.) in liquid ammonia (400 c.c.). After 15 min. ammonium chloride was added. The product (2 g.), isolated after evaporation of the ammonia, had b. p. 97°/0·25 mm., $n_D^{20}$ 1·5165, and gave the 3,5-dinitrobenzoate, m. p. 68°, as noted in (i).

1α-*Formyl*-1β,10β-*dimethyl*-$\Delta^{8,9}$-*octalin* (XXXII).—1α-Hydroxymethyl-1β,10β-dimethyl-$\Delta^{8,9}$-octalin (0·68 g.) with chromium trioxide (1·4 g.) in pyridine (14 c.c.) was kept overnight and then treated with water, ice, and sulphur dioxide. The product, which contained very little material extracted by sodium hydrogen carbonate solution, was purified by chromatography on alumina. Elution by light petroleum gave the 1α-*aldehyde* (0·33 g.), b. p. 80°/0·7 mm., $n_D^{20}$ 1·5052, $\nu_{max.}$ 1724 (CHO), 3025, 1639 cm.$^{-1}$ (double bond) (Found: C, 80·7; H, 10·6. $C_{13}H_{20}O$ requires C, 81·1; H, 10·4%). The 2,4-*dinitrophenylhydrazone* formed yellow prisms, m. p. 162°, from methanol (Found: C, 60·8; H, 6·8. $C_{19}H_{24}N_4O_4$ requires C, 61·1; H, 6·7%). The remainder of the oxidation product, eluted from alumina with benzene, had $\lambda_{max.}$ 235 mμ (log ε 3·45) and on analysis (Found: C, 76·1; H, 10·4%) gave evidence of being more highly oxidised.

1α-*Hydroxymethyl*-1β,10β-*dimethyldecalin* (XXXIV).—1α-Benzyloxymethyl-1β,10β-dimethyl-$\Delta^{8,9}$-octalin (1·2 g.) in alcohol (35 c.c.) with palladised charcoal (1·2 g.) absorbed 2 mol. of hydrogen (190 c.c.) in 7 days, to give 1α-*hydroxymethyl*-1β,10β-*dimethyldecalin*, b. p. 95°/0·15 mm., $n_D^{20}$ 1·5037 (Found: C, 79·2; H, 12·5. $C_{13}H_{24}O$ requires C, 79·5; H, 12·3%). The 3,5-*dinitrobenzoate* formed prisms, m. p. 79°, from methanol (Found: C, 61·2; H, 6·8. $C_{20}H_{26}N_2O_6$ requires C, 61·5; H, 6·7%).

1β,10β-*Dimethyldecalin*-1α-*carboxylic Acid* (XXXV).—1α-Hydroxymethyl-1β,10β-dimethyldecalin (0·47 g.) with chromium trioxide (0·4 g.) in slightly aqueous acetic acid (6 c.c.) was kept overnight. After destruction of the excess of chromic acid with sulphur dioxide, most of the acetic acid was removed *in vacuo* and the acidic oxidation product (0·32 g.) was isolated as an oil, b. p. 140°/0·2 mm., $n_D^{20}$ 1·4978, which gave the *carboxylic acid*, m. p. 103° (from aqueous methanol), $\nu_{max.}$ 1685, 1269 cm.$^{-1}$ (Found: C, 74·6; H, 10·6. $C_{13}H_{22}O_2$ requires C, 74·4; H, 10·5%). This acid was chromatographed on a silica-coated plate by means of 4 : 1 benzene–alcohol, and detected by spraying the plate with ethanolic 4% phosphomolybdic acid and heating it at 110° for 5—15 min. The methyl ester, prepared on the mg. scale by use of diazomethane, was similarly chromatographed in benzene. It was found by this means that the crystalline acid, m. p. 103°, formed the major constituent of the total oxidation acid, and that the sample kindly provided by Professor Dutta (cf. ref. 22) moved rather more slowly on the silica-coated plate. By this chromatographic technique, hydrolysis of the methyl esters of the acid, m. p. 103°, of the whole acid product, of methyl abietate and of methyl *O*-methylpodocarpate could be followed by sampling, acidification with acetic acid, and recovery by extraction. The esters (*ca.* 2 mg.) were heated in 0·5N-alcoholic potassium hydroxide (1—2 c.c.). Methyl abietate and the esters of our acids were extensively hydrolysed after *ca.* 6 hr.; methyl *O*-methylpodocarpate was apparently unchanged after this treatment for 12 hr. The hydrolysis was followed by disappearance of the ester and appearance of the acid, the silica-coated plate being developed in benzene (the acid then remained near the origin).

1,10-*Dimethyl*-$\Delta^{1,9}$-2ξ-*octalol*.—1,10-Dimethyl-$\Delta^{1,9}$-2-octalone (0·6 g.) was reduced with sodium borohydride (0·53 g.) in alcohol (5 c.c.) to the *alcohol*, b. p. 85—90°/0·3 mm., $n_D^{20}$ 1·5080 (Found: C, 79·6; H, 11·4. $C_{12}H_{20}O$ requires C, 79·9; H, 11·1%).

1,2,3,7,8,9-*Hexahydro*-5,9-*dimethylnaphthalene* (XXXVII).—The last-mentioned alcohol (0·4 g.) was kept in dioxan (4 c.c.) with 60% perchloric acid (2 drops) at 60° for 2 hr. The *product* had b. p. 95°/22 mm., $n_D^{20}$ 1·5290, $\lambda_{max.}$ 238 mμ (ε 24,800), shoulders at 233 (ε 21,800) and 246 mμ (ε 17,500) and $\nu_{max.}$ 3029, 1639, 824, 784, 743 cm.$^{-1}$ (Found: C, 89·0; H, 11·0. $C_{12}H_{18}$ requires C, 88·9; H, 11·1%).

*Oxidation of* 1α-*Formyl*-1β,10β-*dimethyl*-$\Delta^{8,9}$-*octalin* (XXXII) *by Silver Oxide*.—The aldehyde was stirred with fresh silver oxide (1 mol.) in a 5% solution of sodium hydroxide in 50% aqueous alcohol at 50°, or similarly in aqueous dioxan at 20°, or in water at 20°. In each case the product was almost entirely neutral material although the amount of reduced silver was *ca.* 40% of that expected for complete oxidation to the acid. Chromatography of the product gave a fraction, b. p. 80—90°/0·2 mm., $n_D^{20}$ 1·5120, $\nu_{max.}$ 3346 (OH) and 3030 cm.$^{-1}$ (C=C), $\lambda_{max.}$ 202 mμ in hexane, and in alcohol after contact with a little perchloric acid 239 mμ (ε 9300) with shoulder 234 (ε 7900) and 246 mμ (ε 7400).

1α-*Benzyloxymethyl*-8,9-*epoxy*-1β,10β-*dimethyldecalin.*—1α-Benzyloxymethyl-1β,10β-dimethyl-$\Delta^{8,9}$-octalin (0·7 g.) with perbenzoic acid (0·35 g.) in chloroform (15 c.c.) was kept for 24 hr. at 0°; the whole of the peracid was consumed. The *epoxide* produced (0·63 g.) was an oil, b. p. 155—160°/0·4 mm., $n_D^{20}$ 1·5290 (Found: C, 80·0; H, 9·6. $C_{20}H_{28}O_2$ requires C, 80·0; H, 9·4%).

1α-*Benzyloxymethyl*-1β,10β-*dimethyldecalin*-9α,8β-*diol* (XXXIII; R = Ph·CH$_2$).—This *diol* was obtained, m. p. 89°, from pentane, by hydrolysis of the epoxide (0·7 g.) in aqueous acetone (8 c.c.)containing 10% perchloric acid (0·4 c.c.) for 36 hr. (Found: C, 75·2; H, 9·4. $C_{20}H_{30}O_3$ requires C, 75·4; H, 9·5%).

8,9-*Epoxy*-1α-*hydroxymethyl*-1β,10β-*dimethyldecalin.*—This *epoxide* was obtained from the corresponding $\Delta^{8,9}$-octalin (0·2 g.) and perbenzoic acid (0·15 g.) in chloroform (5 c.c.), and had b. p. 95°/0·3 mm., $n_D^{20}$ 1·5060 (Found: C, 73·9; H, 10·1. $C_{13}H_{22}O_2$ requires C, 74·3; H, 10·4%). The same product was obtained (b. p. 95°/0·3 mm., $n_D^{20}$ 1·5055) by hydrogenation of the 1α-benzyloxymethyl-8,9-epoxide (0·1 g.) at palladised charcoal (0·05 g.) in alcohol (5 c.c.).

1α-*Hydroxymethyl*-1β,10β-*dimethyldecalin*-9α,8β-*diol* (XXXIII; R = H).—(i) The corresponding epoxide (0·35 g.) in aqueous acetone (4 c.c.) with 10% perchloric acid (0·2 c.c.) was kept for 24 hr. The recovered material crystallised to give the 9α,8β-*diol*, m. p. 128° (from light petroleum) (Found: C, 68·2; H, 10·4. $C_{13}H_{24}O_3$ requires C, 68·4; H, 10·5%). (ii) The 1α-benzyloxymethyl derivative above (0·46 g.) in alcohol (25 c.c.) with palladised charcoal (0·2 g.) absorbed 1 mol. of hydrogen in 5 hr., to give the same diol, m. p. 128°.

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