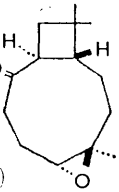
578. *Transannular Reactions in the Caryophyllene Series*

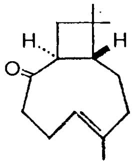
By J. M. GREENWOOD, I. H. QURESHI, and J. K. SUTHERLAND

Two types of transannular cyclisation of caryophyllene derivatives are described, one leading to caryolane, the other to hydrindane derivatives. The caryophyllene ring system has been regenerated from both types by 1,3-elimination.

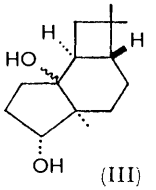
DURING the structural work on carophyllene by Barton and his collaborators, the oxido-ketone (I) was converted into a chlorohydrin,[1] $C_{14}H_{23}ClO_2$, characterised by oxidation to a ketone, $C_{14}H_{21}ClO_2$. We first became interested in this compound as a source of intermediates, such as (II) and (III), which might be useful in the synthesis of caryophyllene. However our initial assumption that the chlorohydrin was derived by simple addition of hydrogen chloride to the oxiran ring was quickly disproved, and chemical [2] and crystallographic evidence [3] has shown it to be (V) which contains the ring system found in caryolan-1-ol [4] (IV), a cyclisation product of caryophyllene.



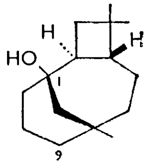
(I)



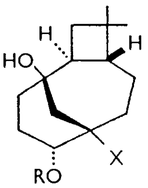
(II)



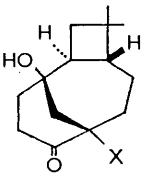
(III)



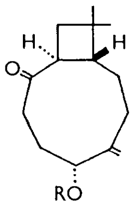
(IV)



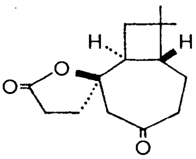
(V: X = Cl, R = H)
(VI: X = Cl, R = Ac)
(VII: X = R = H)
(XVIII: X = OH, R = H)



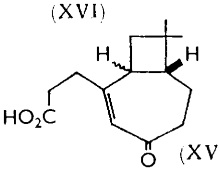
(X: X = OH)
(XI: X = Cl)
(XII: X = H)



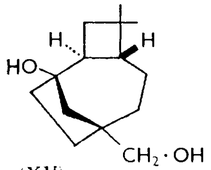
(VIII: R = H)
(IX: R = Ac)



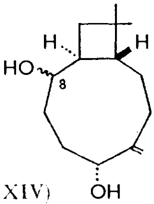
(XVI)



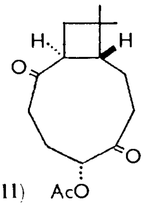
(XVII)



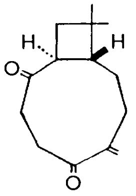
(XV)



(XIV)



(XIII)



(XIX)

The most characteristic reaction of the chlorohydrin is a 1,3-elimination [5] of hydrogen chloride to give the ketol (VIII).* This reaction is best accomplished with N-ethanolic potassium hydroxide at room temperature but also occurs on filtering a solution through

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* This compound has recently been prepared by alumina isomerisation of the oxido-ketone (I) (E. W. Warnhoff, *Canad. J. Chem.*, 1964, **42**, 1664).

[1] D. H. R. Barton and A. S. Lindsey, *J.*, 1951, 2988.

[2] J. M. Greenwood, I. H. Qureshi, and J. K. Sutherland, *Proc. Chem. Soc.*, 1963, 372.

[3] D. Rogers and Mazhar-ul-Haque, *Proc. Chem. Soc.*, 1963, 371.

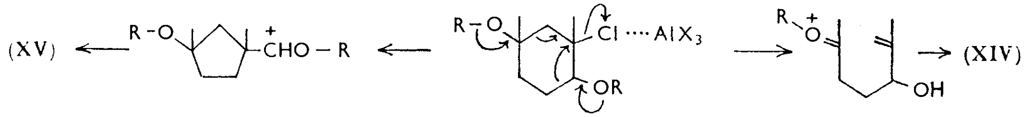
[4] D. H. R. Barton, T. Bruun, and A. S. Lindsey, *J.*, 1952, 2210; J. M. Robertson and G. Todd, *J.*, 1955, 1254.

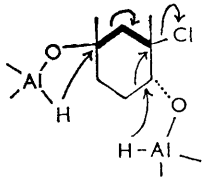
[5] A. Eschenmoser and A. Frey, *Helv. Chim. Acta*, 1952, **35**, 1660; R. B. Clayton, H. B. Henbest, and M. Smith, *J.*, 1957, 1983.

alumina and under the conditions for zinc dust–acetic acid and catalytic reductions. Unlike the chlorohydrin, the ketol (VIII) absorbs in the carbonyl region of the infrared and contains an unsaturated methylene group (n.m.r. and ozonlysis to formaldehyde). When the ketol (VIII) is treated with hydrogen chloride in chloroform [the conditions for conversion of the oxido-ketone (I) into (V)], the chlorohydrin is regenerated, suggesting the intermediacy of the ketol (VIII) in the original formation of the chlorohydrin (V). Further support for this pathway came from the isomerisation of the oxido-ketone (I) to the ketol (VIII) by sodium iodide in acetic acid; this type of elimination to form an exocyclic, rather than endocyclic, double bond appears to be characteristic of the caryophyllene and humulene ring systems.[6] The cyclisation of (VIII) to (V) (a type of Prins reaction) undoubtedly occurs so readily because the geometry of the nine-membered ring places the two reacting centres in almost ideal positions for the cyclisation. Stereochemically two modes of cyclisation are possible but only one is observed, that leading to the β-methylene bridge. This is understandable since the transition state leading to the chair form of the six-membered ring with the β-methylene bridge shows appreciably less H–H interaction than the transition states leading to the α-bridge chair form or the two possible boat forms.

The chlorohydrin monoacetate (VI) also underwent 1,3-elimination, yielding the ketol acetate (IX) which on ozonolysis gave formaldehyde and the acetoxy-dione (XIII). The acetate was also prepared by acetylation of the ketol (VIII).

The great ease with which the chlorohydrin (V) was converted into the ketol (VIII) under a wide variety of experimental conditions led us to study the reduction of (V), as removal of the chlorine would stabilise the ring system. In the light of the known structure of the chlorohydrin (V) it would not be expected that lithium aluminium hydride reduction would give the derived diol (VII); instead two other diols (XV) and (XIV) were isolated. The structure of (XV) follows from the 2-proton singlet in the n.m.r. spectrum at $6{\cdot}64\ \tau$, consistent only with the presence of a $CH_2{\cdot}OH$ group attached to a quaternary carbon. The other diol (XIV) was identical with one of the diols obtained on lithium aluminium hydride reduction of the ketol (VIII). It appears that the aluminium hydride is first acting as a Lewis acid (see arrows), initiating, in one case, a 1,3-elimination to give the ketol-complex, and, in the other, a 1,2-migration * to yield the aldehyde complex. Hydride migrations in the complexes then produce the diols (XV) and (XVI). It is interesting that the lithium aluminium hydride–ketol complex produced by 1,3-elimination must be different from that formed by mixing the ketol and reagent, since the diol (XIV), obtained by reduction of the chlorohydrin, is the minor product formed on reduction of the ketol, the major one being the epimer at C-8. An alternative explanation which would account for the exclusive formation of the 8β-hydroxy-compound is that the C–C bonds are directly displaced by hydride without prior isomerisation to the carbonyl complexes. Reduction of (V) with lithium in ammonia did give the diol (VII) which was characterised by oxidation to the ketone (XII). More vigorous oxidation converted the ketone into a key degradation product in this series, the keto-lactone (XVI). Base catalysed isomerisation of (XVI) yielded the unsaturated keto-acid (XVII). The γ-lactone (XVI) was useful in proving the structure of the triol (XVIII)





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* A similar ring-contraction of a bridgehead α-bromo-ketone on lithium aluminium hydride reduction has been reported by Cope, Graham, and Marshall, *J. Amer. Chem. Soc.*, 1954, **76**, 6159.

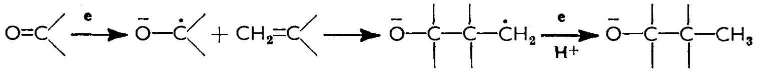
[6] F. Sorm, L. Dolejs, and J. Pliva, *Coll. Czech. Chem. Comm.*, 1950, **15**, 186; N. P. Damodaran and Sukh Dev, *Tetrahedron Letters*, 1963, 1941.

obtained from the ketol (VIII) on heating with aqueous acetic acid; oxidation of (XVIII), even with the Jones reagent, gave the lactone.

As mentioned before, the chlorohydrin (V) was oxidised to a ketone (XI). On repeating this work we were unable to isolate the ketone described; instead the dihydroxy-ketone (X) was obtained, and its structure was proven by its oxidation to the γ-lactone (XVI) and its reduction to the triol (XVIII). The difference in products obtained on oxidation of the chlorohydrin (V) was due to the quality of alumina used in purification. When an authentic sample of the chloro-ketone (XI) in solution was filtered through our alumina the dihydroxy-ketone (X) was formed. The mechanism of this displacement is interesting but at present we are unable to distinguish amongst the variety of unattractive processes which can be written, except to say that the stability of the dione (XIX) [7] on alumina appears to exclude an elimination–addition mechanism.

While the structural work was going on we had not lost sight of our original objective, namely, the preparation of the tricyclic compound (III), and this was eventually achieved by lithium–ammonia reduction of the ketol (VIII). The reduction product (III), obtained in 30% yield, showed three quaternary methyl groups in its n.m.r. spectrum, two at 8·89 and one at 8·94 τ, and could be oxidised to a hydroxy-ketone which again showed two quaternary methyl groups at 8·89 τ with the other shifted to 8·85 τ. About this time Corey *et al.*[8] reported their total synthesis of caryophyllene, including the preparation of a diol with the carbon skeleton of (III) and the conversion of its monotosylate into the ketone (II) with dimethylsulphinyl carbanion. Under these reaction conditions, the monotosylate of (III) was transformed into the ketone (II), whose structure and stereochemistry were proven by its perphthalic acid oxidation to the oxido-ketone (I). The stereochemistry of the secondary hydroxyl group of (III) is certain since it must be the same as that in the chlorohydrin (V), while the configuration indicated for the angular methyl is required to account for the generation of the *trans*-double bond of (II).[9] We believe that the fusion of the four- and six-membered rings is *trans* since Corey *et al.* showed [10] that conversion of the *cis*-fused compound into the ketone (II) involves formation of the *cis*-fused bicyclic ketone which can be isolated and detected by gas chromatography. Examination of our reaction product after 5 and 15 minutes' reaction showed that only the *trans*-compound (II) was present.

The mechanism of formation of the diol (III) is unknown but the stability of the diols (XIV) under the conditions where the ketol (VIII) is reduced to (III) makes addition of the radical anion [11] (derived from the carbonyl group) to the methylene group a plausible suggestion. An anionic addition to the double bond seems improbable, though the orientation of addition supports this. The stereochemistry of (III) (with a *trans*-5,6 ring junction) is understandable as the chair-type transition state leading to this isomer appears to involve less H–H and H–O (of the secondary hydroxyl) interactions. We also studied the lithium–ammonia reduction of the oxido-ketone (I), the main product being the derived oxido-alcohol.[1] The other product was the diol (VII), initially obtained by reduction of the chlorohydrin, the proportion of which could be increased by carrying out the reduction in the presence of ammonium chloride. This surprising result we are unable to explain at present, as the obvious intermediate, the ketol (VIII), does not give any of the diol (VII) when reduced under identical conditions, and the reduction product of the ketol (VIII) is not formed on reduction of the oxido-ketone (I).



$$O{=}C\langle \xrightarrow{e} \bar{O}{-}\dot{C}\langle + CH_2{=}C\langle \longrightarrow \bar{O}{-}C{-}C{-}\dot{C}H_2 \xrightarrow[H^+]{e} \bar{O}{-}C{-}C{-}CH_3$$

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[7] E. W. Warnhoff, *Canad. J. Chem.*, 1964, **42**, 1664.

[8] E. J. Corey, R. B. Mitra, and H. Uda, *J. Amer. Chem. Soc.*, 1963, **85**, 362.

[9] P. S. Wharton, *J. Org. Chem.*, 1961, **26**, 4781.

[10] E. J. Corey, R. B. Mitra, and H. Uda, *J. Amer. Chem. Soc.*, 1964, **86**, 485.

[11] C. B. Wooster, *J. Amer. Chem. Soc.*, 1928, **50**, 1388.

Attempts to generate caryophyllene by reductive 1,4-elimination reactions on 1-chloro-9α- and -9β-methanesulphonyloxycaryolane using lithium–ammonia, magnesium–ether, and zinc–pyridine or –acetic acid were unsuccessful.

EXPERIMENTAL

Optical rotations were measured in chloroform except where otherwise stated. Ultraviolet spectra were determined in ethanol using a Perkin-Elmer 4000 spectrophotometer, infrared spectra on a Unicam S.P. 200 in chloroform solution, and n.m.r. spectra on deuterochloroform solutions using tetramethylsilane as internal standard on a Varian A-60 spectrometer.

Preparation of the Ketol (VIII).—(*a*) A mixture of the oxido-ketone (I)[12] (250 mg.), sodium iodide (230 mg.), and sodium acetate (20 mg.) in acetic acid (0·7 ml.) was set aside at room temperature overnight. The resulting dark red mixture was poured into saturated sodium hydrogen carbonate solution and extracted with ether. After washing with sodium hydrogen sulphite solution, the dried ether extract was concentrated to give the *ketol* (VIII) (230 mg.), m. p. 110—111° [from light petroleum (b. p. 60—80°)], $[\alpha]_D$ −41° (*c* 1·05), $\lambda_{max.}$ 287 mμ (ε 27), $\nu_{max.}$ 3450, 1690 cm.$^{-1}$ (Found: C, 75·3; H, 10·0. $C_{14}H_{22}O_2$ requires C, 75·6; H, 10·0%). It gave a 3,5-*dinitrobenzoate*, m. p. 133—134° (from aqueous methanol) (Found: C, 60·2; H, 6·1; N, 6·8. $C_{21}H_{26}N_2O_7$ requires C, 60·3; H, 6·2; N, 6·7%).

(*b*) The chlorohydrin (V) (100 mg.) was dissolved in ethanol (1 ml.), and 2N-potassium hydroxide (1 ml.) added. After standing overnight at room temperature, the mixture was diluted with water and extracted with ether. Concentration of the ether extract gave the ketol (VIII) (80 mg.) identified by m. p., mixed m. p., and i.r. spectrum. On ozonolysis it gave formaldehyde, identified as the dimedone derivative.

The ketol was also prepared from the chlorohydrin by passing a benzene solution of the latter through a column of Spence Grade H neutral alumina, by shaking with zinc dust in acetic acid at room temperature overnight, and by attempted catalytic hydrogenation.

Conversion of the Ketol (VIII) *into the Chlorohydrin* (V).—A stream of dry hydrogen chloride was passed into a solution of the ketol (VIII) (66 mg.) in chloroform (20 ml.). Removal of the solvent *in vacuo* and recrystallisation of the residue from chloroform–light petroleum (b. p. 60—80°) gave the chlorohydrin (V) in quantitative yield, identified by m. p., mixed m. p., and i.r. spectrum.

Chlorohydrin Monoacetate (VI).—The chlorohydrin (V) (200 mg.) was left overnight in pyridine (1·5 ml.) and acetic anhydride (0·5 ml.). Removal of the solvents *in vacuo* gave a residue which was decolourised by charcoal in chloroform and then crystallised from chloroform–light petroleum (b. p. 60—80°), to give the *acetate* (VI) (150 mg.), m. p. 150—151°, $[\alpha]_D$ −6·4° (*c* 1·72), $\nu_{max.}$ (Nujol) 3550, 1710 cm.$^{-1}$ (Found: C, 64·0; H, 8·5; Cl, 12·1. $C_{16}H_{25}ClO_3$ requires C, 63·9; H, 8·3; Cl, 11·8%).

When filtered in benzene solution through Spence Grade H alumina the acetate (VI) was converted into the *ketol acetate* (IX), m. p. 125° [from light petroleum (b. p. 60—80°)], $[\alpha]_D$ −17° (*c* 1·1), $\nu_{max.}$ 1720, 1690 cm.$^{-1}$ (Found: C, 72·9; H, 9·2. $C_{16}H_{24}O_3$ requires C, 72·8; H, 9·1%), identical with the product obtained on acetylation of the ketol by the procedure above; it could be hydrolysed back to the ketol with methanolic potassium hydroxide.

Ozonolysis of the Ketol Acetate (IX).—The acetate (IX) (500 mg.) was ozonised at 0° for 2 hr. in methylene dichloride (20 ml.). After warming with water (10 ml.) for 10 min. the organic layer was removed and the aqueous phase extracted with ether. The combined extracts were dried and concentrated *in vacuo*, to give an *oil* which crystallised from ether–light petroleum (b. p. 40—60°) (400 mg.), m. p. 78—79°, $[\alpha]_D$ −31° (*c* 0·16), $\nu_{max.}$ 1740, 1720, 1690 cm.$^{-1}$ (Found: C, 67·8; H, 8·5. $C_{15}H_{22}O_4$ requires C, 67·7; H, 8·3%). In another experiment, steam-distillation of the reaction mixture into dimedone gave the formaldehyde derivative.

Lithium Aluminium Hydride Reduction of the Chlorohydrin (V).—The chlorohydrin (V) (2·3 g.) in dry ether (250 ml.) was refluxed with lithium aluminium hydride (1 g.) for 1½ hr. and set aside overnight. Excess of reagent was destroyed by addition of ethyl acetate followed by a saturated aqueous ammonium chloride. The two layers were separated, and the aqueous phase was thrice extracted with ether. The combined ethereal extracts were dried and concentrated, to give an oil which was chromatographed on grade V neutral alumina (100 g.).

[12] W. Treibs, *Ber.*, 1947, **80**, 56.

Elution with benzene and benzene–ethyl acetate (3 : 1) gave two crystalline products. The first was the *diol* (XIV) (735 mg.), m. p. 160—161° (from ethyl acetate), $[\alpha]_D$ +39° (*c* 1·15), $\nu_{max.}$ 3570, 3400, 1640 cm.$^{-1}$ (Found: C, 75·0; H, 11·2. $C_{14}H_{24}O_2$ requires C, 75·0; H, 10·8%). On ozonolysis it gave formaldehyde, identified as the dimedone derivative. The second compound, the *diol* (XV) (398 mg.), crystallised from ether–light petroleum (b. p. 40—60°) m. p. 140—141°, $[\alpha]_D$ +61° (*c* 0·95), $\nu_{max.}$ 3650, 3500 cm.$^{-1}$ (Found: C, 74·4; H, 11·4%).

Lithium–Ammonia Reduction of the Chlorohydrin (V).—The chlorohydrin (V) (1 g.) in dry tetrahydrofuran (10 ml.) was added during 20 min. to a stirred solution of lithium (1 g.) in liquid ammonia (500 ml.). After stirring for 2 hr. the excess lithium was destroyed by addition of ammonium chloride, and the ammonia allowed to evaporate. Water (50 ml.) was added to the residue, and, after acidification with 2N-hydrochloric acid, the solution was extracted with ether. Evaporation of the ether gave the *diol* (VII) (598 mg.), m. p. 192° (from ethyl acetate), $[\alpha]_D$ +2·3° (*c* 1·75), $\nu_{max.}$ 3670, 3500 cm.$^{-1}$ (Found: C, 74·7; H, 10·8%).

Oxidation of the Diol (VII).—The diol (VII) (400 mg.) in pyridine (1 ml.) was added to chromium trioxide (600 mg.) in pyridine (5 ml.). After 16 hr. at room temperature the mixture was poured into an ice–4N-hydrochloric acid mixture. The solid which separated was filtered off and the filtrate extracted with ether. After washing the ethereal extract with saturated sodium hydrogen carbonate solution, drying, and concentration gave the *hydroxy-ketone* (XII) (246 mg.), m. p. 125° [from ether–light petroleum (b. p. 40—60°)], $[\alpha]_D$ +49·5° (*c* 1·4), $\nu_{max.}$ 3510, 1710 cm.$^{-1}$, $\lambda_{max.}$ 286 mμ (ε 23) (Found: C, 75·7; H, 9·8. $C_{14}H_{22}O_2$ requires C, 75·7; H, 9·9%). Sodium borohydride reduction of the hydroxy-ketone (XII) regenerated the diol (VII).

Keto-γ-lactone (XVI).—(*a*) The hydroxy-ketone (XII) (25 mg.) in acetic acid (0·5 ml.) was added to a solution of chromium trioxide (18 mg.) in water (0·1 ml.) and acetic acid (1·5 ml.). After 4 days at room temperature the mixture was poured into water and extracted with ether. Concentration of the ether extract gave the *keto-γ-lactone* (XVI) (18 mg.), m. p. 123—124° [from chloroform–light petroleum (b. p. 60—80°)], $[\alpha]_D$ +20° (*c* 0·68), $\nu_{max.}$ 1765, 1710 cm.$^{-1}$ (Found: C, 71·2; H, 8·4. $C_{14}H_{20}O_3$ requires C, 71·2; H, 8·5%).

(*b*) The triol (XVIII) (50 mg.) in acetone (4 ml.) was added to chromium trioxide (30 mg.) in water (0·5 ml.), concentrated sulphuric acid (2 drops), and acetone (2 ml.). After standing at room temperature for 12 hr. the mixture was worked up as before, to give the γ-lactone (XVI) (48 mg.).

(*c*) The keto-diol (X), oxidised as in (*b*), also gave the γ-lactone.

Oxidation of the Chlorohydrin (V).—The chlorohydrin (V) (255 mg.) was oxidised as described before. The crude product was chromatographed on Spence Grade H alumina, elution with methanol giving a solid which was sublimed at 10^{-2} mm. to give the *keto-diol* (X) (115 mg.), m. p. 138—139°, $[\alpha]_D$ +64° (*c* 0·85), $\nu_{max.}$ 3620, 3450, 1705 cm.$^{-1}$ (Found: C, 70·1; H, 9·4. $C_{14}H_{22}O_3$ requires C, 70·5; H, 9·3%).

The Triol (XVIII).—(*a*) The ketol (VIII) (500 mg.) was dissolved in ether, and a solution of acetic acid (5 ml.) and water (5 ml.) added. The ether was slowly distilled off and the temperature of the solution raised to 100°. After 30 min. the solvents were removed *in vacuo* and the oily residue triturated with ether to give the *triol* (XVIII) (100 mg.), m. p. 209—210° (after sublimation) (from ethyl acetate), $\nu_{max.}$ 3620, 3400 cm.$^{-1}$ (Found: C, 69·7; H, 10·2. $C_{14}H_{24}O_3$ requires C, 70·0; H, 10·1%).

(*b*) The keto-diol (X) (30 mg.) was dissolved in methanol (2 ml.), and water (0·2 ml.) added, followed by sodium borohydride (20 mg.). After standing for 15 hr. 4N-hydrochloric acid (6 ml.) was added, and the solution extracted with ether. Concentration of the extract gave a boron-containing compound, m. p. 278—284° (decomp.), which was warmed in acetic acid (3 ml.) and water (1 ml.) for 15 min. Dilution with water and ether extraction, followed by evaporation of the ether extract, gave the triol (XVIII), identified by m. p., mixed m. p., and i.r. spectrum.

Isomerisation of the Keto-γ-lactone (XVI).—N-Sodium hydroxide was added to the γ-lactone (XVI) (30 mg.) in ethanol (3 ml.) until a permanent yellow colour developed (*ca.* 5 drops). After standing for 15 hr. water was added and the solution extracted with ether. The aqueous solution was then acidified and the solution again extracted with ether. Evaporation of this extract gave the *keto-acid* (XVII) (17 mg.), m. p. 128—129° [from chloroform–light petroleum (b. p. 40—60°)], $[\alpha]_D$ +23° (*c* 0·66), $\nu_{max.}$ 1710, 1650, 1620 cm.$^{-1}$, $\lambda_{max.}$ 246 mμ (ε 11000) (Found: C, 71·3; H, 8·5. $C_{14}H_{20}O_3$ requires C, 71·2; H, 8·5%).

Lithium Aluminium Hydride Reduction of the Ketol (VIII).—A suspension of lithium aluminium hydride (60 mg.) in ether (10 ml.) was added to an ice cold solution of the ketol (VIII) (150 mg.) in dry ether (10 ml.). After stirring for 1 hr. it was set aside at 0° overnight. A saturated solution of ammonium chloride was added to the mixture, and the ethereal layer separated. The aqueous portion was again extracted with ether, and the combined extracts were concentrated to give an oil which on trituration with chloroform–light petroleum (b. p. 40—60°) gave a white solid (11 mg.), m. p. 159—160° (from ethyl acetate), identical with the diol (XIV) obtained from similar reduction of the chlorohydrin.

The filtrate was kept at 0° for 24 hr., when the *epimeric diol* separated, m. p. 56—58° [from light petroleum (b. p. 40—60°), $[\alpha]_D$ $-27°$ (c 1·0), $\nu_{max.}$ 3620, 3450, 1640 cm.$^{-1}$, 1-proton peaks at 4·82, 4·88, 5·75, and 6·32 τ (Found: C, 74·5; H, 10·7%).

Lithium–Ammonia Reduction of the Oxido-ketone (I).—The oxido-ketone (I) (1 g.) in ether (25 ml.) was added during 15 min. to a solution of lithium (1 g.) in liquid ammonia (500 ml.) containing ammonium chloride (2·5 g.). After 2 hr. the mixture was worked up as in previous reductions and the residue chromatographed on Spence Grade H alumina (60 g.). Elution with benzene and benzene–ether (3 : 1) gave, first, the oxido-alcohol (219 mg.), m. p. 140—141°, identical with the product previously obtained by lithium aluminium hydride reduction of the oxido-ketone (I), and then the diol (VII) (107 mg.), m. p. 192°, identical with the product obtained on lithium–ammonia reduction of the chlorohydrin (V).

When the reduction was carried out in the presence of 2 mol. of ammonium chloride the ratio of oxido-alcohol to (VII) increased to 3, and was 4 in the absence of ammonium chloride.

Lithium–Ammonia Reduction of the Ketol (VIII).—The ketol (VIII) (200 mg.) in ether (25 ml.) was added to a stirred solution of lithium (200 mg.) in liquid ammonia. After 90 min. the mixture was worked up as in previous reductions. The diol (III) (60 mg.) was obtained on crystallising the residue from ether–light petroleum (b. p. 40—60°), m. p. 171—172° (sublimation), $[\alpha]_D$ $+33°$ (c 1·26), $\nu_{max.}$ 3650, 3550 cm.$^{-1}$, M (Bendix mass spectrometer), 224 (Found: C, 74·9; H, 10·7. $C_{14}H_{24}O_2$ requires C, 75·0; H, 10·8%).

Oxidation of the Diol (III).—The diol (III) (150 mg.) in acetone (12 ml.) was added to a solution of chromium trioxide (75 mg.) in acetone (3 ml.), water (0·5 ml.), and concentrated sulphuric acid (2 drops). After 12 hr. at room temperature the mixture was diluted with water and extracted with ether. Concentration of the ether extract gave the *ketol* (70 mg.), m. p. 154—155° [from chloroform–light petroleum (b. p. 40—60°)], $[\alpha]_D$ $-22°$ (c 0·8), $\nu_{max.}$ 3390, 1735 cm.$^{-1}$ (Found: C, 75·7; H, 9·9. $C_{14}H_{22}O_2$ requires C, 75·6; H, 10·0%).

Tosylation of the Diol (III).—The diol (III) (300 mg.) in pyridine (2 ml.) containing toluene-*p*-sulphonyl chloride (290 mg.) was set aside for 12 hr. The pyridine was removed *in vacuo* and saturated sodium hydrogen carbonate and water were added to the residue which was then warmed at 50° for 30 min. The precipitate was filtered off, and crystallised from chloroform–light petroleum (b. p. 40—60°), to give the *monotosylate* (400 mg.), m. p. 131—132°, $[\alpha]_D$ $-44°$ (c 0·95), $\nu_{max.}$ 3620 cm.$^{-1}$ (Found: C, 66·5; H, 7·9. $C_{21}H_{30}O_4S$ requires C, 66·6; H, 8·0%).

Norcaryophyllene Ketone (II).—The tosylate of (III) (300 mg.) was converted into the unsaturated ketone (II) (120 mg.) with dimethyl sulphoxide–sodium hydride, as described for its isomer.[10] The ketone had b. p. 0·3 mm./125° (bath), $[\alpha]_D$ $-5°$ (c 0·83), $\nu_{max.}$ 1690 cm.$^{-1}$, n_D^{24} 1·4955, and gave a semicarbazone, m. p. 177—178°.

The ketone (II) (40 mg.), on oxidation with monoperphthalic acid in ether, gave, after chromatography on alumina, the oxido-ketone (I) (10 mg.), m. p. 65—66°.

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