Tetrahedron Letters No. 10, pp. 429-432, 1962. Pergamon Press Ltd. Printed in Great Britain.

A SYNTHESIS OF THE OLEANANE SKELETON

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(Received 3 April 1962)

SCLAREOL (I), the synthesis of which has been described elsewhere,[1] has been used as a starting material for the synthesis of hydrocarbons of the oleanane series. Permanganate oxidation[2] under controlled conditions gave either the hydroxyketone (II, X = $-CH_2COCH_3$; $R = {<}^{\cdot\cdot OH}_{Me}$),[1] m.p. 78°-80°, or the enolether (III), b.p. 130°-134°/0.06 mm. Ozonolysis of the latter, in ethyl acetate at -70° gave a mixture of an aldehyde (II, X = -CHO; $R = {<}^{\cdot\cdot OAc}_{Me}$) and the corresponding acid.[3] Lithium aluminium hydride reduction of this product, without purification gave two products; the glycol (II, X = $-CH_2OH$; $R = {<}^{\cdot\cdot OH}_{Me}$), m.p. 132°, and the unsaturated alcohol (II, X = $-CH_2OH$; R = CH_2). Treatment of either with phosphorus oxybromide in pyridine gave, in good yield, the unsaturated bromide (II, X = $-CH_2Br$; R = CH_2), b.p. 145°-150°/0.05 mm; $[\alpha]_D^{15}$ +31°.

This bromide, in presence of sodium t-amyloxide, alkylated the racemic octalone (IV).[4] The product, obtained as a viscous oil in 68 per cent yield, was the mixture of epimeric ketones (V), the synthesis of which, by a different route, has already been described.[5] This mixture had λ_{max} 250 mμ,

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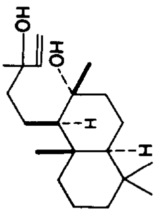
[1] D.B. Bigley, N.A.J. Rogers and J.A. Barltrop, <u>J. Chem. Soc.</u> 4613 (1960).

[2] L. Ruzicka, C.F. Seidel and L.L. Engel, <u>Helv. Chim. Acta</u> <u>25</u>, 621 (1942).

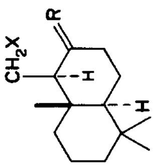
[3] M. Stoll and M. Hinder, <u>Helv. Chim. Acta</u> <u>34</u>, 1251, 1308 (1950).

[4] T.G. Halsall and D.B. Thomas, <u>J. Chem. Soc.</u> 2431 (1956).

[5] E.J. Corey, H.J. Hess and S. Proskow, <u>J. Amer. Chem. Soc.</u> <u>81</u>, 5258 (1959).



I



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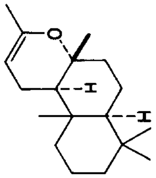

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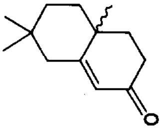

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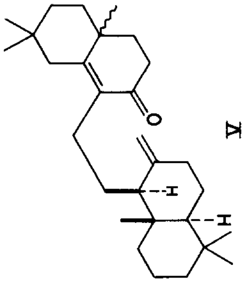

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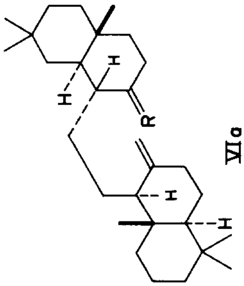
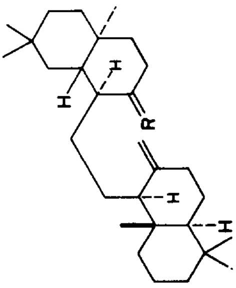
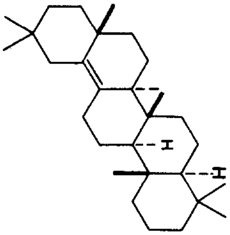


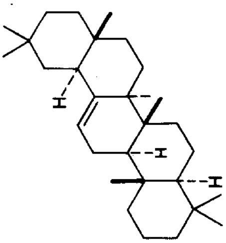
VIa



VIb



VII



VIII

ε_{max} 12,810; $[\alpha]_D^{20}$ +10°. (Lit.[5] gives λ_{max} 252 mμ, ε_{max} 14,000). Reduction with lithium in liquid ammonia gave, in 97 per cent yield, the mixture of <u>trans</u>-β-decalones (VIa and b, R = O) which, without further separation was treated with lithium methyl to give the alcohols (VIa and b, $R = {<}^{\mathrm{OH}}_{\mathrm{Me}}$) as a glass. The most effective reagent for the cyclodehydration of these alcohols was found to be aluminium chloride in a mixture (4:1) of nitromethane and ether at room temperature.

The product, which was obtained as a viscous oil, was examined with the aid of gas-liquid chromatography. The trace, which showed two groups of peaks attributable to tetracyclic and pentacyclic hydrocarbons, suggested that cyclization had occurred to the extent of about 35 per cent. Further, the pentacyclic region was well resolved into two peaks, of approximately equal strength, which could be assigned to hydrocarbons of the natural series, and of the 17-α-series.

Gas-liquid chromatography on a preparative scale, with collection of the appropriate band at the jet gave, after repeated crystallization, a small yield of a solid, m.p. 188°-189°, identical in all respects with the mixed crystals of (-)-olean-13(18)-ene (VII) and (+)-18-α-olean-12-ene (VIII) obtained on isomerization of (-)-olean-12-ene.[6] On an analytical gas-liquid chromatographic column, the synthetic mixture showed a pattern identical with that given by the mixture obtained from natural sources, and identity was further established by comparison of m.p., mixed m.p., infra-red and ultra-violet spectra, optical rotatory dispersion, and mass spectrometric fragmentation pattern.

It is thought possible that the components (VII and VIII) of the mixed crystals may be separable on a preparative gas-liquid chromatographic column, and this work is in hand. It is hoped to present these results, together with work bearing on the resolution and absolute configuration of the

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[6] G. Brownlie, M.B.E. Fayez, F.S. Spring, R. Stevenson and W.S. Strachen, <u>J. Chem. Soc.</u> 1377 (1956).

ketones (IV), and hence on the structures of the ketones (V) in greater detail elsewhere.

Satisfactory analyses were obtained for all new compounds described. We are grateful to Dr. R.I. Reed for measurement of fragmentation patterns, and to Prof. W. Klyne for measurement of optical rotatory dispersion curves.