Tetrahedron. Vol. 23, pp. 3847 to 3849. Pergamon Press Ltd. 1967. Printed in Great Britain

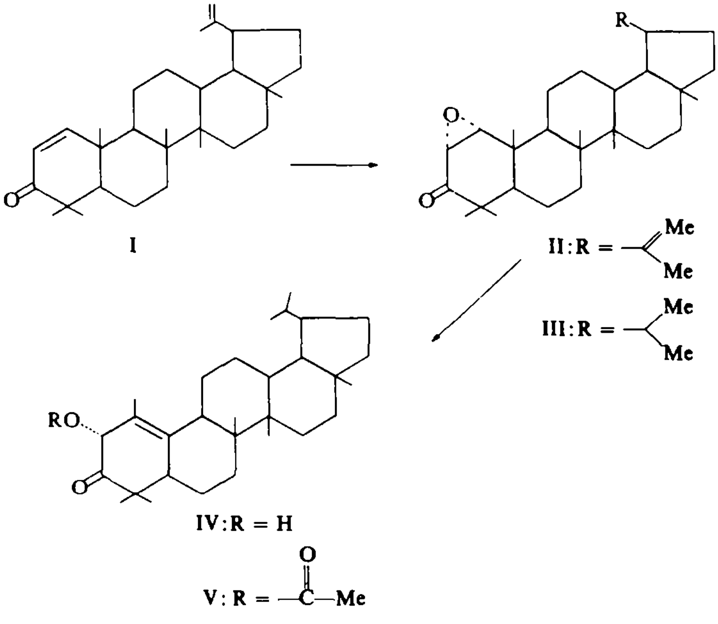
BORON TRIFLUORIDE CATALYSED REARRANGEMENT OF 1,2-EPOXY LUPAN-3-ONE*

A. K. GANGULY, T. R. GOVINDACHARI and A. MANMADE
CIBA Research Centre, Goregaon, Bombay

(*Received* 8 *November* 1966; *accepted for publication* 26 *January* 1967)

Abstract—Boron trifluoride catalysed rearrangement of 1,2-epoxy-lupan-3-one (III) yielded IV. Oxidation of IV with pyridine-chromium trioxide yielded IX.

EARLIER[1], we reported that glochidone (I) on treatment with alkaline hydrogen peroxide yields the epoxide II which on catalytic hydrogenation afforded the dihydro derivative III. In the present communication we wish to report the acid catalysed rearrangement of III. A benzene solution of III was treated with BF_3–Et_2O and the crude product chromatographed over alumina. Elution of the column with ether yielded a colourless crystalline compound $C_{30}H_{48}O_2$, m.p. 225°, ν_{max} 3500 cm^{-1} (OH), 1712 cm^{-1} (cyclohexanone) and in the UV it had end absorption at 208 mμ. On acetylation using acetic anhydride and pyridine at room temperature, a crystalline acetate $C_{32}H_{50}O_3$ was obtained. The acetate did not show any selective absorption



I

II:R = $-C(=CH_2)Me$

III:R = $-CH(Me)Me$

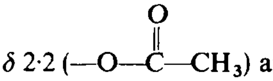
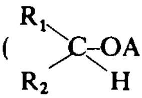
IV:R = H

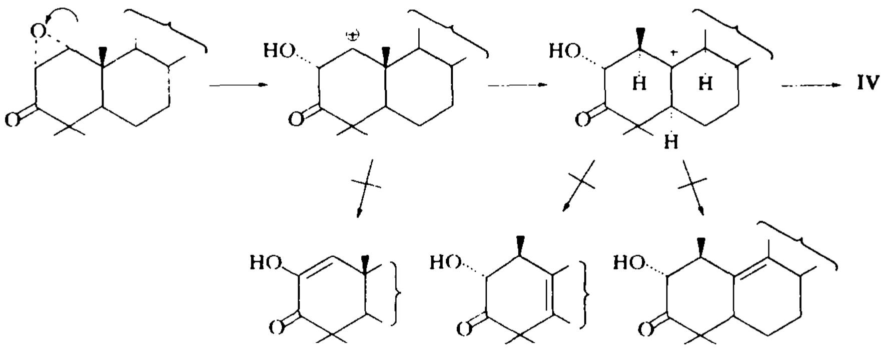
V:R = $-\overset{\overset{\displaystyle O}{\|}}{C}-Me$

---

* Contribution No. 87 from CIBA Research Centre.

[1] A. K. Ganguly, T. R. Govindachari, P. A. Mohamed, A. D. Rahimtulla and N. Viswanathan, *Tetrahedron* **22**, 1513 (1966).

in the UV beyond 208 mμ and in the IR it had bands at 1740, 1220 cm^{-1} (acetate) and 1725 cm^{-1} (cyclohexanone). The NMR spectrum of the acetate showed signals at δ 2·2  ($-O-\overset{\overset{O}{\|}}{C}-CH_3$) and a sharp singlet at δ 5·45  ($\overset{R_1}{\underset{R_2}{>}}C\overset{OAc}{\underset{H}{<}}$) which prior to acetylation appeared at δ 4·5. Finally, the olefinic Me signal in the rearranged product appeared as a singlet at δ 1·3. Based on the above observations we have formulated the rearrangement product as IV and its acetate as V. Alternative structures such as VI and VII or any other structures resulting from backbone rearrangement[2] of III were ruled out because in all such structures the axial proton at C_2 would be coupled with C_1 axial proton showing a doublet at δ 5·45 whereas in reality we see only a sharp singlet. The diosphenol structure VIII is also ruled out from the UV and IR spectral characteristics of the rearrangement product IV.*

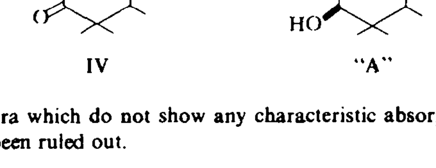


VIII VI VII

The rearrangement product IV on oxidation using pyridine-chromium trioxide afforded a colourless crystalline compound $C_{28}H_{44}O_3$, m.p. 215°, $[\alpha]_D$ +97·02°, λ_{max} 235 mμ (ε, 1019), ν_{max} 1750, 1800 cm^{-1} (6-membered cyclic anhydride). Its NMR spectrum showed the loss of a Me group and the presence of a one proton quartet at δ 3·6 (J = 7 c/s) ascribed to the C_{10} proton being coupled with C_5 and C_9 hydrogens.

---

* Although allylic oxidation of the keto alcohol IV to an enedione is possible, this further evidence is not required for the structure assignment. Rearrangement of an epoxide ketone such as III involving a methyl shift from C_{10} to C_1 could give rise to structures sich as VI, VII and VIII, none of which, as argued explain the NMR spectrum. The following rearrangement has also been considered:

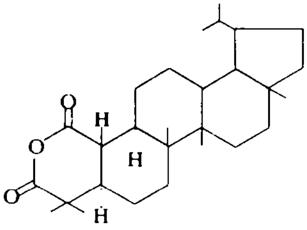


IV "A"

Based on UV and IR spectra which do not show any characteristic absorption for an α:β unsaturated ketone, structure "A" has been ruled out.

[2] M. P. Hartshorn and D. N. Kirk, *Tetrahedron Letters* 3913 (1966).

Based on its mode of formation, elemental composition and spectral characteristics, the above oxidation product has been assigned structure IX.



IX

EXPERIMENTAL

All m.ps are uncorrected. IR spectra were run on a Perkin-Elmer 421 spectrophotometer and the UV spectra in 95% EtOH on a Beckman DB spectrophotometer. NMR spectra were run in a Varian A-60 instrument in $CDCl_3$ soln.

Boron trifluoride-etherate catalysed rearrangement of 1,2 *epoxy-lupan-3-one* (III).

To a soln of III (150 mg) in dry benzene (1·5 ml) BF_3-etherate (1 ml)was added and kept at room temp for 3 hr. The reaction mixture was poured into ice, extracted with ether and the ether layer washed with $NaHCO_3$aq and finally with water. It was dried over Na_2SO_4 and on evaporation a glassy material was obtained which was dissolved in benzene and chromatographed on alumina. Elution of the column with hexane and benzene yielded gummy material. Subsequent elution with ether yielded a colourless crystalline compound (100 mg). Crystallization from MeOH gave colourless needles, m.p. 225°, ν_{max} 1712, 3500 cm^{-1}. (Found: C, 81·9; H, 11·07. $C_{30}H_{48}O_2$ requires: C, 81·76; H, 10·98%.)

Acetylation. The product IV (50 mg) when acetylated using Ac_2O (1 ml) and pyridine (1 ml) at room temp yielded V. It crystallized from $CHCl_3$-MeOH as colourless needles, m.p. 265°, ν_{max} 1725, 1740 cm^{-1}. (Found: C, 79·48; H, 10·39. $C_{32}H_{50}O_3$ requires: C, 79·62; H, 10·44%.)

Pyridine-chromium trioxide oxidation of IV.

A soln of IV (100 mg) in pyridine was added to a suspension of pyridine–CrO_3 complex prepared from CrO_3 (100 mg) and pyridine (1 ml). After allowing the reaction mixture to stand at room temp it yielded a colourless solid (60% yield) which crystallized from MeOH, m.p. 215°, $[\alpha]_D$ +97·02, ν_{max} 1750, 1800 cm^{-1}, λ_{max} 235 mμ (ε, 1019). (Found: C, 78·43; H, 10·50. $C_{28}H_{44}O_3$ requires: C, 78·45; H, 10·35%.)

Acknowledgement—The authors express their sincere thanks to Dr. S. Selvavinayakam and his staff for microanalyses and for the determination of UV, IR and NMR spectra.