

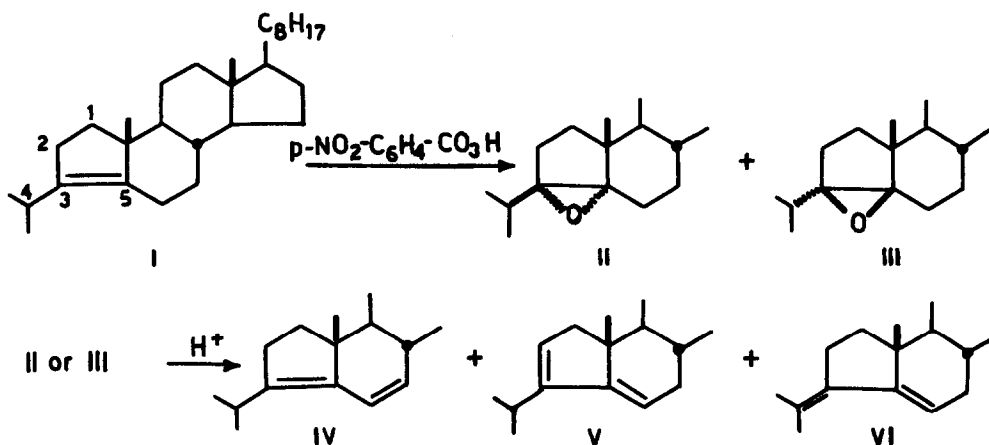
THE REACTION OF 3 α -ISOPROPYL-3,5 β -EPOXY-A-NORCHOLESTANE WITH BF_3
 A NOVEL FRAGMENTATION OF AN EPOXIDE

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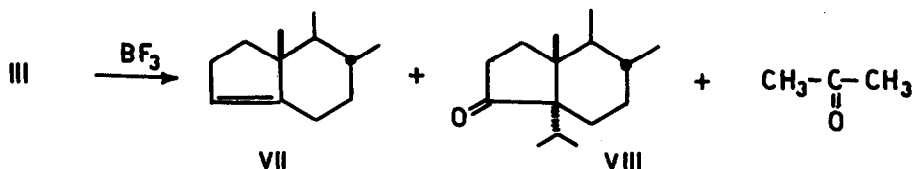
3-Isopropyl-A-norcholest-3(5)-ene (I)[§] affords a mixture of the two α - and β -epoxides (II and III) on treatment with *p*-nitroperoxybenzoic acid. The β -epimer (m.p. 90-92°, $[\alpha]_D^{25} + 50.9^\circ$ ^{§§}) which is formed as the minor reaction product (~8%), gives the same dienes as the major one¹ when treated with protic acids. For instance, it was converted into diene IV by ethanolic HCl, and into dienes V and VI by pyridinium chloride. On the basis of previous results,^{1,2} this should constitute a proof that the epoxide function in III is located in the 3,5 position.



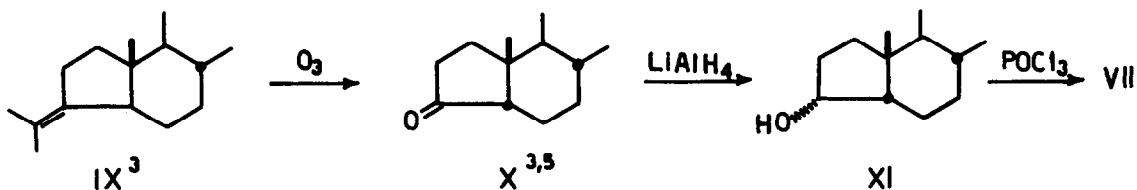
[§] Olefin I has been described in the literature.³ The compound, prepared by us by two independent syntheses, showed different physical data: m.p. 60-62°, $[\alpha]_D^{25} + 53^\circ$.

^{§§} All specific rotations were measured in CHCl_3 at 25°, (c 1).

Completely different results were obtained when III was treated for one minute with BF_3 -ether complex in CHCl_3 solution. Chromatography of the reaction mixture led to isolation of a trisubstituted olefin (δ 5.11 ppm) and a 5-membered ketone (λ_{CO} 5.77 μ) in the ratio 85:15.³ Structure VIII was attributed to the latter (m.p. 134-135°, $[\alpha]_{\text{D}} - 20.3^\circ$) on the basis of the analytical and spectral data, and of the well established retention of configuration in 1,2 shifts.⁴ The mass spectrum of the olefin (VII, m.p. 73-75°, $[\alpha]_{\text{D}} + 56.6^\circ$) unexpectedly showed a molecular peak at m/e 356, indicating the loss of a $\text{C}_3\text{H}_6\text{O}$



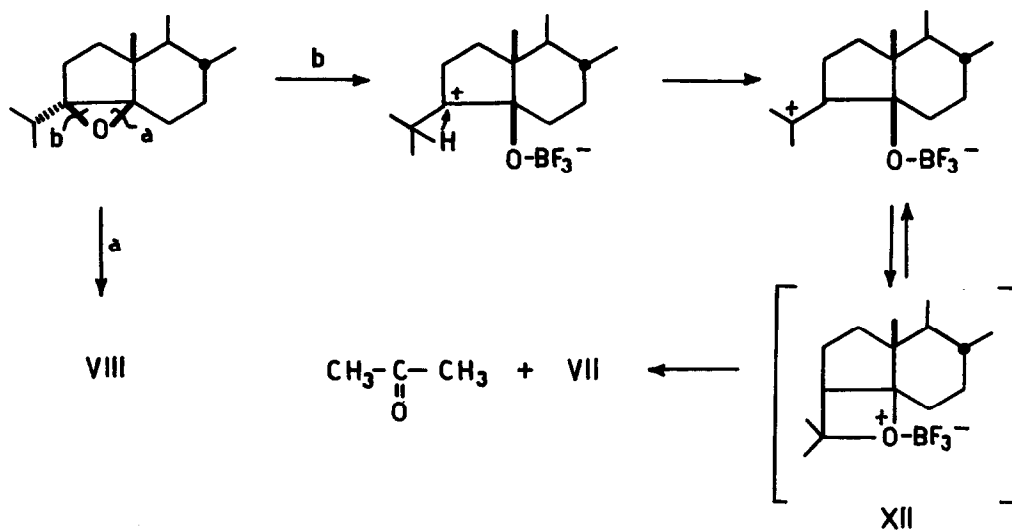
fragment from the original epoxide in the reaction with BF_3 . Careful examination of the reaction mixture led to the revelation of acetone. The olefin VII is known,⁵ and its identity was verified by its independent synthesis as outlined.



Incidentally our results in the reduction of X do not agree with those reported in the literature,⁵ since determination of the configuration of the alcohol XI by Horeau's method,⁶ indicates that the OH group should be α and not β , as reported.

Whereas the rearrangement of the epoxide III to ketone VIII is quite normal,⁷ little can be said, with the data in our hands, about the mechanism of the fragmentation leading to olefin VII. However, since the formation of acetone must involve a shift of oxygen from C-3 to C-4, it appears as rather likely that the conversion of III into VII proceeds through the oxetane XII, originated as outlined. It is indeed known that hindered oxetanes undergo fragmentation into ketones and alkenes when treated with acids.⁸

³ Treatment of 3 α -methyl-3,5 β -epoxy-A-norcholestane with BF_3 affords 5 α -methyl-A-norcholestan-3-one⁹ as the sole reaction product.



Although it has not yet been possible to isolate an oxetane from the reaction of III with $\text{BF}_3 \cdot \text{Et}_2\text{O}$, work is in progress to obtain proofs in support of the proposed mechanism.

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