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REACTIONS OF EPOXIDES - XXV[1]. BF_3-CATALYSED REARRANGEMENT OF 3,3-ETHYLENEDIOXY-5,6α-EPOXY-5α-CHOLESTANE

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Bowers et al.[2] have reported the isolation of a 3-ketal-6β-fluoro-5α-hydroxy compound (1) as the product (> 60%) of the treatment of the 3-ketal-5α, 6α-epoxide (2) with BF_3-etherate in benzene-ether (1:1) solution. Any attempt to compare this result with other BF_3-epoxide rearrangements carried out in benzene solution must now be viewed with caution since it has been shown[1] that the products of BF_3-catalysed rearrangement of 4β,5-epoxy-5β-cholestane are markedly dependent upon the benzene:ether ratio of the solvent.

We now report the results of the BF_3-catalysed rearrangement (1.5 min.) of 3,3-ethylenedioxy-5,6α-epoxy-5α-cholestane in benzene solution. The major products, separated by chromatography, were as follows: fluorohydrin (1; 21%), m.p. 102-103°, $[\alpha]_D$ - 17°, ν_{max} 3500 cm.$^{-1}$, NMR[*] δ 4.20 ppm (OH), 4.23 (6α-H; $J_{H,F}$ = 50 cps), 3.95 (ketal), 1.06 ($C^{19}H_3$; $J_{CH_3,F}$ = 5 cps), 0.67 ($C^{18}H_3$); 5α-and 5β-3-ketal-6-ketones (3; 20%), ν_{max} 1710 cm.$^{-1}$, NMR δ 0.67 ppm ($C^{18}H_3$), 0.76 ($C^{19}H_3$, 5α-), 0.86 ($C^{19}H_3$, 5β-), and hydrolysis to the known[3] 5α-cholesta-3,6-dione; rearranged Δ^9-olefin (4; 9%), a gum, $[\alpha]_D$ + 6°, ν_{max} 3420 cm.$^{-1}$, $\varepsilon_{200\ nm}$ 10,000, NMR δ 3.50 ppm (6β-H; J = 12.5 cps, J′ = 5 cps), 0.92 (5β-CH_3), 0.77 ($C^{18}H_3$), and CrO_3-pyridine oxidation gave the 6-ketone NMR δ 1.32 ppm (5β-CH_3), followed by hydrolysis to the known[4] diketone (5); ester (6; 35%), a gum, $[\alpha]_D$ + 5°, $\nu_{max.}$ 3400, 1730, 1620 cm.$^{-1}$, NMR δ 5.16, 4.83 ppm (CH_2=C<), 4.27 (6β-H, -CH_2-$C\underline{\underline{H}}_2OH$), 3.82 (-$C\underline{\underline{H}}_2$-$CH_2OH$), 1.01 ($C^{19}H_3$), 0.69 ($C^{18}H_3$), and reduction with $LiAlH_4$ to the diol (7), m.p. 89-91°, $[\alpha]_D$ + 19°,

$\nu_{max.}$ 3300, 1620 cm.$^{-1}$, NMR δ 5.13, 4.80 ppm ($CH_2=C<$), 4.25 (6β-H; J = 11 cps, J′ = 4 cps), 3.62 ($-C^3\underline{H}_2OH$), 0.98 ($C^{19}H_3$), 0.69 ($C^{18}H_3$).

We believe that the ester (6) constitutes a further example of a product formed *via* a discrete C-5 carbonium ion.

References

* Determined at 60 Mc for $CDCl_3$ solutions.

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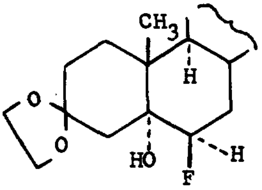

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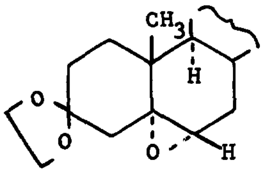

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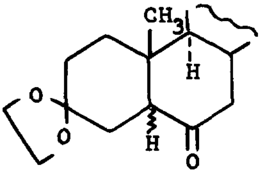

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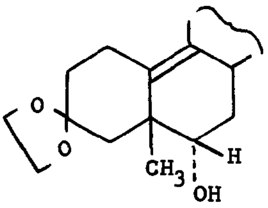

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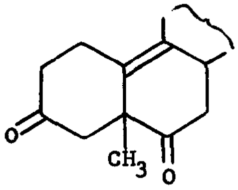

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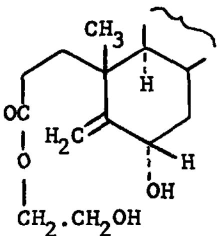

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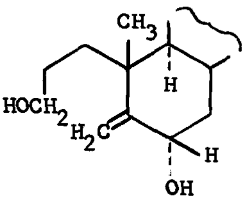

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