CHEMISTRY LETTERS, pp. 1171-1172, 1983.

19-METHYL vs. 18-METHYL GROUP MIGRATION IN THE REARRANGEMENT OF 3β-ACETOXY-9α,11α-EPOXY-5α-LANOSTAN-7-ONE

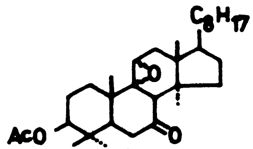
Zdzisław PARYZEK*, Roman WYDRA, and Krzysztof BŁASZCZYK
Department of Chemistry, A. Mickiewicz University, 60-780 Poznań,
Poland

$BF_3 \cdot Et_2O$-catalyzed rearrangement of the keto-epoxide (1b) was found to be a complex reaction leading to compounds (2), (4), and (5) having the rearranged carbon skeletons; spectral and chemical evidences are presented to confirm their structures.

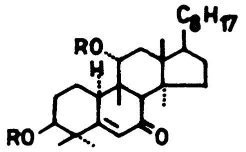
The $BF_3 \cdot Et_2O$-catalyzed rearrangement of the epoxide (1a) has been reported[1,2] to give in high total yield compounds having the cucurbitane skeleton. On the other hand, similar reaction of the 9α,11α-epoxide (1b) afforded compound (5) as the only isolable product.[2] We found, however, that this rearrangement is more complex reaction and gives products resulting from the two possible modes of the opening of the epoxide ring.

The $BF_3 \cdot Et_2O$-catalyzed rearrangement of epoxy-ketone (1b) carried out in acetic anhydride (r.t.; 5 min) gave after isolation and chromatography four products, (2) (mp 148-150°C; yield 13%), (4) (oil; yield 10%), (5)[2] (yield 44%), and 3β-acetoxy-5α,9β-lanostan-7,11-dione[3] (yield 12%).

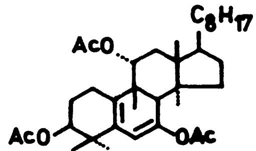
The structure of cucurbitane (2) was inferred from its spectral properties [δ 6.06, 5.18, and 4.85; ν_{max} 1750 and 1658 cm^{-1}; λ_{max} 244 nm (ε 11600)] and their comparison with the known properties of the 3β,11β-diacetoxy-19(10→9β)abeo-10α-lanost-5-en-7-one.[1]



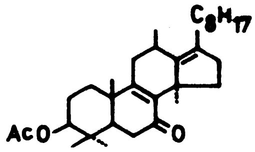
(1a) 9β-isomer
(1b) 9α-isomer



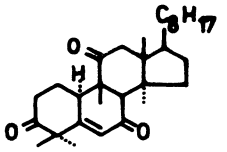
(2) R=Ac
(3) R=H



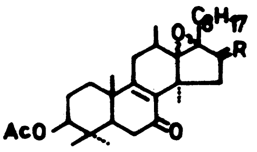
(4)



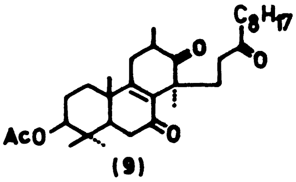
(5)



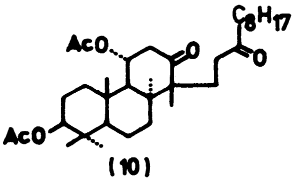
(6)



(7) R=H_2
(8) R=O



(9)



(10)

The compound (2) was hydrolyzed to (3) (amorphous, δ 6.06, 3.90, and 3.58; λ_{max} 248 nm) which was oxidized to the triketone (6) [mp 175-178 °C; ν_{max} 1718, 1698, and 1658 cm^{-1}; λ_{max} 248 nm (ε 8800); m/z 454(M^+), 439, 411, 291, and 205] identical with the product obtained from (2) (11β-OAc isomer)[1] by similar transformations.

The structure of compound (4) follows from the spectral data; m/z 584(M^+); δ 5.86(s, 6-H), 5.15(m, 11β-H), 4.71(t, J 6.5Hz, 3α-H), 2.09, 2.06, and 2.02 (three CH_3COO); and λ_{max} 275 nm. Compound (4) was probably formed via 3β-acetoxy-19(10⟶9β) abeo-lanost-5(10)-en-7-one, since pure (2) could not be transformed to (4) when treated with $BF_3 \cdot Et_2O$ in acetic anhydride.

The structure of compound (5) which was proposed solely on the basis of its spectral properties[2] is now supported by chemical transformations. Epoxidation of (5) with m-chloroperbenzoic acid gave epoxide (7) [mp 162-164 °C; δ 4.49, 2.49, and 2.05; ν_{max} 1728, 1658, 1610, and 1255 cm^{-1}; λ_{max} 251 nm (ε 10000); m/z 498, 385, 372, 164, and 149] while oxidation with CrO_3 in AcOH afforded low yield of the D-ring epoxy-ketone (8) [mp 172-174 °C; λ_{max} 247 nm (ε 12500); ν_{max} 1728, 1715, and 1665 cm^{-1}; m/z 512, 496, 481, and 301]. The oxidation of the allylic position 11 was not detected in contrast to the easy oxidation of 3β-acetoxy-5α-lanost-8-en-7-one to the respective 8-en-7,11-dione.

Ruthenium tetraoxide - sodium metaperiodate oxidation of (5) yielded the seco-compound (9) [oil, yield 58% after preparative TLC; δ 4.53(m, 3α-H), 3.12 (br s, 11β-H), 3.02(br s, 11α-H), and 2.07(s, CH_3COO); ν_{max} 1728, 1715, 1663, and 1620 cm^{-1}; λ_{max} 248 nm (ε 8200)]. Mass spectral fragmentation of compound (9) was similar to those of seco-compound (10)[4] and contained all major fragments arising from McLafferty rearrangement as well as from α- and β-cleavages, characteristic of saturated ketones. Additionally, fragment m/z 57, arising from the rupture of C_{13} - C_{14} and C_{11} - C_{12} bonds was very intense (71%).

The presented results indicate that the described rearrangement proceeds via C-9 and C-11 carbocationic species. It is proposed therefore, that electronic and conformational factors[5] compete in directing the course of the rearrangements of the epoxides (1).

We thank the Polish Academy of Sciences for financial support within the Project MR.I.12.1.5.

References

1) Z. Paryzek, Tetrahedron Lett., 1976, 4761;
Z. Paryzek, J. Chem. Soc., Perkin Trans. 1, 1979, 1222.

2) G. V. Baddeley, H. J. Samaan, J. J. H. Simes, and Tu Hoa Ai, J. Chem. Soc., Perkin Trans. 1, 1979, 7.

3) Z. Paryzek, J. Chem. Soc., Perkin Trans. 1, 1978, 329.

4) Z. Paryzek and R. Wydra, Bull. Acad. Polon. Sci., Ser. Sci. Chim., 26, 591 (1978).

5) D. N. Kirk, Chem. Ind., 1973, 109; for other examples see also "Specialist Periodical Reports - Terpenoids and Steroids," Vol. 1-11, Part II, Molecular Rearrangements; The Chemical Society, London(1971-1982).

(Received May 9, 1983)