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# STRUCTURE REVISION FOR THE PRODUCT DERIVED FROM THE BASE-PROMOTED REARRANGEMENT OF *exo*-2,3-EPOXYNORBORNANE-*endo*-5,6-CARBONATE

Anil K. Saksena,* Pietro Mangiaracina, and Raymond Brambilla
Chemical Research Department, Schering Corporation, Bloomfield, New Jersey 07003
Andrew T. McPhail* and Kay D. Onan
Paul M. Gross Chemical Laboratory, Duke University, Durham, North Carolina 27706

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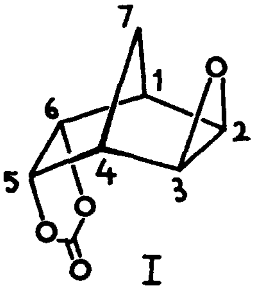
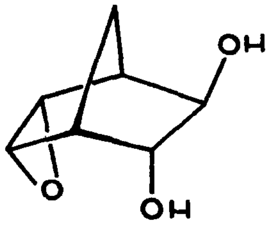
In an attempted saponification of (I),[1,2] Paasivirita and Äyräs isolated a rearrangement product to which they assigned the *endo*-epoxide structure (II) on the basis of spin decoupled $^1$H nmr and infrared spectra; this product was reported to be surprisingly stable to $LiAlH_4$ in THF and to aqueous HCl or $HClO_4$ (0.2$N$) at 100°. A reinvestigation of this reaction in connection with an unrelated problem gave us a compound (m.p. 215-217° dec.) which had an $^1$H nmr spectrum (pyridine-$d_5$) identical with that reported for (II). However, based on mechanistic considerations as well as detailed $^1$H and $^{13}$C nmr spectral analyses, we have concluded that the rearrangement product should be reformulated as the tricyclic oxetane (III). This revised structure assignment has been confirmed by the results of a single-crystal $X$-ray analysis of diacetate (IV).

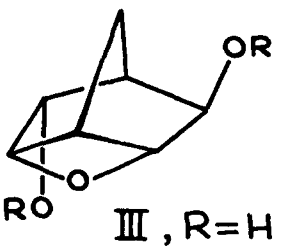
Our $^1$H nmr [see structure (V) for hydrogen atom labels] and $^{13}$C nmr spectral assignments for (III), obtained with the aid of corresponding spectra for (IV),[3] (VI),[4,5] (VII),[6] and (VIII),[7] are reported in Tables 1 and 2, respectively. By reference to structure (V) the identical relative configurations of the individual hydrogen atoms in *endo*-epoxide (II) and oxetane (III), as well as in the isomeric oxolane (IX), become apparent. Consequently, it is easy to understand how the ambiguous nature of the $^1$H nmr spectrum could have led to the earlier erroneous assignments in favor of structure (II).[1] The most notable difference in the $^{13}$C nmr spectra of *exo*- and *endo*-epoxynorbornanes is a significant deshielding (20 ppm) of the C-7 resonance in the latter.[13] We did not observe an effect of this magnitude with any of the oxetanes studied here, but we did note a relatively small deshielding of the C-7 resonance for diol (III) with respect to the corresponding signal for *exo*-epoxycarbonate (I). Ketone (VIII) was prepared[7] in order to confirm the C-3 and C-5 resonances, and also to examine the influence of the 2-keto group upon the C-7 resonance.[14] Whereas the C-1 and C-7 resonances in (VIII) manifested only a small downfield trend, a pronounced deshielding (16 ppm) of the C-3 resonance was observed. We have assigned the C-4 and C-6 resonances in (VIII) based on comparison of their relative γ upfield shift values with those for 2-*exo*-alcohol (VI). Further support for the revised structure assignment was derived from the fact that the infrared spectrum (Nujol) of (III) exhibited a fairly strong absorption (960 cm$^{-1}$) which compared well with those for oxetane (VI)[4] and 2,2-dimethyloxetane.



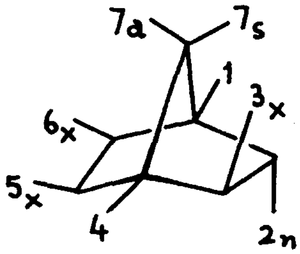
I



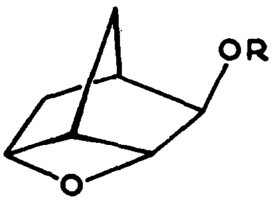
II



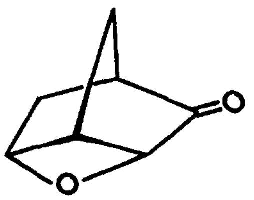
III, R=H
IV, R=Ac



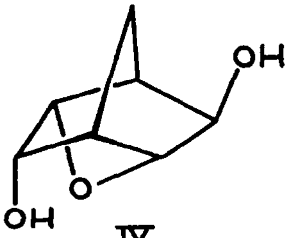
V



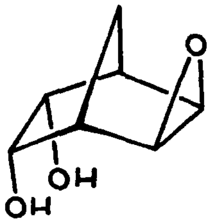
VI, R=H
VII, R=Ac



VIII



IX



X

Table 1 $^1$H NMR Chemical Shifts[10,11,12]

| Compound | $H_1$ | $H_{2n}$ | $H_{3x}$ | $H_4$ | $H_{5x}$ | $H_{6x}$ | $H_{6n}$ | $H_{7a}$ | $H_{7s}$ |
|---|---|---|---|---|---|---|---|---|---|
| (III) | 2.75 | 4.38 | 4.52 | 3.82 | 4.35 | 3.9 | - | 1.28 | 1.76 |
| (IV) | 3.0 | 5.44 | 4.74 | 3.9 | 4.58 | 4.62 | - | 1.42 | 1.74 |
| (VI) | 2.75 | 4.08 | 4.65 | 3.75 | 4.34 | 1.94 | 1.52 | 1.25 | 1.86 |
| (VII) | 2.9 | 5.0 | 4.66 | 3.78 | 4.48 | 2.08 | 1.56 | 1.30 | 1.78 |
| (VIII) | 3.3 | - | 5.84 | 3.8 | 5.11 | 1.67 | 2.0 | 1.8 | 2.38 |

Table 2 $^{13}$C NMR Chemical Shifts[10,11]

| Compound | C-1 | C-2 | C-3 | C-4 | C-5 | C-6 | C-7 | C=O (endo) | C=O (exo) | $CH_3$ |
|---|---|---|---|---|---|---|---|---|---|---|
| (I) | 40.0 | 46.4 | 46.4 | 40.0 | 78.9 | 78.9 | 20.7 | 155.04 | - | - |
| (III) | 47.5 | 74.0 | 87.1 | 44.9 | 80.7 | 72.5 | 27.6 | - | - | - |
| (IV) | 43.6 | 75.7 | 84.6 | 45.3 | 78.6 | 74.6 | 28.0 | 170.7 | 169.6 | 21.0 |
| (VI) | 43.1 | 75.6 | 86.5 | 43.8 | 82.5 | 37.0 | 33.0 | - | - | - |
| (VII) | 41.1 | 77.5 | 84.5 | 44.0 | 82.2 | 37.2 | 33.4 | - | 169.7 | 21.0 |
| (VIII) | 43.9 | 174.9 | 102.5 | 41.0 | 83.4 | 28.7 | 36.4 | - | - | - |

The constitution of (III) was established unequivocally by single-crystal *X*-ray analysis of diacetate (IV). Crystals of (IV) belong to the triclinic system, space group $P\bar{1}$, with $a = 7.320(5)$, $b = 13.315(8)$, $c = 6.294(5)$ Å, $\alpha = 96.94(5)$, $\beta = 92.41(5)$, $\gamma = 114.91(5)°$, $Z = 2$. The structure was solved by direct methods using MULTAN.[15] Full-matrix least-squares refinement of atomic positional and thermal (anisotropic C, O; isotropic H) parameters converged at $R = 0.088$ over 1646 statistically significant $[I > 2.0\sigma(I)]$ reflections measured by diffractometer (Ni-filtered Cu-$K_\alpha$ radiation; $\theta$-$2\theta$ scans). Bond lengths and valency angles have expected values; torsion angles defining the ring conformations are shown in the Figure. Owing to constraints imposed by the oxetane ring and the presence of the acetoxy substituents, the cyclopentane ring conformations deviate significantly from envelope forms and approximate to half-chair ($C_2$) forms in which C(4) and C(7) are displaced to opposite sides of the plane through the other three ring atoms. The oxetane ring has a mean dihedral angle of 20.2° and consequently is quite puckered.

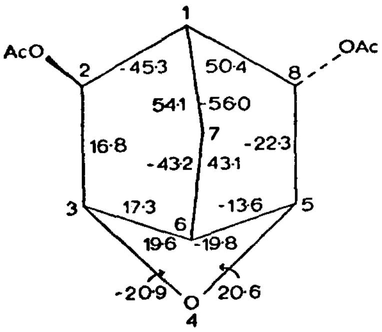


Figure. Endocyclic torsion angles (deg.) in (IV)

Masamune and coworkers[16] have recently reported a new non-photochemical synthesis of oxetanes by regiospecific ring opening of certain 3,4-epoxyalcohols under hydrolytic conditions. The formation of (III) and (VI)[4,5] are particularly good examples of such epoxide ring opening reactions. Although we have not studied this reaction under anhydrous conditions,[16] we expect that steric constraints would severely limit the alternative mode of attack of the alkoxy anion at C-6 to give the oxolane (IX).

We have also found that thermolysis (160°) of (X) for 1 hour results in the formation of (III) to the extent of about 50% as determined by $^1$H nmr and t.l.c., the only other major component being unchanged (X). Isolation of (III) and (X) and their direct spectral comparison with authentic samples confirmed our observation. First detected during m.p. determination of (X), this, to our knowledge, is representative of a new oxetane-forming reaction from a 3,4-epoxyalcohol.

Acknowledgements. We thank Dr. Ashit K. Ganguly and Professor J. Meinwald for their interest and valuable comments.

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2. The reaction conditions (*viz.* methanol/50% aqueous KOH, reflux, 4 hours) for mere hydrolysis of the cyclic carbonate (I) were surprisingly rather drastic.[1] Thus, on treatment of (I) in THF with aqueous $Na_2CO_3$(10%) at room temperature overnight, we obtained an 80% yield of the expected *exo*-2,3-epoxy-*endo*-5,6-norbornanediol (X), m.p. undefined ($CH_2Cl_2$/*n*-hexane). $^1H$ nmr, $\delta$ ($CDCl_3$): $H_{2,3}$ 4.08; $H_{5,6}$ 3.44; $H_{1,4}$ 2.72; $H_{7s}$ 1.25; $H_{7a}$ 0.55 ($J_{7a,7s}$ 11.0 Hz). The rearranged oxetane (III) must, no doubt, come from this *exo*-epoxydiol (X).

3. Diacetate (IV), m.p. 68-69° (acetone/*n*-hexane); (Found: C, 58.48; H, 6.51. $C_{11}H_{14}O_5$ requires C, 58.41; H, 6.20).

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5. We obtained (VI) from *exo*-2,3-epoxy-*endo*-5-norbornanol[4] under the same conditions[1] that caused the rearrangement of (I) to give (III).

6. Monoacetate (VII), a colorless oil, had consistent infrared and mass spectral data.

7. Ketone (VIII) was obtained in a rather modest yield as a waxy solid by either $RuO_4/CCl_4$[8] or $CrO_3$/pyridine complex[9] oxidations; it had consistent infrared and mass spectral data.

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10. To aid comparison of the numerical data, we have used norbornane numbering system in the Tables. The correct numbering of these tricyclic oxetanes is exemplified in the Figure. Accordingly, oxetane (III) should be named, 2-*exo*-8-*endo*-4-oxatricyclo $[3,2,1,0^{3,6}]$-octanediol.

11. Fourier transform $^1H$ and $^{13}C$ nmr spectra were obtained on a Varian XL-100-15 equipped with a Varian 620L-100 disk-based computer system. The chemical shifts (ppm) are recorded downfield from TMS used for solutions in $CDCl_3$.

12. $^1H$ nmr coupling constants: (IV) $J_{7s,7a} = 13.5$; $J_{2,7a} = 2.3$; $J_{2,7s} = < 0.5$; $J_{4,7s} = 1.3$; $J_{4,7a} = < 0.3$; $J_{3,5} = {\sim}2$; $J_{1,7a} = 3.8$; $J_{1,7s} = 1.5$; $J_{1,2} = < 0.7$; $J_{1,3} = 2.7$; $J_{1,4} = 1.5$; $J_{1,5} = 2.5$; $J_{2,3} = < 0.5$; $J_{3,4} = 4.5$; $J_{4,5} = 2.8$. (VII) $J_{1,6x} = {\sim}1$; $J_{1,6n} = < 0.5$; $J_{6x,5} = 4.8$; $J_{6n,5} = < 0.5$; $J_{6x,6n} = 13.5$; $J_{6x,4} = 0.5$; $J_{6n,4} = 1.9$; $J_{6x,3} = J_{6n,3} = J_{2,5} = < 0.5$.

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