Unexpected Acid-catalysed Rearrangement of a Vinylcyclopropane Derivative

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A vinylcyclopropane carboxylic acid derivative undergoes a novel type of rearrangement under mild acidic conditions; X-ray diffraction study of the rearrangement product confirms the structure as (1*SR*,4*SR*,7*SR*)-4-methyl-3,9-dioxabicyclo[5.3.0]dec-5-ene-2,10-dione.

In connection with a research programme aimed at the synthesis of functionally substituted 1-aminocyclopropane-1-carboxylic acids **1**,[1] we desired access to the vinylic cyclopropane lactones exemplified by compound **2**. Our route is based on the Curtius-type rearrangement of the corresponding lactonic acid **4**, which is obtained from the corresponding *tert*-butyl ester **3** by acid hydrolysis.

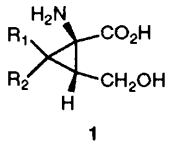
When compound **3** was subjected to acidic conditions (trifluoroacetic acid, TFA in dichloromethane or neat TFA) in order to cleave the *tert*-butyl ester to give the acid **4**, the product (m.p. 94–95 °C) did not show the spectral features characteristic of a cyclopropane derivative, but the rearranged structure **5** was indicated.

The ^{1}H NMR spectrum of the product shows seven one-proton signals together with a doublet corresponding to the methyl group. Assignment of signals was performed using both homonuclear and heteronuclear shift correlations (COSY, XHCORRD and COLOC). Additionally, in order to check some small proton correlations that were unclear in the COSY spectrum, the ^{1}H NMR spectrum was iterated with a LAOCOON-type program[2] and all the coupling constants were obtained.†

When the spectra were recorded in CD_3OD, the H-1 exchanges with deuterium from methanol and the doublet at δ 4.20 is lost in the ^{1}H NMR spectrum, and the multiplet at δ 3.62 (due to H-5) is modified correspondingly. Simultaneously, the δ 49.01 signal in the ^{13}C NMR spectrum disappears in the DEPT spectrum. The same exchange effect can be seen in $CDCl_3$ when a drop of D_2O, together with a phase-transfer catalyst, is added.

The rearrangement to produce **5** is quite remarkable in its facility (room temperature) and mildness of the reaction conditions. The rearranged product was obtained as the sole product in purified yields varying between 35 and 50%.

The presence of compound **4** can be detected by NMR when a solution of **1** in $CDCl_3$ is treated with TFA. After cleavage of



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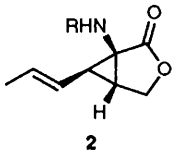

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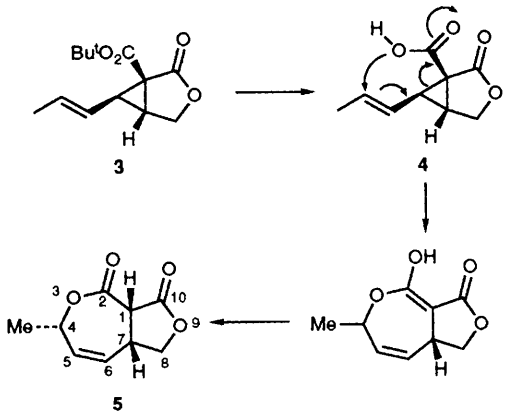
† *Spectroscopic data* for compound **5**: ^{1}H NMR ($CDCl_3$, 200.13 MHz) δ 1.51 (d, 3H, *J* 6.5 Hz, Me), 3.62 (m, 1H, *J* 9.4, 11.9, 7.7, 2.4, 3.0, 2.5 Hz, H-7), 3.97 (dd, 1H, *J* 11.9, 8.8 Hz, H-8a), 4.20 (d, 1H, *J* 9.3 Hz, H-1), 4.59 (dd, 1H, *J* 7.7, 8.8 Hz, H-8b), 5.19 (m, 1H, *J* 6.5, 5.2, 2.1, 2.5 Hz, H-4), 5.70 (bdt, 1H, *J* 2.1, 2.4, 10.7 Hz, H-6), 5.88 (dq, 1H, *J* 3.0, 5.2, 10.7 Hz, H-5); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 20.30 (q, Me), 38.81 (d, C-7), 49.02 (d, C-1), 70.40 (d, C-4), 70.56 (t, C-8), 128.82 (d, C-6), 133.85 (d, C-5), 166.18 (s, C-10), 171.16 (s, C-2). *m/z* (electron impact): 182 (12%, M^+), 164(39), 137(42), 123(27), 98(68), 79(100). HRMS: Calc. for $C_9H_{10}O_4$ 182.0579, found: 182.0564.



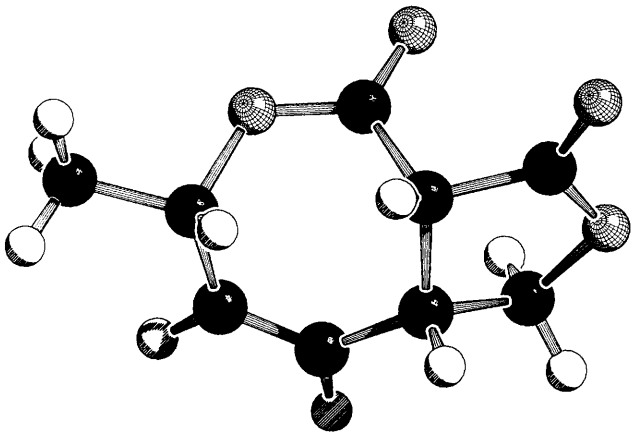


Fig. 1 Compound **5**

the ester a mixture of both products **4** and **5** can be detected. Compound **5** can be purified easily by FC (EtOAc : diethyl ether 1 : 1–3 : 2) and crystallized from EtOAc–hexanes as a colourless solid.

The stereochemistry at positions 1 and 7 relative to position 4 cannot be deduced unambiguously from the NMR data. Compound **3** is a single diastereoisomer, as evidenced by the NMR spectra. In order to verify the structure of the rearrangement product, a suitable crystal was obtained and subjected to X-ray analysis‡ (Fig. 1) which determines unequivocally the stereochemistry of all three appendages in the seven-membered ring.

The X-ray analysis shows no abnormal bond distances or angles. The three hydrogens at positions 1, 4 and 7 are all located on the same side of the dilactone skeleton, thus defining the stereochemistry at the stereogenic carbons as 1*S*,4*S*,7*S* or 1*R*,4*R*,7*R*. Compound **5** was found to crystallize in a centric space group as a racemic crystal, therefore both enantiomers are present in the crystal.

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References

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2 R. Laatikainen, *J. Magn. Reson.*, 1988, **78**, 127.

‡ *Crystal structure* of **5**: $C_9H_{10}O_4$: M_r = 182.06; monoclinic, space group $P2_1/c$ (no. 14); a = 1369.3(2), b = 802.5(1), c = 823.6(2) pm, β = 102.62(2)°, V = 883.1(3) × 10^6 pm^3; Z = 4; D_c = 1.370 g cm^{-3}; Mo-Kα (λ = 0.71073 Å); μ = 0.102 mm^{-1}; F(000) = 384, T = 296 ± 1 K; crystal dimensions, 0.20 × 0.30 × 0.30 mm; CAD4 (Enraf-Nonius) diffractometer; corrections: Lorentz polarization, empirical absorption corrections [(DIFABS: N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158): minimum and maximum correction coefficients 0.722 and 1.194]; 2θ = 50°; *hkl* range: h 0 → 16, k = 0 → 9 and l = −9 → 9; 1744 measured reflections, 1547 unique (R_{int} = 0.007), 1207 with $I > 3\sigma I$. The structure was solved by direct methods [SHELXS, G. M. Sheldrick, in *Crystallographic Computing 3*, ed. G. M. Sheldrick, C. Kruger and R. Goddard, Oxford University Press, 1985, p. 175]. Refinement: R = 0.035, R_W = 0.030, non-hydrogen atoms anisotropically, H atoms located from difference Fourier map and refined with isotropic temperature factors (CRYSTALS program, D. Watkin J. R. Carruthers and P. W. Betteridge, Chemical Crystallography Laboratory, Oxford, 1990). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.