71. Unexpected Hydroxyspirolactone Formation upon *Baeyer-Villiger* Oxidation of a *trans*-α-Decalone (*trans*-Octahydronaphthalen-1(2*H*)-one) and X-Ray Structure of the Product

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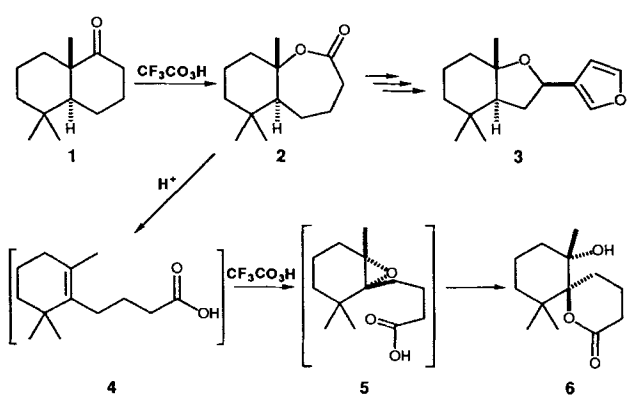
(20. III. 95)

trans-4,4,10-Trimethyl-9-decalone (= *trans*-5,5,8a-trimethyl-octahydronaphthalen-1(2*H*)-one; **1**), when treated with trifluoroperacetic acid, gave the unexpected hydroxyspirolactone 7-hydroxy-7,11,11-trimethyl-1-oxaspiro[5.5]undecan-2-one (**6**), in which the two new O-atoms were introduced in a 1,2-*trans* relationship. The structure of this compound was conclusively proven by X-ray crystallography. The process involves the intermediacy of 7-membered lactone **2**, the expected *Baeyer-Villiger* product, which could also be succesfully prepared under controlled conditions at 0° in a buffered medium containing Na_2HPO_4.

Introduction. – Decalone **1** [1] has been entertained as a key intermediate in a number of terpene syntheses. We envisaged **1** as a starting point for a synthesis of the sesquiterpene ancistrofuran (**3**) [2], a termite defence pheromone [3], *via* lactone **2** (*Scheme*).

Results and Discussion. – *Peracid Oxidation of 4,4,10-Trimethyl-9-decalone* (**1**). When **1** was treated with trifluoroperacetic acid [4a] in an attempt to regioselectively prepare **2** [5a, b], we were surprised to find that the product contained none of the desired 7-membered lactone. One equivalent or an excess of the peracid provided one major product **6** along with a series of unidentified by-products. The ease of this process was reflected in the fact that the same result was observed upon buffering the reaction medium with Na_2HPO_4 [4b] to remove the (strong) trifluoroacetic acid. In this case, the reaction

Scheme



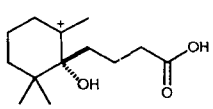
[1]) 'Praktikantin' from the University of Vienna, Austria, October 1991 to March 1992.

proceeded more slowly providing the same product **6** in 48% yield, accompanied, however, by lactone **2**[2]) (18%) and unreacted starting decalone **1** (20%)[3]).

Spectral evidence of the unexpected material **6** indicated an alcohol function ($\tilde{\nu}_{max}$ 3457 cm^{-1}) whose tertiary nature was reflected in its resistance to acetylation as well as in its ^{1}H-NMR (*no* CH_n-OH signals), ^{13}C-NMR (δ 74.9), and mass spectra (facile loss of H_2O). The δ-lactone unit followed from the IR ($\tilde{\nu}_{max}$ 1698 cm^{-1}) and ^{13}C-NMR spectra (δ 172.5, 89.6). The MS (M^+ 226) showed that *two* O-atoms had been incorporated into the molecule on trifluoroperacetic-acid treatment, and conclusive evidence for this interpretation was provided by combustion analysis indicating an empirical formula of $C_{13}H_{22}O_3$.

Our speculations that the structure of the unexpected product could reasonably *only* be that of hydroxylactone **6** were fully supported by extensive NMR experiments (COSY, ROESY, HCCORR, NOE). However, we were not able to unambiguously nail down the relative configuration of the two asymmetric centres in the molecule, despite the fact that our mechanistic explanation for this reaction only allowed for a *trans*-1,2-dioxy substitution.

As shown in the experiments using buffered trifluoroperacetic acid, (CF_3CO_3H/Na_2HPO_4/CH_2Cl_2) [4b], the first step in this reaction is a normal *Baeyer-Villiger* process giving lactone **2**. In the acidic medium, this lactone **2** suffers internal elimination giving the cyclohexene-carboxylic acid **4** which in turn is epoxidized to **5** (*Scheme*). Internal epoxide opening with back-side attack finally affords **6**. Although no products arrising from 'S_N1' or '$E1$'-like processes (*via* tertiary carbenium ions **7** or **8**) were isolated, such a process cannot be ruled out as occurring.



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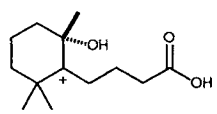

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Conclusive structural proof for the hydroxy-spirolactone structure **6** was obtained from an X-ray crystal structure.

X-Ray Structure of Hydroxyspirolactone **6**. A stereoscopic view of the molecular conformation of **6** is shown in the *Figure* displaying the 50% probability thermal ellipsoids for the C- and O-atoms (the H-atoms are set in theoretical positions and given a constant radius of 0.15 Å). There are no unusual features in the crystal structure; noteworthy, however, may be the 'envelope' conformation of the lactone ring and the axial position of the OH group. A summary of the crystallographic analysis is given in the *Exper. Part*, and full details of the X-ray analysis including coordinates were deposited at the *Cambridge Crystallographic Data Center*.

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[2]) Satisfactory analytical data were obtained for compound **2** (NMR, MS, IR, microanalysis, m.p. 88–89° (hexane)).

[3]) The formation of **6** could be suppressed by performing the reaction at 0° in the presence of an excess of Na_2HPO_4 buffer. In this case, it was possible to prepare lactone **2** in 72% based on recovered starting decalone.

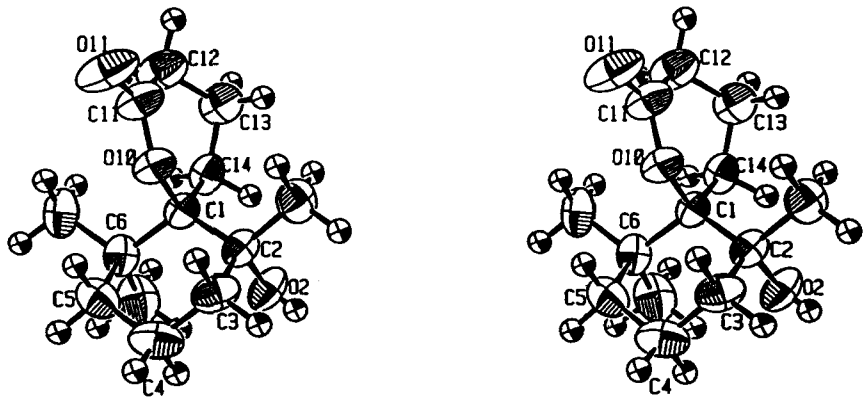

Figure. *Stereoscopic ORTEP drawing of compound* **6**

Experiment Part

7-Hydroxy-7,11,11-trimethyl-1-oxaspiro[5.5]undecan-2-one (**6**). A stirred soln. of **1** [1] (105 mg, 0.54 mmol) in CH_2Cl_2 (12 ml) at 0° was treated with *ca.* 0.2M CF_3CO_3H in CH_2Cl_2 (3.3 ml, 0.67 mmol) (prepared from CH_2Cl_2 (23 ml), 60% H_2O_2 soln. (0.25 ml), and trifluoroacetic anhydride (1.75 ml)). After 1.5 h at 0°, more CF_3CO_3H soln. (3.3 ml) was added and stirring continued overnight with gradual warming to r.t. Several spatulas of Na_2SO_3 were added, and vigorous stirring was continued for a further 30 min. Filtration, washing of the filtrate with sat. aq. $NaHCO_3$ soln., drying (Na_2SO_4), filtration, and evaporation afforded a colourless gum which slowly crystallised to fine needles. Recrystallisation from *i*-Pr_2O gave colourless needles (65 mg, 55%). M.p. 132–134°. IR (KBr): 3457*s*, 1698*s*, 1396*m*, 1351*m*, 1297*s*, 1038*s*, 1005*s*. ^{1}H-NMR (360 MHz, $CDCl_3$): 2.49 (*m*, 1 H); 2.34–2.21 (*m*, 2 H); 2.09–1.99 (*m*, 1 H); 1.95–1.71 (*m*, 6 H); 1.49–1.35 (*m*, 2 H); 1.22 (*s*, 3 H); 1.19–1.12 (*m*, 1 H); 1.15 (*s*, 3 H); 0.89 (*s*, 3 H). ^{1}H-NMR (400 MHz, (D_6)benzene): 2.28 (*m*, H–C(3)); 2.11 (*ddd*, *J* = 13.5, 13.5 4.5, H–C(8)); 2.03–1.90 (*m*, H–C(3), H–C(5), H–C(10)); 1.82 (*ddddd*, *J* = 13.5, 13.5, 13.5, 3.5, 3.5, H–C(9)); 1.45–1.27 (*m*, 2 H–C(4), H–C(5), H–C(9)); 1.22–1.09 (*m*, H–C(10), H–C(8)); 1.18 (*s*, Me–C(11)); 1.02 (*s*, Me–C(7)); 0.85 *s*, Me–C(11)). ^{13}C-NMR (90 MHz, $CDCl_3$): 172.5, 89.6, 74.9, 40.2, 36.2, 35.6, 30.4, 27.2, 26.8, 23.5, 21.8, 19.8, 17.6. EI-MS: 226 (17, M^+), 208 (37), 193 (20), 109 (64), 86 (85), 71 (66), 43 (100). Anal. calc. for $C_{13}H_{22}O_3$: C 68.99, H 9.80; found: C 68.7, H 9.5.

Crystallographic Data for **6**: Diffraction data was measured on a *CAD4-F* diffractometer (*Nonius*, Delft) using CuK_α radiation. Some details are summarized in *Table 1*.

The structure was solved by direct methods (SHELX86) and refined by full-matrix least-squares methods using the program SHELX76. H-Atoms were included in the SF-calculation in theoretical positions ('riding' on the connected heavy atom).

Table 1. *Crystal Data for* **6**

Crystallized from	AcOEt
Chemical formula	$C_{13}H_{22}O_3$
Molecular weight	226.3
Crystal form	prismatic, *ca.* 0.3 × 0.2 × 0.1 mm
Crystal colour	colourless
Crystal system	orthorhombic, primitive
Space group	$P2_12_12_1$
Cell dimensions	a = 13.388(1) Å, b = 13.477(1) Å, c = 14.154(2) Å, Vol = 2553.9 Å^3
Z (molecules per cell)	8
Density (calc.)	1.176 g/cm^3

Table 1 *(cont.)*

Diffractometry	
Type of diffractometer	*CDA4-F*, $\omega/2\theta$-scans
Temperature	*T* 295K
Radiation	CuK_α, $\lambda = 1.54060$ Å
θ-Range	$2.1 < \theta < 77.5°$
Intensity decay	8.4%
Absorption corr.	T_{min} 0.980, T_{max} 1.023 (empirical)
No. of measured reflexions	3030
No. of unique deflexions	3005
No. of reflexions $\|F\| > 3\,\sigma(F)$	2701
Refinement	
No. of parameters	297
Treatment of H	no refinement ('riding' on connected atom)
Final *R*	0.0618
Final R_w	0.0741
Weighting scheme	$w = [\sigma^2(F) + 0.0007\,F^2]^{-1}$
S (goodness of fit)	3.099
Final $\Delta\,\max/\sigma$	0.0205
$\Delta\rho$ (min, max) [eA^{-3}]	0.216, −0.234

The crystal structure contains two molecules in the asymmetric unit of the cell. The two independent molecules are identical within experimental error: the r.m.s. of fitting the C- and O-atoms is 0.039 Å. There are two *inter* molecular H-bonds which link the molecules in chains along the *a*-axis (*Table 2*).

Table 2. *Intermolecular H-Bonds of* **6**[a])

D	A	D···A	DH···A	angle (D–H···A)
O(2)–H	O(61)	2.85	2.14	165
O(52)–H	O(11)	2.96	2.14	163

[a]) D = Donor, A = acceptor

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