Unusual Formation of an Oxetane Ring.
Molecular and Crystal Structure of
2a-Acetyl-3-(1-methoxyethylidene)-5a-methylcyclopenta[b]oxetan-4-one

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Received August 24, 1981

The reaction between 2,3-diacetyl-4-hydroxy-4-methylcyclopent-2-en-1-one, **2**, and diazomethane gave a mixture of four compounds, two of which, **5** and **6**, resulted to be cyclopenta[b]oxetane derivatives. The structure of **5** was determined by X-ray analysis. Some aspects of the mechanism are discussed.

In the course of our studies on tetraacetylethylene **1**, a highly reactive system (1-4), we became interested in the reactivity of 2,3-diacetyl-4-hydroxy-4-methylcyclopent-2-en-1-one, **2**, prepared from **1** under basic conditions (5).

Scheme 1
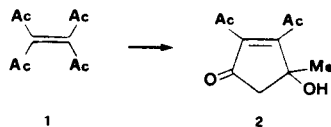
The cyclopentenone **2** with a double bond activated by three carbonyl groups reacted easily with an excess of diazomethane to yield a mixture of four products which were resolved by column chromatography. The main product, **3**, mp 100-101°, and the isomer **4**, mp 77-78°, had formula $C_{11}H_{14}O_4$, whereas compounds **5**, mp 128-130°, and **6**, mp 94-96°, had formula $C_{12}H_{16}O_4$. The combined evidence of spectral data and identity with the products obtained by treating 1,1,2,2-tetraacetylcyclopropane in a basic medium (6) indicated that the isomers **3** and **4** were 1α,5α-diacetyl-4α-hydroxy- and 1α,5α-diacetyl-4β-hydroxy-4-methylbicyclo[3.1.0]hexan-2-one, respectively. The absence of any appreciable absorption (except a band of low intensity due to the carbonyl groups) in the uv spectra and the presence of a band at *ca.* 3090 cm⁻¹ in the ir spectra strongly supported the presence of a cyclopropane

ring. Its formation resulted from an attack by diazomethane on the double bond C(2)=C(3) of compound **2** followed by nitrogen elimination. The pmr spectra presented an AX system for the methylene protons of the cyclopropane ring, beside four singlets for a hydroxyl group and three methyl groups, and a multiplet due to a methylene system.

Scheme 2
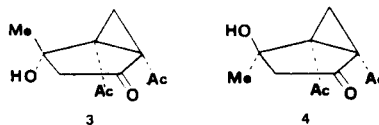
The ir spectrum of compound **5** showed sharp bands at 1710 and 1680 cm⁻¹ attributable to CO groups and a very strong band at 1580 cm⁻¹ which was indicative of a conjugated -CO-C=C-O- system (3,4), confirmed by the uv absorption at 280 nm. The pmr spectrum displayed four singlets attributable to three methyl groups and a methoxy group, an AB system centered at δ 2.63 (J = 18 Hz) and two mutually coupled doublets (1 H each, J = 5.6 Hz) at δ 3.98 and 5.34 ppm.

The spectral data of compound **6** were similar. The ir spectrum presented strong bands at 1705 (CO), 1640 (CO), and 1600 (-CO-C=C-O-) cm⁻¹, and the uv spectrum showed a maximum at 269 nm. In the pmr spectrum, besides four

Table 1

Positional Parameters (× 10⁴) and Thermal Parameters (A² × 10⁴) With the Estimated Standard Deviations in Parenthesis

Atom	X/A	Y/B	Z/C	U11	U22	U33	U12	U13	U23
O(1)	5632(3)	-2369(5)	3830(4)	470(24)	840(33)	471(25)	48(22)	-24(19)	156(24)
O(8)	3102(3)	-3729(5)	2463(5)	585(28)	468(26)	855(33)	-179(22)	70(24)	148(26)
O(12)	2884(3)	112(4)	3438(5)	483(23)	476(24)	713(29)	73(20)	265(21)	-92(23)
O(14)	5314(3)	1992(5)	1856(5)	904(34)	437(28)	896(35)	-220(24)	361(28)	-1(26)

| Atom	X/A	Y/B	Z/C	U	Atom	X/A	Y/B	Z/C	U
C(2)	4658(4)	-2293(7)	4137(6)	506(17)	C(6)	5378(4)	-3703(8)	1614(7)	661(20)
C(2a)	4275(3)	-1731(6)	2699(5)	341(14)	C(7)	3426(4)	-2611(7)	1950(6)	410(14)
C(3)	4248(4)	49(6)	2559(6)	351(14)	C(9)	3033(4)	-2093(8)	532(7)	633(19)
C(4)	5101(4)	615(8)	2053(6)	467(16)	C(10)	3570(4)	928(7)	2972(6)	422(15)
C(5)	5717(4)	-743(7)	1809(6)	486(16)	C(11)	3508(4)	2678(7)	2907(6)	594(18)
C(5a)	5289(4)	-2186(6)	2373(6)	417(15)	C(13)	2194(4)	897(8)	4136(7)	694(20)

singlets for the methyl groups and an AB system attributable to a methylene group, there were two mutually coupled doublets (1 H each, J = 6.0 Hz) at δ 4.10 and 5.30 ppm.

The evidence presented above was not sufficient to assign the correct structures to the isomers **5** and **6**. Consequently an X-ray structure determination was undertaken on compound **5**, which presented more suitable crystals. The X-ray analysis established that it had the 2a-acetyl-3-(1-methoxyethylidene)-5a-methylcyclopenta[b]oxetan-4-one structure. The details of the X-ray analysis are reported in the Experimental, coordinates of non-hydrogen atoms in Table 1 and non-hydrogen atoms bond lengths and angles in Table 2, and the shortest intermolecular distances in Table 3.

The two rings of the structure (Figure) are essentially planar; the most significant puckering is present in the cyclopentane ring with the C(5a) atom projecting (0.177 Å) out of the plane of the four other atoms. The puckering angle of the oxetane ring was 16.4°, not significantly different from those of uncondensed oxetane rings (7,8). Comparison with analogous systems was not possible since to our knowledge no crystal structure of cyclopenta-oxetanes was reported in the literature. The most interesting feature in this molecule is the short length (1.468 Å) of the C(3)-C(4) bond of the conjugated system O(12)-C(10)=C(3)-C(4)=O(14), which had been expected on the basis of the uv and ir spectra. This structure explains the great difference between the chemical shifts of the hydrogen atoms in the oxetane ring. In fact, on the basis of crystallographic data, H(21) is situated in the deshielded region of the C(7)=O(8) group, whereas H(22) is situated in the shielded region of the C(3)=C(10) double bond (see Scheme 3).

Whereas **6** was stable, the methoxy-derivative **5** changed into the isomer **7** in a few hours when absorbed on silica gel. This behavior explained the erratic ratio between **5** and **7** we obtained in different experiments: it must be ascribed to the time we left the reaction mixture in contact with the chromatographic column.

Scheme 3
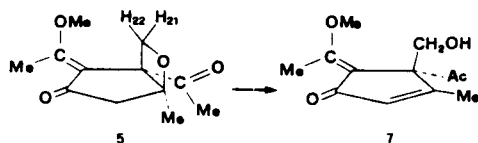
On the basis of its formation and of the following spectroscopic properties we formulate **7** as 3-acetyl-2-(1-methoxyethylidene)-3-hydroxymethyl-4-methylcyclopent-4-en-1-one. The compound showed a complex uv spectrum with maxima at 221, 253, 291, and 310 nm. The ir included absorptions at 3360 attributable to an OH group, 1715 and 1665 due to CO groups and a very strong band at 1590

Table 2
Bond Lengths (Å) and Bond Angles (°) (a)

O(1)-C(5a)	1.453(6)	C(2)-O(1)-C(5a)	91.5(4)
O(1)-C(2)	1.469(6)	C(10)-O(12)-C(13)	120.9(4)
O(8)-C(7)	1.205(6)	O(1)-C(2)-C(2a)	91.4(4)
O(12)-C(10)	1.339(6)	C(4)-C(3)-C(2a)	110.3(5)
O(12)-C(13)	1.453(7)	C(4)-C(3)-C(10)	126.8(5)
O(14)-C(4)	1.233(7)	C(10)-C(3)-C(2a)	122.6(5)
C(2)-C(2a)	1.517(7)	O(14)-C(4)-C(5)	122.8(5)
C(3)-C(4)	1.468(7)	O(14)-C(4)-C(3)	127.1(5)
C(3)-C(2a)	1.519(7)	C(3)-C(4)-C(5)	110.0(5)
C(3)-C(10)	1.336(7)	C(4)-C(5)-C(5a)	106.5(5)
C(4)-C(5)	1.492(8)	O(8)-C(7)-C(2a)	121.0(5)
C(5)-C(5a)	1.517(7)	O(8)-C(7)-C(9)	121.3(5)
C(6)-C(5a)	1.508(8)	C(9)-C(7)-C(2a)	117.6(5)
C(7)-C(9)	1.490(8)	O(12)-C(10)-C(3)	114.8(5)
C(7)-C(2a)	1.508(7)	O(12)-C(10)-C(11)	119.4(5)
C(10)-C(11)	1.491(8)	C(3)-C(10)-C(11)	125.8(6)
C(2a)-C(5a)	1.577(7)	C(3)-C(2a)-C(5a)	103.7(4)
		C(2)-C(2a)-C(5a)	85.1(4)
		C(2)-C(2a)-C(3)	113.5(4)
		C(7)-C(2a)-C(5a)	117.6(5)
		C(3)-C(2a)-C(7)	116.3(4)
		C(2)-C(2a)-C(7)	116.1(5)
		O(1)-C(5a)-C(5)	111.3(5)
		O(1)-C(5a)-C(2a)	89.6(4)
		C(5)-C(5a)-C(2a)	108.2(4)
		O(1)-C(5a)-C(6)	111.2(5)
		C(5)-C(5a)-C(6)	115.9(5)
		C(6)-C(5a)-C(2a)	117.8(5)

(a) The e.s.d.'s are given in parentheses.

Table 3
Intermolecular Distances Shorter than 3.65 Å

C(11)...O(8)	(x, 1+y, z)	3.122
C(11)...O(1)	(1-x, -y, 1-z)	3.277
C(5)...O(8)	(0.5 + x, -0.5-x, z)	3.380
C(10)...O(1)	(1-x, -y, 1-z)	3.417
C(13)...O(8)	(0.5-x, 0.5 + y, 1-z)	3.479
C(11)...C(2)	(1-x, -y, 1-z)	3.605
C(9)...O(14)	(1-x, -y, -z)	3.613

cm⁻¹ characteristic of a CO-C=C-O-system. The pmr spectrum showed three singlets attributable to three methyl groups, a doublet for a methyl group coupled with a CH, which resonated as a quartet, and a multiplet for a methylene system.

For the isomer **6** two structures, **6a** and **6b**, could be considered on the basis of the structure of **5** and the spectral data:
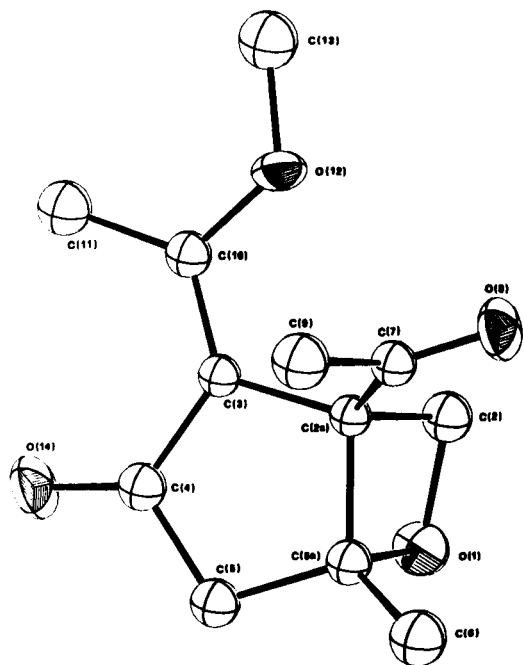
Scheme 4
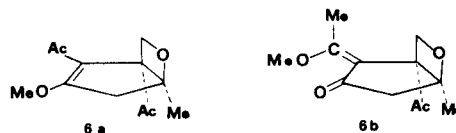
Figure. ORTEP drawing of the molecule with 30% probability thermal ellipsoids and atom labelling system used in the crystallographic analysis.

It seems reasonable to suppose that compound **6** would have structure **a**, in view of the differences in chemical stability and in spectral data in comparison with those of compound **5** (for instance see δ 2.99 and 2.63 ppm respectively for the methylene group of the cyclopentane ring in the pmr spectra).

Reaction Mechanism.

For the formation of the cyclopenta-oxetane ring system we can exclude a nucleophilic attack of the OH group at the methylene of the cyclopentane ring of compound **4**. In fact **4** was recovered unchanged when it was treated with diazomethane under the same conditions. Thus a nucleophilic attack from the OH group on the methylene of the expected intermediate pyrazoline seems more attractive. Out of the expected cyclopentapyrazolines **8** and **9** only

Scheme 5
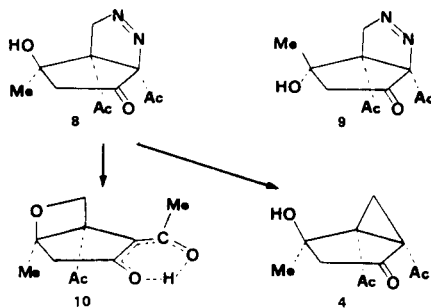
the first one has the correct stereochemistry for such an attack. Thus decomposition of the pyrazoline **8** gives compound **10** and the bicyclo[3.1.0]hexane **4**.

Under the reaction conditions **10** reacts with diazomethane to give the methoxy-derivatives **5** and **6**.

In the case of the pyrazoline **9** the nitrogen elimination can lead only to the bicyclo[3.1.0]hexane **3**.

From a consideration of the relative amounts (9) of compounds **3,4,5,6** we must conclude that the presence of the OH group in β position is very effective.

EXPERIMENTAL

Ir spectra were measured for dispersions in potassium bromide with a Perkin-Elmer 457 spectrometer and uv spectra for solutions in methanol with a Cary 14 recording spectrophotometer. The pmr spectra were recorded for solutions of deuteriochloroform with a Perkin-Elmer R 32; chemical shifts are reported in ppm down-field from tetramethylsilane as internal reference and coupling constants in Hz.

Reaction of 2,3-Diacetyl-4-hydroxy-4-methylcyclopent-2-en-1-one (**2**) with Diazomethane.

A solution of the cyclopentenone **2** (1 g) in ether (30 ml) was treated with ethereal diazomethane (0.43 g) at 0° and allowed to stand at this temperature for 3 hours. The solvent was evaporated and the residue (9) was chromatographed on silica gel with ether/petroleum ether (3:1, v:v) as eluent.

The first fraction consisted of compound **4**, mp 77-78° (from cyclohexane) (41 mg, 3.8%).

The second fraction consisted of the isomer **3**, mp 100-101° (from benzene) (290 mg, 27%).

The third fraction consisted of compound **5**, mp 128-130° (from petroleum ether) (58 mg, 5.1%); ir: 1710 (CO), 1680 (CO), 1580 cm⁻¹ (CO-C=C-O-); uv: λ max 280 nm (log ε 4.10); pmr δ 1.43 (s, 3H, CH₃), 1.94 (s, 3H, CH₃), 2.56 (s, 3H, CH₃), 2.63 (AB, 2H, CH₂, J = 18 Hz), 3.72 (s, 3H, OCH₃), 3.98 (d, 1H, CH, J = 5.6 Hz), 5.34 (d, 1H, CH, J = 5.6 Hz).

Anal. Calcd. for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19. Found: C, 64.42; H, 7.17.

The fourth fraction consisted of compound **6**, mp 94-96° (from cyclohexane) (40 mg, 3.5%); ir: 1705 (CO), 1640 (CO), 1600 cm⁻¹ (CO-C=C-O-); uv: λ max 269 nm (log ε 4.12); pmr: δ 1.42 (s, 3H, CH₃), 2.04 (s, 3H, CH₃), 2.38 (s, 3H, CH₃), 2.99 (AB, 2H, CH₂, J = 18 Hz), 3.96 (s, 3H, OCH₃), 4.1 (d, 1H, CH, J = 6.0 Hz), 5.30 (d, 1H, CH, J = 6.0 Hz).

Anal. Calcd. for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19. Found: C, 64.12; H, 7.06.

Isomerisation of the Cyclopenta[b]oxetane **5**.

Compound **5** was not very stable and when absorbed on silica gel for a few hours isomerised into 2-(1-methoxyethylidene)-3-acetyl-3-hydroxymethyl-4-methylcyclopent-4-en-1-one **7**, mp 172-173° (from cyclohexane) (quantitative yield); ir: 3360 (OH), 1715 (CO), 1665 (ring CO), 1590 cm⁻¹ (CO-C=C-O-); uv: λ max 221, 230 sh, 253, 291, and 310 sh nm (log ε 3.87, 3.83, 3.91, 3.99, and 3.84); pmr: δ 1.90 (s, 3H, CH₃), 2.03 (d, 3H, CH₃, J = 1.2 Hz), 2.56 (s, 3H, CH₃), 3.76 (s, overlapping a very broad signal, 4H, OCH₃ + OH), 4.25 (m, 2H, CH₂), 6.24 (q, 1H, CH, J = 1.2 Hz).

Anal. Calcd. for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19. Found: C, 64.56; H, 6.98.

Crystal Data.

Compound **5** has the molecular formula $C_{12}H_{16}O_4$, molecular weight 224.26, and occurs as monoclinic crystals with cell dimensions: a = 14.230(9), b = 8.499(5), c = 9.896(9) Å, β = 99.43(8)° (from least squares refinement of 2θ values of 18 reflections). The crystals are in the space group $P2_{1/a}$, V = 1182.27 Å³, D_x = 1.26 g.cm⁻³ (Z = 4). A small crystal of approximate dimensions 0.07 × 0.15 × 0.08 mm was mounted on a Philips automated diffractometer (graphite monochromator, Mo-Kα radiation, λ = 0.7107°).

The reflection were collected within $2\theta < 60°$ by $\omega/2\theta$ step-scan (scan speed 0.03° /second⁻¹, scan range 1.2°). Two standard reflections monitored periodically showed no significant variation. After correction for Lorentz and polarization effects, 662 reflections with $I > 2\sigma$ (I) were considered observed and used in the structure solution and refinement.

Structure Refinement.

The structure was solved by use of automatic centrosymmetric direct methods of the SHELX (1976) program system (10). All the non-hydrogen atoms were located in the E-map. Two cycles of full matrix least squares refinement with unit weight and isotropic temperature factors reduced R to 0.11. Two cycles of least squares refinement with anisotropic temperature factors for all the oxygen atoms reduced R factor to 0.089. A difference Fourier synthesis calculated at this point showed all the hydrogen atoms. Introduction of these atoms with a temperature factor of U of 0.07 Å² without any further refinement gave an R factor of 0.07. Two additional least squares cycles on non-hydrogen atom parameters gave the final R factor of 0.043. The weighting scheme used was w = $(\sigma^2(F_o) + 0.007\ F_o^2)^{-1}$, where $\sigma(F_o)$ is the individual estimated standard deviation for each reflection from diffractometer counting statistics. The corresponding R_w was 0.049.

Hydrogen atom coordinates, bond distances and angles involving hydrogen atoms, least squares plane equations from the planes and angles between selected planes as well as observed and calculated structure factors are reported in Tables 4-7 (11).

Acknowledgement.

The authors wish to thank Professor Mammi for the use of a diffractometer at the Istituto di Chimica Organica dell'Università di Padova.

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(9) In order to ascertain the relative amounts of the products, the residue was dissolved in ether/petroleum ether (1:1, v/v) and filtrated through silica gel. The relative ratios were determined by pmr spectroscopy and they resulted to be **3:4:5:6** = 42:19:17:20.

(10) G. M. Sheldrick, SHELX program system. University Chemical Laboratory, Lensfield Road, Cambridge, England.

(11) Tables 4-7 are available from the authors.