X-Ray Crystal Structure of 9-Methyl-3-oxo-2-oxabicyclo[4.4.0]dec-4-ene-6,9-carbolactone. Revised Structure of Iodolactonization Product of 9-Methyl-3-oxo-2-oxabicyclo[4.4.0]deca-4,8-diene-6-carboxylic Acid

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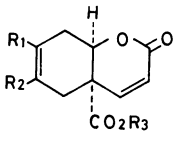
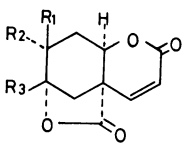
Synopsis. The structure of the title compound, deiodo lactone compound, was determined by X-ray crystallographic analysis: The results lead to a revision of the previously proposed structure for iodolactonization product of 9-methyl-3-oxo-2-oxabicyclo[4.4.0]deca-4,8-diene-6-carboxylic acid.

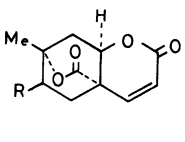
Previously, we have reported that hydrolysis of the Diels-Alder adducts (**1a** and **1b**) of methyl 2-oxo-2*H*-pyran-5-carboxylate with isoprene to the corresponding acids, 9- and 8-methyl-3-oxo-2-oxabicyclo-[4.4.0]deca-4,8-diene-6-carboxylic acid (**2a** and **2b**), followed by iodolactonization, gave iodo lactones (**3a** and **3b**), respectively.[1] Since the proposed structure **3a** was inconsistent in some respects with a recent examination of the off-resonance ^{13}C-NMR spectrum, which showed doublet signal at δ 22.5 due to CH–I and singlet signal at δ 84.3 due to C–O,[2] the structure of the iodo lactone was reinvestigated in detail, resulting in a revision to 8-iodo-9-methyl-3-oxo-2-oxabicyclo-[4.4.0]dec-4-ene-6,9-carbolactone (**4**) from **3a**.[3] In addition, reduction of the iodo lactone with tributyltin hydride afforded the deiodonation product, whose structure was confirmed unambiguously to be 5,9-dioxatricyclo [6.2.2.0^{1,6}]dodecane compound (**5**) by X-ray crystallographic analysis. In this paper, we report on the crystal structure of **5** and the structural revision of iodolactonization product (**3a**→**4**).



1a R1=R3=Me, R2=H
1b R1=H, R2=R3=Me
2a R1=Me, R2=R3=H
2b R1=R3=H, R2=Me



3a R1=I, R2=Me, R3=H
3b R1=I, R2=H, R3=Me



4 R=I
5 R=H
6 R=SePh

Experimental

9-Methyl-3-oxo-2-oxabicyclo[4.4.0]dec-4-ene-6,9-carbolactone (5). To a solution of 120 mg of iodo lactone **4**[1] in 5 ml of dry toluene was added 200 mg of tributyltin hydride (97%) with stirring at 5 °C under N_2. After stirring was continued for 7 h at 5 °C and then for 24 h at room temperature, methanol was added to the reaction mixture. The solvent was removed *in vacuo* at room temperature to give colorless oil which was chromatographed on silica gel using dichloromethane as eluent to afford 55 mg of **5**; colorless prisms, mp 97—99 °C recrystd from benzene–hexane; IR($CHCl_3$) 1760—1730 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ=1.46 (3H, s, C_9–CH_3), 1.72—2.66 (6H, m, 3×–CH_2–), 4.62 (1H, dd, J=4.8 and 9.6 Hz, C_1–H), 5.96 and 7.24 (each 1H, d, J=10.2 Hz, C_4– and C_5–H); MS m/z 208 (M^+); Found: C, 63.56; H, 5.81%. Calcd for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81%.

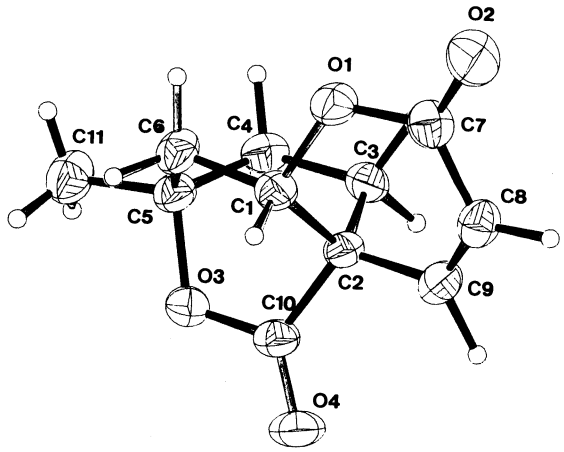


Fig. 1. Perspective view of the X molecule.

X-Ray Measurement. A colorless, single crystal with dimensions of about 0.4×0.4×0.4 mm^3 was used. The crystal data are as follows: $C_{11}H_{12}O_4$, mol wt 208.2, triclinic, space group $P\bar{1}$, a=7.601(1), b=11.179(1), c=12.147(1) Å, α=85.26(1), β=80.18(1), γ=80.57(1)°, Z=4, D_c=1.38 g cm^{-3}. The cell dimensions and diffraction intensities were measured on an automated, four-circle diffractometer with graphite-monochromated, Mo $K\alpha$ radiation (λ=0.7107 Å). The 2θ—ω scan technique was applied at a variable scan rate. Three standard reflections, measured at intervals of every 200 reflections, showed no significant decrease in intensities during the course of data collection. The intensities were corrected for the Lorentz and polarization factors, but not for the absorption or extinction effect. In the range of 2θ values up to 55°, 3707 unique structure factor magnitudes above the $3\sigma(F)$ level were selected for the structure determination.

Structure Determination

The structure was solved by direct method, MULTAN 78.[4] Tangent procedure was carried out using 220 $|E|$ values above 2.03. E-map revealed the locations of 24 non-hydrogen atoms. The rest 6 non-hydrogen atoms had been located in difference Fourier map. Some of hydrogen atoms had also been located in the above map and other hydrogen ones at calculated position. The structure refined by the block-diagonal least-squares method in UNICS III[5] program system with anisotropic temperature factor for non-hydrogen

Table 1. The final atomic parameters and estimated standard deviations[a)]

Atom	x	y	z	B_{eq}/Å^2[b)]
O(1)X	3530(3)	2819(2)	6232(2)	4.85
O(2)X	6230(4)	2267(2)	5293(2)	7.16
O(3)X	67(3)	5140(2)	8390(2)	4.51
O(4)X	1816(4)	6544(2)	7900(2)	5.85
C(1)X	2242(4)	3840(2)	6676(2)	4.00
C(2)X	3063(4)	4449(2)	7503(2)	3.72
C(3)X	3332(4)	3583(3)	8543(2)	4.23
C(4)X	1514(5)	3256(3)	9120(3)	4.63
C(5)X	61(4)	3809(3)	8441(3)	4.21
C(6)X	515(4)	3399(3)	7248(3)	4.70
C(7)X	5236(5)	3031(3)	5831(3)	4.99
C(8)X	5769(4)	4157(3)	6119(3)	4.78
C(9)X	4791(4)	4820(3)	6915(3)	4.58
C(10)X	1639(4)	5492(2)	7926(2)	4.18
C(11)X	−1822(5)	3652(3)	8994(3)	6.06
O(1)Y	2708(3)	2900(2)	2892(2)	5.80
O(2)Y	776(4)	3831(2)	4217(2)	6.79
O(3)Y	5243(3)	−325(2)	1518(2)	5.85
O(4)Y	2717(4)	−1089(2)	2053(2)	7.13
C(1)Y	3100(5)	1868(3)	2159(3)	5.11
C(2)Y	3082(4)	716(2)	2894(3)	4.26
C(3)Y	4576(5)	577(3)	3635(3)	5.65
C(4)Y	6389(6)	550(4)	2908(3)	6.51
C(5)Y	6178(5)	680(3)	1708(3)	5.11
C(6)Y	4984(5)	1852(3)	1426(3)	5.66
C(7)Y	1276(5)	2911(3)	3737(3)	5.41
C(8)Y	421(5)	1829(3)	3954(3)	6.02
C(9)Y	1268(5)	771(3)	3585(3)	6.23
C(10)Y	3611(5)	−321(3)	2134(3)	4.81
C(11)Y	7974(6)	522(4)	943(4)	8.45

a) The atomic coordinates are multiplied by 10^4. b) W.C. Hamilton, *Acta Crystallogr.*, **12**, 609 (1959).

atoms and isotropic ones for hydrogen atoms. The final R value was 0.071.[6)] Atomic scattering factors were taken from the International Tables for X-Ray Crystallography.[7)] The final atomic parameters are listed in Table 1. The two crystallographically independent molecules of **5**, X and Y, have the almost same geometries containing those absolute configurations.[6)] From the above results, the structure of **5** was shown to be 9-methyl-3-oxo-2-oxabicyclo-[4.4.0]dec-4-ene-6,9-carbolactone.

References

1) T. Matsui, T. Inoue, M. Nakayama, and J. D. White, *Bull. Chem. Soc. Jpn.*, **56**, 647 (1983).

2) Preliminary assignments of the ^{13}C-NMR spectra for these compounds are corrected as follows; **4**: δ=22.5 (C_8), 26.4 (C_9–CH_3), 33.9 and 35.5 (C_7 and/or C_{10}), 43.4 (C_6), 74.5 (C_1), 84.3 (C_9), 122.3 (C_4), 143.6 (C_5), 161.9 (C_3), 169.6 (–CO_2– of C_6); **3b**: δ=20.7 (C_9), 25.5 (C_8–CH_3), 36.1 and 37.9 (C_7 and/or C_{10}), 49.4 (C_6), 73.6 (C_1), 86.7 (C_8), 123.5 (C_4), 144.4 (C_5), 162.8 (C_3), 172.7 (–CO_2– of C_6).

3) More recently, Colvin and Brown reported that both iodo- and seleno-lactonization of acid (**2a**) gave the corresponding lactones (**4** and **6**); B. A. Brown and E. W. Colvin, *J. Chem. Soc., Chem. Commun.*, **1984**, 1514.

4) P. Main, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq, and M. M. Woolfson, 1978, "MULTAN 78, A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data," University of York, England.

5) T. Sakurai and K. Kobayashi, *Rikagaku Kenkyusho Hokoku*, **55**, 69 (1979).

6) The complete *Fo* and *Fc* data, a table of bond length, and a figure of the cell contents perpendicular to bc plane are deposited at the Office of the Editor of the Bulletin of the Chemical Society of Japan (Document No. 8548).

7) "International Tables for X-Ray Crystallography," The Kynoch Press, Birmingham (1974), Vol. IV.