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ONE-STEP SYNTHESIS AND CRYSTAL STRUCTURE OF A NEW MONOTERPENE DERIVATIVE WITH THREE DIFFERENT HETEROATOMS

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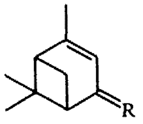
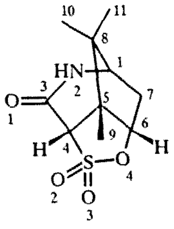
The reaction of the oxime of verbenone, a bicyclic ketone, with sulfuric acid in acetonitrile gives a lactamsultone, which is readily separated and whose structure was demonstrated by x-ray diffraction structural analysis.

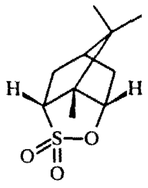
The bicyclic ketone, verbenone (Ia), is a well known natural monoterpenoid [1]. The oxime of this ketone Ib [2] undergoes the Beckmann rearrangement upon reaction with toluenesulfonyl chloride in pyridine to give the corresponding lactam in 72% yield [3]. We have found that the reaction of oxime Ib with concentrated sulfuric acid in acetonitrile is more complicated and a readily isolable crystalline product $C_{10}H_{15}NO_4S$ (II) is formed in 38% yield. The structure of II was established by x-ray diffraction structural analysis (a single numbering system for this compound shown below was used for the x-ray diffraction structural analysis and spectral data).



Ia–c



II



III

Ia R = O, b R = NOH, c R = H_2

The crystal of lactamsultone II is formed by two independent molecules. The structure of one of these types is shown in Fig. 1. The bond lengths and angles of the two independent molecules are identical within the error margins. The differences in the torsion angles are more significant and reach 5.7(6)° for $C_{(4)}$—S—$O_{(4)}$—$C_{(6)}$. The bond lengths are similar to the corresponding standard literature values [4], although there is some elongation of the $C_{(4)}$—S (1.806(7) and 1.793(6) Å vs. 1.75 Å) and $C_{(6)}$—$O_{(4)}$ bonds (1.485(9) and 1.474(8) Å vs. 1.43 Å), apparently as a consequence of steric strain [5]. The amide fragment is planar and the departures of $C_{(5)}$ and $C_{(8)}$ from this plane are 0.16(1), 0.20(1) and 1.02(1), 1.05(1) Å, respectively, indicating that the conformation of this ring is close to half-boat. The five-membered heterocycle has envelope conformation with extrusion of $C_{(4)}$ from the ring plane by 0.68(1) and 0.69(1) Å. The molecules are linked in the crystal to form infinite chains along the *a*-axis by NH···O=C hydrogen bonds (N—H, 0.86; H···O, 1.97, 1.94; N···O, 2.830(7), 2.782(8) Å; N—H···O, 176°, 167°).

The starting oxime Ib was a racemic mixture with predominance of the (+)-enantiomer and a chromatographically uniform 3:1 crystalline mixture of the *syn* and *anti* isomers as indicated by the ratio of the integral intensities of the olefinic proton signals, which are identical in form and appear at 6.43 ppm for the *syn* isomer and 5.77 ppm for the *anti* isomer [6].

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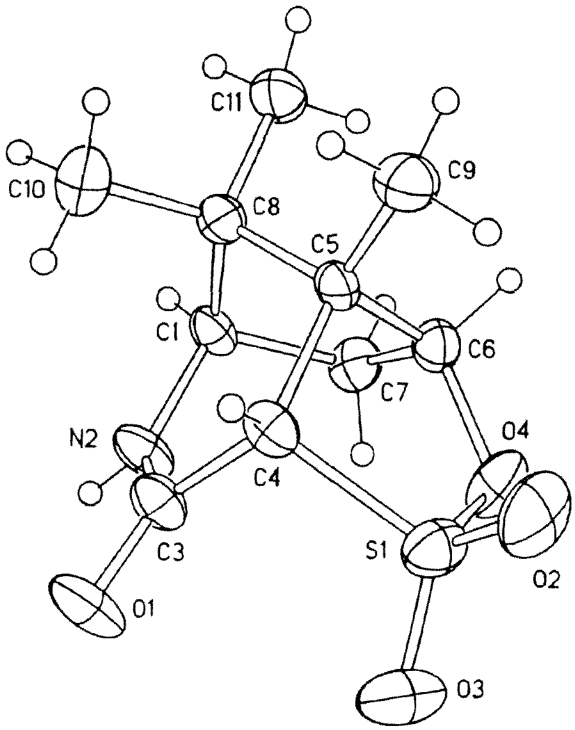

Fig. 1. Structure and numbering of the atoms in lactamsultone II. Some bond lengths (Å): $C_{(4)}$—S, 1.793(6), 1.806(7); S—$O_{(2)}$, 1.433(5), 1.413(6); S—$O_{(3)}$, 1.420(6), 1.419(7); S—$O_{(4)}$, 1.571(5), 1.577(7); $O_{(2)}$—$C_{(6)}$, 1.474(8), 1.485(9); $C_{(4)}$—$C_{(5)}$, 1.564(9), 1.576(9) Å.

In light of the molecular structure of lactamsultone II, oxime Ib undergoes a Beckmann rearrangement and addition of a $^{+}SO_3H$ cation at the carbon—carbon double bond with subsequent isomerization of the carbon skeleton and intramolecular neutralization of the carbocation site at the secondary carbon atom as proposed in the formation of γ-sultones from 1-(1-adamantyl)-1-alkanols [7]. The simplest γ-sultone with such bornane structure (III), was obtained in only 7.3% upon the treatment of α-pinene (Ic) SO_3·dioxane at −78°C in dioxane [8].

In light of the ease of isolating lactamsultone II, this reaction opens a simple and rather inexpensive pathway to a highly functionalized heteroatomic derivative of secobornane.

EXPERIMENTAL

The electron impact mass spectrum at 70 eV was taken on an MKh-1320 mass spectrometer. The IR spectrum was taken on UR-20 spectrometer for KBr pellets. The ^{1}H and ^{13}C NMR spectra were taken on a Bruker AM-400 spectrometer with TMS as the internal standard. The signals in the ^{13}C NMR spectrum were interpreted on the basis of the broadening of the carbon atom signals upon off-resonance irradiation (SFORD) and data of the two-dimensional ^{13}C—^{1}H NMR spectrum (COLOC). The optical rotation values were obtained using a POLAMAT polarimeter.

Oxime Ib was obtained according to Wienhaus and Schumm [2], mp 119-120°C, $[\alpha]_{580}^{23}$ +27.6° (c 3.41, ether) (mp 119-120°C, $[\alpha]_D$ +80° (ether) [2]). The ^{1H} NMR spectrum was taken in $CDCl_3$.

9,10,10-Trimethyl-2-oxo-7-oxa-8-thia-3-azatricyclo[4.2.1.1^{4,9}]decane 8,8-dioxide. A sample of 7 ml concentrated sulfuric acid was added over 1 h to a stirred solution of 2.5 g (0.015 mole) oxime Ib in 10 ml acetonitrile at 20-25°C. Stirring was continued for 6 h. The mixture was then maintained on a bath at 90°C for 12 h, cooled, and poured into 200 ml 10% aqueous ammonia. The solution was extracted with chloroform. The extract was dried over $MgSO_4$ and evaporated until a crystalline precipitate formed. The crystals were filtered off and washed on the filter with chloroform to give 1.4 g (38%) II, mp 276-278°C. IR spectrum: 770, 945, 1036, 1165 (SO_3), 1212, 1358, 1670 (NH), 1705 (C=O), 2890, 2980, 3080, 3200 cm^{-1} (NH). ^{1}H NMR spectrum (in pyridine-d_5): 0.78 (3H, s, CH_3), 0.98 (3H, s, CH_3), 1.39 (3H, s, 5-CH_3), 2.16 (1H, d.d,

TABLE 1. Coordinates ($\times 10^4$) and Equivalent Temperature Factors (Å^2, $\times 10^3$) of the Non-Hydrogen Atoms of Lactamsultone II

Atom	x/a	y/b	z/c	U_{eq}	x/a	y/b	z/c	U_{eq}
	Molecule 1				Molecule 2			
$C_{(1)}$	-8066(9)	12964(6)	1395(5)	41(2)	-2915(8)	7907(6)	3416(5)	42(2)
$N_{(2)}$	-7721(7)	14201(5)	1753(5)	48(2)	-2647(8)	6928(5)	2718(5)	46(1)
$C_{(3)}$	-6123(10)	14611(6)	1975(6)	45(2)	-1049(9)	6560(6)	2453(5)	41(2)
$C_{(4)}$	-4517(9)	13754(6)	1930(5)	40(2)	589(8)	7296(6)	2774(4)	35(1)
$C_{(5)}$	-4955(9)	12478(6)	1486(4)	37(1)	226(8)	8270(6)	3553(4)	40(1)
$C_{(6)}$	-5876(9)	11800(7)	2298(5)	44(2)	-650(9)	9339(6)	2974(5)	39(1)
$C_{(7)}$	-7876(10)	12054(7)	2212(5)	49(2)	-2686(9)	9147(7)	2965(6)	44(2)
$C_{(8)}$	-6552(9)	12627(6)	723(5)	40(2)	-1357(9)	7863(6)	4184(5)	42(2)
$C_{(9)}$	-3278(11)	11892(8)	1110(6)	59(2)	1964(10)	8619(8)	4123(6)	57(2)
$C_{(10)}$	-6170(12)	13533(8)	-54(6)	67(2)	-1057(12)	6624(8)	4657(7)	64(2)
$C_{(11)}$	-7032(12)	11404(7)	264(6)	61(2)	-1707(12)	8793(9)	4973(6)	65(2)
$O_{(1)}$	-5806(7)	15684(5)	2207(5)	66(2)	-837(6)	5651(5)	1959(4)	52(1)
$O_{(2)}$	-1971(7)	12916(8)	3143(4)	80(2)	3134(7)	8633(6)	2002(4)	66(2)
$O_{(3)}$	-4255(9)	14209(8)	3821(5)	86(2)	866(8)	7758(6)	876(4)	70(2)
$O_{(4)}$	-5115(8)	12242(6)	3232(4)	66(2)	-27(7)	9273(5)	1984(4)	55(1)
$S_{(1)}$	-3778(2)	13338(2)	3132(1)	57(1)	1325(2)	8211(2)	1804(1)	48(1)

J = 15.7 and 2.2 Hz, 7-H_{endo}), 2.56 (1H, d.d.d, J = 1.57, 9.0, 5.5 Hz, H_{exo}), 3.35 (1H, br.t, J = 6 Hz, 1-H), 4.57 (1H, br.s, 4-H), 5.04 (1H, d.d, J = 9.0 and 2.2 Hz, 6-H), 9.67 (1H, br.d, J = 6 Hz, NH). ^{13}C NMR spectrum (in pyridine-d_5): 16.07 ($C_{(9)}$), 19.48 and 21.46 ($C_{(10)}$ and $C_{(11)}$), 39.78 ($C_{(7)}$), 46.80 ($C_{(8)}$), 56.08 ($C_{(5)}$), 69.50 ($C_{(4)}$), 60.07 ($C_{(1)}$), 90.74 ($C_{(6)}$), 162.30 ppm ($C_{(3)}$). Mass spectrum, *m/z* (*I*, %): 245 (30, M^+), 217, 202, 166, 152, 138, 110 (100), 95, 84, 63. For the x-ray diffraction structural analysis, the product was recrystallized from acetone—ethyl acetate, mp 287-288°C, $[\alpha]_{580}^{20}$ +9.5° (c 1.05, pyridine). Found: C, 48.99, 49.02; H, 6.38, 6.41; N, 5.72, 5.75; S, 13.07, 13.23%. Calculated for $C_{10}H_{15}NO_4S$: C, 48.96; H, 6.16; N, 5.71; S, 13.07%.

X-ray Diffraction Structural Analysis of Lactamsultone II. The analysis was carried out on a Syntex $P2_1$ diffractometer using CuK_α radiation and a graphite monochromator. The unit cell parameters for the monoclinic crystals of II: a = 7.381(1), b = 11.108(2), c = 13.965 Å, V = 1144.2(4) Å^3, $C_{10}H_{15}NO_4S$, Z = 4, space group $P2_1$, d_{calc} = 1.424 g/cm^3. A total of 1800 independent reflections with $2\theta < 120°$ were measured by ω scanning (scan interval 1.5°) for a 0.05 × 0.3 × 1.2-mm^3 crystal. A correction was introduced for the diminution (95.7%) of the intensities of the control reflections and for absorption (using the SHELX-76 program, μ = 2.54 mm^{-1}, transmission 0.47-0.88). The structure was deciphered by the direct method using the SHELX-86 program and refined by the method of least squares over all F^2 using the SHELX-93 program in the full-matrix anisotropic—isotropic approximation to wR_2 = 0.1718, S = 1.00 (R = 0.0608 for 1599 $F > 4\delta$). The positions of the hydrogen atoms in each refinement cycle were calculated geometrically. The coordinates of the non-hydrogen atoms are given in Table 1.

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