Chemistry of Natural Compounds, Vol. 46, No. 4, 2010

ADDITION PRODUCTS OF CHLOROSULFONYLISOCYANATE TO (+)-3-CARENE AND α-PINENE ENANTIOMERS

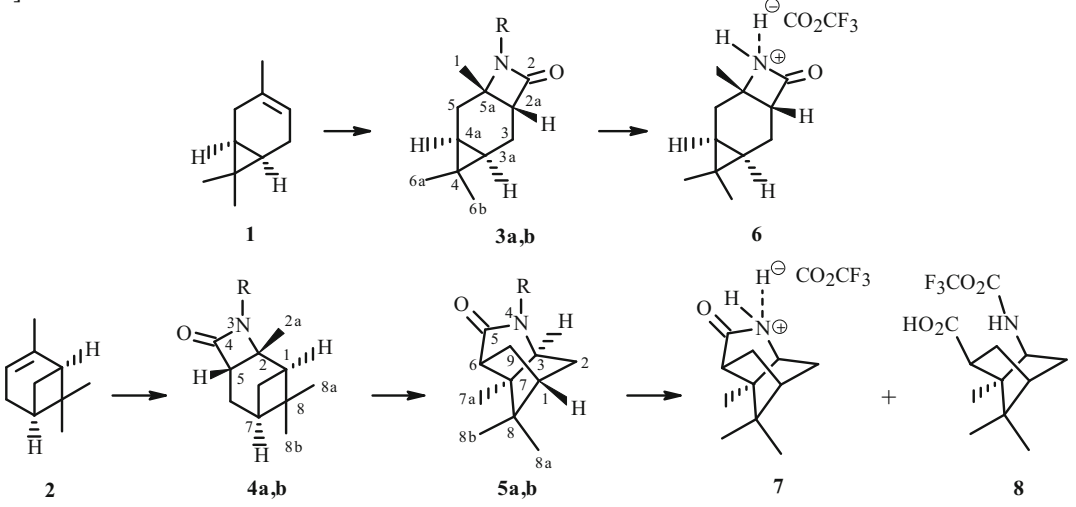
F. Z. Makaev,[1*] L. A. Vlad,[1] L. P. Bets,[1] S. T. Malinovskii,[1†]
K. N. Gavrilov,[2] and M. Gdanets[3]

UDC 547.318

Optically active lactams were synthesized from (+)-3-carene and α-pinene enantiomers. Their properties and structures were characterized. A pathway for preparing their trifluoroacetate salts was demonstrated.

Keywords: chlorosulfonylisocyanate, (+)-3-carene, (-)- and (+)-α-pinene, lactam-functionalized ionic liquids.

The reaction of chlorosulfonylisocyanate with (+)-3-carene (**1**) or α-pinene enantiomers (**2**) is known to form the corresponding β-lactams **3a** and **4a** [1]. The tendency of **4a** to undergo skeletal rearrangement into γ-lactam **5a** has been reported [1, 2].



The synthesis of **3b** was repeated during the development of an approach to optically active lactam-functionalized ionic liquids [3]. As it turned out, a compound with mp 66–67°C was isolated instead of the expected product with mp 108–111°C. Distinguishing features of the PMR spectrum of the isolated product were 3H singlets for a *gem*-dimethyl group of a cyclopropane ring, a C-1 methyl (here and henceforth the atomic numbering is given for sake of discussion and does not agree with IUPAC rules), and two 1H resonances for C-5 group in the ranges 2.22–2.31 and 2.57–2.65 ppm.

The weak-field region (at 3.08 ppm) contained a resonance for H-2a and no amide proton resonance. The resonance for C-2 in the ^{13}C NMR spectrum was located at weaker field (164.5) than that reported (148.3) [3]. The IR spectrum showed amide bands and characteristic bands for sulfonylchloride (see Experimental). These features in combination with the elemental analysis were consistent with structure **3a**.

In addition, we performed a full x-ray structure analysis (XSA) of the obtained product (Table 1).

†Deceased.

1) Institute of Chemistry of the Academy of Sciences of Moldova, Kishinev, MD-2028, Moldova, fax: 373 22 73 97 75, e-mail: flmacaev@cc.acad.md; 2) S. A. Esenin Ryazan State Pedagogical University, ul. Svobody, 46, 390000, Ryazan, Russian Federation; 3) A. Mickiewicz University, 60-780, Poznan, Poland. Translated from Khimiya Prirodnykh Soedinenii, No. 4, pp. 447–451, July–August, 2010. Original article submitted January 15, 2010.

 0009-3130/10/4604-0528

TABLE 1. Crystallographic Data, Experimental Conditions, and Structure Refinement of **3a** and **5a**

Compound	**3a**	**5a**
Empirical formula	$C_{11}H_{16}ClNO_3S$	$C_{11}H_{16}ClNO_3S$
Molecular weight	277.76	277.76
Temperature, K	294 (2)	100 (2)
Wave length, Å	0.71073	0.71073
System	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$
a, Å	7.2922 (8)	7.7694 (5)
b, Å	13.7364 (13)	11.7285 (8)
c, Å	13.7978 (14)	13.9317 (10)
V, Å^3	1382.1 (2)	1269.50 (15)
Z	4	4
ρ_{calcd}, g/cm^3	1.335	1.453
F (000)	584	584
Crystal size, mm	0.6 × 0.2 × 0.2	0.5 × 0.2 × 0.05
Absorption coefficient, mm^{-1}	0.424	0.461
θ measurement range, deg	4.08–25.02	4.30–26.37
Indices range	–6 ≤ h ≤ 8; –15 ≤ k ≤ 16; –16 ≤ l ≤ 11	–9 ≤ h ≤ 9; –13 ≤ k ≤ 14; –17 ≤ l ≤ 17
Number of measured reflections	7513	15148
Number of independent reflections	2431 [*R*(int) = 0.0247]	2583 [*R*(int) = 0.0244]
Number of refined parameters	173	154
GOOF over F^2 (S)	1.017	1.129
R-factor [$I \geq 2\sigma(I)$]	*R*1 = 0.0389, w*R*2 = 0.0998	*R*1 = 0.0347, w*R*2 = 0.0954
R-factor (over whole data set)	*R*1 = 0.0531, w*R*2 = 0.1091	*R*1 = 0.0363, w*R*2 = 0.0966

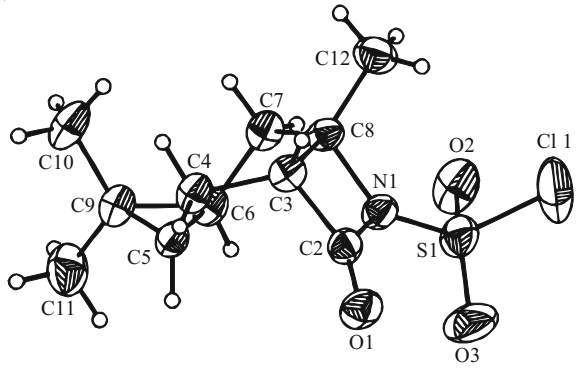


Fig. 1. Molecular structure of **3a**.

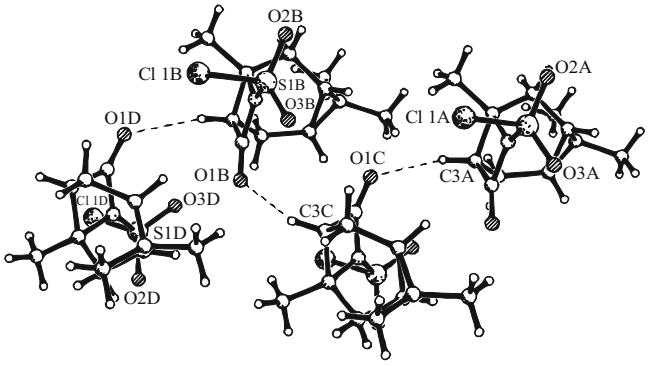


Fig. 2. A portion of the crystal packing of **3a**.

The molecule of **3a** consists of methylcyclohexane, *gem*-dimethylcyclopropane, and *β*-lactam rings. It should be noted that the last ring contains a statistically disordered sulfonylchloride group with occupancy factor 0.833(3). This indicates that the crystal contains a mixture of two conformers in a 0.833:0.167 ratio that differ in the torsion angle along the S–N bond and are situated relative to each other by 180° around this bond. Moreover, the Cl–S and S–O interatomic distances are less than 2.000(2) and 1.430(3) Å, respectively, whereas the S atom deviates from the plane of the lactam ring by 0.216(5) Å. The conformation of the methylcyclohexane ring can be described as a distorted half-chair. The dihedral angle formed by the C4–C5–C6–C7 and C3–C4–C7–C8 fragments is 45.6(2)°. The cyclopropane and *β*-lactam rings are fused to the cyclohexane ring through C5–C6 and C3–C8 bonds, respectively, forming dihedral angles of 41.1(2) and 87.5(1)° with the mean-square plane of the cyclohexane ring. The torsion angle H5–C5–C6–H6 is –0.1°. The two substituents C10 and C11 deviate from the plane of the cyclopropane ring by 1.206(7) and –1.293(7) Å (Fig. 1).

Hydrogen-bonding plays an important role in the crystal packing. H-bond C3–H3...O1 [0.5 + x, –0.5 – y, –1 –z] has parameters 3.292(7) Å; C3–H3 0.98; H3...O1 2.49. The angle at H3 is 140°. Figure 2 shows a portion of the chain structure in the crystal packing.

Other researchers have reported without giving the NMR spectra that the compound is a liquid [1].

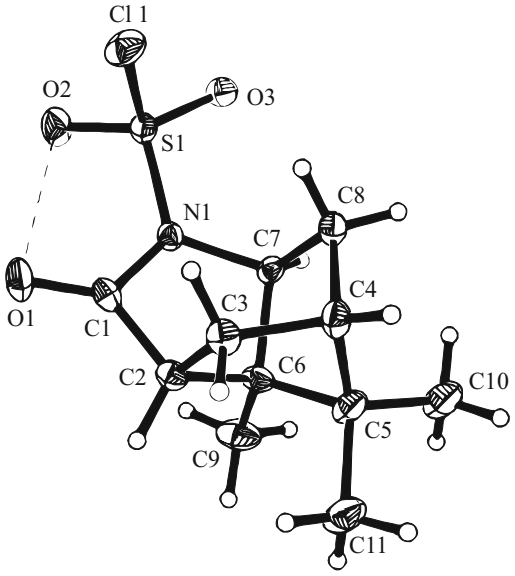


Fig. 3. Molecular structure of **5a**.

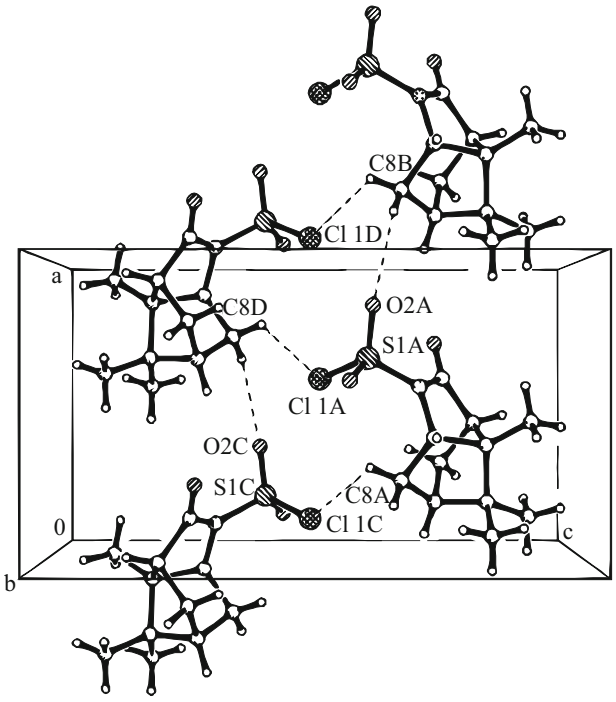


Fig. 4. A portion of the crystal packing of **5a**.

Subsequent work up of **3a** with Et_3N and H_2O gave lactam **3b**, which was also synthesized from **1** without isolating **3a**. However, the overall yield was 8% lower than for the chain of transformations **1** → **3a** → **3b**.

Monitoring of the course of the addition of chlorosulfonylisocyanate to (–)-pinene (**2**) (TLC and GC) showed that the solution contained several products, the ratio of which varied with time (24 h). These observations agreed with those of other researchers [4].

The product that crystallized after distilling off solvent had mp 74–76°C and was identified as sulfonylchloride **5a** [5] whereas recrystallization from hexane gave a product that melted at 82–84°C and did not agree with data for **4a** [2]. The IR and PMR spectra agreed with those for **5a**. However, the melting point of our sample differed from that reported [5], for which an XSA was performed. This prompted us to perform our own XSA. The rather high (0.0938) *R*-factor given before [5] probably did not enable the H atom to be objectively located. Therefore, the configuration of the resulting chiral centers and the crystal packing of the compound were not discussed.

Figure 3 shows the isolated molecule containing sulfonylchloride, $C_{11}H_{16}ClNO_3S$, which consists of three cyclopentane rings fused to each other. The conformations of the cyclopentane rings are described as an envelope with atom C5 deviating from the planes of C2,C3,C4,C6 and C4,C6,C7,C8 by 0.852(4) and 0.845(4) Å, respectively. Atom C6 deviates from the plane of C1,N1,C7,C2 by –0.649(4) Å. The C10 and C11 methyls are situated on different sides of the three-atom plane C4,C5,C6 at distances of –1.229(6) and 1.253(6) Å, respectively. The sulfonylchloride group is bonded to N1. The S atom deviates from the plane of C1,N1,C7,C2 by 0.508(4) Å.

Figure 4 shows a portion of the crystal packing of **5a** that includes intermolecular H-bonds C8–H8...Cl1 [0.5 + x, 1.5 – y, –z] of 3.510(2) Å and C8–H8...O2 [1 + x, y, z] of 3.201(2). The H8...Cl1 and H8...O2 distances are 2.85 and 2.56 Å, respectively. The angles around H8 are 125 and 122°, respectively.

Reaction of **5b** with trifluoroacetic acid gave a mixture of products **7** and **8**. According to an analysis of the PMR signal strengths for methyl protons H-7a at 1.56 and 1.78 ppm, the ratio of compounds was 3:1. The spectrum of the major product had a doublet for the C-3 proton (5.05 ppm) and 1H singlets for the trifluoroacetate and amide (7.19, 7.83). Moreover, the PMR exhibited a 6H multiplet at 1.33–2.94 for H-1, H-2, H-9, and H-6. The ^{13}C NMR spectrum in the weak-field region had doubled resonances for two C=O groups at 177.57, 177.58, 181.95 and 187.11 ppm. The mixture of **7** and **8** was synthesized alternately by storing **4b** in trifluoroacetic-acid solution at room temperature (see Experimental). Under these conditions, skeletal rearrangement occurred in addition to salt formation.

The reaction of **3b** in trifluoroacetic acid gave trifluoroacetate **6** in quantitative yield. It was identified based on analytical and spectral data.

Thus, addition products of chlorosulfonylisocyanate to (+)-3-carene and α-pinene enantiomers were synthesized; characterized by physical constants, structures, and properties; and hydrolyzed. A pathway for preparing trifluoroacetate salts of optically active lactams was demonstrated. The catalytic properties of the synthesized lactam-functionalized ionic liquids are currently under study. The results will be reported separately.

EXPERIMENTAL

Melting points were measured on a Kofler heating stage. IR spectra were recorded on a Perkin–Elmer Spectrum 100 FTIR spectrometer. PMR and ^{13}C NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 solutions (2–3%) on Bruker Avance III (400.13 and 100.61 MHz) and AC-80 (80 and 20 MHz) spectrometers with TMS internal standard. Specific rotation was recorded in $CHCl_3$ or MeOH on an automated Jasco-2000 polarimeter. Elemental analyses of all compounds were performed on an Elementar Vario LIII instrument and agreed with those calculated.

Column chromatography used silica gel (SiO_2, 40/63 μm, Fluka); TLC, silica gel 60 F_{254} plates (Merck). Compounds were detected with phosphotungstic acid (5%) in EtOH.

(+)-3-Carene {**1**, Aldrich, 90%, $[\alpha]_D^{20}$ +14.72° (*c* 0.0339)}; (+)-α-pinene {**2**, Fluka, 98%, $[\alpha]_D^{20}$ +50.32° (*c* 0.064)}, (–)-λ-pinene {**2**, Fluka, 98%, $[\alpha]_D^{20}$ –58.48° (*c* 0.046)} and chlorosulfonylisocyanate (Aldrich, 98%) were purchased commercially.

(–)-(2a*R*,3a*R*,4a*S*,5a*S*)-4,4,5a-Trimethyl-2-oxoperhydrocyclopropa[4,5]benzo[*b*]azet-1-sulfonylchloride (3a). A. A mixture of **1** (2.72 g, 20 mmol) and chlorosulfonylisocyanate (2.84 g, 20 mmol) in ether (50 mL) was stirred for 9 h and then treated dropwise with Na_2SO_3 (3.78 g) solution and then aqueous KOH (20%) until the pH was 8 [3]. The usual work up gave an oily product (3 g) that crystallized from hexane (5 mL) to afford **3a** (1.87 g, 34%), mp 66–67°C (hexane), lit. [1] colorless oil, $[\alpha]_D^{20}$ –7.11° (*c* 0.1, $CHCl_3$). IR spectrum (mineral oil, ν, cm^{-1}): 1812 (CON), 1401, 1170 (SO_2Cl).

PMR spectrum (400 MHz, $CDCl_3$, δ, ppm, J/Hz): 0.80 (2H, m, H-3a, H-4a), 0.99, 1.07 (6H, ss, H-6a, H-6b), 1.11 (2H, m, H_α-3, H_α-5), 1.69 (3H, s, H-1), 2.28 (1H, ddd, J = 2.36, 7.81, 17.79, H_β-3), 2.66 (1H, dd, J = 7.83, 16.47, H_β-5), 3.09 (1H, dd, J = 2.39, 4.62, H-2a).

^{13}C NMR spectrum (100 MHz, $CDCl_3$, δ, ppm): 16.76 (C-6a), 16.89 (C-1), 16.89 (C-4), 17.36 (C-6b), 18.23 (C-3), 23.80 (C-3a), 26.60 (C-5), 27.96 (C-4a), 55.82 (C-2a), 68.78 (C-5a), 164.46 (C-2).

B. A mixture of **1** (5 g, 37 mmol) and chlorosulfonylisocyanate (5.25 g, 37 mmol) in ether (65 mL) was stored for 12 h. The solvent was distilled off to give an oil (10 g) that crystallized from hexane (25 mL) to afford **3a** (8.2 g, 81%) that was identical to that from method A.

(+)-β-Lactam 3b. A. A mixture of **3a** (0.5 g, 2 mmol) and Et_3N (0.48 g, 2 mmol) in ether (5 mL) was stirred for 30 min, treated with H_2O (2 mL), and stirred for another 3 h. The usual work up with Na_2SO_3 and KOH solutions isolated an oil (0.32 g) that crystallized from hexane (3 mL), mp 105–108°C. Repeated crystallization from hexane gave **3b** (0.29 g, 91%), mp 109–110°C, lit. mp 111–114°C [1] and 108–111°C [3], $[\alpha]_D^{20}$ +30.14° (*c* 0.106, $CHCl_3$). IR spectrum (mineral oil, ν, cm^{-1}): 3233 (NH), 1769 (CON).

PMR spectrum (400 MHz, $CDCl_3$, δ, ppm, J/Hz): 0.6 (2H, m, H-3a, H-4a), 0.93, 1.02 (6H, ss, H-6a, H-6b), 1.25 (2H, m, H_α-3, H_α-5), 1.36 (3H, s, H-1), 2.00 (1H, ddd, J = 2.36, 7.81, 17.79, H_β-3), 2.16 (1H, dd, J = 7.83, 16.47, H_β-5), 2.68 (1H, dd, J = 2.5, 4.5, H-2a), 6.0 (br.s, NH).

^{13}C NMR spectrum (100 MHz, $CDCl_3$): 15.10 (C-6a), 16.71 (C-1), 17.25 (C-4), 17.27 (C-6b), 17.64 (C-3), 25.79 (C-3a), 27.94 (C-5), 28.23 (C-4a), 52.90 (C-2a), 53.48 (C-5a), 170.90 (C-2).

B. A mixture of 3-carene (**1**, 2.72 g, 20 mmol) and chlorosulfonylisocyanate (2.84 g, 20 mmol) in ether (50 mL) was stirred at room temperature for 18 h and then treated dropwise with Et_3N (2.84 g, 20 mmol). A white fluffy precipitate formed and disappeared upon adding H_2O (10 mL). Stirring was continued for an additional 30 min. The usual work up isolated an oily product (3 g) that crystallized from hexane to afford **3b** (1.79 g, 50%) that was identical to that from method A.

(–)-β-Lactam 4b. A mixture of (–)-α-pinene (**2**, 1.36 g, 10 mmol) and chlorosulfonylisocyanate (1.43 g, 10.12 mmol) in ether (25 mL) was stirred for 1 h at room temperature, treated dropwise with Et_3N (4.08 g, 40 mmol), stirred for another 3 h, treated dropwise with H_2O (15 mL), and left overnight. The usual work up isolated an oily product (1.61 g) that crystallized from benzene (5 mL) to afford **4b** (1.48 g, 83%), mp 150–153°C, $[\alpha]_D^{20}$ –94.5° (*c* 0.1, MeOH), lit. mp 110–112°C [1] and 144–147°C [6], $[\alpha]_D^{20}$ –96.0° (*c* 0.1, MeOH). IR spectrum (mineral oil, ν, cm^{-1}): 3200 (NH), 1720 (CON).

PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 0.92, 1.30 (6H, ss, H-8a, H-8b), 1.43 (3H, s, H-2a), 1.51 (1H, d, J = 0.92, H_α-9), 1.87 (1H, m, H_α-6), 1.97 (1H, m, H-7), 2.05 (1H, dd, J = 4.66, 6.04, H-1), 2.20 (2H, m, H_β-6, H_β-9), 2.84 (1H, d, J = 10.22, H-5), 5.96 (1H, br.s, NH).

^{13}C NMR spectrum (20 MHz, $CDCl_3$): 23.40 (C-8a), 25.09 (C-9), 25.54 (C-2a), 25.79 (C-8b), 27.88 (C-6), 42.34 (C-8), 50.38 (C-7), 50.49 (C-5), 59.31 (C-2), 59.20 (C-1), 173.90 (C-4).

(+)-β-Lactam 4b. A mixture of (+)-α-pinene (**2,** 1.36 g, 10 mmol) and chlorosulfonylisocyanate (1.43 g, 10.12 mmol) in ether (25 mL) was stirred for 1 h at room temperature, treated dropwise successively with Et_3N (1.5 g, 15 mmol) and H_2O (10 mL), stirred for another 6 h, and left overnight. The usual work up gave a product (1.61 g) that crystallized from benzene to afford **4b** (0.93 g, 52%), mp 149–150°C, $[\alpha]_D^{20}$ +92.31° (*c* 0.13, $CHCl_3$), lit. [5] $[\alpha]_D^{20}$ +96.5° (*c* 0.1). IR spectrum (mineral oil, ν, cm^{-1}): 1720 (CON), 3200 (NH).

(+)-Sulfonylchloride 5a. A mixture of (–)-α-pinene (**2**, 5 g, 37 mmol) and chlorosulfonylisocyanate (5.25 g, 37 mmol) in ether (50 mL) was stirred for 3 h at room temperature and left overnight to give a crystalline product, mp 74–76°C. Crystallization from hexane afforded **5a** (6.48 g, 64%), mp 83–85°C, $[\alpha]_D^{20}$ +48.73° (*c* 0.16, $CHCl_3$), lit. mp 85–87°C [1] and 75–76°C [5]. IR spectrum (mineral oil, ν, cm^{-1}): 1768 (CON), 1400, 1165 (SO_2Cl).

PMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 0.89, 0.92 (6H, ss, H-8a, H-8b), 1.07 (3H, s, H-7a), 1.62 (1H, d, J = 14, H_β-2), 1.54 (1H, d, J = 13.2, H_β-9), 1.96 (1H, m, H-1), 2.27 (2H, m, H_α-2, H_α-9), 2.60 (1H, dd, J = 11.1, 11.2, H-6), 4.34 (1H, d, J = 8, H-3).

^{13}C NMR spectrum (20 MHz, DMSO-d_6): 11.17 (C-7a), 18.60 (C-8a), 19.32 (C-8b), 32.68 (C-2), 34.15 (C-9), 45.91 (C-6), 47.56 (C-8), 48.79 (C-1), 68.18 (C-7), 95.86 (C-3), 173.01 (C-5).

(–)-Sulfonylchloride 5a. (+)-α-Pinene (**2**, 5 g, 37 mmol) and chlorosulfonylisocyanate (5.25 g, 37 mmol) were reacted analogously as for (+)-**5a** to afford the (–)-**5a** product (6.48 g, 61%), mp 82–85°C (hexane), $[\alpha]_D^{20}$ –52.05° (*c* 0.19, $CHCl_3$). The spectral properties agreed completely with those for the (+)-**5a** enantiomer.

(+)-Lactam 5b. (+)-α-Pinene **2** (1.36 g, 10 mmol) and chlorosulfonylisocyanate (1.43 g, 10.12 mmol) in dry ether (25 mL) were stirred for 24 h, treated dropwise with Et_3N (4.08 g, 40 mmol), stirred for an additional hour, treated with H_2O (15 mL), and left overnight. The usual work up gave a product (1.63 g) that crystallized from benzene to afford (+)-**5b** (0.86 g, 48%), mp 153°C, $[\alpha]_D^{20}$ +87.18° (*c* 0.64, $CHCl_3$), lit. [5] mp 160–210°C (hexane). IR spectrum (mineral oil, ν, cm^{-1}): 1730 (CON), 3200 (NH).

PMR spectrum (100 MHz, $CDCl_3$, δ, ppm, J/Hz): 0.86, 1.27 (6H, ss, H-8a, H-8b), 1.36 (3H, s, H-7a), 1.74-1.94 (2H, m, Hβ-2, Hβ-9), 1.94–1.98 (1H, tt, J = 4.02, 4.4, H-1), 2.11 (2H, m, Hα-2, Hα-9), 2.50 (1H, m, H-6), 2.80 (1H, dd, J = 9.2, 12.4, H-3), 7.75 (1H, br.s, NH).

(–)-Lactam 5b. A mixture of (–)-α-pinene (**2**, 1.36 g, 10 mmol) and chlorosulfonylisocyanate (1.43 g, 10.1 mmol) in ether (25 mL) was stirred for 24 h at room temperature, treatd with Et_3N (4.08 g, 40 mmol), stirred for 3 h, treated with H_2O (15 mL), and left overnight. The usual work up gave an oily product (1.63 g) that crystallized from benzene (5 mL) to afford lactam **5b** (0.86 g, 48%), mp 135–139°C, $[\alpha]_D^{20}$ –77.86° (*c* 0.4, $CHCl_3$), lit. mp 218–220°C [1] and 160–210°C [5]. IR spectrum (mineral oil, ν, cm^{-1}): 1695 (CON), 3215 (NH).

(–)-(2a*R*,3a*R*,4a*S*,5a*S*)-4,4,5a-Trimethylperhydrocyclopropa[4,5]benzo[*b*]azet-2-one Trifluoroacetate (6). A solution of (+)-**3b** (0.1 g) in trifluoroacetic acid (1 mL) was stirred for 3 d at room temperature. The solvent was vacuum distilled to afford in quantitative yield a colorless oil, $[\alpha]_D^{20}$ –4.16° (*c* 0.29, MeOH).

PMR spectrum (80 MHz, DMSO-d_6, δ, ppm): 0.6 (2H, m, H-3a, H-4a), 0.89, 0.97 (6H, ss, H-6a, H-6b), 1.29 (2H, m, H_α-3, H_α-5), 1.48 (3H, s, H-1), 2.44 (3H, m, H_β-3, H_β-5, H-2a), 7.22, 7.86 (2H, br.s, s, CF_3CO_2-NH_2^+).

Mixture of 7,8,8-Trimethyl-4-azatricyclo[4.2.1.0^{3,7}]nonan-5-one (7) and 6-Amino-1,7,7-trimethylbicyclo[2.2.1]heptan-2-carboxylic Acid (8) Trifluoroacetates. A. Lactam (+)-**4b** (0.1 g) was dissolved in trifluoroacetic acid (1 mL) and stirred for 3 d. The solvent was vacuum distilled to afford in quantitative yield a mixture of the trifluoroacetates as a colorless oil, $[\alpha]_D^{20}$ +77.02° (*c* 0.024, MeOH).

PMR spectrum of the major product (80 MHz, DMSO-d_6, δ, ppm, J/Hz): 0.85, 0.88 (6H, ss, H-8a, H-8b), 1.78 (3H, s, H-7a), 2.13 (6H, m, H-1, H-2, H-9, H-6), 5.05 (1H, d, J = 6.95, H-3), 7.19, 7.83 (2H, br.s, s, CF_3CO_2-NH_2^+).

^{13}C NMR spectrum of the major product (20 MHz, DMSO-d_6): 16.11 (C-7a), 16.66 (C-8a), 18.95 (C-8b), 20.91 (C-2), 33.68 (C-9), 47.11 (C-8), 48.92 (C-1), 68.59 (C-6), 96.64 (C-7), 101.83 (C-3), 150.30 (C-F), 177.57 (C=O), 187.11 (C-5).

PMR spectrum of the major product (80 MHz, DMSO-d_6, δ, ppm, J/Hz): 0.85, 0.88 (6H, ss, H-8a, H-8b), 1.56 (3H, s, H-7a), 1.78 (3H, s, H-7a), 2.13 (6H, m, H-1, H-2, H-9, H-6), 5.40 (1H, m, H-3), 11.84, 12.74 (2H, br.s, s, NH, CO_2H).

^{13}C NMR spectrum of the major product (20 MHz, DMSO-d_6): 16.23 (C-7a), 16.52 (C-8a), 19.41 (C-8b), 21.13 (C-2), 34.48 (C-9), 47.11 (C-8), 48.92 (C-1), 60.71 (C-6), 108.30 (C-7), 122.53 (C-3), 159.56 (C-F), 177.57 (C=O), 181.95 (C-5).

B. Lactam (+)-**5b** (0.1 g) was dissolved in trifluoroacetic acid (1 mL) and stirred for 3 d. The solvent was vacuum distilled to afford in quantitative yield a product identical to that obtained by method A.

X-ray Structure Analysis. X-ray data sets were collected on a KM4CCD diffractometer using ω-scanning. Table 1 presents the principal crystallographic data, experimental conditions, and structure refinement. The structure was solved and refined using the SHELXS-97 and SHELXL-97 programs [7].

Atomic coordinates and bond lengths and angles were deposited in the Cambridge Crystallographic Data Centre (CCDC 670927 and 670928).

ACKNOWLEDGMENT

The work was performed under the auspices of bilateral project ASM-MESU-01/UA.

REFERENCES

1. T. Sasaki, S. Eguchi, and H. Yamada, *J. Org. Chem.*, **38**, 679 (1973).
2. J. R. Malass, *Tetrahedron Lett.*, **49**, 4951 (1972).
3. S. Gyonfalvi, Z. Szakonyi, and F. Fulop, *Tetrahedron: Asymmetry*, **14**, 3965 (2003).
4. E. A. Koneva, K. P. Volchko, D. V. Korchagina, N. I. Komarova, A. I. Kochnev, N. F. Salakhutdinov, and A. G. Tolstikov, *Izv. Akad. Nauk, Ser. Khim.*, **1**, 105 (2008).
5. G. T. Furst, M. A. Wachsman, J. Pieroni, J. G. White, and E. J. Moriconi, *Tetrahedron*, **12**, 1675 (1973).
6. Z. Szakonyi, T. Martinek, A. Hetenyl, and F. Fulop, *Tetrahedron: Asymmetry*, **11**, 4571 (2000).
7. G. M. Sheldrick, *SHELXS-97* and *SHELXL-97*, University of Goettingen, Germany, 1997.