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Diastereoselective Addition of Allyltrimethylsilane to N-Glyoxyloyl-(2R)-bornane-10,2-sultam. A new synthesis of (S)-1,2-Pentanediol

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DIASTEREOSELECTIVE ADDITION OF ALLYLTRIMETHYLSILANE TO *N*-GLYOXYLOYL-(2*R*)-BORNANE-10,2-SULTAM. A NEW SYNTHESIS OF (*S*)-1,2-PENTANEDIOL

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Abstract: Addition of allyltrimethylsilane (**3**) to *N*-glyoxyloyl-(2*R*)-bornane-10,2-sultam (**4**) in the presence of Lewis acid afforded, in high diastereoselectivity, adduct (2'*S*)-**6** which, after recrystallization, was hydrogenated to give optically pure (*S*)-1,2-pentanediol (**1**).

Recently, Mori and Takaishi[1] presented the highly stereocontrolled synthesis of (+)-monocerin (**2**), an antifungal metabolite,[2,3] starting from (*S*)-1,2-pentanediol (**1**)[4] as a useful chiral building block (Scheme 1).

This approach prompted us to propose a convenient route to optically active 1,2-diols, based on the diastereoselective addition of allyltrimethylsilane (**3**) to *N*-glyoxyloyl-(2*R*)-bornane-10,2-sultam (**4**). In the present communication, we would like to report our results on asymmetric induction in this type of allylic addition, and finally an efficient way to optically pure (*S*)-1,2-pentanediol (**1**) (Scheme 2).

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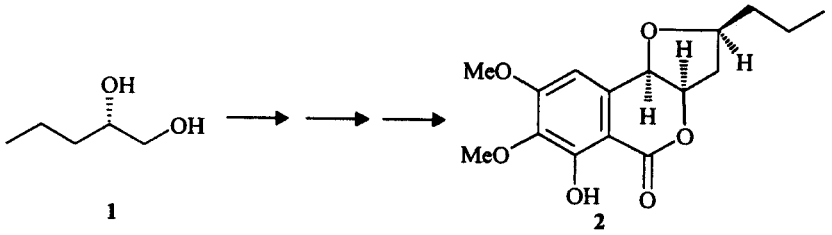
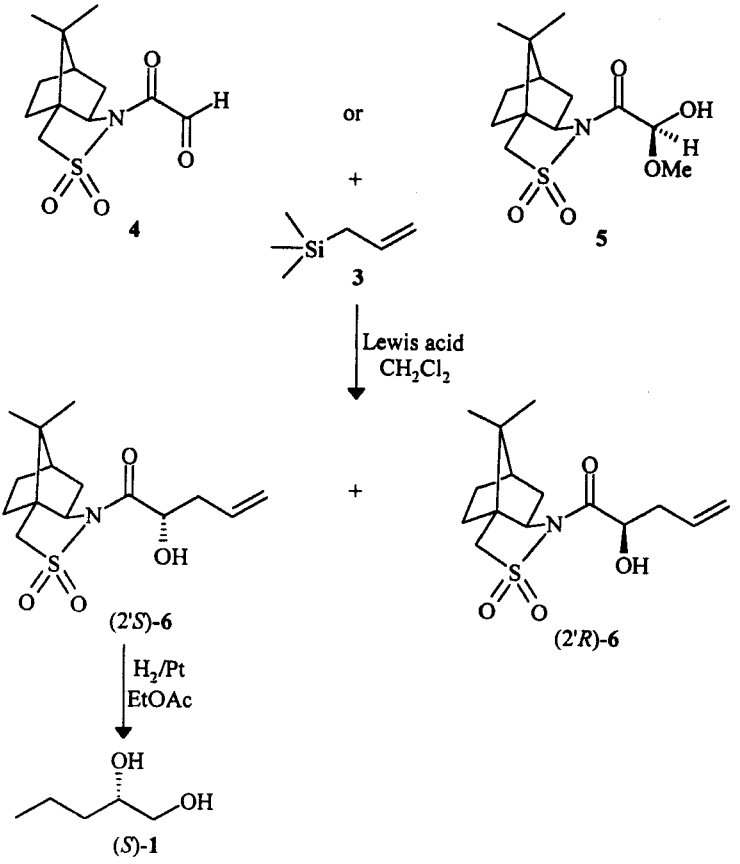


Scheme 1



Scheme 2

Table 1. Results of reactions of **3** with **4** or **5**, carried out in the presence of one equivalent of Lewis acid in CH_2Cl_2.

Entry	Substrate	Lewis acid	Temp. [ŞC]	Time [h]	Yield [%]	Diastereoisomer Ratio	Absolute Configuration
1	**4**	$SnCl_4$	-78	18	45	69:31	*S*
2	**4**	$TiCl_4$	-78	65	55	65:35	*S*
3	**4**	$BF_3 \cdot Et_2O$	-20	1	65	80:20	*S*
4	**4**	$MgBr_2 \cdot 2Et_2O$	25	21	70	80:20	*S*
5	**4**	$ZnCl_2$	0	2	70	89:11	*S*
6	**5**	$ZnCl_2$	0	3	85	86:14	*S*
7	**4**	$ZnBr_2$	0	2	75	91:9	*S*
8	**5**	$ZnBr_2$	0	6	95	92:8	*S*

N-Glyoxyloyl-(2*R*)-bornane-10,2-sultam (**4**) or its hemiacetal **5**[5] were reacted with silane **3** in the presence of various Lewis acids. Additions were carried out under an argon atmosphere in methylene chloride as a solvent, and at various temperatures. After work-up, the crude reaction mixtures were analysed by ^{1}H NMR to establish the diastereoisomeric ratio of the adducts (2'*S*)-**6** and (2'*R*)-**6**. The relative configuration of the major diastereoisomer (2'*S*)-**6** was determined by X-ray analysis.[6] The results of experiments are shown in Table 1.

Several aspects of the data presented in Table 1 are noteworthy. The addition carried out in the presence of strongly chelating Lewis acids (Entries 1 and 2) afforded the mixture of diastereoisomers **6** in a moderate yield, but with low (30-38% de) asymmetric induction. The use of nonchelating Lewis acid

(Entries 3 and 4) improved diastereoselectivity substantially (60% de). The best results in terms of both the chemical yield (95%) and diastereoisomeric excess (84%) were obtained when the addition was performed in the presence of $ZnBr_2$ and when the hemiacetal **5** was used as a substrate (Entry 8). The major diastereoisomer (2'*S*)-**6** was readily isolated in optically pure form by simple recrystallization. Its direct hydrogenation in the presence of the Adams catalyst led to the desired (*S*)-1,2-pentanediol (**1**) in very high yield (81%). Enantiomeric purity of **1** was justified by comparison of its optical rotation with the literature data[4a] and using the ^{1}H NMR experiments, carried out in the presence of tris(3-((heptafluoropropyl)-hydroxymethylene)-*d*-camphorato)europium (III) in acetonitrile-d_3 and aceton-d_6, according to Whitesides *et al.*[7]

The presented efficient synthesis of enantiomerically pure compound **1** could be easily extended to other chiral 1,2-diols.

Experimental

General. Melting points were determined using a Kofler hot stage apparatus and are not corrected. Rotations were recorded using a JASCO DIP-360 polarimeter. IR spectra were obtained with a Perkin-Elmer 1640 FTIR spectrometer in KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded using a Varian Gemini (200 MHz or 50 MHz, respectively) spectrometer. Mass spectra were recorded on an ADM-604 Inectra instrument using the electron impact (EI) technique.

Synthesis of adducts (2'*S*)-**6** *and* (2'*R*)-**6** - *a typical procedure*:

To a stirred solution of **4** or **5** (1 mmol) in dry CH_2Cl_2 (15 ml) at temperature indicated in Table 1, under argon, the Lewis acid (1 mmol) was added slowly.

After additional stirring (5 min), allyltrimethylsilane (**3**) (0.32 ml, 2 mmol) was added dropwise. The stirring was continued for the period of time indicated in Table 1. The reaction was quenched with sat. NH_4Cl and was extracted with Et_2O (3 × 30 ml). The organic layers were pooled, dried ($MgSO_4$) and concentrated *in vacuo*. Flash chromatography (hexane/ethyl acetate) afforded homoallyl alcohols **6**.

Analytical and spectral data for compound (*2'S*)-**6**: mp 138-139°C; $[\alpha]_D^{20}$=-105 (*c* 2.2, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$), δ: 5.9-5.7 (m, 1H, C*H*=CH_2), 5.2-5.05 (m, 2H, C=C*H*$_2$), 4.83 (dd, J=11.8, 6.2 Hz, 1H, C*H*OH), 3.94 (dd, J=7.4, 5.0 Hz, 1H, C*H*N), 3.51 ($^1/_2$ABq, J=13.8 Hz, 1H, C*H*SO_2), 3.47 ($^1/_2$ABq, J=13.8 Hz, 1H, C*H*$_2SO_2$), 3.08 (d, J=7.7 Hz, 1H, O*H*), 2.8-1.2 (m, 9H, 4×C*H*$_2$ and 1×C*H*), 1.14 (s, 3H, C*H*$_3$), 0.98 (s, 3H, C*H*$_3$); ^{13}C NMR (50 MHz, $CDCl_3$), δ: 174.2, 132.0, 118.9, 70.3, 64.9, 52.9, 48.9, 47.8, 44.5, 39.8, 38.2, 32.7, 26.4, 20.6, 19.8; IR (KBr) : 3552, 3001, 2959, 1696,1641, 1331, 1058, 774; EIMS m/z (%): 313 (M^+, 1.3), 295 (1.8), 272 (33), 199 (9), 135 (100), 93 (47), 71 (13), 55 (6); Anal. calcd for $C_{15}H_{23}NO_4S$: C 57.5, H 7.4, N 4.0, S 10.2, found: C 57.3, H 7.5, N 4.4, S 10.2.

Analytical and spectral data for compound (*2'R*)-**6**: mp 69-70°C; $[\alpha]_D^{20}$ =-97.7 (*c* 1.08, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ: 6.0-5.7 (m, 1H, C*H*=CH_2), 5.3-5.1 (m, 2H, C=C*H*$_2$), 4.57 (dd, J=7.6, 4.7 Hz, 1H, C*H*OH), 3.90 (dd, J=7.7, 5.1 Hz, 1H, C*H*N), 3.9 (ABq, J=14.0 Hz, 2H, C*H*$_2SO_2$), 2.8-1.2 (m, 9H, 4×C*H*$_2$ and 1×C*H*), 1.15 (s, 3H, C*H*$_3$), 0.97 (s, 3H, C*H*$_3$); ^{13}C NMR (50 MHz, $CDCl_3$): δ: 171.8, 133.1, 118.5, 70.3, 65.3, 52.9, 49.3, 47.9, 44.5, 38.1, 37.0, 32.8, 26.5, 20.7,

19.9; IR (KBr): 3561, 3078, 2964, 1699, 1640, 1134, 1056, 764; EIMS m/z (%): 313 (M^+, 3), 295 (6), 272 (31), 199 (8), 135 (100), 93 (48), 71 (15), 55 (8); HR-EIMS Calcd. for $C_{15}H_{23}NO_4S$ (M^+): 313.13478, found: 313.1352, Calcd. for $C_{12}H_{18}NO_4S$ (M^+-C_3H_5): 272.09565, found: 272.0951.

Synthesis of (S)-1,2-pentanediol (**1**):

To a solution of (*S*)-**6** (130 mg, 0.42 mmol) in dry ethyl acetate was added PtO_2 (ca 20 mg). The suspension was stirred under hydrogen atmosphere for 2 h at room temperature. After filtration of the catalyst through Celite, the solution was concentrated *in vacuo*. The resulting residue was purified by column chromatography on silica gel. Elution with hexane/ethyl acetate (7:3→4:6) gave the appropriate alcohol **1** (35 mg, 81%) as a colorless oil.

Analytical and spectral data for compound (*S*)-**1**: $[\alpha]_D^{20}$ =-15.5 (*c* 0.81, EtOH), lit. {$[\alpha]_D^{20}$ =-16.1 (*c* 3, EtOH)}[4a]; ^{1}H NMR (500 MHz, $CDCl_3$), δ: 3.76 (m, 1H, C*H*OH), 3.66 (dd, J=11.1, 3.0 Hz, 2H, C*H*$_2$OH), 2.36 (bs, 2H, O*H*), 1.52-1.33 (m, 4H, 2×C*H*$_2$), 0.94 (t, 3H, C*H*$_3$), ^{13}C NMR (125 MHz, $CDCl_3$), δ: 72.0, 66.8, 35.3, 18.7, 14.0; IR (film): 3379, 2970, 2932, 1720, 1134, 799; EIMS m/z (%): 73 (M^+-CH_2OH, 54), 61 (18), 55 (100), 43 (32).

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