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Diastereoselective Addition of Allyl Reagents to *N*-Tosyl- and *N*-Benzyl-*N*-tosyl-L-alaninal

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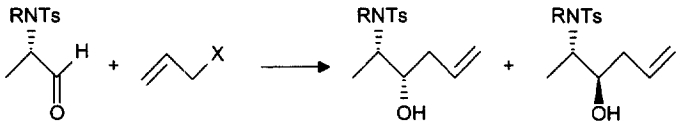
Abstract: Diastereoselective C_3-elongation processes of *N*-tosyl- (**1**) and *N*-benzyl-*N*-tosyl-L-alaninal (**2**), using various allyl reagents and different reaction conditions, are described. A large difference between effects of the *N*-protecting groups replacing either one or two amino protons was observed. © 1997 Elsevier Science Ltd.

α-Amino aldehydes are the versatile chirons, frequently used in the stereocontrolled synthesis of natural products,[1-3] including amino sugars.[4-7] Stereoselective elongation of the carbon skeleton is the crucial point of the synthesis of amino sugars from amino acids and their derivatives.[8-10] We recently described several C_4-elongations of α-amino aldehydes *via* high-pressure [4+2] cycloaddition,[11,12] Lewis acid-mediated cyclocondensation,[12,13] and furyllithium addition.[14] We observed a large difference between the *N*-protecting groups replacing either one or two amino protons. When we used *N,N*-diprotected α-amino aldehydes instead of *N*-monoprotected ones, the direction of asymmetric induction was reversed. We explained this was a result of substantial changes in the nature of the amino group: from steric to chelating character.[15]

We considered this very interesting, especially from the synthetic point of view, to study other types of reactions of variously *N*-protected α-amino aldehydes. Therefore, we resolved to investigate the addition reaction of various allyl reagents (**3-5**) to *N*-tosyl- (**1**) and *N*-benzyl-*N*-tosyl-L-alaninal (**2**) under different conditions (Scheme 1, Table 1). In this study we decided to use the derivatives of L-alaninal as the simplest example of chiral α-amino aldehydes. *N*-Tosyl-L-alaninal (**1**) was selected as a typical *N*-monoprotected derivative, and *N*-benzyl-*N*-tosyl-L-alaninal (**2**) as a typical *N,N*-diprotected one. Both alaninals were obtained from the respective α-amino alcohols, using the TEMPO oxidation method.[16,17] In all reactions shown in Table 1, mixtures of *syn* and *anti* diastereoisomeric products were obtained (throughout this paper we follow the *syn/anti* convention as proposed by Masamune *et al.*[18,19]).



1 R=H **3** X=MgCl *syn*-**6** R=H *anti*-**7**
2 R=Bn **4** X= Br *syn*-**8** R=Bn *anti*-**9**
5 X= $SiCl_3$

Scheme 1

Table 1. Results of the addition of allyl reagents (**3-5**) to *N*-protected L-alaninals **1** and **2**.

Entry	Aldehyde	Allyl reagent	Reaction conditions	Yield (%)	Product ratio
1	**1**	**3**	THF, 0°C, 4 h	46	*syn*-**6**:*anti*-**7**=60:40
2	**2**	**3**	THF, -78°C, 18 h	81	*syn*-**8**:*anti*-**9**=12:88
3	**1**	**4**	Zn/NH_4Cl, THF, RT, 3 h	66	*syn*-**6**:*anti*-**7**=50:50
4	**2**	**4**	Zn/NH_4Cl, THF, RT, 22 h	71	*syn*-**8**:*anti*-**9**=14:86
5	**1**	**4**	Zn/$AlCl_3$, THF, RT, 1 h	93	*syn*-**6**:*anti*-**7**=45:55
6	**2**	**4**	Zn/$AlCl_3$, THF, RT, 1 h	87	*syn*-**8**:*anti*-**9**= 5:95
7	**1**	**4**	$SnCl_2 \cdot 2H_2O$/NaI, DMF, RT, 1.5 h	65	*syn*-**6**:*anti*-**7**=50:50
8	**2**	**4**	$SnCl_2 \cdot 2H_2O$/NaI, DMF, RT, 3 h	100	*syn*-**8**:*anti*-**9**= 7:93
9	**1**	**4**	Mg/$CuCl_2 \cdot 2H_2O$, THF, RT, 23 h	56	*syn*-**6**:*anti*-**7**=36:64
10	**2**	**4**	Mg/$CuCl_2 \cdot 2H_2O$, THF, RT, 22 h	39	*syn*-**8**:*anti*-**9**=12:88
11	**1**	**5**	DMF, 0°C, 2 h	43	*syn*-**6**:*anti*-**7**=77:23
12	**2**	**5**	DMF, 0°C, 20 h	64	*syn*-**8**:*anti*-**9**=23:77

Addition of allylmagnesium chloride (**3**) to *N*-monoprotected α-amino aldehyde **1** (Table 1, Entry 1) resulted in the low *syn*-diastereoselectivity, accordingly to the literature data.[20] In the case of *N,N*-diprotected-L-alaninal **2**, the same addition (Entry 2) afforded the moderate *anti*-diastereoselectivity.[21] The pure crystalline adducts *syn*-**6** and *anti*-**9** were used for the final proof of the structure and stereochemistry by the single-crystal X-ray analysis (Figures 1, 2 and 3).

According to X-ray studies the two major diastereoisomers obtained in the above reactions: *syn*-**6** and *anti*-**9**, have C1(R), C3(R) and C1(S),C3(R) configuration, respectively (confirmed by low absolute structure parameters, Table 2). That proves the *syn* and *anti* configuration assignment. As might be seen from Figure 2,

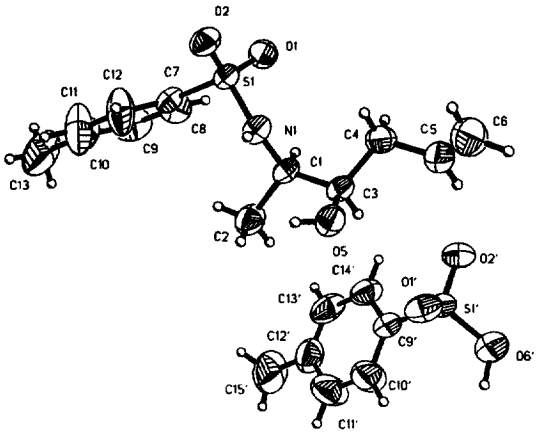


Fig. 1 ORTEP diagram of *syn*-**6** showing asymmetric unit.

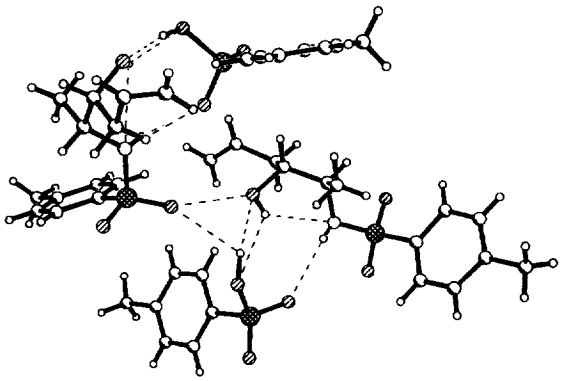


Fig. 2. Hydrogen bonding pattern observed in the crystal of compound *syn*-**6**.

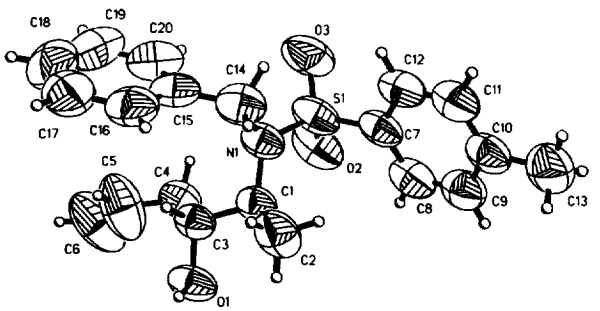


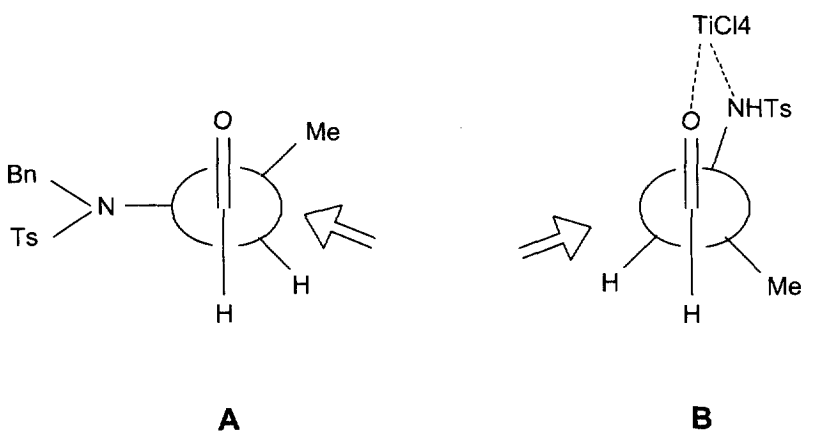
Fig. 3. ORTEP diagram of the molecule of compound *anti*-**9**.

an extensive hydrogen bonding between hydrogen bond donors and acceptors in *syn*-**6** and *p*-toluenesulfonic acid molecule is observed in the crystals.

Relatively poor results of the above-mentioned Grignard additions prompted us to turn our attention to other allylation procedures. Among many allylation methods, we have chosen four versions of the Barbier reaction, using allyl bromide (**4**) modified by Zn/NH_4Cl[22,23] (Tabel 1,ntries 3 and 4), $Zn/AlCl_3$[24] (Entries 5 and 6), $SnCl_2{\cdot}2H_2O/NaI$[25] (Entries 7 and 8), and $Mg/CuCl_2{\cdot}2H_2O$[26] (Entries 9 and 10).

Additionally, we decided to check the addition of allyltrichlorosilane (**5**)[27] (Entries 11 and 12). In all cases of additions to *N,N*-diprotected α-amino aldehyde **2** studied, *anti*-diastereoselectivity was observed as an evidence of nonchelation control of the reaction. Contrary to these results, additions to *N*-monoprotected α-amino aldehyde **1** afforded rather poor diastereoselectivities; the best *syn*-diastereoselectivity was obtained for addition of reagent **5** (Entry 11).

The stereochemical results can be rationalized by the transition state models **A** and **B**, as shown in Scheme 2. In the case of *N,N*-diprotected α-amino aldehyde **2**, additions of allyl reagents led to *anti*-adduct **9**, according to the Felkin-Anh model **A**.[28,29] To achieve *syn*-diastereoselection, the chelation-controlled model **B**[30] should operate, what is favorable in the case of additions to *N*-monoprotected α-amino aldehyde **1**.



Scheme 2

Solution of the problem under consideration calls for further studies, extended for other allylation methods as well as for variously *N*-mono- and *N,N*-diprotected α-amino aldehydes, which are now in progress.

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Experimental

General

Melting points were determined using a Kofler hot stage apparatus and are uncorrected. Optical rotations were recorded using a JASCO DIP-360 polarimeter with a thermally jacketed 10 cm cell. ^{1}H NMR spectra were recorded using a Bruker AM 500 (500 MHz) spectrometer, and ^{13}C NMR spectra were recorded using also a Bruker AM 500 (125 MHz) spectrometer. All chemical shifts are quoted in parts per million relative to tetramethylsilane (δ, 0.00 ppm), and coupling constants (J) are measured in Hertz. IR spectra were obtained on a Perkin-Elmer 1640 FTIR spectrophotometer in KBr pellets. Mass spectra were recorded on an AMD-604 Intectra instrument using the electron impact (EI) technique. Single-crystal X-ray diffraction analysis was performed on an Enraf-Nonius MACH 3 diffractometer. Flash-column chromatography was performed according to Still *et al.*[31] on silica gel (Kieselgel-60, Merck, 200-400 mesh).

*Addition of the allyl reagents to N-protected α-amino aldehydes **1** and **2**. General procedures.*

*A. Addition of allylmagnesium chloride (**3**).*

A precooled solution of allylmagnesium chloride (2 mmol in 10 mL of dry THF) was added dropwise to a cold (0°C or -78°C) solution of an α-amino aldehyde (1 mmol in 2.5 mL of dry THF). After stirring for the period given in Table 1, saturated aqueous solution of ammonium chloride (10 mL) was added and the reaction mixture was allowed to reach room temperature. Then it was diluted with water (25 mL) and extracted with Et_2O (2 x 10 mL). The combined extracts were washed with brine (10 mL), 1N hydrochloric acid (10 mL), saturated sodium bicarbonate (10 mL), and again with brine (10 mL), dried ($MgSO_4$) and evaporated in vacuo. Flash chromatography (hexane-EtOAc 9:1→1:1) afforded a mixture of appropriate *syn* and *anti* diastereoisomers.

*B. Addition of allyl bromide (**4**) in the presence of Zn/NH_4Cl.*

Allyl bromide (**4**, 2 mmol) was added dropwise at room temperature to the stirred suspension of zinc (powder, 2 equiv.), an α-amino aldehyde (1 mmol), saturated aqueous solution of ammonium chloride (0.5 mL), and THF (10 mL). After stirring at room temperature for several h, until the substrate disappeared (by TLC), the reaction mixture was extracted with Et_2O (2 x 10 mL), the combined extracts were dried ($MgSO_4$), evaporated in vacuo, and the residue was worked up as in the former procedure.

*C. Addition of allyl bromide (**4**) in the presence of Zn/$AlCl_3$.*

Allyl bromide (**4**, 1.2 mmol) was added dropwise at room temperature under argon to the stirred suspension of zinc (powder, 1.2 equiv.), $AlCl_3$ (0.1 equiv.), and THF (3 mL). After 5 min of stirring, a solution of an aldehyde (1mmol) in THF (2 mL) was added, and the mixture was stirred to stirr until the

disappearance of the substrate (TLC). Further workup was similar to that used in the above-described procedures.

D. Addition of allyl bromide (4) in the presence of $SnCl_2 \cdot 2H_2O$/NaI.

To a stirred solution of an aldehyde (1 mmol) and allyl bromide (**4**, 1.5 mmol) in DMF (10 mL) was added $SnCl_2 \cdot 2H_2O$ (1.5 mmol) followed by sodium iodide (1.5 mmol). After stirring for several h (until disappearance of the substrate in TCL) a saturated aqueous solution of ammonium fluoride (10 mL) and Et_2O (10 mL) were added and the mixture was transferred into a separatory funnel. The aqueous layer was reextracted with Et_2O (2 x 10 mL) and combined extracts were worked up as in the former procedures.

E. Addition of allyl bromide (4) in the presence of $Mg/CuCl_2 \cdot 2H_2O$.

Allyl bromide (**4**, 2.5 mmol) was added dropwise at room temperature, under argon, to a stirred suspension of magnesium (powder, 2.5 equiv.), $CuCl_2 \cdot 2H_2O$ (2.5 mmol), an aldehyde (1 mmol), and THF (5 mL). The reaction mixture was stirred for several h (until disappearance of the substrate in TCL), then it was quenched with 1 N hydrochloric acid, and extracted with Et_2O (3 x 10 mL). Combined extracts were worked up as in the former procedures.

F. Addition of allyltrichlorosilane (5).

A solution of an aldehyde (1 mmol) and allyltrichlorosilane (**5**, 1.2 mmol) in DMF (6 mL) was stirred at 0°C for several h (until disappearance of the substrate in TCL), then it was quenched with saturated aqueous solution of ammonium chloride (10 mL), and extracted with Et_2O (3 x 10 mL). Combined extracts were worked up as in the former procedures.

Analytical and spectral data for compound syn-6.

mp 110-112°C (from *n*-hexane-AcOEt); $[\alpha]_D^{20}$-1.5 (*c* 0.95, $CHCl_3$); IR (KBr), ν, 3490, 1641, 1316, 1160, 968, 812, 676 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz), δ, 7.76 (1/2ABq, J=8.3, 2H), 7.28 (1/2ABq, J=8.3, 2H), 5.75 (m, 1H), 5.09 (m, 2H), 4.92 (d, J=8.4, 1H), 3.48 (m, 1H), 3.29 (dddd, J_1=3.7, J_2=6.7, J_3=8.5, J_4=15.2, 1H), 2.26 (m, 1H), 2.16 (m, 1H), 2.05 (bs, 1H), 1.00 (d, J=6.7, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz), δ, 143.3, 138.1, 133.9, 129.7, 127.0, 118.7, 73.4, 53.1, 38.3, 21.5, 18.5; LSIMS HR (m/z) calculated for $C_{13}H_{19}NO_3S$ $(M+Na)^+$ 292.0983, found 292.0982.

Analytical and spectral data for compound anti-7.

oil (compound *anti*-**7** contaminated by compound *syn*-**6**); ^1H NMR ($CDCl_3$, 500 MHz), δ, 7.76 (1/2ABq, J=8.4, 2H), 7.28 (1/2ABq, J=8.4, 2H), 5.75 (m, 1H), 5.40 (d, J=8.4, 1H), 5.09 (m, 2H), 3.64 (ddd,

J_1=3.2, J_2=5.5, J_3=8.0, 1H), 3.47 (m, 1H), 2.26 (m, H), 2.16 (m, 1H), 2.05 (bs, 1H), 0.96 (d, J=6.6, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz), δ, 143.2, 137.8, 134.1, 129.6, 129.5, 126.9, 117.9, 73.0, 53.0, 37.7, 21.4, 14.4; LSIMS HR (m/z) calculated for $C_{13}H_{19}NO_3S$ $(M+Na)^+$ 292.0983, found 292.0977.

*Analytical and spectral data for compound syn-**8**.*

mp 88-89°C (from *n*-hexane-AcOEt); $[\alpha]_D^{20}$ +21.1 (*c* 1.08, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz), δ, 7.71 (m, 2H), 7.30 (m, 5H), 5.78 (m, 1H), 5.02 (m, 2H), 4.63 (1/2ABq, J=15.6, 1H), 4.15 (1/2ABq, J=15.6, 1H), 3.78 (m, 1H), 3.28 (m, 1H), 2.43 (s, 3H), 2.24 (m, 1H), 2.08 (d, J=4.1, 1H), 2.17 (m, 1H), 0.92 (d, J=6.9, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz), δ, 143.4, 137.7, 137.5, 133.8, 129.8, 128.7, 128.2, 127.8, 127.2, 117.7, 71.9, 58.8, 47.9, 38.0, 21.5, 14.6; Analysis calculated for $C_{20}H_{25}NO_3S$: C, 66.8; H, 7.0; N, 3.9; found: C, 66.8; H, 7.1; N, 3.7%.

*Analytical and spectral data for compound anti-**9**.*

mp 110-111°C (from *n*-hexane-AcOEt); $[\alpha]_D^{20}$ +25.4 (*c* 1.15, $CHCl_3$); IR (KBr), ν, 3526, 1644, 1331, 1159, 995, 862, 735, 659 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz), δ, 7.71 (m, 2H), 7.40 (m, 2H), 7.30 (m, 5H), 5.45 (m, 1H), 4.98 (m, 2H), 4.67 (1/2ABq, J=15.5, 1H), 4.11 (1/2ABq, J=15.5, 1H), 3.80 (dq, J_1=6.0, J_2=6.9, 1H), 3.30 (ddt, J_1=4.0, J_2=5.7, J_3=8.7, 1H), 2.43 (s, 3H), 3.28 (m, 1H), 2.00 (m, 1H), 1.66 (d, J=3.9, 1H), 0.99 (d, J=7.0, 3H); ^{13}C NMR ($CDCl_3$, 500 MHz), δ, 143.3, 137.8, 137.7, 134.6, 129.7, 128.6, 128.4, 127.7, 127.0, 118.2, 73.0, 57.9, 48.3, 39.1, 21.5, 12.2; Analysis calculated for $C_{20}H_{25}NO_3S$: C, 66.8; H, 7.0; N, 3.9; S, 8.9; found C, 66.6; H, 7.0; N, 4.1; S, 8.9%.

*X-Ray structure determination of compounds syn-**6** and anti-**9**.*

Monocrystals of compounds *syn*-**6** and *anti*-**9** suitable for X-ray structure determination were obtained from the methanol/*n*-hexane solutions. Diffraction data were collected at room temperature on an Enraf-Nonius MACH 3 diffractometer. Details of data collection and refinement procedures are shown in Table 2. Programs used during structure analysis were: SHELXS 86[32] for structure solution and SHELXL 93[33] for structure refinement. All but hydroxyl and sulfonyl H-atoms were placed in ideal positions and refined with the riding model and fixed isotropic displacement parameters. Refined atomic coordinates, and geometrical parameters for compounds *syn*-**6** and *anti*-**9** were deposited in the Cambridge Crystallographic Data Centre.

Table 2. Crystal data and structure refinement for compounds *syn*-**6** and *anti*-**9**

Compound	*syn*-**6**	*anti*-**9**
Empirical formula	$C_{13}H_{19}NO_3S \cdot C_7H_8O_3S$	$C_{20}H_{25}NO_3S$
Formula weight	441.55	359.47
Temperature (K)	293(2)	
Wavelength (Å)	1.54178	
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_1$
Unit cell dimensions (Å, °):		
a:	17.5210(10) .	9.3053(5)
b:	12.8930(10) .	7.2649(6)
c:	9.923(3)	15.1244(10).
β:		103.570(3)
Volume ($Å^3$)	2241.6(7)	993.9(1)
Z	4	2
Density (calculated) (Mg m^{-3})	1.308	1.201
Absorption coefficient (mm^{-1})	2.454	1.584
F(000)	936	384
Crystal size (mm)	0.2 x 0.2 x 0.25	0.15 x 0.20 x 0.30
θ-range for data collection (°)	4.26 to 69.74	3.01 to 74.85
Index ranges	$0 \le h \le 19$, $0 \le k \le 15$, $-11 \le l \le 0$	$-10 \le h \le 11$, $0 \le k \le 9$, $-18 \le l \le 0$
Reflections collected	1771	1720
Independent reflections	1771 [R(int) = 0.0000]	1660 [R(int) = 0.0306]
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1770 / 0 / 271	1660 / 0 / 230
Goodness-of-fit on F^2	1.057	0.876
Final R indices [$I>2\sigma$ (I)]	$R_1 = 0.0425$, $wR_2 = 0.1104$	$R_1 = 0.0439$, $wR_2 = 0.1266$
R indices (all data)	$R_1 = 0.0434$, $wR_2 = 0.1134$	$R_1 = 0.0447$, $wR_2 = 0.1287$
Absolute structure parameter	0.00(4)	-0.02(3)
Extinction coefficient	0.00026(13)	0.009(2)
Largest diff. peak and hole ($e \cdot Å^{-3}$)	0.314 and -0.268.	0.143 and -0.158

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