Tetrahedron Vol. 47, No. 6, pp. 1037-1044, 1991
Printed in Great Britain

0040-4020/91 $3.00+.00

HIGH-PRESSURE [4+2] CYCLOADDITION OF 1-METHOXY-1,3-BUTADIENE TO *N,O*-PROTECTED D-THREONINALS AND D-*ALLO*-THREONINALS‡

A. Golebiowski and J. Jurczak*

Institute of Organic Chemistry, Polish Academy of Sciences,
01-224 Warszawa, Poland

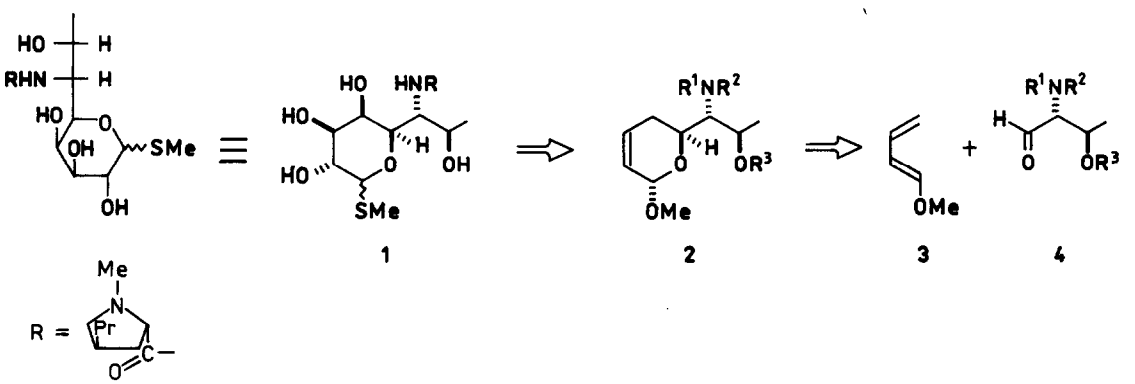
(*Received in UK* 19 *October* 1990)

Abstract. High-pressure [4+2]cycloadditions of *trans*-1-methoxy-1,3-butadiene (**3**) to *N,O*-protected D-*allo*-threoninals (**4**) and D-threoninals (**8**) were studied. In all cases, 5,6-*syn*-adducts were the major products. The results are explained by α-chelation with Eu(fod)$_3$ or by intramolecular hydrogen bonding.

The hetero-Diels-Alder reaction of 1-oxygenated or 1,3-dioxygenated 1,3-butadiene derivatives with carbonyl compounds is a convenient method for the preparation of sugars.[1-3] There are only a few published works concerned with the application of this methodology to lincosamine chemistry.[4-6]

Retrosynthetic analysis of lincosamine (**1**) (Scheme 1), reveals the possibility of the application of a [4+2]cycloaddition reaction between diene **3** and *N,O*-protected D-*allo*-threoninal **4** as the key step. Moreover, the use of each of the four threonine diastereoisomers, combined with stereocontrol of cycloaddition, should give easy access to diastereoisomers of lincosamine modified at the C5, C6, or C7 position.

Scheme 1



It is readily seen from Scheme 1 that the correct stereochemistry of the major product obtained by the Diels-Alder reaction is the critical factor in this strategy. The problem was extensively studied in our laboratory.

The choice of N-protecting groups (replacing either one or two amino protons) has a large influence on the stereochemical course of the [4+2]cycloaddition between diene **3** and *N*-protected D-alaninals. When *N,N*-diprotected α-amino aldehydes were used instead of *N*-monoprotected ones, the direction of asymmetric induction was reversed.[7,8] In light of these results, it seemed evident that the required *erythro* selectivity might be obtained

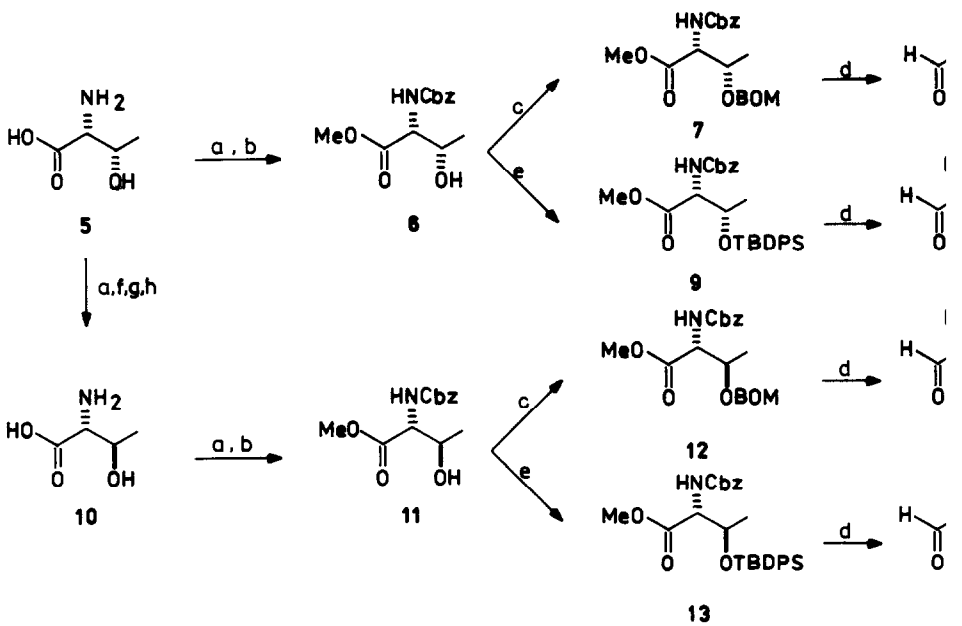
by the use of *N,N*-diprotected derivatives of D-*allo* threoninal **4** as the heterodienophiles. Subs question arose as to whether the stereochemistry of high-pressure [4+2]cycloaddition of diene **2** could be controlled by β-chelating interactions.

RESULTS

Preparation of model α-amino aldehydes

Suitable *N,O*-protected D-*allo*-threoninals **4** and D-threoninals **8** were prepared by DIBAL rec appropriate *N,O*-protected methyl esters (Scheme 2).[9]

Scheme 2

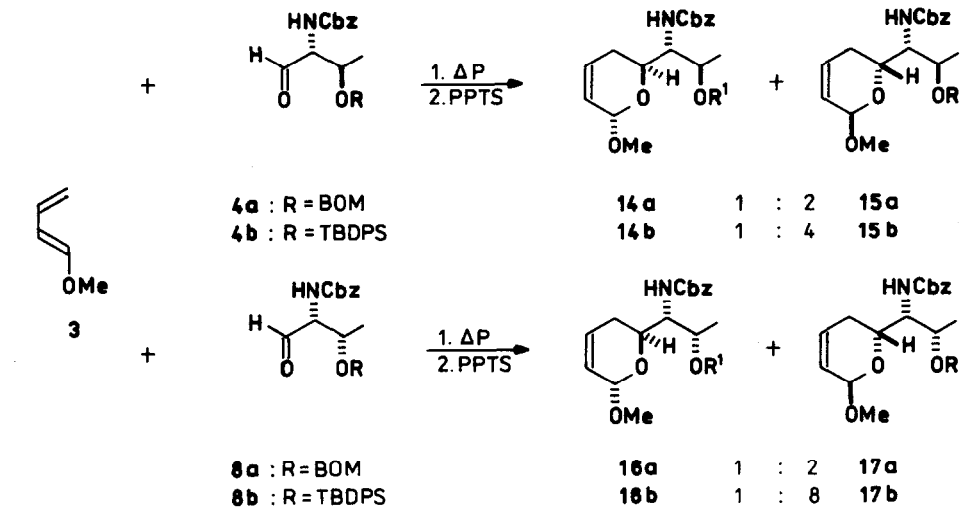


Scheme 2. a: MeOH, $SOCl_2$, RT, 3 days; b: CbzCl, sat-$NaHCO_3$ RT, 3 h; c: BOMCl, DIPEA, CH 3 h; d: DIBAL, Et_2O, -78 °C; e: TBDPSCl, Imidazole, DMF, 70 °C; f: BzCl, Py, $CHCl_3$; g: SOC 24h; h: 6N HCl, reflux, then Py.

High-pressure [4+2]cycloaddition studies

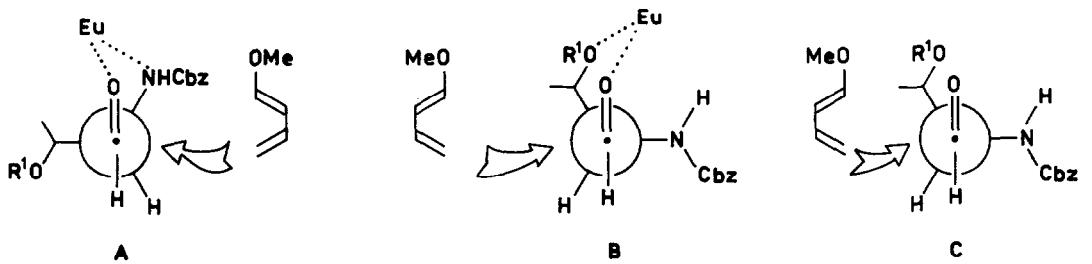
The Eu(fod)$_3$-mediated[10,11] high-pressure reactions of diene **3** with various *N*-protected D-*allo*- and D-threoninals **8** were carried out in diethyl ether as solvent at 15 kbar and 50°C to afford, in 70 mixtures of all four possible diastereoisomers: two *cis*-adducts formed by *endo* addition and two formed by *exo* addition.[12] Acidic isomerisation[13] of these mixtures, followed by chromatographic s to the thermodynamically more stable *trans*-adducts (Scheme 3). The configurations of these established using ^{1}H NMR spectroscopy.[14]

Scheme 3



The stereochemical results can be rationalized by transition-state models A, B, and C, as shown in Scheme 4.[15-17]

Scheme 4



In the case of aldehydes **4b** and **8b** (R^1= *tert*-butyldiphenylsilyl), conformation A predominates over conformation B and C. When the bulky silyl group is replaced by the strongly chelating benzyloxymethyl group (aldehydes **4a** and **8a**), the population of conformer B substantially increases, giving rise to a higher yield of *erythro* diastereoisomers **14a** and **16a**.

The use of *N,N*-diprotected D-*allo*-threoninal having a chelating group protecting the β-hydroxyl function, should lead to the predominance of conformations B and C. Our first attempts to realize this approach failed, since *N,N*-diprotected D-*allo*-threoninals are rather unreactive under the reaction conditions studied.

Further transformation of adducts of type **14** will involve oxidative shift of the double bond, using Noyori's method[18] followed by *cis*-hydroxylation, to afford the lincosamine derivative . This work is currently in progress in our laboratory.

Our preliminary study on this problem showed that a change in protection of the β-hydroxy function from the bulky *tert*-butyldiphenylsilyl group to the chelating benzyloxymethyl group caused a substantial increase in formation of the required (5S)-diastereoisomer; the direction of asymmetric induction remained, however, unchanged.

Experimental Section:

^{1}H NMR Spectra were recorded at 500 MHz with a Bruker AM 500 spectrometer in $CDCl_3$ as solvent. ^{13}C NMR spectra were measured at 125 MHz with a Bruker AM 500 spectrometer. Infrared spectra were recorded on a Beckman IR-4240 spectrometer. Optical rotations were determined with a Perkin-Elmer 141 polarimeter.

Column chromatography was carried out with Merck Kieselgel 60 (230-400 mesh), according to Still's procedure.[19] All chromatographic separations were monitored by TLC analyses, performed on Merck DC Alufolien Kieselgel 60F-254. Yields are reported for chromatographically pure compounds.

High-pressure reactions were carried out in a piston-cylinder type apparatus with a working volume of about 90 mL. Construction details have been reported previously.[20] The pressure was measured with a manganine coil calibrated to 0.1 kbar. The temperature was measured with a thermocouple calibrated to 1°C.

trans-1-Methoxy-1,3-butadiene[21] (**3**) and D-*allo*-threonine[22] were prepared according to literature procedures.

Preparation of D-*allo*-Threoninals (4a, 4b) and D-Threoninals (8a, 8b).
Esterification. Typical Procedure.

D-Threonine (**5**) (40.0 g, 0.34 mol) was suspended in methanol (400 mL) and cooled to -30 °C. Thionyl chloride (40.0 g, 0.34 mol) was added dropwise, and the reaction mixture was allowed to warm to room temperature; stirring was continued for 48 h. The solvent was evaporated and the crude oily product was used without purification.

Protection of the Amine Group. Typical Procedure.

The crude hydrochloride of D-threonine methyl ester (16.9 g, 0.1 mol) was added to a two-phase system of ethyl acetate (50 mL) and an aqueous saturated solution of sodium bicarbonate (250 mL). The magnetic stirring was commenced and benzyl chloroformate (17.0 g, 0.095 mol) was added dropwise. The reaction mixture was stirred for 24 h. After addition of ethyl acetate (200 mL) the organic layer was extracted with 1 *N* HCl (2x50 mL) and then with a saturated solution of sodium bicarbonate (2x100 mL), filtered and evaporated. The product was crystallised (ethyl acetate - hexane) giving 22.7 g (85 % yield) of *N*-Cbz-D-threonine methyl ester (**6**): mp 90.0-90.5°C; $[\alpha]^{17}$ +13.2° (c 4, $CHCl_3$). $[\alpha]^{17}$ +14.8° (c 4, MeOH). [For L-enantiomer lit.[23] mp 90°C; $[\alpha]^{20}$ -14.2° (c 4.25, MeOH), lit.[24] $[\alpha]^{20}$ -16.1° (c 4.25, MeOH)]. IR ($CHCl_3$): 3600, 3420, 1720, 1500, 1200, 1060. Anal. calcd for $C_{13}H_{17}NO_5$: C 58.41; H 6.41; N 5.24. Found: C 58.31; H 6.59; N 5.34. ^{1}H NMR: 7.34-7.26(m, 5H); 5.91(d, J= 9.0 Hz, 1H); 5.09(bs, 2H); 4.29(m, 2H); 3.70(s, 3H); 3.10(bs, 1H); 1.18(d, J= 6.4 Hz, 3H). ^{13}C NMR: 171.6, 156.7, 136.1, 128.3, 128.0, 127.8, 67.7, 67.0, 59.2, 52.3, 19.7.

Using this procedure, the crude hydrochloride of D-*allo*-threonine methyl ester (8.45 g, 0.05 mol) was transformed into *N*-Cbz-D-*allo*-threonine methyl ester (**11**) (11.6 g, 87% yield): mp 54.0-55.0°C; $[\alpha]^{20}$= -14.5° (c 10, $CHCl_3$). IR ($CHCl_3$): 3600, 3400, 1700, 1500, 1220, 1080. Anal. calcd for $C_{13}H_{17}NO_5$: C 58.41; H 6.41; N 5.24. Found: C 58.54; H 6.45; N 5.52. ^{1}H NMR: 7.34-7.25(m, 5H); 5.95(d, J=8.2 Hz, 1H); 5.09(bs,

2H); 4.41(bdd, J=8.0, 3.6 Hz, 1H); 4.12 (m, 1H); 3.72(s, 3H); 3.40(m, 1H); 1.19(d, J=6.4 Hz, 3H). ^{13}C NMR: 170.8, 156.4, 135.9, 128.4, 128.1, 127.9, 68.5, 67.1, 59.4, 52.3, 18.8.

Protection of the Hydroxy Group with Benzyl chloromethyl Ether. Typical Procedure.

N-Cbz-D-Threonine methyl ester (**5**) (13.3 g, 0.05 mol) was dissolved in methylene chloride (40 mL), diisopropylethylamine (17.2 mL, 12.9 g, 0.1 mol) was added, followed by benzyl chloromethyl ether (85% pure, 11.7 g, *ca* 0.075 mol). The reaction mixture was refluxed for 3 h, then cooled to room temperature and ethyl ether (150 mL) was added. Extraction with 1*N* HCl (3x75 mL), then with saturated aqueous solution of sodium bicarbonate (2x50 mL), followed by drying ($MgSO_4$), filtering and evaporation of the solvent, gave an oil which was chromatographed (hexane - ethyl acetate; 85:15 to 7:3) to afford 13.5 g (70% yield) of product **7**: oil; $[\alpha]^{17}$ +19.3° (c 2, $CHCl_3$). IR (film): 3350, 1740, 1040. Anal. calcd for $C_{21}H_{25}NO_6$: C 65.12; H 6.46; N 3.62. Found: C 65.01; H 6.58; N 3.54. ^1H NMR: 7.40-7.20(m, 10H); 5.51(d, J= 9.4 Hz, 1H); 5.15(bs, 2H); 4.74(d_{AB}, J= 7.1 Hz, 1H); 4.64(d_{AB}, J= 11.8 Hz, 1H); 4.54(d_{AB}, J=11.8 Hz, 1H); 4.47(d_{AB}, J= 11.8 Hz, 1H); 4.40(m, 2H); 3.69(s, 3H); 1.27(d, J= 6.5 Hz, 3H).

Using this procedure, followed by crystallization (hexane-ethyl acetate) *N*-Cbz-D-*allo*-Threonine methyl ester (**11**) (2.66 g, 10 mmol) was transformed into 2.75 g (72% yield) of *N*-Cbz-*O*-BOM-D-*allo*-threonine methyl ester (**12**): mp 65.5-66.5°C; $[\alpha]^{17}$ -15.4° (c 1, $CHCl_3$). IR (film): 3460, 1740, 1040. Anal. calcd for $C_{21}H_{25}NO_6$: C 65.12; H 6.46; N 3.62. Found: C 65.24; H 6.77; N 3.50. ^1H NMR: 7.40-7.20(m, 10H); 5.75(bd, J= 8.9 Hz, 1H); 5.11(d_{AB}, J= 12.2 Hz, 1H); 5.07(d_{AB}, J= 12.2 Hz, 1H); 4.81(d_{AB}, J=7.2 Hz, 1H); 4.77(d_{AB}, J= 7.2 Hz, 1H); 4.67(d_{AB}, J= 11.7 Hz, 1H); 4.55(d_{AB}, J= 11.7 Hz, 1H); 4.50(dd, J= 8.9, 3.2 Hz, 1H); 4.09(qd, J= 6.5, 3.2 Hz, 1H); 3.77(s, 3H); 1.28(d, J= 6.5 Hz, 3H).

Protection of the Hydroxy Group with *tert*-Butyldiphenylsilyl Chloride. Typical Procedure.

N-Cbz-D-*allo*-Threonine methyl ester (**6**) (13.3 g, 0.05 mol) was dissolved in DMF (30 mL); imidazole (6.8 g, 0.1 mol) was added, followed by *tert*-butyldiphenylsilyl chloride (15.6 mL, 16.0 g, 0.06 mol). The reaction mixture was stirred at 70 °C for 30 min. The disappearance of substrate was monitored using TLC (hexane - ethyl acetate; 7:3). The reaction was cooled to room temperature and ethyl ether (150 mL) and water (150 mL) were added. The organic layer was extracted with 1*N* HCl (2x50 mL), water (2x50 mL) and saturated aqueous solution of sodium bicarbonate (100 mL), dried ($MgSO_4$), filtered and evaporated. The oily residue was chromatographed (hexane - ethyl acetate, 85:15) affording 22.5 g (90% yield) of ester **9**: oil; $[\alpha]^{17}$ +15.0° (c 1, $CHCl_3$). IR (film): 3350, 1735, 1070. Anal. calcd for $C_{29}H_{35}NO_5Si$: C 68.88; H 6.98; N 2.77. Found: C 68.65; H 6.92; N 2.40. ^1H NMR: 7.65-7.25(m, 15H); 5.57(d, J= 9.7 Hz, 1H); 5.16(bs, 2H); 4.44(qd, J=6.5 Hz, 1.8 Hz, 1H); 4.26(dd, J= 9.7 Hz, 1.7 Hz, 1H); 3.62(s, 3H); 1.05(d, 6.5 Hz, 3H); 1.00(s, 9H).

Using this procedure, *N*-Cbz-D-*allo*-Threonine methyl ester (**11**) was transformed into 23 g (92% yield) of ester **13** an oil, $[\alpha]^{17}$ -9.1° (c 2, $CHCl_3$). IR (film): 3350, 1740, 1080. Anal. calcd for $C_{29}H_{35}NO_5Si$: C 68.88; H 6.98; N 2.77. Found: C 68.84; H 6.99; N 2.42. ^1H NMR: 7.80-7.25(m, 15H); 5.49(d, J=8.9 Hz, 1H); 5.06(bs, 2H); 4.33(dd, J= 8.9, 3.5 Hz, 1H); 4.12(qd, J= 6.5, 3.5 Hz, 1H); 3.76(s, 3H); 1.07(s, 9H); 1.02(d, J=6.5 Hz, 3H).

Reduction of the Ester Group. Typical Procedure.

Ester **7** (3.87 g, 10 mmol) was dissolved in dry ethyl ether (25 mL). The reaction mixture was cooled to -78°C under argon atmosphere. A solution of diisobutylaluminium hydride (DIBAL) in toluene (1.5 M solution, 13.5 mL, 20 mmol) was added dropwise while maintaining the temperature below -70°C. After 1.5h, methanol (*ca.* 2mL) was added dropwise, followed by ethyl ether (150 mL) and saturated aqueous solution of sodium-potassium tartrate (400 mL). Vigorous stirring was continued for *ca.*2 h, until all white solids had dissolved. The organic layer was separated, dried ($MgSO_4$) and evaporated. The oily residue was purified by flash chromatography (hexane - ethyl acetate; 8:2) to give 2.5 g of aldehyde **8a** (70% yield). Since NHCbz α-amino aldehydes are unstable[9,25,26] this product was used without any further purification.

Synthesis of adducts 3 and 4. General Procedure.

A Teflon ampoule containing a solution of diene **3** (0.67g, 8 mmol), aldehyde **4** or **8** (4 mmol), and $Eu(fod)_3$ (83.2 mg, 0.08 mmol) in ethyl ether (5 mL) was placed in a high-pressure vessel filled with pentane. The pressure was slowly (10 min) elevated to 15 kbar at 50 °C. After 24 h the reaction mixture was cooled and decompressed; the solvent was evaporated and the residue was filtered through a short silica gel pad using hexane-ethyl acetate (85:15). The solvents were evaporated, and the residue was dissolved in methanol (10 mL). A catalytic amount of pyridinium p-toluenesulphonate (25.1 mg, 0.1 mmol) was added and the reaction mixture was maintained at room temperature with monitoring by TLC. After disappearance of the starting alcohol, ethyl ether was added (40 mL) and the mixture was washed with aqueous solution of sodium bicarbonate. The aqueous layer was extracted with diethyl ether (3x20 mL). The organic layers were combined, dried over $MgSO_4$, concentrated and purified by flash chromatography.

Adducts **14a** and **15a**: oil, IR (film): 3350, 1460, 1030, 690. Anal. calcd for $C_{25}H_{31}NO_6$: C 68.98; H 5.80; N 3.21. Found: C 68.91; H 5.71; N 3.29.

14a: ^1H NMR: 7.40-7.22(m, 10H); 6.00(m, 1H); 5.72(m, 1H); 5.14(bd, J= 9.0 Hz, 1H); 5.12(bs, 2H); 4.86(bs, 1H); 4.81(d_{AB}, J= 6.8 Hz, 1H); 4.79(d_{AB}, J= 6.8 Hz, 1H); 4.67(d_{AB}, J=12.2 Hz, 1H); 4.56(d_{AB}, J= 12.2 HZ, 1H); 4.31(q, J= 6.4 Hz, 1H); 3.88(m,1H); 3.63(m,1H); 3.41(s,3H); 2.19-2.02(m,2H); 1.26(d, J=6.4 Hz, 3H).

15a: ^1H NMR: 7.37-7.23(m, 10H); 6.00(m, 1H); 5.70(m, 1H); 5.27(bd, J=9.3 Hz, 1H); 5.12(d_{AB}, J= 12.2 Hz, 1H); 5.09(d_{AB}, J= 12.2 Hz, 1H); 4.88(d_{AB}, J= 7.1 Hz, 1H); 4.82(d_{AB}, J= 7.1 Hz, 1H); 4.81(bs, 1H); 4.71(d_{AB}, J= 11.9 Hz, 1H); 4.60(d_{AB}, J=11.9 Hz, 1H); 4.26(dd, J= 11.3, 2.9 Hz, 1H); 3.88(dq, J= 9.2, 6.3 Hz, 1H); 3.68(dd, J=9.3, 9.2 Hz, 1H); 3.38(s, 3H); 2.20-2.16(m, 1H); 1.90-1.84(m, 1H); 1.31(d, J= 6.3 Hz, 3H).

Adducts 14b and 15b: oil, IR (film): 3450, 1730, 1450, 1040, 690. Anal. calcd for $C_{33}H_{41}NO_5Si$: C 70.80; H 7.38; N 2.50. Found: C 70.69; H 7.45; N 2.50.

14b: ^1H NMR: 7.70-7.25(m, 15H); 6.00-5.90(m, 1H); 5.69-5.62(m, 1H); 5.14(d_{AB}, J=12.3 Hz, 1H); 5.06(d_{AB}, J= 12.3 Hz, 1H); 4.83(bd, J= 9.9 Hz, 1H); 4.74(bs, 1H); 4.20(dd, J= 6.3, 2.9 Hz, 1H); 3.95(ddd, J=9.8, 9.0, 2.8 Hz, 1H); 3.87(m, 1H); 3.25(s, 3H); 2.12-1.88(m, 2H); 1.05(s, 9H); 1.04(d, J= 6.3 Hz, 3H).

15b: ^1H NMR: 7.75-7.20(m, 15H); 5.97(m, 1H); 5.68(m, 1H); 5.22(bd, J= 9.9 Hz, 1H); 5.11(d_{AB}, J= 12.4 Hz, 1H); 5.05(d_{AB}, J=12.4 Hz, 1H); 4.77(bs, 1H); 4.33(dd, J= 11.7, 2.3 Hz, 1H); 4.07(dq, J= 6.6, 6.1 Hz,

1H); 3.68(dd, J= 9.9, 6.6 Hz, 1H); 3.26(s, 3H); 2.20-2.10(m, 1H); 1.90-1.80(m, 1H); 1.10(d, J=6.1 Hz, 3H); 1.03(s, 9H).

Adducts 16a and 17a: oil, IR (film): 3350, 1730, 1455, 1040, 670. Anal. calcd for $C_{25}H_{31}NO_6$: C 68.98; H 5.80; N3.21. Found: C 69.07; H 5.81; N 3.25.

16a: ^{1}H NMR: 7.40-7.25(m, 10H); 6.00(m, 1H); 5.71(m, 1H); 5.17(bd, J=9.6 Hz, 1H); 5.13(bs, 2H); 4.86(bs, 1H); 4.81(d_{AB}, J=7.0 Hz, 1H); 4.78(d_{AB}, J= 7.0 Hz, 1H); 4.67(d_{AB}, J= 12.Hz, 1H); 4.56(d_{AB}, J= 12.0 Hz, 1H); 4.31(q, J= 6.4 Hz, 1H); 3.89(ddd, J=11.0, 9.6, 1.5 Hz, 1H); 3.62(dd, J=9.6, 9.6 Hz, 1H); 3.40(s, 3H); 2.19-2.00(m, 2H); 1.27(d, J=6.4 Hz, 1H).

17a: ^{1}H NMR: 7.40-7.20(m, 10H); 5.96(m, 1H); 5.69(m, 1H); 5.17(d, J= 9.5 Hz, 1H); 5.15(bs, 2H); 4.81(s, 1H); 4.80(d_{AB}, J= 7.1 Hz, 1H); 4.72(d_{AB}, J= 7.1 Hz, 1H); 4.58(d_{AB}, J= 11.7 Hz, 1H); 4.53(d_{AB}, J= 11.7, 1H); 4.06(ddd, J= 11.2, 3.4, 1.2 Hz, 1H); 3.97(qd, J= 6.2, 6.0 Hz, 1H); 3.73(ddd, J= 9.5, 6.0, 3.4 Hz, 1H); 3.37(s, 3H); 2.22-2.14(m, 1H); 1.97-1.90(m, 1H); 1.29(d, J= 6.2 Hz, 3H).

Adducts 16b and 17b: oil, IR (film): 3420, 1730, 1450, 1020, 690. Anal. calcd for $C_{33}H_{41}NO_5Si$: C 70.80; H 7.38; N 2.50. Found: C 70.82; H 7.41; N 2.61.

16b: ^{1}H NMR: 7.70-7.25(m, 15H); 5.99(m, 1H); 5.71(m, 1H); 5.30(d, J=10.2 Hz, 1H); 5.19(d_{AB}, J= 12.4 Hz, 1H); 5.14(d_{AB}, J= 12.4 Hz, 1H); 4.80(bs, 1H); 4.49(dd, J= 6.3, 0.5 Hz, 1H); 4.06(m, 1H); 3.56(ddd, J= 10.2, 10.0, 0.5 Hz, 1H); 3.20(s, 3H); 2.13-2.03(m, 2H); 1.06(s, 9H); 1.00(d,J=6.3 Hz, 3H).

17b: ^{1}H NMR: 7.70-7.20(m, 15H); 5.93-5.85(m, 1H); 5.67-5.62(m, 1H); 5.14(d_{AB}, J= 12.1 Hz, 1H); 5.04(d, J= 10.0 Hz, 1H); 5.00(d_{AB}, J=12.1 Hz, 1H); 4.73(bs, 1H); 4.09(ddd, J=10.8, 4.8, 2.7 Hz, 1H); 4.01(qd, J= 6.2, 5.0 Hz, 1H); 3.65(ddd, J= 10.0, 5.0, 4.8 Hz, 1H); 3.26(s, 3H); 2.08-1.97(m, 1H): 1.68-1.62(m, 1H); 1.14(d, J= 6.2 Hz, 3H); 1.05(s, 9H).

ACKNOWLEDGMENT. This work was supported by the Polish Academy of Sciences (Grant CPBP-01.13).

REFERENCES AND NOTES

‡ Studies on the total synthesis of lincosamine. Part 2

1. Golebiowski, A.; Jurczak, J.; Pikul,S. in *High-Pressure Chemical Synthesis;* Jurczak, J.; Baranowski, B., Eds; Elsevier: Amsterdam, **1989**, p 210-254.
2. Danishefsky, S.; Larson, E.; Askin, D.; Kato, N. *J. Am. Chem. Soc.* **1985**, *107*, 1246-1256.
3. Zamojski, A.; Banaszek, A.; Grynkiewicz, G. *Adv. Carbohydr. Chem. Biochem.* **1982**, *40*, 1-112.
4. Golebiowski,A.; Jurczak, J. in *Recent Progress in the Chemical Synthesis of Antibiotics*. Lukacs, G. Ohno, M. Eds.; Springer-Verlag: Berlin, in press.
5. Danishefsky, S.; Larson, E.; Springer, J.P. *J. Am. Chem. Soc.* **1985**, *107*, 1274-1280.
6. Chmielewski, M.; Doboszewski, B.; Achmatowicz, O.Jr.; Zamojski, A. *Bull. Pol. Ac. :Chem.* **1984**, *32*, 423-427.
7. Jurczak, J.; Golebiowski, A.; Raczko, J. *Tetrahedron Lett.* **1988**, *29*, 5975-5978.
8. Jurczak, J.; Golebiowski, A.; Raczko, J. *J. Org. Chem.* **1989**, *54*, 2495-2496.

9. Ito, A.; Takahashi, R.; Baba, Y. *Chem. Pharm. Bull.* **1975**, *23*, 3081-3087.
10. Bednarski, M.; Danishefsky, S. *J. Am. Chem. Soc.* **1983**, *105*, 3716-3717.
11. Jurczak, J.; Golebiowski, A.; Bauer,T. *Synthesis* **1985**, 928-929.
12. Jurczak, J.; Bauer, T. *Tetrahedron* **1986**, *42*, 5045-5049.
13. Jurczak, J. Bauer, T.; Golebiowski, A. *Bull. Pol. Ac. :Chem.* **1985**, *33*, 397-401.
14. Golebiowski, A.; Jacobsson, U.; Jurczak, J. *Carbohydr. Res.* to be published.
15. Cram, D.J.; Abd Elhafez, F.A. *J. Am. Chem. Soc.* **1952**, *74*, 5827-5829.
16. Cherest, M.; Felkin, H.; Prudent, N. *Tetrahedron Lett.* **1966**, 2199-2203.
17. Anh, N.T. *Top. Curr. Chem.* **1980**, *88*, 145-168 .
18. Noyori, R.; Murata, S.; Suzuki, M. *Tetrahedron* **1981** *37*, 3899-3903.
19. Still, W.C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923-2925.
20. Jurczak, J.; Chmielewski, M.; Filipek, S. *Synthesis* **1979**, 41-42.
21. Montagna, A.E.; Hirsch, D.H., U. S. Pat. **1959**, 2,902,722.
22. Elliott, D.F. *J. Chem. Soc.* **1950**, 62-68.
23. Jones, J.K.N.; Millington, J.P.; Perry, M.B. *Can. J. Chem.* **1962**, *40*, 2229-2235.
24. Kozikowski, A.P.; Nieduzak, T.R.; Konoike, T.; Springer, J.P. *J. Am. Chem. Soc.* **1987**, *109*, 5167-5175.
25. Rittle, K.E.; Homnick, C.F.; Ponticello, G.S.; Evans, B.E. *J. Org. Chem.* **1982**, *47*, 3016-3018.
26. Jurczak, J.; Golebiowski, A. *Chem. Rev.* **1989**, *89*, 149-164.