20, 130121-17-4; **21**, 130121-18-5; (±)-(*R**,*R**)-**23a**, 130194-11-5; (±)-(*R**,*S**)-**23a**, 130194-12-6; (±)-(*R**,*R**)-**23b**, 130121-31-2; (±)-(*R**,*S**)-**23b**, 130121-32-3; **24a**, 58697-26-0; **24b**, 76700-84-0; **25a**, 130121-22-1; **25b**, 89682-40-6; **26a**, 130121-19-6; **26b**, 89682-39-3; **27a**, 130121-20-9; **27b**, 130121-23-2; **28** (R = Me), 130121-21-0; **29a**, 114730-45-9; **29b**, 104226-89-3; **30a**, 87517-46-2; **30b**, 130121-24-3; **30c**, 104227-38-5; **30d**, 37497-13-5; **31a**, 130121-26-5; **31b**, 130121-25-4; **31c**, 114730-22-2; **32a**, 130121-27-6; **32b**, 130121-28-7; **33a**, 130121-29-8; **33b**, 130121-30-1; **34b**, 5941-45-7; **35a**, 552-86-3; **35b**, 51490-07-4; **35c**, 36707-31-0; **36**, 130121-33-4; **37a**, 130121-34-5; (*R**,*R**)-**37b**, 130121-36-7; (*R**,*S**)-**37b**, 130194-13-7; **38**, 130121-35-6; (*R**,*R**)-**39**, 130121-37-8; (*R**,*S**)-**39**, 130194-14-8; ethyl diazoacetate, 623-73-4; furan, 110-00-9; 2,5-dimethylfuran, 625-86-5; 2-methylfuran, 534-22-5; 2-*n*-octylfuran, 4179-38-8; methyl 2-furoate, 611-13-2; methyl β-(2-furyl)acrylate, 623-18-7; ethyl α-diazopropionate, 6111-99-5; triethyl α-phosphonopropionate, 3699-66-9; trimethyl phosphonoacetate, 5927-18-4; pelargonyl chloride, 764-85-2; methyl glutaryl chloride, 1501-26-4; *tert*-butyl methyl glutarate, 59378-98-2; dimethyl methanephosphonate, 756-79-6.

Notes

New Chemoenzymatic Synthesis of (*R*)- and (*S*)-4-(Phenylsulfonyl)-2-methyl-1-butanol: A Chiral C_5 Isoprenoid Synthon

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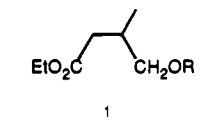
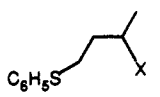
The chiral C_5 isoprenoid synthon of general formula **1** is a useful intermediate for the synthesis of various natural products and has been prepared by several chemoenzymatic approaches.[1] We had already prepared one of the possible synthetic equivalents of **1**, namely, (*S*)-(−)-1-(ethoxymethoxy)-2-methyl-4-(phenylthio)butane (**2a**), and used it for a new synthesis of (25*S*)-26-hydroxycholesterol.[2]



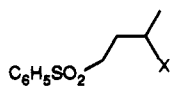
1

a. R= H
b. R= CH_2OEt



2

a. X= $CH_2OCH_2OC_2H_5$
b. X= COOH
c. X= $COOCH_3$
d. X= CH_2OH
e. X= CH_2OCOCH_3
f. X= $CH_2OCOC_3H_7$



3

a. X= $COOCH_3$
b. X= CH_2OH
c. X= CH_2OCOCH_3
d. X= $CH_2OCH_2OC_2H_5$

In that synthesis we used the biohydrogenation of ethyl 4,4-dimethoxy-3-methylbut-2-enoate with fermenting bakers' yeast for the preparation of ethyl (*S*)-(−)-4-hydroxy-3-methylbutanoate (**1a**),[3] which was further transformed into the chiral synthon **2a**. The above biotransformation, however, was not always reproducible, and the chiral intermediates had sometimes variable optical purities.[4] We therefore conceived a different approach for the preparation of enantiomerically pure (*S*)-(−)-**2a** and considered feasible the enzymatic hydrolysis of suitable esters related to the structure of the required intermediate. By this route, the recovery of the unreacted substrate should lead to the preparation of the other stereoisomer, (*R*)-(+)-**2a**. Benzenethiolate opening of commerically available (*R*,*S*)-2-methyl-γ-butyrolactone[5] afforded the racemic thio acid **2b**. Attempted hydrolysis of the methyl ester **2c** to optically active acid **2b**[6] in the presence of pig liver esterase (PLE) proceeded in good chemical yields, but with virtually no enantioselectivity. The ester **2c** was not a substrate for α-chymotrypsin, and the same negative results were obtained from the enzymatic hydrolysis of the methyl ester of phenylsulfonyl acid **3a**, easily obtained by *m*-chloroperbenzoic acid oxidation of the ester **2c**.

We then prepared the phenythio alcohol **2d** and its acetate **2e** and butanoate **2f**, in order to submit these esters to the action of a few hydrolases which have been successfully used for enantioselective hydrolysis of a great variety of substrates.[7] Aqueous hydrolysis was carried out in the presence of a lipase from *Pseudomonas fluorescens* and acetyl cholinesterase from electric eel on the acetate **2e** and with lipase from *Candida cylindracea* and butyryl cholinesterase from horse serum on the butanoate **2f**, prepared by direct esterification of the alcohol **2d** with butyryl chloride in pyridine. In no case did the enantiomeric excess (ee) of the product exceed a mere 20–30%. At this point, the recently published lipase-catalyzed irreversible transesterification using enol esters as acylating reagents[8] was considfered for the resolution of our alcohol.

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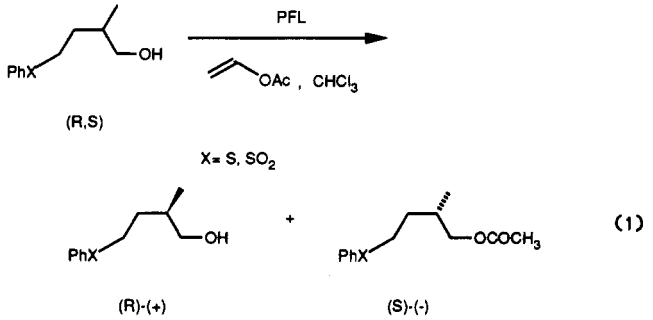
(1) Fuganti, C.; Grasselli, P.; Servi, S.; Hogberg, H. E. *J. Chem. Soc., Perkin Trans. 1* **1988**, 3061 and references cited therein.
(2) Ferraboschi, P.; Fiecchi, A.; Grisenti, P.; Santaniello, E. *J. Chem. Soc., Perkin Trans. 1* **1987**, 1749.
(3) Ferraboschi, P.; Grisenti, P.; Casati, R.; Fiecchi, A.; Santaniello, E. *J. Chem. Soc., Perkin Trans. 1* **1987**, 1743.
(4) The optical rotations of the phenylthio and phenylsulfonyl derivatives **2a** and **3d** reported in ref 2 do not correspond to optically pure material. The values reported in the present paper must, therefore, be considered for reference to optically pure compounds.
(5) The experimental conditions were essentially as descried for ring opening of 3-methyl-γ-butyrolactone: Ferraboschi, P.; Santaniello, E. *Synth. Commun.* **1984**, 1199.
(6) The *R* acid **2b** has already been prepared by enantioselective bakers' yeast hydrogenation: Sato, T.; Hanayama, K.; Fujisawa, T. *Tetrahedron Lett.* **1988**,*29*, 2197.
(7) For a recent review on the use of enzymes in organic synthesis, see: *Enzymes as Catalysts in Organic Synthesis*; Proc. NATO Adv. Res. Workshop; Schneider, M., Ed.; Reidel: Dorchrecht,Holland, 1986.
(8) Wang, Y. F.; Lalonde, J. J.; Momongan, M.; Bergbreiter, D. E.; Wong, C. H. *J. Am. Chem. Soc.* **1988**, *110*, 7200.

0022-3263/90/1955-6214$02.50/0

According to this report, a few alcohols were enantioselectively acylated with vinyl esters, whereas for others the method did not work in an entirely enantioselective fashion. In some cases, the ee of the first hydrolysis could be enhanced by a second enzymatic reaction, thus lowering the chemical yield of the procedure. In our case, by esterification of alcohols **2d** and **3b** with vinyl acetate in the presence of a lipase from *P. fluorescens* (PFL) in chloroform at 60% conversion (followed by ^1H NMR), nearly quantitative yields of alcohols **2d** and **3b** were obtained (eq 1). The ee of these alcohols was established as 98%, by 500-MHz ^1H NMR spectra of (*S*)-(−)-MTPA esters.[9]



(1)

For the quantitative determination of the *R*/*S* ratio it was necessary to decouple the signals corresponding to the C-2 methyl hydrogens (double doublet centered at 0.95 ppm for **2d**), by irradiation of the resonance at 2.04 ppm due to the corresponding hydrogen at the tertiary carbon. In this way, the resonances of the methyl groups of the *R* and *S* stereoisomers in racemic **2d** were at 0.925 and 0.936 ppm, and thus integration of the two singlets allowed us to determine the ee of samples from enzymatic reaction. In order to establish the stereochemical outcome of the PFL transesterification, the optically active alcohols **2d** and **3b** were converted into the corresponding ethoxymethoxy ethers **2a** and **3d**[2] and the optical rotations were compared with those of the same compounds prepared from ethyl (*S*)-4-(ethoxymethoxy)-3-methylbutanoate (**1b**) of known configuration.[3] This established an *R* configuration for (+)-**2d** and (+)-**3b**, and the absence of the resonance at 0.936 ppm in the NMR spectrum of the MTPA ester of **2d** establishes a 98% optical purity for the sample. The same results were obtained for (+)-**3b**, since in the MTPA ester of racemic **3b** two doublets were observed at 0.900 and 0.912 ppm. This separation was sufficient for the analysis of optically active **3b**, since its MTPA ester showed only the doublet at 0.900 ppm.

The *S* enantiomers of **2d** and **3b** can, in principle, be obained by bakers' yeast reduction,[2] but some variation of the optical purities of ethyl (*S*)-4-hydroxy-3-methylbutanoate (**1a**) and the corresponding (*S*)-3-methyl-γ-butyrolactone was often observed by us.[4,10] By the transesterification procedure described in this paper, optically pure acetates (*S*)-(−)-**2e** and (*S*)-(−)-**3c** were prepared at a 40% conversion in nearly quantitative yields. (*S*)-(−)-Acetates **2e** and **3c** showed an optical rotation of the same absolute value as the samples obtained by acetylation of optically pure alcohols **2d** and **3b**.

In summary, transesterification of racemic 4-(phenylthio)- and 4-(phenylsulfonyl)-2-methyl-1-butanol (**2d** and **3b**) with vinyl acetate in chloroform in the presence of *P. fluorescens* lipase (PFL) proceeded with high enantioselectivity and excellent yields. By this enzymatic route, enantiomerically pure alcohols (*R*)-(+)-**2d** and (*R*)-(+)-**3b** together with acetates (*S*)-(−)-**2e** and (*S*)-(−)-**3c** can be obtained and used as valuable C_5 isoprenoid chiral synthons.

Experimental Section

PLE was purchased from Boehringer Mannheim (Mannheim, West Germany), and acyl cholinesterases were purchased from Sigma (St. Louis, MO) α-chymotrypsin and lipases from Fluka (Buchs, Switzerland). (*S*)-(−)-MTPA chloride was obtained from JPS Chimie (Bevaix, Switzerland). TLC analyses were carried out on Merck 60 F_{254} silica gel plates.

Methyl (*R*,*S*)-4-(Phenylthio)-2-methylbutanoate (2c). A solution of thiophenol (1.6 mL, 15.6 mmol) in anhydrous tetrahydrofuran (4 mL) was added into a flask containing a suspension of sodium hydride (80%, 0.45 g) in tetrahydrofuran (10 mL) under nitrogen. After complete evolution of hydrogen, absolute ethanol (2.5 mL) was added in order to dissolve the sodium benzenethiolate. To this solution was added commercial α-methyl-γ-butyrolactone dropwise (1 g, 0.94 mL, 10 mmol), and the final solution was refluxed (24 h). The reaction mixture was worked up by addition of concentrated HCl, and excess thiophenol was distilled with the solvent into a flask containing a cold solution of potassium hydroxide. Water was added (10 mL), and the product was extracted with diethyl ether (3 × 10 mL). The acid **2b** was purified by silica gel chromatography, by elution with hexane/ethyl acetate (7/3) (1.95 g, 92%). The acid **2b** was quantitatively converted into its methyl ester **2c** by reaction with an ethereal solution of diazomethane: bp 220 °C (12 mmHg); ^1H NMR δ 1.2 (d, 3 H, J = 7 Hz, CH_3), 1.6–2.3 (m, 2 H, CH_2), 2.5–2.8 (m, 1 H, CH), 2.9 (t, 2 H, J = 8 Hz, CH_2S), 3.7 (s, 3 H, CH_3O), 7.35 (m, 5 H, Ar). Anal. Calcd for $C_{12}H_{16}O_2S$: C, 64.28; H, 7.14. Found: C, 64.42; H, 7.24.

(*R*,*S*)-4-(Phenylthio)-2-methyl-1-butanol (2d). A solution of the methyl ester **2c** (0.7 g, 3.12 mmol) in anhydrous tetrahydrofuran (5 mL) was added to a flask containing a suspension of lithium aluminum hydride (0.37 g, 9.5 mmol) in tetrahydrofuran (10 mL). The suspension was stirred at room temperature (3 h) and worked up under the usual conditions (addition of water, 15% NaOH, filtration of the lithium salts, and evaporation of the solvent). Pure title alcohol **2d** was obtained (0.58 g, 95%): bp 200 °C (10 mmHg); ^1H NMR δ 1.0 (d, 3 H, J = 7 Hz, CH_3), 1.5–2.2 (m, 4 H, CH_2, CH, and OH), 3.0 (t, 2 H, J = 8 Hz, CH_2S), 3.5 (d, 2 H, J = 6 Hz, CH_2O), 7.35 (m, 5 H, Ar). Anal. Calcd for $C_{11}H_{16}OS$: C, 67.35; H, 8.16. Found: C, 67.48; H, 8.28.

(*R*,*S*)-4-(Phenylsulfonyl)-2-methyl-1-butanol (3b). To a solution of the above phenylthio alcohol **2d** (2.36 g, 12 mmol) in dichloromethane (65 mL) was added *m*-chloroperbenzoic acid (55%, 3.75 g, 12 mmol). The solution was left at room temperature (8 h) and then washed with 5% ammonia solution. The solution was dried on sodium sulfate and then evaporated, and the reaction mixture was purified by column chromatography. The sulfone **3b** was eluted with ethyl acetate (2.27 g, 83%): bp 245 °C (12 mmHg); ^1H NMR δ 0.9 (d, 3 H, J = 7 Hz, CH_3), 1.2–2.0 (m, 3 H, CH_2 and CH), 2.8–3.5 (m, 5 H, CH_2O, CH_2SO_2, and OH), 7.6–7.9 (m, 3 H, Ar), 7.9–8.2 (m, 3 H, Ar). Anal. Calcd for $C_{11}H_{16}O_3S$: C, 57.89; H, 7.01. Found: C, 57.98; H, 7.1.

General Procedure for PFL-Catalyzed Transesterification of Alcohols 2d and 3b. The alcohol used as substrate and vinyl acetate were dissolved in chloroform, and the enzyme PFL (42 units/mg) was added. The suspension was stirred at 30 °C, and the reaction was monitored by ^1H NMR for the conversion. When the conversion desired was reached, the enzyme was filtered off and the solvent was evaporated. The ester obtained as product and the unreacted alcohol were separated by silica gel chromatography.

(*R*)-(+)-4-(Phenylthio)-2-methyl-1-butanol (2d). A solution of the racemic alcohol **2d** (0.385 g, 1.96 mmol), vinyl acetate (0.75 mL, 8.12 mmol), and PFL (22 mg, 924 units) in chloroform (10 mL) was stirred for 18 h. After workup and purification, fractions eluted with hexane/ethyl acetate (9/1) contained the acetate **2e** (0.27 g, 58%), $[\alpha]_D$ −12° (*c* 4, $CHCl_3$). Fractions eluted with hexane/ethyl acetate (8/2) contained the alcohol **2d**, with chemicophysical characteristics in complete agreement with those of

(9) Dale, J. A.; Mosher, H. S. *J. Am. Chem. Soc.* **1973**, *95*, 512.

(10) Recently, we have prepared the β-methyl lactone with constant >90% optical purity by bakers' yeast reduction of potassium 4,4-dimethoxy-3-methylbut-2-enoate: Ferraboschi, P.; Grisenti, P.; Fiecchi, A.; Santaniello, E. *Org. Prep. Proced. Int.* **1989**, *21*, 371.

the racemic compound (0.15 g, 39%), $[\alpha]_D$ +21° (c 4, $CHCl_3$). The (S)-(-)-MTPA ester of racemic **2d**, prepared as described in ref 9, showed, with decoupling of the C-2 methyl signals (double doublet at 0.945 ppm) by irradiation of the resonance at 2.04 ppm due to the corresponding hydrogen at the tertiary carbon, the resonances of the C-2 methyl groups for (R)- and (S)-**2d** at 0.925 and 0.936 ppm. In the spectrum of the corresponding derivative from (R)-(+)-**2d**, the resonance of the methyl group at 0.936 ppm was absent. In a control, this signal could be detected when 2% of racemate was added to (R)-**2d**, corresponding to 1% of the S isomer, and 98% ee was therefore established for the enzymatically produced (R)-(+)-**2d**.

(R)-(+)-4-(Phenylsulfonyl)-2-methyl-1-butanol (3b). A solution of the racemic alcohol **3b** (0.25 g, 1.1 mmol), vinyl acetate (0.42 mL, 4.55 mmol), and PFL (12.3 mg, 517 units) in chloroform (2.5 mL) was stirred for 16 h. After workup and purification, fractions eluted with hexane/ethyl acetate(6/4) contained the acetate **3c** (0.125 g, 42%), $[\alpha]_D$ -5° (c 4, $CHCl_3$). Fractions eluted with hexane/ethyl acetate (4/6) contained the alcohol **3b**, with chemicophysical characteristics in complete agreement with those of the racemic compound (0.140 g, 56%), $[\alpha]_D$ +10° (c 4, $CHCl_3$). The (S)-(-)-MTPA ester of racemic **3b** showed the resonances of the C-2 methyl groups for (R)- and (S)-**3b** as two overlapped doublets (J = 6.93 Hz) centered at 0.900 and 0.912 ppm. In the spectrum of the corresponding derivative from (R)-(+)-**3b**, the resonance of the methyl group at 0.912 ppm was absent. In a control, this signal could be detected when 2% of racemate was added to (R)-**3b**, corresponding to 1% of the S isomer, and 98% ee could be established for (R)-(+)-**3d**.

(S)-(-)-Acetate 2e. In order to prepare enantiomerically pure (S)-(-)-**2e**, the hydrolysis was repeated as described for the preparation of (R)-(+)-**2d**, with the same amounts of substrate and enzyme, the reaction being stopped at 40% conversion. Pure acetate **2e** was obtained by column chromatography (0.177 g, 38%): bp 240 °C (16 mm Hg); $[\alpha]_D$ -15° (c 4, $CHCl_3$); ^1H NMR δ 1.0 (d, 3 H, J = 7 Hz, CH_3), 1.5-1.9 (m, 3 H, CH_2 and CH), 2.0 (s, 3 H, CH_3CO), 2.95 (t, 2 H, J = 8 Hz, CH_2S), 4.0 (d, 2 H, J = 6 Hz, CH_2O), 7.35 (m, 5 H, Ar). Anal. Calcd for $C_{13}H_{18}O_2S$: 65.55; H, 7.56. Found: C, 65.7; H, 7.65.

(S)-(-)-Acetate 3c. The hydrolysis was repeated as described for the preparation of (R)-(+)-**3b**, with the same amounts of substrate and enzyme, the reaction being stopped at 40% conversion. Pure acetate **3c** was obtained by column chromatography (0.104 g, 36%): bp 205 °C (0.3 mm Hg); $[\alpha]_D$ -10.5° (c 4, $CHCl_3$); ^1H NMR δ 0.95 (d, 3 H, J = 7 Hz, CH_3), 1.2-2.0 (m, 3 H, CH_2 and CH), 2.0 (s, 3 H, CH_3CO), 3.2 (t, 2 H, J = 8 Hz, CH_2SO_2), 3.95 (d, 2 H, J = 6 Hz, CH_2O), 7.65-7.9 (m, 3 H, Ar), 7.9-8.2 (m, 2 H, Ar). Anal. Calcd for $C_{13}H_{18}O_4S$: C, 57.75; H, 6.66. Found: C, 57.88; H, 6.75.

(R)-(+)-1-(Ethoxymethoxy)-2-methyl-4-(phenylthio)butane (2a). This compound was synthesized from enzymatically prepared (R)-(+)-**2d** as described in ref 3. The purified compound had characteristics in agreement with those of a standard sample. Starting from alcohol **2d** of $[\alpha]_D$ +21°, the derivative **2a** presented $[\alpha]_D$ +11.5° (c 2, $CHCl_3$).

(R)-(+)-1-(Ethoxymethoxy)-2-methyl-4-(phenylsulfonyl)butane (3d). This compound was synthesized from enzymatically prepared (R)-(+)-**3b** as described in ref 3. The purified compound had characteristics in agreement with those of a standard sample. Starting from alcohol **3b** of $[\alpha]_D$ +10.5°, the derivative **3d** presented $[\alpha]_D$ +5.2° (c 2, $CHCl_3$).

Acknowledgment. We thank Ministero della Pubblica Istruzione for financial help, Dr. Maurizio Anastasio for his participation at the latest stages of the work, and Mr. Carlo Cavarretta and Miss Elisa Verza for technical assistance.

Registry No. (R)-(+)-**2a**, 129423-06-9; (±)-**2b**, 129518-64-5; (±)-**2c**, 129518-65-6; (R)-**2e**, 129423-10-5; (±)-**2d**, 129423-00-3; (R)-(+)-**2d**, 129518-67-8; (R)-**2d** ((S)-(-)-MTPA ester), 129423-04-7; (S)-**2d** ((S)-(-)-MTPA ester), 129423-08-1; (S)-(-)-**2e**, 129423-01-4; (±)-**3b**, 129518-66-7; (R)-(+)-**3b**, 129423-03-6; (R)-**3b** ((S)-(-)-MTPA ester), 129423-05-8; (S)-**3b** ((S)-(-)-MTPA ester), 129423-09-2; (S)-(-)-**3c**, 129423-02-5; (R)-(+)-**3d**, 129423-07-0; PFL, 9001-62-1; PhSH, 108-98-5; α-methyl-γ-butyrolactone, 69010-09-9.

Addition of Activated Grignard Reagents to 2-Phenyloxazolines

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Introduction

The role of amino sugars and amino deoxy sugars as parts of biologically active molecules is well recognized, and numerous efforts have been devoted to their synthesis in enantiomerically pure form.[1] Recently[2] we have been using an approach to isomeric 2,4,6-trideoxy-4-C-methyl-4-amino-L-hexose derivatives starting from L-threonine (1) (Scheme I).

Thus oxazoline **2** obtained as described from L-threonine[3] was methylated to give the aldehyde **3**. Treatment of **3** with allylmagnesium bromide gave the isomeric alcohols **4**. Ozonization of the terminal double bond and deprotection of the β-amino alcohol gave 4-C-methyl amino deoxy sugars of type **5** in enantiomerically pure form. Under the conditions used, even with an excess of nucleophile, addition to the C=N double bond was never observed, as expected from the known stability of 2-oxazolines to Grignard reagents.[4]

In order to prepare differently substituted 2,3,4,6-tetradeoxy-4-aminohexoses of the L series, we considered an approach similar to the one described in Scheme I, namely, the preparation of the tosylates **6a-d**, chain elongation with allyl Grignard reagent, double-bond oxidation, and final deprotection. This procedure should eventually lead to isomeric compounds of type **8** through acyclic precursors like **7** (Scheme II).

Results and Discussion

In contrast to our expectations, reaction of tosylates **6** with allyl Grignard reagents under various conditions,[5] did not affect chain elongation[6] but gave bicyclic compounds **9a-d** as the only products. Structural assignement was made on the basis of high resolution ^1H NMR spectroscopy (Table I) combined with IR and MS data. The formation of a three-membered ring is evident from the chemical shifts and coupling constants of the protons H-4, H-6a, and H-6b.[7] In particular, the magnitude of the geminal coupling constants ^2J(6a,6b), <0.5 Hz, is characteristic of the aziridine ring.[8] The erythro or threo stereochemistry of C-4 and C-5 in **9a,b** reflects the stereochemistry of the starting materials and can be easily recognized from the vicinal coupling constants ^3J(4,5). In the erythro compound **9b** with the protons H-4 and H-5 cis oriented in the five-membered ring, ^3J(4,5) is 3.0 Hz, while for the threo compound **9a** with H-4 and H-5 in a trans relationship, the value of ^3J(4,5) is ~0. In the latter case the two

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(2) Fronza, G.; Fuganti, C.; Pedrocchi-Fantoni, G. *J. Carbohydr. Chem.* **1989**, *8*, 85.
(3) Seebach, D.; Aebi, J. D. *Tetrahedron Lett.* **1983**, *24*, 3211.
(4) Meyers, A. I.; Mihelich, E. D. *Angew. Chem. Int. Ed. Engl.* **1976**, *15*, 270.
(5) No difference was oserved by using THF or diethyl ether with commercially available Grignard solutions or fresly prepared in the presence of Li_2CuCl_4 (ref 6) or without the latter reagent.
(6) Fouquet, G.; Schlosser, M. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 82.
(7) Jackman, L. A.; Sternhell, S. In *Application of NMR Spectroscopy in Organic Chemistry*, 2nd ed.; Pergamon Press: Oxford, 1969; p 272.
(8) Manatt, S. L.; Ellemann, D. D.; Brois, S. J. *J. Am. Chem. Soc.* **1965**, *87*, 2220.

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