Pergamon

Tetrahedron: Asymmetry, Vol. 7, No. 12, pp. 3527-3534, 1996

0957-4166/96 $15.00 + 0.00

PII: S0957-4166(96)00460-0

Organoboranes for Synthesis 17. Generality of Hydroboration-Amination for the Conversion of Terpenes into Enantiomerically Pure Terpenylamines. Their Utility for Gas Chromatographic Analysis of Chiral Carboxylic Acids

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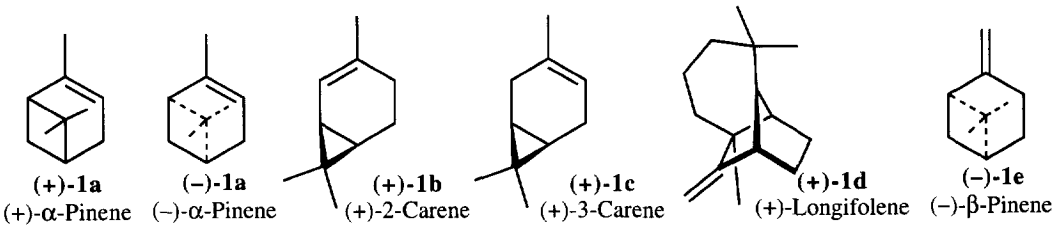
Abstract: The generality of our new convenient synthesis of isopinocampheylamines by hydroboration-amination of α-pinene has been established by converting representative terpenes into optically pure terpenylamines, such as (–)-*cis*-caran-*trans*-2-amine, (–)-*cis*-caran-*trans*-4-amine, (–)-longifolamine, and (+)-*cis*-myrtanylamine. The synthesis involves converting the terpene into the *B*-chloroditerpenylborane by treatment with chloroborane-methyl sulfide. This is treated with trimethylaluminum to form the *B*-methylditerpenylborane, and the latter is converted into the amine by treatment with hydroxylamine-*O*-sulfonic acid. *cis*-Myrtanylamine has been shown to be as effective as isopinocampheylamine for the gas chromatographic analysis of racemic carboxylic acids as their diastereomeric amides, suggesting the generality of this application of terpenylamines as chiral derivatizing agents.

INTRODUCTION

Enantiomerically pure primary and secondary amines, traditional reagents for the kinetic resolution of racemic carboxylic acids, are gaining major importance in asymmetric synthesis, serving as chiral auxiliaries and intermediates.[2] Accordingly several new chiral amines have been synthesized in the recent past.[3,4] We recently reported an optimized extremely efficient synthesis, in very high yields, of both enantiomers of isopinocampheylamines, (**(–)-** and **(+)-4a**) from the corresponding antipodes of the super chiral auxiliary[5] α-pinene (**(+)-** and **(–)-1a**), respectively, via the corresponding *B*-chlorodiisopinocampheylboranes (**(–)-** and **(+)-2a**), respectively, and the corresponding *B*-methyldiisopinocampheylboranes (**(–)-** and **(+)-3a**), respectively.[6] The utility of this amine in organic synthesis is being tested in our laboratory. Our experience in asymmetric synthesis via organoboranes[7] using terpenes as chiral auxiliaries has shown that terpenes, such as 2- and 3-carenes and 2-alkylapopinenes, provide superior results in asymmetric hydroboration,[8] asymmetric reduction[9] and asymmetric allylboration.[10,11] On this basis, to test the generality of our new convenient synthesis of **4a**, and to make several stereoisomerically pure terpenylamines available to organic chemists, we decided to extend our methodology to several representative terpenes, such as 2-carene (**1b**), 3-carene (**1c**), longifolene (**1d**), and β-pinene (**1e**).



Previously we reported the utility of isopinocampheylamines ((−)- and (+)-**4a**) as chiral derivatizing agents for the gas chromatographic analysis of optically active acids.[6] We were interested in testing the utility of other terpenylamines for this purpose and have now shown that even *cis*-myrtanylamine (**4e**), which has the amine moiety separated by a $-CH_2-$ group from the chiral center, is as effective a derivatizing agent as isopinocampheylamine. This paper discusses the synthesis of optically pure terpenylamines and the utility of (+)-*cis*-myrtanylamine as a chiral derivatizing agent for the gas chromatographic analysis of optically active carboxylic acids.

RESULTS AND DISCUSSION

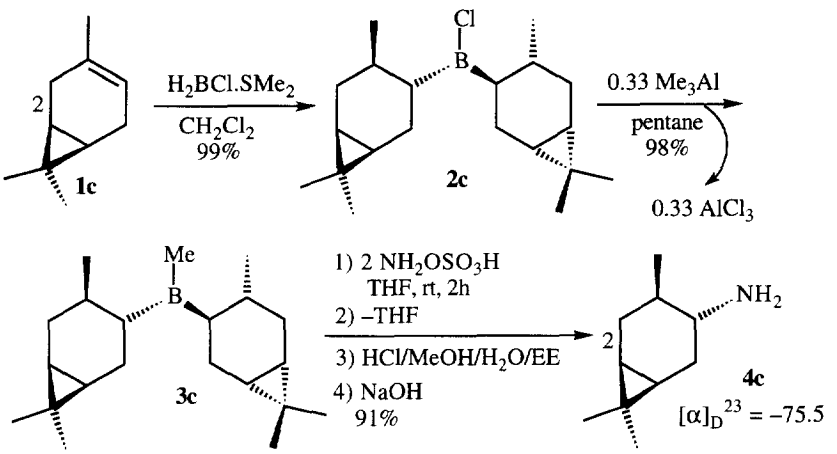
Synthesis of Terpenylamines via Hydroboration-Amination of Terpenes

Treatment of the four selected terpenes (**1b-e**) with chloroborane-methyl sulfide complex ($ClBH_2{\bullet}SMe_2$) in CH_2Cl_2 at room temperature (rt) provides the corresponding *B*-chloroditerpenylboranes (**2b-e**) in essentially quantitative yields. Treatment of these chloroboranes with 0.33 equiv of Me_3Al provides the corresponding *B*-methylditerpenylboranes (**3b-e**). These intermediates, upon treatment with hydroxylamine-*O*-sulfonic acid (HSA) in THF, followed by hydrolysis with HCl/MeOH/H_2O/EE readily provide the corresponding terpenylamines in excellent yield (eq 1).

$$\underset{\textbf{1a-e}}{2\ \text{Terpene}} \xrightarrow[CH_2Cl_2]{H_2BCl{\bullet}SMe_2} \underset{\textbf{2a-e}}{Terp_2BCl} \xrightarrow[\substack{\text{pentane}\\ -0.33\ AlCl_3}]{0.33\ Me_3Al} \underset{\textbf{3a-e}}{Terp_2BMe} \xrightarrow[\substack{2)\ -THF\\ 3)\ HCl/MeOH/H_2O/EE\\ 4)\ NaOH}]{\substack{1)\ 2\ NH_2OSO_3H\\ THF,\ rt,\ 2h}} \underset{\textbf{4a-e}}{2\ TerpNH_2} \qquad (1)$$

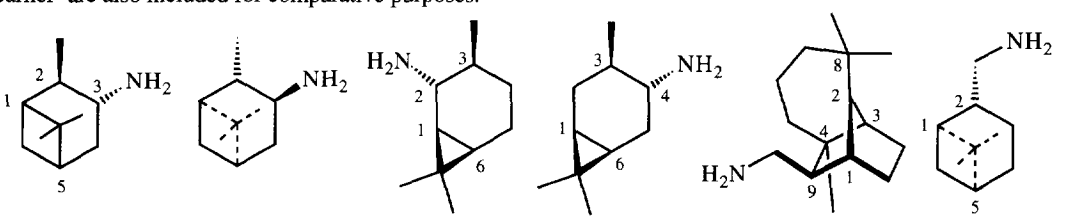
Although the commercial $ClBH_2{\bullet}SMe_2$ is an equilibrium mixture containing ~5-7% of both $Cl_2BH{\bullet}SMe_2$ and $BH_3{\bullet}SMe_2$, the equilibrium is shifted towards $ClBH_2{\bullet}SMe_2$ in hydroborations of hindered olefins.[12] This hydroboration reaction provides chemically pure *B*-chloroditerpenylboranes from the two α-pinenes, (+)- and (−)-**1a**,[13] 2-carene (**1b**), and 3-carene (**1c**). In the case of unhindered exocyclic olefins, such as longifolene (**1d**) and β-pinene (**1e**), ≤5 % of *B,B*-dichloroterpenylborane is also formed. However, this does not affect the yield of the amine since these dichloroboranes are converted to the corresponding dimethyl derivatives upon treatment with trimethylaluminum in the next step, and the methyl groups do not migrate in competition with the terpenyl groups in the amination step.[14] Irrespective of the structure of the terpenes, all of these amines are obtained in satisfactory yields (75-96%).

For example, 3-carene (**1c**) is converted to *B*-chlorodiiso-4-caranylborane (**2c**) in 99% yield by treatment with $ClBH_2{\bullet}SMe_2$. This is then converted to *B*-methyldiiso-4-caranylborane (**3c**) in 98% yield by treatment with 0.33 equiv of trimethylaluminum, which is then transformed to the corresponding amine, (−)-*cis*-caran-*trans*-4-amine (**4c**) in 91% isolated yield (eq 2).



(2)

As previously noted for the amination of (+)- and (−)-**3a**, the amination of **3b-e** proceeds with retention of configuration without any detectable loss of optical activity. It is especially noteworthy that even 2-carene (**1b**) retains the integrity of the cyclopropane ring at the 2-position without cleavage during the entire process, providing a good yield of the corresponding amine. The enantiomeric purities of these amines, determined by the gas chromatographic analysis of their α-methoxy(trifluoromethyl)phenylacetamide derivatives (MTPA amides), using a SPB-5 capillary column (30 m), are ≥ 99%. The isolated yields and the physical properties of the amines **4b-e** shown below are summarized in Table 1. The data for (−)- and (+)-**4a** reported earlier[6] are also included for comparative purposes.



(−)-4a (−)-IpcNH$_2$ | **(+)-4a** (+)-IpcNH$_2$ | **(−)-4b** (−)-2-CarNH$_2$ | **(−)-4c** (−)-4-CarNH$_2$ | **(−)-4d** (−)-LgfNH$_2$ | **(+)-4e** (+)-MyrNH$_2$

Table 1. Synthesis of Enantiomerically Pure Terpenylamines

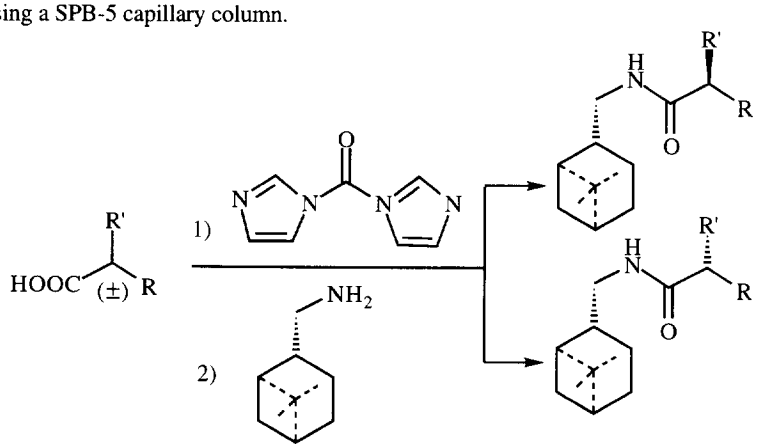
terpene	terp$_2$BCl yield[a] %	terp$_2$BCl ^{11}B NMR δ (ppm)	terp$_2$BMe yield[a] %	terp$_2$BMe ^{11}B NMR δ (ppm)	terpNH$_2$ yield[a] %	ee[b] %	bp (°C/mm Hg)	$[\alpha]_D^{23}$ (neat)
(+)-α-pinene, **(+)-1a**	99	74	98	81	96	≥99	90/18	−44.0[c]
(−)-α-pinene, **(−)-1a**	99	74	97	81	94	≥99	90/18	+44.0[c]
(+)-2-carene, **1b**	93	74	93	79	75	≥99	35/0.4	−29.8
(+)-3-carene, **1c**	99	77	98	83	91	≥99	36/0.4	−75.5
(+)-longifolene, **1d**	97	68	98	87	91	≥99	198/1	−11.3
(−)-β-pinene, **1e**	92	67	89	87	84	≥99	95/27	+30.5

[a]Isolated yield. [b]Determined as the MTPA amide on a SPB-5 capillary column. [c]From ref. 6.

These results support the generality of our optimized synthesis of terpenylamines, so that this convenient procedure should be applicable to other terpenes, such as sabinene, thujene, α- and β-cedrene, thujopsene, etc., to convert them into the corresponding stereoisomerically pure amines.

(–)-cis-Myrtanylamine as a Chiral Derivatizing Agent

An application of the isopinocampheylamines which we recently reported is the gas chromatographic separation of racemic carboxylic acids as their isopinocampheylamides prepared by treating the chiral acids in THF with 1,1'-carbonyldiimidazole (CDI),[15] followed by $IpcNH_2$ (**4a**). From among the new series of terpenylamines (**4b-e**) that we synthesized, we selected (–)-*cis*-myrtanylamine (**4e**) as a difficult candidate to test the generality of the applicability of terpenylamines for this purpose, since the amino group in this terpenylamine is one carbon away from the nearest chiral center. It is gratifying to observe that the corresponding amides prepared from **4e** (eq 3) could be readily separated by gas chromatography. The results of the GC analysis are summarized in Table 2. The data realized with **4a** reported earlier[6] are also included for comparison. It is interesting to note that while the amide from mandelic acid and $IpcNH_2$ could not be separated on this column, the corresponding amide with $MyrNH_2$ could be easily separated (entry #3). However, the reverse was the case for the amides from *N*-trifluoroacetylproline (entry #5). This supports the advantage of having a number of terpenylamines available to overcome the problem of acids that cannot be separated by a particular terpenylamine. Figure 1 shows a representative chromatogram of *N*-(*cis*-myrtanyl)mandelamide analyzed using a SPB-5 capillary column.



The results obtained with the *N*-(*cis*-myrtanyl)amides suggest that the diastereomeric carboxylic amides prepared from all of the other terpenylamines (**4b-d**) and racemic carboxylic acids should also be separated by gas chromatography. By the selection of a proper terpenylamine, it should now be possible to determine the optical purity of almost any type of chiral carboxylic acid by the gas chromatographic analysis of its terpenylamide. This application should be valuable in asymmetric syntheses.

Table 2. Column Temperatures and Retention Times for the Separation of Terpenylamides of Racemic Carboxylic Acids on a SPB-5 Capillary Column[a]

acid	myrtanylamide temp °C	myrtanylamide ret. time (min.) t_1	myrtanylamide ret. time (min.) t_2	isopinocampheylamide temp °C	isopinocampheylamide ret. time (min.) t_1	isopinocampheylamide ret. time (min.) t_2
(±)-α-methoxyphenylacetic acid	180	94.3	98.0	180	67.3	69.5
(±)-2-phenylbutyric acid	170	126.7	128.7	180	93.8	95.2
(±)-mandelic acid	185	95.8	97.6	no separation		
(±)-tetrahydro-2-furoic acid	130	251.1	259.8	130	168.2	171.2
(±)-*N*-trifluoroacetylproline	no separation			140	175.9	180.1
(±)-methoxy(trifluoromethyl)phenyl-acetic acid	180	91.5	94.9	180	52.4	53.5

[a]Column inlet pressure: 14.5 psi for myrtanylamide and 26 psi for isopinocampheylamide; linear flow rate 20 cm/min.; split ratio 100:1.

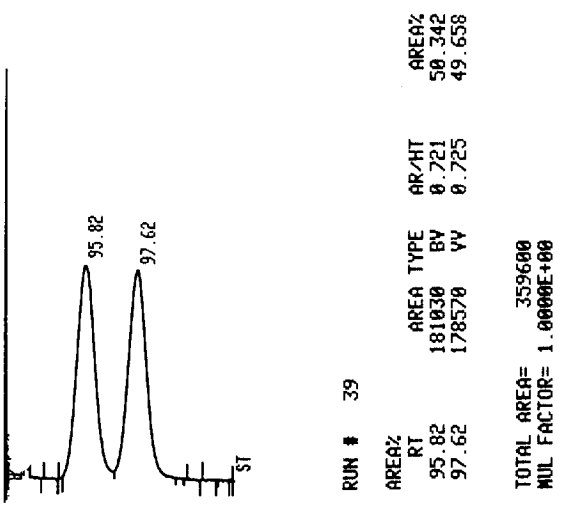


Fig. 1. Gas Chromatogram of Diastereomeric *N*-(*cis*-myrtanyl)mandelamides on a SPB-5 (30 m) Column at 185 °C.

CONCLUSIONS

In conclusion, we have established the generality of our new convenient synthesis of isopinocampheylamine by extending the hydroboration-amination methodology for the synthesis of a series of optically pure terpenylamines, such as (–)-*cis*-caran-*trans*-2-amine, (–)-*cis*-caran-*trans*-4-amine, (–)-

longifolamine, and (+)-*cis*-myrtanylamine, in satisfactory yields from the corresponding readily available terpenes. Application of *cis*-MyrNH$_2$ for determining the enatiomeric purity of chiral carboxylic acids as their diastereomeric amides using capillary gas chromatography has been demonstrated, suggesting the generality of the use of terpenylamines as chiral derivatizing agents. We do not foresee any difficulty in utilizing other terpenylamines for this purpose. The selected terpenylamines readily synthesized from terpenes, as reported in this paper, and other amines that should be conveniently synthesized using this procedure from readily available terpenes, all should enrich the pool of chiral auxilaries available to organic chemists. Further research exploiting the potential of these amines in asymmetric syntheses is under way.

Acknowledgment. Financial support from the United States Office of Naval Research is gratefully acknowledged.

EXPERIMENTAL

General Methods. All operations were carried out under an inert atmosphere. Techniques for handling air- and moisture-sensitive materials have been previously described.[16] The ^{1}H and ^{11}B NMR spectra were plotted on a Varian Gemini-300 spectrometer with a Nalorac-Quad probe. Analysis of the enantiomeric purity of amines **4b-e** as the diastereomeric amides prepared by reaction with MTPA-chloride and the analyses of the diastereomeric amides prepared from racemic carboxylic acids and **4e** were performed on a Hewlett-Packard 5890A gas chromatograph (GC) using a SPB-5 capillary column (30m) at appropriate temperatures and integrated using a Hewlett-Packard 3390 A integrator. The infrared spectra were recorded on a Perkin-Elmer 1420 ratio recording spectrophotometer. The mass spectra were obtained on a Finnigan Model 4000 gas chromatograph mass spectrometer. The optical rotations were measured using a Rudolph Autopol III polarimeter.

Materials. Anhydrous ethyl ether purchased from Mallinckrodt, Inc. was used as received. THF was distilled from sodium benzophenone ketyl. 2- and 3-carenes, (+)-longifolene, (–)-β-pinene (upgraded)[17], trimethylaluminum, hydroxylamine-*O*-sulfonic acid, (±)-methoxyphenylacetic acid, (±)-α-methoxy-α-(trifluoromethyl)-phenylacetic acid, (±)-tetrahydro-2-furoic acid, DL-mandelic acid, (±)-2-phenylbutyric acid, and 1,1'-carbonydiimidazole were all obtained from the Aldrich Chemical Co. (*R*)-(+)-α-methoxy-α-(trifluoromethyl)phenylacetic acid was purchased from the Aldrich Chemical Co. and converted to the acid chloride using Mosher's procedure.[18]

Preparation of Terpenylamines.

General Procedure. Preparation of *B*-Chloroditerpenylborane (2). To a 250 ml round bottom flask containing the terpene **1** (210 mmol) in 75 mL of CH_2Cl_2 was added $ClBH_2$•SMe_2 (100 mmol) at 0 °C, and the mixture was warmed to rt and stirred for 10 hrs. The ^{11}B NMR spectrum of an aliquot of the mixture revealed a singlet at δ ~74, which was shifted to δ 52 after methanolysis. The solvent was removed under aspirator vacuum to provide the *B*-chloroditerpenylborane (**2**), which was used as such in the next step.

Preparation of *B*-Methylditerpenylborane (3). Trimethylaluminum (10 mL of 2 M (calculated as monomer) solution in hexane, 20 mmol) was added, dropwise, to a stirred solution of $Terp_2BCl$ (60 mmol) in pentane (50 mL) at 0 °C. The reaction is mildly exothermic and the temperature was controlled by the slow addition of Me_3Al. Upon addition of Me_3Al, the colorless reaction mixture became pale yellow and a brown viscous mass (presumably $AlCl_3$) precipitated out of the hexane-pentane mixture. The reaction mixture was warmed to rt and allowed to stir for 0.5 h. The ^{11}B NMR spectrum of an aliquot of the supernatant showed the total disappearance of $Terp_2BCl$ (δ 74 ppm) and the formation of $Terp_2BMe$ (δ 81 ppm). The hexane-pentane mixture was separated by means of a cannula, washed with NH_4Cl solution (20 mL) under nitrogen, and dried over $MgSO_4$. Upon washing with NH_4Cl solution, the pale yellow solution became colorless. Removal of the volatiles furnished **3** which was used as such for the preparation of the amine.

Preparation of Terpenylamine (4). Hydroxylamine-*O*-sulfonic acid (126 mmol, 2.1 equiv), with the help of an addition tube for solids, was added slowly to 60.0 mmol of the *B*-methylditerpenylborane prepared above dissolved in freshly distilled THF (60 mL). The temperature of the reaction was controlled by the slow addition of HSA. The reaction mixture was stirred at rt, until the initial slurry became a clear solution (2 h). The completion of the reaction was ascertained by ^{11}B NMR spectroscopy and the solvent was pumped of *in vacuo* (20 mm). The residual viscous mass was treated with methanol (5 mL), conc. HCl (13 mL), and water (10mL), and to this mixture 60 mL EE was added. The reaction mixture was allowed to stir at 25 °C for 0.5 h. The ^{11}B NMR spectrum of the organic portion showed a sharp singlet at δ 32 ppm $MeB(OMe)_2$. The acidic aqueous layer was separated, cooled to 0 °C and layered with EE (40 mL). It was then made strongly alkaline by adding solid NaOH with stirring. The EE layer was separated and the aqueous layer was extracted with EE (3 x 40 mL), combined, dried over Na_2SO_4, concentrated, and distilled to furnish the corresponding terpenylamine **4**. The amines were characterized by ^1H NMR, and mass spectrometry. The MTPA amides of these amines were prepared and analyzed on a GC using a SPB-5 capillary column at appropriate temperatures. All of the amines showed an ee of ≥99%.

(–)-*cis*-Caran-*trans*-2-amine (4b): overall yield, 65%; bp 35 °C/0.4 mm Hg (lit.[19] bp 80-82 °C/8 mm Hg); IR ν_{max}^{cm-1} 3000, 2910, 1610; ^1H NMR δ ($CDCl_3$), 0.91 (d, J = 4 Hz, C$\underline{H}_3$), 0.98 (s, gem C$\underline{H}_3$), 1.03 (s, gem C$\underline{H}_3$), 2.78 (N$\underline{H}_2$); MS, m/z 154 (M+H), 153 (M^+); $[\alpha]_D^{23}$ (neat) –29.9 (lit.[20] $[\alpha]_D$ (neat) –30.5).

(–)-*cis*-Caran-*trans*-4-amine (4c): overall yield, 88.3%; bp 36 °C/0.4 mm Hg (lit.[19] bp 80-82 °C/8 mm Hg); IR ν_{max}^{cm-1} 3000, 2910, 1610; ^1H NMR δ ($CDCl_3$), 0.82 (d, J = 3 Hz, C$\underline{H}_3$), 0.97 (s, gem C$\underline{H}_3$), 1.03 (s, gem C$\underline{H}_3$), 2.79 (N$\underline{H}_2$); MS, m/z 154 (M+H), 153 (M^+). $[\alpha]_D^{23}$ (neat) –75.5 (lit.[20] $[\alpha]_D$ (neat) –77.1).

(–)-Longifolamine (4d): overall yield, 86.5%; bp 195-198 °C/1.0 mm Hg (lit.[21] bp 200 °C/1.0 mm Hg); IR ν_{max}^{cm-1} 3370, 3180, 1670; ^1H NMR δ ($CDCl_3$), 0.96 (s, C$\underline{H}_3$), 1.00 (s, gem C$\underline{H}_3$), 1.10 (s, gem C$\underline{H}_3$), 2.98 (N$\underline{H}_2$).); Ms, m/z 221 (M+H), 206 (M-CH_3); $[\alpha]_D^{23}$ (neat) –11.3.

(+)-cis-Myrtanylamine (4e): overall yield, 68.8%; bp 95 °C/27 mm Hg (lit.[22] bp 60-61 °C/2 mm Hg); IR ν_{max}^{cm-1} 2990, 2905, 1610, 1470; ^{1}H NMR δ ($CDCl_3$), 1.00 (s, gem $C\underline{H}_3$), 2.75 ($N\underline{H}_2$); MS, m/z 154 (M+H), 153 (M^+); $[\alpha]_D^{23}$ (neat) +30.5 (lit.[22] $[\alpha]_D^{26}$ (neat) –27.9 for the (–)-isomer).

Preparation and Analysis of Diastereomeric Amides.

General Procedure. The racemic carboxylic acid (0.1 mmol) was added to a vial containing 0.016 g (0.1 mmol) of CDI in 3 mL of dry THF. To this solution, 0.015 g (0.1 mmol) of **(–)-4e** was added and stirred for 1 h. (In those cases where the acid is a solid, the acid (0.1mmol) and CDI (0.1 mmol) were weighed into a vial and dissolved in 3 mL of THF, followed by the addition of **(–)-4e**.) 1 μL of the THF solution of the resulting diastereomeric amides was injected directly into a gas chromatograph fitted with an appropriate capillary column maintained isothermally at the required temperature. The diastereomeric amides revealed a 1:1 correspondence with the correpsonding retention times. The details of the GC analyses are presented in Table 2.

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(*Received in USA* 30 *September* 1996)