An Efficient Route to Both Enantiomers of *N*-(*p*-Tolylsulfonyl)benzenesulfonimidamide and Their Use for Asymmetric Allylic Amination of Olefins

Susumu TSUSHIMA,§ Yasuhiro YAMADA,§ Tetsuo ONAMI,*,† Koichiro OSHIMA,††,§ Michael O. CHANEY,†††
Noel D. JONES,††† and John K. SWARTZENDRUBER†††
Department of Chemistry, Stanford University, Stanford, CA 94305, U.S.A.
†Department of Chemistry, Fukushima Medical College, Hikarigaoka, Fukushima-shi 960-12
††Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139, U.S.A.
†††Lilly Research Laboratories, A Division of Eli Lilly and Company, Lilly Corporate Center, Indianapolis, IN 46285, U.S.A.

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The chiral compounds (*R*)- and (*S*)-*N*-(*p*-tolylsulfonyl)benzenesulfonimidamide have been prepared efficiently from *N*-(*p*-tolylsulfonyl)benzenesulfonimidoyl chloride and both enantiomers were transformed into chiral selenium diimide reagents, (*S*)- and (*R*)-*N*,*N'*-bis[*N*-(*p*-tolylsulfonyl)benzenesulfonimidoyl]selenium diimide, respectively, for the asymmetric allylic amination of olefins. Asymmetric allylic amination of methylenecyclohexane with the *S*-configured selenium diimide reagent afforded allylic amide, (1*S*)-*N*-[(*R*)-*N*-(*p*-tolylsulfonyl)benzenesulfonimidoyl]-2-methylenecyclohexylamine as a major diastereomer (42% diastereomeric excess). Similarly, cyclohexene, 1-heptene, and cyclooctene gave chiral allylic amides with 34%, 32%, and 20% diastereomeric excess, respectively. It is apparent that the *S*-configured diimido selenium reagent gives *S*-configured allylic amides, and that the *R*-configured reagent affords *R*-configured allylic amides as the major diastereomers in all of the cases investigated.

Great progress has been made in the area of asymmetric oxygenations of prochiral olefins since the finding of the enantioselective epoxidation of allylic alcohols by Sharpless and Katsuki in 1980.[1)] However, the aza analogues of direct asymmetric oxygenations of olefins have not been studied extensively, and only chiral aziridination of the special olefins such as α-methylene-γ-butyrolactone is reported[2)] to date as a direct asymmetric nitrogenation of prochiral olefins, although an indirect but excellent method for the synthesis of chiral primary amines through 2-alkyl-1,3,2-dioxaborinanes is developed by Brown et al.[3)]

In 1976, we reported a method for the direct allylic amination of olefins and acetylenes by selenium diimide compounds.[4)] The probable mechanism for the allylic amination is the aza analogue of the well-established mechanism for the allylic oxygenation of olefins by selenium dioxide.[5)] If the substituent on the nitrogen atom in the selenium diimide reagent were chiral, some asymmetric induction would be anticipated in the allylic amination. This report describes the application of this concept to achieve asymmetric allylic amination of olefins. It must be admitted at the outset that this approach to asymmetric allylic amination by means of the chiral substituent on the nitrogen introduced is not likely to be of much practical value, for it involves the stoichiometric use of a resolved chiral reagent. However, the area of asymmetric amination is new enough that the factors which enable one to achieve good enantioselectivities are poorly understood, and there are only a few literatures[6,7)] to refer to about it. In this circumstance it seems defensible, even desirable, to engage in studies which involve the stoichiometric use of a chiral agent which is not a commercially available natural product. Of course, the real future for a practical asymmetric allylic amination process lies in the development of highly effective chiral catalysts.

Jones and Cram have reported the synthesis of the chiral *N*-(menthyloxycarbonyl)-*p*-toluenesulfonimidamide (**1**).[8)] The amide **1** was prepared following their procedure and transformed into its sodiochloramine derivative **2**, which was found to be effective in the selenium mediated allylic amination of methylenecyclohexane, as shown in Scheme 1. Although the allylic amination product **3** was shown to have a diastereomeric purity of about 48%,[9)] it was very difficult to obtain more than a few hundred milligrams of the optically pure amide **1** due to the difficulty of its isolation from the diastereomeric mixture. However, this preliminary result encouraged us to devise a more practical route to other chiral alkylbenzenesulfonimidamides.

Results and Discussion

After several false starts, the exceedingly efficient sequence shown in Scheme 2 for the preparation of chiral *N*-(*p*-tolylsulfonyl)benzenesulfonimidamide [(*R*)-**8** and (*S*)-**8**] was developed. The racemic sulfonimidoyl chloride **6** is readily available from diphenyl disulfide (**4**) by sequential application of two literature procedures.[10)] The nitrogen was introduced into sulfonimidamide **7** in the form of (*S*)-α-methylbenzylamine. At this point we had the good fortune to expe-

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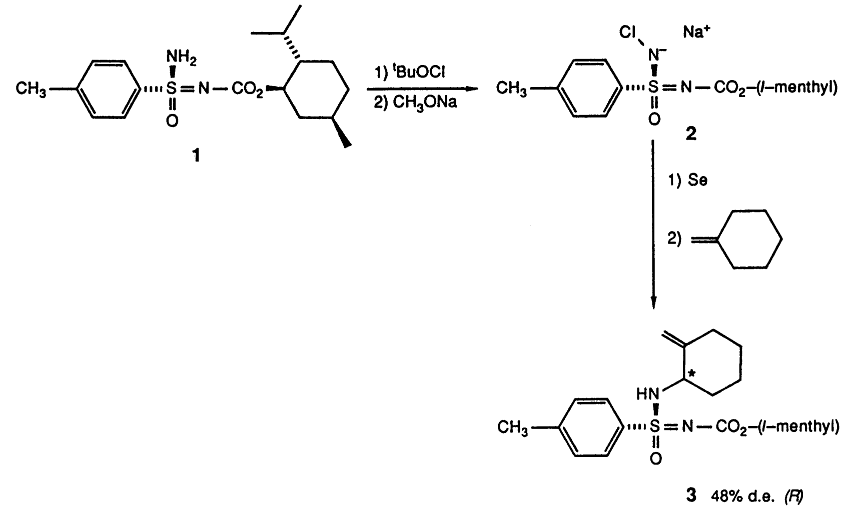
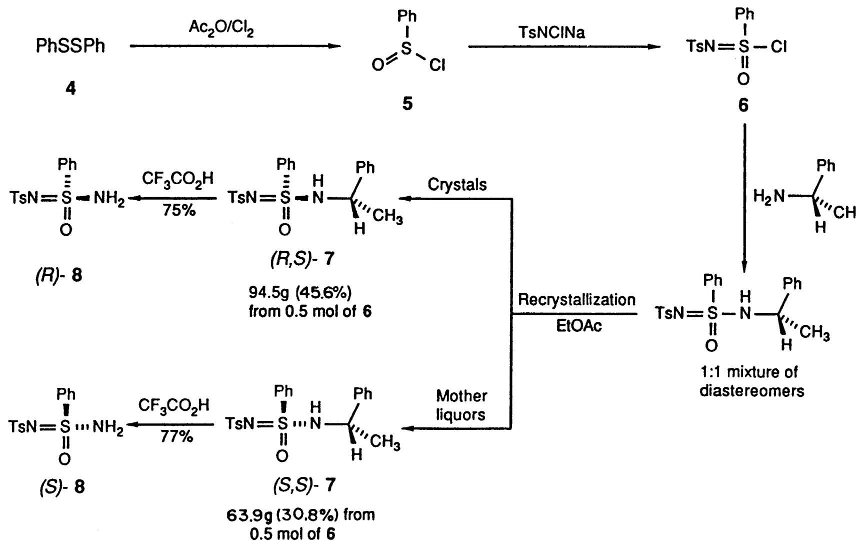
§ Present address: S. T.: Chemistry Laboratories, Central Research Division, Takeda Chemical Industries, Ltd., Jusohommachi, Yodogawa, Osaka 532; Y. Y.: Department of Fermentation Technology, Faculty of Engineering, Osaka University, Yamadaoka, Suita-shi 565; and K. O.: Department of Industrial Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606.



Scheme 1.



Scheme 2.

rience a completely painless resolution. One of the diastereomeric sulfonimidamides [(*R*,*S*)-**7**] is almost completely insoluble in ethyl acetate. Thus, a single recrystallization from ethyl acetate led to its isolation in 45.6% yield. The other diastereomer (*S*,*S*)-**7** was isolated in 30.8% yield by concentrating the mother liquor and adding diethyl ether to induce its crystallization. Therefore, the total yield of the two diastereomers was 76.4% from the sulfonimidoyl chloride **6**, and it will be noted in Scheme 2 that large amounts of (*R*,*S*)-**7** and (*S*,*S*)-**7** were easily obtained by carrying out a 0.5 mole scale reaction. A single-crystal X-ray analysis of (*S*,*S*)-**7** allowed assignment of the absolute stereochemistry at the chiral sulfur center; it is *S* as shown in Fig. 1.

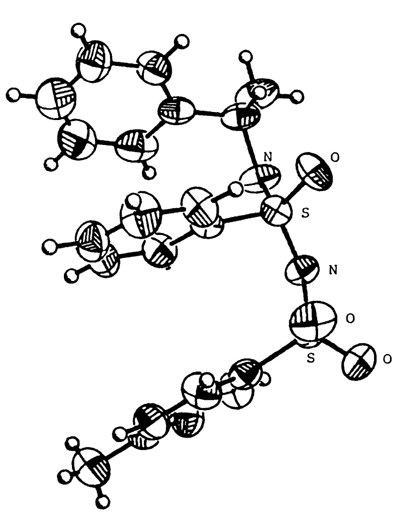
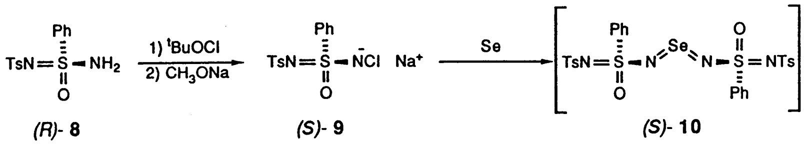


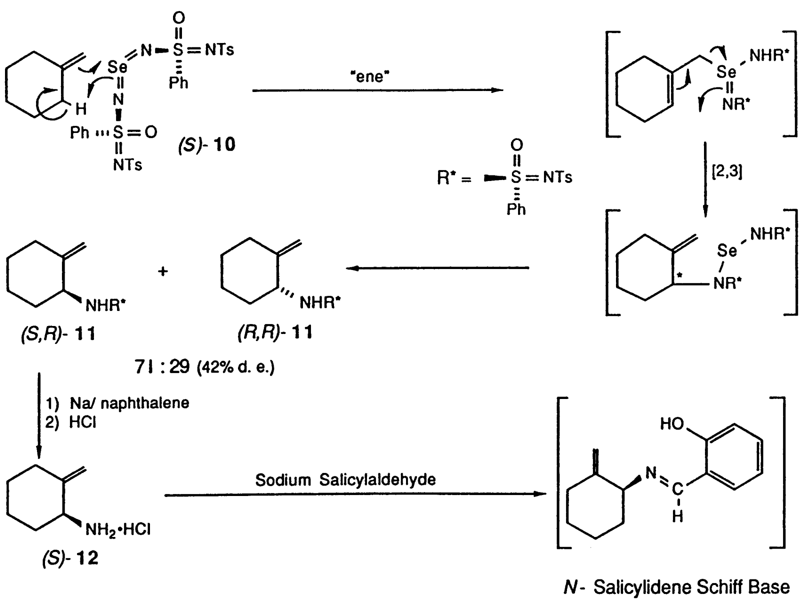
Fig. 1. The perspective drawing of the (*S*,*S*)-**7** molecule.

Numerous unsuccessful attempts were made to cleave the α-methylbenzyl moiety from (*R*,*S*)-**7** and (*S*,*S*)-**7** by hydrogenolysis. Finally, a literature method[11] involving solvolysis in trifluoroacetic acid was found to be very effective. A priori one might have expected these acidic conditions to either racemize or hydrolyze the desired chiral sulfonimidoyl amides (*R*)-**8** and (*S*)-**8**, but no such difficulties were encountered. We, therefore, now had a good route to the chiral benzenesulfonimidamides (*R*)-**8** and (*S*)-**8**.[12] Sulfonimidamide (*R*)-**8** is readily converted to the corresponding chloramine salt (*S*)-**9**, as shown in Scheme 3. The salt (*S*)-**9** is stable for months at room temperature. The salt (*S*)-**9** is slightly soluble in dry dichloromethane, and when exposed to selenium metal in this solvent it reacts to afford an uncharacterized substance which behaves as if it were the selenium(IV) diimide species (*S*)-**10**.[13] The putative diimide reagent (*S*)-**10** is effective for the allylic amination of olefins.

The probable mechanism for the allylic amination process is that shown in Scheme 4, and it is simply the aza analogue of the rather well-established mechanism for the allylic oxygenation of olefins by selenium dioxide.[5] The key events bearing on the question of chirality transfer from the selenium reagent to the allylic

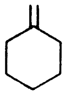
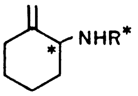
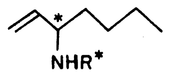
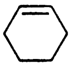
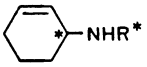
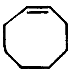
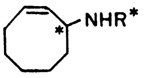


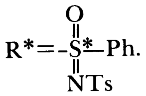
Scheme 3.



Scheme 4.

Table 1. Asymmetric Inductions

Entry	Olefin	Configuration of R*N=Se=NR*[a]	Product	Ratio of diastereomers	Diastereomeric excess	Yield
1		*S*		29 : 71	42% (*S*)	51%
2		*R*		34 : 66	32% (*R*)	25%
3		*R*		33:67	34% (*R*)	29%
4		*R*		4.0 : 6.0	20% (*R*)	30%

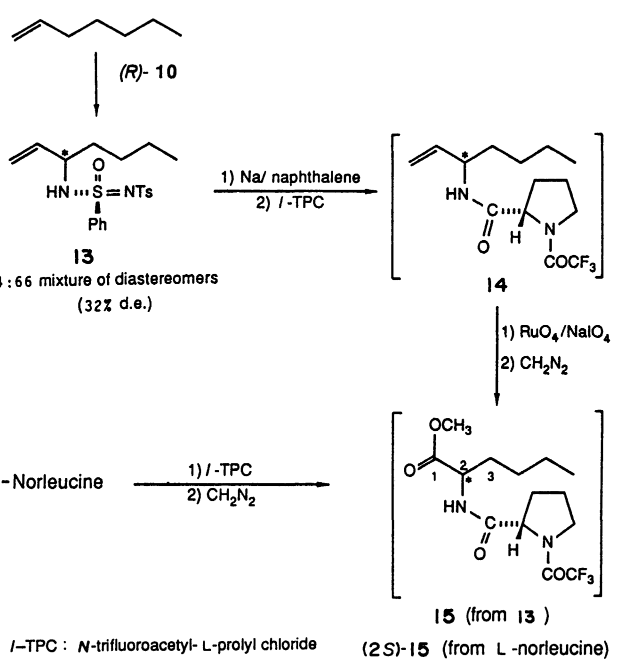
a) 

$\mathrm{R^*}=-\overset{\mathrm{O}}{\underset{\mathrm{NTs}}{\overset{\|}{\underset{\|}{\mathrm{S^*}}}}}-\mathrm{Ph}.$

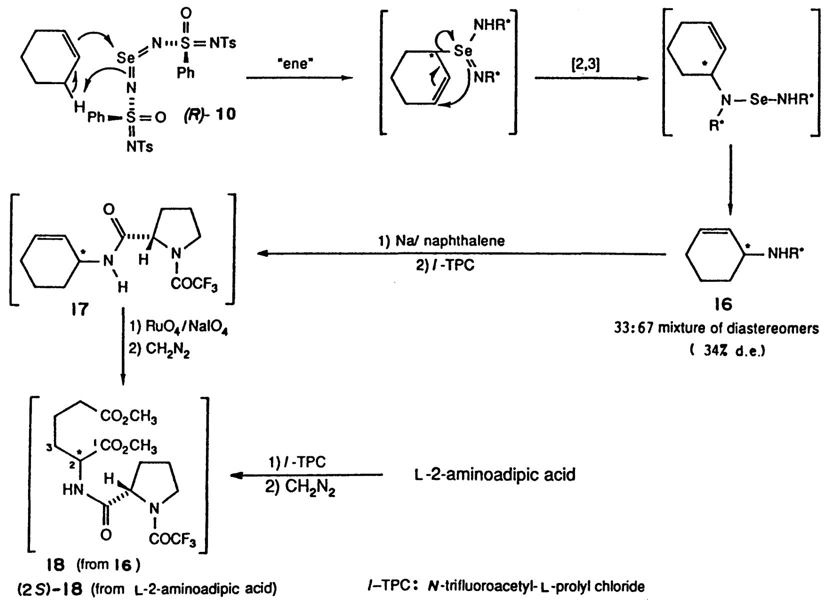
amination product are the ene step and the [2,3]sigmatropic step. For an olefin which bears a terminal double bond such as methylenecyclohexane or 1-heptene (Entry 2, Table 1), the ene step would induce a chiral center at the selenium, but leads to an intermediate which has no chirality in the olefinic part of the structure. In this case, therefore, the asymmetric selection could take place in the [2,3]sigmatropic step.[7] For example, the diimide reagent (*S*)-**10** (*S* configuration at sulfur) derived from the optically active sulfonimidamide (*R*)-**8**, reacted with methylenecyclohexane at 0 °C to give the expected allylic amide **11** as the mixture of diastereomers in the ratio of 29 : 71 (42% diastereomeric excess). The ratio was not changed even when the reaction was performed at various temperatures between −40 °C and 25 °C. The diastereomers were distinguished clearly by their ^{1}H NMR spectra and were separated by column chromatography on silica gel to give (*S*,*R*)-**11** as the major isomer and (*R*,*R*)-**11** as the minor isomer. The circular dichroism of the *N*-salicylidene Schiff base of the allylic amine (*S*)-**12**, which was derived from (*S*,*R*)-**11** by naphthalene-sodium reduction,[14] showed positive Cotton effects at 253 and 317nm. Therefore, the newly induced chiral center at carbon in the major diastereomer was assigned the *S*-configuration[15] following the salicylideneamino chirality rule.[16]

An acyclic olefin such as 1-heptene was aminated with the selenium diimide reagent (*R*)-**10** which contains *R*-configured sulfurs, and a somewhat lower diastereomeric excess (32%) was observed for the allylic amination product **13** (Scheme 5).[17] The absolute configuration of the newly induced chiral center in **13** was correlated to the corresponding chiral center in an authentic sample of *N*-(*N*-trifluoroacetyl-L-prolyl)-L-norleucine methyl ester [(2*S*)-**15**] which was derived from commercially available L-norleucine as shown in Scheme 5. The GC retention time of the major diastereomer of **15** which was derived from the diastereomeric mixture **13** was the same as that of (2*S*)-**15** from L-norleucine. Therefore the induced chiral center in the major diastereomer of **13** was proved to be *S*-configured.

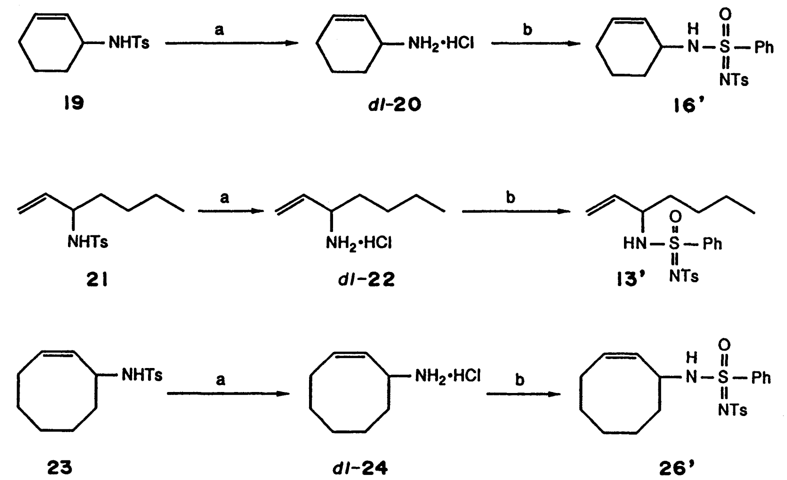
For the majority of olefins which do not bear a terminal double bond (e.g. Entries 3 and 4, Table 1), the ene product possesses chirality in the olefinic part of the structure, and in this case the chirality of the final product is determined only by the asymmetric induction in the ene step. An example is shown in Scheme 6



Scheme 5.

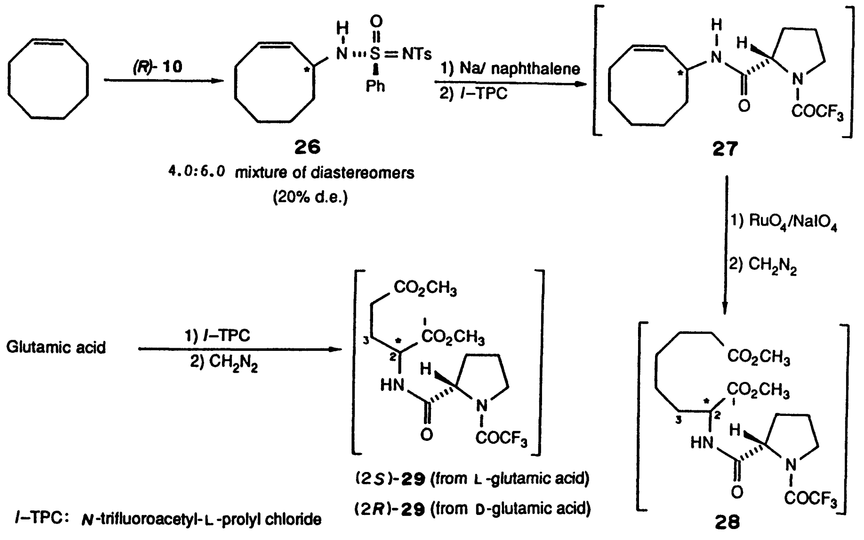


Scheme 6.



a: 1) Na/naphthalene, 2) HCl. b: PhSO(=NTs)Cl.

Scheme 7. Preparation of authentic samples.



Scheme 8.

for cyclohexene as the olefin. When the aminating reagent (*R*)-**10** was used, two diastereomers (**16**) were produced in the ratio of 33:67 (34% diastereomeric excess). As they are not separable by column chromatography on silica gel, the structure was confirmed by comparison of the diastereomeric mixture with an authentic sample of diastereomeric mixture **16′** which was derived from racemic allylic amine *dl*-**20** as shown in Scheme 7. In order to determine the absolute configuration of the newly induced chiral center in the major diastereomer of **16**, the diastereomeric mixture (**16**) was converted to methyl *N*-(*N*-trifluoroacetyl-L-prolyl)-2-aminoadipate (**18**) as shown in Scheme 6. As the GC retention time of the major diastereomer of **18** was the same as that of an authentic sample of methyl *N*-(*N*-trifluoroacetyl-L-prolyl)-L-2-aminoadipate [(2*S*)-**18**], which was derived from L-2-aminoadipic acid, the induced chiral center in the major diastereomer of **16** must be *S*-configured.

A medium-sized cyclic olefin such as cyclooctene afforded two diastereomers (**26**) upon the asymmetric allylic amination with the diimido selenium reagent (*R*)-**10** (Scheme 8). However, the asymmetric induction (20% diastereomeric excess) was somewhat lower than for the other olefins already described. As shown in Scheme 8, the diastereomeric mixture **26** was converted to **28** in order to assign the absolute configuration of the induced chiral center in the major diastereomer of the allylic amide. The GC analysis of **28** showed two peaks on PEG, and the major diastereomer eluted before the minor one. While diastereomers with *S*-configuration at C-2, such as (2*S*)-**18** (Scheme 6), (2*S*)-**15** (Scheme 5), and (2*S*)-**29** (Scheme 8) have in all cases longer retention times than the corresponding diastereomers with *R*-configuration at C-2 on the same GC column as shown in Table 2.[18] Therefore, as the major diastereomer of **28** has a shorter retention time than the minor one, the *R*-configuration was assigned

Table 2. GC Retention Times of *N*-(*N*-Trifluoroacetyl-L-prolyl) Derivatives of Amino Acid Methyl Ester

Amino acid	D-Enantiomer	L-Enantiomer	Column temp, flow rate[a)]
Norleucine	7.80 min	10.50 min	170 °C, 24 mL min^{-1}
Glutamic acid	18.20 min	22.20 min	180 °C, 45 mL min^{-1}
2-Aminoadipic acid	15.17 min	17.40 min	200 °C, 24 mL min^{-1}

a) 1m 1% PEG-20M-P.

to C-2 in the major diastereomer of **28**, and accordingly the induced chiral center in the major diastereomer of **26** was assigned the same *R*-configuration.

It seems noteworthy that the *R*-configured selenium reagent (*R*)-**10** gives the *R*-configured allylic amides in all four cases examined (Table 1). As can also be seen in Table 1 the asymmetric inductions we have observed are in the unimpressive 20—42% range. We had hoped for better inductions as chiral transfer is known to be excellent for [2,3]sigmatropic processes.[19)] There are at present far too many unknown factors to support any speculation about the reasons for the modest inductions we have observed. However, since the relative bulk of the substituents around the chiral sulfurs in the imido selenium reagent could play an important part in determining the geometry of the transition states, the asymmetric inductions might be improved by exploring structural variations in the chiral sulfonimidamide **8** (Scheme 2). Fortunately, the synthetic route to the chiral sulfonimidamides (*R*)-**8** and (*S*)-**8** is straight-forward and should lend itself to the introduction of structural modifications.

Experimental

Melting points were determined on a capillary tube melting point apparatus and are uncorrected. Optical rotations were measured using a Perkin-Elmer 241 polarimeter. Infrared (IR) spectra were recorded on a Jasco A-100 grating infrared spectrometer and proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Jeol FX-90Q spectrometer (90 MHz). Tetramethylsilane (TMS) was used as an internal standard; however, when the solvent was D_2O, the standard was sodium 3-(trimethylsilyl)propionate-d_4 (TSP-d_4); chemical shifts are denoted in ppm downfield from TMS or TSP-d_4 at δ=0. Elemental analyses were performed by Stanford university or Takeda Chemical Industries Ltd., Chemistry Laboratories. Gas chromatographic (GC) analyses were performed on a Hitachi 163 gas chromatograph with a flame ionization detector using glass columns (3 mm i.d.) and nitrogen carrier gas. All the column packings used were purchased from Gasukuro Kogyo Inc. Analytical high-performance liquid chromatography (HPLC) was carried out on a Jasco BIP-1 high-performance liquid chromatograph equipped with a UV detector (adjusted to 260 nm). The CD spectrum was recorded on a Jasco J-20 spectropolarimeter at Takeda Chemical Industries Ltd., Chemistry Laboratories. Analytical thin-layer chromatography was performed on precoated silica-gel glass plates (0.25 mm, Kieselgel 60, F-254, E. Merck) and siica gel (Wakogel C-300, Wako Pure Chemical Industries Ltd.) was used for column chromatography.

(*R*)-*N*-[(*S*)-α-Methylbenzyl]-*N*′-(*p*-tolylsulfonyl)benzenesulfonimidamide [(*R*,*S*)-7] and (*S*)-*N*-[(*S*)-α-Methybenzyl]-*N*′-(*p*-tolylsulfonyl)benzenesulfonimidamide [(*S*,*S*)-7]. To an ice-cooled solution of 165 g (0.5 mol) of *N*-(*p*-tolylsulfonyl)benzenesulfonimidoyl chloride (prepared according to the published procedure[10)]) in 1 L of dichloromethane was added a mixture of 66.5 g (0.55 mol) of (*S*)-(−)-α-methylbenzylamine (Aldrich) and 50.4 g (0.6 mol) of sodium hydrogencarbonate in 550 ml of water, and the mixture was stirred at room temperature overnight. After the separation of the organic layer, it was washed with 10% HCl, and water, successively, and concentrated in vacuo to afford crude crystals. Recrystallization from 1.5 L of ethyl acetate gave 94.5 g (45.6%) of (*R*,*S*)-**7** as needles (mp 166.5—168.0 °C), which was diastereomerically pure by ^{1}H NMR. An analytical sample was obtained by recrystallization from ethyl acetate: mp 167.5—168.5 °C; $[\alpha]_D^{23}$ −60.3° (*c* 1.02, acetone); IR (KBr) 3240, 1600, 1450, 1430, 1306, 1265, 1150, 1092, 1055, and 952 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.33 (3H, d, *J*=6.9 Hz, methyl), 2.37 (3H, s, aryl methyl), 4.50 (1H, q, *J*=6.9 Hz, CH-N), 7.0—8.0 (15H, NH and aromatic). Found: C, 60.84; H, 5.32; N, 6.77%. Calcd for $C_{21}H_{22}N_2O_3S_2$: C, 60.85; H, 5.35; N, 6.76%.

The mother liquor was concentrated and 1.2 L of diethyl ether was added to the residue to give 69.8 g of the other diastereomer (*S*,*S*)-**7** as prisms (mp 89.5—91.5 °C, contains approximately 1% of (*R*,*S*)-**7** judging from its ^{1}H NMR spectrum). Concentration of the mother liquor afforded a second crop of 17.2 g of crude crystals, which were dissolved in 75 mL of hot ethyl acetate and 3.29 g of crystals (mp 164—166.5 °C) were precipitated on cooling to room temperature. [These precipitated crystals were further recrystallized from 50 mL of ethyl acetate to give 2.9 g of diastereomerically pure (*R*,*S*)-**7**, mp 167.5—168.5 °C. Therefore, the total yield of (*R*,*S*)-**7** is 97.4 g (47%).] After separating the crystals, the mother liquor was concentrated and 200 mL of diethyl ether was added to the residue to give 13.1 g of (*S*,*S*)-**7** (mp 89.5—91.5 °C, contains approximately 2% of (*R*,*S*)-**7** judging from its ^{1}H NMR spectrum). The combined (*S*,*S*)-**7** (82.9 g) was dissolved in 100 mL of hot ethanol, and addition of hexane (100 mL) afforded 63.9 g (30.8%) of diastereomerically pure (*S*,*S*)-**7**: mp 91.5—92.5 °C; $[\alpha]_D^{23}$ −70.6° (*c* 1.08, acetone); IR (KBr) 3240, 1600, 1450, 1290, 1260, 1150, 1092, 1062, and 967 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.54 (3H, d, *J*=6.9 Hz, methyl), 2.37 (3H, s, aryl methyl), 4.48 (1H, d of q, *J*=6.9 and 6.9 Hz, CH-N), 6.71 (1H, d, *J*=6.9 Hz, NH), 6.9—8.0 (14H, aromatic). Found: C, 60.55; H, 5.47; N, 6.57%. Calcd for $C_{21}H_{22}N_2O_3S_2$: C, 60.85; H, 5.35; N, 6.76%.

X-Ray Diffraction Studies on (*S*)-*N*-[(*S*)-α-Methylbenzyl]-*N*′-(*p*-tolylsulfonyl)benzenesulfonimidamide [(*S*,*S*)]-7].

Compound (*S*,*S*)-**7** exists as colorless prisms in the space group $P2_12_12_1$, with four molecules in a unit cell having the dimensions: a =11.500±0.003; b=8.254±0.002; c=21.384±0.005 Å. The calculated density is 1.356 g cm^{-3}. A total of 1626 reflections were measured on an automated four-circle diffractometer, using monochromatic copper radiation. A partial solution was found using the direct method routines of the SHELXTL program library, with the remaining peaks being located through successive difference E maps. The solution was refined by the least squares method to R=0.0755, with anisotropic temperature factors for all atoms except hydrogen. Hydrogen atoms were included with isotropic temperature factors at calculated positions. Supplementary materials (unit cell atomic coordinates, bond lengths, bond angles, anisotropic temperature factors, hydrogen atom coordinates, and nonbonded distances) are deposited as Document No. 8864 at the Office of the Editor of the Bulletin of the Chemical Society of Japan.

(*R*)-*N*-(*p*-Tolylsulfonyl)benzenesulfonimidamide [(*R*)-8] and (*S*)-*N*-(*p*-Tolylsulfonyl)benzenesulfonimidamide [(*S*)-8]. To 40 mL of trifluoroacetic acid was added 16.56 g (40 mmol) of (*R*,*S*)-**7**. After stirring for 40 h at 35 °C, trifluoroacetic acid was removed in vacuo to give crude crystals. Recrystallization of the crystals from 600 mL of ethyl acetate afforded 10.63 g (86%) of (*R*)-**8** ($[\alpha]_D^{23}$ +97.8°), which was further recrystallized from the same solvent to give 9.3 g (75%) of pure (*R*)-**8**, mp 178.5—179.5 °C,[20] $[\alpha]_D^{23}$ +103° (c 1.03, acetone). Further recrystallization of this material did not change the rotation: IR (KBr) 3220 (sh), 3170, 3060, 1590, 1558, 1448, 1388, 1290, 1259, 1135, 1042, 930, 800, and 750 cm^{-1}; ^{1}H NMR (CDCl$_3$/DMSO-d_6, ca. 1 : 1) δ=2.36 (3H, s, aryl methyl), 4.39 (2H, broad s, NH), and 7.0—8.0 (9H, aromatic). Found: C, 50.47; H, 4.48; N, 8.93%. Calcd for $C_{13}H_{14}N_2O_3S_2$: C, 50.31; H, 4.55; N, 9.02%.

The other enantiomer (*S*)-**8** (6.3 g, 77%) was obtained from 12.52 g (30 mmol) of (*S*,*S*)-**7** following the same procedure: mp 178.5—179.5 °C, $[\alpha]_D^{23}$ −103° (c 1.03, acetone). The ^{1}H NMR and IR spectra were identical to those of (*R*)-**8**.

Sodium Salt of (*R*)-*N*-Chloro-*N'*-(*p*-tolylsulfonyl)benzenesulfonimidamide [(*R*)-9] and Sodium Salt of (*S*)-*N*-Chloro-*N'*-(*p*-tolylsulfonyl)benzenesulfonimidamide [(*S*)-9]. To an ice-cooled, stirred suspension of 14.23 g (46 mmol) of (*S*)-**8** in 115 mL of methanol was added dropwise 5.21 mL (4.99 g, 46 mmol) of *t*-butyl hypochlorite (Tokyo Kasei Kogyo Co., Ltd.) under a nitrogen atmosphere. After stirring for 15 min, 2.53 g (47 mmol) of sodium methoxide was added while still stirring under ice-bath cooling. The solution was concentrated on a rotary evaporator at 30 °C to a volume of approximately 30 mL, and addition of 300 mL of diethyl ether to the concentrated solution induced crystallization. After standing overnight at room temperature, the crystals were separated and washed with diethyl ether under nitrogen to avoid contact with moisture (if this procedure is done without nitrogen, some of the crystals melt presumably due to the absorption of moisture), and dried at 80 °C in vacuo (ca. 1 mmHg; 1 mmHg≈133.322 Pa) for 1 h, to give 15.62 g (93%) of (*R*)-**9**. Titration of this material with 0.1 M (1 M=1 mol dm^{-3}) sodium thiosulfate showed a purity of 96%, and this anhydrous (*R*)-**9** was stable for months at room temperature if protected from the atmosphere in a well-sealed bottle. An analytical sample of these crystals was obtained by recrystallization from isopropyl alcohol, which afforded fine needles: mp 175.5—176.5 °C (decomp). Found: C, 42.32; H, 3.19; N, 7.58%. Calcd for $C_{13}H_{12}ClN_2NaO_3S_2$: C, 42.57; H, 3.30; N, 7.64%.

The other enantiomer (*S*)-**9** was prepared from (*R*)-**8** in the same manner.

Preparation of Diimido Selenium Reagents (*S*)-10 and (*R*)-10. To a stirred suspension of 3.67 g (10 mmol) of the chloramide salt (*S*)-**9** (dried at 80 °C in vacuo for 1 h) in 20 mL of dry dichloromethane (methanol-free dichloromethane was passed through a column of neutral aluminum oxide, activity grade I, Woelm, and stored over 3A Molecular Sieves) was added 474 mg (6 mmol) of selenium powder (dried at 80 °C in vacuo for 1 h) under a nitrogen atmosphere. The resulting mixture was stirred vigorously at room temperature and almost all the solids in the solution disappeared within 30 min, only a small amount of the excess selenium powder remained. After stirring for an additional 3 h, the reaction mixture was used as reagent (*S*)-**10** for the amination of olefins.

Reagent (*R*)-**10** was similarly prepared from the chloramide salt (*R*)-**9**.

Allylic Amination of Methylenecyclohexane with the Diimido Selenium Reagent (*S*)-10. To reagent (*S*)-**10**, which was prepared from 3.67 g (10 mmol) of chloramide salt (*S*)-**9** and 6 mmol of selenium powder according to the method described above, was added dropwise 768 mg (8 mmol) of methylenecyclohexane at 0 °C (an ice bath) while stirring under a nitrogen atmosphere. After stirring for 24 h in the refrigerator (0 °C), the reaction mixture was allowed to warm to room temperature (15 min), and stirring was continued for 1 h. the reaction mixture was then diluted with 200 mL of 1 : 1 ethyl acetate/diethyl ether and 50 mL of an alkaline aqueous solution consisting of 2 parts 1 M NaOH and 1 part saturated NaCl solution. After stirring for 30 min, the red mixture was filtered through Celite 545 and the organic layer of the filtrate was washed again with 50 mL of the above mentioned alkaline brine solution (2×50 mL), dried (Na$_2$SO$_4$) and concentrated to give an oil. The crude product was chromatographed on 60 g of silica gel (dichloromethane/ethyl acetate, 95 : 5 as eluent) to give 1.66 g (51% based on the olefin) of a crystalline diastereomeric mixture of (*S*,*R*)-**11** and (*R*,*R*)-**11**, which showed two spots by TLC analysis [hexane/ethyl acetate, 3:2, R_f 0.464 (major) and R_f 0.536 (minor)]. GC analysis (1m 1% PEG-HT on 60/80 mesh Uniport HP, 270 °C, flow rate: 38 mL min^{-1}) of the crystalline diastereomeric mixture showed two peaks at 10.03 min and 12.50 min in a ratio of 29 : 71, respectively. The ratio matched that obtained by comparison of the integrated vinyl proton resonances for each of the diastereomers in the ^{1}H NMR spectrum.

A part of the diastereomeric mixture (0.1 g) was chromatographed on 20 g of silica gel (elution with 10—20% ethyl acetate/hexane) to yield two fractions. Eluting first was the minor diastereomer (*R*,*R*)-**11**, which was recrystallized from ethyl acetate/hexane to give 21 mg of pure crystals: mp 92—93 °C; $[\alpha]_D^{23}$ + 25.4° (c 1.00, acetone); IR (KBr) 3196, 1651, 1599, 1450, 1311, 1255, 1154, 1124, 1090, and 1069 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.1—2.3 (8H, m, methylene), 2.39 (3H, s, aryl methyl), 3.76 (1H, m, CH-N), 4.57 (2H, s, vinyl), 6.40 (1H, d, J=8 Hz, NH), 7.0—8.1 (9H, m, aromatic). Found: C, 59.34; H, 5.91; N, 7.04%. Calcd for $C_{20}H_{24}N_2O_3S_2$: C, 59.38; H, 5.98; N, 6.92%.

Eluting second was the major diastereomer (*S*,*R*)-**11**, which was recrystallized from ethyl acetate/hexane to afford

39 mg of pure crystals: mp 132—133 °C; $[\alpha]_D^{23}$ +6.9° (*c* 1.01, acetone); IR (KBr) 3246, 1648, 1599, 1450, 1313, 1303, 1252, 1156, 1119, and 1080 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.1—2.3 (8H, m, methylene), 2.39 (3H, s, aryl methyl), 3.76 (1H, m, CH-N), 4.80 (1H, s, vinyl), 5.04 (1H, s, vinyl), 6.22 (1H, d, *J*=8.0 Hz, NH), 7.0—8.1 (9H, m, aromatic). Found: C, 59.38; H, 5.84; N, 7.05%. Calcd for $C_{20}H_{24}N_2O_3S_2$: C, 59.38; H, 5.98; N, 6.92%.

Determination of the Absolute Configuration of (*S,R*)-11. To a stirred solution of naphthalene-sodium reagent[14] [prepared by stirring a mixture of 11 mg (0.49 mmol) of sodium metal and 66 mg (0.51 mmol) of naphthalene in 1 mL of freshly distilled dry 1,2-dimethoxyethane for 2 h at room temperature under nitrogen] was added 20 mg (0.049 mmol) of (*S,R*)-**11** under nitrogen at room temperature, and stirring was continued for 2 h. After addition of chilled water (3 mL) to the reaction mixture cooled in an ice bath, 1 M HCl was added until the solution became acidic (pH<1), and the resulting mixture was washed twice with 10 mL of diethyl ether. The aqueous layer was separated, made strongly basic (pH>11) with aqueous 30% NaOH and extracted with chloroform (3×5 mL). After drying the combined extracts with sodium sulfate, 0.05 mL of concd HCl was added and the resulting mixture was evaporated to dryness in vacuo to give 4.2 mg of crude crystals, which was recrystallized from 1-propanol/hexane to afford 1.3 mg of (*S*)-**12**. The ^{1}H NMR spectrum was identical with that of *dl*-2-methylenecyclohexylamine hydrochloride (*dl*-**12**), which was prepared as described below.

For observation of the circular dichroism, the *N*-salicylidene derivative of (*S*)-**12** was prepared in situ according to Smith's procedure.[21] Sodium salicylaldehyde[22] (1.26 mg, 8.74 μmol) and 1.14 mg (7.72 μmol) of (*S*)-**12** were weighed into a 5-mL volumetric flask on a microgram balance. Methanol (3 mL) was added and the mixture was warmed for 15 min with steam, cooled, and made up to 5 mL. This solution was diluted (1 : 10) for observation of the CD maxima: CD (*c* 0.0033, MeOH, 25 °C) $[\theta]_{317}^{\text{peak}}$ +7800, $[\theta]_{253}^{\text{peak}}$ +16000.[23]

Allylic Amination of Methylenecyclohexane at Various Temperatures. Four test tubes (10 cm, 13 mm i.d.) containing 0.25 mmol of diimido selenium reagent (*R*)-**10** in 2 ml of dichloromethane were kept at −40 °C (Dry Ice-aqueous ethanol bath), −20 °C (Dry Ice-carbon tetrachloride bath), −5 °C (ice-salt bath), and 25 °C, respectively. After an addition of 60 μL (0.5 mmol) of methylenecyclohexane to each of the tubes under nitrogen, they were stirred magnetically for 1 week maintaining their initial temperatures in freezers (−40, −20, or −5 °C) or in the room (25 °C). One drop of water was added to each tube to destroy the reagent and the resulting mixtures were then diluted with 4 mL of diethyl ether and 1 mL of an alkaline aqueous solution consisting of 2 parts 1 M NaOH and 1 part saturated NaCl solution. After stirring for 30 min at room temperature, the reaction mixtures were filtered through Celite 545 and the organic layers of the filtrates were concentrated to give oils. Each crude product was analyzed by GC (1 m 1% PEG-HT on 60/80 mesh Uniport HP, 270 °C, flow rate: 38 mL min^{-1}), and the diastereomeric ratios were determined as 29 : 71 (42% diastereomeric excess) in four cases.

Allylic Amination of Cyclohexene with Diimido Selenium Reagent (*R*)-10. Cyclohexene (493 mg, 6 mmol) was aminated with reagent (*R*)-**10** according to the method and conditions described for allylic amination of methylenecyclohexane with reagent (*S*)-**10**. The crude product (oil) was chromatographed on 60 g of silica gel using 50—60% dichloromethane/hexane to give 686 mg (29%) of a diastereomeric mixture (**16**) as crystals in a ratio of 33:67 (34% diastereomeric excess); mp 160—166 °C; IR (KBr) 3245, 1647, 1599, 1452, 1311, 1303, 1154, 1117, 1090, 1060, and 1050 cm^{-1}. The NMR spectrum was identical with an authentic sample of a 73 : 27 diastereomeric mixture of **16′** (vide infra) with the exception of differing peak intensities in the olefinic proton region. HPLC (4 mm i.d. 250 mm LiChrosorb Si 60, 5 μm, 55 : 1 hexane/isopropyl alcohol, 1 mL min^{-1}) retention times of the major (t_r=17.20 min) and minor (t_r=16.00 min) diastereomers in the mixture were identical with those of the authentic sample of **16′**. The above diastereomeric ratio (33 : 67) was determined by GC analysis of *N*-trifluoroacetyl-L-prolyl derivative **17**, which was derived by reductive cleavage of the diastereomeric mixture **16** and subsequent acylation with *N*-trifluoroacetyl-L-prolyl chloride as shown in Scheme 6 (see the following general method for the determination of diastereomeric ratios).

General Method for the Determination of Diastereomeric Ratios. As diastereomeric mixture **16** was not well-resolved either by analytical GC or by analysis of its NMR spectrum, *N*-trifluoroactyl-L-prolyl chloride was used to derivatize[24] the amine enantiomers which were derived by reductive cleavage of the diastereomeric mixture **16**. Separation of the newly derived diastereomeric mixture **17** was achieved by GC. This method was also applied to diastereomeric mixtures **13** and **26**.

To a 0.01 mmol diastereomeric mixture of asymmetric amination product was added 0.4 mL (0.2 mmol) of naphthalene-sodium reagent[14] at room temperature [the reagent was prepared by stirring a mixture of 115 mg (5 mmol) of sodium metal and 673 mg (5.25 mmol) of naphthalene in 10 mL of freshly distilled dry 1,2-dimethoxyethane for 2 h under a nitrogen atmosphere, and 0.4 mL of the resulting deep green solution was used. The rest was stored at 0 °C in the refrigerator for the next use]. After stirring for 1 h, 1 mL of water was added to the ice-chilled (ca. 0 °C) reaction mixture to quench the reaction and the mixture was acidified with an addition of 3 drops of 6 M HCl to pH<1. The resulting solution was washed with diethyl ether (2×1 mL), made strongly basic (pH>11) with 30% aqueous NaOH (ca. 4 drops), saturated with NaCl, and extracted with diethyl ether (2 mL), and the extract was dried (Na_2SO_4). To the ethereal solution was added 0.1 mL (0.01 mmol) of *N*-trifluoroactyl-L-prolyl chloride solution (Regis, 0.1 M in chloroform, contains 6.2% D-isomer), and the resulting mixture was stirred for 30 min. Fifteen minutes after addition of 1 drop of triethylamine and 1 drop of water, the organic layer was separated, dried (Na_2SO_4), and evaporated. A diastereomeric ratio of the diastereomers in the resulting product was analyzed by GC.

Determination of Absolute Configuration of the Major Diastereomer of 16. To the mixture of 8 mg (0.05 mmol) of L-2-aminoadipic acid (Calbiochem) and 5.5 mg of magnesium oxide (heavy) in 0.2 mL of water was added 0.5 mL (0.05 mmol) of *N*-trifluoroacetyl-L-prolyl chloride solution (Regis, 0.1 M in chloroform, contains 6.2% D-isomer) at 0 °C (ice bath), and the mixture was stirred for 2 h at 0 °C, and then for 4 h at room temperature. After dilution with 2 mL of ethyl acetate, the solid material (MgO) was filtered off through Celite 545 (water wash, 0.5 mL). To the filtrate was added 6 M HCl until the aqueous layer became acidic (pH<1) with stirring. The organic layer was separated, dried (Na_2SO_4), and treated with excess diazomethane (diethyl ether solution). After stirring for 5 min, the excess diazomethane and solvents were removed in vacuo to afford 9 mg of an oil. Analysis by GC (1 m 1% PEG-20M-P on 80/100 mesh Uniport HP, 200 °C, flow rate: 24 mL min^{-1}) afforded single peak[25] (t_r=17.40 min) due to (2*S*)-**18** (*S*-configuration at the asterisk in Scheme 6). The reaction was repeated with *dl*-2-aminoadipic acid and GC analysis of the product showed a 1.0 : 1.0 ratio of (2*R*)-**18** (t_r=15.17 min) to (2*S*)-**18** (t_r=17.40 min).

To 1.2 mL of the naphthalene-sodium reagent (see above) was added 12 mg (0.03 mmol) of the diastereomeric mixture **16** (33 : 67) under a nitrogen atmosphere. After stirring for 1 h, the reaction mixture was cooled to 0 °C (ice bath), quenched by addition of 2 mL of ice-water, and acidified to pH<1 with concd HCl (ca. 3 drops). The resulting mixture was washed with diethyl ether (3×1 mL) to remove naphthalene and other nonbasic substances. The separated aqueous layer was made strongly basic (pH>11) with 30% aqueous NaOH (ca. 6 drops), saturated with NaCl, and extracted into diethyl ether (3×2 mL). The ethereal solution (dried with Na_2SO_4) was treated with 0.3 mL (0.03 mmol) of *N*-trifluoroacetyl-L-prolyl chloride (Regis, 0.1 M in chloroform, contains 6.2% D-isomer) and allowed to stand for 1 h. After addition of 1 drop of triethylamine and 3 drops of water, the reaction mixture was stirred for 30 min, and successively washed with 1 mL of 1 M HCl, 1 mL of 1 M NaOH, and brine (2×2 mL), dried (Na_2SO_4), and concentrated to give amide **17** as an oil. The oil was dissolved in 1 mL of ethyl acetate. To this solution was added $RuO_4/NaIO_4$ reagent [a mixture of 52 mg (0.24 mmol) of $NaIO_4$, 0.3 mg (0.0018 mmol) of $RuO_2\cdot 2H_2O$, 0.5 mL of CCl_4, and 1 mL of water was stirred until all the $RuO_2\cdot 2H_2O$ dissolved (ca. 2 min) and the resulting mixture was used as the reagent] to cleave the carbon-carbon double bond and the mixture was stirred vigorously for 3 h. Then isopropyl alcohol (3 drops) was added and the reaction mixture was stirred for 30 min. After acidification of the aqueous layer with 3 M sulfuric acid to pH<1, the organic layer was extracted with 3 mL of ethyl acetate, and dried ($MgSO_4$). The ethyl acetate solution was treated with excess diazomethane (diethyl ether solution). After standing for 5 min, the excess diazomethane and solvent were removed in vacuo to afford 8 mg of a crude oil. Analysis by GC (1 m 1% PEG-20M-P, the same conditions as above) showed a 67 : 33 ratio of (2*R*)-**18** (t_r=15.17 min) to (2*S*)-**18** (t_r=17.40 min), thus establishing the *R*-configuration at the carbon bearing the nitrogen in the major diastereomer of the amination product **16**.

Allylic Amination of 1-Heptene with Diimido Selenium Reagent (*R*)-10. 1-Heptene (471 mg, 4.8 mmol) was aminated with reagent (*R*)-**10** according to the method and conditions described for the allylic amination of methylenecyclohexane with diimido selenium reagent (*S*)-**10**. The crude product (oil) was chromatographed on 70 g of silica gel using 5—10% EtOAc/hexane to give 488 mg (25%) of the diastereomeric mixture **13** in a ratio of 34:66 (32% diastereomeric excess) as an oil: IR (neat) 3228, 2962, 2938, 2864, 1601, 1451, 1318, 1303, 1290, 1263, 1155, 1114, 1095, 1020, and 929 cm^{-1}. The NMR spectrum was identical with an authentic sample of a 1.0 : 1.0 diastereomeric mixture of **13′** (vide infra) except for intensities of the peaks in the olefinic proton region. HPLC (4.6 mm i.d. 150 mm Finepak SIL C_{18} S; 3 : 7 H_2O/MeOH, 1 mL min^{-1}) retention times of the major (t_r=8.35 min) and minor (t_r=9.23 min) diastereomers in the mixture were identical with those of the authentic sample of **13′**. The above diastereomeric ratio (34 : 66) was determined by GC analysis of the *N*-trifluoroacetyl-L-prolyl derivative **14**, which was derived by reductive cleavage of the diastereomeric mixture **13** and subsequent acylation with *N*-trifluoroacetyl-L-prolyl chloride as shown in Scheme 5 (see general method for the determination of diastereomeric ratios).

Determination of the Absolute Configuration of the Major Diastereomer of 13. L-Norleucine (L-2-aminohexanoic acid, 6 mg) was acylated with *N*-trifluoroacetyl-L-prolyl chloride and the resulting amide was then methylated with diazomethane (Scheme 5) according to the method and conditions described for the determination of absolute configuration of the major diastereomer of **16**. GC analysis (2 m 3% Silicone OV-17 on 80/100 mesh Uniport HP, 180 °C, flow rate: 50 mL min^{-1}) of the crude product revealed a single peak[25] (t_r=39.60 min) attributed to (2*S*)-**15**. The reaction was repeated with *dl*-norleucine and GC analysis of the product showed a 1.0 : 1.0 ratio of (2*R*)-**15** (t_r=34.60 min) to (2*S*)-**15** (t_r=39.60 min).

The diastereomeric mixture **13** (34 : 66, 12 mg) was converted to amido ester **15** according to the method and conditions described for the conversion of diastereomeric mixture **16** to amido ester **18**. GC analysis (2 m 3% Silicone OV-17 on 80/100 mesh Uniport HP, 180 °C, flow rate: 50 mL min^{-1}) of the crude product showed a 66:34 ratio of (2*R*)-**15** (t_r=34.60 min) to (2*S*)-**15** (t_r=39.60 min), thus providing the *R*-configuration at the carbon bearing the nitrogen in the major diastereomer of **13**.

Allylic Amination of Cyclooctene with Diimido Selenium Reagent (*R*)-10. Cyclooctene (330 mg, 3 mmol) was aminated with reagent (*R*)-**10** according to the method and conditions described for allylic amination of methylenecyclohexane with reagent (*S*)-**10**. The crude product (oil) was chromatographed on 40 g of silica gel using 5—10% EtOAc/hexane to give 379 mg (30%) of the diastereomeric mixture **26** in a ratio of 4.0 : 6.0 (20% diastereomeric excess) as crystals: mp 117—127 °C; IR (KBr) 3205, 2920, 2850, 1650, 1599, 1447, 1326, 1302, 1217, 1150, 1113, 1088, 1052, and 1023 cm^{-1}. The NMR spectrum was identical with an authentic sample of a 62 : 38 diastereomeric mixture of **26′** (vide infra) with the exception of differing peak intensities in the olefinic proton region and the shape of proton signal due to the NH. The NH proton signal appeared at 6.10 ppm as a broad singlet. HPLC (4.6 mm i.d. 150 mm Finepak SIL C_{18} S; 3 : 7 H_2O/MeOH, 1 mL min^{-1}) retention times of the major (t_r=7.95 min) and minor (t_r=8.41 min) diastereomers in the mixture were identical with those of the authentic sample of **26′**. The above diastereomeric ratio (4.0 : 6.0) was determined by GC analysis of *N*-trifluoroacetyl-L-prolyl derivative **27**, which was obtained by reductive cleavage of the diastereomeric mixture **26** and subsequent acylation with *N*-trifluoroacetyl-L-prolyl chloride as shown in Scheme 8 (see general method for the determination of diastereomeric ratio).

GC Studies for the Determination of Absolute Configuration of the Major Diastereomer of 26. The diastereomeric mixture **26** (4.0 : 6.0, 13 mg) was converted to amido ester **28** (Scheme 8) according to the method and conditions described for the conversion of diastereomeric mixture **16** to amido ester **18**. GC analysis (1 m 1% PEG-20M-P on 80/100 mesh Uniport HP, 195 °C, flow rate: 45 mL min^{-1}) of the product showed a 4.0 : 6.0 ratio of the minor (t_r=23.02 min) to the major diastereomer (t_r=28.17 min).

L-Glutamic acid (7 mg) was acylated with *N*-trifluoroacetyl-L-prolyl chloride and the resulting amide was then methylated with diazomethane according to the method and conditions described for the determination of absolute configuration of the major diastereomer of **16**. GC analysis (the same column as above, 180 °C, flow rate: 45 mL min^{-1}) of the product afforded a single peak[25] (t_r=22.20 min) assigned to (2*S*)-**29**. The reaction was repeated with *dl*-glutamic acid and GC analysis of the product showed a 1.0 : 1.0 ratio of (2*R*)-**29** (t_r=18.20 min) to (2*S*)-**29** (t_r= 22.20 min).

A 1 : 1 diastereomeric mixture of (2*R*)-**15** and (2*S*)-**15** were analyzed by GC using the same column as above (170 °C, flow rate: 24 mL min^{-1}). Retention times of (2*R*)-**15** and (2*S*)-**15** were 7.80 and 10.50 min, respectively.

***dl*-2-Cyclohexenylamine Hydrochloride (*dl*-20).** To naphthalene-sodium reagent[14] [prepared by stirring the mixture of 276 mg (12 mmol) of sodium metal, 1.62 g (12.6 mmol) of naphthalene and 24 mL of freshly distilled dry 1,2-dimethoxyethane for 2 h under nitrogen] was added 503 mg (2 mmol) of *dl*-*N*-*p*-tolylsulfonyl-2-cyclohexenylamine (**19**).[4] After stirring for 1 h, the reaction was quenched by addition of ice-water (10 mL), acidified with 1 M HCl to pH<1, and the resulting solution was washed with diethyl ether (3×35 mL) to eliminate naphthalene and other nonbasic substances. The aqueous layer was then made strongly basic (pH>11) with 30% NaOH, saturated with NaCl, and extracted with chloroform three times (30, 10, and 10 mL). The combined chloroform extracts were dried by passing through a cone of anhydrous sodium sulfate. After addition of 0.5 mL of concd HCl, the mixture was concentrated and the crystalline residue was washed succesively with 1 mL of hexane and 1 mL of benzene to give 187 mg (70%) of *dl*-**20** as off-white crystals. An analytical sample was obtained by recrystallization from 1-propanol/hexane to afford white crystals, mp 159.5—160.5 °C; IR (KBr) 2910, 2714, 2604, 2516, 2042, 1653, 1600, 1502, 1450, 1400, 729, and 670 cm^{-1}; ^{1}H NMR (D$_2$O) δ=1.4—2.3 (6H, methylene), 3.87 (1H, m, CH-N), 4.78 (3H, s, NH$_2$·HCl), 5.62 (1H, m, C=CH-C-N), 6.10 (1H, m, CH=C-C-N). Found: C, 54.01; H, 8.79; N, 10.40%. Calcd for $C_6H_{12}ClN$: C, 53.93; H, 9.05; N, 10.48%.

***N*-(2-Cyclohexenyl)-*N*′-(*p*-tolylsulfonyl)benzenesulfonimidamide (16′).** To the stirred mixture of 134 mg (1 mmol) of *dl*-2-cyclohexenylamine hydrochloride (*dl*-**20**), 1 g of ice, 2 mL of dichloromethane, and 330 mg (1 mmol) of *N*-(*p*-tolylsulfonyl)benzenesulfonimidoyl chloride (**6**)[10] was added 1 mL of 17% aqueous sodium hydrogencarbonate solution under ice-bath cooling. The reaction mixture was allowed to warm to room temperature (ca. 1 h) and stirred for an additional 24 h. The reaction mixture was twice extracted with ethyl acetate (10 mL, 5 mL), and the combined extracts were dried (Na$_2$SO$_4$). Evaporation of the solvent gave crude product which was then passed through a short plug of silica gel (3 g) using 1 : 1 EtOAc/hexane as eluent. Polar impurities were thus removed and evaporation of the solvent gave crystals, which were further recrystallized from EtOH/hexane to give 169 mg (43%) of optically inactive diastereomeric mixture **16′** (73 : 27[26]): mp 147—153 °C; HPLC (4 mm i.d. 250 mm LiChrosorb Si 60, 5 μm, 55 : 1 hexane/isopropyl alcohol, 1 mL min^{-1}) t_r=17.20 min (major), t_r=16.00 min (minor); IR (KBr) 3245, 1647, 1599, 1452, 1311, 1303, 1154, 1117, 1090, 1060, and 1050 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.2—2.1 (6H, methylene), 2.40 (3H, s, aryl methyl), 3.85 (1H, m, CH-N), 5.45—6.20 (3H, m, two vinyl protons and NH), and 7.10—8.10 (9H, aromatic). Found: C, 58.34; H, 5.86; N, 7.17%. Calcd for $C_{19}H_{22}N_2O_3S_2$: C, 58.44; H, 5.68; N, 7.17%.

***dl*-*N*-*p*-Tolylsulfonyl-2-cyclooctenylamine (23).** A mixture of 729 mg (10.5 mmol) of dry selenium powder (dried in vacuo at 80 °C for 1 h) and 4.55 g (10 mmol) of anhydrous Chloramine-T (commercially available Chloramine-T was dehydrated in vacuo at 80 °C for 1 h) in 35 mL of dry dichloromethane (methanol-free dichloromethane was passed through activated alumina, Woelm neutral alumina activity I and stored over 3A Molecular Sieves) was vigorously stirred (magnetically) for 14 h at room temperature under a nitrogen atmosphere (a white or white-gray slurry was usually produced after stirring for 2 to 4 h). Several minutes after addition of 1.56 mL (1.32 g, 12 mmol) of cyclooctene to the stirred slurry at room temperature, a gentle exothermic reaction was observed and the stirring was continued overnight (for about 14 h). The solvent was then removed in vacuo, and the residue was dissolved in a mixture of 150 mL 1 : 1 ethyl acetate/diethyl ether and 90 mL of an alkaline aqueous solution consisting of 2 parts 1 M NaOH and 1 part saturated NaCl solution. After stirring for 30 min, the entire reaction mixture was filtered through Celite 545 and the organic layer of the filtrate was washed again with the above mentioned alkaline brine solution (2×50 mL), dried (Na$_2$SO$_4$), and concentrated to give crude crystals. The crystals were dissolved in 20 mL of acetone. The acetone solution was refluxed for 2 min with 30 mg of activated charcoal and the mixture was passed through a two layered column (13 mm i.d.) consisting of 1.3 g of Celite 545 (lower layer) and 100 mg of activated charcoal (upper layer). More acetone (30 mL) was used to ensure elution of **23** and the combined eluates were concentrated to give white crystals, which were recrystallized from carbon tetrachloride/hexane (ca. 10 mL : 15 mL) to give 2.66 g (84%) of **23**: mp 125.0—125.5 °C; IR (KBr) 3230, 2910, 2845, 1595, 1437, 1300, 1144, 1087, and 1060 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.0—2.2 (10H, methylene), 2.41 (3H, s, aryl methyl), 4.19 (1H, m, CH-N), 4.92 (1H, d, *J*=6.81 Hz, NH), 5.14 (1H, d of d, *J*=7.69 and 10.55 Hz, C=CH-C-N), 5.54 (1H, d of t, *J*=10.55 and 5.54 Hz, CH=C-C-N), 7.1—7.9 (4H, aromatic). Found: C, 64.44; H, 7.66; N, 5.02%. Calcd for $C_{15}H_{21}NO_2S$: C, 64.48; H, 7.58; N, 5.01%.

***dl*-2-Cyclooctenylamine Hydrochloride (*dl*-24).** *dl*-2-Cyclooctenylamine hydrochloride (*dl*-**24**) was prepared from 1 g (3.58 mmol) of **23** according to the method and conditions described for the preparation of *dl*-2-cyclohexenylamine hydrochloride (*dl*-**20**), and the crude crystalline hydrochloride was recrystallized from isopropyl alcohol/hexane to give 407 mg (70%) of *dl*-**24**: mp 268—269 °C (sealed tube under nitrogen); IR (KBr) 2926, 2652, 2576, 2040, 1655, 1609, 1586, 1519, 1457, 1410, 758, and 716 cm^{-1}; ^{1}H NMR (D$_2$O) δ=1.2—2.4 (10H, methylene), 4.26 (1H, m, CH-N), 4.80 (3H, s, NH$_2$·HCl), 5.47 (1H, d of d, *J*=7.91 and 10.54 Hz, C=CH-C-N), 5.96 (1H, m, CH=C-C-N). Found: C, 59.54; H, 10.20; N, 8.62%. Calcd for $C_8H_{16}ClN$: C, 59.43; H; 9.97; N, 8.66%.

***N*-(2-Cyclooctenyl)-*N*′-(*p*-tolylsulfonyl)benzenesulfonimidamide (26′).** Compound **26′** was prepared from 162 mg (1 mmol) of *dl*-**24** according to the method and conditions described for the preparation of *N*-(2-cyclohexenyl)-*N'*-(*p*-tolylsulfonyl)benzenesulfonimidamide (**16'**), and recrystallization from ethanol/hexane gave 307 mg (73%) of diastereomeric mixture **26'** (62 : 38[26]): mp 123—134 °C; HPLC (4.6 mm i.d. 150 mm Finepak SIL C_{18} S; 3 : 7 H_2O/MeOH, 1 mL min^{-1}) t_r=7.95 min (major), t_r=8.41 min (minor); IR (KBr) 3205, 2920, 2850, 1650, 1599, 1447, 1326, 1302, 1217, 1150, 1113, 1088, 1052, and 1023 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.0—2.2 (10H, methylene), 2.39 (3H, s, aryl methyl), 4.14 (1H, m, CH-N), 4.8—5.8 (2H, m, CH=CH), 5.98 (0.62H, d, J=6.8 Hz, NH in the major diastereomer), 6.20 (0.38H, d, J=7.3 Hz, NH in the minor diastereomer), 7.1—8.0 (9H, aromatic). Found: C, 60.12; H, 6.23; N, 6.49%. Calcd for $C_{21}H_{26}N_2O_3S_2$: C, 60.26; H, 6.26; N, 6.69%.

***dl*-*N*-*p*-Tolylsulfonyl-1-butyl-2-propenylamine (21).** *dl*-*N*-*p*-Tolylsulfonyl-1-butyl-2-propenylamine (**21**) was prepared by allylic amination of 1-heptene (1.18 g, 12 mmol) according to the method and conditions described for the preparation of *dl*-*N*-*p*-tolylsulfonyl-2-cyclooctenylamine (**23**). The crude product (oil) was chromatographed on 80 g of silica gel using 50—75% benzene/hexane to give 2.08 g (65%) of **21** as an oil. An analytical sample was obtained by Kugelrohr distillation of a portion of this oil (180 °C, 13 Pa): IR (neat) 3280, 2970, 2940, 2860, 1648, 1600, 1500, 1432, 1330, 1163, 1098, 923, and 817 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.80 (3H, diffuse t, J=5.9 Hz, methyl), 1.0—1.7 (6H, methylene), 2.41 (3H, s, aryl methyl), 3.72 (1H, m, CH-N), 4.8—5.1 (2H, three peaks, CH=C), 5.18 (1H, d, J=7.0 Hz, NH), 5.55 (1H, m, C=CH-N), 7.1—7.9 (4H, aromatic). Found: C, 62.80; H, 8.13; N, 5.14%. Calcd for $C_{14}H_{21}NO_2S$: C, 62.98; H, 7.92; N, 5.24%.

***dl*-1-Butyl-2-propenylamine Hydrochloride (*dl*-22).** *dl*-1-Butyl-2-propenylamine hydrochloride (*dl*-**22**) was prepared from 1 g (3.74 mmol) of **21** according to the method and conditions described for the preparation of *dl*-2-cyclohexenylamine hydrochloride (*dl*-**20**). the crude crystalline hydrochloride was recrystallized from isopropyl alcohol/hexane to give 243 mg (43%) of *dl*-**22**: mp 118—119 °C; IR (KBr) 2928, 2666, 2548, 2060, 1617, 1504, 1439, 1000, and 960 cm^{-1}; ^1H NMR (D_2O) δ=0.887 (3H, t, J=5.93 Hz, methyl), 1.1—1.9 (6H, methylene), 3.78 (1H, d of t, J=6.81 and 6.81 Hz, CH-N), 4.79 (3H, s, aryl methyl), 5.2—5.5 (2H, m, CH=C), 5.6—6.1 (1H, m, C=CH-C-N). Found: C, 56.30; H, 11.06; N, 9.22%. Calcd for $C_7H_{16}ClN$: C, 56.18; H, 10.78; N, 9.36%.

***N*-(1-Butyl-2-propenyl)-*N'*-(*p*-tolylsulfonyl)benzenesulfonimidamide (13').** *N*-(1-Butyl-2-propenyl)-*N'*-(*p*-tolylsulfonyl)benzenesulfonimidamide (**13'**) was prepared from 150 mg (1 mmol) of *dl*-**22** according to the method and conditions described for the preparation of *N*-(2-cyclohexenyl)-*N'*-(*p*-tolylsulfonyl)benzenesulfonimidamide (**16'**). The crude product (oil) was purified by preparative TLC (silicagel plates, 1 : 2 EtOAc/hexane) to give 124 mg (30%) of diastereomeric mixture **13'** (1.0 : 1.0) as an oil: HPLC (4 mm i.d. 150 mm Finepak SIL C_{18} S; 3 : 7 H_2O/MeOH, 1 ml min^{-1}) t_r=8.35 min (major), t_r=9.23 min (minor); IR (neat) 3228, 2962, 2938, 2864, 1601, 1451, 1318, 1303, 1290, 1263, 1155, 1114, 1095, 1020, and 929 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.6—1.8 (9H, methyl and methylene), 2.38 (3H, s, aryl methyl), 3.65 (1H, m, CH-N), 4.6—6.0 (3H, m, vinyl), 6.30 (1H, broad s, NH), 7.0—8.1 (9H, aromatic); Anal. by high resolution MS (Hitachi M-80A mass spectrometer): Found: m/z 406.1372. Calcd for $C_{20}H_{26}N_2O_3S_2$: M, 406.1362.

***dl*-2-Methylenecyclohexylamine Hydrochloride (*dl*-12).** *dl*-2-Methylenecyclohexylamine hydrochloride (*dl*-**12**) was prepared from 500 mg (1.88 mmol) of *dl*-*N*-(*p*-tolylsulfonyl)-2-methylenecyclohexylamine (**25**)[4] according to the method and conditions described for the preparation of *dl*-2-cyclohexenylamine hydrochloride (*dl*-**20**). The crude crystalline hydrochloride was recrystallized from isopropyl alcohol/hexane to give 154 mg (55%) of *dl*-**12**: mp 218—220 °C; IR (KBr) 2936, 2056, 1659, 1595, 1513, 1452, 1399, and 910 cm^{-1}; ^1H NMR (D_2O) δ=1.2—2.6 (8H, methylene), 3.75 (1H, m, CH-N), 4.72 (1H, s, vinyl), 4.79 (3H, s, $NH_2 \cdot HCl$), 5.01 (1H, s, vinyl). Found: C, 56.57; H, 9.52; N, 9.37%. Calcd for $C_7H_{14}ClN$: C, 56.94; H, 9.56; N, 9.49%.

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