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HIGHLY REGIO AND CHEMOSELECTIVE RING OPENING OF EPOXIDES WITH TRIMETHYLSILYL AZIDE IN THE PRESENCE OF ALUMINIUM ISOPROPOXIDE AND TITANIUM ISOPROPOXIDE

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The ring-opening of functionalized epoxides with trimethylsilyl azide in the presence of a catalytic amount of Ti(O-*i*-Pr)$_4$ or Al(O-*i*-Pr)$_3$ is described. The reaction is stereospecific and highly regiospecific, leading generally to the formation of the carbon-azido bond on the less substituted carbon. The mechanism of this reaction is also discussed.

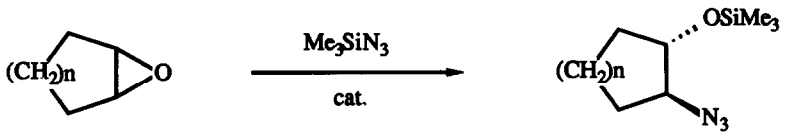
Introduction

Vicinal azidohydrines are the precursors of β-aminoalcohols, whose structures are present in numerous natural products.[1] Elaboration of the 1,2-azido functionality could be achieved by nucleophilic oxirane-ring cleavage with alkali azide in a suitable solvent.[2] The increasing availability of a number of enantiomerically pure functionalized epoxides[3] make them powerful intermediates in the synthesis of optically pure multifunctionalized amino-alcohols. However these reactions were often carried out under alkaline or sometimes acidic conditions, and usually required long reaction times and high temperatures; furthermore side reactions, such as isomerization, epimerization and rearrangements occured. So, there is still a problem in finding a regio and chemoselective reagent, which is specific towards the oxirane ring and inactive towards other functional groups.

During the last decade, the combined use of trimethylsilyl azide or sodium azide and a Lewis acid or a transition-metal complex has been successfully applied to the ring-opening of epoxides and 2,3-epoxy-alcohols.[4] We have recently reported some preliminary results on a mild procedure for the regioselective ring-opening of functionalized epoxides using trimethylsilyl azide mediated by catalytic amounts of Ti(O-*i*-Pr)$_4$ or Al(O-*i*-Pr)$_3$.[4k,l] The present paper describes this study in more details.

Results and Discussion

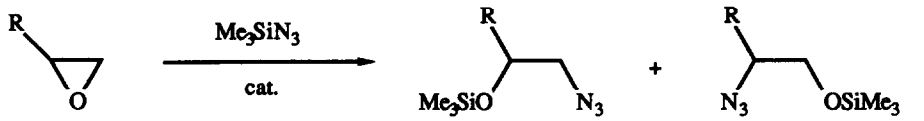
In a typical run, a mixture of an epoxide (10 mmol) and trimethylsilyl azide (15 mmol) in an appropriate solvent was stirred under nitrogen in the presence of Ti(O-*i*-Pr)$_4$ (0.15 mmol) or Al(O-*i*-Pr)$_3$ (0.98 mmol). As described in Tables 1 and 2, ring-opening of the epoxides proceeded under very mild conditions in fairly good yields. Reaction of epoxycycloalkane **1a-1d** afforded *trans*-1-azido-2-trimethylsilyloxy cycloalkanes **2a-2d** exclusively (Table I), as shown on the basis of ^{1}H and ^{13}C NMR spectra; effectively, ^{13}C NMR showed characteristic signals for C-N$_3$ and C-OSiMe$_3$ carbons at about δ 68 and 77 ppm respectively.The *trans* stereochemistry of the product was easily confirmed from the vicinal coupling constant between the α-protons of



1 **2**

a : n = 1 ; **b** : n = 2 ; **c** : n = 3 ; **d** : n = 4

Scheme I



3 **4** **5**

a : R = *n*-C_6H_{13}- ; **b** : R = CH_2=CH-$(CH_2)_2$- ; **c** : R = $HOCH_2$- ; **d** : R = CH_3OCH_2- ; **e** : R = *t*-$BuOCH_2$- ; **f** : R = $PhOCH_2$- ; **g** : R = $TsOCH_2$- ; **h** : R = $AcOCH_2$- ; **i** : R = AcO-$(CH_2)_3$- ; **j** : R = AcO-$(CH_2)_9$- ; **k** : R = Cl- ; **l** : R = Br- ; **m** : R = C_6H_5- ; **n** : R = *p*-CH_3-C_6H_4- ; **o** : R = *p*-Br-C_6H_4- ; **p** : R = *p*-NO_2-C_6H_4- ; **q** : R = furyl-

Scheme II

Table 1. Reaction of Epoxides **1** with Trimethylsilyl Azide.[a]

run	epoxide	catalyst	solvent	time, d	T°C	yield, %[b]
1	**1a**	Ti(O-*i*-Pr)$_4$	THF	6	25	84
2	**1a**	Al(O-*i*-Pr)$_3$	THF	1	25	73
3	**1b**	Ti(O-*i*-Pr)$_4$	THF	7	25	74
4	**1b**	Al(O-*i*-Pr)$_3$	no	1	25	74
5	**1b**	$SnCl_2$	CH_2Cl_2	1	25	75
6	**1b**	$Pd(CN)_2$	CH_2Cl_2	3	reflux	69
7	**1b**	$PdCl_2(CH_3CN)_2$	CH_2Cl_2	3	reflux	64
8	**1c**	Ti(O-*i*-Pr)$_4$	THF	6	25	15
9	**1c**	Ti(O-*i*-Pr)$_4$	THF	6	60	72
10	**1c**	Ti(O-*i*-Pr)$_4$	THF	1	60	81
11	**1d**	Ti(O-*i*-Pr)$_4$	THF	6	25	0
12	**1d**	Ti(O-*i*-Pr)$_4$	THF	6	60	53
13	**1d**	Al(O-*i*-Pr)$_3$	THF	1	60	0

[a] Conditions: Me_3SiN_3 (1.5 equiv), **1** (1 equiv), Ti(O-*i*-Pr)$_4$ (0.015 equiv); Al(O-*i*-Pr)$_3$ (0.098 equiv); $SnCl_2$ (0.05 equiv); $Pd(CN)_2$ (0.05 equiv); $PdCl_2(CH_3CN)_2$ (0.05 equiv). [b] Isolated by column chromatography.

Table 2. Reaction of Epoxides 3 with Trimethylsilyl Azide.[a]

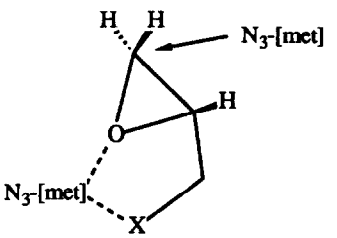
run	epoxide	catalyst	solvent	time, d	yield, %[b]	4:5[c,d]
1	**3a**	$Ti(O\text{-}i\text{-}Pr)_4$	THF	6	74	92:8
2	**3a**	$Al(O\text{-}i\text{-}Pr)_3$	none	1	74	85:15
3	**3b**	$Ti(O\text{-}i\text{-}Pr)_4$	THF	6	86	99:1
4	**3b**	$Al(O\text{-}i\text{-}Pr)_3$	CH_2Cl_2	1	70	99:1
5	**3c**	$Ti(O\text{-}i\text{-}Pr)_4$	THF	6	50	99:1
6	**3c**	$Ti(O\text{-}i\text{-}Pr)_4$	THF	6	90[e]	99:1
7	**3c**	$Al(O\text{-}i\text{-}Pr)_3$	CH_2Cl_2	5	59[e]	99:1
8	**3d**	$Ti(O\text{-}i\text{-}Pr)_4$	THF	6	60	99:1
9	**3d**	$Al(O\text{-}i\text{-}Pr)_3$	CH_2Cl_2	2	90	99:1
10	**3e**	$Ti(O\text{-}i\text{-}Pr)_4$	THF	6	79	99:1
11	**3e**	$Al(O\text{-}i\text{-}Pr)_3$	CH_2Cl_2	1	82	99:1
12	**3e**	$SnCl_2$	CH_2Cl_2	1	70	95:5
13	**3f**	$Ti(O\text{-}i\text{-}Pr)_4$	THF	6	72	99:1
14	**3f**	$Al(O\text{-}i\text{-}Pr)_3$	CH_2Cl_2	1	70	99:1
15	**3g**	$Ti(O\text{-}i\text{-}Pr)_4$	THF	6	76	99:1
16	**3g**	$Al(O\text{-}i\text{-}Pr)_3$	CH_2Cl_2	1	93	99:1
17	**3h**	$Ti(O\text{-}i\text{-}Pr)_4$	THF	6	54[f]	99:1
18	**3h**	$Al(O\text{-}i\text{-}Pr)_3$	CH_2Cl_2	1	83	99:1
19	**3i**	$Ti(O\text{-}i\text{-}Pr)_4$	THF	6	82	70:30
20	**3i**	$Al(O\text{-}i\text{-}Pr)_3$	CH_2Cl_2	1	80	85:15
21	**3j**	$Ti(O\text{-}i\text{-}Pr)_4$	THF	6	72	99:1
22	**3k**	$Ti(O\text{-}i\text{-}Pr)_4$	THF	6	75	99:1
23	**3k**	$Al(O\text{-}i\text{-}Pr)_3$	CH_2Cl_2	1	83	99:1
24	**3l**	$Ti(O\text{-}i\text{-}Pr)_4$	THF	6	86	99:1
25	**3l**	$Al(O\text{-}i\text{-}Pr)_3$	CH_2Cl_2	1	81	99:1
26	**3m**	$Ti(O\text{-}i\text{-}Pr)_4$	THF	6	74	1:99
27	**3m**	$Al(O\text{-}i\text{-}Pr)_3$	CH_2Cl_2	1	73	7:93
28	**3n**	$Ti(O\text{-}i\text{-}Pr)_4$	THF	6	57	1:99
29	**3n**	$Al(O\text{-}i\text{-}Pr)_3$	CH_2Cl_2	1	60	1:99
30	**3o**	$Ti(O\text{-}i\text{-}Pr)_4$	THF	6	67	5:95
31	**3o**	$Al(O\text{-}i\text{-}Pr)_3$	CH_2Cl_2	1	53	3:97
32	**3p**	$Ti(O\text{-}i\text{-}Pr)_4$	THF	6	70	44:56
33	**3p**	$Al(O\text{-}i\text{-}Pr)_3$	CH_2Cl_2	1	94	60:40
34	**3q**	none	THF	6	74	1:99

[a] Conditions: Me_3SiN_3 (1.5 equiv), **3** (1 equiv), $Ti(O\text{-}i\text{-}Pr)_4$ (0.015 equiv); $Al(O\text{-}i\text{-}Pr)_3$ (0.098 equiv); $SnCl_2$ (0.05 equiv); room temperature. [b] Isolated by column chromatography. [c] Determined by NMR and GLC. [d] 99:1 means that only one regioisomer could be detected. [e] Me_3SiN_3 (2.0 equiv). [f] Another compound **8** was obtained in 36% chemical yield after column chromatography.

the azido and the trimethylsilyloxy groups (J_{HH} = 6.6 Hz for **2a**, J_{HH} = 9.0 Hz for **2b** and J_{HH} = 7.9 Hz for **2c**). However we noticed that medium-ring epoxides **1c-1d** were less reactive than cyclohexene oxide and required higher temperatures, affording the desired products in lower yields (runs 8-13). Instead of Ti(O-*i*-Pr)$_4$ or Al(O-*i*-Pr)$_3$, $SnCl_2$, $Pd(CN)_2$ and $PdCl_2(CH_3CN)_2$ were also effective catalysts for the stereoselective ring-opening of **1b** (Table I, runs 5-7).

Table 2 exhibits the results obtained in the ring-opening of acyclic, eventually functionalized, 1,2-epoxides **3**. In all cases, except for aryl glycidols **3m-3p** and butadiene monoepoxide **11**, the nucleophilic attack occurred at the unsubstituted methylene, and a wide variety of functional groups, including hydroxy, alcoxy, phenoxy, tosyloxy, acetate, chloro, bromo, were tolerated under our reaction conditions. Of special interest is the improvement of the regioselectivity with the epoxides bearing an electron-withdrawing group at the C-3 position (runs 5-11, 13-18 and 22-25). The regiochemistry was unambiguously assigned using ^{13}C NMR[5] (see experimental section); the signals corresponding to -CH_2N_3 and >$CHOSiMe_3$ for isomer **4** appeared at about δ 53-56 ppm and 70-72 ppm, and the signals corresponding to -CH_2OSiMe_3 and >CHN_3 for isomer **5** at about δ 65-70 ppm and 63-65 ppm, respectively. This regiochemistry was also confirmed for some compounds by hydrolysis; for example, ^1H NMR analysis in DMSO of the azidohydrine obtained by hydrolysis of the compound occuring from the ring-opening of epoxide **3k** showed a doublet at δ 5.6 ppm for the hydroxylic proton. The regioselectivity did not seem to be solvent dependent; for example, the ring-opening of epoxide **3d**, catalyzed by Ti(O-*i*-Pr)$_4$, is regiospecific, when using tetrahydrofuran (THF), *n*-hexane, benzene, acetonitrile or dichloromethane as the solvent. The ring-opening of glycidol **3c** needed at least two equivalents of trimethylsilyl azide, due to silylation of the glycidol.[6] Using $SnCl_2$ as a catalyst gave lower regioselectivity (run 12); however we obtained in this case the reverse regiochemistry than that observed by Imi and coll. in the ring-opening of non functionalized epoxides by cyanotrimethylsilane under the same catalytic conditions.[7]

This very high regioselectivity observed in the ring opening of these functionalized epoxides catalyzed by Ti(O-*i*-Pr)$_4$ or Al(O-*i*-Pr)$_3$ could be rationalized by invoking the formation of a coordinated structure around the metal center in a similar manner to that proposed by Sharpless[4c] and Onaka[4i] (Scheme III). Opening at C-3 could occur preferentially for the reasons invoked by Onaka: in this case a five-membered chelation structure remains, instead of a six-membered chelation structure, which seems less stable, for the opening at C-2. This chelation could also explain the reversal observed in the opening of **3e** using $SnCl_2$ as the catalyst, compared to the litterature data.

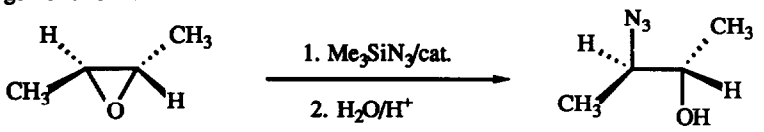


Scheme III

If we have no information about the exact nature of the active azido species in the case of Al(O-*i*-Pr)$_3$, formation of Al(O-*i*-Pr)$_2$(N$_3$) could be expected by analogy with the formation of Al(O-*i*-Pr)$_2$CN by reaction of Al(O-*i*-Pr)$_3$ with Me_3SiN_3.[4i] On the other hand, for the ring-opening using Ti(O-*i*-Pr)$_4$ as the catalyst, it was recently shown that the active species was Ti(O-*i*-Pr)$_2$(N$_3$)$_2$.[4b,c,e]

To acquire more knowledge about the mechanism of this ring-opening, we ran two experiments using

(2S,3S)-epoxybutane **6** as the substrate and Al(O-*i*-Pr)$_3$ or Ti(O-*i*-Pr)$_4$ as the catalyst. In both cases, we obtained the azido alcohol **7** having the same optical rotation (Scheme IV). As it has been shown that ring opening of epoxides using Al(O-*i*-Pr)$_3$ was an S_N2 intermolecular process,[4i] we expected that the same S_N2 intermolecular mechanism occured for the ring opening using Ti(O-*i*-Pr)$_4$. The rigorous *trans* stereochemistry of the *trans*-1-azido-2-trimethylsilyloxy cycloalkanes obtained effectively suggested an S_N2-type attack on a Lewis acid complexed epoxide. However it still remains unclear to us whether the active azido species exists in its monomeric or oligomeric form.



6 **7**

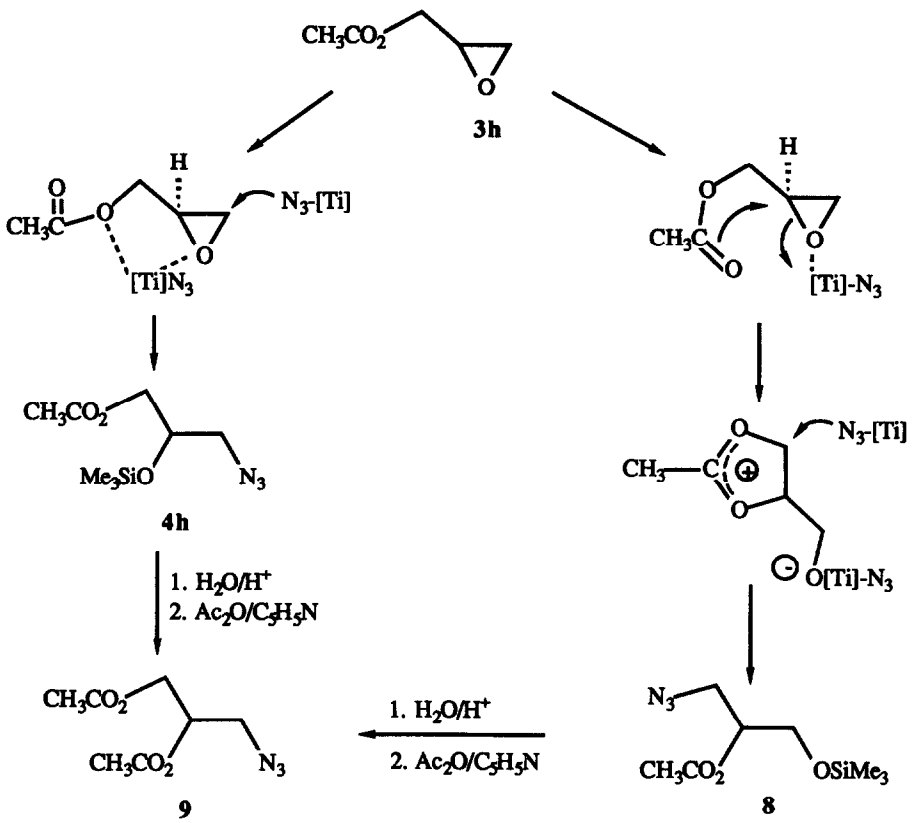
cat. Al(O-*i*-Pr)$_3$ $[\alpha]_D^{20}$ -16.6°

cat. Ti(O-*i*-Pr)$_4$ $[\alpha]_D^{20}$ -15.7°

Scheme IV

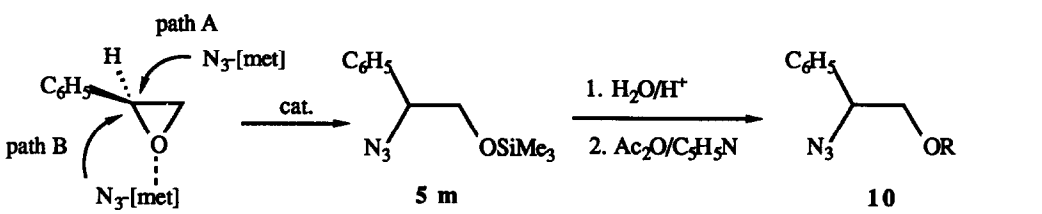
Acetoxy glycidol **3h** gave a more complex reaction under the catalytic action of Ti(O-*i*-Pr)$_4$; besides the expected compound **4h** obtained as the only regioisomer in 54% chemical yield, we observed the formation of a second compound in 36% chemical yield to which we assigned structure **8**. This assignement was not only based on ^{13}C NMR data, but mainly on the chemical transformation of **8** by hydrolysis and acetylation into the compound **9** whose analytical data are identical to that of the compound obtained from **4h** using the same procedure.The formation of compound **8** could be explained by intramolecular acetate participation in the epoxide opening (Scheme V). Complexation of the titanium species followed by participation of the acetate in the cleavage of the epoxide C-O bond results in the formation of a dioxolenium ion which upon attack by the Ti(N$_3$)$_2$(O-*i*-Pr)$_2$ species on the less subtituted carbon gives the azido compound **8**. Such a participation already had some precedent in the opening of acetoxy epoxides in the presence of Lewis acids.[8]

Styrene oxide **3m** gave only the azido alcohol **5m**, resulting from C-2 attack, with complete reversal in the regioselectivity in the presence of Ti(O-*i*-Pr)$_4$. However in the presence of Al(O-*i*-Pr)$_3$, a small amount of the other regioisomer **4m** was detected. Due to some discrepencies in the litterature about this ring-opening using trimethylsilyl azide or sodium azide,[2a,4a] the structure of compound **5m** was unambiguously confirmed by hydrolysis and acetylation according to Scheme VI. The ^1H NMR spectrum of the azido alcohol **10a** in DMSO as the solvent showed a triplet at δ 5.45 ppm for the hydroxyl function; and for the acetate **10b**, we observed a deshielding effect of 0.5 ppm for the methylene protons. However, this regioselectivity was modified by the introduction of a withdrawing group on the aromatic ring; for example, the ring-opening of 2-(4-nitrophenyl) oxirane **3p** gave a mixture of regioisomers (runs 32-33). These results clearly show that in this case electronic factors play a crucial role, and that probably partial ionization of the epoxide oxygen in the transition state, via coordination of the catalyst at the oxygen ring, was involved in this mechanism. Using optically active styrene oxide as the substrate provided more information (Table 3). Ring-opening using Al(O-*i*-Pr)$_3$ as the catalyst occured with inversion of configuration at the benzylic carbon in all of the solvents used. A reasonable mechanism in this case is an intermolecular transfer of the azido group as shown in Scheme VI. When Ti(O-*i*-Pr)$_4$ was used as the catalyst, inversion was observed in hexane and methane, and retention in tetrahydrofuran (THF), dimethoxyethane (DME) and tetrahydropyran (THP). This implies that two mechanisms are operative: one is the



Scheme V

same as the mechanism previously described for Al(O-*i*-Pr)$_3$ (path A); the other is the complexation of the reactive species at the epoxide oxygen atom followed by an intramolecular transfer of the azido group in close proximity via a four-center transition state affording a retention of configuration (path B). Eventually, epoxide ring-opening could also occur via a carbonium ion intermediate which can lead to a benzylic substitution with a lower selectivity.[9-12] These two later mechanisms would be more favoured in a solvent like tetrahydrofuran.



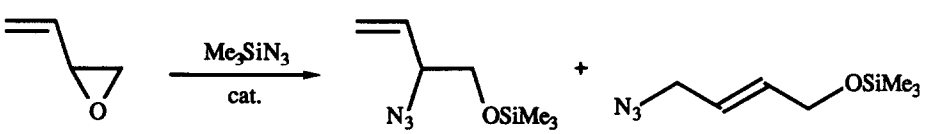
Scheme VI

Table 3. Reaction of Epoxide **3m** (R) with Trimethylsilyl Azide.[a]

catalyst	solvent	yield, %[b]	$[\alpha]_D^{20}$ of **5m**[c]	e.e(%)(conf.)[d]
Al(O-*i*-Pr)$_3$	Hexane	59	+55	76(S)
Ti(O-*i*-Pr)$_4$	Hexane	37	+52	72(S)
Al(O-*i*-Pr)$_3$	CH_2Cl_2	50	+65	90(S)
Ti(O-*i*-Pr)$_4$	CH_2Cl_2	56	+31	43(S)
Al(O-*i*-Pr)$_3$	Ether	48	+58	80(S)
Ti(O-*i*-Pr)$_4$	Ether	45	+22	31(S)
Al(O-*i*-Pr)$_3$	DME	44	+55	76(S)
Ti(O-*i*-Pr)$_4$	DME	58	-46	64(R)
Al(O-*i*-Pr)$_3$	THF	47	+60	83(S)
Ti(O-*i*-Pr)$_4$	THF	50	-60	83(R)
Ti(O-*i*-Pr)$_4$	THP	45	-45	63(R)

[a] Conditions: Me_3SiN_3 (1.5 equiv), **3m** (1 equiv), Ti(O-*i*-Pr)$_4$ (0.04 equiv); Al(O-*i*-Pr)$_3$ (0.1 equiv). [b] After purification by flash chromatography. [c] c=1, CH_2Cl_2. [d] The enantomeric excesses of **5m** were determined by conversion of the silylated product into it's amino alcohol derivative and compared with the optical rotation of the corresponding pure R-amino alcohol:$[\alpha]_D^{20}$ = -25.8°(c= 6.6; MeOH)[18].

The reaction of butadiene monoxide **11** with trimethylsilyl azide in the presence of a catalyst showed some similarities with the ring-opening of styrene oxide. Two products **12** and **13** were formed practically in the same ratio (Scheme VII). Compound **12** occured from the attack of the azide on the more electrophilic center, as for styrene oxide; the other compound **13** was formed by an S_N2' mechanism. These two products were also obtained using sodium azide as the reagent.[2b]



11 **12** **13**

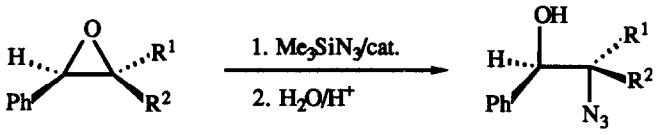
cat. Ti(O-*i*-Pr)$_4$	48%	52%
cat. Al(O-*i*-Pr)$_3$	45%	55%

Scheme VII

We also noticed that the ring-opening of 2-furyl oxirane **3q** in the presence of Ti(O-*i*-Pr)$_4$ or Al(O-*i*-Pr)$_3$ gave only polymers; however, at 0 °C, without catalyst, ring-opening occured very cleanly leading after

hydrolysis to 2-azido-2-furyl ethanol **5q**. The structure of this azidohydrine was again confirmed by ^1H and ^{13}C NMR; in DMSO as the solvent, the hydroxylic proton showed a triplet at δ 5.0 ppm, and in ^{13}C NMR two signals appeared for the CN_3 and CH_2OH carbon atoms at δ 60.6 and 63.4 ppm respectively. This easier ring-opening of 2-furyl oxirane and the regiospecificity observed were also recently shown for halosilanes.[13]

We finally examined the ring-opening of stilbene oxides **14a** *cis* and **14b** *trans* by using trimethylsilyl azide in the presence of Ti(O-*i*-Pr)$_4$ (Scheme VIII). The *threo* azidohydrine **15b** was stereospecifically obtained from the *cis* isomer ($J_{H,H}$ = 8.4 Hz), whereas the *trans* epoxide **14b** gave a mixture of *threo* and *erythro* azidohydrine ($J_{H,H}$= 6.0 Hz) in a ratio of 45/55. Here again it seems likely that ring-opening of the *cis* epoxide **14a** occured only in the S_N2 fashion, although in the case of the *trans* isomer, the intermediate of a four-center transition state could explain the formation of the *erythro* isomer; the slower rate of the ring-opening for the *trans* isomer is in good agreement with this mechanism.



11 **12**

a : R^1 = H, R^2 = Ph ; **b** : R^1 = Ph, R^2 = H

Scheme VIII

In conclusion, ring-opening of functionalised epoxides with trimethylsilyl azide in the presence of a catalytic amount of Ti(O-*i*-Pr)$_4$ or Al(O-*i*-Pr)$_3$ occured under very mild conditions in a stereospecific manner and with a very high regioselectivity, the formation of the carbon-nitrogen bond occuring generally at the less hindered carbon of the epoxide. In the case of styrene oxide, the regioselectivity observed was the reversed; if inversion was only observed using Al(O-*i*-Pr)$_3$ as the catalyst, Ti(O-*i*-Pr)$_4$ gave inversion or retention, depending on the solvent.

Experimental Section

General Procedures. Column chromatography was carried out on silica gel GF_{254} (230-400 mesh Merck). Analytical gas chromatograms were obtained on a Girdel 330 apparatus with a flame ionization detector (10% Carbowax 20 M on Chromosorb W 60/80 mesh, 3 m). Infrared spectra were obtained using a Perkin-Elmer 681 instrument. Optical rotations were measured on a Perkin-Elmer 241 polarimeter. ^1H-NMR spectra were recorded on either a Bruker AM 300 (300 MHz) or a Bruker W 80 (80 MHz) in $CDCl_3$ solution, the δ values calculated being based on δ 7.26 ppm for $CHCl_3$ for the silylated products; ^{13}C-NMR spectra were obtained at 75.47 MHz on a Bruker AM 300 spectrometer, the δ values calculated being based on δ 77.0 ppm for $CDCl_3$ (central resonance) for the silylated products. Microanalysis were performed by the Laboratoire Central de Microanalyse du CNRS, Vernaison, France. All solvents were distilled from an appropriate drying agent and stored under an atmosphere of nitrogen. All air-sensitive reactions were performed under an atmosphere of nitrogen. 1,2-epoxycycloheptane **1c**,[14] 1,2-epoxycyclooctane **1d**,[14] tosyloxy glycidol **3g**,[15] acetoxy glycidol **3h**,[15] 1-acetoxy-4,5-epoxypentane **3i**,[14] 1-acetoxy-10,11-epoxyundecane **3j**,[14] 2-(4-methylphenyl) oxirane **3n**,[16] 2-(4-bromophenyl) oxirane **3o**[16] and 2-(4-nitrophenyl) oxirane **3p**[16] were prepared by reported procedures. All the other chemicals are commercially available.

General Procedure for Ring Opening of Epoxides with Trimethylsilyl Azide Catalyzed by Ti(O-*i*-Pr)$_4$. To a mixture of Ti(O-*i*-Pr)$_4$ (42 mg, 0.15 mmol, 0.015 equiv) and Me_3SiN_3 (1.7 g, 15 mmol,

1.5 equiv) in 3 mL of tetrahydrofuran was added the epoxide (10 mmol), and the mixture was stirred at room temperature. The reaction is complete after about 6 days (GC). This is due to the slow formation of the active species $Ti(O\text{-}i\text{-}Pr)_2(N_3)_2$ which requires 2 to 3 days at room temperature.[4b] The catalyst was removed from the reaction mixture by flash-chromatography using a mixture of hexane and ethyle acetate as the eluent.

General Procedure for Ring Opening of Epoxides with Trimethylsilyl Azide Catalyzed by $Al(O\text{-}i\text{-}Pr)_3$. A mixture of $Al(O\text{-}i\text{-}Pr)_3$ (0.2 g, 0.98 mmol, 0.1 equiv) and Me_3SiN_3 (1.7 g, 15 mmol, 1.5 equiv) in 2 mL of dichloromethane was stirred at room temperature for 2 h. The epoxide (10 mmol) was added to the mixture and the solution was stirred at room temperature. The reaction was worked up as previously described.

***trans*-1-Azido-2-trimethylsilyloxy cyclopentane 2a.** IR (neat) 2090 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.07 (9H, s), 1.40-1.97 (6H, m), 3.56 (1H, dt, J = 6.0, 6.0 Hz), 3.93 (1H, dt, J = 6.6, 6.6 Hz); ^{13}C NMR ($CDCl_3$) δ - 0.3 ($SiMe_3$), 20.0 (C-4), 28.0 (C-5), 32.4 (C-3), 68.5 (C-1), 77.7 (C-2). Anal. Calcd for $C_8H_{17}N_3OSi$: C, 48.21; H, 8.60. Found: C, 48.15; H, 8.31.

***trans*-1-Azido-2-trimethylsilyloxy cyclohexane 2b.** IR (neat) 2100 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.16 (9H, s), 1.10-1.14 (4H, m), 1.70-1.75 (2H, m), 1.83-1.95 (2H, m), 3.19 (1H, ddd, J = 10.7, 9.0, 4.3 Hz), 3.43 (1H, ddd, J = 10.7, 9.0, 4.3 Hz); ^{13}C NMR ($CDCl_3$) δ 0.1 ($SiMe_3$), 23.8 (C-5), 24.0 (C-4), 30.4 (C-6), 34.5 (C-3), 66.6 (C-1), 75.1 (C-2) in agreement with the litterature.[4b]

***trans*-1-Azido-2-trimethylsilyloxy cycloheptane 2c.** IR (neat) 2090 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.15 (9H, s), 1.40-1.83 (10H, m), 3.34 (1H, ddd, J = 8.0, 7.9, 3.7 Hz), 3.59 (1H, ddd, J = 7.9, 7.9, 3.3 Hz); ^{13}C NMR ($CDCl_3$) δ 0.1 ($SiMe_3$), 22.0 (C-5), 23.1 (C-6), 27.4 (C-4), 29.8 (C-7), 34.3 (C-3), 70.1 (C-1), 77.8 (C-2). Anal. Calcd for $C_7H_{13}N_3O$ (hydrolyzed product): C, 54.17; H, 8.44. Found: C, 54.43; H, 8.49.

***trans*-1-Azido-2-trimethylsilyloxy cyclooctane 2d.** IR (neat) 2090 cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) δ 0.1 (9H, s), 1.2-1.9 (12H, m), 3.2-3.9 (2H, m); ^{13}C NMR ($CDCl_3$) δ 0.3 ($SiMe_3$), 24.1 (C-6), 24.7 (C-5), 25.7 (C-4, C-7), 29.7 (C-8), 33.1 (C-3), 68.7 (C-1), 76.4 (C-2). Anal. Calcd for $C_8H_{15}N_3O$ (hydrolyzed product): C, 56.78; H, 8.93. Found: C, 56.99; H, 8.91.

1-Azido-2-trimethylsilyloxy octane 4a and 1-Trimethylsilyloxy-2-azido octane 5a. A mixture of **4a** and **5a** was obtained, but separation of each component in a pure state was unsuccessful. Elemental analysis of the two components was determined by NMR and GLC. Anal. Calcd for $C_{11}H_{25}N_3OSi$: C, 54.28; H, 10.35. Found: C, 54.60; H, 10.68.

4a: IR (neat) 2090 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.15 (9H, s), 0.88 (3H, t, J = 6.7 Hz), 1.27 (8H, m), 1.46 (2H, m), 3.14 (1H, dd, J = 12.5, 6.0 Hz), 3.16 (1H, ddd, J = 12.5, 4.5 Hz), 3.76 (1H, tdd, J = 6.0, 6.0, 4.5 Hz); ^{13}C NMR ($CDCl_3$) δ 0.1 ($SiMe_3$), 13.9 (C-8), 22.5 (C-7), 25.3 (C-6), 29.3 (C-5), 31.7 (C-4), 35.1 (C-3), 56.7 (C-1), 71.8 (C-2).

5a: ^1H NMR (300 MHz, $CDCl_3$) δ 0.13 (9H, s), 0.88 (3H, t, J = 6.7 Hz), 1.27 (8H, m), 1.46 (2H, m), 3.33 (1H, m), 3.56 (1H, dd, J = 10.5, 7.0 Hz), 3.67 (1H, dd, J = 10.5, 4.0 Hz); ^{13}C NMR ($CDCl_3$) δ - 0.8 ($SiMe_3$), 13.9 (C-8), 22.5 (C-7), 26.0 (C-6), 29.0 (C-5), 30.4 (C-4), 31.6 (C-3), 63.6 (C-2), 65.7 (C-1).

1-Azido-2-trimethylsilyloxy-5-hexene 4b. IR (neat) 2090 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.14 (9H, s), 1.57 (2H, dt, J = 7.7, 6.2 Hz), 2.07 (2H, m), 3.14 (1H, dd, J = 12.5, 6.2 Hz), 3.19 (1H, dd, J = 12.5, 4.3 Hz), 3.79 (1H, ddt, J = 6.2, 6.2, 4.3 Hz), 4.96 (1H, ddt, J = 17.0, 1.6, 1.6 Hz), 5.77 (1H, ddt, J = 17.0, 10.4, 6.5 Hz); ^{13}C NMR ($CDCl_3$) δ - 0.1 ($SiMe_3$), 29.3 (C-3), 34.0 (C-4), 56.4 (C-1), 71.0 (C-2), 114.6 (C-6), 137.6 (C-5). Anal. Calcd for $C_9H_{19}N_3OSi$: C, 50.67; H, 8.98. Found: C, 50.78; H, 9.01.

1-Azido-2,3-bis(trimethylsilyloxy) propane 4c. IR (neat) 2090 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.10 (9H, s), 0.15 (9H, s), 3.21 (1H, dd, J = 12.6, 6.3 Hz), 3.29 (1H, dd, J = 12.6, 3.6 Hz), 3.48 (1H, dd, J = 10.3, 6.8 Hz), 3.51 (1H, dd, J = 10.3, 5.4 Hz), 3.82 (1H, dddd, J = 6.8, 6.3, 5.4, 3.6 Hz); ^{13}C NMR ($CDCl_3$) δ - 0.6 ($SiMe_3$), 0.1 ($SiMe_3$), 53.9 (C-1), 64.1 (C-3), 72.4 (C-2). Anal. Calcd for $C_9H_{23}N_3O_2Si_2$: C, 41.34; H, 8.87. Found: C, 41.42; H, 8.61.

1-Azido-2-trimethylsilyloxy-3-methoxy propane 4d. IR (neat) 2100 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.14 (9H, s), 3.22 (1H, dd, J = 12.5, 6.0 Hz), 3.25 (1H, dd, J = 12.5, 4.3 Hz), 3.32 (3H, s), 3.33 (2H, d, J = 5.5 Hz), 3.91 (1H, ddt, J = 6.0, 5.5, 4.3 Hz); ^{13}C NMR ($CDCl_3$) δ - 0.4 ($SiMe_3$), 53.8 (C-1), 58.6 (OMe), 70.5 (C-2), 74.0 (C-3). Anal. Calcd for $C_7H_{17}N_3O_2Si$: C, 41.35; H, 8.43. Found: C, 41.65; H, 8.38.

1-Azido-2-trimethylsilyloxy-3-*t*-butyloxy propane 4e. IR (neat) 2090 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.07 (9H, s), 1.07 (9H, s), 3.10 (1H, dd, *J* = 12.5, 6.3 Hz), 3.18 (1H, dd, *J* = 9.0, 6.8 Hz), 3.18 (1H, dd, *J* = 12.5, 3.4 Hz), 3.21 (1H, dd, *J* = 9.0, 5.6 Hz), 3.77 (1H, dddd, *J* = 6.8, 6.3, 5.6, 3.4 Hz); ^{13}C NMR ($CDCl_3$) δ - 0.1 ($SiMe_3$), 27.2 (Me), 54.3 (C-1), 63.4 (C-3), 71.5 (C-2), 72.7 (*C*Me_3). Anal. Calcd for $C_{10}H_{23}N_3O_2Si$: C, 48.94; H, 9.45. Found: C, 49.25; H, 9.67.

1-Azido-2-trimethylsilyloxy-3-phenoxy propane 4f. IR (neat) 2090 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.30 (9H, s), 3.40 (1H, dd, *J* = 12.6, 6.0 Hz), 3.45 (1H, dd, *J* = 12.6, 4.0 Hz), 3.99 (2H, d, *J* = 5.8 Hz), 4.25(1H, ddt, *J* = 6.0, 5.8, 4.0 Hz), 7.01-7.06 (3H,m), 7.26-7.39 (2H, m); ^{13}C NMR ($CDCl_3$) δ 0.03 ($SiMe_3$), 54.0 (C-1), 69.1 (C-3), 70.4 (C-2), 114.2, 120.9, 129.5, 158.2 (C_6H_5). Anal. Calcd for $C_{12}H_{19}N_3O_2Si$: C, 54.31; H, 7.22. Found: C, 54.62; H, 7.37.

1-Azido-2-trimethylsilyloxy-3-tosyloxy propane 4g. IR (neat) 2090 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.04 (9H, s), 2.36 (3H,s), 3.12 (1H, dd, *J* = 12.8, 5.5 Hz), 3.19 (1H, dd, *J* = 12.8, 3.8 Hz), 3.86 (1H, dd,*J* = 9.3, 6.3 Hz), 3.88 (1H, dd, *J* = 9.3, 4.7 Hz), 3.93 (1H, ddm, *J* = 6.3, 4.7 Hz), 7.27 (2H, m), 7.70 (2H, m); ^{13}C NMR ($CDCl_3$) δ - 0.4 ($SiMe_3$), 21.4 (Me), 53.1 (C-1), 69.2 (C-2), 70.1 (C-3), 127.7, 129.7, 132.3, 144.9 (C_6H_4). Anal. Calcd for $C_{13}H_{21}N_3O_4SSi$: C, 45.46; H, 6.16. Found: C, 45.58; H, 6.23.

1-Azido-2-trimethylsilyloxy-3-acetoxy propane 4h. IR (neat) 2090 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.16 (9H, s), 2.05 (3H, s), 3.22 (1H, dd, *J* = 12.4, 5.6 Hz), 3.24 (1H, dd, *J* = 12.4, 4.4 Hz), 3.96-4.03 (3H, m); ^{13}C NMR ($CDCl_3$) δ - 0.1 ($SiMe_3$), 20.7 (Me), 54.0 (C-1), 65.5 (C-3), 69.6 (C-2), 170.4 (CO). Anal. Calcd for $C_8H_{17}N_3O_3Si$: C, 41.54; H, 7.41. Found: C, 41.52; H, 7.33.

1-Azido-2-acetoxy-3-trimethylsilyloxy propane 8. ^1H NMR (80 MHz, $CDCl_3$) δ 0.15 (9H, s), 2.13 (3H, s), 3.51 (2H, d, *J* = 5.2 Hz), 3.72 (2H, d, *J* = 5.3 Hz), 5.00 (1H, q); ^{13}C NMR ($CDCl_3$) δ 0.5 ($SiMe_3$), 20.5 (Me), 50.2 (C-1), 60.6 (C-3), 72.4 (C-2), 172.0 (CO).

1-Azido-2,3-diacetoxy propane 9. A solution of **4h** (231 mg, 1mmol) (or **8**) was hydrolyzed in 5 mL of methanol containing a trace of HCl. After evaporation of the solvent, the residu was dissolved in 5 mL of pyridine and acetic anhydride (102 mg, 3 mmol) was added. After 24 h at room temperature, usual work-up gave the diacetate **9** (160 mg, 80% yield). ^1H NMR (80 MHz, $CDCl_3$) δ 0.10 (9H, s), 2.15 (3H, s), 2.20 (3H, s), 3.57 (2H, d, *J* = 5.2 Hz), 4.30 (2H, d, *J* = 6.0 Hz), 5.3 (1H, q); ^{13}C NMR ($CDCl_3$) δ 20.7 (Me), 20.8 (Me), 50.5 (C-1), 62.3 (C-3), 69.9 (C-2), 170.3 (CO), 170.4 (CO).

1-Azido-2-trimethylsilyloxy-6-acetoxy pentane 4i. IR (neat) 2100 cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) δ 0.11 (9H, s), 1.45-1.72 (4H, m), 2.00 (3H, s), 3.14 (2H, m), 3.77 (1H, bq, *J* = 6 Hz), 4.02 (2H, bt, *J* = 6 Hz); ^{13}C NMR ($CDCl_3$) δ 0.1 ($SiMe_3$), 20.8 (Me), 24.5 (C-4), 31.2 (C-3), 56.5 (C-1), 64.4 (C-5), 71.1 (C-2), 170.8 (CO). Anal. Calcd for $C_{10}H_{21}N_3O_3Si$: C, 46.31; H, 8.16. Found: C, 46.10; H, 8.12.

1-Azido-2-trimethylsilyloxy-11-acetoxy undecane 4j. IR (neat) 2100 cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) δ 0.1 (9H, s), 1.0-1.6 (14H, m), 1.9 (3H, s), 3.1 (2H, m), 3.8-4.1 (3H, m); ^{13}C NMR ($CDCl_3$) δ 0.0 ($SiMe_3$), 20.9 (Me), 25.4, 25.9, 28.7, 29.2, 29.4, 29.6 (C-4, C-5, C-6, C-7, C-8, C-9, C-10), 35.2 (C-3), 56.8 (C-1), 64.5 (C-11), 71.9 (C-2), 170.8 (CO). Anal. Calcd for $C_{16}H_{33}N_3O_3Si$: C, 55.94; H, 9.68. Found: C, 56.01; H, 9.71.

1-Azido-2-trimethylsilyloxy-3-chloro propane 4k. IR (neat) 2100 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.16 (9H, s), 3.28 (1H, dd, *J* = 12.7, 5.7 Hz), 3.36 (1H, dd, *J* = 12.7, 3.9 Hz), 3.44 (1H, dd, *J* = 11.1, 5.5 Hz), 3.47 (1H, dd, *J* = 11.1, 6.5 Hz), 3.95 (1H, dddd, *J* = 6.5, 5.7, 5.5, 3.9 Hz); ^{13}C NMR ($CDCl_3$) δ - 0.1 ($SiMe_3$), 45.2 (C-3), 54.0 (C-1), 71.8 (C-2). Anal. Calcd for $C_6H_{14}ClN_3OSi$: C, 34.69; H, 6.79. Found: C, 34.66; H, 6.79.

1-Azido-2-hydroxy-3-chloro propane. A solution of **4k** (0.5 g, 0.26 mmol) in 10 mL of dioxanne containing 5 mL HCl 1N was stirred at room temperature for 30 mn. Removal of the solvent and flash chromatography of the crude mixture with AcOEt/hexane (1:2) as the eluent afforded the pure azidohydrine (0.28 g, 90% yield).[17] IR (neat) 3390 and 2100 cm^{-1}; ^1H NMR (60 MHz, DMSO d_6) δ 3.1-3.5 (4H, m), 3.5-3.9 (1H, m), 5.6 (1H, d, *J* = 6.0 Hz).

1-Azido-2-trimethylsilyloxy-3-bromo propane 4l. IR (neat) 2100 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.17 (9H, s), 3.30 (1H, dd, *J* = 10.4, 5.1 Hz), 3.32 (1H, dd, *J* = 12.6, 5.7 Hz), 3.34 (1H, dd, *J* = 10.4, 6.7 Hz), 3.39 (1H, dd, *J* = 12.6, 3.9 Hz), 3.96 (1H, dddd, *J* = 6.7, 5.7, 5.1, 3.9 Hz); ^{13}C NMR ($CDCl_3$) δ 0.1 ($SiMe_3$), 33.6 (C-3), 54.2 (C-1), 71.5 (C-2). Anal. Calcd for $C_6H_{14}BrN_3OSi$: C, 28.58; H, 5.60. Found: C, 28.42; H, 5.51.

1-Trimethylsilyloxy-2-azido-2-phenyl ethane 5m. I.R. (neat) 2100 cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) δ 0.1 (9H, s), 3.5-3.7 (2H, m), 4.5 (1H, m), 7.3 (5H, m); ^{13}C NMR ($CDCl_3$) δ - 0.7 ($SiMe_3$), 67.2 (C-2), 67.4 (C-1), 126.9, 128.2, 128.5, and 136.7 (C_6H_5).

1-Azido-2-phenyl-2-trimethylsilyloxy ethane 4m. ^{13}C NMR ($CDCl_3$) (in the mixture of **4m** and **5m**) δ - 0.1 ($SiMe_3$), 58.4 (C-1), 74.4 (C-2), 126.9, 128.2, 128.5, and 136.7 (C_6H_5).

2-Azido-2-phenyl ethanol 8a. A solution of **5m** (1.0 g, 4.2 mmol) was hydrolyzed in a mixture of dioxane (5mL) and water (5mL) containing a trace of HCl. After evaporation, flash chromatography of the crude mixture afforded the azido alcohol **8a** (0.54 g, 70% yield). I.R. (neat) 3390 and 2100 cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) δ 2.45 (1H, s), 3.68 (2H, d, J = 6.2 Hz), 4.67 (1H, t, J = 6.2 Hz), 7.30 (5H, m); (80 MHz, DMSO d_6) d 3.73 (2H, m), 4.7 (1H, dd, J = 7.2, 5.8 Hz), 5.40 (1H, t, J = 5.8 Hz), 7.50 (5H, m). Anal. Calcd for $C_8H_9CN_3O$: C, 58.88; H, 5.56. Found: C, 59.15; H, 5.81.

1-Acetoxy-2-azido-2-phenyl ethane 8b. Acetylation of **8a** (0.54 g, 3.3 mmol) in pyridine using the usual procedure afforded compound **8b** (0.55 g, 81% yield). I.R. (neat) 2100 and 1740 cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) δ 2.05 (3H, s), 4.12 (1H, dd, J = 12.0, 8.0 Hz), 4.30 (1H, dd, J = 12.0, 5.0 Hz), 4.72 (1H, dd, J = 8.0, 5.0 Hz), 7.30 (5H, m).

Determination of the e.e. of the Azido Compound 5m. Hydrolysis of 1-trimethylsilyloxy-2-azido-2-phenyl ethane **5m** of $[\alpha]_D^{20}$ - 60° (*c* 1, CH_2Cl_2) according to the preceeding procedure gave 2-azido-2-phenyl ethanol (**8a**) with $[\alpha]_D^{20}$ - 173° (*c* 1, CH_2Cl_2). Hydrogenation of this compound in ethanol using Pd/C as the catalyst afforded 2-phenyl-2-amino ethanol (yield 90%) of $[\alpha]_D^{20}$ - 21.5° (*c* 2.5, MeOH) corresponding to 83% e.e.[18]

1-Trimethylsilyloxy-2-azido-2-(4-methylphenyl) ethane 5n. IR (neat) 2100 cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) δ 0.0 (9H, s), 2.2 (3H, s), 3.4-3.6 (1H, m), 4.3-4.6 (1H, m), 7.1 (1H, m); ^{13}C NMR ($CDCl_3$) δ - 0.8 ($SiMe_3$), 20.9 (Me), 67.0 (C-2), 67.3 (C-1), 126.8, 129.2, 133.7 and 137.9 (C_6H_4). Anal. Calcd for $C_9H_{11}N_3O$ (hydrolyzed product): C, 61.00; H, 6.26. Found: C, 61.55; H, 6.62.

1-Trimethylsilyloxy-2-azido-2-(4-bromophenyl) ethane 5o. IR (neat) 2100 cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) δ 0.06 (9H, s), 3.5 (1H, dd, J = 11.0, 7.5 Hz), 3.5 (1H, dd, J = 11.0, 5.0 Hz), 4.43 (1H, dd, J = 7.5, 5.0 Hz), 7.1 (2H, d, J = 8 Hz), 7.4 (2H, d, J = 8 Hz); ^{13}C NMR ($CDCl_3$) δ - 0.9 ($SiMe_3$), 66.2 (C-2), 67.0 (C-1), 122.0, 128.5, 131.5 and 135.7 (C_6H_4). Anal. Calcd for $C_8H_8N_3OBr$ (hydrolyzed product): C, 39.69; H, 3.33. Found: C, 39.49; H, 3.53.

1-Trimethylsilyloxy-2-azido-2-(4-nitrophenyl) ethane 5p and 1-Azido-2-(4-nitrophenyl)-2-trimethylsilyloxy ethane 4p. IR (neat) 2100 cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) δ 0.1 (9H, s), 3.0-3.2 (1H, m), 3.5-3.6 (1H, m), 4.3-4.9 (1H, m), 7.0 (2H, d), 8.1 (2H, d); ^{13}C NMR ($CDCl_3$) for **5p** δ - 0.9 ($SiMe_3$), 65.9 (C-2), 66.8 (C-1), 123.4, 127.9, 144.1 and 148.8 (C_6H_4); for **4p** δ - 0.4 ($SiMe_3$), 57.9 (C-1), 73.7 (C-2), 123.5, 126.7, 147.4 and 148.8 (C_6H_4). Anal. Calcd for $C_8H_8N_4O_3$ (hydrolyzed product): C, 46.16; H, 3.87. Found: C, 46.26; H, 3.68.

2-Azido-2-(1-furanyl) ethanol 5q. IR (neat) 2100 cm^{-1}; ^1H NMR (80 MHz, DMSO d_6) δ 3.30 (1H, dd, J = 6.0, 6.0 Hz), 3.43 (1H, dd, J = 6.0, 6.0 Hz), 4.26 (1H, t, J = 6.0 Hz), 5.0 (1H, t, J = 6.0 Hz), 6.16 (2H, s), 7.40 (1H, s); ^{13}C NMR ($CDCl_3$) δ 60.6 (C-2), 63.4 (C-1), 108.8, 110.5, 143.2 and 149.8 (furyl). Anal. Calcd for $C_6H_7N_3O_2$: C, 47.06; H, 4.61. Found: C, 46.85; H, 4.65.

2-Azido-3-hydroxy butane 7. Ring-opening of epoxide **6** using the normal procedure was achieved after 15 days. Hydrolysis in 5 mL of methanol containing a trace of HCl followed by evaporation and flash chromatography afforded the azido alcohol **7**. $[\alpha]_D^{20}$ - 15.7° (*c* 1.1, CH_2Cl_2) using $Ti(O\text{-}i\text{-}Pr)_4$ and $[\alpha]_D^{20}$ - 16.6° (*c* 1.1, CH_2Cl_2) using $Al(O\text{-}i\text{-}Pr)_3$; ^1H NMR (300 MHz, $CDCl_3$) δ 1.12 (3H, d, J = 6.1 Hz), 1.15 (3H, d, J = 6.5 Hz), 2.45 (1H, s), 3.95 (2H, m); ^{13}C NMR ($CDCl_3$) δ 15.7 (Me), 18.6 (Me), 66.3 (*C*H-N_3), 76.2 (*C*H-OH).

Ring-opening of 3,4-Epoxy-1-butene 11. A mixture of 2-azido-1-trimethylsilyloxy-3-buten **12** and 1-azido-4-trimethylsilyloxy-2-butene **13** was obtained and separation of each compound in a pure state was unsuccessful. Elemental analysis of the two components was determined by NMR and GLC. Anal. Calcd for $C_7H_{15}N_3OSi$: C, 45.37; H, 8.16. Found: C, 45.24; H, 8.22.

12: ^1H NMR (80 MHz, $CDCl_3$) δ 0.1 (9H, s), 3.55-3.70 (2H, m), 3.95-4.00 (1H, m), 5.68-5.90 (3H, m); ^{13}C NMR ($CDCl_3$) δ 0.2 ($SiMe_3$), 65.4 (C-1), 65.5 (C-2), 118.7 (C-4), 123.7 (C-3).

13: ^{1}H NMR (80 MHz, $CDCl_3$) δ 0.1 (9H, s), 3.77-3.79 (2H, m), 4.16-4.19 (2H, m), 5.28-5.39 (2H, m); ^{13}C NMR ($CDCl_3$) δ 0.0 ($SiMe_3$), 52.2 (C-1), 65.1 (C-4), 134.3 (C-2), 134.5 (C-3).

Ring-opening of Stilbene Oxide 14. The ring-opening of stilbene oxide **14** was performed at 60 °C for 10 days according to the general procedure. After separation of the azidohydrine and hydrolysis, the azido alcohol **15** was separated by flash-chromatography . Ring-opening of **14a** gave only the isomer **15b** with 66% chemical yield, although the epoxide 14b gave a mixture of isomers **15a** and **15b** with 51% chemical yield. Elemental analysis of the two compounds was determined by NMR and GLC on the pure **15b** and on the mixture **15a** + **15b**. Anal. Calcd for $C_{14}H_{13}N_3O$: C, 70.20; H, 5.48. Found: C, 69.59; H, 5.65.

15a : IR (neat) 3040 and 2100 cm^{-1}; ^{1}H NMR (80 MHz, CCl_4) δ 4.5 (1H, d, J = 6.0 Hz), 4.65 (1H, d, J = 6.0 Hz), 7.0 (10H, m); ^{13}C NMR ($CDCl_3$) δ 71.2 (C-1), 76.9 (C-2), 127.3, 127.7, 127.8, 128.0, 137.4 and 139.2 (C_6H_5).

15b : IR (neat) 3040 and 2100 cm^{-1}; ^{1}H NMR (80 MHz, CCl_4) δ 3.9 (1H, d, J = 8.4 Hz), 4.6 (1H, d, J = 8.4 Hz), 7.0 (10H, m); ^{13}C NMR ($CDCl_3$) δ 72.8 (C-1), 77.5 (C-2), 127.3, 127.7, 127.8, 128.0, 137.4 and 139.2 (C_6H_5).

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