The Reaction of 1,2-Epoxyalkylsilanes with Azidotrimethylsilane. A Novel Stereoselective Synthesis of (Z)-1-Alkenyl Azides

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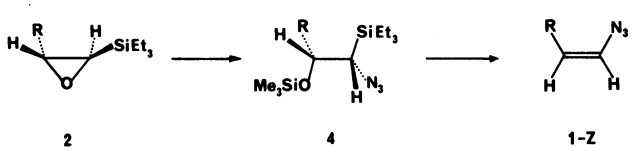
Synopsis. The reaction of *trans*-1,2-epoxyalkylsilanes with azidotrimethylsilane in the presence of boron trifluoride-diethyl ether complex afforded regio- and stereoselectively (*Z*)-1-alkenyl azides.

1-Alkenyl azides, or more commonly vinyl azides, constitute an intriguing class of compounds because of their versatile utility in organic synthesis[1] as well as theoretical interests.[2] Methods available for the synthesis of these are rather limited, among which Hassner's procedure involving 2-iodoalkyl azides, prepared by addition of iodine azide to alkenes, has been most frequently employed.[3] Since this method fails to provide 2-substituted vinyl azides (**1**) except 3,3-dimethyl-1-butenyl azide, several attempts at synthesizing **1** have been made including azidoselenenylation[4] and azidosulfenylation[5] of alkenes.

In a synthetic project, we required stereochemically defined 2-substituted vinyl azides. With regard to the well-known stereoselective alkene synthesis originally reported by Peterson,[6] we thought that the reaction of 1,2-epoxyalkylsilanes (**2**)[7] with azide ion might ultimately afford the desired vinyl azides (**1**) stereoselectively. Herein we wish to report the novel reaction.

The azide ion source we have employed was azidotrimethylsilane (**3**).[8] Initial attempts at the reaction between **2** and **3** were uniformly unsuccessful in the absence of catalysts. After thorough screening of catalysts, it was found that boron trifluoride–diethyl ether is most effective for this reaction. Thus a 1:2 mixture of **2** and **3** was allowed to react at 0 °C to room temperature for 0.5 h in the presence of excess boron trifluoride-diethyl ether. The usual ethereal workup followed by chromatography provided **1** in the yields and stereoselectivities shown in Table 1. Five *trans*-1,2-epoxyalkylsilanes (**2a—e**) were employed. It should be noted that controlled experiments in NMR tube showed essentially quantitative conversion in all cases except **2e**, which gave mainly polymeric materials.



2 4 1-Z

As shown in Table 1, the stereoselectivity of the reaction is greater than 93%. ^{1}H NMR spectral analysis has shown that the olefinic proton resonances at C-2 of (*Z*)-isomers (δ=4.81—4.82) occur at higher field than those of (*E*)-isomers (δ=5.29—5.32) and that the coupling constants between the vinylic protons for (*Z*)-isomers (J=7.5—7.8 Hz) are less than those for (*E*)-isomers (J=13.5—14 Hz), thus confirming the stereochemical assignments discussed above. Virtually exclusive formation of (*Z*)-isomers is entirely consistent with the results of related reactions of **2** previously reported by Hudrlik et al.[9] As shown in Eq. 1, selective nucleophilic displacement by azide ion at the C-1 of **2** would produce intermediate **4**, which would then undergo *trans*-elimination to afford **1-Z**.

Table 1. Synthesis of 2-Substituted Vinyl Azide (**1**) from *trans*-1,2-Epoxyalkylsilanes (**2**)[a]

	2 R	**1** Isolated Yield/%	$Z:E$[b]
a	n-C_8H_{17}	91	93:7
b	n-C_6H_{13}	95	93:7
c	$Me_2CH(CH_2)_2$	88	95:5
d	$Ph(CH_2)_2$	93	95:5
e	Ph	8	100:0

a) Reactions were performed as described in Experimental Section. b) Determined by ^{1}H NMR.

It should be mentioned that the present method cannot be applied to *cis*-1,2-epoxyalkylsilanes, which generally undergo rapid polymerization in the presence of Lewis acids. For example, the cis isomer of **2a** was much less reactive toward **3** under the above conditions to provide a 2:3 mixture of **1-Z** and **1-E** in 12% isolated yield in addition to untractable white solids.

In summary, we have shown that (*Z*)-1-alkenyl azides (**1**) can be easily and stereoselectively obtained by a one-pot reaction from *trans*-1,2-epoxyalkylsilanes (**2**) in good yields. Although the reaction is not very successful for the case of **2e** (R=Ph), it clearly compensates the existing method.[3]

Experimental

Measurements and Materials. All reactions were performed under dry inert conditions. Solvents used were purified by distillation over appropriate drying agent under argon atmosphere. 1,2-epoxyalkylsilanes (**2**) were prepared from the corresponding alkenylsilanes according to the method of Stork.[7,10] Azidotrimethylsilane (**3**) was purchased from Chisso Chem. Co. and was distilled once under argon before use. Infrared spectra were measured on a JASCO DS403G spectrometer. ^{1}H NMR spectra were obtained as $CDCl_3$ solutions with a Varian EM-390 spectrometer at 90 MHz. ^{13}C NMR spectra were recorded in $CDCl_3$ on a JEOL FX90-Q spectrometer operated at 22.5 MHz. All chemical shifts were reported in relative to internal tetramethylsilane.

General Procedure to Prepare 1-Alkenyl Azides (1). To a mixture of **2** and **3** (2 molar equivalent) was added boron trifluoride–etherate (2 molar equivalent) at 0 °C and the mixture was stirred for 0.5 h at room temperature. It was then diluted with ether. The usual aqueous workup with saturated sodium hydrogencarbonate solution and anhydrous magnesium sulfate provided an oil after evaporation of the

solvent, which was purified by column chromatography on silica gel (Kieselgel 60, eluent hexane).

The yields of 1-alkenyl azides (**1**) are shown in Table 1. Analytical and spectroscopic data of the products **1** follow.

(Z)-1-Decenyl Azide (1a). Bp 43 °C/67 Pa. IR (liquid film) 2100 (s, $-N_3$), 1645 (m, C=C), and 725 (m, *cis*-CH=CH–) cm^{-1}. ^1H NMR ($CDCl_3$) δ=0.9 (m, 3H), 1.3 (br. s, 12H), 2.0 (m, 2H), 4.82 (d of t, J=7.5 and 7.5Hz, 1H) and 6.05 (d, J=7.5Hz, 1H). ^{13}C NMR ($CDCl_3$) δ= 14.1 (q), 22.7 (t), 25.8 (t), 29.2 (t), 29.3 (t), 29.4 (t), 31.9 (t), 121.2 (d), and 125.2 (d).

Found: C, 66.43; H, 10.39; N, 23.22%. Calcd for $C_{10}H_{19}N_3$: C, 66.26; H, 10.56; N, 23.18%.

(Z)-1-Octenyl Azide (1b). Bp 34 °C/52 Pa. IR (liquid film) 2100 (s, -N3), 1642 (m, C=C) and 727 (m, *cis*-CH=CH–) cm^{-1}. ^1H NMR ($CDCl_3$) δ=0.9 (m, 3H), 1.3 (br. s, 8H), 2.0 (m, 2H), 4.82 (d of t, J=7.5 and 7.5Hz, 1H) and 6.05 (d, J=7.5Hz, 1H). ^{13}C NMR ($CDCl_3$) δ=14.1 (q), 22.7 (t), 25.8 (t), 28.9 (t), 29.2 (t), 31.7 (t), 121.1 (d) and 125.3 (d).

Found: C, 62.76; H, 10.12; N, 27.51%. Calcd for $C_8H_{15}N_3$: C, 62.71; H, 9.87; N, 27.42%.

(Z)-5-Methyl-1-hexenyl Azide (1c). IR (liquid film) 2110 (s, $-N_3$), 1645 (m, C=C) and 728 (m, *cis*-CH=CH–) cm^{-1}. ^1H NMR ($CDCl_3$) δ=0.9 (m,6H), 1.3 (m,2H), 1.6 (m,1H), 2.1 (m, 2H), 4.81 (d of t, J=7.5 and 7.5 Hz, 1H) and 6.03 (d, J=7.5 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ=22.4 (q), 23.7 (t), 27.6 (d), 38.3 (t), 121.1 (d), and 125.1 (d).

Found: C, 60.29; H, 9.58; N, 29.91%. Calcd for $C_7H_{13}N_3$: C, 60.40; H, 9.41; N, 30.19%.

(Z)-4-Phenyl-1-butenyl Azide (1d). Bp 70 °C/0.4 Torr (1 Torr=133.322 Pa). IR (liquid film) 2110 (s, $-N_3$), 1645 (m, C=C), 1605 (m, Ph), 1502 (m, Ph), 750 (m, Ph), 728 (m, *cis*-CH=CH–) and 700 (m, Ph) cm^{-1}. ^1H NMR ($CDCl_3$) δ=2.4 (m, 2H), 2.6 (m, 2H), 4.81 (d of t, J=7.5 and 7.0 Hz, 1H), 6.02 (d, 1H, J=7.5) and 7.4 (m, 5H). ^{13}C NMR($CDCl_3$) δ=27.4 (t), 35.4 (t), 119.8 (d), 125.9 (d), 126.0 (d), 128.5 (d), and 141.6 (s).

Found: C, 69.43; H, 6.14; N, 24.35%. Calcd for $C_{10}H_{11}N_3$: C, 69.34; H, 6.40; N, 24.26%.

(Z)-2-Phenylethenyl Azide (1e). IR (liquid film) 2120 (s, N_3), 1644 (s, C=C), 1602 (m, Ph), 1500 (m, Ph), 750 (m, Ph), 735 (m, *cis*-CH=CH–) and 695 (m, Ph). ^1H NMR ($CDCl_3$) δ=5.22 (d, J=6.7 Hz, 6.22 (d, J=6.7 Hz, 1H), 7.21 (m, 3H), and 7.60 (m, 2H).

Found: C, 66.31; H, 4.98; N, 28.64%. Calcd for $C_8H_7N_3$: C, 66.19; H, 4.86; N, 28.95%.

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