non-6-en-3-one (13). To a stirred, yellow solution of 534 mg (1.00 mmol) of $(\eta^3$ -cyclohexenyl)palladium complex 6 and 2.10 g (8.01 mmol) of triphenylphosphine in 40 mL of anhydrous THF (freshly distilled from sodium-benzophenone ketyl radical) under a N2 atmosphere was added a solution containing 4.0 mmol of sodium dimethyl malonate in 30 mL of anhydrous THF.¹⁸ After 40 h at 21 °C, the resulting yellow-green slurry was diluted with 200 mL of water and extracted twice with 200-mL portions of Et_2O . The combined organic phase was washed with 200 mL of water and dried (MgSO₄), and the solvent was removed at reduced pressure (water aspirator) on a rotary evaporator to afford a red-black oil, which was flash chromatographed $(2.5 \times 15$ -cm column packed and eluted with EtOAc-hexane, 3:7). Removal of solvent at reduced pressure (water aspirator) afforded 236 mg (1.05 mmol, 53%) of 13 as a pale yellow oil: IR (film) 2950, 2910, 2860, 1730, 1440, 1385, 1235, 1220, 1065, 1020, 960 cm⁻¹; ¹NMR (400 MHz) δ 4.92 (1 H, H-1, 10-line m, J = ca. 1.5 Hz), 3.78 (3 H, s), 3.51 (1 H, H-4_{endo}, t, J = ca. 1.6 Hz), 2.64–2.60 (1 H, H-5, m), 2.36–2.34 (1 H, H-8_{endo}, m with fine splitting, J = 0.9 Hz), 2.28 [1 H, H-9_{sym} (lactone), ddd with further fine splitting, J = 13.6, 4.7, 2.3 Hz], 1.81 [1 H, H-9_{anti} (lactone), ddt, J = 13.6, 4.1, 1.4 Hz], 1.74–1.72 (1 H, H-8_{exo}, m with fine splitting, J = 0.9 Hz), 1.62 (3 H, br s with fine splitting, J = 0.9 Hz), 1.54 (3 H, s); homonuclear decoupling, irradiation at δ 4.92 affected the signal at δ 2.36–2.34 and collapsed the signals at δ 2.28 to a dd and at δ 1.81 to a ddd, irradiation at δ 3.51 affected the signal at δ 2.64–2.60 and collapsed the signal at δ 1.81 to a ddd, irradiation at δ 2.62 collapsed the signals at δ 3.51 to a d and at δ 2.28 to a dd and at δ 1.81 to a dt, irradiation at δ 2.35 simplified the signal at δ 4.92 and sharpened

the signal at δ 1.74–1.72, irradiation at δ 2.28 simplified the signal at δ 4.92 and sharpened the signal at δ 2.64–2.60 and collapsed the signal at δ 1.81 to a dt, irradiation at δ 1.81 affected the signals at δ 4.92 and 2.64–2.60 and collapsed the signals at δ 4.92 and 2.64–2.60 and collapsed the signals at δ 3.51 to a d and at δ 2.28 to a dd, irradiation at δ 1.73 sharpened the signal at δ 2.36–2.34 to a d with further fine splitting and affected the signal at δ 2.36–2.34 to a d with further fine splitting and affected the signal at δ 1.62, irradiation at δ 1.62 affected the signal at δ 2.36–2.34 and collapsed the signal at δ 1.74–1.72 to a t; 13 C NMR (100 MHz) 168.90 (s), 165.95 (s), 126.53 (s), 124.15 (s), 75.24 (d), 52.50 (q), 50.75 (d), 38.26 (t), 35.73 (d), 24.48 (t), 18.02 (q), 17.13 (q); mass spectrum, m/z (relative intensity) 224 (M⁺, 9), 180 (6), 165 (6), 149 (7), 121 (14), 119 (16), 118 (15), 108 (9), 107 (99), 106 (100), 105 (21), 95 (22), 93 (17), 91 (54), 79 (20), 77 (18), 67 (15), 55 (15), 53 (13), 43 (11), 41 (29), 39 (21). Anal. Calcd for C₁₂H₁₆O₄: C, 64.28; H, 7.19. Found: C, 64.20; H, 7.10.

Acknowledgment. We are grateful to the Swedish Natural Science Research Council, the Swedish Board for Technical Development, Hoffmann-La Roche Inc., the Rutgers University Graduate School, and the Rutgers University President's Coordinating Council on International Programs for supporting this research. We also thank the Knut and Alice Wallenberg Foundation and the Swedish Council for Planning and Coordination of Research (FRN) for grants for the 400-MHz NMR instrument, Johnson Matthey, Inc. for palladium dichloride (Loan Program), and Tobias Rein for the 400-MHz ¹H NMR spectra.

Solid-Supported Sodium Azide Reagents: Their Preparation and Reactions with Epoxides

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Received April 4, 1988

Sodium azide is supported on three types of porous solid acids (zeolite, alumina, and silica gel) and applied to several reactions with epoxides. A systematic investigation reveals that the reactivities of the supported reagents are greatly influenced by loading amounts of NaN_3 , amounts of adsorbed water in the reagents, acidic properties of the solid acids, and reaction solvents. For demonstrating the utility of supported NaN₃ reagents in selective organic syntheses, nucleophilic ring-opening reactions of 2,3-epoxy alcohols with the supported reagents are examined. Among the supported reagents, only the Ca^{2+} -exchanged zeolite-supported reagent induces a C-3 ring opening in a highly regioselective manner (>90%). It is deduced that the role of calcium ions in the zeolite is to increase the acid strength of the zeolite facilitating the ring cleavage of epoxides and to fix the conformation of epoxy alcohols through forming chelate complexes with calcium ions.

The elaborate design of supported reagents for liquidphase organic reactions is now an intriguing area of current research in organic synthesis since the impregnation of inorganic reagents, which are insoluble in organic solvents, on porous solid supports is as efficient to activate the reagents as the use of phase-transfer catalysts such as onium salts and crown compounds.¹ Effectiveness of these supported reagents is ascribed to a combination of several factors. (1) An increase in the effective surface area of the reagent owing to high dispersion on the support. (2) An activation of the reagent by the interaction between the support surface and the reagent. (3) A decrease in activation entropy of reactions due to preadsorption of substrates in close proximity. (4) Synergistic effect of acid and base sites of the support on substrates.

The present paper describes the characteristics of a supported sodium azide reagent in regioselective ringopening reactions of unsymmetrical epoxides.²

Azides are important precursors of nitrenes or amino compounds and also belong to a large family of 1,3-dipoles, which undergo cycloaddition to alkenes.³ Nucleophilic

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Figure 1. The reaction of 1 with NaN₃/Al₂O₃. NaN₃ (1 mmol) was supported on Al_2O_3 (0.62 or 1.3 g) and treated with 1 (1 mmol) in benzene at 80 °C for 5 h. (•), 4.8 wt % loading of NaN_3 ; (•), 9.5 wt % loading of NaN₃. Figures in parentheses and brackets indicate ratios of 2a to 2b and yields of 1,2-diol 2c, respectively.

substitution is a particularly useful method for preparation of alkyl azides.⁴ Alkali azides like NaN₃ and LiN₃ are good nucleophiles in dipolar aprotic solvents, while trimethylsilyl azide (Me_3SiN_3) has been employed with advantages of high solubility in nonpolar solvent and good stability.⁵

Here we impregnate various solid acids such as zeolite, alumina, and silica gel with sodium azide and investigate nucleophilic ring-opening reactions of epoxides with the supported NaN₃ reagents, discussing what factors affect activities of the supported reagents.

In order to demonstrate the utility of the supported NaN₃ reagent, the reagent is utilized in regioselective ring opening of 2,3-epoxy alcohols. Since a discovery of an efficient method for the synthesis of enantiomerically pure 2,3-epoxy alcohols,⁶ regioselective ring-opening reactions of epoxy alcohols with various nucleophiles have been developed as a promising route for synthesizing multifunctionalized chiral molecules.⁷ For instance, the combined use of a variety of nucleophiles and Ti(O-i-Pr)₄ has been successfully applied to the reactions with 2,3-epoxy alcohols.8

By applying solid-supported NaN_3 to reactions with 2,3-epoxy alcohols, we disclose the important participation

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Figure 2. The reaction of 1 with NaN₃/CaY. NaN₃ (1 mmol) was supported on zeolite CaY (0.26 to 0.51 g) and treated with 1 (1 mmol) in benzene at 80 °C for 2 h. (\bullet), 11 wt % loading of NaN_3 ; (**m**), 20 wt % loading of NaN_3 . Figures in parentheses indicate ratios of 2a to 2b.



Figure 3. The reaction of 1 with NaN_3/SiO_2 . NaN_3 (1 mmol) was supported on SiO_2 (0.43 or 0.89 g) and treated with 1 (1 mmol) in benzene at 80 °C for 10 h. (\bullet), 6.8 wt % loading of NaN₃; (\blacksquare), 13 wt % loading of NaN₃. Figures in parentheses and brackets indicate ratios of 2a to 2b and yields of 1,2-diol 2c, respectively.

of cations in solid supports in regioselective ring openings.

Results and Discussion

I. Reactions of Supported NaN₃ Reagents with 1,2-Epoxyoctane. Effects of the Loading Amount of NaN3. Various solid supports (alumina, calcium ion-exchanged Y-type zeolite (CaY), and silica gel) were impregnated with aqueous solutions of sodium azide followed by evaporation of the bulk of water under different drying conditions. The reactions of 1,2-epoxyoctane (1) with the resulting supported reagents were conducted in a benzene suspension at 80 °C to give azido alcohols 2a and 2b (eq 1). With any support, a supported reagent with a low loading of NaN₃ showed greater reactivity than a high

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loading reagent (Figures 1-3).

Azide ions (N_3^-) have strong and diagnostically useful infrared bands in the region of 2100 cm⁻¹ arising from the asymmetric stretching mode.⁹ Figures 4-6 illustrate the variations in IR absorption bands of azide ions on each supported reagent at various loadings and residual water levels. Parent solid NaN₃ has characteristic absorption at 2130 cm⁻¹ (Figure 4a). A 9.5 wt % loading of NaN₃ on alumina (ALO-4) shows a new absorption peak of 2060 cm⁻¹ in addition to the parent peak of 2130 cm⁻¹ in Nujol mull (Figure 4c). After the alumina-supported reagent with a 9.5 wt % loading of NaN_3 was treated with 1,2epoxyoctane, the supported reagent was immediately analyzed with IR spectroscopy.¹⁰ It was found that the peak of 2060 cm⁻¹ sharply decreased compared with the parent peak of 2130 cm⁻¹ (Figure 4d). This result indicates that the azide ions showing a lower frequency of 2060 cm^{-1} are much more reactive for the nucleophilic ring opening of the epoxide than the azide ions characterized by 2130 cm^{-1} . We can speculate that a finely dispersed form of NaN₃ gives absorption at 2060 cm⁻¹, while coagulated NaN₃ crystals on the support has absorption at 2130 cm⁻¹.

By the addition of a small amount of water to solid NaN₃, the absorption peak of the azide ions was found to be shifted from 2130 to 2060 cm⁻¹. Accordingly, it is reasonable to explain that for the alumina-supported reagent, both hydroxyl groups and residual water on the alumina surface interact with dispersed sodium azides to improve their nucleophilicity.

An alumina-supported sample with a lower loading (4.8 wt %) of NaN₃ shows only a lower frequency peak at 2060 cm⁻¹ (Figure 4b), and it gives higher reactivity than a highly loaded sample (9.5 wt %). Namely, under the same reaction conditions, the low-loading reagent gave 74% yield of the products, while the high-loading sample showed 47% yield.¹⁰

When NaN₃ is supported on zeolite CaY (20 wt %), two IR absorption peaks appear at 2060 and 2110 cm⁻¹ (Figure 5b). The 2060-cm⁻¹ peak corresponds to reactive NaN₃, which diminished after the reaction with 1 (Figure 5c).¹¹ A low-loading (11 wt %) sample shows only a peak at 2060 cm⁻¹ (Figure 5a) and gives higher reactivity (71% yield) compared with a 20 wt % loading sample (40% yield).¹¹

Two types of silica-supported reagents were prepared with 6.8 and 13 wt % loadings of NaN₃. Both reagents give a single adsorption peak at 2060 cm⁻¹, differing from the alumina- or zeolite-supported reagent mentioned above. However, the reactivity of a low-loading sample is superior to that of a highly loaded one (58 versus 35% yield).¹²

Effects of Residual Water in a Supported Reagent. The amount of residual water in the supported NaN_3 reagent is adjustable by a choice of evaporating conditions (evaporation temperature, reduced pressure, evaporation time), and greatly influences the reactivity of the reagent.



Figure 4. IR spectra of NaN_3/Al_2O_3 . (a) Nonsupported NaN_3 . (b) NaN_3 (4.8 wt %) supported on Al_2O_3 (residual water content: 21 wt %). (c) NaN_3 (9.5 wt %) supported on Al_2O_3 (residual water content: 7.0 wt %). (d) After treatment of (c) with 1.

It is noted that an optimal quantity of water is required for each reagent to possess highest activity as shown in Figures 1–3.

In previous studies on supported reagents the role of a small amount of water in the reagent, being associated with reactivities of those reagents, has been discussed.¹³ On the basis of those discussions, it is probable that the water molecules as well as hydroxyl groups on solid supports coordinate to the dispersed NaN₃ to loosen the ion-pairing of Na⁺-N₃⁻, leading to some enhancement in nucleophilicity of the azide anion.

In contrast, the presence of an excess amount of water lowers the acid strength of solid supports through coordination of water to acid sites on the supports and retards the ring opening of epoxides (vide infra).

A general tendency is also recognized that the product ratio (2a/2b) gradually increases with the content of water, owing to a change in acidic properties of supports. It is interesting to point out that with alumina- and silicasupported reagents octane-1,2-diol (2c), a hydrolyzed product, was a serious byproduct when the content of residual water was low. An excess amount of water also suppressed hydrolysis of the epoxide, owing to the reduction in acid strength of the supports. In striking con-

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⁽¹⁰⁾ Alumina (ALO-4) supported NaN_3 (1 mmol) was treated with 1 (1 mmol) in benzene under reflux for 5 h.

⁽¹¹⁾ CaY-supported NaN₃ (1 mmol) was treated with 1 (1 mmol) in benzene under reflux for 2 h.

⁽¹²⁾ Silica-supported NaN_3 (1 mmol) was treated with 1 (1 mmol) in benzene under reflux for 10 h.

⁽¹³⁾ Ando, T.; Kawate, T.; Yamawaki, J.; Hanafusa, T. Chem. Lett. 1982, 935 and references cited therein.



Figure 5. IR spectra of NaN₃/CaY. (a) NaN₃ (11 wt %) sup-

ported on CaY (residual water content: 20 wt %). (b) NaN₃ (20 wt %) supported on CaY (residual water content: 17 wt %). (c) After treatment of (b) with 1.



Figure 6. IR spectra of NaN_3/SiO_2 . (a) NaN_3 (6.8 wt %) supported on SiO_2 (residual water content: 29 wt %). (b) NaN_3 (13 wt %) supported on SiO_2 (residual water content: 38 wt %).

trast to the alumina- and silica-supported reagents, the zeolite-supported reagent gave no hydrolyzed product with any content of water.

Effects of Acid Strength of a Solid Acid Support. The solid acid supports surveyed in the present study are supposed to work not only as supports that finely disperse NaN₃ on their surfaces to enhance the reactivity of NaN₃ but also as acid catalysts to promote the cleavage of C–O bonds of epoxides.

Table I summarizes the relationship between the maximum acid strength¹⁴ of a zeolite support and the reactivity

Table I. Effects of Acid Strength of Solid Acida

solid acid (NaN ₃ loading, wt %)	maximum acid strength ^b	reaction time, h	yield, %	2a/2b
CaY (20) ^c	$H_0 \leq -8.2$	2	90	7.0
NaY (20)°	$+0.8 < H_0 \le +1.5$	5.	49	12
KY (20) ^c	$+2.0 < H_{0} \le +3.3$	5	7.5	14

^aReaction of 1 (1 mmol) with NaN₃ (3 mmol) supported on solid acid was carried out in benzene at 80 °C. ^bAcid strength of nonsupported solid acids, which were dried at 450 °C in air was measured by use of Hammett indicators in benzene. ^cAll NaN₃/solid acid reagents contained 21 wt % of residual water.

Table II. Effects of Solvent^a

yield, %	2a/2b
90	7.0
93	7.0
97	7.2
90	6.6
43	9.6
23 (89) ^b	$13 (12)^{b}$
8.0	13
7.6	10
	yield, % 90 93 97 90 43 23 (89) ^b 8.0 7.6

^aRing-opening reaction was carried out at 80 °C for 2 h by use of a NaN₃ (3 mmol)/CaY reagent (20 wt % loading) with 21 wt % of residual water. ^bReaction was carried out for 20 h.

of the NaN₃ on the zeolite for the ring opening of epoxide $1.^{15}$ Both the combined yield of **2a** and **2b** and the ratio of **2a** and **2b** are closely interrelated to the acid properties of zeolite. As the acid strength of zeolite increases, an increase in the yield and a decrease in the ratio are observed.¹⁶ These trends substantiate the idea that the solid support plays an important role in activating an epoxide as well as supporting NaN₃.

It is noteworthy that NaN₃/CaY completed the ring opening within 2 h because zeolite CaY is most acidic ($H_0 \leq -8.2$ in benzene) among the three zeolites listed in Table I.¹⁷

Effects of Reaction Solvent. Even in a heterogeneous reaction system where a supported reagent, a reactant, and a solvent were suspended, the solvent greatly influences the reaction rate because the solvent is also adsorbed on the support affecting changes in the acid properties of the support.

Table II summarizes the results of the reactions of a NaN_3/CaY reagent with epoxide 1 in various solvents. The more polar and the more basic the solvent is, the lower the yield and the higher the 2a/2b ratio. Polar solvents weaken the acid strength of the support, resulting in poor acid catalysis.

As a summary, in order to prepare a reactive supported NaN₃ reagent we should pay much attention to the following items: (1) a loading amount of NaN₃, (2) the coexistence of a certain amount of water, (3) a selection of a solid support from the viewpoint of acid properties, and (4) a choice of a reaction solvent.

When a nucleophilic ring opening is desired at an end position of a terminal epoxide like 1, it is recommended

⁽¹⁴⁾ Benesi, H. A. J. Am. Chem. Soc. 1956, 78, 5490.

⁽¹⁵⁾ The acidic properties of the zeolite depend on the sort of cation in the zeolite, and can be altered by cation exchange without any change of crystalline structure. Thus zeolites are suitable materials for examining the correlation between acidic properties of supports and their catalytic activities.

⁽¹⁶⁾ Internal ring opening of terminal epoxides is generally facilitated under acidic conditions. Parker, R. E.; Isaacs, N. S. Chem. Rev. 1959, 737.

⁽¹⁷⁾ Among zeolites, alumina, and silica, zeolite CaY is most acidic and shows the highest activities for ring opening of epoxides (Figures 1-3).

Table III. Reactions of 3-Cyclohexyl-1,2-epoxypropan-1-ol(3) with Azide

run	solid acid	time, h	yield, %	4a:4b
1	CaY ^{a,b}	1.5	85	94:6
2	$MgY^{a,b}$	6	70	86:14
3	BaY ^{a,b}	9	45	83:17
4	LaY ^{a,b}	6	69	79:21
5	HY ^{a,b}	5	45	76:24
6	$NaY^{a,b}$	7	65	77:23
7	Ca-Mont ^{a,b}	31	26	86:14
8	Al-Mont ^{a,b}	12	18	80:20
9	$SiO_2^{a,c}$	10	35	78:22
10	$Al_2O_3^{a,d}$	5	65	66:34
11	NaN ₃ -NH ₄ Cl ^e	21	88	76:24
12	Me ₃ SiN ₃ -Ti(O-i-Pr) ₄ ^f	7	91	89:11

^aReaction of 3 (1 mmol) with NaN₃ (3 mmol) supported on solid acid was carried out in benzene at 80 °C. ^b The supported reagent contained a 20 wt % loading of NaN₃ and a 20 wt % of residual water. ^cThe supported reagent contained a 7.0 wt % loading of NaN₃ and a 18 wt % of residual water. ^dThe supported reagent contained a 9.5 wt % loading of NaN₃ and a 9.2 wt % of residual water. ^eReaction of 3 (1 mmol) with NaN₃ (10 mmol) and NH₄Cl (2.2 mmol) was carried out in MeOH/H₂O (8:1) at 80 °C. ^fReaction of 3 (1 mmol) with Me₃SiN₃ (3 mmol) was cararied out in benzene at 80 °C.

to employ any of the following reaction systems: NaN_3/CaY in 2-propanol, NaN_3/NaY in benzene, or NaN_3/SiO_2 in benzene.

II. Application of Supported NaN₃ Reagents to Regioselective Ring Openings of 2,3-Epoxy Alcohols. To further explore the synthetic potential of the supported NaN₃ reagents, we have applied the reagents to regioselective ring opening of 2,3-epoxy 1-ols.¹⁸ As a model compound, racemic 3-cyclohexyl-*trans*-2,3-epoxypropan-1-ol (3) was chosen and treated with the NaN₃ supported on various solid supports (Table III). We prepared each supported reagent to show high reactivity by adjusting the amounts of loaded NaN₃ and residual water (detailed data shown in Table III).

In order to compare homogeneous reagent systems with the supported reagent system, NaN₃ and NH₄Cl^{8a} were treated with 3 in aqueous methanol at 80 °C to afford a mixture (76:24) of 3-azido 1,2-diol **4a** and 2-azido 1,3-diol **4b** in a total yield of 88% (run 11) (eq 2). Although the

C-2 position of 3 is less sterically hindered than the C-3 site, the ring opening at C-2 is retarded by the inductive electron-withdrawing effect of a C-1 hydroxyl.^{7b}

When Me₃SiN₃ and Ti(O-i-Pr)₄ were treated with 3,^{8a} a good regioselectivity (89:11) and a good total yield of 91% were obtained (run 12). The Ti(O-i-Pr)₄-mediated procedure is characterized as follows. (1) Me₃SiN₃ is very soluble in organic solvents and therefore effective as an azide source. (2) Ti(O-i-Pr)₄ facilitates the ring opening of epoxides and also induces a regioselective attack of the azide at C-3.¹⁹

Alumina-supported NaN₃ has modest reactivity for the ring opening of 3 but somewhat lower regioselectivity toward the C-3 opening than NH_4N_3 (run 10). A silica-supported reagent is not so effective for the reaction,



showing a similar selectivity to that with NH_4N_3 (run 9).

In striking contrast, NaN₃ supported on zeolite demonstrates peculiar reactivities (runs 1–6). Various cationic forms of the same zeolite exhibit very different reactivities and selectivities, suggesting that the interaction between the substrate and cations in zeolite is decisive for promotion of the ring opening. Among the cation-exchanged zeolites surveyed, calcium ion-exchanged Y-type zeolite (CaY) shows the most remarkable catalysis. Although NaN₃ on CaY (NaN₃/CaY) was suspended in a benzene solution, the ring opening was complete within 1.5 h at 80 °C, and a mixture of azido diols (4a and 4b) was isolated in 85% yield. After peracetylation of the diols with Ac₂O and pyridine, the products were analyzed by GLC to be a mixture (94:6) of 4a and 4b, which is comparable to the result with the Sharpless procedure.

In practice, 0.195 g (3 mmol) of NaN₃ was supported on 0.78 g of zeolite CaY (specific surface area: $680 \text{ m}^2/\text{g}$) and treated with 1 mmol of 3. Zeolite Y consists of small, uniform cavities (1.3 nm in diameter), and the exterior surface area of zeolite Y is only 0.5–1.3% of the total surface area.²⁰ Thereby most of the supported NaN₃ seems to be finely dispersed inside the small cavities and interacts with hydroxyls on the zeolite surfaces to be activated (vide supra).

Since the two regioisomeric products (4a and 4b) have almost the same size, it is difficult to discriminate the two isomers on the basis of three-dimensional molecular sizes. Therefore, the selectivity is closely related with the nature of cations in the zeolite rather than the geometric constraints imposed by the pore geometry and cation locations in the zeolite.

As another example of regioselective ring opening, instead of using the CaY-supported NaN₃ reagent, nonsupported CaY (predried at 400 °C, 3 h, in air), the epoxy alcohol, and Me₃SiN₃ were vigorously mixed in benzene at 80 °C for 2 h, giving a 91:9 mixture of 4a and 4b in 20% yield and a hydrolyzed product, 1-cyclohexylpropane-1,2,3-triol (4c, 20% yield), as well.

In order to confirm whether calcium ions induce specific selectivity only in zeolite, we employed clay montmorillonite²¹ as another type of silicate with cation-exchange ability. NaN₃ was supported on calcium ion and aluminium ion exchanged montmorillonites (abbreviated as Ca-Mont and Al-Mont, respectively)²² and applied to the reaction with 3 (runs 7 and 8). The Ca²⁺-exchanged form gave higher selectivity compared with the Al³⁺-exchanged form, although the reactivity was far inferior to that of a CaY-supported reagent. These results reveal that calcium

 ⁽¹⁸⁾ Our preliminary communication: Onaka, M.; Sugita, K.; Izumi,
 Y. Chem. Lett. 1986, 1327.

⁽¹⁹⁾ The use of Et₂AlF in place of Ti(O-i-Pr)₄ enabled much higher regioselection. Maruoka, K.; Sano, H.; Yamamoto, H. Chem. Lett. 1985, 599.

⁽²⁰⁾ Venuto, P. B.; Landis, P. S. In Advances in Catalysis; Eley, D. D., Pines, H., Weisz, P. B., Eds.; Academic Press: New York, 1968; Vol. 18, p 259.

⁽²¹⁾ Thomas, A. J. In Intercalation Chemistry; Whittingham, M. S., Jacobson, A. J., Eds.; Academic Press: New York, 1982; p 55.

⁽²²⁾ Cations in montmorillonite are easily exchanged with various cations in a similar way to that of zeolite. See: Kawai, M.; Onaka, M.; Izumi, Y. Bull. Chem. Soc. Jpn. 1988, 61, 1237.

Table IV. Regioselective Ring Opening of 3-Monoalkyl-trans-2,3-epoxy Alcohols (7, 9, 11) with Azide Reagents

	$R = {}^{n}C_{7}H_{15}$		$\mathbf{R} = {}^{\mathbf{i}}\mathbf{C}_{3}\mathbf{H}_{7}$		$R = PhCH_2OCH_2$				
NaN_3 -reagent	time, h	yield, %	(8a:8b)	time, h	yield, %	(10a:10b)	time, h	yield, %	(12a:12b)
NaN ₃ /CaY ^{a,b}	1.5	82	(97:3)	2.0 16.0°	86 81	(88:12)	2.5	88	42:58
$NaN_3/Al_2O_3^{a,d}$	5.0	64	(78:22)	10.0	79	(47:53)			
$NaN_3/SiO_2^{a,e}$	7.0	56	(86:14)	10.0	62	(68:32)		~ -	15 50
NaN ₃ -NH4Cl' Me ₃ SiN ₃ -Ti(O-i-Pr)4 ^g	7.0 4.0	84 58	(87:13) (94:6)	21.0 7.0	58 86	(64:36) (87:13)	6.0 2.0	95 80	47:53 71:29

^aReaction of 7, 9, or 11 (1 mmol) with NaN₃ (3 mmol) supported on solid acid was carried out in benzene at 80 °C. ^bThe supported reagent contained a 20 wt % loading of NaN3 and a 20 wt % of residual water. Reaction was carried out at 50 °C. The supported reagent contained a 9.5 wt % loading of NaN3 and a 9.2 wt % of residual water. "The supported reagent contained a 7.0 wt % loading of NaN3 and a 20 wt % of residual water. ⁷Reaction of 7, 9, or 11 (1 mmol) with NaN₃ (10 mmol) and NH₄Cl (2.2 mmol) was carried out in MeOH/H₂O (8:1) at 80 °C. "Reaction of 7, 9, or 11 (1 mmol) with Me₃SiN₃ (3 mmol) was cararied out in benzene at 80 °C in the presence of Ti(O-i-Pr)₄ (1.5 mmol).

Table V. Chemical Properties of Solid Acids

	PV,ª mL g ⁻¹	${}^{\text{SA},b}_{\text{m}^2\text{ g}^{-1}}$	Fe ₂ O ₃ , %	SiO ₂ , %	Na ₂ O, %
ALO-4	0.66	177	0.01	0.01	0.01
SiO ₂	0.744	585			
NaŸ	0.35	670	(SiO ₂ /.	$Al_2O_3 = 4$.8)

^a Pore volume. ^b Specific surface area.

ions are indispensable for selective ring openings.

 $Ti(O-i-Pr)_4$ -mediated highly regioselective ring opening of epoxy alcohols is rationalized by the coordination of the epoxy alcohols to the titanium alkoxide in the rigid, bidentate chelation structure depicted in Chart Ia.⁸

It is well known that sugars and polyols form weak to tight complexes with calcium ions in an aqueous solution, and different mobilities of those sugars with paper electrophoresis result from the different complexation abilities.²³ Calcium ion exchanged zeolites have been also employed as sorbents in carbohydrate separations.²⁴ On the ground of a peculiar affinity between calcium ions and polyoxygenated compounds, we suppose that in our system the epoxy alcohol probably forms a coordinated structure around a calcium ion in the zeolite in a similar manner to that of $Ti(O-i-Pr)_4$ as shown in Chart Ib. If the C–O bond cleavage of the epoxide ring takes place at C-3, a fivemembered chelation structure remains. On the other hand, the C-O bond at C-2 is cleaved to give a new six-membered chelation compound. The stability difference between the two chelation forms may be a predominant factor to determine the regioselection in ring opening.²⁵

In order to examine whether a hydroxyl group is requisite to afford high regioselectivity, the methyl ether (5)of 3 was subjected to ring opening with NaN_3/CaY . The ring opening was slowed down but still maintained high C-3 selectivity (6a:6b = 91:9) (eq 3). Thus the presence

$$\bigcap_{\substack{\text{benzene, 80 *C}\\6 \text{ hr}}} OMe \xrightarrow[6 \text{ hr}]{} OMe \xrightarrow[7]{I} OMe \xrightarrow[7]{I} OMe \xrightarrow[7]{I} OMe \xrightarrow[7]{I} OMe \xrightarrow[7]{I} OHe \xrightarrow[7]{I} OHe \xrightarrow[7]{I} OHe \xrightarrow[7]{I} OHe \xrightarrow[7]{I} OHe \xrightarrow[6]{I} OHe \xrightarrow[6]{I}$$

of a hydroxyl group is not necessarily required to accomplish high regioselection but is indispensable in accelerating the ring opening with NaN₃.

Another role of calcium ions is to increase the acid strength of zeolite. When calcium ions are introduced into

zeolite Y, the zeolite becomes a strong acid and an efficient acid catalyst for promoting the ring opening with a nucleophile.

Table IV summarizes the results of regioselective ring openings of 3-monoalkyl-trans-2,3-epoxypropan-1-ols with NaN₃/CaY, NaN₃/Al₂O₃, NaN₃/SiO₂, NH₄N₃, and Me₃SiN₃-Ti(O-i-Pr)₄. Except for 11, NaN₃/CaY presents the highest C-3 regioselectivity (>90%) among the reagents (eq 4); 11 is presumed to form a chelate ring between an

R 0H	R N ₃ OH OH N	R OH	(4)
$R = {}^{n}C_{7}H_{15}(7)$	8a	8b	
$R = {}^{1}C_{3}H_{7}(9)$	10a	10 Б	
$R = PhCH_2OCH_2(11)$	12a	12 b	

epoxy oxygen and a hydroxyl or benzyloxy group. Thus the NaN_3/CaY system is difficult to discriminate the C-2 and C-3 positions of 11 resulting in nonselective ring opening.

Use of supported reagents in organic syntheses has several merits. (1) Stable and cheap inorganic reagents can be effectively employed in liquid-phase organic reactions (for example, the use of NaN_3 in place of Me_3SiN_3). (2) Workup procedures are simple. (3) Specific properties of the solid surfaces (high surface area, variable acid properties, participation of surface hydroxyls, and effects of cations in solids) can be utilized to promote organic reactions under mild conditions.

Experimental Section

Analysis. Infrared (IR) spectra were measured in CHCl₃ or CCl₄ with a JASCO IRA-2 spectrometer. IR spectra of a NaN₃-supported reagent were recorded in Nujol mull. Thermogravimetric analysis was conducted on a Rigakudenki TG-DTA (Cat. M8075). ¹H NMR spectra were measured in CDCl₃ with Hitachi R-600 (60 MHz) and Varian GEMINI 200 (200 MHz) spectrometers. Tetramethylsilane (TMS) was used as an internal standard. The chemical shifts are given in δ (ppm) downfield from TMS, and the coupling constants are in hertz. Gas chromatograms were obtained on a Shimadzu GC-8A instrument with a flame ionization detector and a capillary column (OV-1 bonded, 25 m, OV-17 bonded, 50 m, or PEG-HT bonded, 25 m).

Materials. As solid supports, Y-type zeolite, γ -alumina (JRC-ALO-4: "Reference catalyst" supplied from Catalysis Society of Japan), and silica gel (Fuji-Davison B-type) were selected. Various cation-exchanged Y-type zeolites were prepared from commercially available sodium ion exchanged Y-type zeolite (NaY, Shokubai Kasei Co.) by ion-exchange treatment as described previously.²⁶ The cation content in zeolites CaY and KY was determined by atomic absorption analysis: CaY (Ca²⁺ 67%, Na⁺

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(24) (a) Sherman, J. D.; Cho C. C. In New developments in zeolite science and technology; Murakami, Y., Iijima, A., Ward, J. W., Eds.; Kodansha-Elsevier: New York, 1986; p 1025. (b) Wortel, Th. M.; van Derhouer H. Beet, Terre M., Berg, 1972, 62, 1972. Bekkum, H. Recl. Trav. Chim. Pays-Bas 1978, 97, 156. (25) Sugars predominantly form a five-membered chelation with a

calcium ion. See ref 23.

⁽²⁶⁾ Onaka, M.; Kawai, M.; Izumi, Y. Bull. Chem. Soc. Jpn. 1986, 57, 1761.

33%), KY (K⁺ 99%, Na⁺ 1%). Other zeolites were not determined. Chemical properties of the supports are listed in Table V. Calcium ion and aluminium ion exchanged montmorillonites were prepared from sodium ion exchanged montmorillonite (Kunipia-F, Kunimine Co.) by ion exchange.²²

Organic solvents were dried over molecular sieves 3A. $(2S^*,3S^*)$ -2,3-Epoxy 1-ols were preapred from trans allylic alcohols with *m*-chloroperbenzoic acid.

Preparation of Supported NaN₃ **Reagents.** NaN₃ (1 or 3 mmol) was dissolved in deionized water (5 mL) in a 30-mL flask. A solid support (a variable amount) was then added and stirred for a while. The water was removed on a rotary evaporator under different conditions (temperature, 40–80 °C; reduced pressure, 1–20 Torr; evaporation time, 0.5–2 h).

The loading amount (X wt %) of NaN₃ on a support and the amount (Y wt %) of residual water in the supported reagent are defined as follows:

$$X = [a/\{a + (1 - \alpha/100)b\}] \times 100$$

 $Y = [\{W - W_{\rm o} - a - (1 - \alpha/100)b\}/(W - W_{\rm o})] \times 100$

where a (g) is the weight of NaN₃ supported, b (g) is the weight of a solid support used, α (%) is wt % of physisorbed water in a solid support (α was determined by thermal gravimetric analysis of a support in the temperature range of 30–220 °C.²⁷), W_{o} (g) is a tare of a flask used for the preparation of a supported reagent, and W (g) is the weight of a flask containing a supported reagent after evaporating the bulk of impregnation solvent (water).

Acid Strength Measurements of Solid Acid Supports.¹⁴ The following Hammett indicators (pK_a value) were employed. 4-(Dimethylamino)azobenzene (butter yellow) (+3.3), 4'-amino-2,3'-dimethylazobenzene (+2.0), 4-(phenylazo)-N-phenylaniline (+1.5), crystal violet (+0.8), and anthraquinone (-8.2).

Solid support was dried at 450 °C for 3 h in air. In a test tube was placed 0.1 g of the solid, and 2 mL of dry benzene was added. Then a few drops of a 0.1% solution of the indicator in benzene were added. After 1 day color changes were determined visually.

Reactions of Supported NaN₃ Reagents with 1,2-Epoxyoctane. To a suspended mixture of the NaN₃ (1 or 3 mmol) supported reagent and dry solvent (3 mL) was added 1,2-epoxyoctane (1 mmol) in a solvent (3 mL), and the mixture was heated at 80 °C with stirring under nitrogen atmosphere. As workup, water (3 mL) was added,²⁸ and the mixture was stirred at room temperature for 0.5 h and filtered through a Büchner funnel. The solid support was washed with AcOEt. Organic products were extracted with AcOEt from the filtrate, dried with Na₂SO₄, and analyzed by GLC with use of naphthalene as an internal standard.

1-Azidooctan-2-ol (2a): bp 95 °C (bath temperature)/1 Torr; ¹H NMR (CDCl₃) δ 0.87 (t, J = 5.2 Hz, 3 H, CH₃), 1.10–1.80 (br, 10 H, (CH₂)₅), 2.60 (d, J = 4.4 Hz, 1 H, OH), 3.15–3.40 (m, 2 H, CH₂N₃), 3.55–4.00 (br, 1 H, CHOH); IR (CHCl₃) 3630, 3450 (br), 2920, 2850, 2130, 1470, 1445, 1380, 1280, 1210, 1065, 910 cm⁻¹.

2-Azidooctan-1-ol (2b): bp 95 °C (bath temperature)/1 Torr; ¹H NMR (CDCl₃) δ 0.90 (t, J = 5.2 Hz, 3 H, CH₃), 1.10–1.80 (br, 10 H, (CH₂)₅, 2.10–2.50 (br, 1 H, OH), 3.30–4.00 (br, 3 H, CHN₃ and CH₂OH); IR (CHCl₃) 3630, 3430 (br), 2930, 2860, 1470, 1340, 1260, 1040 cm⁻¹. Anal. Calcd for C₈H₁₇ON₃: C, 56.11; H, 10.01; N, 24.54. Found: C, 56.26; H, 9.72; N, 24.72.

Octane-1,2-diol (2c): ¹H NMR (CDCl₃) δ 0.89 (t, J = 5 Hz, 3 H, CH₃), 1.00–1.65 (br, 10 H, (CH₂)₅), 2.50–3.10 (br, 2 H, OH), 3.15–3.90 (m, 3 H, CH₂OH and CHOH); IR (CHCl₃) 3630, 3450 (br), 2920, 2850, 1470, 1380, 1060 cm⁻¹.

Reactions of Supported NaN₃ **Reagents with** (2S*,3S*)-2,3-Epoxy Alcohols. To a suspended mixture of a NaN₃ (3 mmol) supported reagent and benzene (3 mL) was added a benzene (2 mL) solution of $(2S*,3S^*)$ -2,3-epoxy 1-ol (1 mmol), and the mixture was stirred at 80 °C under nitrogen atmosphere. As workup, water (3 mL) was added,²⁸ and the mixture was stirred for 0.5 h and filtered through a suction funnel. The solid support was washed with AcOEt. Organic products were extracted with AcOEt from the filtrate, dried with Na_2SO_4 , and purified by chromatography on silica gel to afford a regioisomeric mixture of azido diols. The regioselectivity of the reaction was determined by GLC after the azido diols were converted to diacetates. The azido diols were treated with Ac_2O (0.5 mL) and pyridine (0.5 mL) in CH₂Cl₂ (1 mL) in the presence of catalytic 4-(N,N-dimethylamino)pyridine. After the reaction was complete, the mixture was washed with 1 M HCl solution and brine, dried with Na_2SO_4 , and distilled with a Kugelrohr apparatus to yield azido diacetates.

The two regioisomers of azido diols were identical with those obtained from the reactions of epoxy alcohols with NH_4N_3 or Me_3SiN_3 -Ti(O-i-Pr)₄ by GLC and NMR analyses.

Reaction of Trimethylsilyl Azide with 3 in the Presence of Zeolite CaY. Zeolite CaY (1.07 g) was placed in a 30-mL flask and dried in an electric furnace at 400 °C for 3 h in air. After cooling, the zeolite was immersed in dry benzene (6 mL) under an argon atmosphere, and 3 (1 mmol) and Me₃SiN₃ (3 mmol) were added successively. The suspended mixture was stirred at 80 °C for 4 h. After the addition of water (3 mL), the mixture was stirred at room temperature for 1 h and filtered. Organic products were extracted with AcOEt from the filtrate, dried over Na₂SO₄, and concentrated. Azido diols (4a and 4b) and triol (4c) were purified by thin-layer chromatography.

Reaction of $(2S^*,3S^*)$ -2,3-Epoxy 1-Alcohol with NaN₃ and NH₄Cl. To a solution of NaN₃ (10 mmol) and NH₄Cl (2.2 mmol) in H₂O (1 mL) was added a solution of an epoxy alcohol (1 mmol) in MeOH (8 mL). The mixture was stirred at 80 °C. After the completion of the reaction was monitored with TLC, the mixture was evaporated and dissolved in AcOEt. The AcOEt solution was washed with water, dried with Na₂SO₄, and concentrated. The azido diols were purified on silica gel and analyzed.

Reaction of $(2S^*, 3S^*)$ -2,3-Epoxy 1-Alcohol with Me₃SiN₃ and Ti(O-i-Pr)₄. Under a nitrogen atmosphere, Ti(O-i-Pr)₄ (1.5 mmol) was added to a solution of an epoxy alcohol (1 mmol) and Me₃SiN₃ (3 mmol) in benzene (5 mL) at room temperature. The mixture was stirred at 80 °C until the epoxy alcohol was consumed. After benzene was evaporated, the reaction mixture was diluted with Et₂O (5 mL), and 5% H₂SO₄ (5 mL) was added. The twophase mixture was stirred vigorously until two clear layers formed. The azido diols were extracted with AcOEt, dried with Na₂SO₄, and purified on silica gel.

 $(2R^*, 3R^*)$ -3-Azido-3-cyclohexylpropane-1,2-diol (4a): bp 148 °C (bath temperature/0.6 Torr; ¹H (CDCl₃) δ 0.70–2.10 (br, 11 H, cyclohexyl), 2.20–2.55 (br, 2 H, OH), 3.20–3.60 (br, 1 H, CHN₃), 3.60–4.05 (br, 3 H, CH₂OH and CHOH); IR (CCl₄) 3400 (br), 2930, 2850, 2100, 1450, 1270, 1070 cm⁻¹. Anal. Calcd for C₉H₁₇O₂N₃: C, 54.25; H, 8.60; N, 21.09. Found: C, 54.22; H, 8.89; N, 21.25.

(2*R**,3*R**)-3-Azido-3-cyclohexylpropane-1,2-diol diacetate (4a'): bp 150 °C (bath temperature)/0.6 Torr; ¹H NMR (CDCl₃) δ 0.90–2.00 (br, 11 H, cyclohexyl), 2.05 (s, 3 H, Ac), 2.08 (s, 3 H, Ac), 3.24–3.55 (br, 1 H, CHN₃), 4.10 (dd, *J* = 12.0, 6.6 Hz, 1 H, C(*H*)HOAc), 4.42 (dd, *J* = 12.0, 3.0 Hz, 1 H, C(*H*)HOAc), 5.20 (ddd, *J* = 6.6, 4.8, 3.0 Hz, CHOAc); ¹H NMR (CDCl₃, decoupled at 3.40 δ) δ 0.90–2.00 (br, 11 H, cyclohexyl), 2.05 (s, 3 H, Ac), 2.08 (s, 3 H, Ac), 4.10 (dd, *J* = 12.0, 6.6 Hz, 1 H, C(*H*)HOAc), 4.42 (dd, *J* = 12.0, 3.0 Hz, 1 H, C(*H*)HOAc), 5.20 (dd, *J* = 6.6, 3.0 Hz, 1 H, CHOAc); ¹H NMR (CDCl₃ decoupled at 5.20 δ) δ 0.90–2.00 (br, 11 H, cyclohexyl), 2.05 (s, 3 H, Ac), 2.08 (s, 3 H, Ac), 3.24–3.55 (br, 1 H, CHN₃), 4.10 (d, *J* = 12.0 Hz, 1 H, C(*H*)HOAc), 4.42 (d, *J* = 12.0 Hz, 1 H, C(*H*)HOAc); IR (CCl₄) 2930, 2860, 2110, 1750, 1450, 1370, 1240, 1220, 1050 cm⁻¹.

1-Cyclohexylpropane-1,2,3-triol (4c): IR (CCl₄) 3400 (br), 2920, 2840, 1070 cm⁻¹.

1-Cyclohexylpropane-1,2,3-triol triacetate (4c'): bp 170 °C (bath temperature)/1 Torr; ¹H NMR (CDCl₃) δ 0.70–1.90 (br, 11 H, cyclohexyl), 2.03 (s, 6 H, Ac), 2.07 (s, 3 H, Ac), 4.10 (dd, J = 12.0, 6.8 Hz, 1 H, C(H)HOAc), 4.40 (dd, J = 12.0, 3.0 Hz, 1 H, C(H)HOAc), 4.80–5.45 (m, 2 H, CHOAc); IR (CCl₄) 2920, 1740, 1360, 1220, 1030 cm⁻¹.

 $(2R^*, 3R^*)$ -3-Azido-3-cyclohexyl-1-methoxypropan-2-ol (6a): bp 130 °C (bath temperature)/0.3 Torr; ¹H NMR (CDCl₃) δ 0.90–2.00 (br, 11 H, cyclohexyl), 2.30–2.80 (br, 1 H, OH), 3.40 (s, 3 H, OCH₃), 3.20–3.65 (m, 3 H, CHN₃ and CH₂OMe) 3.65–3.95 (br, 1 H, CHOH); IR (CCl₄) 3360 (br), 2920, 2850, 2090, 1430, 1250,

⁽²⁷⁾ The content of physisorbed water can also be easily estimated by the weight loss of a support after the drying treatment (200 $^{\circ}C/0.5$ Torr for 3 h).

⁽²⁸⁾ This procedure is necessary to desorb organic products from solid surfaces completely.

1100, 1040 cm⁻¹. Anal. Calcd for $C_{10}H_{19}O_2N_3$: C, 56.32; H, 8.89; N, 19.70. Found: C, 56.23; H, 8.93; N, 19.84.

 $(2R^*, 3R^*)$ -3-Azidodecane-1,2-diol (8a): bp 149 °C (bath temperature)/0.5 Torr; ¹H NMR (CDCl₃) δ 0.90 (br t, 3 H, CH₃), 1.10–1.85 (br, 12 H, (CH₂)₆), 2.10–3.00 (br, 2 H, OH), 3.20–3.55 (br, 1 H, CHN₃), 3.55–4.15 (br, 3 H, CH₂OH, CHOH); IR (CCl₄) 3400 (br), 2930, 2860, 2120, 1470, 1270, 1070 cm⁻¹. Anal. Calcd for C₁₀H₂₁O₂N₃: C, 55.79; H, 9.83; N, 19.52. Found: C, 55.79; H, 9.73; N, 19.64.

(2*R**,3*R**)-3-Azidodecane-1,2-diol diacetate (8a'): bp 150 °C (bath temperature)/0.3 Torr; ¹H NMR (CDCl₃) δ 0.89 (t, *J* = 6.0, Hz, 3 H, CH₃), 1.10–1.70 (br, 12 H, (CH₂)₆), 2.06 (s, 3 H, Ac), 2.11 (s, 3 H, Ac), 3.35–3.80 (br, 1 H, CHN₃), 4.13 (dd, *J* = 11.8, 6.0 Hz, 1 H, C(*H*)HOAc), 4.43 (dd, *J* = 11.8, 3.0 Hz, 1 H, C(*H*)HOAc), 5.10 (ddd, *J* = 6.0, 5.2, 3.0 Hz, 1 H, CHOAc); ¹H NMR (CDCl₃, decoupled at 3.55 δ) δ 0.89 (t, *J* = 6.0 Hz, 3 H, Ac), 1.10–1.70 (br, 12 H, (CH₂)₆), 2.06 (s, 3 H, Ac), 2.11 (s, 3 H, Ac), 4.13 (dd, *J* = 11.8, 6.0 Hz, 1 H, C(*H*)HOAc, 4.43 (dd, *J* = 11.8, 3.0 Hz, 1 H, CH₃), 1.10–1.70 (br, 12 H, (CH₂)₆), 2.06 (s, 3 H, Ac), 2.11 (s, 3 H, Ac), 4.13 (dd, *J* = 11.8, 6.0 Hz, 1 H, C(*H*)HOAc, 4.43 (dd, *J* = 11.8, 3.0 Hz, 1 H, C(H)HOAc), 5.10 (dd, *J* = 6.0, 3.0 Hz, 1 H, CHOAc); ¹H NMR (CDCl₃, decoupled at 5.10 δ) δ 0.89 (t, *J* = 6.0 Hz, 3 H, CH₃), 1.10–1.70 (br, 12 H, (CH₂)₆), 2.06 (s, 3 H, Ac), 2.11 (s, 3 H, Ac), 3.35–3.80 (br, 1 H, CH₃), 4.13 (d, *J* = 11.8 Hz, 1 H, C-(H)HOAc), 4.43 (d, *J* = 11.8 Hz, 1 H, C(H)HOAc); IR (CCl₄) 2900, 2850, 2120, 1730, 1470, 1370, 1240, 1040, 950 cm⁻¹.

 $(2R^{*,3}R^{*})$ -3-Azido-4-methylpentane-1,2-diol (10a): bp 115 °C (bath temperature)/0.5 Torr; ¹H NMR (CDCl₃) δ 0.89 (d, J = 6.4 Hz, 3 H, CH₃), 1.05 (d, J = 6.4 Hz, 3 H, CH₃), 1.98 (sept, J = 6.4 Hz, 1 H, CHMe₂), 2.75–3.20 (br, 2 H, OH), 3.13–3.55 (br, 1 H, CHN₃), 3.55–4.15 (br, 3 H, CH₂OH, CHOH); IR (CCl₄) 3400 (br), 2970, 2930, 2880, 2120, 1470, 1270, 1070 cm⁻¹. Anal. Calcd for C₆H₁₃O₂N₃: C, 45.27; H, 8.23; N, 26.40. Found: C, 45.57; H, 8.20; N, 26.11.

(2*R**,3*R**)-3-Azido-4-methylpentane-1,2-diol diacetate (10a'): bp 130 °C (bath temperature)/0.7 Torr; ¹H NMR (CDCl₃) δ 0.97 (d, J = 6.2 Hz, 3 H, CH₃), 1.08 (d, J = 6.0 Hz, 3 H, CH₃), 1.40–1.95 (m, 1 H, CHMe₂), 2.07 (s, 3 H, Ac), 2.10 (s, 3 H, Ac), 3.40 (t, J = 6.0 Hz, 1 H, CHM₃), 4.14 (dd, J = 12.4, 6.0 Hz, 1 H, C(H)HOAc), 4.47 (dd, J = 12.4, 3.2 Hz, 1 H, C(H)HOAc), 5.17 (ddd, J = 6.0, 6.0, 3.2 Hz, 1 H, CHOAc); ¹H NMR (CDCl₃, decoupled at 3.40 δ) δ 0.97 (d, J = 6.2 Hz, 3 H, CH₃), 1.08 (d, J = 6.0 Hz, 3 H, CH₃), 1.40–1.95 (m, 1 H, CHMe₂), 2.07 (s, 3 H, Ac), 2.10 (s, 3 H, Ac), 4.14 (dd, J = 12.4, 6.0 Hz, 1 H, C(H)HOAc), 4.47 (dd, J = 12.4, 3.2 Hz, 1 H, C(H)HOAc), 5.17 (dd, J = 6.0, 3.2 Hz, 1 H, CHOAc); ¹H NMR (CDCl₃, decoupled at 5.17 δ) δ 0.97 (d, J = 6.2 Hz, 3 H, CH₃), 1.08 (d, J = 6.0 Hz, 3 H, CH₃), 1.40–1.95 (m, 1 H, CHMe₂), 2.07 (s, 3 H, Ac), 2.10 (s, 3 H, Ac), 3.40 (d, J = 6.0 Hz, 1 H, CHN₃), 4.14 (d, J = 12.4 Hz, 1 H, C(H)HOAc), 4.47 (d, J = 12.4 Hz, 1 H, C(H)HOAc); IR (CCl₄) 2970, 2120, 1755, 1375, 1240, 1220, 1050 cm⁻¹.

 $(2R^*, 3R^*)$ -3-Azido-4-(benzyloxy)butane-1,2-diol (12a): Compound 12a was separated from 12b by preparative TLC (3:1 Et₂O/hexane): R_t 0.16; ¹H NMR (CDCl₃) δ 3.00-3.40 (br, 2 H, OH), 3.45-4.00 (br, 6 H, CHN₃, BnOCH₂, CH₂OH, CHOH), 4.57 (s, 2 H, PhCH₂), 7.33 (s, 5 H, Ph); IR (CCl₄) 3400 (br), 3075, 3040, 2940, 2875, 2120, 1460, 1270, 1100 cm⁻¹. Anal. Calcd for $C_{11}H_{15}O_{3}N_{3}$: C, 55.69; H, 6.37; N, 17.71. Found: C, 55.75; H, 6.26; N, 17.42.

 $(2R^*, 3R^*)$ -3-Azido-4-(benzyloxy)butane-1,2-diol diacetate (12a'): bp 185 °C (bath temperature)/0.5 Torr; ¹H NMR (CDCl₃) δ 2.05 (s, 3 H, Ac), 2.06 (s, 3 H, Ac), 3.57 (dd, J = 10.2, 6.8 Hz, 1 H, C(H)HOBn), 3.67 (dd, J = 10.2, 3.8 Hz, C(H)HOBn), 3.85 (ddd, J = 6.8, 6.8, 3.8 Hz, 1 H CHN₃), 4.16 (dd, J = 12.2, 6.0 Hz, 1 H, C(H)HOAc), 4.40 (dd, J = 12.2, 3.0 Hz, 1 H, C(H)HOAc), 4.57 (s, 2 H, PhCH₂O), 5.17 (ddd, J = 6.8, 6.0, 3.0 Hz, 1 H, CHOAc), 7.28–7.42 (m, 5 H, Ph); IR (CCl₄) 3040, 2870, 2110, 1755, 1460, 1370, 1240, 1220, 1105, 1050 cm⁻¹.

 $(2R^*, 3R^*)$ -2-Azido-4-(benzyloxy)butane-1,3-diol (12b): R_f 0.25 (3:1 Et₂O/hexane); ¹H NMR (CDCl₃) δ 2.35–2.75 (br, 2 H, OH), 3.35–4.10 (m, 6 H, CHN₃, BnOCH₂, CH₂OH, CHOH), 4.59 (s, 2 H, PhCH₂), 7.35 (s, 5 H, Ph); IR (CCl₄) 3425 (br), 3075, 3040, 2930, 2870, 2120, 1460, 1265, 1090 cm⁻¹.

(2*R**,3*R**)-2-Azido-4-(benzyloxy)butane-1,3-diol diacetate (12b'): bp 175 °C (bath temperature)/1 Torr; ¹H NMR (CDCl₃) δ 2.09 (s, 3 H, Ac), 2.10 (s, 3 H, Ac), 3.63 (dd, J = 10.8, 4.2 Hz, 1 H, C(H)HOBn), 3.70 (dd, J = 10.8, 4.2 Hz, 1 H, C(H)HOBn), 4.02 (ddd, J = 7.0, 7.0, 3.8 Hz, 1 H, CHN₃), 4.19 (dd, J = 11.6, 7.0 Hz, 1 H, C(H)HOAc), 4.30 (dd, J = 11.6, 3.8 Hz, 1 H, C-(H)HOAc), 4.55 (s, 2 H, PhCH₂O), 5.03 (ddd, J = 7.0, 4.2, 4.2 Hz, 1 H, CHOAc), 7.27–7.42 (m, 5 H, Ph); IR (CCl₄) 3040, 2875, 2120, 1755, 1460, 1375, 1230, 1090, 1050 cm⁻¹

Registry No. 1, 2984-50-1; **2a**, 118043-38-2; **2b**, 118043-39-3; **2c**, 1117-86-8; **3**, 86990-94-5; **4a**, 116911-20-7; **4a**', 118043-41-7; **4b**, 118043-40-6; **4b** (acetate), 118043-42-8; **4c**, 118043-43-9; **4c'**, 118043-49-5; **5**, 118043-44-0; **6a**, 118043-45-1; **6b**, 118043-46-2; **7**, 81096-86-8; **8a**, 118043-47-3; **8a'**, 118043-50-8; **8b**, 118043-48-4; **9**, 89459-99-4; 10a, 118242-98-1; 10a', 118043-51-9; 10b, 118242-99-2; 11, 98048-62-5; **12a**, 118203-36-4; **12a'**, 118138-64-0; **12b**, 118138-63-9; **12b'**, 118138-65-1; sodium azide, 26628-22-8; alumina, 1344-28-1.

Attachment of Phenyl Radicals, Generated from Halobenzenes and Solvated Electrons, to Alkenes in Ammonia Solution¹

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Received May 12, 1988

The four phenyl halides react with 1-alkenes and potassium metal, in an ammonia/t-BuOH solvent, to form the corresponding 1-phenylalkanes in yields up to 45%. The key bond-forming step is believed to be attachment of phenyl radical to C-1 of the alkene.

We recently reported² that the addition of alkali metals to liquid ammonia solutions of o-3-butenylhalobenzenes (1f-i) causes formation of two principal products, cyclized 3 and uncyclized 4, in proportions that depend on the identity of the halogen. Radical 2 was implicated as an intermediate, one that in part underwent intramolecular addition of the aryl radical center to the alkene double bond³ en route to cyclized product 3. The variation in 3/4ratio with halogen identity was ascribed mainly to differences in the time interval between formation of 2 and termination of its life by reaction with a solvated electron. This termination step forms the carbanion corresponding

⁽¹⁾ Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work.

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