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Reaction of 1,2-Epoxyalkylsilanes with Azides. Stereoselective Synthesis of 1-Azide-2-hydroxyalkylsilanes as a Synthetic Equivalent of 1-Aminoalkene

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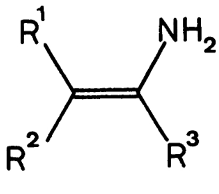
The reaction of 1,2-epoxyalkylsilanes with azidotrimethylsilane or sodium azide provided 1-azido-2-hydroxyalkylsilanes stereoselectively, one of which was successfully converted into a 2-aza-1,3-diene by a three-step reaction sequence.

Despite considerable potential utility of 1-aminoalkenes (**1**) in organic synthesis, they have received little attention not only because of their thermal instability (stable only at -50 °C) but also because of their difficult accessibility.[1)] Especially intriguing area of their application would be the general synthesis of 2-aza-1,3-butadienes (**2**),[2)] which have recently attracted much attention in view of their potential use as an effective component for the heterodiene synthesis[2)] as well as precursors to lithio enamines.[3)] Since **1** presents enormous difficulties of handling, the use of 1-aminoalkene equivalents would be more profitable for the general synthesis of **2** rather than direct use of **1** itself. Such an approach has been little investigated to date.[4)] We wish to report herein the synthesis of 1-azido-2-hydroxyalkylsilanes (**3**), a new synthetic equivalent of **1**, by the title reaction along with an example of its successful conversion into a 2-aza-1,3-diene.



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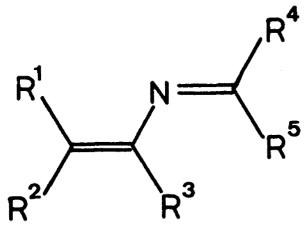

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The synthesis of **3** initially employed azidotrimethylsilane (**4**)[5)] as the azide ion source. When 1,2-epoxyalkylsilanes (**5**) were allowed to react with **4** without solvent in the presence of a Lewis acid, they provided a variety of products.[6)]

Only in two cases involving 1,2-epoxyethyltrimethylsilanes (**5a**) and trans-1,2-epoxy-2-(1-hydroxycyclohexyl)ethyltriethylsilane (**5b**) afforded desired 1-azido-2-trimethylsiloxyalkysilanes (**6a** and **6b**, respectively) in excellent yields when boron trifluoride etherate was used as the catalyst(Entries 1 and 2 in Table 1). Compounds **6a** and **6b** could be easily converted into the corresponding alcohols **3a** and **3b**, respectively, by treatment with trace amount of hydrogen chloride in methanol. It should be noted that **3b** was obtained as a single stereoisomer.

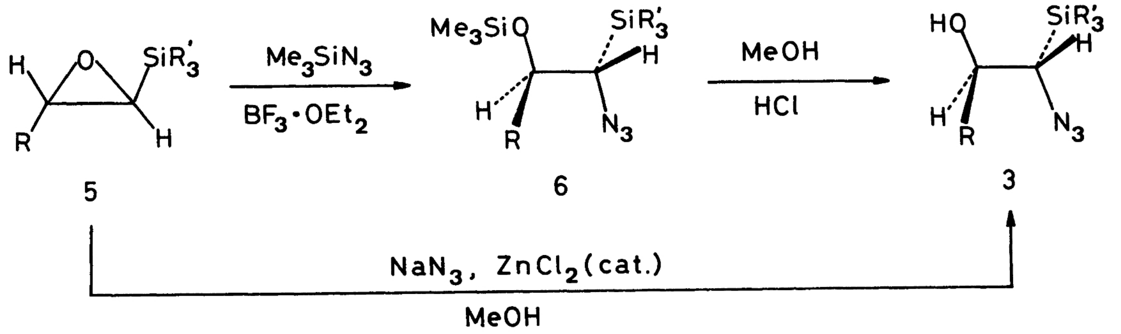
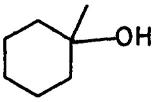


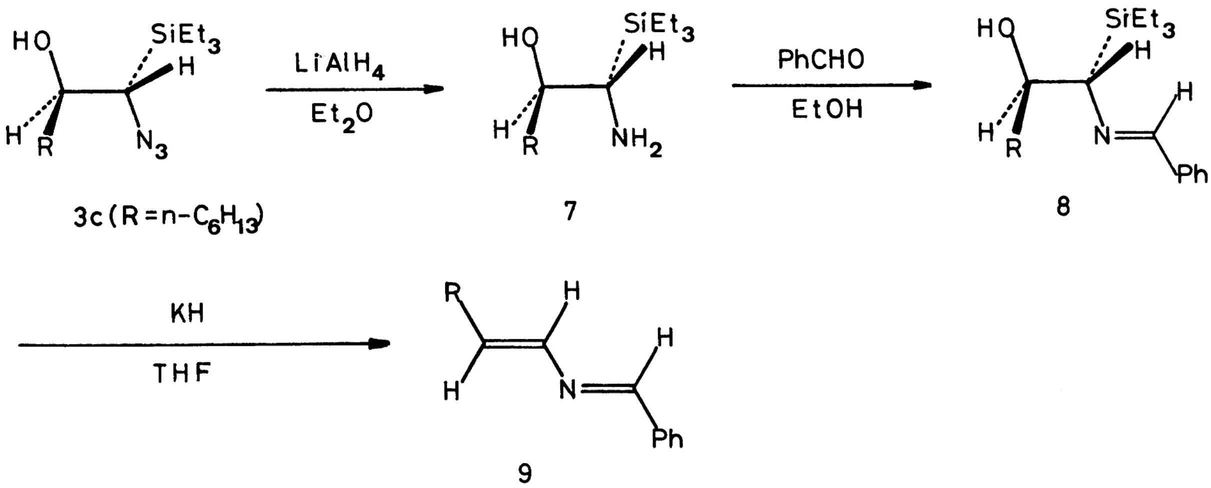
Table 1. Synthesis of **3** by the reaction between **5** and azide$^{a)}$

Entry		5		Azide	Catalyst	Temp,	Time	3
		R	R'	(mol equiv.)	(mol equiv.)	°C	h	Yield/%$^{b)}$
1	**a**	H	Me	Me_3SiN_3 (2)	BF_3-OEt_2 (0.1)	0,	0.5	86$^{c)}$
2	**b**		Et	Me_3SiN_3 (3)	BF_3-OEt_2 (0.3)	0,	0.1	74$^{c)}$
3	**c**	n-C_6H_{13}	Et	NaN_3 (10)	none	rt,	43	48
4	**c**	n-C_6H_{13}	Et	NaN_3 (12)	$ZnCl_2$ (0.2)	rt,	50	62
5	**d**	$Me_2CH(CH_2)_2$	Et	NaN_3 (10)	$ZnCl_2$ (0.1)	rt,	44	66
6	**e**	n-C_6H_{13}	Me	NaN_3 (10)	$ZnCl_2$ (0.1)	rt,	41	61

a) The reactions of **5** with azidotrimethylsilane (**4**) were performed without solvent, while those with sodium azide were run in absolute methanol.
b) Isolated yield after column chromatography on silica gel. c) Initial product was converted into azido-alcohol **3** by treatment with trace amount of hydrogen chloride in methanol. d) Structures of **3** were identified by IR, ^1H- and ^{13}C-NMR, and MS.

Since the reaction of other 1,2-epoxyalkylsilanes (**5c**, **5d**, and **5e**: each single trans isomer) with azidotrimethylsilane (**4**) failed to give corresponding desired **6**, we next turned our attention to the use of other azides. When a large excess of sodium azide was allowed to react with **5c** in methanol in the absence of Lewis acid catalyst, **3c** was obtained in 48% yield in addition to a small amount (6%) of (**E**)-1-azido-1-octene, presumably as a result of the Peterson elimination.$^{7)}$ Such an elimination could be completely circumvented by adding catalytic amount of zinc(II) chloride (Table 1). In all cases (Entries 3 to 6), products, in which methoxy groups are incorporated, were not obtained. The reaction proceeded stereoselectively; in each case a single isomer was obtained.$^{8)}$ The structures of these azido alcohols **6** were identified by IR, NMR(^{1}H and ^{13}C),and MS.

The azido alcohol **3** thus obtained can be utilized as a synthetic equivalent of 1-aminoalkene (**1**). For example, **3c** was reduced with lithium tetrahydridoaluminate to afford aminoalcohol **7** in 90% yield. Compound **7** was then allowed to react with benzaldehyde in ethanol in the presence of 4A molecular sieves to give Schiff base **8** in 88% yield. Treatment of **8** with potassium hydride in tetrahydrofuran provided 1-phenyl-2-aza-1,3-decadiene (**9**)$^{9)}$ in 60% yield as a single isomer. The structure of **9** was consistent with the spectroscopic data (IR, NMR and MS). The presence of azomethine bond(C=N) is indicated by ^{1}H NMR(δ =8.1, s, 1H) as well as by ^{13}C NMR(δ =158.9, d). Trans C=C bond is confirmed by the two ^{1}H nmr absorptions at δ =6.1 and 6.8, which couple to each other with a coupling constant of 13 Hz.



3c(R=n-C_6H_{13})

7

8

9

Further utility of **3** as well as synthetic application of 2-aza-1,3-dienes will be reported in due course.

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8) That SN2 reaction in 1,2-epoxyalkylsilanes proceeds regio- and stereoselectively has been demonstrated by Hudrlik; P. F. Hudrlik, A. M. Hudrlik, R. J. Rona, R. N. Misra, and G. P. Withers, J. Am. Chem. Soc., 99, 1933(1977) and A. P. Davis, G. J. Hughes, P. R. Lowndes, C. M. Robbins, E. J. Thomas, and G. H. Whitham, J. Chem. Soc., Perkin Trans. 1, 1981, 1934. The present reaction is considered to belong to this type of reactions.

9) Spectral data; bp 75 $^{\circ}$C ($5\mathrm{x}10^{-2}$ Pa); IR(liq film) 1650(m), 1600(m), 970(m), 755(m) and 690(m) cm^{-1}; ^{1}H NMR(CDCl$_3$) δ=0.9(3H, t, J=7 Hz), 1.3(8H, m), 2.2(2H, m), 6.1(1H, dt, J=13 and 7 Hz), 6.8(1H, d, J=13 Hz), 7.4(3H, m), 7.7(2H, m), 8.1(1H, s); ^{13}C NMR(CDCl$_3$) δ=14.0(q), 22.5(t), 28.8(t), 29.4(t)30.2(t), 31.7(t), 128.3(d), 128.5(d), 128.5(d), 130.5(d), 133.1(d), 136.3(s), 142.7(d), 158.9(d).

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