IODOSYLBENZENE-TRIMETHYLSILYL AZIDE-BORON TRIFLUORIDE ETHERATE: A HIGHLY EFFICIENT SYSTEM FOR DIRECT SYNTHESIS OF ALLYL AZIDES FROM ALLYLSILANES

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<u>Summary</u>: Simple method for the synthesis of allyl azides from allyltrimethylsilanes utilizing the combination of iodosylbenzene-trimethylsilyl azide-boron trifluoride etherate in dichloromethane was developed. A reaction mechanism involving the allyliodine(III) species was proposed.

Combination of (diacetoxyiodo)benzene and trimethylsilyl azide (TMSA) in dichloromethane has been reported by Zbiral and co-workers to undergo an oxidative azidation of simple olefins such as styrene and cyclohexene yielding α -azidoketones.^{1,2} Recently we found an exclusive formation of vicinal diazide 2 in the reaction of allylsilane 1 with iodosylbenzene (ISB) and TMSA in dichloromethane and proposed a reaction pathway involving 1,3-dipolar cycloadditions of hypervalent azidoiodine(III) species.³ Fluoride ion-induced β -elimination of trimethylsilyl and azido groups of 2 gave a good yield of allyl azide 3, which has been shown to serve as an important precursor of primary allylic amines.⁴ Vicinal diazides were also produced from alkenes by the reaction with ISB and sodium azide in acetic acid.⁵ We are interested in devising a more efficient method for the synthesis of allyl azide 3 and report herein the development of novel reagent system, ISB-TMSA-boron trifluoride etherate, for effecting the direct conversion of allylsilane 1 to allyl azide 3.



Scheme 1

Table 1. Synthesis of Allyl Azides 3 from Allylsilanes 1^a

Ally1silane 1		Conditions Time(h)	Allyl Azide	3 ~	Ύi	eld(%) ^b
Me SiMe ₃	la ~~	0.5	Me N ₃		3a ~~	(82)
Ac0 SiMe ₃	lb ∼~	0.5	Aco N ₃		3b ~~	68 ^C
c ₆ H ₅	1c ~~	2	C ₆ H ₅ Aco N ₃		3c	70 ^d
SiMe ₃	ld	0.5	N_3 + N_3	α -3d	+ γ-3₫	(67)
C ₆ H ₅ SiMe ₃]g	0.5	C ₆ H ₅ N ₃		3g ~~	53
SiMe ₃	1h ~~	0.25	Ŋ−N ₃		3h ~~	(57)
SiMe ₃	li ~~	0.5	∽-N ₃		3i ~~	(64)
(81 : 19) ^f	le ~~	ı W	$\bigvee_{\left(\begin{smallmatrix}30\\N\end{array}\right)}^{N_3} + \bigvee_{\left(\begin{smallmatrix}30\\N\end{array}\right)}^{P} e$	√ ^N 3 α-3ౖలౖ	+ γ-3e	65
^C 6 ^H 5 (83:17) ^f	lf ~~	¹ с ₆ н ₅	$(29:71)^{e}$	N ₃ α-3f	+ y-3f	63

a) Reactions were performed as described in the text. b) Isolated yield (GLC yield). c) Rearranged β -silyl ketone 10 (R = 3-acetoxydecyl) was obtained in 8% yield. d) Ketone 10 (R = 2-acetoxy-4-phenylbutyl) was produced in 8% yield. e) Ratios were determined by H-NMR spectra. f) <u>E:Z</u> Ratios.

Boron trifluoride etherate highly activates polymeric ISB by coordination to the oxygen atom.⁶ The use of boron trifluoride etherate plays an essential role in direct synthesis of allyl azide 3. To a suspension of ISB (1.2 equiv.) and TMSA (1.2 equiv.) in dichloromethane was added boron trifluoride etherate (1.2 equiv.) at -78 °C under nitrogen. The original yellow color of the suspension turned into bright orange. After being stirred for 30 min, a solution of allylsilane 1c in dichloromethane was added dropwise and the mixture was stirred for $\tilde{2}$ h at -78 °C. The resulting pale yellow solution was quenched with a cold aqueous sodium hydrogencarbonate solution and extracted with dichloromethane. Silica gel chromatography (hexane-ethyl acetate, 7:1) of the extract afforded the allyl azide 3c in 70% yield. As a minor product of the reaction, a rearranged B-trimethylsilyl ketone 10 (R = 2-acetoxy-4-phenylbutyl) was produced in 8% yield. The results on the synthesis of allyl azides 3 are summarized in Table 1. A variety of substituted allylsilanes 1 including cyclic compounds such as 3-trimethylsilylcyclohexene (1i) smoothly undergo the formal substitution reaction to yield the corresponding azides 3 in good yield.

Allylsilanes ld-f gave a regioisomeric mixture of azides and γ -alkylated allyl azides were obtained as a major product in all cases. Since the facile allylic rearrangement of allyl azides has been shown to occur at room temperature in various solvents <u>via</u> a six-membered cyclic transition state, the isomeric ratios of 3d-f, shown in Table 1, probably reflect the difference of thermodynamic stability between both regioisomers.⁷ For the regioselective synthesis of γ -substituted allyl amines by the reduction of azides 3d-f, the product complexity may not suffer serious disadvantage, because of the facile 1,3-rearrangement during reduction.⁸

We propose the reaction pathway involving the highly reactive 8-I-2 species 5, produced probably by the complexation of [azido(trimethylsiloxy)-iodo]benzene 4 with boron trifluoride etherate. Electrophilic attack of 5 upon double bond of allylsilanes affords the carbocation 6 stabilized by hyperconjugative interaction with the adjacent carbon-silicon σ bond.⁹ Detrimethylsilylation of 6, followed by nucleophilic substitution of resulting hypervalent allyliodine(III) intermediates 7 with TMSA, may give the allyl azides. On the other hand, nucleophilic attack of azide anion to 6 and subsequent 1,2-migration of the trimethylsilylmethyl group of 8 with



Scheme 2

concomitant reductive elimination of iodobenzene may account for the formation of rearranged ketone 10. 10

In order to obtain positive evidence in support of the above reaction process, a large excess of TMSA (5 equiv.) was employed on the azidation of allylsilane lc in the hope of increasing the amount of rearranged ketone 10 (R = 2-acetoxy-4-phenylbutyl) in the product mixture. The reaction gave rise to the ketone 10 in only 5% yield but the rearranged geminal diazide 11 (R = 2-acetoxy-4-phenylbutyl) in 31% yield. Since the diazide 11 is mechanistically equivalent to the ketone 10, 11 these results may support the reaction pathway shown in Scheme 2.

References and Notes

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- 4. For a recent few examples, see: (a) S. Murahashi, Y. Tanigawa, Y. Imada, and Y. Taniguchi, <u>Tetrahedron Lett.</u>, 27, 227 (1986); (b) S. N. Maiti, M. P. Singh, and R. G. Micetich, <u>ibid.</u>, 27, 1423 (1986).
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 $\begin{array}{c} \text{Me} \\ \text{R} \\ 12 \\ 13 \\ \text{I} \\ \text{R} \\ \text{R}$

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