Diazidation of Allylsilanes with a Combination of Iodosylbenzene and Trimethylsilyl Azide, and Synthesis of Allyl Azides

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Reaction of allytrimethylsilane with iodosylbenzene and trimethylsilyl azide in dichloromethane at −78°C to room temperature affords vicinal diazides, which undergo fluoride ion-catalyzed β-elimination of azide and trimethylsilyl groups, providing allyl azides in good yields.

Keywords iodosylbenzene; trimethylsilyl azide; allyltrimethylsilane; vicinal diazide; β-elimination; allyl azide

Zbiral and co-workers have reported that the oxidation of simple olefins with (diacetoxyiodo)benzene and trimethylsilyl azide (TMSA) in dichloromethane produces azidoalkanes. 13 For example, cyclohexene gave 2-azidocyclohexanone in 95% yield. 14 However, such reactions depend on the structure of the olefin. With functionalized olefins such as 1-acetoxy- and 1-chlorocyclohexenes, oxidative ring cleavage occurs to give α-cyano acid derivatives. With methyl cinnamate, methyl 2,3-diazidol-3-phenylpropionate was obtained in low yield (25%). 14a On the other hand, Moriarty and Khosrowshahi have observed that the treatment of olefins with iodosylbenzene and sodium azide in acetic acid gives 1,2-diazides. 2a

We recently reported a direct synthesis of allyl azides from allyltrimethylsilane with a combination of iodosylbenzene, TMSA, and boron trifluoride-diethyl ether in dichloromethane. 31 It was suggested that allyl azide formation probably involves highly reactive alkylidine(III) intermediates 2, 41 produced by the reactions of allyltrimethylsilanes with initially formed [azido(trimethylsilyloxy)iodo]benzene (1a), and nucleophilic substitution of 2 with TMSA may give allyl azides (Chart 1).

In this paper, we report that allyltrimethylsilanes react with iodosylbenzene and TMSA in the absence of boron trifluoride-diethyl ether to give good yields of vicinal diazides, useful precursors of allyl azides.

Results and Discussion

Iodosylbenzene and TMSA by themselves do not react with allyltrimethylsilane 3a at room temperature. When TMSA was added under nitrogen to a pale yellow suspension of iodosylbenzene in dichloromethane at −78°C and the mixture was stirred for 3 h at that temperature, a bright orange suspension resulted which was reactive with 3a. Based on the observation that the treatment of (diacetoxy-iodo)benzene with TMSA in dichloromethane produces (acetoxyazidoiodo)benzene, 1b, 4a it seems reasonable to consider that iodosylbenzene reacts with TMSA to give either 1a 4b and/or (diaziodo)iodo benzene (1b) 4b depending on the relative amounts of TMSA and iodosylbenzene.

These azidioidine(III) species were not detected in dichloromethane-d2 at −78°C by low temperature proton nuclear magnetic resonance (1H-NMR) experiments. They seem to be thermally labile. When the bright orange suspension of iodosylbenzene and TMSA at −78°C was allowed to warm to −30°C, the mixture decomposed with evolution of gas, presumably nitrogen, and no longer reacted with allyltrimethylsilanes 3.

Treatment of the β-substituted allylsilane 3a with the bright orange suspension formed from 1.5 eq of iodosylbenzene and 2 eq of TMSA at −78°C to room temperature afforded the 1,2-diazide 4a in 59% yield and a small amount of the ketone 5. With 3−5 eq of TMSA, the yield of 4a

![Chart 1](image)

<table>
<thead>
<tr>
<th>3</th>
<th>TMSA (eq)</th>
<th>Reactin. temp. (°C)</th>
<th>4</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>2</td>
<td>−78 to r.t.</td>
<td>4a</td>
<td>59b</td>
</tr>
<tr>
<td>3a</td>
<td>3</td>
<td>−78 to −30</td>
<td>4a</td>
<td>84b</td>
</tr>
<tr>
<td>3a</td>
<td>5</td>
<td>−78 to r.t.</td>
<td>4a</td>
<td>86</td>
</tr>
<tr>
<td>3b</td>
<td>5</td>
<td>−78 to r.t.</td>
<td>4b</td>
<td>75</td>
</tr>
<tr>
<td>3c</td>
<td>5</td>
<td>−78 to r.t.</td>
<td>4c</td>
<td>48a</td>
</tr>
<tr>
<td>3d (81:19)b</td>
<td>5</td>
<td>−78 to r.t.</td>
<td>4d</td>
<td>46b</td>
</tr>
<tr>
<td>3e (83:17)b</td>
<td>5</td>
<td>−78 to r.t.</td>
<td>4e</td>
<td>52</td>
</tr>
</tbody>
</table>

a) 1.5 mol eq of iodosylbenzene was used. b) r.t. = room temperature. c) Isolated yield. d) The ketone 5 was isolated as a minor product (5−12% yield). e) The triazole 6 was obtained in 8% yield with 19% recovery of 3c. f) 1H-13C ratios. g) The (E)-allyl azides 7 and 8 were isolated in 9% and 5% yields, respectively.

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increased to more than 80%. The reaction was monitored by following the disappearance of the orange color, and the products were separated by preparative thin layer chromatography (TLC). The results are summarized in Table I.

With 1,13-tetradecadiene 3e, chemoselective azidation was observed, and the double bond activated with the trimethylsilyl group was preferentially functionalized. Thus, the vicinal diazide 4e was the major product and was accompanied by an 8% yield of the triazole 6. The γ-substituted allylsilane 3d afforded the 1,2-diazide 4d in 46% yield and the (E)-allyl azides 7 and 8 as minor products. The attempted diazidation of 3-trimethylsilylcyclohex-1-ene led to the formation of a complex mixture of products, and 2,3-diazido-1-trimethylsilylcyclohexane was not isolated.

The 1H- and 13C-NMR spectra support the structures of the 1,2-diazides 4 (see Experimental). All of the diazides 4 were mixtures of two diastereoisomers (13C-NMR analysis). The structures were further confirmed by their conversion to the corresponding allyl azides 9 and 10 (Chart 3).

1,2-Elimination of β-functionalized organosilicon compounds provides a highly efficient and valuable route to olefins of defined stereochemistry. In β-eliminations mediated by nucleophilic attack at silicon, oxygen (hydroxy, tosloxy, and acetox), sulfur (phenylsulphenyl and phenylsulfonyl), and carbon (cyano) nucleофugal groups have proven to be good leaving groups. We have now found that the azido group of β-azidosilanes is a good leaving group in fluoride induced eliminations. Exposure of 4a to tetrabutylammonium fluoride in tetrahydrofuran at room temperature for 10 min caused the β-elimination of the trimethylsilyl and azido groups to give the allyl azide 9a in 80% yield. The syntheses of allyl azides from diazides 4 are summarized in Table II.

The diazides 4d and 4e yielded mixtures of regioisomers 9 and (E)-10. The ratio of 9 to 10 is similar to that obtained in reactions of allylsilanes 3d and 3e with iodosobenzene-TMSA–BF3, and probably reflects the difference in thermodynamic stability between the regioisomers because of the facile allylic rearrangement of allyl azides at room temperature.

The reduction of azides to amines is documented, and vicinal diazides serve as useful precursors of 1,2-diamines which are otherwise difficult to obtain. For example, hydrogenation of 4a with Lindlar catalyst in ethanol® gave the diamine 11 in 84% yield. The structure of 11 was confirmed by its conversion to the diamide 12. Furthermore, lithium aluminum hydride reduction of allyl azides 9a and 9b gave the corresponding primary allylic amines 13a and 13b in good yields. Primary allyl amines are important intermediates in organic synthesis and constitute a partial structure of many biologically active natural products such as gabaculine® and cytisinine.® The present method provides easy access to primary allyl amines from allylsilanes.

For the oxidation of olefins with iodosobenzene and sodium azide in acetic acid, yielding vicinal diazides, an ion reaction pathway involving initial electrophilic attack of hypervalent iodine species analogous to 1 upon the double bond has been proposed. A similar ionic mechanism, shown in Chart 4, involving the formation of allyl iodide(III) species can reasonably explain the desilylative azidation of allylsilanes in the presence of BF3 leading to allyl azides directly. The ionic mechanism, however, is not compatible with the formation of vicinal diazides 4 from allylsilanes 3 with iodosobenzene and TMSA in the absence of BF3. The fact that the allyl azides 9 and 10 expected from the ionic mechanism through facile desilylation of the presumed cationic intermediate 14 were not detected in the reaction provides evidence against the ionic mechanism.

We propose the cycloaddition pathway shown in Chart 5. 1,3-Dipolar cycloadditions of hypervalent azidodioxide(III) species 1a or 1b to allylsilanes 3 may produce A2,1,2,3-triazolines 15. Nucleophilic cleavage of the C5–N bond of 15 with the azido group and concomitant reductive elimina-
ion of iodobenzene would give vicinal diazides 4. Cycloadditions of organic azides to alkenes are well established\(^1\) and are accelerated by electron-withdrawing substituents on the azide.\(^2\) The desilylative Grob fragmentation\(^3\) of 15 may account for the formation of the minor ketone 5.

**Experimental**

Infrared spectra (IR) were recorded with a JASCO IR-A1 spectrometer. \(^1\)H- and \(^1\)C-NMR spectra were determined on a Varian XL-300 spectrometer in CDCl\(_3\) solution with (CD\(_3\))\(_2\)SO as an internal standard. Mass spectra (MS) were taken on a JOEL JMS-DX 300 spectrometer. For column chromatography, Merck silica gel 60 (70–230 mesh) was used. Preparative TLC was carried out on Merck silica gel 60 F254. All reactions were performed under nitrogen.

**Materials**

5-Acetoxy-2-(trimethylsilylmethyl)-1-dodecene (3a), 4-acetoxy-6-phenyl-2-(trimethylsilylmethyl)-1-hexene (3b), and 4-acetoxy-2-(trimethylsilylmethyl)-1,3-tetradecadiene (3e) were prepared by the method described previously.\(^1\) The 2-trimethylsilyl-2-pentene (3e) were prepared by the Wittig reaction developed by Seyferth and his co-workers.\(^2\) The 5- and 7-(1H)-inden-2-ones (7) were synthesized from the corresponding aldehydes and phenylmagnesium bromide.

**General Procedure for Synthesis of Vicinal Diazides**

Trimethylsilyl azide (3.0 mmol) was added dropwise to a pale yellow suspension of iodobenzene (0.99 mmol) in dichloromethane (5 ml) at 78 °C and the mixture was stirred for 3 h. The mixture turned to a bright orange suspension. Allylsilane (3.0 mmol) was added to the suspension at 78 °C and the reaction temperature was gradually raised to room temperature for 5–6 h. The mixture was poured into cold water and extracted with dichloromethane. The organic phase was dried (Na2SO4) and evaporated under reduced pressure. The products were isolated by preparative TLC.

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**References**

1. F. Seiyer and Co-workers, J. Chem. Soc., 1645, 1460, 1250, 1150, 850 cm\(^{-1}\). 2. H. NMR: 3.54–2.52 (2H, m), 2.05 (2H, q, J = 7.5 Hz). 3. A. N. Bag, J. Chem. Soc., 1507, 1450, 1250, 835 cm\(^{-1}\). 4. H. NMR: 7.36–7.14 (5H, m), 5.16 (1H, m), 3.41–3.27 (2H), 2.64 (2H, t, J = 7.5 Hz), 2.07 and 2.05 (total 3H, eac., 2.14–1.44 (4H), 1.29–1.50 (9H), 0.11, 0.10 (9H, each). 5. A. N. Bag, J. Chem. Soc., 1507, 1450, 1250, 835 cm\(^{-1}\). 6. H. NMR: 7.34–7.14 (5H, m), 5.16 (1H, m), 3.41–3.27 (2H), 2.64 (2H, t, J = 7.5 Hz), 2.07 and 2.05 (total 3H, eac., 2.14–1.44 (4H), 1.29–1.50 (9H), 0.11, 0.10 (9H, each). 7. A. N. Bag, J. Chem. Soc., 1507, 1450, 1250, 835 cm\(^{-1}\). 8. H. NMR: 5.81 (1H, ddt, J = 17, 10, 7.2 Hz), 5.08 (1H, m), 5.04–4.90 (2H, m), 3.41–3.26 (2H), 2.06 (3H, s), 2.05–1.90 (3H), 1.80–1.70 (1H, m). 9. M. A. N. Bag, J. Chem. Soc., 1507, 1450, 1250, 835 cm\(^{-1}\). 10. H. NMR: 5.75 (1H, C2-H of C3 and C4 of 10d), 5.51 (ddt, J = 16, 6, 1.5 Hz, C2-H of 10d), 5.29–5.23 (m, C1-H, of 9d), 3.80 (q, J = 7 Hz, C3-H of 9d), 3.69 (d, J = 6 Hz, C2-H of 10d), 2.08 (2H, q, J = 7 Hz, C4-H of 9d).
and 10d), 1.60—1.20 (16H), 0.88 (3H, t, J = 7 Hz, C3-H3 of 9a and 10d).
H, 11.43; N, 18.93.

3-Azido-5-phenyl-1-pentene (9e) and (E)-1-Azido-5-phenyl-2-pentene
(10e) H NMR: 7.32—7.16 (5H, m, aromatic—H, of 9e and 10e), 5.78 (1H, C2-H of 9e and C3-H of 10e), 5.55 (dt, J = 15, 7, 1.5 Hz, C2-H of 10e), 5.32—5.25 (m, C1-H of 9e), 3.82 (q, J = 7 Hz, C3-H of 9e), 3.69 (d, J = 6 Hz, C1-H of 10e), 2.76—2.62 (2H, C5-H2 of 9e and 10e), 2.41 (q, J = 7 Hz, C4-H of 10e), 1.85 (m, C4-H of 9e). Anal. Calcd for C14H18N3: C, 70.56; H, 7.00; N, 22.44. Found: C, 70.38; H, 7.02; N, 22.55.

Reduction of 4a with Lindlar Catalyst
Hydrogenation of 4a (59 mg, 0.15 mmol) with Lindlar catalyst (5%, Pd/CaCO3, 24 mg) in ethanol (5 ml) gave 5-acetoxy-1,2-diamino-2-(trimethylsilylmethyl)dodecane (11) (43 mg, 84% yield). Its structure was confirmed by the conversion to the diamide 12 (R, CH2Cl2): 3440, 3320, 1720, 1650, 1530, 1490, 1250, 840, 700 cm−1.

H NMR: 8.07 (1H), 7.98—7.76 (4H, m), 7.56—7.20 (6H, m), 7.28, 6.95 (total 1H, each s), 4.82, 4.50 (total 1H, m), 3.92—3.50 (2H, 2.0, 1.98 (total 3H, each s), 0.87 (3H, t, J = 6.8 Hz), 0.13, 0.11 (total 9H, each s).

Lithium Aluminum Hydride Reduction of 9a
Reduction of 9a (20 mg, 0.07 mmol) with lithium aluminum hydride (14 mg, 0.35 mmol) in diethyl ether (2 ml) at room temperature for 1 h afforded 2-aminomethyl-5-hydroxy-1-dodecene (13a) (3.9 mg, 62% yield), colorless oil (CHCl3); 3670, 3600, 3380, 1650, 1460, 900 cm−1.

H NMR: 4.95, 4.86 (each 1H), 3.61 (1H, m), 3.27 (2H), 2.21 (2H, m), 1.72—1.18 (15H), 0.89 (3H, t, J = 7.2 Hz).

Lithium Aluminum Hydride Reduction of 9b
Reduction of 9b (19 mg, 0.07 mmol) with lithium aluminum hydride (14 mg, 0.35 mmol) in diethyl ether (3 ml) at room temperature for 1 h afforded 2-aminomethyl-4-hydroxy-6-phenyl-1-hexene (13b) (10.3 mg, 72% yield), colorless oil (CHCl3); 3380, 1645, 1495, 1455, 910 cm−1.

H NMR: 7.34—7.14 (5H, m), 4.97, 4.90 (each 1H), 3.65 (1H, m), 3.37, 2.32 (2H, AB type, J = 13.2 Hz), 2.92—2.62 (2H, m), 2.44 (1H, dd, J = 13.5, 2.6 Hz), 2.20 (1H, dd, J = 13.5, 8.6 Hz), 1.90—1.70 (2H).

References