

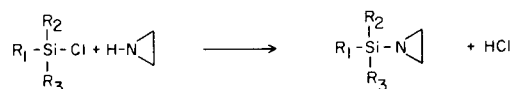
Organosilicon Compounds VI.
The Preparation of Silylaziridines and Silyldiaziridines by Silicon-Carbon Cleavage (1)

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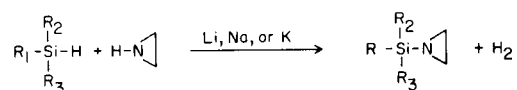
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The preparation of several 2-furyl-, 2-thienyl-, benzyl-, and allylsubstituted silanes is reported. Such derivatives, when treated with aziridine in the presence of a metal catalyst, afford good yields of silylaziridines and silyldiaziridines. A qualitative study of electronic and steric requirements of the displacement reaction is reported.

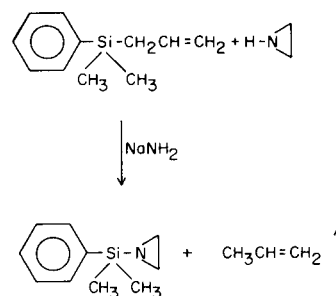
The chemistry of silylamines has received considerable attention in recent years; however, such is not the case with silylaziridines. This lack of research activity with silylaziridines is probably a result of earlier laborious and unreliable syntheses. The silylaziridines were reported in the patent literature first in 1952 by Heyna and Bauer (2) and in 1958 by Birr and Walther (3). These investigators, as well as Scherer and Schmidt (4), employed chlorosilanes and aziridine for their preparations. This method has serious drawbacks in that the evolution of hydrogen chloride, during the reaction, causes cleavage of the aziridine ring with a concomitant loss in product yield (5).



An improved procedure for the preparation of silylaziridines was reported by Nametkin, Perchenko, and Batalova (4). These investigators employed a condensation reaction between aziridine and an appropriate silane, catalyzed by lithium, sodium, or potassium. The yields varied between 40-80% with optimum reaction rates being obtained when the organosilicon substituents were phenyl or benzyl groups; aliphatic substituents produced a rate decrease.

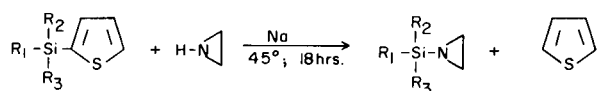


In an effort to add aziridine to unsaturated silanes, Nametkin, *et al.* (6) reported that phenyldimethylallylsilane gave 10% of dimethylphenyl-*N*-aziridinylsilane and propene rather than the desired addition product.



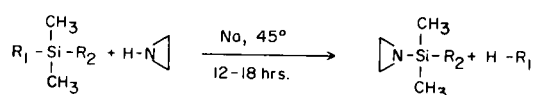
This latter report concerning silicon-carbon cleavage, and the fact that the majority of such cleavages occur by the action of electrophilic reagents, prompted us to report our findings. We have established that selective, nucleophilic cleavage of the silicon-carbon bond can be readily accomplished, and when certain structural limitations are employed, the yields of resulting silylaziridines are quite good (60-100%). A number of 2-furyl-, 2-thienyl-, benzyl-, allyl- and phenyl-substituted silanes have been prepared and their reactivity with aziridine in the presence of a catalyst (lithium, sodium, potassium) have been studied qualitatively (Schemes A, B & C).

The substrates employed efficaciously in this reaction sequence suggest that the ease of nucleophilic cleavage of a substituent is somewhat dependent upon the acidity of the liberated group, *e.g.*, in the following case, thiophene.



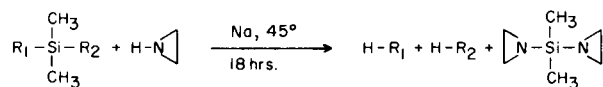
Such rationale is not without precedent as silicon-carbon cleavage by hydroxide ion has been shown to be dependent on the acidity or electron-attracting properties of the corresponding leaving groups (7). Thus, in the present case, as with treatment by hydroxide ion, silicon-carbon cleavage is facilitated when the departing group is an aromatic heterocycle rather than a phenyl group (Schemes A & B). Under the conditions of the reaction reported herein, no silicon-phenyl cleavage could be detected, while our qualitative study (Scheme C) indicates that the 2-furyl and 2-thienyl moieties are similar in their effectiveness as leaving groups. Both the 2-furyl and 2-thienyl groups are more effective than the benzyl group. Such an observation coincides with the marked ease with which these heterocycles can be metalated in the 2-position (8), and is in agreement with the earlier conclusion for required acidity of the related hydrocarbon.

Scheme A



	Cmpd.	Yield %
I. $\text{R}_1 = \text{C}_2\text{H}_4\text{S}$; $\text{R}_2 = \text{C}_2\text{H}_5$	XIII	80
II. $\text{R}_1 = \text{C}_2\text{H}_4\text{O}$; $\text{R}_2 = \text{C}_2\text{H}_5$	XIII	81
XII. $\text{R}_1 = \text{C}_6\text{H}_5\text{CH}_2$; $\text{R}_2 = \text{CH}_3$	XV	61

Scheme B

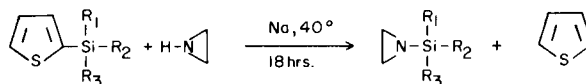


X. $\text{R}_1 = \text{R}_2 = \text{C}_2\text{H}_4\text{S}$	XIV	Yield, %
XI. $\text{R}_1 = \text{C}_2\text{H}_4\text{S}$; $\text{R}_2 = -\text{CH}_2\text{CH}=\text{CH}_2$		98

A comparison of the reactivity of the 2-thienyl- and allyl-substituted silanes emphasizes the importance of resonance stabilization of the resulting carbanion and, perhaps to a lesser extent, the influence of steric requirements upon this reaction. Allylic displacement (Scheme B) would be facilitated by both its tendency for resonance

stabilization of the resulting carbanion and its smaller bulk as opposed to the heterocyclic moiety, thereby allowing the incoming nucleophile easy access to the reaction center.

Scheme C



	Cmpd.	Yield, %
VII. $\text{R}_1 = \text{R}_2 = \text{R}_3 = -\text{CH}_3$	XV	81
I. $\text{R}_1 = \text{R}_2 = -\text{CH}_3$; $\text{R}_3 = \text{C}_2\text{H}_5$	XIII	80
III. $\text{R}_1 = \text{R}_2 = \text{R}_3 = -\text{CH}_2\text{CH}_3$	XVI	98
IX. $\text{R}_1 = \text{R}_2 = \text{R}_3 = -\text{CH}_2\text{CH}_2\text{CH}_3$	XVII	90
IV. $\text{R}_1 = \text{R}_2 = \text{CH}_3$; $\text{R}_3 = \text{C}_6\text{H}_5$	XVIII	60
V. $\text{R}_1 = \text{R}_2 = -\text{C}_2\text{H}_5$; $\text{R}_3 = \text{C}_6\text{H}_5$	XIX	68
VI. $\text{R}_1 = \text{CH}_3$; $\text{R}_2 = \text{R}_3 = -\text{C}_6\text{H}_5$	XX	34
VIII. $\text{R}_1 = \text{R}_2 = \text{R}_3 = -\text{C}_6\text{H}_5$	XXI	no pure product was isolated

The nature of the steric requirements alone was investigated (Scheme C) when a variety of alkyl- and aryl-substituted thienylsilanes was employed as substrate materials. On the basis of pure product yield the lower alkyl substitutions afforded good product yield with a substantial yield decrease with the introduction of phenyl groups into the system. It is interesting to note that such a trend is in contrast to the structural requirements of the condensation reaction (5).

EXPERIMENTAL

The infrared spectra were determined with a Beckman IR-5 spectrophotometer. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee. All chlorosilanes were distilled prior to use (10" Vigreux column) and all metalation reactions were conducted under strictly anhydrous conditions under an atmosphere of nitrogen.

2-Thienyldimethylethylsilane (I).

Thiophene, (40 g., 0.475 mole) in 200 ml. of anhydrous ether, was metalated with *n*-butyllithium (250 ml.; 1.6 M) and the solution boiled under reflux for 3 hours. To this was added dropwise dimethylethylchlorosilane (50 g.; 0.41 mole) and the resulting mixture was refluxed for 6 hours at which time the lithium chloride was filtered, the solution concentrated *in vacuo* and the residue distilled to afford 50.3 g. (74%) of I boiling at 82°/25 mm.

Anal. Calcd. for $\text{C}_8\text{H}_{14}\text{SSi}$: C, 56.41; H, 8.28; Si, 16.49. Found: C, 56.48; H, 8.41; Si, 16.33.

The above method was employed as a standard procedure for the synthesis of the following silanes.

2-Furyldimethylethylsilane (II).

Furan (13.6 g.; 0.2 mole), *n*-butyllithium (125 ml.; 1.6 M) and dimethylethylchlorosilane (22.4 g.; 0.2 mole) afforded 25 g.

(81%) of II boiling at 53°/25 mm., $n_D^{26} = 1.4490$.

Anal. Calcd. for $C_8H_{14}OSi$: C, 62.28; H, 9.15; Si, 18.20. Found: C, 62.34; H, 9.21; Si, 17.98.

2-Thienyltriethylsilane (III).

Thiophene (33.6 g.; 0.4 mole), *n*-butyllithium (250 ml.; 1.6 *M*) and triethylchlorosilane (60.0 g.; 0.40 mole) afforded 70 g. (89%) of III boiling at 114-116°/23 mm.

Anal. Calcd. for $C_{10}H_{18}SSi$: C, 60.54; H, 9.14; Si, 14.16. Found: C, 60.30; H, 9.01; Si, 14.29.

2-Thienyldimethylphenylsilane (IV).

Thiophene (8.4 g.; 0.1 mole), *n*-butyllithium (62.5 ml.; 1.6 *M*) and dimethylphenylchlorosilane (23.2 g.; 0.1 mole) gave 18.3 g. (84%) of IV boiling at 124°/0.025 mm., $n_D^{30} = 1.5635$.

Anal. Calcd. for $C_{12}H_{14}SSi$: C, 66.00; H, 6.46; Si, 12.86. Found: C, 66.08; H, 6.62; Si, 12.63.

2-Thienylphenyldiethylsilane (V).

Thiophene (8.4 g., 0.1 mole), *n*-butyllithium (62.5 ml.; 1.6 *M*) and phenyldiethylchlorosilane (19.8 g.; 0.1 mole) afforded 20 g. (81%) of V boiling at 135°/2 mm.

Anal. Calcd. for $C_{14}H_{18}SSi$: C, 68.23; H, 7.36; Si, 11.40. Found: C, 68.14; H, 7.34; Si, 11.17.

2-Thienyldiphenylmethylsilane (VI).

Thiophene (8.4 g.; 0.1 mole), *n*-butyllithium (62.4 ml.; 1.6 *M*) and diphenylmethylchlorosilane (23.2 g.; 0.1 mole) gave 20 g. (71%) of VI boiling at 124°/0.025 mm.; $n_D^{22} = 1.6142$.

Anal. Calcd. for $C_{17}H_{16}SSi$: C, 72.80; H, 5.75; Si, 10.01. Found: C, 73.00; H, 5.73; Si, 10.14.

2-Thienyltrimethylsilane (VII).

Thiophene (0.8 mole; 67.2 g.), *n*-butyllithium (500 ml.; 1.6 *M*) and trimethylchlorosilane (0.8 mole; 86.5 g.) afforded 93 g. (75%) of VII boiling at 68°/25 mm.; Lit. (10) gives 159-160°/748 mm.

The following compounds were prepared according to the procedure outlined previously for the synthesis of I with the exception that an inverted order of addition was employed, e.g., an ether solution of the organometal was added to an ether solution of the desired chlorosilane.

2-Thienyltriphenylsilane, (VIII).

Thiophene (8.4 g.; 0.1 mole), *n*-butyllithium (62.5 ml.; 1.6 *M*) and triphenylchlorosilane (29.4 g.; 0.1 mole), gave VIII melting at 197-198°.

Anal. Calcd. for $C_{22}H_{18}SSi$: C, 77.14; H, 5.30; Si, 8.20. Found: C, 76.89; H, 5.22; Si, 7.97.

2-Thienyltri-*n*-propylsilane (IX).

Thiophene (33.6 g.; 0.4 mole), *n*-butyllithium (250 ml.; 1.6 *M*) and tri-*n*-propylchlorosilane (76.0 g.; 0.4 mole) gave 70 g. (73%) of IX boiling at 98°/1.25 mm.

Anal. Calcd. for $C_{13}H_{24}SSi$: C, 64.93; H, 10.06; Si, 11.68. Found: C, 64.78; H, 10.09; Si, 11.84.

Bis-(2-thienyl)dimethylsilane (X).

Thiophene (16.8 g.; 0.2 mole), *n*-butyllithium (125 ml.; 1.6 *M*) and dimethyldichlorosilane (25.6 g.; 0.2 mole) afforded 18.5 g. (82%) of X boiling at 106°/1.3 mm.; $n_D^{25} = 1.5770$.

Anal. Calcd. for $C_{10}H_{12}S_2Si$: C, 53.52; H, 5.39; Si, 12.51. Found: C, 53.68; H, 5.27; Si, 12.41.

2-Thienyldimethylallylsilane (XI).

Thiophene (16.8 g.; 0.2 mole), *n*-butyllithium (125 ml.; 1.6 *M*) and dimethylallylchlorosilane (26.8 g.; 0.2 mole) gave 27 g. (74%) of XI boiling at 92-94°/25 mm.; $n_D^{22} = 1.5105$.

Anal. Calcd. for $C_9H_{14}SSi$: C, 59.28; H, 7.74; Si, 15.40. Found: C, 59.10; H, 7.77; Si, 15.27.

Benzyltrimethylsilane (XII).

Benzyl chloride (19 g.; 0.15 mole) in 30 ml. of anhydrous ether was reacted with magnesium (4.1 g.; 0.17 mole) to form the Grignard reagent. To this was added dropwise trimethylchlorosilane (16.2 g.; 0.15 mole) and the mixture was allowed to stir overnight. The magnesium chloride was filtered and the ether layer washed with water and then dried over sodium sulfate. The ether was removed by distillation and the residue distilled *in vacuo* to afford 15 g. (61%) boiling at 82°/20 mm. Lit. (9) gives 93°/35 mm.

Silylaziridines and Silyldiaziridines.

In a typical reaction procedure a hetero-, benzyl-, or allyl-substituted silane was added to one equivalent excess of aziridine and a catalytic amount (0.1 g. or less) of lithium, sodium, or potassium. (Sodium was employed for the majority of the reactions for it is easy to handle and affords good results). The reaction mixture was heated for approximately 18 hours between 45 and 50° at which time the excess aziridine was removed *in vacuo* and the residue distilled to afford the desired product.

The following silylaziridines and silyldiaziridines were prepared according to the above general procedure:

1. Dimethylethylsilylaziridine (XIII).

Yield 80% boiling at 117°/760 mm., $n_D^{22} = 1.4192$.

Anal. Calcd. for $C_6H_{15}NSi$: C, 55.74; H, 11.70; Si, 21.73. Found: C, 55.45; H, 11.76; Si, 21.55.

2. Dimethylsilyldiaziridine (XIV).

Yield 92% boiling at 85°/100 mm.; $n_D^{22} = 1.4405$.

Anal. Calcd. for $C_6H_{14}N_2Si$: C, 50.65; H, 9.92; Si, 19.74. Found: C, 50.41; H, 10.10; Si, 19.91.

3. Trimethylsilylaziridine (XV).

Yield 81% boiling at 83°/760 mm.; Lit. (4) gives 88-96°/760 mm.

4. Triethylsilylaziridine (XVI).

Yield 98% boiling at 105°/95 mm.; Lit. (5) gives 81.5-83°/59 mm.

5. Tri-*n*-propylsilylaziridine (XVII).

Yield 90% boiling at 85°/5 mm.; $n_D^{22} = 1.4454$.

Anal. Calcd. for $C_{11}H_{25}NSi$: C, 66.25; H, 12.64; Si, 14.08. Found: C, 66.32; H, 12.78; Si, 14.21.

6. Dimethylphenylsilylaziridine (XVIII).

Yield 60% boiling at 104°/0.20 mm.; Lit. (6) gives 74-75°/5 mm.

7. Diethylphenylsilylaziridine (XIX).

Yield 68% boiling at 130°/25 mm.; $n_D^{25} = 1.5095$.

Anal. Calcd. for $C_{12}H_{19}NSi$: C, 70.18; H, 9.33; Si, 13.68. Found: C, 69.97; H, 9.41; Si, 13.95.

8. Diphenylmethylsilylaziridine (XX).

Yield 34% boiling at 94°/0.03 mm.; Lit. (5) gives 142-145°/4 mm.

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- (1) This investigation was supported by the U. S. Army Medical Research and Development Command, Department of the Army, under contract number DA-49-193-MD-2910, and in part by the National Aeronautics and Space Administration who provided PLK with a predoctoral research fellowship. Presented in part at the First International Congress of Heterocyclic Chemistry, June, 1967, Albuquerque, New Mexico.
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