Synthesis of Vinylsilanes from Benzenesulfonylhydrazones

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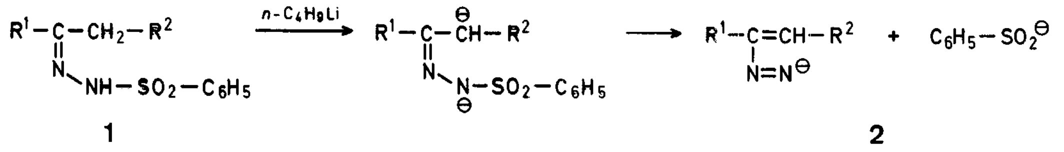
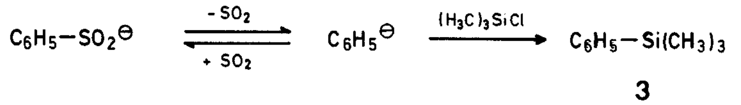
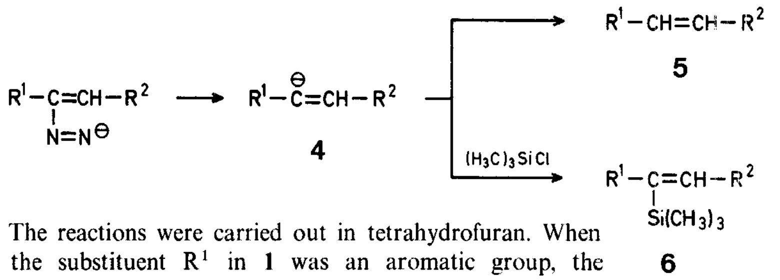
Vinylsilanes have recently become useful intermediates in organic synthesis. They have been used as precursors to α-silyl carbanions[1]. Epoxidation of vinylsilanes followed by ring opening can lead to carbonyl compounds[2] and their derivatives[3]. Dihalocyclopropanation of vinylsilanes with subsequent elimination of β-halosilanes can serve as a mild method for the generation of cyclopropenes[5]. Entry into the allene oxide/cyclopropanone system via vinylsilanes has been reported[6]. Electrophilic substitution of the silyl group in vinylsilanes by proton[7, 8], halogen[9], or acyl cation[10] can give substituted olefins often with defined stereochemistry[11].

Only a limited number of methods are available for the preparation of vinylsilanes. These are the reduction of acetylenic compounds either by semi-hydrogenation[2, 4] or by hydrosilylation[9]; the reaction of carbonyl compounds with bis-[α-silyl]-carbanions[12], and the reaction of vinylorganometallic compounds with halosilanes[13]. We wish to report here a convenient method for the conversion of carbonyl compounds into vinylsilanes via the benzenesulfonylhydrazones.

Reactions of aromatic sulfonylhydrazones (**1**) with alkyl lithium have been reported to give the vinyl carbanions (**4**) which have been trapped with various electrophiles[14, 15]. Quenching of the vinyl carbanions **4** with chlorotrimethylsilane gives the expected vinylsilanes **6**.



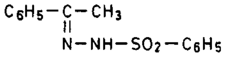
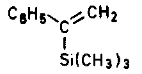
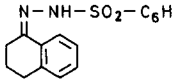
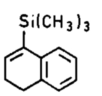
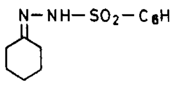
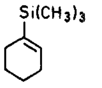
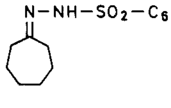
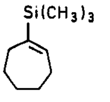
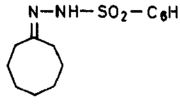
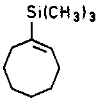
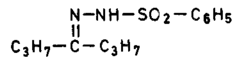
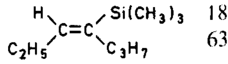




The reactions were carried out in tetrahydrofuran. When the substituent R^1 in **1** was an aromatic group, the product **6** could be obtained in good yield. For aliphatic compounds (R^1 = alkyl), the conversion of **1** to **3** was, however, poor. This was due to the formation of the alkene **5**. The yield of **6** could be improved with the use of tetramethylethylenediamine (TMEDA) as solvent (Table). The use of tetramethylethylenediamine is beneficial not only in improving the yield of **6**, but also in suppressing the formation of a side product, phenyltrimethylsilane (**3**), which could only be separated with difficulty from **6**. The formation of **3** is attributed to the decomposition of phenylsulfinate anion (**2**) to sulfur dioxide and phenyl carbanion (as phenyllithium) which reacts with chlorotrimethylsilane. In tetramethylethylenediamine, the phenylsulfinate anion is stabilized and is eventually removed from the reaction mixture by aqueous extraction. The compounds **6c–e** have been prepared from the carbonyl precursors by an independent route[13] with vinyl chloride as the intermediate. While the overall yields of the products were comparable by both methods, the benzenesulfonylhydrazone route appears to be more convenient.

The conversion of **1f** to **6f** by the benzenesulfonylhydrazone method gave apparently only one isomer. The stereochemistry of **6f** has been assigned to be (*E*) by comparison of

Table. Physical Data for Benzenesulfonylhydrazones **1** and Vinylsilanes **6**

Benzenesulfonylhydrazone			Vinylsilanes					
		m.p.			Yield [%][a]	b.p./torr (Lit. b.p./torr)	Molecular formula[b]	^{1}H-N.M.R. (CCl_4)[c] δ [ppm]
1a		125–127°	**6a**		62[d,e]	73–77°/8 (52°/3)[17]	$C_{10}H_{16}Si$ (164.3)	0.72 (s, 9H), 6.02 (AB, 3H, J=3Hz), 7.47 (m, 5H_{arom})
1b		185–186.5°	**6b**		70[d,f]	81–84°/0.85	$C_{13}H_{18}Si$ (202.4)	0.62 (s, 9H), 2.4–3.1 (m, 4H), 6.52 (t, 1H, J=4Hz), 7.0–7.4 (m, 4H_{arom})
1c		143–145°	**6c**		33[d] 43[g] 48[h]	81–83°/38 (74–75°/30)[18]	$C_9H_{18}Si$ (154.3)	0.13 (s, 9H), 1.5–2.2 (m, 8H, 5.95 (br, 1H)
1d		146–148°	**6d**		19[d] 30[g]	50–52°/8	$C_{10}H_{20}Si$ (168.4)	0.30 (s, 9H), 1.4–2.6 (m, 10H), 6.17 (t, 1H, J=6Hz)
1e		119–121°	**6e**		16[d] 23[g,i] 40[h]	92–94°/11 (73–74°/7)[19]	$C_{11}H_{22}Si$ (182.4)	0.30 (s, 9H), 1.7–2.6 (m, 12H), 6.07 (t, 1H, J=10Hz)
1f		102–103°	**6f**		18[d] 63[h]	86–87°/47	$C_{10}H_{22}Si$ (170.4)	0.29 (s, 9H), 0.9–2.6 (m, 12H), 5.87 (t, 1H, J=6Hz)

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[a] Yield of product isolated by distillation.

[b] All products gave satisfactory spectral analyses with purity established by G.L.C. to be >98%.

[c] Dichloromethane used as internal standard; shifts obtained using function $\delta_{CH_2Cl_2} - \delta_{TMS} = 5.28$ ppm.

[d] Tetrahydrofuran used as reaction solvent.

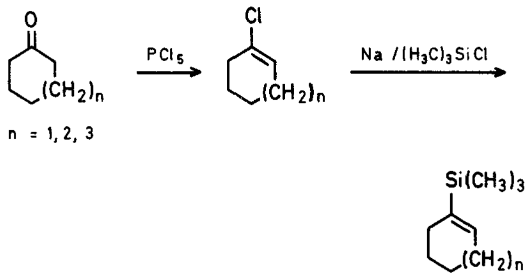
[e] Side product: styrene, yield not determined.

[f] Side product: 1,2-dihydronaphthalene, yield: 20%.

[g] Tetrahydrofuran and tetramethylethylenediamine (4 equiv) used as reaction solvent.

[h] Tetramethylethylenediamine used as reaction solvent.

[i] Side product: cyclooctene, yield: 36%.



its ^{1}H-N.M.R. spectrum with those of similar compounds of known stereochemistry[11].

Tetramethylethylenediamine (TMEDA) was dried over calcium hydride and distilled. Benzenesulfonylhydrazones of carbonyl compounds were prepared according to the general procedures reported[16] in essentially quantitative yields. The conversion of the hydrazones to vinylsilanes was carried out under nitrogen.

Preparation of α-Trimethylsilylstyrene (6a):

A solution of the benzenesulfonylhydrazone of acetophenone (20 mmol) in tetrahydrofuran (90 ml) was stirred and cooled to −78°. To the mixture, a solution of *n*-butyllithium (80 mmol, 2.4 *M* in hexane) was added dropwise. After 1.5 h, the reaction mixture was allowed to warm to room temperature. After 40 min. the reaction mixture was cooled back to −78°. Chlorotrimethylsilane (80 mmol) was added dropwise and the mixture was allowed to warm to room temperature overnight. The reaction mixture was extracted with ether. The ether solution was washed with 3% hydrochloric acid, then with saturated salt solution. The ether solution was dried ($MgSO_4$) and distilled to give α-trimethylsilylstyrene; yield: 62%; b.p. 73–77°/8 torr.

Preparation of 4-Trimethylsilyl-3-heptene (6f):

A solution of the benzenesulfonylhydrazone of 4-heptanone (**1f**, 20 mmol) in tetramethylethylenediamine (90 ml) was cooled to −78°. To the mixture, a solution of *n*-butyllithium (80 mmol, 2.4 *M* in hexane) was added dropwise. Five minutes after addition, the reaction mixture was allowed to warm to room temperature and left for 40 min. To the reaction mixture, chlorotrimethylsilane (12 ml) was added dropwise. After completion of addition, the reaction mixture was stirred for 1.5 h. The mixture was dissolved in dichloromethane. The solution was washed with dilute hydrochlorid acid, then 10% aqueous sodium hydrogen carbonate solution and finally with saturated salt solution. The organic layer was dried ($MgSO_4$), evaporated, and distilled to give 4-trimethylsilyl-3-heptene; yield: 63%; b.p. 86–87°/47 torr.

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Erratum

T. H. Chan, A. Baldassarre, D. Massuda, *Synthesis* **1976**, 801–803.

The last sentence starting on p. 802 should be:

The stereochemistry of **6f** has been assigned to be (*Z*) by comparison of its ^{1}H-N.M.R. spectrum with those of similar compounds of known stereochemistry[11].