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PRACTICAL SYNTHESES OF ALLYLSILANES FROM 1-BENZENESULFONYL-2-TRIMETHYLSILYLETHANE

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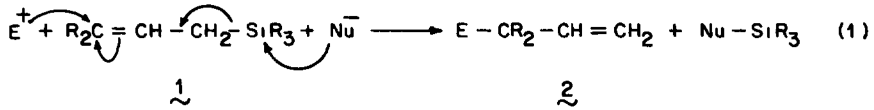
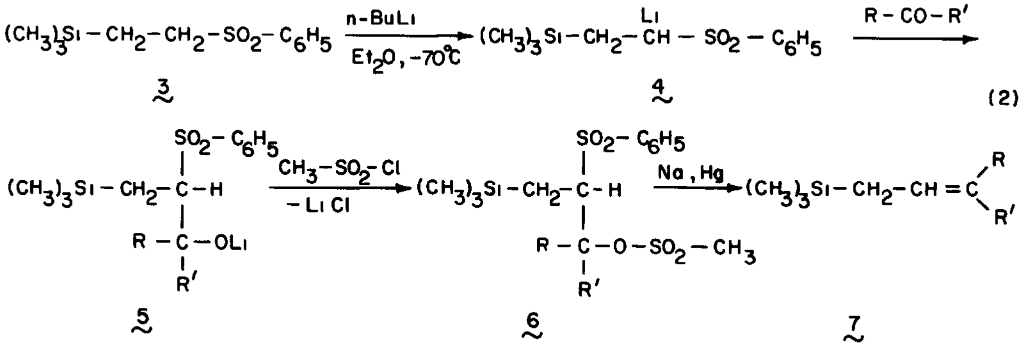
Abstract *The methanesulfonates of the adducts of aldehydes and ketones with 1-(1-benzenesulfonyl-2-trimethylsilyl)ethyllithium are converted by sodium-amalgam to allylsilanes.*

Allylsilanes (1) have become of intense interest in synthesis.[1] Of particular value are their reactions with various electrophiles to give allyl derivatives as in Equation 1.[1]



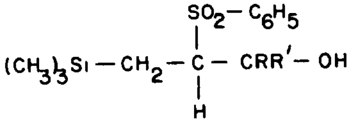
Routes to specific allylsilanes have been described[2] The methods however are inefficient, expensive and not general. In this communication we describe the synthesis and utility of 1-benzenesulfonyl-2-trimethylsilylethane (3)[3] for conversion of a wide variety of aldehydes and ketones to allylsilanes (7)[4a] in excellent yields (85-95%) and on large scale. The sequence for preparation of 7 from 3 is summarized in Equation 2



Silylsulfone 3 (BSTMSE) is prepared by addition of thiophenol to vinyltrimethylsilane (8)[4b] at 90°C in the presence of azoisobutyronitrile (AIBN) and oxidation of the resulting 1-trimethylsilyl-2-thiophenoxyethane (9)[4a] with 30% hydrogen peroxide (Equation 3) The overall synthesis of 3 is convenient, essentially quantitative and usable for large quantities

$$\underset{\mathbf{8}}{(CH_3)_3Si-CH=CH_2} + H-S-C_6H_5 \xrightarrow{AIBN} \underset{\mathbf{9}}{(CH_3)_3Si-CH_2-CH_2-S-C_6H_5} \xrightarrow{H_2O_2} \mathbf{3} \quad (3)$$

The methodology for preparation of 7 from 3 as in Equation 2 is elaborated as follows Reaction of 3 with n-butyllithium at -70°C in anhydrous ethyl ether yields 1-(1-benzenesulfonyl-2-trimethylsilyl)ethyllithium (4),[3] a highly reactive carbanionic reagent. Addition of 4 to the carbonyl groups of a wide variety of aldehydes and ketones occurs readily to give 5 and then the corresponding 2-benzenesulfonyl-3-trimethylsilyl alcohols (10, > 95%) upon neutralization. Of particular significance is conversion of 5 in situ by methanesulfonyl



$(CH_3)_3Si-CH_2-C(SO_2-C_6H_5)(H)-CRR'-OH$

10

chloride to methanesulfonates 6 which, after washing with water, dilution with methanol and reduction with sodium-amalgam (6%) in the presence of disodium hydrogen phosphate results in the desired allylsilanes (7).[5] The allylsilanes prepared from the indicated aldehydes and ketones, their yields from 3 and their ^{1}H NMR spectra are summarized in Table 1. Procedures for synthesis of 9, 3 and a typical allylsilane are described below

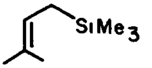
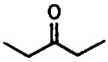
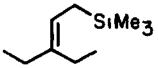
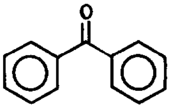
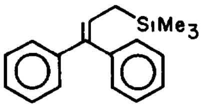
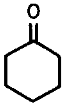
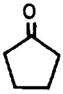
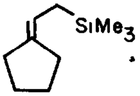
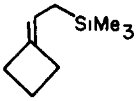
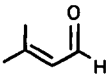
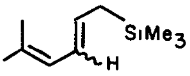
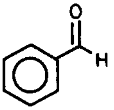
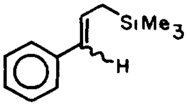
1-Trimethylsilyl-2-thiophenoxyethane(9) A solution of trimethylvinylsilane (8, 350g, 3.50 mol), thiophenol (600g, 5 44 mol) and azoisobutyronitrile (0.5g) was heated under nitrogen to 90°C to initiate reaction. After the exothermic reaction subsided (~1 hr), the mixture was cooled, diluted with ethyl ether (1000 mL), and washed with aqueous potassium hydroxide (1N) to remove excess thiophenol and then with saturated brine Evaporation, concentration and vacuum distillation of the dried ether extract ($MgSO_4$) gave 9 (733g, 99.2% yield) as a colorless liquid, bp 123-125°C (3.5 mm Hg), NMR (CCl_4, δ) 0.13 (s, 9H), 0 93 (m, 2H) 2 93 (m, 2H) and 7.33 (m, 5H).

1-Benzenesulfonyl-2-trimethylsilylethane(3). Hydrogen peroxide (30%, 200g, 1 75 mol) was added to 9 (210g, 1.0 mol) in commercial glacial acetic acid (450 mL) The two-layered mixture was heated until an exothermic reaction initiated After ~20 min., additional hydrogen peroxide (30%; 350g, 3 08 mol) was added slowly The mixture was then heated to 100°C for 2 hr, cooled and vacuum evaporated After most of the acetic acid and water had been removed, the residue was diluted with ether, washed with saturated aqueous sodium bicarbonate and then saturated aqueous sodium chloride, dried ($MgSO_4$) and filtered After evaporation, 3 (240g, 99 2% yield; analytically pure) crystallized; mp 52°C, IR (cm^{-1}, neat) 3100, 2900, 1600, 1490, 1460, 1330, 1270, 1160, 1100, 870, 750 and 710, NMR (CCL_4, δ) 0.03 (s, 9H), 0.93 (m, 2H), 2.93 (m, 2H), 7 53 (m, 3H) and 7 83 (m, 2H)

(2-Trimethylsilylethylidene)cyclopentane n-Butyllithium (40 mL, 1 6 M solution in hexane, 64 mmol) was syringed slowly into a suspension of 3 (15.0g, 62 mmol) in anhydrous ethyl ether (70 mL) at -70°C The white suspension changed immediately to a light yellow solution After the mixture had been stirred 25 min , cyclopentanone (5 4g, 62 mmol) was added The solution was warmed to room temperature in 20 min , cooled to -10°C and methanesulfonyl chloride (7 1g, 62 mmol) in anhydrous ethyl ether (5 mL) was introduced A white precipitate of lithium chloride formed instantly The suspension was refluxed 25 min , cooled, diluted with ethyl ether (100 mL), washed with aqueous sodium chloride, dried ($MgSO_4$), filtered and evaporated

Table 1

CONVERSIONS OF ALDEHYDES AND KETONES TO ALLYLSILANES (**7**, Eq 2)

Carbonyl	Allylsilane (**7**)	Yield(%)[a]	^{1}H NMR (δ)[b]
		92	0.03 (s,9H) 1.39 (bd, 2H) 1.55 (bs,3H) 1.72 (bs,3H) 5.09 (bt,1H)
		92	0.05 (s,9H) 0.97 (m,6H) 1.50 (m,2H) 2.01 (bq,4H) 5.05 (bt,1H)
		95	0 05 (s,9H)[c] 1.65 (d, 2H) 6.10 (t,1H) 7.25 (m,10H)
		94	0.00 (s,9H) 1.38 (d,2H) 1.53 (m,6H) 2.04 (m,4H) 5.04 (bt,1H)
		94	-0.06 (s,9H) 1.29 (bd,2H) 1 59 (m,2H) 2.09 (m,2H) 5.19 (bt, 1H)
		95	-0 06 (s,9H) 1.14 (bd,2H) 1.84 (m, 2H) 2.54 (bq,4H) 4.94 (bt, 1H)
	 (E/Z)	85	0.05 (s,9H) 1.69 (m,8H) 5.70 (m,3H)
	 (E/Z)	92	0.20 (s,9H)[c] 1.90 (m,2H) 6.27 (m,2H) 7.30 (m,5H)

[a] The yields cited are based on the initial carbonyl compounds and refer to isolated pure **7**

[b] Spectra were recorded on a Varian EM-390 NMR spectrometer with CCl_4 as solvent Unless indicated, benzene was used as an internal NMR standard

[c] p-Dioxane was used as an internal standard

The colorless residue was dissolved without further purification in a mixture of methanol (50 mL) and disodium hydrogen phosphate (Na_2HPO_4; 35.2g, 0.25 mol) While cooling the resulting suspension to ~0°C, sodium-amalgam (6%, 75g) was added in small portions The reductive-elimination was completed in 1 hr The suspension was diluted with ethyl ether, decanted and vacuum-evaporated. The residue was diluted with petroleum ether (35-60°C, 100 mL), washed with water, dried ($MgSO_4$) and passed through a short silica gel column. After evaporation of the solvents, (2-trimethylsilylethylidene)cyclopentane (9.8g, 58.3 mmol, 94% yield; Table 1) was obtained Gas-liquid chromatography revealed that the product was greater than 98% pure.

Acknowledgement. This research was supported by the National Science Foundation and the State of Ohio

References and Footnotes

1 (a) T. H Chan and I Fleming, *Synthesis*, 761 (1979) (b) P. Magnus, *Aldrichimica Acta*, **13**, No 3, 43 (1980) and references therein

2. Syntheses of allylsilanes along with the references are reviewed in ref 1a. The principal present methodology for synthesis of allylsilanes involves (a) Wittig reactions of aldehydes and ketones with β-trimethylsilylethyltriphenylphosphonium salt-derived ylides, (b) silylation of allyl metal compounds, (c) equilibrative isomerization of allylsilanes by heat or fluoride ion, (d) reductive silylation of dienes, (e) thermal rearrangement of cyclopropyltrimethylsilanes and (f) Diels-Alder reactions of trimethylsilylbutadienes.[1a]

3 P J. Kocienski, *Tetrahedron Lett.*, 2649 (1979) reports reactions of alkyl halides with **4**, as derived from **3** and n-butyllithium, to give β-silylsulfones which undergo fluoride-induced elimination yielding terminal olefins. Similar findings were made independently in this laboratory See P J Kocienski, *J Org Chem* , **45**, 2037 (1980)

4. (a) All new compounds reported give satisfactory elemental analyses. (b) R K. Boeckman, Jr., D M Blum, B Ganem and N. Halvey, *Organic Syntheses*, **58**, 152 (1978)

5 The method of M Julia and J.-M Paris, *Tetrahedron Lett* , 4833 (1973) as modified by B M. Trost, H C Arndt, P E Strege, and T R VerHoeven, *ibid.*, 3477 (1976).

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