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1-BENZENESULFONYL-2-TRIMETHYLSILYLETHANE AND 1-BENZENESULFONYL-1-CHLORO-2-TRIMETHYLSILYLETHANE; EFFICIENT REAGENTS FOR SULFONYL-$\underline{\alpha}$-VINYLATION

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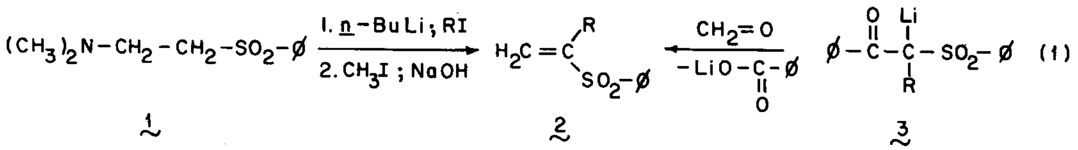
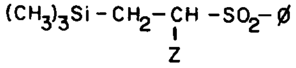
Abstract: 1-Benzenesulfonyl-2-trimethylsilylethane and 1-benzenesulfonyl-1-chloro-2-trimethylsilylethane are convertable to 1-benzenesulfonyl-1-chloro-1-substituted-2-trimethylsilylethanes which undergo elimination by fluoride ion to give phenyl $\underline{\alpha}$-substituted-vinyl sulfones.

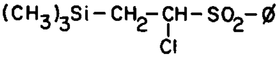
Vinyl sulfones ($H_2C{=}CH{-}SO_2{-}Ar$) are important in synthesis because of their varied addition reactions and the subsequent transformations about sulfone functionalities.[1] Recently 1-alkenyl aryl sulfones ($RCH{=}CH{-}SO_2Ar$) and methyllithium were found to give $\underline{\alpha}$-lithio derivatives ($RCH{=}CLi{-}SO_2{-}Ar$) at -95°C which react well with various electrophiles (RI, $R_2C{=}O$ and $(CH_3)_3SiCl$).[2a] Such methodology is inapplicable however to vinyl sulfones because of their Michael polymerization by alkyllithium reagents.[2b] Partial solutions which have been developed for synthesis of vinylic sulfones[2c] (2, Eq 1) are: (1) lithiation and monoalkylation of the Michael adduct (1) of dimethylamine and phenyl vinyl sulfone, quaternization and then Hofmann elimination[2b] and (2) condensation of formaldehyde with salts (3) of 1-benzoyl-1-alkyl phenyl sulfones, intramolecular benzoyl transfer and then benzoate elimination.[2d-e] Recently, 1-benzenesulfonyl-2-trimethylsilylethane (BSTMSE, 4)[3a-b] and its utility for preparing olefins[3a] and allyltrimethylsilanes[3b] via 1-benzenesulfonyl-1-lithio-2-trimethylsilylethane (5) were described. Practical syntheses of 2 from 5 are now reported.[4a] Further, 1-benzenesulfonyl-1-chloro-2-trimethylsilylethane (6), an even more versatile reagent, has been developed for general preparation of 2 and for 2-(benzenesulfonyl)allyl alcohols (7).[4a]





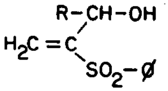
$(CH_3)_3Si-CH_2-\underset{Z}{CH}-SO_2-\phi$

4, Z = H
5, Z = Li



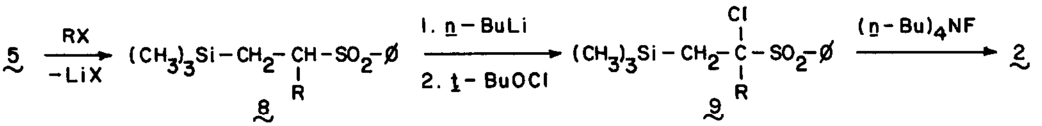
$(CH_3)_3Si-CH_2-\underset{Cl}{CH}-SO_2-\phi$

6



7

Vinyl sulfones 2 are now preparable (Eq 2) from 5 by alkylation at -70 to 25°C in ethyl ether,[4b] deprotonation of the resulting 2-benzenesulfonyl-1-trimethylsilylalkanes (8) with $\underline{n}$-butyllithium (1 equiv) at -70°C in ethyl ether, chlorination with $\underline{t}$-butyl hypochlorite (1 equiv) at -70°C (~3 sec) and elimination of chlorotrimethylsilane from the resulting 2-benzenesulfonyl-2-chloro-1-trimethylsilylalkanes (9) with tetra-$\underline{n}$-butylammonium fluoride at ~25°C (10 min) in tetrahydrofuran. The operations summarized in Table 1 are remarkably effective and satisfying.



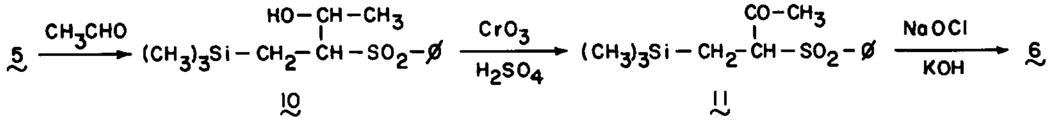
$$5 \xrightarrow[-\text{LiX}]{\text{RX}} \underset{8}{(CH_3)_3Si-CH_2-\underset{R}{\underset{|}{CH}}-SO_2-\varnothing} \xrightarrow[2.\ t\text{-BuOCl}]{1.\ n\text{-BuLi}} \underset{9}{(CH_3)_3Si-CH_2-\overset{Cl}{\overset{|}{\underset{R}{\underset{|}{C}}}}-SO_2-\varnothing} \xrightarrow{(n\text{-Bu})_4NF} 2 \qquad (2)$$

Table 1

Yields of 8, 9 and 2 from 1-Benzenesulfonyl-1-lithio-2-trimethylsilylethane (5; Eq 2)

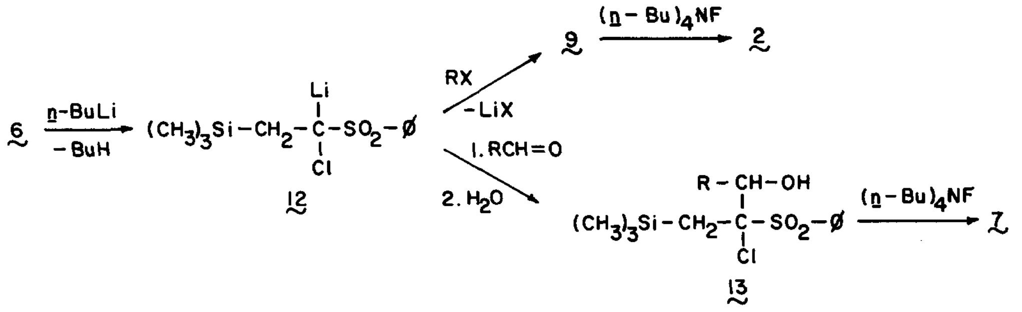
RX	8, %	9, %	2, %	RX	8, %	9, %	2, %
CH_3CH_2Br	95	95	> 99	$(CH_3)_3C(CH_2)_2Br$	89	90	> 99
$CH_3(CH_2)_3Br$	93	95	> 99	$H_2C=CHCH_2Br$	96	92	> 99
$CH_3(CH_2)_5I$	97	92	> 99	$\varnothing CH_2Br$	90	65	> 99

Synthesis of 6 was then developed. Monochloride 6 is obtainable from 5 and *t*-butyl hypochlorite. Under various conditions, however, the 6 is contaminated with 1-benzenesulfonyl-1,1-dichloro-2-trimethylsilylethane $[\phi\text{-}SO_2\text{-}CCl_2\text{-}CH_2\text{-}Si(CH_3)_3]$[4a] as derived by deprotonation of 6 and subsequent chlorination. Condensation of 5 with acetaldehyde (Eq 3) and aqueous work-up to give 3-benzenesulfonyl-4-trimethylsilyl-2-butanol (10), oxidation of 10 with chromic acid/acetone (Jones oxidation) to 3-benzenesulfonyl-4-trimethylsilyl-2-butanone (11) and then chlorination of 11 in suspension in potassium hydroxide/*p*-dioxane with supermarket sodium hypochlorite result in pure 6, a readily-handled solid (mp 53°C). The preparative sequence (Eq 3) is efficient, rapid, usable on large scale and highly recommended.



$$5 \xrightarrow{CH_3CHO} \underset{10}{(CH_3)_3Si-CH_2-\overset{HO-CH-CH_3}{\overset{|}{CH}}-SO_2-\varnothing} \xrightarrow[H_2SO_4]{CrO_3} \underset{11}{(CH_3)_3Si-CH_2-\overset{CO-CH_3}{\overset{|}{CH}}-SO_2-\varnothing} \xrightarrow[KOH]{NaOCl} 6 \qquad (3)$$

Chlorosulfonylsilane 6 in ethyl ether is converted quantitatively to 1-benzenesulfonyl-1-chloro-1-lithio-2-trimethylsilylethane (12) by *n*-butyllithium at -70°C. Lithio reagent 12 is storable for at least 5 hr without change at -70°C but decomposes upon warming to room temperature. In the presence of added HMPA, 12 effects efficient displacement of varied primary halides (Eq 4).[4b] The alkylation products, 9, are identical with those of Equation 2 and are converted to pure vinyl sulfones 2 in impressive yields by fluoride ion (Eq 4). Examples which illustrate the general method are summarized in Table 2. When synthesis of more than one vinylic sulfone (2) is an objective, the methodology of Equation 4 is preferable to that of Equation 2 because by use of 6 as a general reagent the number of different chlorinations is kept minimal.



(4)

(5)

Table 2

Yields of 2 and 7 from 1-Benzenesulfonyl-1-chloro-1-lithio-2-trimethylsilylethane(12; Eq 4 and 5).

RX	2, %	RCH=O	7, %
$CH_3(CH_2)_3Br$	94	$(CH_3)_2CHCHO$	92
$CH_3(CH_2)_5I$	96	$CH_3(CH_2)_2CHO$	95
$CH_2=CHCH_2Br$	94	c-$C_6H_{11}CHO$	95
øCH_2Br	96	øCHO	90
CH_3OCH_2Cl	97	$CH_2=CHCHO$	94

Lithio reagent 12 also reacts well with other electrophiles. Thus 12 adds rapidly to the carbonyl groups of varied aldehydes[4c] in ethyl ether at -70°C (HMPA is not necessary) to give, after hydrolysis, 2-benzenesulfonyl-2-chloro-3-trimethylsilyl-1-propanols (13, Eq 5) in high yields and excellent purities. Alcohols 13 then undergo elimination smoothly with tetra-*n*-butylammonium fluoride to give 7 efficiently. Table 2 reveals typical results for conversion of 6 to 7 as in Equation 5. The present methods thus extend significantly previous routes to 2 and 7. Procedures for synthesis of 6 (Eq 3) and a representative of 2 (Eq 4) and 7 (Eq 5), respectively, are described below.[4d]

1-Benzenesulfonyl-1-chloro-2-trimethylsilylethane (6). Acetaldehyde (10 g, 0.227 mol) was added to 5 prepared by syringing *n*-butyllithium (53.5 ml, 1.7 M in hexane, 90.9 mmol) into 4 (20.0 g, 82.6 mmol) suspended in ethyl ether at -70°C. After 20 min and then addition of aqueous ammonium chloride at -70°C, the resulting ether solution was washed with brine, dried, filtered and concentrated to 10, a colorless oil. Acetone (100 mL) and then Jones reagent (1.86 M, 200 mL)[5] were added (20 min) to 10 at 0-5°C and, after 1 hr, the resulting suspension was washed with water and with aqueous sodium bicarbonate, dried, filtered and concentrated to 11 (22.7 g, 97%), white crystals (mp 67°C, from petroleum ether).[4a]

Potassium hydroxide (10 g) and chlorine bleach (5.25% NaOCl, 300 mL) were added to 11 (20 g, 70.42 mmol) in dioxane (70 mL). The heterogeneous mixture was stirred 2.5 hr, diluted with ethyl ether and washed with water. The ether extract was dried, filtered and concentrated to 6 (19.3 g, 99%), an oil which crystallized completely, mp 53°C (from hexane/ethyl acetate; 20:1).[4a]

2-Benzenesulfonyl-3-phenyl-1-propene. n-Butyllithium (1.6 mL, 1.7 M in hexane, 2.72 mmol) was syringed under nitrogen into **6** (0.7 g, 2.53 mmol) in ethyl ether (10 mL) at -70°C. The yellow solution was stirred 15 min and benzyl bromide (0.6 g, 3.50 mmol) and then HMPA (2.5 mL) were added. The mixture was warmed to -30°C, stirred 15 min, diluted with ethyl ether (200 mL), washed with water, dried and evaporated. The residue was dissolved in tetrahydrofuran (4 mL) and tetra-n-butylammonium fluoride (5 mL, 1 M in THF, 5 mmol) was added. After 10 min the mixture was diluted with ethyl ether, washed with water, dried, concentrated and passed through a silica gel column. Elution with petroleum ether (35-60°C) and then methylene chloride and evaporation yielded 2-benzenesulfonyl-3-phenyl-1-propene (0.63 g, 2.44 mmol, 96%), a light yellow oil,^{4a} ^{1}H-NMR (δ, CCl_4) 3.50 (bs, 2 H), 5.30 (t, 1 H, J=1.5 Hz), 6.27 (bs, 1 H) and 6.85-7.95 (m, 10 H).

2-Benzenesulfonyl-1-cyclohexyl-2-propen-1-ol. Cyclohexanecarboxaldehyde (0.3 g, 2.67 mmol) was added to **12** prepared from **6** (0.7 g, 2.53 mmol) and n-butyllithium (1.6 mL, 1.7 M in hexane, 2.72 mmol) in ethyl ether (10 mL) at -70°C. The mixture was stirred at -70°C for 30 min, quenched with aqueous ammonium chloride (10 mL) and extracted with ethyl ether (100 mL)/ methylene chloride (50 mL). The organic phase was dried, concentrated, treated in tetrahydrofuran (5 mL) with tetra-n-butylammonium fluoride (5 mL, 1 M solution in THF, 5 mmol) at ~25°C (10 min), diluted with water and extracted with ethyl ether. Evaporation of the dried ether extract gave a colorless oil which crystallized to 2-benzenesulfonyl-1-cyclohexyl-2-propen-1-ol (0.67 g, 95%), mp 76°C from petroleum ether (35-65°C)/ethyl acetate (5:1).^{4a}

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4. (a) All new compounds give proper analyses and appropriate mass, NMR and IR spectra. (b) Displacements do not occur satisfactorily with secondary halides. (c) 3-Benzenesulfonyl-2-methyl-3-buten-2-ol is preparable (91%) from acetone and **12** as in Eq 5. However, 2-butanone condenses poorly with 12 and 3-pentanone does not, apparently because of steric factors. (d) Reactions of **12** with other kinds of electrophiles will be summarized in a subsequent publication.

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