Tetrahedron Letters,Vol.24,No.23,pp 2371-2374,1983 0040-4039/83 $3.00 + .00
Printed in Great Britain

1-LITHIO-1-BENZENESULFINYL-2-TRIMETHYLSILYLETHANE AS A 2-TRIMETHYLSILYLVINYL ANION EQUIVALENT IN REACTIONS WITH ALDEHYDES, KETONES AND EPOXIDES

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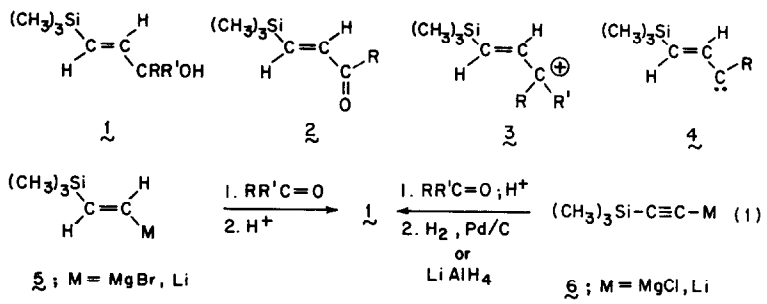
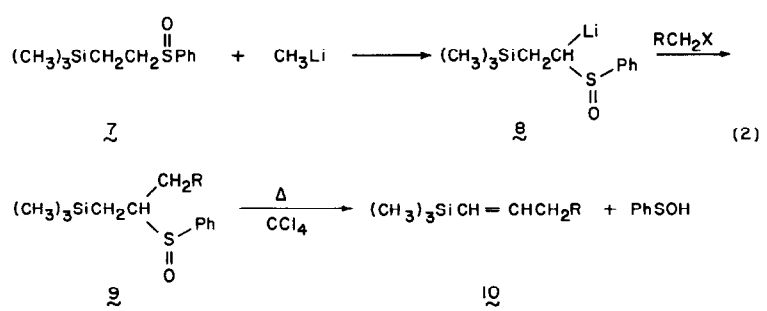
Abstract: Aldehydes, ketones and epoxides give adducts with 1-lithio-1-benzenesulfinyl-2-trimethylsilylethane which upon neutralization eliminate benzenesulfenic acid efficiently at 76°C to yield trans-3-(trimethylsilyl)allyl alcohols and trans-4-(trimethylsilyl)-3-alken-1-ols.

3-(Trimethylsilyl)allyl alcohols (1) and β-trimethylsilylvinyl aldehydes (2, R=H) and ketones (2, R=alkyl and aryl) are important in synthesis.[1a-g] In this laboratory derivatives of 1 and 2 are of interest with respect to their cationic (3) and carbenic (4) intermediates. Preparations of 1 have previously involved (1) condensations of carbonyl compounds with trans-2-trimethylsilylvinylmetallo reagents (5, Eq. 1),[1c,e,g] (2) reactions of aldehydes and ketones with metallotrimethylsilylacetylenes (6, Eq. 1) followed by partial reduction (H_2/Pd/C or $LiAlH_4$) of the triple bonds[1a,b,d,f] and (3) addition of organometallics to 2.[1f] Although the conversions to 1 are generally acceptable, method 1 suffers because the precursors to 5 are not readily available,[2] method 2 is extended because of the hydrogenation step and method 3 usually involves synthesis of lower primary and secondary 3-(trimethylsilyl)allyl alcohols (1, R=H) and their oxidations to 2 with pyridinium dichromate, manganese dioxide or nickel peroxide.[1d,f]

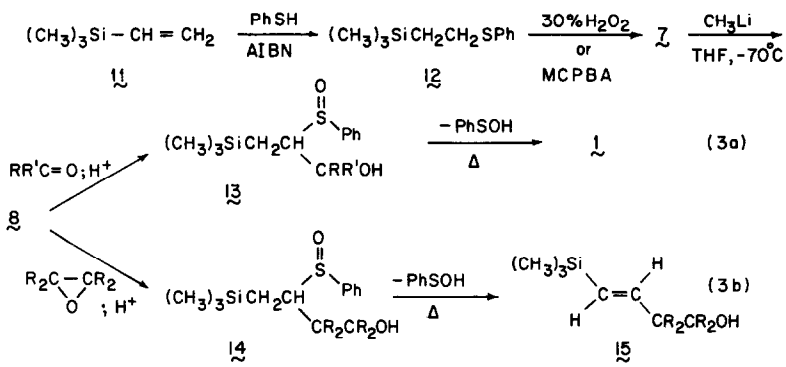


Recently 1-benzenesulfinyl-2-trimethylsilylethane (7, Eq. 2), prepared (58%) from methyl



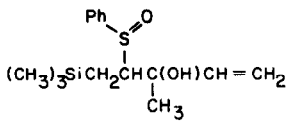
phenyl sulfoxide and n-butyllithium and then trimethylsilylmethyl iodide in tetrahydrofuran/hexamethylphosphoramide, has been converted by methyllithium to 1-lithio-1-benzenesulfinyl-2-trimethylsilylethane (8), alkylation of which by propyl and by benzyl halides yields 2-benzenesulfinyl-1-trimethylsilylalkanes (9).[3] Of note is that 9 eliminates benzenesulfenic acid regiospecifically (98-88%) at 76°C to give (E)- and (Z)-1-trimethylsilyl-1-alkenes (10).[3]

As a continuation of previous development of 1-thiophenoxy-2-trimethylsilylethane (12)[4a,b] as a reagent, we now describe an advantageous large-scale synthesis of 7 and its use via 8 as a convenient, efficient equivalent for 5 for conversion of varied aldehydes and ketones to 1. Such allyl alcohols (1) which are primary and secondary are efficiently oxidized to 2 by pyridinium dichromate. The value of 8 as a synthon is illustrated further by its reactions with epoxides leading to trans-4-(trimethylsilyl)-3-alken-1-ols (15) in good yields. Preparation of 7 and the sequences for conversion of 8 to 1 and 15 are summarized in Eq. 3a,b.



As described earlier, 12 is readily obtained in quantity by homolytic addition of thiophenol to trimethylvinylsilane (11).[4a] Upon oxidation with meta-chloroperbenzoic acid in methylene chloride at -70°C, or with 30% hydrogen peroxide in refluxing acetone, 12 is converted to 7 in 90-98% yields on large scale. Deprotonation of 7 by methyllithium in tetrahydrofuran occurs readily at -70°C to give 8, a reactive nucleophile which adds rapidly to the carbonyl groups of various aldehydes and ketones at -70°C to give 2-benzenesulfinyl-3-trimethylsilyl-1-propanols (13) upon neutralization. If desired, 13 can be isolated pure by crystallization from petroleum ether (35-60°C)/ethyl acetate (10:1). It is convenient however to dissolve the crude alcohols (13) in carbon tetrachloride and effect their decomposition to 1 at reflux (∿20 min). The benzenesulfenic acid produced is removable from 1 by distillation[4c] or by oxidation with 30% hydrogen peroxide to benzenesulfonic acid followed by extraction with aqueous sodium bicarbonate. Table 1 summarizes the overall results of transformations of 7 to 1. Eliminations of 13 occur essentially stereospecifically to give 1 of trans-stereochemistry. The activating effects of the trimethylsilyl groups leading to the specific regiochemistry of decomposition are so great that 13, as derived from 7 and various aldehydes, do not eliminate to any detectable quantities of 1-trimethylsilyl-3-carbonyl derivatives via possible enol intermediates, $RC(OH)=CHCH_2Si(CH_3)_3$.[4d] The conjugated unsaturated aldehydes, acrolein and trans-cinnamaldehyde, undergo 1,2-addition of 8 to their carbonyl groups. Methyl vinyl ketone reacts with 8 however by competitive 1,2 and 1,4-addition processes in 70:30 ratio to give 2-benzenesulfinyl-

3-methyl-1-trimethylsilyl-4-penten-3-ol (16) and 5-benzenesulfinyl-6-trimethylsilyl-2-hexanone (17), decomposition of which yields trans-3-methyl-1-trimethylsilyl-1,4-pentadien-3-ol (18) and trans-6-trimethylsilyl-5-hexen-2-one (19). Reagent 8 is thus of promise in reactions of the Michael type with appropriate activated systems.



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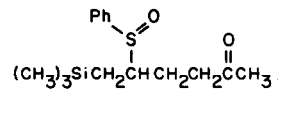

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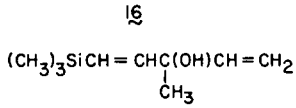

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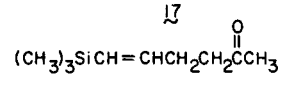

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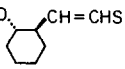
Epoxides undergo nucleophilic ring-opening by 8 in tetrahydrofuran at 25-30°C to yield after hydrolysis, 3-benzenesulfinyl-4-trimethylsilyl-1-alkanols (14). Regiospecific displacement on primary carbon in propylene oxide and in 1-butene oxide occurs with facility (~100%, ~1 hr); cyclohexene oxide is significantly retarded (57%, 36 hr). The resulting silylsulfinylalkanols (14) are readily isolable oils and decompose regiospecifically to 15 in refluxing carbon tetrachloride. The overall conversions of epoxides to 15 are satisfactory and are summarized in Table 1.

Table 1. Conversions of Aldehydes, Ketones and Epoxides by 8 to 1 and 15, Respectively[a]

$CH_2=O$	$HOCH_2CH=CHSi(CH_3)_3$	85[b]	$(CH_2)_3C=O$	$(CH_2)_3C(OH)CH=CHSi(CH_3)_3$	81[c]
$CH_3CH=O$	$CH_3CH(OH)CH=CHSi(CH_3)_3$	70[b]	$(CH_2)_4C=O$	$(CH_2)_4C(OH)CH=CHSi(CH_3)_3$	89[c]
$(CH_3)_2CHCH=O$	$(CH_3)_2CHCH(OH)CH=CHSi(CH_3)_3$	75[b]	$(CH_2)_5C=O$	$(CH_2)_5C(OH)CH=CHSi(CH_3)_3$	84[c]
$H_2C=CHCH=O$	$H_2C=CHCH(OH)CH=CHSi(CH_3)_3$	63[b]	$(CH_2)_{11}C=O$	$(CH_2)_{11}C(OH)CH=CHSi(CH_3)_3$	89[c]
$ØCH=O$	$ØCH(OH)CH=CHSi(CH_3)_3$	79[c]			
$ØCH=CHCH=O$	$ØCH=CHCH(OH)CH=CHSi(CH_3)_3$	84[c]	H_2C-CH_2 (O)	$HOCH_2CH_2CH=CHSi(CH_3)_3$	71[b]
$(CH_3)_2C=O$	$(CH_3)_2CH(OH)CH=CHSi(CH_3)_3$	75[b]	CH_3CH-CH_2 (O)	$CH_3CH(OH)CH_2CH=CHSi(CH_3)_3$	78[b]
$(C_2H_5)_2C=O$	$(C_2H_5)_2C(OH)CH=CHSi(CH_3)_3$	84[c]	$C_2H_5CH-CH_2$ (O)	$C_2H_5CH(OH)CH_2CH=CHSi(CH_3)_3$	83[b]
$Ø_2C=O$	$Ø_2C(OH)CH=CHSi(CH_3)_3$	45[c]			57[c]

[a] All vinyltrimethylsilanes prepared are of trans stereochemistry. [b] Yield of isolated product upon vacuum distillation. [c] Yield of isolated product after column chromatography.

Typical procedures for synthesis of 7[5] and 1 are described subsequently. Many of 1 have been efficiently oxidized to 2 with pyridinium dichromate. Study of 3 and 4 has been initiated.

1-Benzenesulfinyl-2-trimethylsilylethane (7). Meta-chloroperbenzoic acid (MCPBA, 80-85% assay, 52 g) was added slowly to 12 (50 g, 238 mmol) in dichloromethane (750 mL) at -70°C. The white suspension was stirred at -70°C for ∿1 hr, filtered and most of the dichloromethane removed under vacuum. The residue was diluted with ethyl ether (500 mL), washed with 25% aqueous sodium metabisulfite (100 mL), saturated aqueous sodium bicarbonate and brine, dried ($MgSO_4$), filtered and evaporated. The 7 (52.7 g, 98%) obtained is a colorless oil sufficiently pure for efficient conversion to 8 without further purification; ^{1}H NMR (CCl_4, δ) 0.10 (s, 9H), 0.65-1.05 (m, 2H), 2.50-2.90 (m, 2H) and 7.60 (m, 5H).

Trans-1-(2-trimethylsilyl)vinyl-1-cyclohexanol. Methyllithium (20 mL, 1.4 M in ethyl ether, 28.0 mmol) was syringed into a solution of 1-benzenesulfinyl-2-trimethylsilylethane (7, 6.0 g, 26.5 mmol) in anhydrous tetrahydrofuran (45 mL) at -70°C. After the light yellow mixture had stirred 20 min, cyclohexanone (2.60 g, 26.5 mmol) was added. The mixture was stirred 45 min at -70°C, quenched with aqueous ammonium chloride, diluted with ethyl ether/chloroform (1:1) and washed with water. The organic extract was dried ($MgSO_4$), concentrated and the colorless residue diluted with carbon tetrachloride (50 mL), refluxed 20 min and evaporated. The light yellow oily residue was diluted with acetone (35 mL) and sodium bicarbonate (10 g) and 30% hydrogen peroxide (20 g, 176.5 mmol) were added. Upon refluxing the mixture for 30 min and vacuum-removing the acetone, the residue was diluted with ethyl ether, washed with brine, dried ($MgSO_4$), filtered and concentrated. The concentrate was passed through a short silica gel column and eluted with hexane and then benzene. Evaporation gave trans-1-(2-trimethylsilyl)vinyl-1-cyclohexanol (4.4 g, 22.2 mmol, 84%) as a colorless oil which crystallized completely upon standing, mp 38°C; ^{1}H NMR (CCl_4, δ) 0.10 (s, 9H), 1.00 (s, 1H), 1.40-1.90 (m, 10H) and 5.75, 5.95, 6.10, 6.20 (q, AB system, 2H).

Acknowledgement: This research was supported by the National Science Foundation.

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4. (a) C.-N. Hsiao and H. Shechter, Tetrahedron Lett., 1963 (1982). (b) C.-N. Hsiao and H. Shechter, ibid., 3455 (1982). (c) Benzenesulfenic acid converts to benzenesulfinic acid and thiophenol on heating. (d) It is not yet clear whether hydroxyl groups actually retard elimination to enols.

5. Reaction of 12 with 30% hydrogen peroxide (1.5 equiv) in refluxing acetone (3 hr) carried to 95% completion and column chromatography also gives 7 (90%) effectively.

(Received in USA 31 January 1983)