

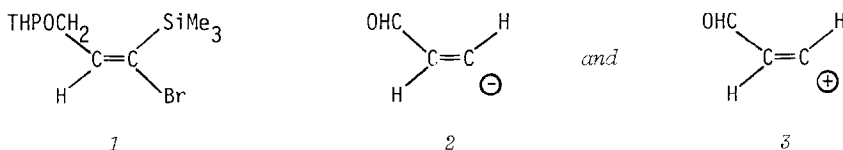
THE TETRAHYDOPYRANYL ETHER OF (E)-3-BROMO-3-TRIMETHYLSILYL-2-PROPEN-1-OL,
 A SINGLE SYNTHON FOR THE (E)- β -FORMYLVINYL ANION AND CATION

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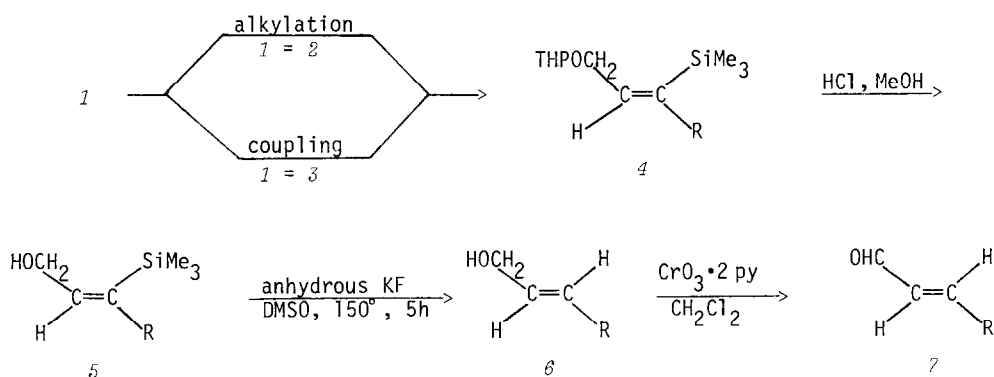
Summary. The tetrahydropyranyl ether of (E)-3-bromo-3-trimethylsilyl-2-propen-1-ol can serve as a single synthon for both the (E)- β -formylvinyl anion and cation depending upon the manner in which the bromine group is stereospecifically replaced by an alkyl group.

Based on our earlier work¹ using 1-bromo-1-trimethylsilyl olefins as intermediates in a highly stereoselective trisubstituted olefin synthesis, it was proposed that the tetrahydropyranyl ether of (E)-3-bromo-3-trimethylsilyl-2-propen-1-ol (**1**) could serve as a single synthon for the (E)- β -formylvinyl anion² (**2**) and cation (**3**) if a stereospecific method for



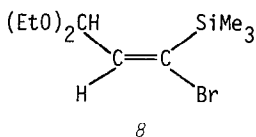
cleaving the vinyl carbon-silicon bond could be found. A successful demonstration of the proposed route is the subject of this communication and is shown in Scheme I.

Scheme I

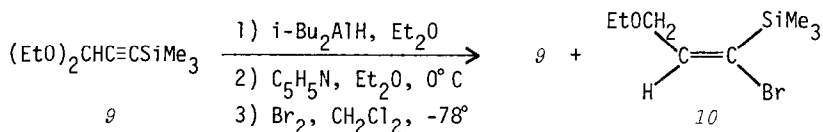


R = Me, *n*-Bu, *sec*-Bu

Originally, it was proposed to use the diethoxy acetal of (E)-3-bromo-3-trimethylsilyl-2-propenal (*8*) as the single synthon for both *2* and *3* but this compound could not be prepared.

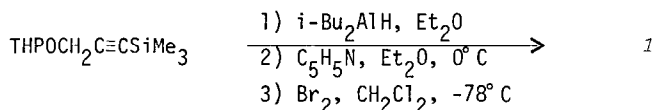


Attempts to prepare *8* by hydroalumination of 1,1-diethoxy-3-trimethylsilyl-2-propyne (*9*)^{3,4} followed by bromination of the intermediate vinylalane were unsuccessful. Instead of the desired acetal *8*, these reaction conditions gave a 4:6 mixture of unreacted *9* and (E)-1-bromo-3-ethoxy-1-trimethylsilyl-1-propene (*10*). The formation of *10* presumably came from

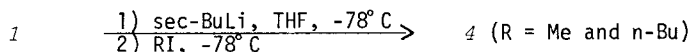


initial diisobutylaluminum hydride cleavage of the acetal⁵ to give a monoethoxy trimethylsilylpropyne which underwent hydroalumination followed by bromination in the expected manner. Because of the inability to prepare *8*, attention was directed to derivatives of (E)-3-bromo-3-trimethylsilyl-2-propen-1-ol in which the protecting group could be easily removed.

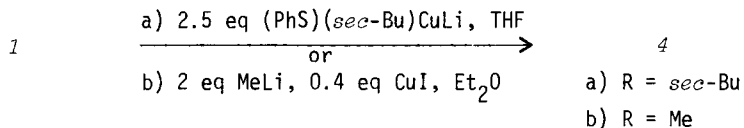
The tetrahydropyranyl ether of (E)-3-bromo-3-trimethylsilyl-2-propen-1-ol (*1*)³ was prepared in 80% isolated yield⁶ with >99% of the (E)-isomer being obtained by hydroalumination-bromination⁷ of the tetrahydropyranyl ether of 3-trimethylsilyl-2-propyn-1-ol.⁸



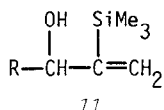
The utilization of *1* as a synthon for the (E)- β -formylvinyl anion (*2*) involved conversion of the vinyl bromide *1* to a vinyl lithium reagent *via* halogen-metal exchange with *sec*-butyllithium (1.2 eq) in tetrahydrofuran at -78°C followed by alkylation with either methyl iodide or *n*-butyl iodide at -78°C .⁹ The desired alkylated products *4* were obtained in 75% isolated yield with >99% of the (Z)-isomer present with no noticeable amount of the protonated material¹ (*4*, R=H) being formed.



To use *1* as a synthon for the (E)- β -formylvinyl cation (*3*), it was necessary to reverse the polarity utilized in the alkylation process. This was accomplished by coupling the vinyl bromide *1* with cuprate reagents.¹ Thus *1* upon reaction with (PhS)(*sec*-Bu)CuLi in tetrahydrofuran gave *4* (R = *sec*-Bu) in 65% isolated yield and upon reaction with methyl lithium and 20 mol % copper iodide in diethyl ether gave *4* (R = Me) in 75% isolated yield.



Attempts at cleavage of the vinyl carbon silicon bond by electrophilic reagents such as hydroiodic acid, either as such or generated *in situ* from iodine and water,¹⁰ or benzene-sulphenic acid¹¹ were unsuccessful on both the tetrahydropyranyl ethers **4** or the corresponding alcohols **5**. However it was found that reaction of the alcohols **5**, prepared in 89-91% isolated yield by treatment of **4** with a few drops of 3*N* hydrochloric acid in methanol at room temperature, with anhydrous potassium fluoride in dimethyl sulfoxide at 150°C gave the allylic alcohols **6** in 70-80% isolated yield with >99% of the (E)-isomer present (see Scheme I). This reaction is similar to Chan's observation¹² that allylic alcohols with the structural requirement shown in **11** can be induced to undergo silicon-vinyl carbon bond cleavage with fluoride ion. In Chan's study, however, if the hydroxyl group and the silicon were more than three bonds apart cleavage



did not occur. In our case the hydroxyl group and silicon are four bonds apart and cleavage not only occurs but does so stereospecifically.

Finally, the allylic alcohols **6** were oxidized to the corresponding (E)-β-substituted acroleins **7** using chromium trioxide-pyridine in methylene chloride¹³ in 80-86% isolated yields with >99% of the (E)-isomer being obtained. Thus **1** can indeed serve as a single synthon for both the (E)-β-formyl vinyl anion (**2**) and cation (**3**) depending on the manner in which the alkyl group in **4** is introduced.

Preparation of the Tetrahydropyranyl Ether of (E)-3-Bromo-3-trimethylsilyl-2-propen-1-ol (1): In a 500 mL, three-necked, round-bottomed flask, fitted with two addition funnels and a low temperature thermometer, was placed 20 g (94 mmol) of the tetrahydropyranyl ether of 3-trimethylsilyl-2-propyn-1-ol⁸ in 95 mL of anhydrous diethyl ether. To this solution was added 19.21 mL of 5.4*M* diisobutylaluminum hydride (103.7 mmol, 1.1 eq, Ethyl Corp.) at such a rate that the temperature did not rise above 5°C (ice bath). The resulting mixture was warmed to room temperature and stirred for 30 min, then stirred at 40°C for 3h. At the end of this time the solution was cooled to 0°C (ice bath) and 95 mL of anhydrous diethyl ether and 15.2 mL (188 mmol) of pyridine were added. The yellow solution was next cooled to -78°C (Dry Ice/acetone bath) and a solution of 22.6 g (141 mmol, 1.5 eq) of bromine in 47 mL of methylene chloride was added at a rate such that a temperature <-60°C was maintained. The resulting bright yellow suspension was washed into a separatory funnel containing 3*N* sodium hydroxide, ice, and pentane. After shaking and separating, the aqueous layer was thoroughly extracted with fresh pentane. The combined organic layers were washed twice with ice-cold 1*N* sulfuric acid and once with saturated sodium bicarbonate solution. After drying over anhydrous sodium sulfate the solvent was removed by rotary evaporation in the presence of some solid sodium carbonate. The colorless residue was distilled under reduced pressure in the presence of solid sodium carbonate to afford 22 g (75

mmol, 80% yield) of colorless product. GLC analysis revealed the product to be >99% the (E)-isomer: bp 68-69°C (10^{-4} torr); IR (neat) 2970 (s), 2890 (m), 1600 (m), 1450 (m), 1250 (s), 1120 (s), 1020 (s), 840 (s), 740 (m) cm^{-1} ; NMR (CCl_4) δ^{*14} 0.00 (s, 9H, $(\text{CH}_3)_3\text{Si}$), 1.35 (m, 6H, $\text{-(CH}_2\text{)}_3\text{-}$), 3.1-3.9 (m, 4H), 4.35 (m, 1H, O-CH-O), 6.6 (t, J = 7Hz, HC=C). Anal. Calcd. for $\text{C}_{11}\text{H}_{21}\text{O}_2\text{Si}$: C, 45.05; H, 7.22. Found: C, 44.96; H, 7.03.

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