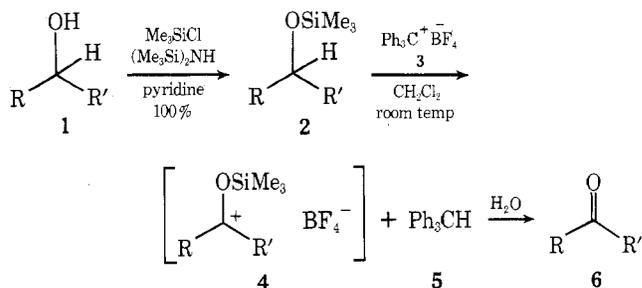


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 (13) Bromination of acetate **8b** is anticipated to be most favorable at the two bridgehead positions labeled A and B in structure **8** shown in Scheme I. Ionic attack of bromine at site A yields the trans isomer **9a**, whereas attack at site B affords the corresponding cis bromoacetate (**10a**). Since the two stereoisomers failed to separate on silica gel TLC and attempts to separate the mixture via fractional crystallization were unsuccessful at this stage as well as after subsequent reactions, no further attempt was made to determine the stereochemistry of the reaction products.
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 (15) Reactions were carried out under a nitrogen atmosphere. The isolation of reaction products was accomplished by extracting the aqueous layer thoroughly with the specified solvent. Anhydrous sodium sulfate was used to dry the combined extracts, and the solvent was removed on a rotary evaporator under reduced pressure. Melting points were determined on a Fisher-Johns block and are corrected. The NMR spectra were recorded with a Varian A-60 NMR spectrometer and infrared spectra were obtained using a Beckman IR-12 spectrophotometer. Elemental analyses were performed by the Analytical Resources and Methods Department, Searle Laboratories, G. D. Searle & Co.



The oxidation of alkyl ethers to carbonyl compounds by trityl salts has been observed previously¹ but only recently has this become a useful synthetic method. Barton has used this technique in the oxidation of ketone acetals and in the deprotection of steroidal benzyl ethers and carbonates.² Doyle has also employed this oxidation in the disproportionation of trityl alkyl ethers by a cationic chain reaction process.³ The trimethylsilyl ethers were chosen for the present study for several reasons. First, they could be quickly and easily prepared in quantitative yields. Secondly, the amount of simple complexation of the trityl salt and the ether oxygen could be lessened because of steric hindrance between the very bulky trimethylsilyl group and the trityl cation. Finally, it was anticipated that the trimethylsilyl group could provide additional stabilization to the carbonium ion β to it by a mechanism of vertical stabilization such as in **7**. This is completely analogous to the all-carbon case, **8**, which has been shown to offer a great deal

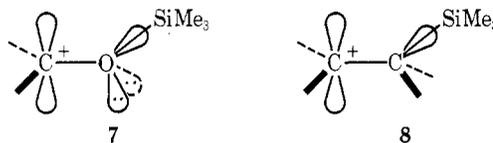
Oxidation of Trimethylsilyl Ethers via Hydride Abstraction. A New Method for Alcohol Oxidation

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Received January 8, 1976

I wish to report a new method for the oxidation of alcohols to ketones and aldehydes under extremely mild conditions in nearly quantitative yields. The key step of this two-step procedure involves the treatment of the trimethylsilyl ethers **2** of the alcohols **1** with a triphenylcarbonium (trityl) salt **3** in methylene chloride at room temperature. The carbonyl compounds **6** are produced cleanly and can be easily isolated from the by-product, triphenylmethane (**5**), by simple distillation or chromatography. A variety of alcohols have been subjected to this new oxidation technique, the products and yields of which are listed in Table I.

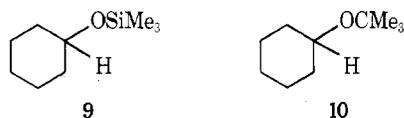


of stabilization.⁴ For example, the Hammett electrophilic para-substitution constant, σ_p^+ , for the trimethylsilylmethyl group (Me_3SiCH_2) is -0.66 .⁴ This very closely approximates the value for the methoxyl group (MeO), $\sigma_p^+ = -0.74$,⁴ implying in a general sense that a trimethylsilyl group β to a carbonium ion stabilizes that ion to about the same extent as a methoxyl group α to it. Therefore it was anticipated that the stability of the carbonium ion, e.g., **4**, could be enhanced by changing the group attached to oxygen from alkyl to trimethylsilyl. In agreement with this expectation the silyl ether **9** is oxidized somewhat faster than the *tert*-butyl ether **10** under identical conditions, although **10** also gives cyclohexanone in reasonable yield. However, this result is not conclusive because the difference in rates may be due to other effects, e.g., steric effects, since the

Table I. Oxidation of Trimethylsilyl Ethers with $\text{Ph}_3\text{C}^+\text{BF}_4^-$ ^a

Starting alcohol	Registry no.	Product ^b	Registry no.	% yield ^c
	123-96-6		111-13-7	95
	108-93-0		108-94-1	99 (92)
	589-82-2		106-35-4	98
	100-51-6		100-52-7	100
	104-54-1		104-55-2	100
	111-70-6		111-71-7	38

^a All reactions were conducted in CH_2Cl_2 at 25 °C under a nitrogen atmosphere. ^b The products were identified by comparison (GC, NMR, ir) with authentic samples. ^c The yields were determined by gas chromatographic analysis through reference to an internal standard, normally mesitylene. The numbers in parentheses are isolated yields. The yields of triphenylmethane are all 100%.

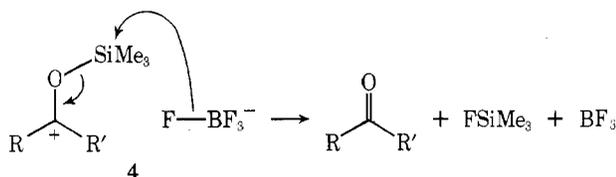


tert-butyl group is somewhat bulkier than the trimethylsilyl group.

The crude trimethylsilyl ether **2**, produced from the alcohol **1** by silylation in a few minutes at room temperature, is generally >95% pure and can be used directly in the oxidation step without further purification.

In all of the reported reactions trityl tetrafluoroborate (**3**) was employed as the hydride abstractor.⁵ It is commercially available,⁶ although it can be easily prepared in two steps from benzene and carbon tetrachloride by the method of Dauben.⁷ The progress of the oxidation can be easily monitored by GC or NMR. Reaction times range from 1 min for the cinnamyl ether to 4 days for the 2-octyl ether. Thus far the reaction is not very useful for saturated aldehydes. The rate of oxidation is very slow and the aldehyde begins to decompose before the reaction is completed. All of these oxidations can be speeded up by using refluxing dichloroethane as solvent, but this causes some decomposition of the carbonyl products.⁸

Analysis of the crude reaction mixtures by NMR indicates the presence of the carbonyl compound before addition of water. This implies that the cation **4** probably decomposes by attack of a fluoride ion from BF_4^- to give the carbonyl compound and Me_3SiF directly. To support this



hypothesis, when the reaction mixture is heated, one can detect the evolution of an acidic gas, probably BF_3 or Me_3SiF . It is postulated that hydride abstraction is a discrete step that precedes fluoride transfer to silicon. The alternative of a concerted pathway involving concomitant hydride abstraction and fluoride transfer is unlikely for entropy reasons, since it would require the correct alignment of three distinct species in the transition state, namely, the trityl cation, the silyl ether, and the tetrafluoroborate anion.

Since the ethers of primary alcohols oxidize slower than those of secondary alcohols (stability of a secondary vs. a tertiary carbonium ion), we are now pursuing the use of this procedure in oxidizing a primary, secondary diol to the primary hydroxy ketone. In addition, the oxidations of silylated amines to carbonyl compounds⁹ and of silyl enol ethers to enones,¹⁰ as well as other oxidations, are currently being investigated.

Experimental Section

The following is a typical experimental procedure.

Cyclohexanone. Cyclohexanol was converted into its trimethylsilyl ether **9** by stirring for a few hours at room temperature with a silylating solution consisting of pyridine, hexamethyldisilazane, and trimethylchlorosilane in the ratio of 10:2:1. A solution of the crude ether **9** (1.72 g, 10 mmol) and Ph_3CBF_4 (**3**, 4.95 g, 15 mmol) in 200 ml of CH_2Cl_2 was allowed to stir at room temperature under nitrogen. After 9 h, GC analysis of an aliquot showed completion of reaction. Addition of water, extraction, and distillation afforded 901 mg of cyclohexanone (92% yield).

Acknowledgment. The author wishes to acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

Registry No.—**2** ($\text{R} = \text{CH}_3$; $\text{R}' = \text{C}_6\text{H}_{13}$), 18023-52-4; **2** ($\text{R} = \text{C}_2\text{H}_5$; $\text{R}' = \text{C}_4\text{H}_9$), 18132-91-7; **2** ($\text{R} = \text{H}$; $\text{R}' = \text{C}_6\text{H}_5$), 14642-79-6; **2** ($\text{R} = \text{H}$; $\text{R}' = \text{PhCH}=\text{CH}$), 18042-41-8; **2** ($\text{R} = \text{H}$; $\text{R}' = \text{C}_6\text{H}_{13}$), 18132-93-9; **3**, 341-02-6; **9**, 13871-89-1; Me_3SiCl , 75-77-4; $(\text{Me}_3\text{Si})_2\text{NH}$, 999-97-3.

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- Trityl salts with different counterions, e.g., PF_6^- , SbF_6^- , were also employed, as well as other hydride abstracting reagents. A comparison of the reactivities will be described elsewhere.
- Commercial samples from both the Aldrich Chemical Co. and Cationics, Inc. were used successfully.
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- Solid Na_2CO_3 was added in an attempt to trap any acidic products which might be causing decomposition (e.g., BF_3), but without significant effects. Acetonitrile was also employed but the oxidation was very slow in this solvent.
- M. E. Jung and G. S. Tennyson, unpublished results.
- M. E. Jung and Y.-G. Pan, unpublished results.

trans- β -Trimethylsilylvinylithium

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Received November 21, 1975

In connection with other investigations we required a synthetically useful preparation of *trans*- β -trimethylsilylvinylithium (**2**). This reagent was unavailable at the time this work was begun, but has since been prepared by the reaction of *trans*- β -bromovinyltrimethylsilane with either lithium metal¹ or *tert*-butyllithium.² Synthetically useful yields of the reagent are realized by only the latter of these two methods. Our approach, different from either of these, but also affording excellent yields of **2**, is presented here.

The preparation of **2** involved the transmetalation reaction between organolithium reagents and vinyltin substrates developed by Seyferth and co-workers.³ Thus, treatment of either *trans*-1-trimethylsilyl-2-triphenylstannylethylene (**1a**) or *trans*-1-trimethylsilyl-2-tri-*n*-butylstannylethylene (**1b**) with respectively phenyllithium or *n*-butyllithium led to high yields of **2**, as determined by subsequent derivatization (eq 1).

Although the transmetalation of **1a** with phenyllithium could be effected at 25 °C to afford, after trimethylchlorosilane derivatization, 84% of *trans*-1,2-bis(trimethylsilyl)ethylene (**3**), the reaction of **1b** with *n*-butyllithium gave better results at low temperature. Thus, **3** was obtained in only 53% yield from the transmetalation of **1b** at 25 °C, but 90% of **3** was afforded when transmetalation was effected at -70 °C.⁴ The reaction of **2** with a variety of other electrophiles was examined in order to assess its utility in this regard. As shown in eq 1, *trans*-1-bromo-2-trimethylsilyl-ethylene (**4**), *trans*-1-trimethylsilyl-1-hexene (**5**), and *trans*-3-trimethylsilylpropenoic acid (**6**) were all obtained in excellent yield. NMR and VPC analysis of these products indicated the absence of detectable amounts of corresponding *cis* isomers.

Of particular interest was the observation that the present procedure led to preparatively useful conversions