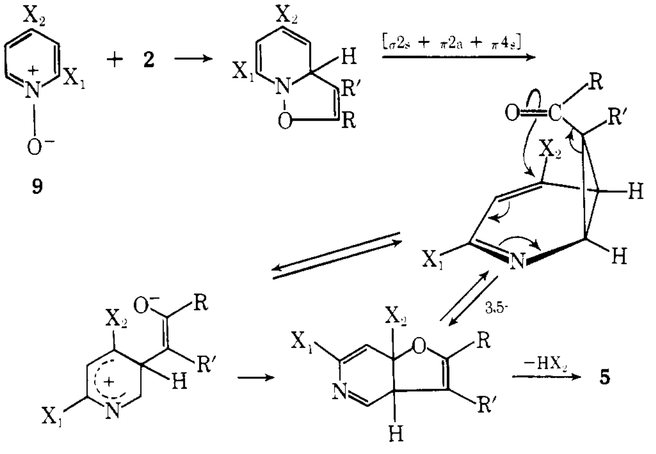
Scheme II



Extension of the synthetic scope of this reaction and investigation of aspects of the mechanisms of the rearrangements observed are under study.

Acknowledgment. We wish to thank the National Institutes of Health (Grant No. GM-16626) for support of this work.

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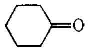
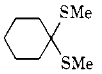
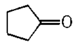
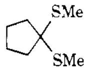
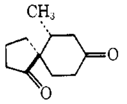
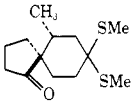
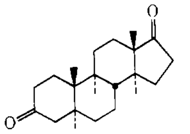
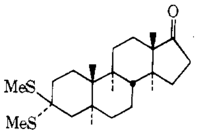
Methylthiotrimethylsilane. A Versatile Reagent for Thioketalization under Neutral Conditions

Sir:

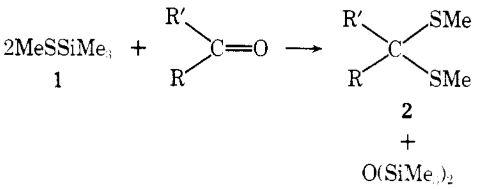
It is now well recognized that silicon is an excellent oxygenophile, and as such, a host of useful synthetic methods have been developed which exploit this property.[1] As a class, alkylthiosilanes[2] have gone virtually unrecognized as potentially useful reagents in organic synthesis[3] although such silicon derivatives are easily prepared by a variety of methods.[2,4]

During an investigation into the chemistry of organosulfur derivatives of silicon, we have developed an exceptionally mild procedure for thioketalization *which proceeds without the apparent requirement of acid catalysis* (eq 1). We have found that methylthiotrimethylsilane, TMS–SMe (**1**),[5] reacts spontaneously at 0° with aldehydes and ketones to give dimethylthioketals, **2**, in excellent yields (Table I). Reaction solvents such as C_6H_6, CH_3CN, CH_2Cl_2, and Et_2O may be employed with equal success; however, the overall reaction rate of thioketalization appears to be proportional to solvent polarity. The following is a general procedure for thioketalization.

Table I. Thioketalization with TMS–SMe (eq 1)

RRC=O	2[a]	% yield[b]	bp (mp), °C
C_6H_5CHO	$C_6H_5CH(SMe)_2$[c]	90	35 (0.04 mm)
$CH_3(CH_2)_5CHO$	$CH_3(CH_2)_5CH(SMe)_2$[d]	88	48 (0.06 mm)
		90	35 (2.0 mm)
		93	39 (2.0 mm)
		93	(70–71)
		92	(156–158)

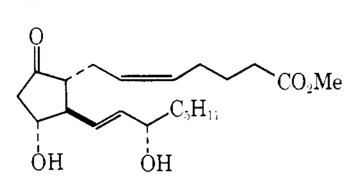
[a] Consistent spectral data and combustion analyses have been obtained on all compounds shown. [b] Isolated yields. [c] A. Schonberg and K. Praefcke, *Chem. Ber.*, **100**, 778 (1967). [d] J. M. Lalancette, Y. Beavregard, and M. Bhereur, *Can. J. Chem.*, **49**, 2983 (1971). [e] V. J. Morgenstern and R. Mayer, *J. Prakt. Chem.*, **34**, 116 (1966). [f] K. Grimm, P. S. Venkatrami, and W. Reusch, *J. Am. Chem. Soc.*, **93**, 270 (1971).



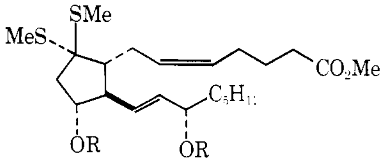
$$\underset{\mathbf{1}}{2MeSSiMe_3} + RR'C{=}O \longrightarrow \underset{\mathbf{2}}{RR'C(SMe)_2} + O(SiMe_3)_2 \qquad (1)$$

To a cooled (0°) solution of ketone or aldehyde in anhydrous ether is added dropwise 2 equiv of TMS–SMe (**1**) over a 15-min period. After the addition is completed, the reaction is allowed to stir at room temperature for 2 hr. Addition of water and extraction with ether or methylene chloride are followed by drying (Na_2SO_4), removal of solvents, and filtration through alumina (activity III) to remove minor impurities.

This mild carbonyl derivatization procedure may be further illustrated by the conversion of PGE_2 methyl ester (**3**) into the dimethylthioketal **4b** in 37% overall yield.[6] Treatment of **3** with 4 equiv of TMS–SMe in acetonitrile at 0° afforded **4a** which was hydrolyzed (MeOH, H_2O, HOAC; 20:2:1) to **4b** following literature precedent.[7]

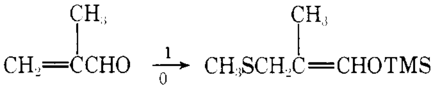


3



4a, R = TMS
b, R = H

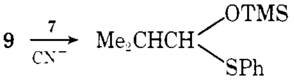
The reactions of thiosilanes such as **1** with α,β-unsaturated aldehydes and ketones depart from the traditional path that is normally observed in thioketalization. For example, **1** spontaneously reacts with methacrolein (**5**) without catalysis at 0° in methylene chloride to give the 1,4-adduct **6** in 82% yield (bp 82-83°, 3 mm) as a 2:1 mixture of *E* and *Z* isomers. This uncatalyzed mode of addition has been observed for a wide variety of unsaturated carbonyl compounds, and in no instance was 1,2-addition detected.



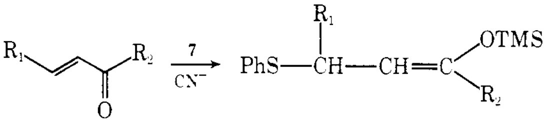
$$CH_2{=}C(CH_3)CHO \xrightarrow[0]{1} CH_3SCH_2C(CH_3){=}CHOTMS$$

5 6

In contrast to TMS-SMe (**1**), other silanes such as phenylthiotrimethylsilane (**7**)[4c] react only slugglishly at elevated temperatures (100-150°, 2-4 days) with carbonyl derivatives. However, in the presence of anionic initiators such as potassium cyanide-18-crown-6 (0.01 equiv) or potassium ethylthiolate-crown complex,[8] stoichiometric amounts of **7** and isobutyraldehyde (**9**) (25°, neat, 20 hr) react to give the adduct **10** (bp 71°, 0.05 mm) in 81% yield. Under similar conditions, unsaturated aldehydes **11a** and **11b** reacted exothermically to give adducts **12a** (86%, bp 87-89°, 0.02 mm) and **12b** (90%, bp 90-92°, 0.02 mm) as a mixture of *E* and *Z* isomers.[9] The catalyzed addition of **7** to methyl vinyl ketone (**11c**) and cyclohexenone (**13**) proceeds with equal facility to give **12c** (86%, bp 85-86°, 0.03 mm) and **14** (88%, bp 117-119°, 0.16 mm), respectively.



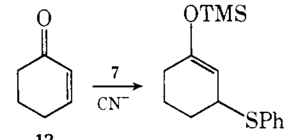
10



11a-c

12a-c

a, $R_1 = H$; $R_2 = H$
b, $R_1 = CH_3$; $R_2 = H$
c, $R_1 = H$; $R_2 = CH_3$



13

14

In conclusion, the high reactivity of TMS-SMe (**1**) is quite surprising. Other silanes such as **7** and even ethylthiotrimethylsilane, TMS-SEt, are quite unreactive by comparison. The mechanistic details of these interesting transformations must await further study.

Acknowledgment. We wish to thank the Upjohn Company for a sample of PGE_2 and the National Institutes of Health and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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(5) TMS–SMe may either be prepared according to ref 4a or more conveniently as follows. To a mechanically stirred suspension of 125 mmol of $LiAlH_4$ in 500 ml of anhydrous ether was added dropwise 250 mmol of dimethyl disulfide. After heating at reflux for 1 hr, a solution of 68 g of Me_3SiCl (distilled from CaH_2) in 50 ml of ether was added dropwise. The resulting gelatinous precipitated aluminum salts may be transformed into a granular solid by heating for several hours followed by stirring at 25° (12 hr). Filtration of the inorganic salts under an inert atmosphere followed by fractional distillation of the filtrate afforded the desired **1,** bp 110–111° in 65–70% yield. TMS–SMe is exceptionally moisture sensitive and should be handled accordingly.

(6) The mass spectrum (70 eV) of **4b** revealed fragment ions at *m/e* 426 (P-18), 408 (P − 36) and 99. The fragment ion at 426 exhibited an exact mass of 426.2263 (calcd for $C_{23}H_{38}O_3S_2$: 426.2262). All other spectral data are consistent with the assigned structure.

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(8) D. A. Evans and L. K. Truesdale, *Tetrahedron Lett.*, 4929 (1973); see footnote 9 for catalyst preparation.

(9) Triphenylphosphine is also an excellent initiator for thiosilane addition to α,β-unsaturated ketones and aldehydes.

(10) Camille and Henry Dreyfus Teacher–Scholar Recipient (1971–1976); Alfred P. Sloan Fellow (1972–1974).

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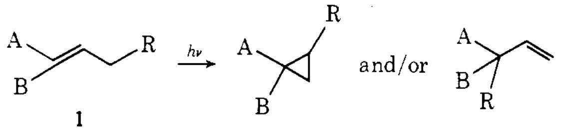
An Unusual Mechanism for 1,3-Hydrogen Migration in the Photochemistry of 4-Methyl-1,1,4-triphenyl-1-pentene

Sir:

Upon irradiation many systems of the type **1**, in which R = H, alkyl, benzyl, or allyl and the olefinic group is either a simple olefin or part of a diene, styrene, or diphenylethylene system, undergo a 1,2- and/or 1,3-shift of the group R (eq 1).[1] As a start in determining the influence of various types of substitution on the course of rearrangement of such systems we chose to study the photochemistry of the diphenylethylene derivative **2**. Our findings, which proved most unusual and interesting, are presented here.



1 (1)

Irradiation[2] of a cyclohexane solution of **2** provided, slowly, one major product isolated in 36% yield at 69% conversion of **2**. The formation of other minor products in quantities too small to allow identification as well as high molecular weight material was also noted. Spectral data on the major product indicated it had the structure **3**. The NMR spectrum showed a singlet for the geminal methyls at τ 8.58, a doublet ($J_{1,2} = 7.0$ Hz) for the benzhydryl hydrogen at 5.24, a doublet ($J_{2,3} = 15.0$ Hz) for the C-3 vinyl hydrogen at 4.28, and a doublet of doublets for the C-2 vinyl hydrogen at 4.05. The magnitude of $J_{2,3}$ is indicative of a trans arrangement of hydrogens on the double bond. This stereochemistry is supported by the strong band at 974 cm^{-1} in the infrared spectrum of **3**. Confirmation of the structure of **3** was provided by its ozonolysis to approxi-