where A is the percent isomer to be determined, A apparent = (cpm in peak A/cpm A + cpm B) × 100, and k is percent optical impurity in the resolving reagent (3.75).[34]

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Thiosilanes, a Promising Class of Reagents for Selective Carbonyl Protection

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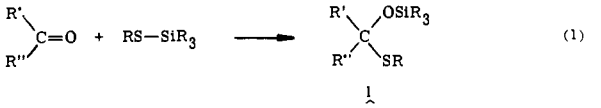
Abstract: The thermal and catalyzed carbonyl addition reactions of alkyl- and arylthiosilanes, $RSSiMe_3$, have been studied. Contrary to earlier literature reports, it has been found that thiosilanes react with aldehydes and ketones to form either thioketals or *O*-silylhemithioketals when various acid catalysts are employed. With α,β-unsaturated ketones and aldehydes anion-initiated reactions result in exclusive 1,4-addition. The synthetic procedures reported in this paper constitute an exceptionally mild procedure for selective carbonyl protection.

In recent years organosilicon derivatives have played an ever increasing role in synthetic organic chemistry.[2] Much of the logic behind the development of organosilane reagents has relied upon the "proton-silicon correlation". For example, organosilanes undergo a number of thermal rearrangements[3] which phenomenologically have their direct counterparts in analogous proton systems.[4] A number of other processes such as olefin hydrosilylation,[5] carbonyl silicon pseudohalide[6] addition,[7] and silicon transfer to Lewis bases[8] are just a few of the other reactions of tetravalent silicon for which the proton analogy can be drawn. Organosulfur derivatives of silicon have been extensively studied over the years and a multitude of methods have been developed for their synthesis.[9,10] Based upon the relatively weak silicon-sulfur bond (ca. 70 kcal/mol)[11] these reagents should be good oxygenophiles. However, little definitive work has been reported on the applications of these reagents to useful synthetic transformations.[12]

The aims at the outset of this study were to develop organosilicon reagents that would selectively mask carbonyl groups under exceptionally mild conditions (eq 1-3). In part, our in-



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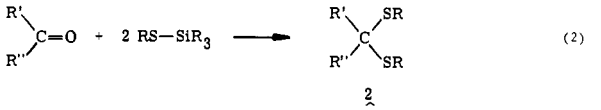

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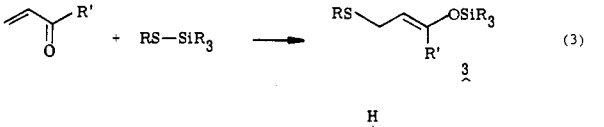

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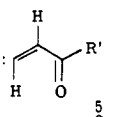
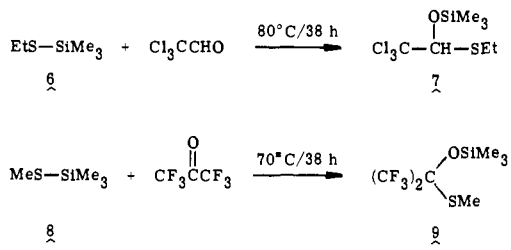


5

terest in these adducts was based upon our anticipation that such adducts could be transformed into the useful "reversed polarity" equivalents such as **4** and **5** upon metalation, and that such carbonyl derivatization reactions should serve as useful selective carbonyl protection operations in chemical synthesis.

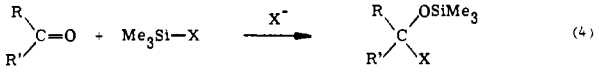
Literature reports that ethylthiotrimethylsilane (**6**) reacted slowly (80 °C, 36 h) with chloral to afford the adduct **7**, and that methylthiotrimethylsilane (**8**)[10a] added to hexafluoroacetone under similar conditions (70 °C, 36 h) to give **9**[12d]



suggest that, even with highly reactive carbonyl substrates, uncatalyzed thiosilane carbonyl addition is not a facile process. Our own previous studies on the carbonyl addition reactions of trimethylsilyl cyanide[14] suggested to us that the conditions employed by previous workers to effect thiosilane carbonyl addition may have been deceptively harsh and that such reactions should be facilitated by anionic as well as Lewis acid catalysts.

Results and Discussion

Nucleophilic Catalysis of Organosilane Carbonyl Insertion Reactions. We have found that a variety of carbonyl addition reactions of silicon derivatives, Me_3SiX, may be effectively initiated by the addition of small amounts (ca. 0.01 equiv) of nucleophiles X^- (eq 4). Typical reactions of this type that have



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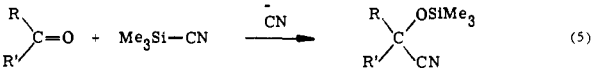
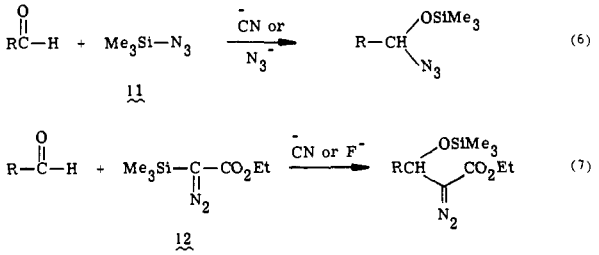
been investigated are the addition of trimethylsilyl cyanide (**10**) to aldehydes and ketones (eq 5), a reaction which is dramati-



(5)

cally catalyzed by traces of cyanide ion.[14] In an analogous fashion the addition of trimethylsilyl azide (**11**) to aldehydes may be initiated by both azide and cyanide ion (eq 6).[14c] More recently we have found that anionic catalysis is effective in promoting the carbonyl insertion reactions of α-silyl diazoacetate **12** where other modes of catalysis have failed (eq 7).[14e]



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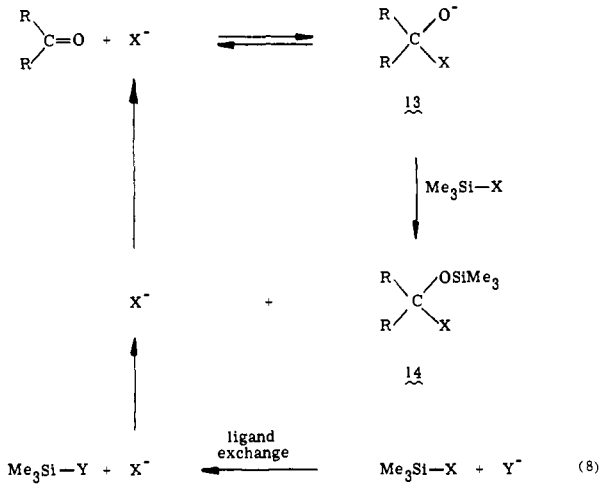
(7)

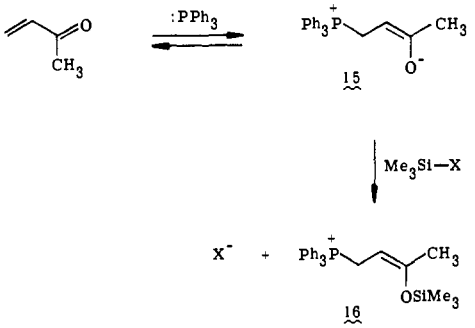
As illustrated in Scheme I, the presumed mode of nucleophilic catalysis in the above cases involves carbonyl addition of X^- affording equilibrium concentrations of **13**, which is converted to adduct **14** by subsequent bimolecular silicon transfer. This catalytic model suggests that any nucleophile, X^- or Y^-, which is either capable of carbonyl addition or of effecting ligand exchange on silicon (eq 8) should initiate the

Scheme I



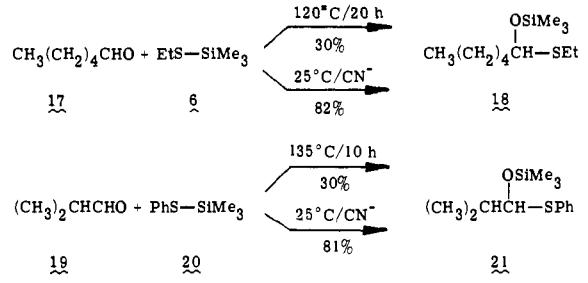
(8)

carbonyl addition process. We have found that potassium cyanide–crown ether complexes, tetra-*n*-butylammonium cyanide, as well as tetra-*n*-butylammonium fluoride all appear to be efficient initiators for organosilane carbonyl addition. For addition reactions with many unsaturated ketones and aldehydes as well as quinones, we have also found that triphenylphosphine (0.01 equiv) is a convenient initiator. The mode of initiation in this instance presumably involves the phosphine-initiated liberation of X^- via the reaction sequence illustrated below. Evidence that phosphonium enolates such as **15** are actually formed and can be trapped by silanes has been demonstrated by treating a benzene solution of methyl vinyl ketone with 1 equiv of triphenylphosphine and chlorotrimethylsilane, whereupon the crystalline phosphonium chloride **16** (X = Cl) has been isolated in excellent yield.[15] In addition



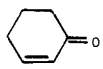
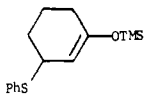
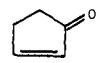
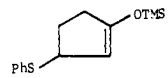
to our own observations on nucleophilic catalysis of organosilane carbonyl addition reactions, several other recorded examples have appeared.[16]

In agreement with earlier reports,[12d,12f] we have found that thiosilanes react slowly with aldehydes at elevated temperatures in the absence of catalysts. For example, heating equimolar amounts of *n*-hexanal (**17**) and ethylthiosilane **6** at 100 °C for 20 h resulted in the formation of only 30% of the adduct **18**. Similar results were obtained on attempted thermal addition of the phenylthiosilane **20** to isobutyraldehyde (**19**) to give adduct **21**. The dramatic effect of anionic initiation in this



addition process was observed when the analogous reactions

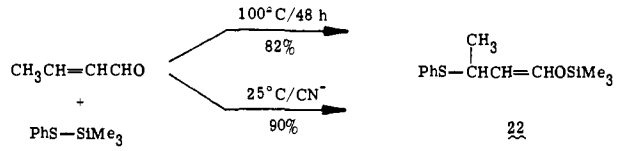
Table I. Anion-Initiated Thiosilane–Carbonyl Addition Reactions (eq 1, 3)[a]

Substrate	RS-TMS[b]	Adduct	% Yield[c]
PhCHO	EtS-TMS	PhCH(OTMS)-SEt 22	95
$CH_3(CH_2)_4CHO$	EtS-TMS	$CH_3(CH_2)_4CH(OTMS)$-SEt 18	82
$(CH_3)_2CHCHO$	PhS-TMS	$(CH_3)_2CH(OTMS)$-SPh 21	81
$CH_2=CHCHO$	PhS-TMS	PhS-CH_2CH=CHOTMS 23	86
$CH_3CH=CHCHO$	PhS-TMS	PhS-CH(CH_3)CH=CHOTMS 24	90
	EtS-TMS	EtS-CH(CH_3)CH=CHOTMS 25	90
$CH_2=C(CH_3)CHO$	PhS-TMS	PhS-CH_2C(CH_3)=CHOTMS[d] 26	91 (> 95)
$CH_3CH=C(CH_3)CHO$	PhS-TMS	PhS-CH(CH_3)C(CH_3)=CHOTMS[d] 27	86
	EtS-TMS	EtS-CH(CH_3)C(CH_3)=CHOTMS 28	92
$CH_2=CHC(=O)CH_3$	PhS-TMS	PhS-CH_2CH=C(CH_3)-OTMS[d] 29	86
	PhS-TMS	 30	88
	PhS-TMS	 31	(> 95)

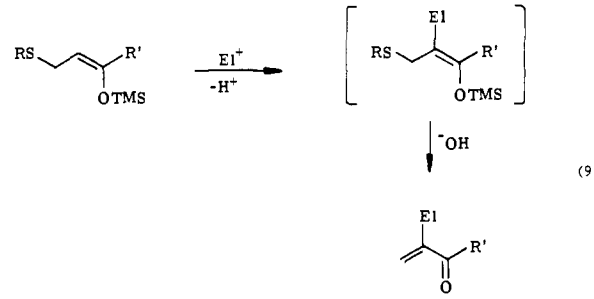
[a] Unless otherwise specified the catalyst employed was cyanide ion. [b] TMS refers to trimethylsilyl (–$SiMe_3$). [c] Values correspond to distilled adduct. Those in parentheses refer to yields determined by GLC. [d] Triphenylphosphine was also employed as an initiator.

were repeated in the presence of small amounts of either tetra-*n*-butylammonium cyanide,[17] tetra-*n*-butylammonium fluoride,[18] or potassium cyanide–18-crown-6 complex.[19] The reaction of hexanal and **6** in the presence of anionic initiators proceeded exothermically at 25 °C to afford the mixed acetal **18** in 82% yield, while the phenylthiosilane **20** and aldehyde **19** gave the adduct **21** in 81% yield. In general, it has been observed that phenylthiosilanes are somewhat less reactive than alkylthiosilanes toward carbonyl addition; however, the reactivity differences are not great. *Both alkyl- and arylthiosilanes show high selectivity toward addition to aldehydes; however, we were unable to effect addition, in general, to ketonic substrates employing anionic initiators.* This could be explained either by assuming that the equilibrium constant for adduct formation is small or that anionic catalysis generally fails with ketone substrates, possibly due to the unfavorable equilibrium in the formation of intermediate **13**, X = SR (Scheme I).

The reactions of α,β-unsaturated aldehydes and ketones with phenylthiosilane **20** and ethylthiosilane **6** proceeded very slowly at elevated temperatures. However, in the presence of cyanide, thiolate, or fluoride ions, the addition process occurred exothermically at 25 °C. *In every case examined 1,4 addition was the exclusive reaction pathway.* These results strongly contrast to the reactions of trimethylsilyl cyanide (**10**) with enones which exhibit exclusive 1,2-addition.[14b,14d] Typical yields and conditions for the thermal as well as anionic initiated addition of **20** to α,β-unsaturated substrates are illustrated below. The list of systems studied is shown in Table I. In all cases the thiosilane addition process was carried out in excellent yield under exceptionally mild conditions. The specific initiator catalyst such as cyanide or fluoride ion does not exhibit any system dependence in the cases studied.



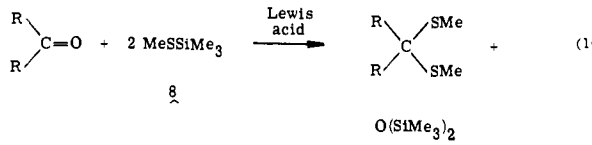
This remarkably facile enone masking operation could prove to be useful in enone–electrophile (El^+) condensation processes of the general type illustrated below (eq 9). The recent silyl enol



(9)

ether mediated carbonyl condensation reactions reported by Mukaiyama might be relevant cases for examination.[20]

Lewis Acid Catalysis of Organosilane Carbonyl Insertion Reactions. In contrast to an earlier literature report,[10a] we have found methylthiotrimethylsilane (**8**) to be exceptionally reactive toward carbonyl substrates, the consequence of this reaction being the dimethylthioketal (eq 10).[21] This observa-

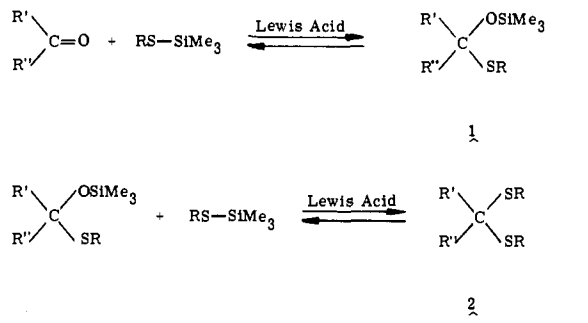


(10)

tion is in marked contrast to the low level of reactivity of both ethylthiosilane **6** and phenylthiosilane **20** toward uncatalyzed carbonyl insertion. As a result of the present study (vide supra) we can now state unequivocally that *the observed reactions of aldehydes and ketones with methylthiotrimethylsilane* (*8*) *were initiated by trace quantities of Lewis acids.*[21]

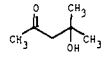
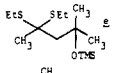
Under the influence of acid catalysts such as zinc iodide, aluminum chloride, or anhydrous hydrogen chloride in solvents such as ether, chloroform, and acetonitrile, thiosilanes react rapidly (ca. 30 min) with both aldehydes and ketones at room temperature to give the *O*-trimethylsilyl hemithioacetals or ketals **1**, respectively (Scheme II). In the presence of a second

Scheme II



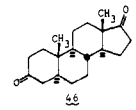
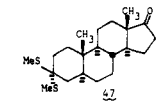
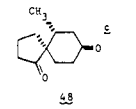
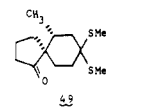
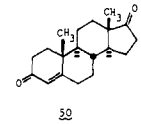
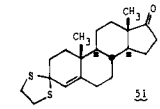
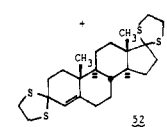
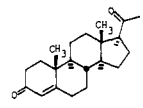
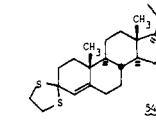
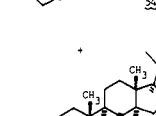
equivalent of thiosilane under the same reaction conditions the

Table II. Acid-Catalyzed Thiosilane Mediated Thioketalization (eq 2)[a]

Entry		RS-TMS[b]	Adduct		Yield (%)[c]
1		MeSTMS (8)	$CH_3(CH_2)_5CH(SMe)_2$[d]	32	88
2	$CH_3(CH_2)_5CHO$	EtSTMS (6)	$CH_3(CH_2)_5CH(SEt)_2$	33	92
3		TMSS$(CH_2)_3$STMS (61)	$CH_3(CH_2)_5CH$ 	34	75
4		8	$(CH_3)_2CH(SMe)_2$	35	85
5	$(CH_3)_2CH-CHO$	6	$(CH_3)_2CH(SEt)_2$	36	92
6		61	$(CH_3)_2CH$ 	37	70
7	C_6H_5CHO	8	$C_6H_5CH(SMe)_2$	38	90
8	$C_6H_5COCH_3$	6	$C_6H_5-C(SEt)_2-CH_3$	39	93
9	$C_2H_5COC_2H_5$	6	$(C_2H_5)_2C(SEt)_2$	40	91
10		61	$(C_2H_5)_2C$ 	41	95
11		8		42	93
12		6		43	98
13		6[d]	 [e]	44	92
14	$CH_2=C(CH_3)-CHO$	8	$MeSCH_2C(CHOTMS)CH_3$	45	82

[a] All reactions were catalyzed with ZnI_2. [b] TMS refers to trimethylsilyl ($SiMe_3$). [c] Values refer to isolated yields. [d] J. M. Lalancette, Y. Beavegard, and J. M. Bhereur, *Can. J. Chem.*, 49, 2983 (1971). [e] Since thiosilanes are effective silylating agents, 3 equiv of thiosilane must be employed in such cases.

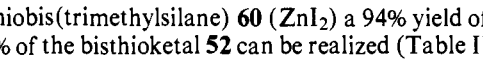
Table III. Selective Thioketalization via Thiosilanes[a]

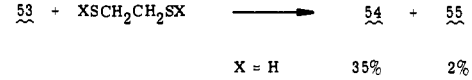
Entry	Carbonyl Substrate	$RSSiMe_3$	Adduct	Yield (%)[b]
1	 46	$MeSSiMe_3$ 8	 47	92
2	 48	$MeSSiMe_3$ 8	 49	93
3	 50	$Me_3SiS(CH_2)_2SSiMe_3$ 61	 51 +  52	94 + 5
4	 53	$Me_3SiS(CH_2)_2SSiMe_3$ 60	 54 +  55	94 + 4

[a] All reactions catalyzed with ZnI_2. [b] Values refer to isolated yields. [c] K. G. Grimm, P. S. Venkatrami, and W. Reuschl, *J. Am. Chem. Soc.*, 93, 270 (1971).

thioketals **2** are produced in nearly quantitative yields after ca. 8–24 h. We have found that the use of thiosilanes in these thioketalization processes holds a great deal of promise as an exceptionally mild procedure for effecting carbonyl derivatization. Although several solvents have been examined (CH_2Cl_2, C_6H_6, CH_3CN) we have found that conditions involving the use of diethyl ether as a solvent and zinc iodide (ca. 10^{-2} molar equiv) as the acid catalyst have been most convenient for effecting thioketalization under mild conditions (0–25 °C). A summary of the scope of this method for carbonyl thioketalization is included in Table II. These data indicate that the structure of the thiosilane, $RSSiMe_3$, does *not* play a significant role in the thioketalization process and that monothiosilanes as well as dithiosilanes may be employed with equal facility. When employing anhydrous zinc iodide as an acid catalyst we have not observed the formation of vinyl sulfides, which frequently arise from subsequent acid-catalyzed elimination of the thioketal adducts of monothiosilanes. In addition, the mildly acidic nature of these reactions is illustrated in the conversion of diacetone alcohol to the corresponding diethylthioketal **44** without any evidence of dehydration (Table II, entry 13). The reactions of α,β-unsaturated aldehydes such as α-methylacrolein with monoalkylthiosilanes (entry 14) under the influence of zinc iodide depart from the traditional reactions that enone substrates follow with thiols. In such cases the Michael adduct **45** is the observed product. This reaction path is the same as that observed under the influence of anionic catalysis (cf. Table I).

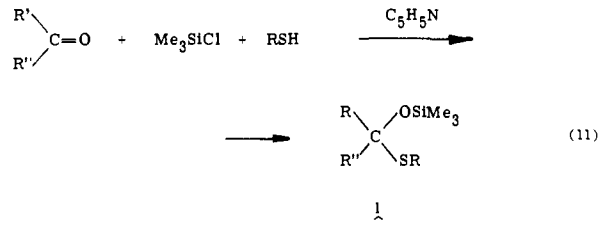
An examination of the general levels of selective monothioketalization of a variety of diketones reveals that high levels of carbonyl differentiation can be expected (Table III). In the selective monothioketalization of 4-androstene-3,17-dione (**50**) with ethanedithiol (*p*-toluenesulfonic acid), a 76% yield of the 3-ethylenethioketal **51** and 10% of the bisthioketal **52** has been reported.[22] In contrast, by employing ethylenedithiobis(trimethylsilane) **60** (ZnI_2) a 94% yield of **51** and only 5% of the bisthioketal **52** can be realized (Table III, entry 3). A similar comparison of the two thioketalization[22] procedures for progesterone (**53**) illustrates the same two points: the yield of monothioketal **54** is higher when the thiosilane reagent is employed; and carbonyl selectivity is enhanced (cf. Table III, entry 4).





The Synthesis of *O*-Silylhemithioacetals and Ketals. Efficient methods for the synthesis of *O*-silylhemithioacetals and ketals **1** would be of general interest, since such carbonyl protective groups could be readily removed under neutral or basic rather than the conventional acidic conditions. During the course of the present study we have demonstrated that *O*-silylhemithioacetals **1** (R′ = H; R = alkyl, aryl) can be efficiently prepared via anion-initiated thiosilane carbonyl insertion (Table I); however, the corresponding ketone adducts could not generally be prepared by this mode of catalysis. Recently, Chan has reported a general synthesis of both *O*-silylhemithioacetals and ketals via the reaction shown below (eq 11).[24] Mechanistically, there are two apparent schemes

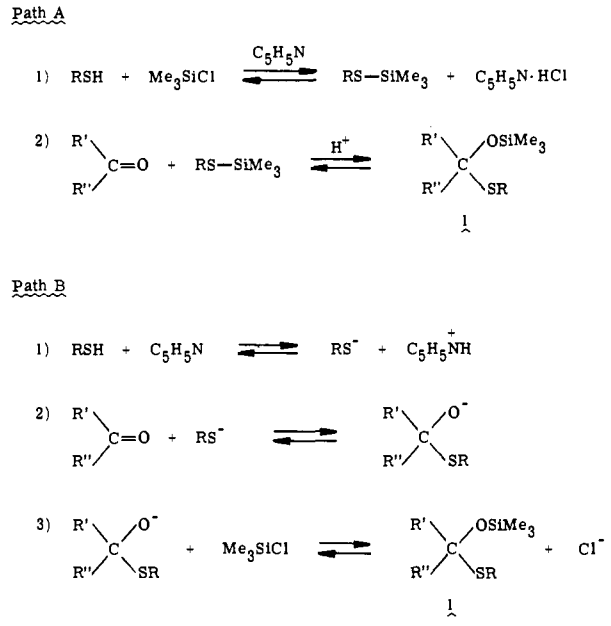
(1)



(11)

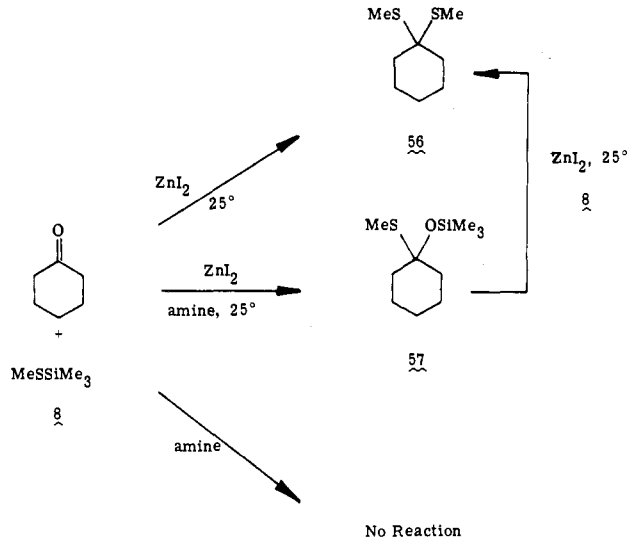
that can be considered for this reaction (Scheme III). In path

Scheme III

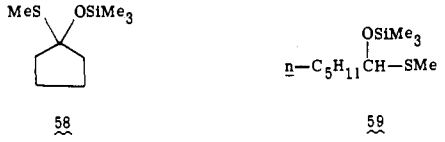


A the thiol could be silylated, giving the thiosilane which could undergo carbonyl insertion via an acid-catalyzed (C_3H_5N·HCl) process. An explanation as to why the *O*-silylhemithioketal **1** is *not* transformed into the thioketal under these conditions *could* be related to the strength of the acid catalyst in the system under study. The alternate mechanism (path B), which was proposed by Chan,[24] could involve thiolate addition to the carbonyl substrate (step 2) followed by subsequent silylation of the hemithioketal or its conjugate base (step 3). As a result of the present investigation, we wish to suggest that the probable course of the reaction of thiols and trimethylsilyl chloride with aldehydes and ketones (eq 11) is not via path B as has been suggested, but via path A. In our earlier discussion (vide supra) we demonstrated that aldehyde *O*-silylhemithioacetals could be prepared by anion-initiated thiosilane carbonyl insertion (Scheme I, X = SR). However, ketones failed to undergo thiosilane insertion by this mode of initiation. Since path B is analogous to this insertion mechanism, it is difficult to explain why the reaction reported by Chan (eq 11) is effective for *both* aldehydes and ketones. Alternatively, if thiosilanes were produced in situ upon treating thiols with trimethylsilyl chloride, and thiosilane carbonyl insertion could be catalyzed by pyridine hydrochloride (path A), one might anticipate that such conditions might not be sufficiently acidic to catalyze the subsequent conversion of the *O*-silylhemithioacetals **1** to the corresponding thioketals. We have verified these projections by demonstrating that the acid-catalyzed thiosilane carbonyl insertion process can be controlled to give *either O*-silylhemithioketals or thioketals by a simple adjustment of the reaction conditions (Scheme IV). Upon treatment of cyclohexanone with methylthiosilane **8** and zinc iodide buffered with an amine (i.e., imidazole or hexamethyldisilazane) the *O*-silylhemithioketal **57** was produced in 88% isolated yield uncontaminated with the dimethylthioketal **56**. In the absence of the amine buffer, cyclohexanone was converted to

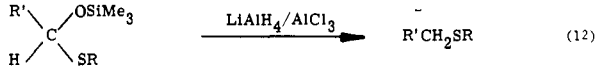
Scheme IV



the dithioketal **56** (2.2 equiv of **8**) under otherwise identical conditions in 92% yield. The intermediacy of **57** in the formation of thioketal **56** was confirmed by GLC analysis. In an independent experiment, it was demonstrated that **57** could be converted in quantitative yield to **56** upon treatment with **8** in the presence of zinc iodide. Although the generality of the amine-buffered, acid-catalyzed thiosilane ketone and aldehyde addition reactions have not been extensively investigated in the present study, both cyclopentanone and *n*-hexanal afford adducts **58** and **59** in good yields under similar conditions.[25]



Recently, Glass has reported the thermal addition of alkylthiosilanes to aliphatic and aromatic aldehydes (eq 1, R″ = H) and the subsequent hydride reduction of the resultant *O*-silylhemithioacetals to unsymmetrical sulfides (eq 12).[26] It is



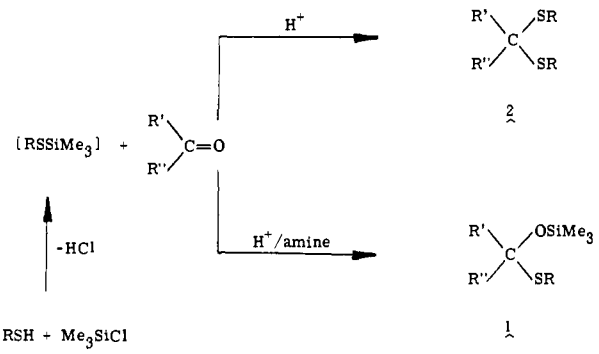
(12)

noteworthy that this study reports the effectiveness of trimethylsilylimidazole as a catalyst for carbonyl insertion with aldehyde substrates. his observation is consistent with our own study (vide supra). Our results also predict that, in general, the analogous ketone carbonyl insertion will *not* be effected by base or anion initiation. This is apparently the case in this study.[26]

The Reactivity of Group 4 Metal Sulfides with Organic Substrates. The reactions of group 4 metal sulfides with a variety of organofunctional groups has been extensively studied.[27] In particular, thiosilanes have been shown to react with acid chlorides,[28,29] anhydrides,[29] isocyanates,[12f] highly reactive ketones and aldehydes,[10a,10d,12f] and strained lactones[12c,12f] without apparent catalysts. In the presence of powerful Lewis acid catalysts such as aluminum chloride or with zinc chloride at elevated temperatures cyclic ethers,[12e] esters,[12b] and α,β-unsaturated acetals[12b] can be induced to react. In general, however, ester interchange does *not* compete with aldehyde and ketone thioketalization when zinc iodide catalysts are employed at 25 °C.[30] Finally, thiosilanes are effective silylating agents (cf. Table II, entry 13). It is thus anticipated that carbonyl protection can be effected in polyfunctional molecules with high selectivity.

Conclusions

In contrast to earlier reports, thiosilanes are not intrinsically unreactive reagents toward carbonyl substrates as this study has demonstrated. On the contrary, when the appropriate initiator catalyst is employed, these reactions occur under exceedingly mild conditions. Prior misconceptions on the low reactivity of the silicon–sulfur bond have been associated with a general lack of understanding of the modes of catalysis that are possible to effect reactions. Depending upon the acid lability of the carbonyl substrate, thiosilanes may be employed either as preformed reagents, as in the present study, or as in situ intermediates[24] in carbonyl protection. Furthermore, an exercised control of the reaction acidity can be instrumental in controlling the nature of carbonyl protection.



Experimental Section

All melting points were taken on a Kofler hot stage or Büchi SMP-20 melting point apparatus and are uncorrected. Boiling points are uncorrected. Infrared spectra were taken on a Perkin-Elmer spectrometer, Model 700. Nuclear magnetic resonance spectra were taken on either a Varian Associates Model T-60 or A-60 spectrometer using 1% tetramethylsilane as an internal standard for non-silicon-containing compounds and either chloroform (437 Hz) or methylene chloride (317 Hz) for silicon-containing derivatives. In NMR descriptions, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Analytical gas chromatographic analyses were carried out on a Varian Model 1400 gas chromatograph using 6-ft columns of 5% SE-30 or 20% Carbowax 20-M on a 60–80 mesh DMCS Chromosorb-W support. Anhydrous sodium sufate was used to dry the organic diethyl ether layer. "Anhydrous" ether is reagent ether distilled from lithium aluminum hydride prior to use. All liquid ketones are aldehydes were freshly distilled prior to use. Solid ketones were sublimed prior to use. Methylthiotrimethylsilane (**8**) was purchased from Petrarch Systems and redistilled prior to use. The commercial material contains ca. 1% hexamethyldisilazane.[25] Phenylthiotrimethylsilane (**20**) was prepared according to the procedure reported by Ojima.[10c]

Ethylthiotrimethylsilane (6). The title compound was prepared in analogy to the general procedure reported by Langer[32] in 68% yield, bp 127–131 °C, and was found to be identical with a sample prepared by the method of Abel.[33]

1,2-Ethanedithiobis(trimethylsilane) (60). Procedure A. The title compound has been prepared by the procedure of Glass via the silylation of ethanedithiol with hexamethyldisilazane employing imidazole as a catalyst.[10d] To obtain amine-free thiosilane by this procedure redistillation of the product through a 10-cm Vigreux column, bp 80 °C (0.3 mmHg), was necessary to remove minor amine contaminants.[25]

Procedure B. To a nitrogen-purged, 100-mL, round-bottom flask equipped with a mechanical stirrer, a reflux condenser, and an addition funnel was added 250 mL of anhydrous ether and 8.4 mL (0.42 g, 0.10 mol) of 1,2-ethanedithiol. While the reaction flask was cooled in an ice bath, 124 mL (0.20 mol) of *n*-butyllithium (1.61 M in hexane) was added dropwise over 0.5 h. The reaction mixture was stirred efficiently during this addition. After the mixture was allowed to stand at room temperature for 3 h, 26.0 mL (21.8 g, 0.20 mol) of chlorotrimethylsilane was added and the mixture was heated at reflux for 12 h. A filtration under nitrogen and a distillation [80 °C (0.3 mm), lit.[10d] bp 145–150 °C (40 mm)], gave 14.2 g (60%) of the desired thiosilane **60**: NMR (CCl_4) 2.60 (s, 4, SCH_2), 0.35 (s, 18, $SiCH_3$).

1,3-Propanedithiobis(trimethylsilane) (61). Procedure A. To a nitrogen-purged, 250-mL, three-necked, round-bottom flask, equipped with a reflux condenser, a mechanical stirrer, and an addition funnel was added 100 mL of anhydrous ether and 5.00 mL (5.40 g, 0.050 mol) of propanedithiol. While the reaction flask was cooled in an ice bath, 50.0 mL of *n*-butyllithium (2.0 M in hexane) was added dropwise over a 0.5-h period. After allowing the reaction mixture to warm to room temperature, 13.0 mL (10.9 g, 0.10 mol) of chlorotrimethylsilane was added over a period of 0.5 h with efficient stirring. After a 24-h reflux period, a filtration under nitrogen followed by a distillation (bp 75 °C (0.02 mm)) afforded 5.0 g (40%) of the desired thiosilane **61**: NMR (CCl_4) δ 2.60 (t, 4, J = 6.0 Hz, SCH_2), 2.92 (m, 2, CH_2), 0.38 (s, 9, $SiCH_3$).

Anal. Calcd for $C_9H_{24}S_2Si_2$: 252.086. Found (MS, 75 eV): 252.086.

Procedure B. The title compound was also prepared via the general procedure of Glass.[10d] To a dry 250-mL flask equipped with a condenser and a static nitrogen atmosphere was added 0.30 g of imidazole, 79.0 mL (61.1 g, 0.38 mol) of hexamethyldisilazane, and 10.0 mL (10.8 g, 0.10 mol) of 1,3-propanedithiol. The reaction mixture was heated at reflux for 24 h and distilled carefully through a 10-cm Vigreux (bp 75 °C (0.02 mm)) to give 21.6 g (85%) of the desired thiosilane **61**.

Preparation of KCN–18-Crown-6 Complex. The potassium cyanide–18-crown-6 complex was prepared by the dissolution of 1 equiv of potassium cyanide in anhydrous methanol followed by the addition of 1 equiv of 18-crown-6.[19] Removal of the solvent under aspirator pressure at 65 °C followed by subsequent drying under high vacuum at room temperature for 5–10 min afforded an active catalyst. The use of other solvents such as carbon tetrachloride or benzene failed due to the apparent insolubility of potassium cyanide. Other soluble salts such as tetra-*n*-butylammonium cyanide[17] are equally effective as anionic initiators.

General Procedure for Cyanide Ion-Initiated Thiosilylation of Saturated and α,β-Unsaturated Ketones and Aldehydes. A dry, nitrogen-purged, round-bottom flask is charged with 1 equiv of ketone or aldehyde and 1.05–1.1 equiv of alkyl or arylthiotrimethylsilane. Upon addition of ca. 5×10^{-4} equiv of the solid potassium cyanide–18-crown-6 complex (ca. 10 mg of complex/60 mmol of ketone) the reaction may be initiated. The reactions involving alkylthiosilanes and carbonyl substrates are generally mildly exothermic and some external cooling may be necessary. Upon completion of the reaction the adducts were isolated by direct distillation of the product from the reaction vessel at reduced pressure.

Ethylthiosilylation of *n*-Hexanal. Following the prescribed general procedure, upon admixture of 3.34 mL (38 mmol) of *n*-hexanal, 7.0 mL (43 mmol) of thiosilane **6**, and ca. 4 mg of the cyanide-crown catalyst a mildly exothermic reaction ensued. Upon cooling to room temperature, the solution was distilled, affording 7.40 g (82%) of the *O*-silylhemithioacetal **18**: bp 75 °C (0.5 mm); IR (neat) 1245, 835, 750 cm^{-1} ($SiCH_3$); NMR (CCl_4) δ 4.72 (t, 1, J = 5.5 Hz, $CHOSi$), 2.45 (q, 2, J = 7 Hz, SCH_2), 0.07 (s, 9, $SiCH_3$).

Anal. ($C_{11}H_{26}OSSi$): C, 56.53; H, 11.25.

Phenylthiosilylation of Isobutyraldehyde. Following the prescribed general procedure, upon admixture of 5.0 mL (55.1 mmol) of isobutyraldehyde, 10.4 g (57 mmol) of phenylthiosilane **20**, and 10 mg of the cyanide-crown catalyst a slow reaction ensued. After 20 h at 25 °C NMR analysis showed the reaction to be 90% complete. Distillation afforded 11.3 g (81%) of the *O*-silylhemithioacetal **21**; bp 71 °C (0.05 mm); NMR (CCl_4) δ 7.45 (m, 5, aromatic H), 4.95 (d, 1, J = 5 Hz, $CHOSi$), 1.98 (m, 1, $CH(CH_3)_2$), 1.12 (d, 6, J = 7 Hz, CH_3), 0.1 (s, 9, $SiCH_3$); exact mass (70 eV) *m/e* calcd for $C_{1221}OSSi$. 254.1161, obsd 254.1157.

Ethylthiosilylation of Benzaldehyde. Following the prescribed general procedure, upon admixture of 5.0 mL (49 mmol) of benzaldehyde, 8.4 mL (52 mmol) of ethylthiotrimethylsilane (**6**), and 10 mg of potassium cyanide–18-crown-6 complex an exothermic reaction ensued. Upon cooling the product was distilled, affording 11.2 g (95%) of the *O*-silylhemithioacetal **22**: bp 73–74 °C (0.02 mm); IR (neat) 1245, 747 cm^{-1} ($SiCH_3$); NMR (CCl_4) δ 7.38 (m, 5, aryl *H*), 6.02 (s, 1, OCH), 2.45 (m, 2, SCH_2), 1.20 (t, 3, J = 7 Hz, CH_2CH_3), 0.20 (s, 9, $SiCH_3$).

Anal. ($C_{12}H_{30}OSSi$): C, 59.68; H, 8.27.

Phenylthiosilylation of Acrolein. Following the prescribed proce-

dure, to a stirred solution of 14.5 g (79.6 mmol) of phenylthiosilane **20** and 5.0 mL (77 mmol) of acrolein (freshly distilled) was added 10 mg of cyanide-crown catalyst with external cooling. After 5 min the reaction was heated at reflux for 15 min. Distillation afforded 5.7 g of starting sulfide and 9.8 g (86%) of a 3:1 mixture of *E/Z* 1,4-adducts **23:** bp 87-89 °C (0.02 mm); IR (neat) 1653, 1248, 842, 737 cm^{-1} ($SiCH_3$); NMR (CCl_4) *E* isomer δ 7.28 (m, 5, aryl *H*), 6.20 (t of d, 1, *J* = 12 and 1 Hz, C=C*H*OSi), 3.42 (d of d, 2, *J* = 8 and 1 Hz, SCH_2), 0.13 (s, 9, $SiCH_3$); NMR *Z* isomer δ 7.28 (m, 5, aryl *H*), 6.21 (t of d, 1, *J* = 6 and 1 Hz, C=C*H*OSi), 3.62 (d of d, 2, *J* = 8 and 1 Hz, SCH_2), 0.22 (s, 9, $SiCH_3$).

Anal. ($C_{11}H_{18}OSSi$): C, 60.36; H, 7.56.

Phenylthiosilylation of Crotonaldehyde. According to the general procedure 10 mg of cyanide-crown catalyst was added to a mixture of 11.5 g (63 mmol) of phenylthiosilane **20** and 5.0 mL (61 mmol) of crotonaldehyde. Upon dissolution an exothermic reaction ensued. Distillation afforded 13.9 (90%) of a 3:1 mixture of *E/Z* 1,4-adducts **24:** bp 90-92 °C (0.02 mm); IR (neat) 1655, 1248, 744 cm^{-1}; NMR (CCl_4) *E* isomer δ 7.31 (m, 5, aryl *H*), 6.02 (d, 1, *J* = 12 Hz, C=C*H*OSi), 4.88 (d of d, 1, *J* = 12 and 8 Hz, =CH), 1.38 (d, 3, *J* = 7 Hz, CCH_3), 0.07 (s, 9, $SiCH_3$).

Anal. ($C_{13}H_{20}OSSi$): C, 61.78; H, 8.06.

Ethylthiosilylation of Crotonaldehyde. The procedure followed in the present case was identical with that described for the preparation of adduct **24.** From 3.0 mL (36.7 mmol) of crotonaldehyde and 7.0 mL (43 mmol) of ethylthiosilane **6** there was obtained 6.75 g (90%) of a 2:1 mixture of *Z* and *E* 1,4-adducts **25:** bp 86-94 °C (9 mm); IR (neat) 1645, 1249, 840, 750 cm^{-1}; NMR (CCl_4) *Z* isomer δ 6.10 (d, 1, *J* = 5.5 Hz, OCH), 4.30 (d of d, 1, *J* = 9 and 5.5 Hz, *H*C=CH-OSi), 1.21 (d, 3, *J* = 7 Hz, $CCCH_3$), 0.12 (s, 9, $SiCH_3$); NMR *E* isomer δ 6.14 (d, 1, *J* = 12 Hz, C=C*H*OSi), 4.75 (dof d, *J* = 12 and 9 Hz, *H*C=CHOSi), 1.15 (d, 3, *J* = 6.5 Hz, $CCCH_3$), 0.12 (s, 9, $SiCH_3$).

Anal. ($C_9H_{20}OSSi$): C, 52.87; H, 9.96.

Phenylthiosilylation of Methacrolein. According to the general procedure 10 mg of cyanide-crown catalyst was added to 3.5 g (50 mmol) of methacrolein and 10.0 g (55 mmol) of phenylthiosilane **20.** Upon catalyst dissolution an exothermic reaction ensued. After stirring at room temperature for 1.5 h, the product was isolated by short-path distillation to give 11.9 g (91%) of a 3.5:1 mixture of *E* and *Z* isomers **26:** bp 99-100 °C (0.05 mm); NMR ($CDCl_3$) *E* isomer δ 7.35 (m, 5, aryl *H*), 6.12 (m, 1, C=C*H*OSi), 3.50 (s, 2, CH_2S), 1.78 (d, 3, *J* = 2 Hz, CH_3), 0.15 (s, 9, CH_3Si); NMR *Z* isomer δ 7.35 (m, 5, aryl *H*), 6.12 (m, 1, C=C*H*Si), 3.60 (s, 2, CH_2S), 1.72 (d, 3, *J* = 2 Hz, CH_3), 0.23 (s, 9, CH_3Si); exact mass (70 eV) *m/e* calcd for $C_{12}H_{20}OSiS$ 252.1004, obsd 252.1001.

Phenylthiosilylation of Tigaldehyde. According to the general procedure 9.9 g (54 mmol) of phenylthiosilane **20,** 5.0 mL (52 mmol) of tigaldehyde, and 0.1 g of triphenylphosphine, upon admixture, resulted in an exothermic reaction. After 30 min the adduct was distilled at reduced pressure to afford 11.9 g (86%) of a mixture of *Z* and *E* isomers of **27** in a 2:7 ratio, respectively: bp 83-84 °C (0.02 mm); IR (neat) 1658, 1249, 845, 745 cm^{-1}; NMR (CCl_4) major isomer δ 7.28 (m, 5, aryl *H*), 5.90 (m, 1, C=C*H*), 2.67 (q, 1, *J* = 7 Hz, SC*H*), 1.63 (d, 3, *J* = 1 Hz, C=CH_2), 1.40 (d, 3, *J* = 7 Hz, SCCH_3). 0.05 (s, 9, $SiCH_3$); NMR minor isomer δ 7.28 (m, 5, aryl *H*), 5.98 (m, 1, C=C*H*), 4.70 (q, 1, *J* = 7 Hz, SC*H*), 1.57 (d, 1, *J* = 1 Hz, C=CCH_3), 1.35 (d, 1, *J* = 7 Hz, SSCH_3), 0.15 (s, 9, $SiCH_3$).

Anal. ($C_{12}H_{22}OSSi$): C, 63.08; H, 8.38.

Ethylthiosilylation of Tigaldehyde. The procedure followed in the present case was identical with that described for the preparation of adduct **27** except that the crown-cyanide initiator (10 mg) was employed. From 8.5 mL (53 mmol) of ethylthiosilane **6** and 5.0 mL (52 mmol) of tigaldehyde there was obtained 10.4 g (92%) of a 3:1 mixture of *E* and *Z* isomers of **28:** bp 62-64 °C (7 mm); IR (neat) 1655, 1248, 750 cm^{-1} ($SiCH_3$); NMR (CCl_4) *E* isomer δ 6.10 (m, 1, C=C*H*), 3.27 (q, 1, *J* = 7 Hz, SC*H*), 1.53 (d, 3, *J* = 1 Hz, C=CH_3), 1.22 (d, 3, *J* = 7 Hz, SCHCH_3), 0.13 (s, 9, $SiCH_3$); NMR *Z* isomer δ 6.08 (m, 1, C=C*H*), 4.22 (q, 1, *J* = 7 Hz, SC*H*), 1.48 (d, 1, *J* = 1 Hz, C=CCH_3), 1.15 (d, 3, *J* = 7 Hz, SCHCH_3), 0.13 (s, 9, $SiCH_3$).

Anal. ($C_{10}H_{22}OSSi$): C, 54.93; H, 10.05.

Phenylthiosilylation of Methyl Vinyl Ketones. Following the prescribed general procedure, to a cooled (0 °C) mixture of 10.01 g (55 mmol) of phenylthiosilane **20** and 3.5 g (50 mmol) of freshly distilled methyl vinyl ketone was added 20 mg of the crown-cyanide catalyst. Upon dissolution of the complex an exothermic reaction ensued. After stirring at 25 °C for 1 h the adduct **29,** 10.95 g (86%), was isolated as an isomeric mixture: bp 85-86 °C (0.02 mm); IR (neat) 1660 cm^{-1}; NMR (CCl_4) δ 7.32 (m, 5, aryl *H*), 4.70 (t, 1, *J* = 7.5 Hz, *H*C=C-OSi), 3.62 (d, *J* = 7.5 Hz, CH_2S, minor isomer), 1.88 (d, *J* = 1 Hz, C=CCH_3, major isomer), 1.76 (s, C=CCH_3, minor isomer), 0.3 (s, $SiCH_2$, major isomer), 0.27 (s, $SiCH_3$, minor isomer); exact mass (70 eV) *m/e* calcd for $C_{12}H_{20}OSSi$ 252.1004, obsd 252.1003.

Phenylthiosilylation of 2-Cyclohexenone. Following the prescribed general procedure, to a mixture of 2.0 mL (10 mmol) of phenylthiosilane **20** and 1.0 mL (10 mmol) of 2-cyclohexenone was added 1 mg of crown-cyanide complex. Upon catalyst dissolution a mild exothermic reaction ensued. After 2 h the reaction had proceeded to completion (<99%) as judged by NMR analysis. With this particular enone triphenylphosphine was not an effective initiator at room temperature. Molecular distillation (150 °C (0.04 mm)) afforded the 1,4-adduct **30** (2.63 g, 95%), contaminated with ca. 5% of 20: IR (neat) 2940, 1650, 1250, 1200, 895, 845 cm^{-1}; NMR (CCl_4) δ 0.30 (s, 9, $siCH_3$), 2.00 (m, 6, CH_2), 3.95 (m, 1, C*H*), 4.95 (d, 1, *J* = 4 Hz, =C*H*), 7.35 (m, 5, aryl *H*). Since adduct **30** appears to be thermally labile, it is advised that the crude reaction mixture be employed in subsequent chemical transformations.

Phenylthiosilylation of 2-Cyclopentenone. Following the prescribed general procedure, to a mixture of 1.03 mL (5 mmol) of phenylthiosilane **20** and 0.4 mL (5 mmol) of 2-cyclopentenone was added 1 mg of crown-cyanide complex. After the exothermic reaction subsided the reaction was allowed to stir for 2 h. NMR analysis indicated that the reaction had proceeded clearly to the desired 1,4-adduct **31.** Molecular distillation (150 °C (0.03 mm)) afforded 1.23 g (87%) of **31** contaminated with ca. 3.5% of **20,** which was formed by thermal reversion: IR (neat) 2955, 1650, 1342, 1263, 1250, 860, 845 cm^{-1}; NMR (CCl_4) δ 0.32 (s, 9, $SiCH_3$), 2.29 (m, 4, CH_2), 4.33 (m, 1, C*H*), 4.73 (d, 1, *J* = 2 Hz, =C*H*), 7.35 (m, 5, aryl *H*).

General Procedure for Zinc Iodide Catalyzed Carbonyl Thioketalization. To a dry, nitrogen-purged, 25-mL flask is added ca. 10 mg (0.03 mmol) of anhydrous zinc iodide and 10 mmol of ketone or aldehyde in 5 mL of anhydrous ether. To this solution is added 22 mmol of the appropriate monothiosilane, $RSSiMe_3$ (**6, 8,** or **20**), or 11 mmol of the appropriate dithiosilane, $R(SSiMe_3)_2$ (**60** or **61**) via syringe over a 1-2-min period. After a reaction time of 12-24 h the reaction is quenched with water and the product isolated by ether extraction. The products may be purified either by distillation or by chromatography on alumina (activity III, hexane elution). Other solvents such as chloroform and acetonitrile are equally effective in this reaction and their use is cited in specific experiments.

***n*-Heptanal Dimethylthioacetal (32).** From 2.28 g (20 mmol) of *n*-heptanal and 5.29 g (44 mmol) of methylthiosilane **8** there was obtained 3.38 g (88%) of **32** as a colorless oil: bp 48 °C (0.06 mm); IR (neat) 2975-2850, 1475-1420, 970, 760 cm^{-1}; NMR ($CDCl_3$) δ 3.60 (t, 3, *J* = 6.5 Hz, C*H*), 2.05 (s, 6, CH_3S), 1.85-0.67 (m, 13).

Anal. ($C_9H_{20}S_2$): C, 56.11; H, 10.58.

***n*-Heptanal Diethylthioacetal (33).** From 1.40 mL (10 mmol) of *n*-heptanal and 3.60 mL (22 mmol) of ethylthiosilane **6** there was obtained 2.03 g (92%) of the thioacetal **33** as a colorless oil after chromatography and molecular distillation (90 °C (0.02 mm)): IR (neat) 2960-2860, 1450, 1260 cm^{-1}; NMR (CCl_4) δ 3.75 (t, 1, *J* = 7.0 Hz, C*H*), 2.68 (q, 4, *J* = 7.0 Hz, SCH_2), 1.40 (m, 13, CH_2), 1.30 (t, 6, *J* = 7.0 Hz, CH_3).

Anal. ($C_{11}H_{24}S_2$): C, 59.78; H, 10.85.

2-Heptyl-1,3-dithiane (34). From 1.40 mL (10 mmol) of *n*-heptanal and 3.01 mL (11 mmol) of bisthiosilane **61** there was obtained 1.53 g (75%) of **34** as a colorless oil after chromatography: IR (neat) 2960-2862, 1462, 1418, 1274, 907 cm^{-1}; NMR (CCl_4) δ 4.00 (t, 1, C*H*), 2.82 (m, 4, SCH_2), 2.00 (m, 2, SCH_2CH_3), 1.50 (m, 10, CH_2), 0.95 (t, 3, CH_3).

Anal. ($C_{10}H_{20}S_2$): C, 58.85; H, 9.79.

1,1-Dimethylthio-2-methylpropane (35). From 0.91 mL (10 mmol) of isobutyraldehyde and 3.2 mL (22 mol) of methylthiosilane **8** there was obtained after chromatography and molecular distillation (80 °C (0.04)) 1.28 g (85%) of thioacetal **35:** IR (neat) 2960-2870, 1460, 1435, 767 cm^{-1}; NMR (CCl_4) δ 3.42 (d, 1, *J* = 6.0 Hz, SC*H*), 2.11 (s, 6, SCH_3), 1.97 (m, 1, C*H*), 1.15 (d, 6, *J* = 6.0 Hz, CH_3).

Anal. ($C_6H_{14}S_2$): C, 47.88; H, 9.42.

1,1-Diethylthio-2-methylpropane (36). From 0.91 mL (10 mmol) of isobutyraldehyde and 3.6 mL (22 mmol) of ethylthiosilane **6** there was obtained after chromatography 1.65 g (92%) of thioacetal **36** as

a colorless oil: IR (neat) 2962-2930, 1450, 1260 cm^{-1}; NMR (CCl_4) δ 3.62 (d, 1, J = 5.0 Hz, C*H*), 2.64 (q, 4, J = 8.0 Hz, SCH_2), 2.05 (m, 1, C*H*), 1.28 (t, 6, J = 8.0 Hz, SCH_2CH_3), 1.10 (d, 6, J = 5.0 Hz, CH_3).

Anal. ($C_8H_{18}S_2$): C, 53.69; H, 9.87.

2-Isopropyl-1,3-dithiane (37). From 0.91 mL (10 mmol) of isobutyraldehyde and 3.01 mL (11 mmol) of bisthiosilane **61** there was obtained after chromatography 0.11 g (70%) of thioacetal 37 as a colorless oil: IR (neat) 2960-2820, 1452, 1415, 1272, 905, 765 cm^{-1}; NMR (CCl_4) δ 3.60 (d, 1, SC*H*), 2.80 (t, 4, SCH_2), 2.05 (m, 1, C*H*), 2.05 (p, 2, SCH_2CH_2), 1.15 (d, 6, CH_3); exact mass (5 eV) *m/e* calcd for $C_7H_{14}S_2$ 162.054, obsd 162.055.

Benzaldehyde Dimethylthioacetal (38). From 2.12 g (20 mmol) of benzaldehyde and 5.29 g (44 mmol) of methylthiosilane **8** there was obtained after molecular distillation (35 °C (0.03 mm)) 3.29 g (90%) of **38** as a pale yellow oil: IR (neat) 3075, 3040, 3000, 2925, 1500, 975, 950, 700 cm^{-1}; NMR ($CDCl_3$) δ 7.47-710 (m, 5, aryl *H*), 4.74 (s, 1, $HC(S)_2$), 2.02 (s, 6, SCH_-).

Anal. ($C_9H_{12}S_2$): C, 58.83; H, 6.64.

Acetophenone Diethylthioketal (39). From 1.16 mL (10 mmol) of acetophenone and 3.60 mL (22 mol) of ethylthiosilane **6** there was obtained after chromatography 2.11 g (93%) of ketal **39** as an oil: IR (neat) 3055, 2965-2930, 1582, 1440, 695 cm^{-1}; NMR (CCl_4) δ 7.60 (m, 5, aryl *H*), 2.62 (q, 4, J = 7.5 Hz, SCH_2), 2.10 (s, 3, CH_3), 1.30 (t, 6, J = 7.5 Hz, CH_3).

Anal. ($C_{12}H_{18}S_2$): C, 63.41; H, 7.80.

3,3-Diethylthiopentane (40). From 1.05 mL (10 mmol) of 3-pentanone and 3.60 mL (22 mmol) of ethylthiosilane **6** there was obtained after chromatography 1.74 g (91%) of **40** as a colorless oil: IR (neat) 2965-2870, 1450, 1370, 812 cm^{-1}; NMR (CCl_4) δ 2.60 (q, 4, J = 7.5 Hz, SCH_2), 1.65 (q, 4, J = 8.0 Hz, CH_2), 1.25 (t, 6, J = 7.5 Hz, CH_3), 1.00 (t, 6, J = 8.0 Hz, CH_3).

Anal. ($C_9H_{20}S_2$): C, 56.41; H, 10.28.

2,2-Diethyl-1,3-dithiane (41). From 1.05 mL (10 mmol) of 3-pentanone and 3.01 mL (11 mmol) of bisthiosilane **61** there was obtained after chromatography 1.67 g (95%) of thiane **41** as a colorless liquid: IR (neat) 2970-2825, 1450, 1418, 903, 877 cm^{-1}; NMR (CCl_4) δ 2.75 (m, 4, SCH_2), 1.95 (m, 2, CH_2), 1.90 (q, 4, CH_2), 0.95 (t, 6, CH_3); exact mass (75 eV) *m/e* calcd for $C_8H_{16}S_2$ 176.069, obsd 176.069.

1,1-Dimethylthiocyclopentane (42). From 0.89 mL (10 mmol) of cyclopentanone and 3.2 mL (22 mmol) of methylthiosilane **8** there was obtained after filtration through alumina and molecular distillation (39 °C (2.0 mm)) 1.52 g (93%) of ketal **42** as a colorless oil: IR (neat) 2960-2870, 1435, 1418 cm^{-1}; NMR (CCl_4) δ 2.05 (s, 6, SCH_3), 1.90 (m, 8, CH_2).

Anal. ($C_7H_{14}S_2$): C, 52.03; H, 8.68.

1,1-Diethylthiocyclohexane (43). From 1.04 mL (10 mmol) of cyclohexanone and 3.60 mL (22 mmol) of ethylthiosilane **6** there was obtained after chromatography 2.00 g (98%) of the ketal **43;** bp 35 °C (2.0 mm); IR (neat) 2970-2860, 1442, 1260, 1257, 1005 cm^{-1}; NMR (CCl_4) δ 2.60 (q, 4, J = 7.5 Hz, SCH_2), 1.75 (m, 10, CH_2), 1.27 (t, 6, J = 7.5 Hz, CH_3).

Anal. ($C_{10}H_{20}S_2$): C, 58.42; H, 9.57.

2,2-Diethylthio-4-methyl-4-trimethylsilyloxypentane (44). From 1.16 g (10 mmol) of diacetone alcohol and 5.4 mL (33 mmol) of ethylthiosilane **6** there was obtained after chromatography 2.72 g (92%) of *O*-silylated diethylthioketal **44** as a colorless liquid: IR (neat) 2980, 2930, 2870, 1445, 1250, 1170, 1035, 858, 840, 750 cm^{-1}; NMR (CCl_4) δ 2.65 (q, 4, J = 7.5 Hz, SCH_2), 2.05 (s, 2, CH_3), 1.70 (s, 3, CH_2), 1.45 (s, 6, CH_3), 1.30 (t, 6, J = 7.5 Hz, SCH_2CH_3), 0.20 (s, 9, $SiCH_3$); exact mass (75 eV) calcd for $C_9H_{18}S_2$ ($P^+ - C_3H_{10}OSi$) 204.101, obsd 204.101.

1-Trimethylsilyloxy-2-methyl-3-thiomethyl-1-propene (45). From 2.1 g (30 mmol) of α-methacrolein, 3.97 g (33 mmol) of methylthiosilane **8,** and 10 mg of anhydrous zinc iodide in ether at 0 °C there was isolated after short-path distillation 4.07 g (82%) of the 1,4-adduct **45** as a colorless oil: bp 82-83 °C (3 mm); IR (neat) 2960, 2930, 1675, 1440, 1260, 1195, 1150, 880, 850, 765 cm^{-1}; the NMR revealed a 34:66 mixture of *E* and *Z* isomers; NMR ($CDCl_3$) δ 6.1 (m, 1, =CH), 3.15 and 2.93 (s, 2, SCH_2), 1.92 and 1.85 (s, 3, SCH_3), 1.57 (m, 3, CH_3).

Anal. ($C_8H_{18}OSSi$): C, 50.44; H, 9.63.

5α-Androstane-3,17-dione 3-Dimethylthioketal (47). From 697 mg (2.58 mmol) of dione **46** and 649 mg (5.42 mmol) of methylthiosilane **8** there was obtained a crystalline monothioketal which was purified by chromatography on silica gel (10% ethyl acetate-benzene). The resultant ketal **47,** mp 156-158 °C, 0.870 g (92%), appeared to be homogeneous on TLC. A small sample was recrystallized from ethyl acetate-hexane to give clear platelets: mp 157-159 °C; IR (KBr) 2980-2840, 1735, 1475-1380, 1062, 1020, 785 cm^{-1}; NMR ($CDCl_3$) δ 2.05 (s, 3), 1.93 (s), 2.42-0.53 (m, 22), 0.83 (s), 0.80 (s).

Anal. ($C_{21}H_{34}OS_2$): C, 68.82; H, 9.22.

10t-Methyl-(5rC')-spiro[4.5]decane-1,7-dione 7-Dimethylthioketal (49). From 1.03 g (5.73 mmol) of dione **48** and 1.57 mL (12 mmol) of methylthiosilane **8** in acetonitrile solvent and zinc iodide as an initiator there was obtained a yellow oil which was chromatographed on silica gel (10% ethyl acetate-pentane elution). The desired crystalline monothioketal **49** which was obtained as a crystalline solid was sublimed (40 °C (0.5 mm)) to give 1.38 g (93%) of fine colorless needles: mp 70-71 °C; IR (CCl_4) 3000-2850, 1735, 1480-1415, 1160, 800, 765 cm^{-1}; NMR (CCl_4) δ 2.42-1.17 (m, 13 H), 2.00 (s), 1.95 (s), 0.68 (d, 3, J = 6.0 Hz).

Anal. ($C_{13}H_{22}OS_2$): C, 60.38; H, 3.54.

Reaction of 4-Androstene-3,17-dione (50) with Ethanebisthiosilane 60. From 274 mg (0.96 mmol) of dione **50** and 0.28 mL (1.1 mmol) of ethanedithiosilane **60** in chloroform (ZnI_2 catalysis) there was obtained a mixture of crystalline adducts. Chromatography on silica gel (1:2 petroleum ether-benzene) afforded 25 mg (5%) of the crystalline bisthioketal **52,** mp 170-174 °C (lit. 174-176 °C);[22] IR ($CHCl_3$) 2962-2850, 1635, 1433, 1130, 1105 cm^{-1}. Further elution with benzene-ethyl acetate (19:1) afforded 328 mg (94%) of the 3-monothioketal **51,** mp 170.5-171.5 °C (lit. mp 173-174.5 °C):[22] IR ($CHCl_3$) 3000-3850, 1735 (s) (C=O), 1635 (w) (C=C), 1433, 1370, 1130, 1105 cm^{-1}; NMR ($CDCl_3$) δ 5.55 (s, 1, =C*H*), 3.35 (m. 4, SCH_2), 2.50-1.20 (m, 19), 1.08 (s, 3, CH_3), 0.90 (s, 3, CH_3).

Reaction of Progesterone (53) with Ethanebisthiosilane 60. From 315 mg (1.0 mmol) of dione **53** and 0.28 mL (1.1 mmol) of ethanebisthiosilane **60** in chloroform (ZnI_2 catalysis) there was obtained a mixture of monoketal **54** and bisketal **55.** Chromatography on silica gel (1:2 petroleum ether-benzene) afforded the crystalline bisthioketal **55** in 4% yield: mp 175-179 °C (lit. 179-181.5 °C):[22] IR ($CHCl_3$) 2970-2860, 1635 (w), 1130, 1105 cm^{-1}. Further elution with benzene-ethyl acetate (19:1) afforded 366 mg (94%) of the crystalline monoketal **54:** mp 177-181 °C (lit. 184-186 °C);[22] IR ($CHCl_3$) 3000-2850, 1690 (s), 1130, 1105 cm^{-1}; NMR ($CDCl_3$) δ 5.50 (s, 1, =C*H*), 3.28 (m, 4, SCH_2), 2.10 (s, 3, $COCH_3$), 2.50-1.00 (m, 20), 1.00 (s, 3, CH_3), 0.60 (s, 3, CH_3).

General Procedure for the Synthesis of *O*-Trimethylsilyl Hemimethylthioketals. To a dry 25-mL flask is added ca. 10 mg (0.03 mmol) of anhydrous zinc iodide, 10 mg (0.15 mmol) of imidazole, and 10 mmol of ketone or aldehyde in 5 mL of anhydrous ether. To this stirred solution is added 22 mmol of the appropriate thiosilane. General reaction time of 1 h at 25 °C are observed. The products may be isolated by dilution of the reaction mixture with ether followed by a water extraction and distillation of the resultant *O*-silylhemithioketal. Variations in the amine buffer (cf. hexamethyldisilazane) and reaction solvent (cf. chloroform) may be made.

1-Trimethylsilyloxy-1-methylthiocyclohexane (57). Following the general procedure outlined for the synthesis of *O*-silylhemithioketals, from 1.96 g (20 mmol) of cyclohexanone and 2.7 g (22 mmol) of methylthiosilane **8** there was obtained the adduct **57.** Filtration of **57** through alumina (activity III) with hexane and molecular distillation (45 °C (0.01 mm)) afforded 3.84 g (88%) of **57** as a colorless liquid which was homogeneous by GLC: IR (neat) 2950-2855, 1441, 1251, 1244, 1089, 1050, 835, 750 cm^{-1}; NMR (CCl_4) δ 2.10 (s, 3, SCH_3), 1.70 (m, 10, CH_2), 0.25 (s, 9, $SiCH_3$); exact mass (75 eV) *m/e* calcd for $C_9H_{19}SiSO$ 203.092, obsd 203.092.

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$$2\ RSH + (Me_3Si)_2NH \xrightarrow{\text{imidazole}} 2\ RSSiMe_3 + NH_3$$

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Reactions of Fluoroethylenes with Strong Bases in the Gas Phase

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Abstract: Ion cyclotron resonance spectroscopy (ICR) has been used to examine reactions of fluoroethylenes with strong bases in the gas phase. Observed reaction types include proton transfer, elimination, and nucleophilic attack leading to substitution and elimination. The latter yields enolate anions as ionic products. Product distributions are determined for reactions of fluoroethylenes with CD_3O^-, $CH_3CH_2O^-$, $(CH_3)_2CHO^-$, $(CH_3)_3CO^-$, and F^-. Acidities of fluoroolefins relative to alcohols and fluoroethanes are reported. Rates for the nucleophilic addition reaction of CF_2CF_2 with alkoxide ions have been measured. In addition, reactions of a series of perhalogenated chlorofluoro- and bromofluoroolefins with CD_3O^- have been studied. Probable mechanisms of the elimination and nucleophilic addition reactions are discussed in terms of observed reactivity.

Introduction

There is evidence for the intermediacy of charged species in many chemical transformations.[2] Accordingly, reactivity is often explained in terms of the thermodynamic stabilities and charge distributions of such intermediates. In solution, the medium of most ionic reactions, these properties are strongly moderated by solvation. Studies of gas phase ionic reactions allow a correlation between intrinsic molecular properties and reactivity. Ion cyclotron resonance spectroscopy (ICR) is well suited for such investigations.

Recently we examined gas phase reactions of fluoroethanes with strong bases such as NH_2^-, OH^-, F^-, and RO^- (R =