TRIMETHYLSILYL ANIONS: STEREOSPECIFIC DEOXYGENATION OF EPOXIDES AND TRIMETHYLSILYLDEHALOGENATION OF ARYL HALIDES

Thesis by

Michael Allen Shippey

In Partial Fulfillment of the Requirements
for the Degree of
Doctor of Philosophy

California Institute of Technology
Pasadena, California
1978

(Submitted January 23, 1978)

ACKNOWLEDGEMENTS

It has been an honor and a joy to experience during my graduate career the friendly, cooperative, and interactive atmosphere that pervades the environment here at Caltech. I am grateful for having shared the wisdom of faculty, staff, and fellow graduate students.

Of the many individuals I should acknowledge, I would particularly like to thank Professors R.G. Bergman, D.A. Evans, J.E. Bercaw, and D. Seebach for helpful discussions and advice, on life in general and chemistry in particular.

Most especially, I owe a debt of thanks to my research advisor, Professor Peter B. Dervan, who spent untold efforts to teach me the difference between a good student of science and a good scientist. Peter -- may Mother Nature always give you the breaks.

I also wish to thank the typist-philosopher, Ms. Deborah Chester, who played a large role in more ways than one in seeing this thesis become a reality, and Dr. Gordon Gribble for proofreading the manuscript.

The National Science Foundation and Caltech are due my gratitude for their financial support.

In the ending lies a new beginning. For Stan Chase, who will continue where I left off, I wish the best of luck and success in pushing back the frontiers of science.

for Karla

ABSTRACT

I. Trimethylsilylpotassium reacts with epoxides to give olefins with inversion of stereochemistry. The reaction appears to proceed via the potassium β-silyl alkoxide (2) formed from the S_N2 attack of the silyl anion on the epoxide. Subsequent stereospecific syn-elimination of 2 affords the olefin of inverted stereochemistry. The reaction is convenient and preparatively useful.

The byproduct of the reaction, potassium trimethylsilanolate (17), effectively cleaves hexamethyldisilane to yield trimethylsilylpotassium. Since the latter reagent is generated and reacted in situ with epoxides, the overall reaction can be carried out with less than one equivalent of potassium methoxide.

II. The reaction of aryl halides with trimethylsilyl anions in HMPT provides good yields of aryltrimethylsilanes, useful synthetic intermediates. The choice of metal cation is unimportant. Chlorides and bromides give high yields of silylated products, while iodides give lower yields, with correspondingly increased amounts of reduced products. Arylammonium and arylphosphonium salts also undergo the reaction.

We have permissive evidence for the reaction proceeding via both aryl radical and aryl anion intermediates.

III. Trimethylsilyl and trimethylstannyl methoxycarbene complexes of chromium and tungsten have been prepared. One of these, $(CO)_5WC(OMe)SnMe_3$, reacts with norbornene at 80° to afford a new olefin polymer. Efforts to effect the alpha-elimination of the nonmetallic carbene ligands have not yet been successful. Reactions of these carbene complexes with acetone have been investigated.

TABLE OF CONTENTS

I. General Introduction. Preparation and Reactivity of Silyl Anions

II. Trimethylsilylpotassium. Deoxygenation of Epoxides with Inversion of Stereochemistry

III. Trimethylsilyl Anions. Direct Synthesis of Aryltrimethylsilanes

I. GENERAL INTRODUCTION

PREPARATION AND REACTIVITY OF SILYL ANIONS

1. Generation of Silyl Anions

A. Silyl Anions from the Alkali-metal Reduction of Silanes and Disilanes

Though compounds with silicon-alkali metal bonds ("silyl anions") were first reported in 1933,[1] extensive exploration of their chemistry awaited the development of more efficient preparative means.[2] Initially, these approaches (which did not appear until 1951) involved the reduction of aryl-silicon[3] and silicon-silicon[4] bonds with alkali metals. The second method results in a clean preparation of silyl anions, whereas the first method generates

$$ArSiR_3 \xrightarrow{2K} ArK + R_3SiK$$

$$R_2ArSiSiArR_2 \xrightarrow{2K} 2\ R_2ArSiK$$

an equimolar amount of aryl anion. The second method is limited to the preparation of aryl-substituted silyl anions, for hexaalkyldisilanes are inert to alkali metals.[2]

Alkali metals have been shown to cleave the silicon-hydrogen bond in arylhydrosilanes, yielding silyl anions plus metal hydrides.[5] Gilman has suggested (Scheme 1) that this probably proceeds via slow reduction of the aryl-silicon bond, yielding R_2SiHM and ArM.[2a] The latter rapidly displaces hydride from the starting material, and the resulting species R_2SiAr_2 can further react with alkali metal to give the observed product R_2SiArM plus ArM, which returns to the catalytic cycle. Provided R_2SiAr_2 undergoes metal reduction much faster than R_2SiArH, this method provides for the generation of silyl anions with only a small amount of aryl-metal species present. Again, trialkylsilyl anions cannot be generated via this procedure.

$$\begin{aligned} ArR_2SiH &\longrightarrow ArLi + R_2SiHLi \\ ArLi + ArR_2SiH &\longrightarrow Ar_2SiR_2 + LiH \\ Ar_2SiR_2 &\longrightarrow ArSiR_2Li + ArLi \end{aligned}$$

Scheme 1

Chlorosilanes also undergo metal reduction, resulting in silyl anions from aryl chlorosilanes. In this instance, disilanes are formed (probably by the initial

$$R_3SiCl \xrightarrow[-MCl]{2M} R_3SiM \xrightarrow{R_3SiCl} R_3SiSiR_3 \xrightarrow{2M} 2R_3SiM$$

generation of silyl anions, followed by their rapid silylation by unreacted chlorosilane), and further cleaved by alkali metal.[2] Chlorosilanes without aryl substituents undergo the reaction to form disilane, which does not react further.[6]

Transformations which may involve the intermediacy of silyl anions result from the reagent systems of magnesium and chlorotrimethylsilane in hexamethylphosphoric triamide (HMPT),[7] and lithium plus chlorotrimethylsilane in tetrahydrofuran.[8] The presence of silyl anions in these systems has not been firmly established, however, and most of the reactions are explained as silylations of anionic intermediates resulting from lithium reduction.

B. Silyl Anions from the Alkali-metal Reduction of Silicon-metal or Metalloid Bonds

Silylmercury and bis(silyl)mercury compounds are cleaved by lithium to give silyllithium compounds.[9] This

$$R_3SiHgR' \xrightarrow{2Li} R_3SiLi + R'Li + Hg$$

$$(R_3Si)_2Hg \xrightarrow{2Li} 2R_3SiLi + Hg$$

method, in contrast to other alkali metal reductions, is successful in the preparation of trialkylsilyl anions. However, this procedure suffers from several disadvantages: the yields of silyl anion are not high, a large excess of lithium metal is required, the procedure is slow and inconvenient, and the bis(silyl)mercurials are themselves not easily obtained and handled.[10]

Silicon-germanium bonds have been reductively cleaved with alkali metals.[11] In fact, this was the method utilized for the first preparation of a trialkylsilyl anion.[1b] The method suffers from low yields and concurrent formation of an equivalent of germyl anion.

C. Silyl Anions from the Heterolytic Cleavage of Disilanes by Nucleophiles

At present, the most general and convenient method for the generation of silyl anions involves the nucleophilic cleavage of disilanes. In 1971, Sakurai reported the first such reaction,[12] the preparation of trimethylsilylsodium from the sodium methoxide cleavage of hexamethyldisilane in HMPT solvent. Later, his group[13] and ours[14] independently discovered that trimethylsilylpotassium can be generated in the absence of HMPT, via the potassium methoxide cleavage of hexamethyldisilane in

$$\mathrm{MeONa} + \mathrm{Me_3SiSiMe_3} \xrightarrow[\mathrm{HMPT}]{} \mathrm{Me_3SiNa} + \mathrm{Me_3SiOMe}$$

$$\mathrm{MeOK} + \mathrm{Me_3SiSiMe_3} \xrightarrow[\substack{\mathrm{HMPT} \\ \text{or} \\ \text{THF, 18-crown-6 ether}}]{} \mathrm{Me_3SiK} + \mathrm{Me_3SiOMe}$$

tetrahydrofuran (THF) in the presence of 18-crown-6 ether, as well as via the HMPT procedure. Other alkoxides also effect the reaction. These cleavage reactions are very fast (complete within minutes at room temperature), and are clean. The only byproduct, methoxytrimethylsilane, is innocuous with respect to further reactions.

This particular preparation of silyl anions deserves further comment. The silicon-silicon bond strength has been revised to 80 kcal/mole,[15] which is not much weaker than a carbon-carbon sigma bond. Its nucleophilic cleavage by methoxide is rendered even more improbable by the higher energy content of the silyl anion, as shown by the relative pK_b values for these two bases (> 35 for the silyl anion,[16] 27.9 for methoxide in DMSO[17]). That the reaction proceeds at all is a tribute to the great susceptibility of silicon toward nucleophilic attack via valence-expanded intermediates or transition states, and to the strength of the silicon-oxygen bond, estimated as high as 129 kcal/mole.[18]

More recently, Still has very nicely shown that organolithium compounds serve equally well in the nucleophilic cleavage of disilanes.[19] Since organolithium and silyllithium species are relatively close in energy, the driving force for this cleavage must stem from the formamation of a new silicon-carbon bond, which has an estimated bond strength of 91 kcal/mole.[20] The cleavage is fast, all of the organolithium reagent is consumed (with

$$Me_3SiSiMe_3 + CH_3Li \xrightarrow[HMPT]{} Me_3SiLi + Me_4Si$$

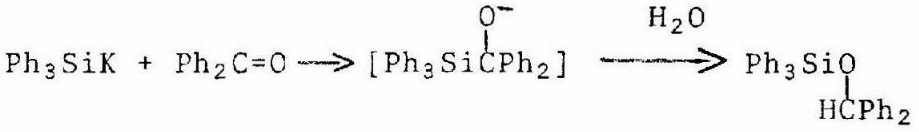
a slight excess of disilane), and the inert tetraalkylsilane is produced as the only byproduct.

2. Reactivity of Silyl Anions

A. Nucleophilic Properties of Silyl Anions

Numerous studies in the triphenylsilyl anion series have revealed the tendency toward nucleophilic displacement at a wide variety of electrophilic sites.[2] Alkyl and aryl halides, epoxides, tosylates, aldehydes, ketones, carboxylic acid derivatives, and inorganic and organometallic halides all react with triphenylsilyl anions to give coupling products, with loss of a good leaving group. However, the analogy with carbon anions is not complete, for competing reactions not found in the carbon case are often important. Also, subsequent reactions can occur so rapidly that the initial product of nucleophilic attack cannot be isolated. A primary example is the reaction of triphenylsilyl anions with carbonyl compounds;

the isolated product often is that resulting from a 1,2-shift of silicon from carbon to oxygen, subsequent to nucleophilic attack.[2,21]

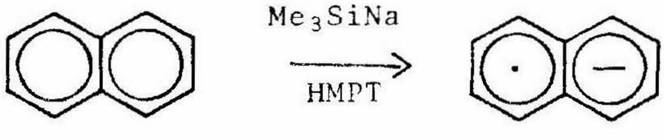


$$\mathrm{Ph_3SiK + Ph_2C{=}O \longrightarrow [Ph_3Si\overset{O^-}{\overset{|}{C}}Ph_2] \xrightarrow{H_2O} Ph_3Si\underset{HCPh_2}{\underset{|}{O}}}$$

The nucleophilic displacement by trialkylsilyl anions has been much less extensively studied. Organic halides[12,13] and ketones,[19] as well as chlorosilanes and stannanes,[9] undergo reaction with trimethylsilyl anions. Trimethylsilyllithium can be carboxylated by carbon dioxide.[22] Trimethylsilyllithium is much more reactive toward nucleophilic cleavage of THF than are its aryl-substituted counterparts.[16b]

B. <u>One-electron Donor Ability of Silyl Anions</u>

The presence of reductive dimer among the products of the reaction of silyl anions with active substrates (notably phosphonates and benzyl halides)[2b] suggests the possibility of an electron transfer mechanism. Sakurai has demonstrated this process in the reaction of trimethylsilylsodium with certain electron acceptors, such as naphthalene, in HMPT solvent. ESR spectra of the



intermediate radical anions were obtained.[12,23] Work by our group[24] and others[19] further substantiates this mechanism. However, these experiments also were conducted in HMPT, a solvent which strongly promotes one-electron donation.[25] Silyl anion reactions may follow different pathways in the ether (diethyl ether, THF, and 1,2-dimethoxyethane) solvents more commonly employed.

C. Silyl Anions as Base

Gilman[16a] measured the extent of metalation of a series of hydrocarbons by triphenylsilyllithium. He concluded that this anion is a stronger base than diphenylmethyllithium (pK_a = 33.45)[26] not as strong as benzyllithium (pK_a = 35)[28]. In a number of other reactions of triphenylsilyllithium with substrates possessing acidic protons, triphenylsilane is produced in significant amounts.[2b] Other arylsilyl anions also readily abstract acidic protons.[2d]

Less is known about the acidity of trialkylsilyl anions. In our group and elsewhere,[12] trimethylsilyl anions have been noted to react with protic acids (e.g., water) to give trimethylsilane. Trimethylsilyllithium efficiently metalates fluorene.[16b] On the basis of silyl anion-disilane redistribution experiments, it has been concluded that (assuming a constant silicon-silicon bond strength) the reactivity of silyl anions decreases with increasing aryl substitution.[2a] This is based on thermodynamic observations, whereas the measurement of reaction kinetics of the metalation of fluorene by silyllithium compounds discovered only a small difference in rate between the reaction of dimethylphenylsilyllithium, methyldiphenylsilyllithium, and triphenylsilyllithium.[16b] The rate of metalation by trimethylsilyllithium was not measured.

II. TRIMETHYLSILYLPOTASSIUM. DEOXYGENATION OF EPOXIDES WITH INVERSION OF STEREOCHEMISTRY

1. Introduction

A. 1,2-Eliminations of β-Functionalized Organosilicon Compounds

Organosilanes bearing a functional group two atoms removed from silicon readily undergo β-elimination[27] to alkenes. Such fragmentation can be induced in appropriate systems by acid, base, or heat, as shown by the examples of Scheme 2.

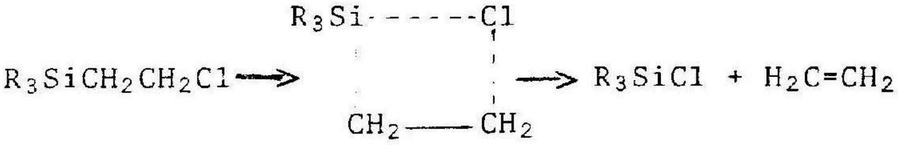
$$Me_3SiCH_2(CH_3)OH \xrightarrow{10\%\ H_2SO_4} H_2C{=}CHCH_3 + Me_3SiOSiMe_3 \qquad \text{Ref } 29$$

$$Et_3SiCH_2CH_2Cl \xrightarrow{NaOH} H_2C{=}CH_2 + EtSiOH + NaCl \qquad \text{Ref } 30$$

$$F_3SiCH_2CHF_2 \xrightarrow{200°} H_2C{=}CHF + SiF_4 \qquad \text{Ref } 31$$

Scheme 2

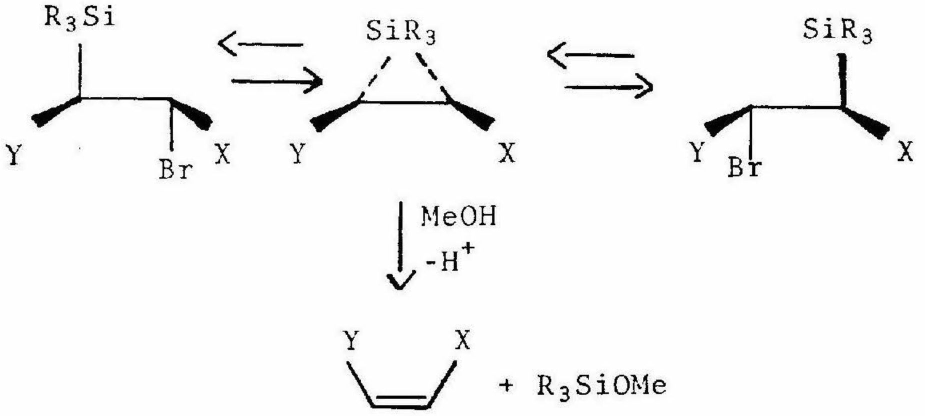
The thermal eliminations are thought to proceed in near-concerted fashion (though perhaps with considerable charge separation) via unimolecular four-centered transition states involving silicon and the leaving group (Scheme 3), based on kinetic studies.[32]



$$R_3SiCH_2CH_2Cl \longrightarrow \begin{matrix} R_3Si \cdots\cdots Cl \\ \vdots \qquad\quad \vdots \\ CH_2 \text{---} CH_2 \end{matrix} \longrightarrow R_3SiCl + H_2C{=}CH_2$$

Scheme 3

The solvolysis of β-bromosilanes proceeds via stereospecific anti-elimination.[33] Evidence has been obtained for some of these reactions passing through a symmetrical intermediate, such as the pentacoordinate siliconium ion intermediate shown in Scheme 4.[33b]

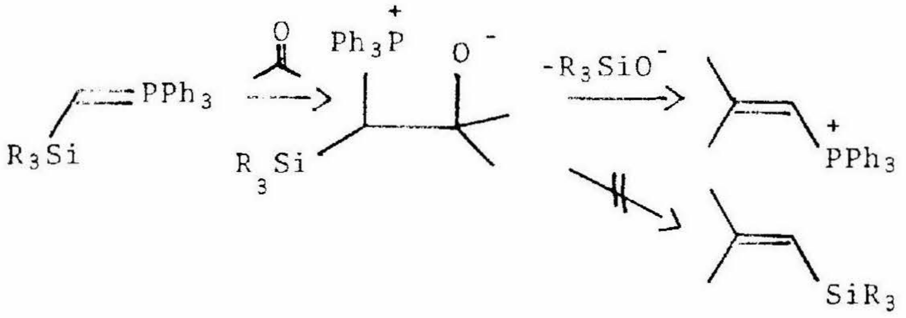


Scheme 4

Similar intermediates have been proposed in the cleavage of aryl, allyl, and vinylsilanes by electrophiles.[34]

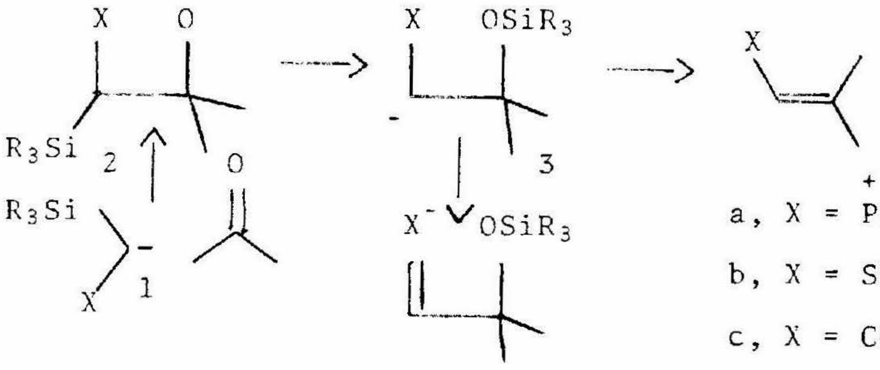
B. Base-induced Elimination of β-hydroxysilanes to Alkenes

Gilman and Tomasi, in an attempt to prepare vinyl silanes via the Wittig reaction of α-silyl phosphorous ylides (1a), observed products consistent with the β-elimination of silyl oxide, in preference to phosphine oxide (Scheme 5).[35]



Scheme 5

This was a surprising finding indeed, for a neutral silicon atom would not be expected to migrate to a β-oxygen anion faster than a positively charged phosphorous atom. These same workers, in fact, had earlier generated a series of β-silyl alkoxide anions from the reactions of triphenylsilyl anions with epoxides. In only one case was any product of elimination found (and then, it was not a major pathway).[36] The authors rationalized the silyl elimination from (2a), but not from simple lithium β-silyl alkoxides (2f), by invoking a stepwise process, in which the intermediate anion (3a) would be stabilized by ylide formation (Scheme 6).



Scheme 6

a, X = $\overset{+}{P}Ph_3$

b, X = SR

c, X = CO_2R

d, X = $SiMe_3$

e, X = $P(S)Ph_2$

f, X = H

Similar eliminations have been observed involving other hypothetical, stabilized anions as intermediates (**3b**,[37] **3c**,[38] **3d**,[39] and **3e**[40]).

C. Reaction of α-Silyl Carbanions with Carbonyl Compounds. The Peterson Olefination Procedure.

That electron-withdrawing groups are not required to effect the base-catalyzed β-elimination of hydroxysilanes was first demonstrated by Peterson in 1968 in his olefination procedure.[40] This method (shown in Scheme 7) represents the first synthetically important transformation involving β-hydroxysilane elimination.

Scheme 7

In addition to effecting the β-elimination with acid, Peterson observed base-catalyzed elimination upon treatment of the hydroxysilane intermediate with sodium or potassium hydride. He suggested the nature of the metal counterion as playing an important role in determining the rate of β-elimination, with potassium better than sodium, which is much better than magnesium. This was also noted by Hudrlik in subsequent work.[42]

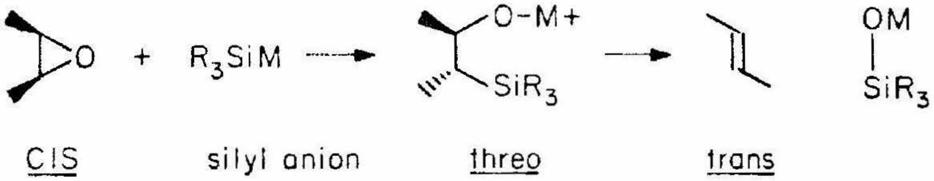
Both cis and trans olefins are produced in about equal amounts from the reactions in Scheme 7 (R and R' ≠ H). The absence of stereoselectivity may well result simply from indiscriminate attack by the α-silyl carbanion on either face of the carbonyl group. Another explanation is that the elimination process occurs in a stepwise manner as in Scheme 6 (2 → 3 → olefin). This is suggested by the accelerating effect of the electron withdrawing groups (a-e). The stabilized carbanion intermediate (3) may suffer racemization more rapidly than elimination.

D. Stereospecific Olefin-forming Reactions of β-hydroxysilanes

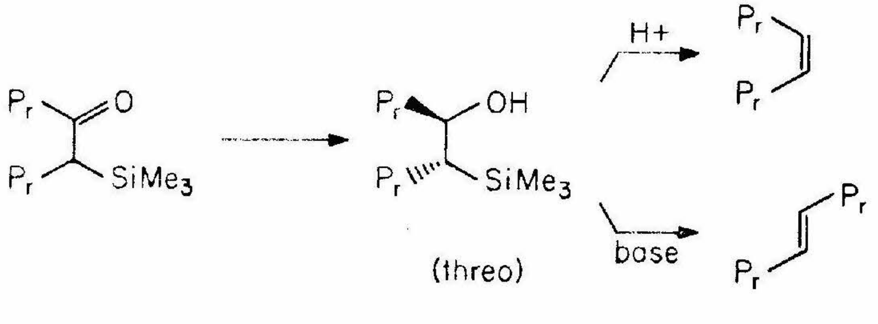
Hudrlik attempted to solve the question of the stereochemistry of β-elimination by constructing a β-hydroxysilane in a stereoselective fashion, and observing the course of base-catalyzed β-elimination. This was first accomplished via the stereoselective reduction of the β-ketosilane 5-oxoprop-4-yltrimethylsilane(4) with diisobutylaluminum hydride at -120° to give one diastereomer of the β-hydroxysilane with very high stereoselectivity.[42] Treatment of this product with KH or NaH gave trans-4-octene selectively; sulfuric or acetic acid treatment provided the cis-isomer. However, since neither the stereochemistry of the β-hydroxysilane diastereomer used, nor the course of the acid-promoted eliminations were known, the stereochemistry involved in the elimination reactions was as yet unproven.

It was at this point that we became involved in this problem. Epoxides can easily be prepared in high stereochemical purity from olefins. Furthermore, most nucleophiles react with epoxides in a strict S_N2 sense.[43] We felt the reaction of trimethylsilyl anion, for which convenient preparations had been recently developed in our group and Sakurai's[12-14] would provide a stereospecific route to erythro and threo β-silyl alkoxides.

$$Me_3SiSiMe_3 + NaOMe \xrightarrow{HMPA} Me_3SiNa$$



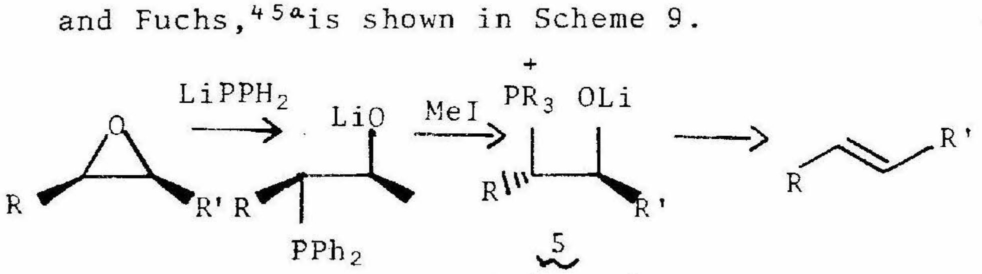
During the course of this work, Hudrlik reported the unambiguous stereochemical synthesis of a diastereomeric pair of β-hydroxysilanes, and their subsequent base-promoted β-elimination.[44] The synthetic route utilized entailed the cis-epoxidation of the isomeric vinyl silanes, with subsequent epoxide ring opening (alpha to silicon) by lithium di-n-propyl cuprate (Scheme 8). Thus, the cis-isomer of 1-trimethylsilyl-1-pentene was converted to the erythro β-hydroxysilane, which gave cis-4-octene on treatment with potassium hydride. The corresponding threo-β-hydroxysilane similarly affords the product from base-induced syn-elimination.



Scheme 8

E. Stereospecific Syn-elimination of β-phosphonium Alkoxide(betaine)intermediates

The comparison of the Peterson and Wittig olefination reactions indicates the similarity between silicon and phosphorous β-elimination reactions. Thus, just as the silyl anion cleaves epoxides and subsequently undergoes β-elimination,[14] a similar sequence involving nucleophilic cleavage of epoxides is known in the phosphorous series. This procedure, developed by Vedejs and Fuchs,[45a] is shown in Scheme 9.



5

Scheme 9

Triphenylphosphine has also been used to effect epoxide ring-opening, and generate the betaine(5) directly.[45b] However, high temperatures are required for the reaction, and at best only 80% inversion of stereochemistry is observed, presumably due to reversible retro-Wittig fragmentation to form the achiral phosphonium ylide and carbonyl compounds. This problem is not encountered with the more nucleophilic lithium diphenylphosphide which reacts with epoxides at 25°. A second reaction is required to alkylate the phosphine in order to generate 5. The yields reported for mono- and dialkyl-substituted epoxides were 75-95% by the route of Scheme 9.

2. Results and Discussion

A. Generation of Trimethylsilylpotassium

The observed counterion dependence of the rate of β-silyl alkoxide elimination,[40,42] increasing in the order Li < Na < K, suggests that a silylpotassium derivative would most readily induce epoxide deoxygenation to olefin.[47] The trimethylsilyl residue was selected as being (on steric grounds[27]) more readily attacked nucleophilically (by the oxygen anion) than more hindered silyl groups. Thus, we chose to investigate the reaction of trimethylsilylpotassium with epoxides.

Trimethylsilylpotassium had previously been prepared only in very low yield from the potassium metal cleavage of the unsymmetrical disilane $Me_3SiSiPh_3$.[51] While this method had previously been valuable in the preparation of arylsilyl anions, hexaalkyldisilanes were found to be inert. That the unsymmetrical disilane was unsuccessful is readily understood, in light of observations suggested by Gilman[2a] of the rapid redistribution of silyl anions and disilanes.[52] Thus, even if formed, the trimethylsilyl anion could rapidly react with the disilane to yield the more stable triphenylsilyl anion, and hexamethyldisilane, which would not be further reduced.

A second method for preparing trimethylsilyl anion, the alkali metal reduction of bis(trimethylsilyl)mercury, had not been used to prepare the potassium derivative. Furthermore, the general inconvenient of the method, the low yields involved, and the prospect of working with volatile organomercury compounds do not recommend this method.[19]

The third method available to generate trimethylsilylpotassium eventually proved the most useful and convenient. This is the cleavage of hexamethyldisilane by potassium methoxide in HMPT solution, in analogy with the trimethylsilyl sodium preparation developed by Sakurai.[12] We found the successful generation of trimethylsilylpotassium required HMPT distilled from lithium wire, and redistilled from calcium hydride as needed.

To avoid the solvent HMPT, which possesses the disadvantages of a high melting point (7°) and suspected carcinogenic properties, we and Sakurai[13] independently developed the 18-crown-6 ether[53] promotion of potassium methoxide-induced cleavage by hexamethyldisilane. This proceeds most readily in tetrahydrofuran, at room temperature or below. The reaction also occurs in less polar solvents, such as dimethoxyethane and benzene, but at a slower rate. Again, the solvents must be rigorously dried prior to use.

It was found that trimethylsilylpotassium was best generated and reacted in situ, rather than prepared prior to addition to epoxide. The reason for this lies in the reactivity of the silyl anion toward these solvents. The reactivity of trimethylsilylpotassium toward THF is not surprising, in view of the previously observed[16b] rapid nucleophilic cleavage of this solvent by trimethylsilyllithium. The partial reaction of trimethylsilylpotassium in HMPT at 65° is more surprising, as this solvent is generally inert to both nucleophiles and strong bases.[25] We found the predominant silicon product of this reaction to be trimethylsilane (via vpc and mass spectral analysis), indicated a proton abstraction by the silyl anion. Though this has not been further investigated, we believe the protons may be coming from methoxytrimethylsilane, the byproduct of methoxide cleavage of the disilane. The silylmethyl protons are somewhat acidic,[46] and it is not unreasonable that trimethylsilylpotassium in HMPT is a strong enough base to remove them. We found 1.5 equivalents of hexamethyldisilane to be the minimum sufficient to generate one equivalent of the silyl anion, based on yields of alkene product from the epoxide deoxygenation reaction.

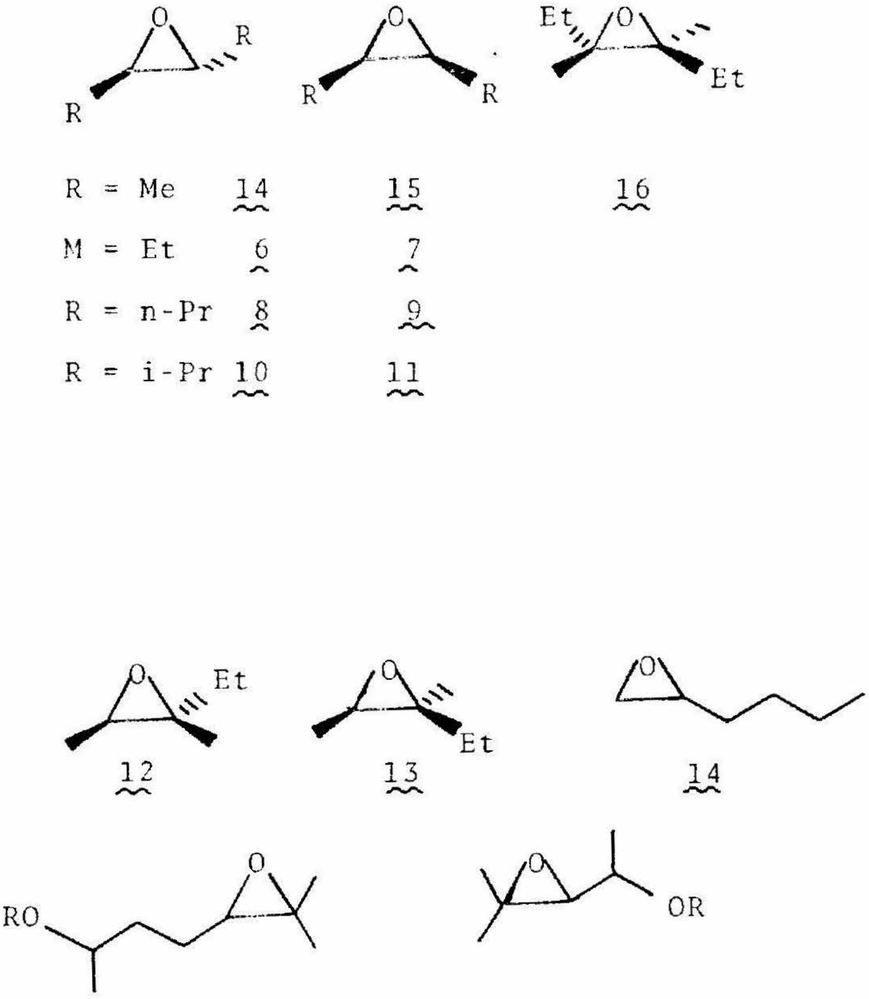
Other potassium alkoxides (but not potassium tert-butoxide) also react with hexamethyldisilane to afford deoxygenation of epoxides. Potassium fluoride does not cleave hexamethyldisilane. All solvents examined (THF, diethyl ether, dimethoxyethane, benzene, dimethyl sulfoxide, and tetramethylethylenediamine) except HMPT were not suitable for hexamethyldisilane cleavage by methoxide. Apparently, the methoxide must be activated by complexation of the potassium counterion by 18-crown-6 ether, or the superlative cation-solvating medium HMPT.

In crown ether mediated reactions, 18-crown-6 is known to complex potassium more effectively than other alkali metal cations.[53] Sodium methoxide is an effective agent for producing trimethylsilylsodium, as shown by Sakurai.[12] We found lithium methoxide to be relatively ineffective in HMPT, requiring elevated temperatures, and resulting in only fair yields. This also is consistent with the previous supposition, for the lithium ion is bound more tightly to methoxide than are sodium or potassium, and more difficult to activate by selective cation complexation.

B. Deoxygenation of Epoxides

1. Method A: Stoichiometric in Potassium Methoxide

i) In HMPT solvent, at 65°: The most convenient method for effecting epoxide deoxygenation with trimethylsilylpotassium is generally the reaction of 1.0 equivalent of epoxide with 1.5 equivalents each of hexamethyldisilane and potassium methoxide in HMPT (epoxide on the order of 0.1 molar concentration), heated at 65° for three h. The results of the reactions of several d,ℓ- and meso-isomeric pairs of epoxides (prepared from the corresponding olefins by m-chloroperbenzoic acid oxidation) are shown in Table I.



R = Me 14 15 16

M = Et 6 7

R = n-Pr 8 9

R = i-Pr 10 11

12

13

14

R = H 23

R = $SiMe_2t$-Bu 25

R = THP 27

R = Ac 29

RO = (=O) 30

R = H 31

R = TMS 33

Scheme 10. Epoxides

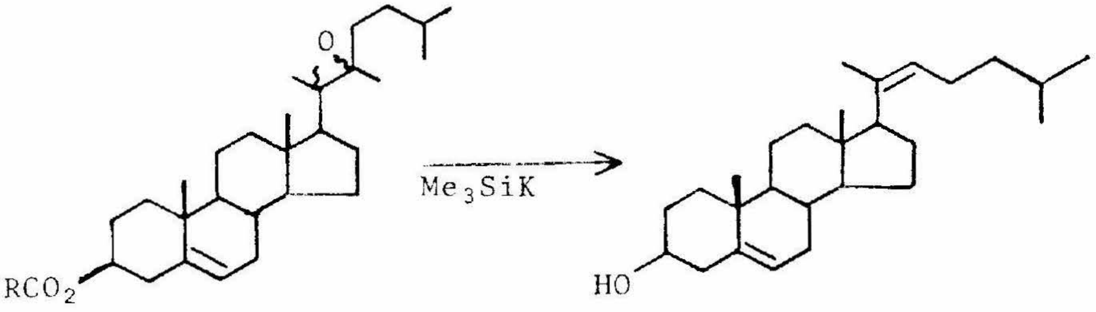
Table I. Epoxide Deoxygenation in HMPT at 65°

Epoxide	Yield[a] of cis olefin,%	Yield of trans olefin,%	Product geometry,%
d,ℓ-3,4-epoxyhexane (6)	99	< 0.5	> 99 cis
meso-3,4-epoxyhexane (7)	< 0.5	86	> 99 trans
d,ℓ-4,5-epoxyoctane (8)	96	< 0.5	> 99 cis
meso-4,5-epoxyoctane (9)	< 0.5	93	> 99 trans
d,ℓ-2,5-dimethyl-3-4-epoxyhexane (10)	93	1.8	> 98 cis
meso-2,5-dimethyl-3-4-epoxyhexane (11)	6	75	> 92 trans
E-3-methyl-2,3-epoxypentane (12)	91	< 0.5	> 99 cis
Z-3-methyl-2,3-epoxypentane (13)	< 0.5	99	> 99 trans

[a] Yield determined by vpc after workup.

As Table I reveals, mono-, di-, and trisubstituted epoxides are deoxygenated in high yield by treatment with trimethylsilylpotassium. The reaction exhibits high stereospecificity, with overall inversion (trans→cis, cis→trans) predominating over retention by greater than 99 to 1 in most cases. Even the hindered 1,2-di(isopropyl)ethylenes are produced in high yield and high stereospecificity from the corresponding epoxides. While most alkenes are inert, cis-diisopropylethylene is isomerized by trimethylsilylpotassium (1.5 equivalent) to the trans isomer to the extent of only 3% after 3 h (HMPT, 65°). This is much slower than the rate of silyl anion attack on epoxides. No products resulting from silyl anion addition to double bonds were observed, in contrast to reports of trialkylsilyllithium to olefins.[9a]

This procedure compares favorably with other epoxide deoxygenation procedures.[45,47] Some advantages include the high yield and high stereospecificity observed, the one-step nature of the reaction, and the point that the reagent is formed directly from commercially available starting materials. The reaction requires only mild temperatures, and short reaction times. Some of these merits are illustrated in the synthesis of Z-20(**22**)-dehydrocholesterol by Koreeda and coworkers.[54] In the last step, the stereoselective synthesis of the trisubstituted Z-20(22) double bond, was accomplished in 95%



yield via trimethylsilylpotassium deoxygenation of the threo epoxides. A double bond and an alkoxide function elsewhere in the molecule did not adversely affect the reaction. The high yield in this deoxygenation of a trisubstituted epoxide, and in others described below, contrasts favorably with the moderate yields obtained from the deoxygenation of trisubstituted epoxides via the Vedejs-Fuchs procedure.[45a]

The deoxygenation procedure, combined with the well-developed methods for stereospecific epoxidation of olefins, constitutes a new olefin inversion procedure,[48] as well as a stereospecific olefin synthesis. Such procedures are of high utility in the field of natural products synthesis.[49]

HMPT need not be the major solvent to promote the generation of trimethylsilylpotassium. As little as 10% by volume of HMPT in THF was found to effect the epoxide deoxygenation reaction. Longer reaction times (24 h) at similar temperatures (refluxing THF) were required. The procedure seemed to offer no advantage over undiluted HMPT.

ii) In THF solvent with 18-crown-6 ether: Trimethylsilylpotassium can also be generated via the 18-crown ether activated potassium methoxide cleavage of hexamethyldisilane in THF, and reacted in situ with epoxides. Reactions were carried out with 1.5 equivalents each of crown ether, potassium methoxide, and hexamethyldisilane with 1.0 equivalent of epoxide, in THF solvent (0.1 molar concentration) at room temperature for three h. The results of several stereochemically pure epoxides subjected to these conditions are displayed in Table II.

The deoxygenation of epoxides in THF is seen from Table II to exhibit the same high stereospecificity as in HMPT. The yields are high in most cases, if somewhat lower than in HMPT. The diisopropyl epoxides, however, required an unusual excess of trimethylsilylpotassium to achieve a high yield of deoxygenation. The tetrasubstituted epoxide (16) failed to react with trimethylsilylpotassium.

No Page 28

Table II. Epoxide Deoxygenation in THF/18-crown-6 ether at 25°

Epoxide	Yield[a] of cis olefin,%	Yield of trans olefin,%	Product geometry,%
1,2-epoxyhexane (14)			
d,ℓ-3,4-epoxyhexane (6)	99	< 0.5	> 99 cis
meso-3,4-epoxyhexane (7)	< 0.5	80	> 99 trans
d,ℓ-4,5-epoxyoctane (8)	76	< 0.5	> 99 cis
meso-4,5-epoxyoctane (9)	< 0.5	90	> 99 trans
d,ℓ-2,5-dimethyl-3-4 epoxyhexane (10)	7[c]	< 0.5	> 99 cis
meso-2,5-dimethyl-3,4 epoxyhexane (11)	< 0.5	19[c]	> 99 trans
E-3-methyl-2,3-epoxypentane (12)	87	< 0.5	> 99 Z
Z-3-methyl-2,3-epoxypentane (13)	< 0.5	80	> 99 E
d,ℓ-2,3-epoxybutane (14)	b	< 0.5	> 99 cis
meso-2,3-epoxybutane (15)	< 0.5	b	> 99 trans
d,ℓ-3,4-dimethyl-3,4-epoxyhexane (16)	1.5	< 0.5[d]	---

[a] Yield determined by vpc analysis with respect to internal standard.

[b] Yield not determined, but estimated > 80%.

[c] Yield improved dramatically (80%) after addition of excess (3 equivalents more) disilane. The product geometry was > 95% inverted.

[d] 92% epoxide unreacted after 48 h.

One other drawback to the above procedure is the use of stoichiometric amounts of 18-crown-6 ether. This compound is commercially available, but expensive. (We chose to prepare it from triethylene glycol via a published procedure.[130]) Furthermore, it is inactive in effecting hexamethyldisilane cleavage by potassium methoxide unless it has been purified via chromatography over alumina. We will later show that catalytic amounts of 18-crown-6 ether (0.1 equivalent) are equally effective in epoxide deoxygenation.

The THF procedure does have some advantages over HMPT, in addition to the question of toxicity. While 65° is required to effect facile epoxide deoxygenation in HMPT, the reactions in THF were commonly run at room temperature. Indeed, we found lower temperatures acceptable. In one instance, **14** was deoxygenated to 1-hexene in 70% yield in six h in THF at -78°, via the crown ether reaction.

THF also may be preferable in instances where the one-electron donor properties of trimethylsilyl anion in HMPT could lead to competing side reactions. For instance, while silyl anions deoxygenate the stilbene epoxides to stilbenes in good yield,[48a] the reaction with trimethylsilylpotassium is not successful in HMPT, apparently because of the tendency for electron transfer into the aromatic system.

2. Method B: "Catalytic" in Potassium Methoxide

Consideration of the mechanism proposed in the next section led to the suggestion that less than one equivalent of potassium methoxide should afford complete epoxide deoxygenation under appropriate conditions. Only hexamethyldisilane is required in stoichiometric quantity. The results of the deoxygenation of various isomeric pairs of epoxides with 0.1 equivalents of potassium methoxide, utilizing both the HMPT and the THF methods, are shown in Table III.

Table III bears out the validity of the above assumption; a "catalytic amount" of potassium methoxide is indeed sufficient to bring about complete epoxide deoxygenation. Yields and stereochemical purity of products are again high. The reaction rate in THF is inconveniently slow at room temperature, as opposed to the case where one equivalent of methoxide is present, such that the catalytic reaction is best performed at reflux temperature, 65°. The diisopropyl epoxides again show low conversion to olefin in THF, although the reactions proceed normally in HMPT. Though not shown in the table, potassium trimethylsilanolate (**17**)[56] was found to effect hexamethyldisilane cleavage and *in situ* epoxide deoxy-

Table III. Epoxide Deoxygenations with "Catalytic" KOCH$_3$

Epoxide	Method[a]	Yield[b] of cis olefin,%	Yield of trans olefin,%	Product geometry,%
1,2-epoxyhexane (14)	A	(85% 1-hexene)		
d,ℓ-3,4-epoxyhexane (6)	A	99	< 0.5	> 99 cis
	B	87	< 0.5	> 99 cis
meso,2,4-epoxyhexane (7)	A	< 0.5	86	> 99 trans
	B	< 0.5	98	> 99 trans
d,ℓ-4,5-epoxyoctane (8)	A	96	2	> 99 cis
	B	87	< 0.5	> 99 cis
meso-4,5-epoxyoctane (9)	A	< 0.5	93	> 99 trans
d,ℓ-2,5-dimethyl-3,4-epoxyhexane (10)	A	83	7	> 92 cis
	B	c		
meso,2,5-dimethyl-3,4-epoxyhexane (11)	A	1.9	95	> 98 trans
	B	c		

Table III, continued.

Epoxide	Method[a]	Yield[b] of cis olefin,%	Yield of trans olefin,%	Product geometry,%
E-3-methyl-2,3-epoxypentane (12)	A	91	0.5	> 99 cis
Z-3-methyl-2,3-epoxypentane (13)	A	< 0.5	99	> 99 trans
	B	< 0.5	99	> 99 trans

[a] Method A: 1.5 equiv. $Me_3SiSiMe_3$, 1.0 equiv. epoxide, 0.1 equiv. $KOCH_3$ in HMPT at 65° for 3 h.

Method B: 1.5 equiv. $Me_3SiSiMe_3$, 1.0 equiv. epoxide, 0.1 equiv. each $KOCH_3$ and 18-crown-6 ether in THF at reflux for 3 h.

[b] Yield determined by vpc with respect to internal standard.

[c] Less than 5% epoxide deoxygenation occurred under these conditions.

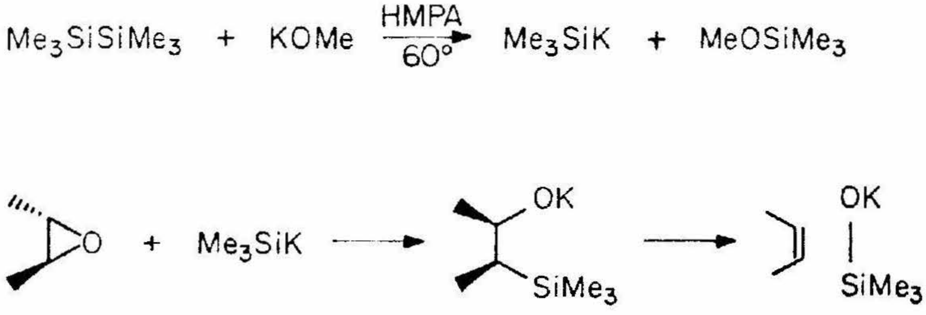
genation under both stoichiometric and catalytic conditions.

In many cases, the catalytic method may prove to be synthetically preferable to the stoichiometric procedure, for the substrate is exposed to the minimum concentration of potassium methoxide and trimethylsilylpotassium. Moreover, the need for "dry" potassium methoxide is no longer necessary since only a catalytic amount is required. This modification of the stoichiometric procedure has practical as well as mechanistic significance.

C. Mechanism

1. Stereochemistry of β-elimination

All experimental evidence is fully in accord with the mechanism proposed in Scheme 11 for epoxide deoxygenation.

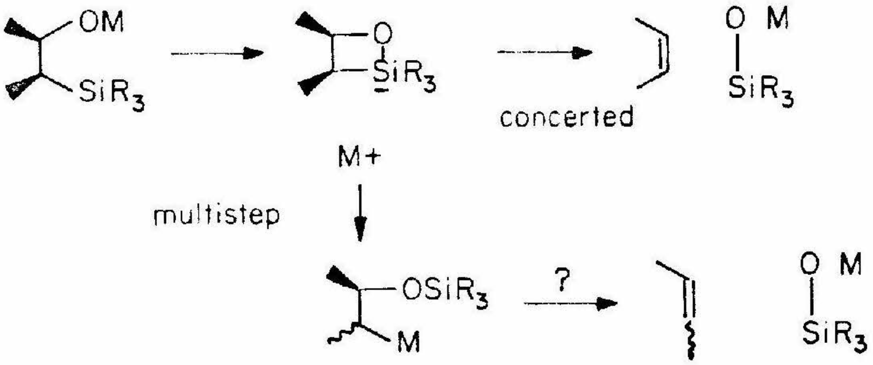


Scheme 11

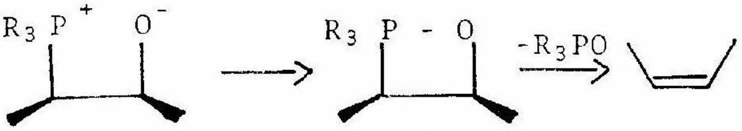
The first step, disilane cleavage, is known from the work of Sakurai.[12] The expected silicon byproduct methoxytrimethylsilane has been observed in the reaction mixture, as has the unexpected byproduct hexamethyldisiloxane. The attack of trimethylsilylpotassium on the epoxide with inversion of configuration is identical to the reaction of triphenylsilyllithium with epoxides.[36] The potassium salt of the β-hydroxysilane thus produced (2) is well known to rapidly form the olefin, with loss of potassium trimethylsilanolate (17).[42] The existence of the latter compound in the reaction medium is indicated by the results of the catalytic reactions, discussed below.

The stereospecific syn-elimination of 2 to olefin is in agreement with the results of Hudrlik, who independently generated 2 via the route discussed previously.[44] Although the syn-elimination of 2 had been previously postulated,[40,42] this was the first experimental demonstration of the stereospecificity of the elimination.

It seems likely that the four membered cyclic structure 18 lies on the mechanistic path from 2 to olefin (Scheme 12). In analogy with the Wittig reaction, 18 may be a true intermediate leading directly to elimination (path a), or an approximation to the transition state involving silicon migration from carbon to oxygen, resulting in a carbanion (19) which subsequently eliminates (path b). A theoretical study of this problem,[57]



considering both the Wittig and Peterson reactions, found in the former case that path a was followed. Ample experimental evidence, including the spectral observation[58] and isolation (followed by thermal elimination to olefin)[59] of oxaphosphetanes (20), confirm this pathway (Scheme 13). However, the same study predicts the



20

Peterson reaction to follow more nearly path b in Scheme 12, resulting in the carbanion 19. Unless the subsequent elimination is much faster than bond rotation, this process results in a mixture of olefin isomers, contrary to experimental observations. Furthermore, β-hydroxy and alkoxy carbanions (analogous to 19), generated via the metal reduction of the corresponding halides, generally give nonstereospecific elimination to olefins.[60] The present evidence thus appears to support a one-step elimination from cyclic intermediate 18. It should be noted that no direct evidence, such as that previously described for oxaphosphetanes in the Wittig reaction, exists for the intermediacy of 18. In fact, silaoxetanes themselves (the neutral counterparts of 18, containing tetravalent silicon) have been reported only as hypothetical intermediates in the thermal reactions of strained silicon compounds with aldehydes and ketones.[61]

2. Catalysis and Initiation

A very interesting aspect of the deoxygenation reaction is the fact that only a "catalytic" amount of methoxide is required to effect complete deoxygenation. A true catalysis would regenerate methoxide after each act of deoxygenation, presumably by displacement from silicon (path A in Scheme 14). Alternatively, the reaction may be initiated by methoxide, the bulk of the disilane cleavage being the result of direct nucleophilic displacement by potassium trimethylsilanolate (17) (path B in Scheme 14).

$$\mathrm{KOMe + Me_3SiSiMe_3 \longrightarrow Me_3SiK + Me_3SiOMe}$$

$$\mathrm{Me_3SiK + epoxide \longrightarrow \underset{17}{Me_3SiOK} + olefin}$$

$$\text{A:}\quad \mathrm{\underset{17}{Me_3SiOK} + Me_3SiOMe \longrightarrow MeOK + Me_3SiOSiMe_3}$$

$$\text{B:}\quad \mathrm{\underset{17}{Me_3SiOK} + Me_3SiSiMe_3 \longrightarrow Me_3SiK + Me_3SiOSiMe_3}$$

Scheme 14

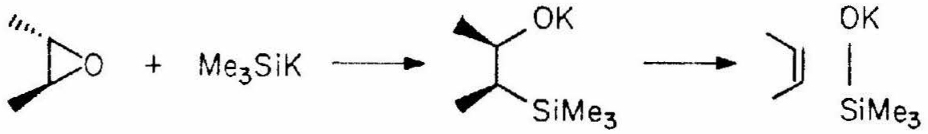
Path A is reasonable, assuming rapid attack of alkoxides on silyl ethers[27] (though this could best be represented as an equilibrium reaction). Our observation that 17 and hexamethyldisilane can be utilized in the absence of methoxide to afford deoxygenation of epoxides, both stoichiometrically and with 0.1 equivalent of 17 at rates similar to the methoxide-induced deoxygenations, shows that path B is permissible. In deoxygenations with a stoichiometric amount of potassium methoxide, hexamethyldisiloxane is observed in about 2:1 ratio to methoxytrimethylsilane: the ratio rises as the relative amount of potassium methoxide falls. Controls revealed that little of the hexamethyldisiloxane arises from the hydrolysis of methoxytrimethylsilane during the workup. In the stoichiometric methoxide case, redistribution of silyl ethers according to path A must be occurring, for potassium methoxide reacts faster with hexamethyldisilane under these conditions than the resulting silyl anion deoxygenates epoxides to produce **17**. Hence, the appearance of hexamethyldisiloxane must arise from reaction of **17** and methoxytrimethylsilane (path A). It can therefore be concluded that the two pathways of Scheme 14 are both reasonable and permissible in the epoxide deoxygenations involving less than one equivalent of potassium methoxide.

3. Nature of Rate-determining Step

Several pieces of information point to the attack on epoxide by trimethylsilylpotassium as being the rate-determining step. In general, although no precise kinetic studies were carried out, vpc analyses of reaction mixtures prior to completion of the reaction indicated that epoxide disappeared at the same rate as appearance of olefin. The inertness of tetrasubstituted epoxides can be attributed to a high barrier to epoxide cleavage.

The proposed mechanism of epoxide deoxygenation (Scheme 15) involves three or more steps: disilane cleavage by potassium methoxide, epoxide cleavage by trimethylsilylpotassium, and elimination (in one or more steps) of the β-silyl alkoxide anion. Disilane cleavage is very fast in HMPT at room temperature,[12] and elimination from the potassium β-silyl alkoxide anion under the same conditions is complete with an hour.[42] Since the epoxide deoxygenation is much slower than either of these (three hours at 65° is required for complete deoxygenation), the remaining step, epoxide cleavage, must be rate-determining.

$$Me_3SiSiMe_3 + KOMe \xrightarrow[60°]{HMPA} Me_3SiK + MeOSiMe_3$$



Scheme 15

D. Limitations

1. *trans*-Cyclooctene

Our attempts to deoxygenate *cis*-cyclooctane epoxide to *trans*-cyclooctene with trimethylsilylpotassium gave unexpected results. The epoxide was cleaved to yield cyclooctyltrimethylsiliane (21), which was isolated and characterized. Only a small amount of trans-

21

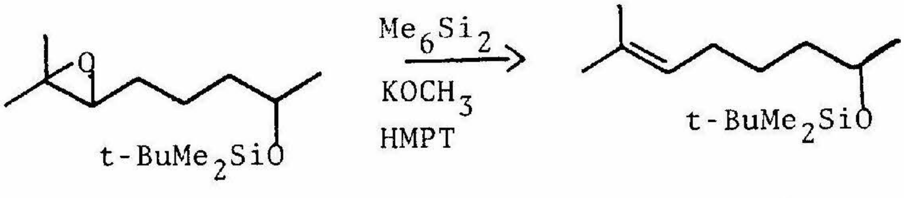
cyclooctene was observed. Half of the epoxide was recovered unreacted, despite the use of the usual excess of hexamethyldisilane.

A straightforward explanation of these results entails the epoxide deoxygenation as the slow step, followed by rapid β-elimination to give the strained trans-cyclooctene. Subsequent reaction of trimethylsilylpotassium with this strained olefin would afford after protonation the observed 21. Each mole of 1,2-epoxycyclooctane thus reacts with two equivalents of trimethylsilylpotassium, as opposed to just the usual one equivalent; the usual amount of trimethylsilylpotassium therefore only reacted with half of the epoxide present.

Trans-cyclooctene is a strained and highly reactive olefin. Reaction of this moiety with trimethylsilylpotassium, a strong nucleophile, is not surprising. Although we have not observed this type of addition to other olefins, similar reactions of trimethylsilyllithium with acyclic olefins have been reported to occur (albeit in low yield).[9a]

2. Functionality

Several derivatives of the trisubstituted epoxide 6-methyl-5,6-epoxyheptane-2-ol, (23) derivatized via the hydroxyl group, were subject to the conditions of epoxide deoxygenation to determine what functional groups were compatible with a trimethylsilylpotassium. The O-tert-butyldimethylsilyl ether (25) gave a 51% yield of olefin (vpc), with the remainder starting material, with



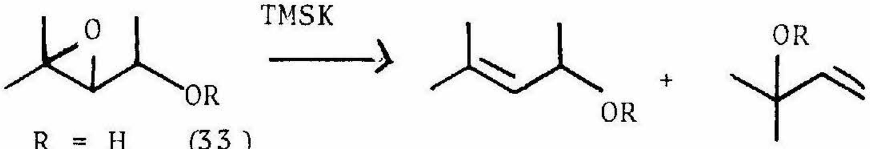
25 24

the "catalytic KOCH$_3$" procedure. The parent alcohol (23), the O-tetrahydropyranyl ether (27), and the O-acetate (29) showed no catalytic deoxygenation. With one equivalent of potassium methoxide, in HMPT at 65°, the parent alcohol and the acetate are consumed to give mixtures containing many products, but little or no product of deoxygenation. The ketone 6-methyl-5,6-epoxyheptan-2-one (31) was recovered from the "catalytic" reaction mixture are 24 h in 68% yield, but less

31

than 1% deoxygenation to olefin had occurred. The reaction of the ketone with one equivalent of potassium methoxide gives complicated mixtures devoid of olefin.

The reaction of the potassium salt (unisolated) of 3,4-epoxy-4-methyl-2-pentanol (33) with hexamethyldisilane, either in HMPT or in THF with crown ether present, produces a mixture of 16 or more products, none of which is major. The reaction of the O-trimethylsilyl ether (35) of the above alcohol gave similar results. Unrearranged and rearranged olefin and epoxide, silylated and not, are among the products. While most alkenes are inert, cis-diisopropylethylene is isomerized by



R = H (33)

R = $SiMe_3$ (35)

trimethylsilylpotassium (1.5 equivalent) to the trans isomer to the extent of 3% after 3 h (HMPT, 65°). This is much slower than the rate of silyl anion attack on epoxides. No products resulting from silyl anion addition to double bonds were observed, in contrast to reports of trialkylsilyllithium addition to styrenes.[9]

3. Conclusion

Trimethylsilylpotassium, a strong base, nucleophile, and one-electron donor, reacts with epoxides to give olefins with inversion of stereochemistry. The reaction appears to proceed via the potassium β-silyl alkoxide (2) formed from the S_N2 attack of the silyl anion on the epoxide. This step appears to be rate determining in the overall procedure. Subsequent stereospecific syn-elimination of 2 affords the olefin of inverted stereochemistry. (Cis epoxide yields trans olefin, and trans epoxide gives cis olefin.) The reaction is convenient and preparatively useful.

The byproduct of the reaction, potassium trimethylsilanolate (17), effectively cleaves hexamethyldisilane to yield trimethylsilylpotassium. Since the latter reagent is generated and reacted in situ with epoxides, the overall reaction can be carried out with a small amount of potassium methoxide (relative to 1.0 equivalent of epoxide and 1.5 equivalents of hexamethyldisilane).

Ethers, tert-butyldimethylsilyl ethers, and remote alkoxide functions survive the reaction conditions. Functional groups which are reactive toward proton abstraction, nucleophilic attack, or reduction by one-electron donor reagents are incompatible with the transformation.

4. Summary

The geometric inversion of olefins has been achieved by the process of syn-epoxidation, and treatment of the epoxides with trimethylsilylpotassium generated in situ from the reaction of hexamethyldisilane with potassium methoxide. The reaction was carried out primarily in THF (with 18-crown-6 ether) or HMPT solvents, with stoichiometric or "catalytic" amounts of methoxide. The scope and limitations of the transformation were investigated and some insight gleaned of the mechanism involved.

III. TRIMETHYLSILYL ANIONS.

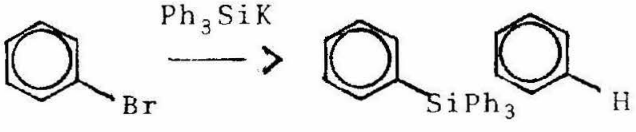
DIRECT SYNTHESIS OF ARYLTRIMETHYLSILANES

1. Introduction

A. Triphenylsilylpotassium and Bromobenzene

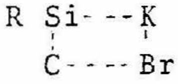
Although the chemistry of trimethylsilyl anions has only recently received attention, triphenylsilyl anions (first prepared in 1933[1]) have been studied for a quarter of a century.[2] Their reactions with aryl halides, particularly bromobenzene, are well known.[3,4,63] Aryltriphenyl silanes, the products of aromatic substitution, are observed in moderate yields, commonly about 50%. The remainder of the silylated products are triphenylsilanol and hexaphenyldisiloxane, the expected products of hydrolysis of triphenylsilyl halides, as well as hexaphenyldisilane, the precursor of triphenylsilyl anion, and benzene (arene).

In 1957, Brook and Wolfe[63] carried out a study of the reaction between triphenylsilylpotassium and bromobenzene in ether. They concluded that the reaction

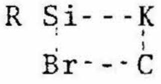


proceeds via two simultaneous pathways, "normal coupling" (resulting in aryltriphenylsilane) and halogen-metal interchange, with relative rates about 60:40 based on product ratios. The metalation reaction leads to phenylpotassium, which is primarily quenched by the solvent to give benzene,[64] plus bromtriphenylsilane, which also is not isolated, but either (a) reacts with more triphenylsilylpotassium to give the disilane, or (b) in the absence of more triphenylsilylpotassium is hydrolyzed on workup to triphenylsilanol and hexaphenyldisiloxane. Path (a) is pursued under conditions of "normal addition" (adding bromobenzene to silyl anion), while (b) is followed during "inverse addition" (adding the silyl anion to bromobenzene) experiments. Although it might be thought that the bromotriphenylsilane could silylate the phenylpotassium via S_N2 displacement, the authors show this to be slow relative to the proton abstraction from ether by phenylpotassium.

The authors propose two cyclic four-centered intermediates (**58** and **59**) as leading to coupling and halogen-metal exchange, respectively



58

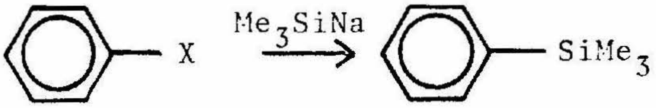


59

Both of these pathways are interesting for a variety of reasons. The halogen-metal interchange represents an unexpected reaction which results in non-isolable products; hence, the authors were forced to utilize indirect methods to demonstrate its existence. The coupling reaction is very important in that it is known to be site-specific;[3] the silyl group becomes bonded to the same carbon atom that formerly held the halogen. Very few reactions are known in which unactivated aryl halides (in the absence of transition metals) couple with nucleophiles,[65] excepting via benzyne intermediates,[66] from which cine substitution is commonly observed.[67]

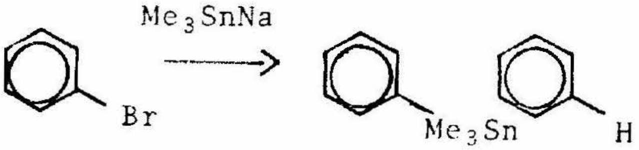
B. *Trimethylsilyl- and Stannylsodium with Aryl Halides*

In his first report of the preparation of trimethylsilylsodium, Sakurai[12] noted its reactions with bromobenzene and chlorobenzene. The substitution product, phenyltrimethylsilane, was found in 44% and 30% yield,



respectively. No other product (e.g., benzene) was reported, though specific mention was made of the absence of biphenyl from the product mixture. This was perhaps deemed of interest because of the presence of the corresponding reductive dimer among the products of the reactions of n-butyl halides and benzyl chloride with trimethylsilylsodium. No mechanism was discussed, although the possibility of one-electron transfer from the silyl anion was suggested, primarily because such a process had been observed with napthalene.

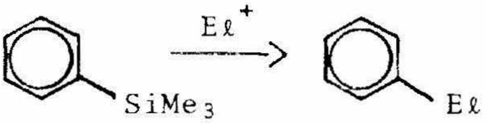
Reactions of the corresponding tin anion, trimethylstannylsodium, have been much more extensively



studied.[2c,d] This reagent effects the nucleophilic substitution of aryl halides, especially bromides. Studies of the mechanism of this reaction by Kuivila[69] have found halogen-metal interchange to be an important pathway. A mechanism involving one-electron transfer and radical anion intermediates was considered and rejected.

C. Aryltrimethylsilanes as Intermediates in Synthesis

The extreme tendency of aryltrimethylsilanes toward electrophilic substitution has been extensively studied by Eaborn, who found rates of substitution 10^4 greater than the parent, unsubstituted arenes.[70] This enables the introduction of electrophilic functions to an aromatic ring under mild conditions, at a specific site (previously occupied by silicon), regardless of



Eℓ = Halogen, H,D,RCO, etc.

the directing effects of other functional groups present. Virtually all types of electrophiles known to replace aromatic hydrogen have been shown to substitute aryltrimethylsilanes.[70] This method has already been put to use in organic synthesis, utilizing aryltrimethylsilanes both as synthetic intermediates,[71] and as reagents to transform other compounds.[72]

During the course of our work in silyl anion chemistry, we chose to further investigate the reactions of trimethylsilyl anions with aryl halides. Our goal was to help elucidate the mechanism of this reaction, and to develop a new preparative method for aryltrimethylsilanes.[73]

2. Results and Discussion

A. Preparation of Trimethylsilyl Anion Reagents

Trimethylsilylpotassium and trimethylsilylsodium were prepared by the methoxide cleavage of hexamethyldisilane in HMPT, as previously described,[12-14] in the presence of the aryl halide. Further reaction occurred *in situ* (Scheme 16).

$$Me_3SiSiMe_3 + MOCH_3 \xrightarrow[\text{HMPT, }25°]{} CH_3OSiMe_3 + Me_3SiM$$

$$M = Na, K$$

$$Me_3SiM + ArX \xrightarrow[\text{in situ}]{} Me_3SiAr + ArH$$

Scheme 16

Trimethylsilyllithium was prepared by the method of Still by the reaction of methyllithium with hexamethyldisilane in HMPT.[19] Solutions of aryl halides in HMPT were then added. (Scheme 17). In this fashion, reaction of methyllithium with aryl halides was avoided.

$$Me_3SiSiMe_3 + CH_3Li \xrightarrow[\text{HMPT, }0°\text{, 15 min}]{} Me_4Si + Me_3SiLi$$

$$Me_3SiLi + ArX \xrightarrow[\text{HMPT, }25°]{} Me_3SiAr + ArH$$

Scheme 17

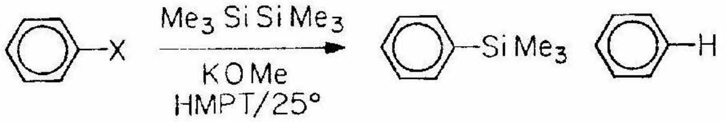
Butyllithium and potassium phenoxide both cleave hexamethyldisilane, and have been used for silylations in the reactions above. Lithium methoxide cleaves hexamethyldisilane only with difficulty, requiring days at elevated temperature (120°) to show a significant amount of reaction.

The generation of trimethylsilylpotassium in THF solvent[13,14] was described in the previous section. This method was also used to effect the silylation of aryl halides as in Scheme 16, substituting THF and 18-crown-6 ether for HMPT. The crown ether was effective in less than stoichiometric quantities. 1.5 Equivalents each of hexamethyldisilane and methoxide (or methyllithium) were used in all of the reactions of Schemes 16 and 17.

B. Reactions of Trimethylsilyllithium, Trimethylsilylsodium, and Trimethylsilylpotassium with Halotoluenes

Unactivated aryl halides can be silylated in good to excellent yields by reaction with trimethylsilyl anions. The yields compare favorably with other methods of direct silylation[73] for aryl bromides and iodides. This may be the superior method for the trimethylsilyldehalogenation of aryl chlorides. The only competing process is reduction of the halide. Table I lists the results of the reactions of p-halotoluenes with trimethylsilyllithium, -sodium and -potassium, in HMPT. Yields were determined after work-up by vapor phase chromatography with decane as internal standard.

The products in Table IV, and indeed of all aromatic nucleophilic silylations examined thus far, give products of formal displacement at aromatic carbon leaving the halogen. No evidence of rearrangement, cine-substitution or other scrambling has been found.



X = Cl, Br, I

REL. RATES: I, Br >> Cl

The nature of the counterion, as is apparent from Table IV, has little effect on the outcome of the reaction. This contrasts with the great counterion effect on the base-catalyzed elimination of β-hydroxysilanes, discussed in the previous section.

Table IV. Reactions of Trimethylsilyl Anions with p-Halotoluenes in HMPT

Reagent	Halide	Yield of **43**,%	Yield of toluene,%	Total Yield,%	Substitution to Reduction Ratio (**43**/toluene)
Me_3SiK	Cl	86	5	91	17
	Br	92	7	99	13
	I	68	26	94	2.6
Me_3SiNa	Cl	87	5	92	17
	Br	91	8	88	11
	I	70	27	97	2.6
Me_3SiLi	Cl	69	4	73	17
	Br	84	7	91	12
	I	63	26	89	2.4

The nature of the halogen atom plays a large role in the course of the reaction. This can best be seen in Table IV from the ratios of silylated product to reduced product. This ratio is highest for the reactions with chlorotoluene, somewhat lower for bromotoluene, and much lower for iodotoluene (a factor of about 7 lower than chlorotoluene). In all cases, increased temperature results in lower silylation to reduction ratios.

Table V discloses the results of the silylation reaction, wherein the metal counterion (potassium) is held constant, while the halogen atoms and their positions on the ring are varied. The silylation to reduction ratio, previously noted to increase in the order I < Br < Cl for the p-halotoluenes, shows the same behavior in both the ortho and the meta series. Furthermore, the change is remarkably constant. The ratio decreases by a factor of between 1 and 2 upon passing from chloride to bromide, and further decreases by a factor of 4-5 between bromide and iodide.

A similar progression obtains in the comparison of positional isomers. The silylation to reduction ratio increases smoothly in the order ortho < meta < para for all halides examined.

Table V. Reactions of Trimethylsilylpotassium with Ortho, Meta, and Parahalotoluenes in HMPT

	Halide	para	meta	ortho
Yield of ArTMS, %	Cl	86	88	69
	Br	92	82	69
	I	68	56	40
Yield of ArH, %	Cl	5	11	20
	Br	7	18	23
	I	26	44	55
Total Yield, %	Cl	91	99	89
	Br	99	100	92
	I	94	100	95
Substitution to Reduction Ratio (ArTMS/ArH)	Cl	17	8.0	3.45
	Br	13	4.5	3.0
	I	2.6	1.3	0.73

The results of the reaction of aryl halides with trimethylsilylpotassium, generated in THF via the 18-crown-6 procedure, are shown in Table VI.

The reaction appears to be less well-behaved using this procedure than in HMPT. The chloride isomers did not fully react, and m- and o-iodotoluene showed very little reaction. Increasing amounts of hexamethyldisilane and potassium methoxide did not affect this pattern. The problem may have to do with the crown ether, which was not used in excess.

p-Iodo- and bromotoluenes reacted completely to give silylated and reduced products. The ratio ArTMS/ArH, however, is much lower in these reactions than in the reactions conducted in HMPT. This is particularly surprising, because this ratio for all three chlorides in THF is somewhat higher than in HMPT.

C. Reaction of Trimethylsilyl Anions with Heteroaromatics

The reaction of aryl halides with trimethylsilyl anions is also useful in the case of halopyridines. Thus, 2-bromopyridine upon reaction with trimethylysilylpotassium gave an 80% isolated yield of 2-pyridyltrimethylsilane (**46**). Similarly, 3-chloropyridine and 4-chloropyridine hydrochloride upon reaction with tri-

Table VI. Reactions of Trimethylsilylpotassium with Halotoluenes in THF[a]

	Yield, %						Recovered Starting Material			ArTMS/ArH		
	Substitution			Reduction								
ArX	Cl	Br	I	Cl	Br	I	Cl	Br	I	Cl	Br	I
para	50	77	48	2.5	23	23	47	0	0	20	3.3	2.1
meta	29[b]	67[c]	--[d]	1.5	33	--	52	0	95	19	2.0	---
ortho	48[b]	44	--[d]	13	52	--	39	4	95	3.7	0.85	---

[a] At room temperature for 24 h, except where indicated

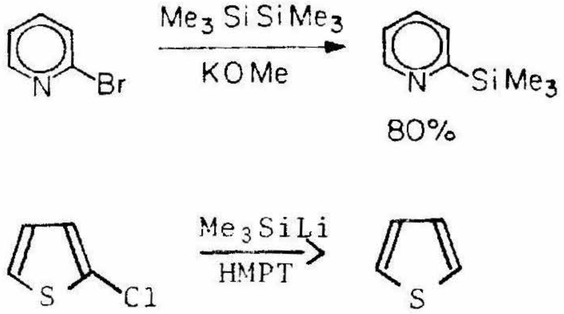
[b] At reflux for 24 h.

[c] 45% isolated yield

[d] Less than 5% reaction occurred.

methylsilyllithium gave respectively 3-pyridyl trimethylsilane (**47**) and 4-pyridyl trimethylsilane (**48**) in somewhat lower yields. No reduction product (pyridine) was found by vpc in any of the reactions of halopyridines examined.

In contrast, the reaction of 2-chlorothiophene with trimethylsilyllithium resulted in a 70% yield of thiophene, the reduction product, with no 2-thienyltrimethylsilane isolated.



D. Reaction of Trimethylsilyl Anions with Arylammonium and Arylphosphonium Salts

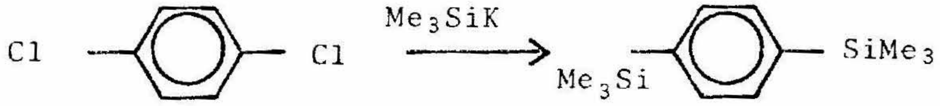
In our efforts to extend the nucleophilic silylation reaction to substrates other than halides, we examined briefly arylammonium salts and arylphosphonium salts. Preliminary experiments revealed that methyltriphenylphosphonium bromide reacted with trimethylsilyllithium to give the silylation product, phenyltrimethylsilane, in 54% yield. Phenyltrimethylammonium bromide reacted with trimethylsilylpotassium to give a 19% yield of phenyltrimethylsilane.

$$R_3\overset{+}{A}\text{-Ar} \xrightarrow[\text{HMPT}]{\text{TMS}^-} \text{Ar-TMS} + R_3A \quad (A = N,P;\ R = Me,Ph)$$

These reactions could eventually prove useful in the indirect substitution of aryl amines and phosphines.

E. Reaction of Trimethylsilyl Anions with Dihalobenzenes. Competition Experiments

Dihalobenzenes react with trimethylsilylpotassium to afford bis-silylated products; the silylation to re-

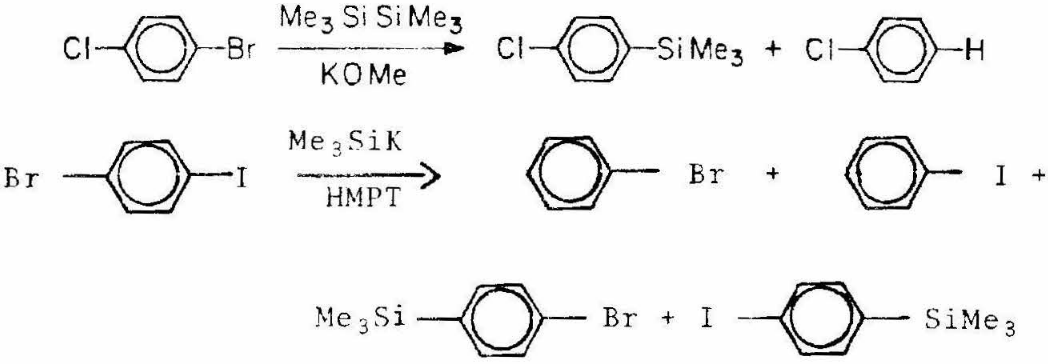


duction ratio is lower than the mono-halotoluenes. Thus, p-dichlorobenzene reacted with excess trimethylsilylpotassium to give a 24% yield of p-bis(trimethylsilyl) benzene (**49**). o-Dichlorobenzene gave solely products of reduction. No evidence for the formation of benzyne was found. The fact that dihalobenzenes undergo the reaction allowed two kinds of competition experiments to be carried out. In the first type, two different halobenzenes were allowed to compete for insufficient silyl anion reagent. Bromobenzene was found to react ten times as fast as chlorobenzene with trimethylsilylpotassium in THF at room temperature. In turn, iodobenzene reacted three times as fast as bromobenzene.

However, under conditions of Scheme 16 (HMPT solvent), iodobenzene reacted only 1.1 times faster than bromobenzene with trimethylsilylpotassium. Bromobenzene reacted only twice as fast as chlorobenzene under these conditions. In an unusual competition, o-chlorotoluene was shown to react with trimethylsilylsodium in HMPT at a rate 1.75 times faster than meso-4,5-epoxyoctane.

The second type of competition experiment utilized was of the intramolecular variety, wherein a p-dihalobenzene with different halogens was allowed to react with insufficient trimethylsilylpotassium in HMPT. In this type of experiment, the relative rates are determined by the product ratios, while in the previous type, relative rates must be derived from the differential loss of starting materials.

In the case of 1-bromo-4-iodobenzene, products arising from iodide loss appeared in about 1.5 times the yield of products derived from bromide loss. 1-Bromo-4-chlorobenzene, in contrast, reacted to give (95%) products of bromide loss (71% of p-chlorophenyltrimethylsilane (50) and 24% of chlorobenzene) plus (3%) products of overreaction (2% of 1,4-bis(trimethylsilyl)-benzene (49), and 1% phenyltrimethylsilane) with less than 1% products of solely chloride loss evident via vpc. Similarly, 1-chloro-4-iodobenzene gave only the products of iodide loss, 49, 50 and chlorobenzene (Scheme 18).



Scheme 18

F. Deuterium Labelling Experiments

Iodobenzene was reacted with trimethylsilylpotassium in HMPT, then quenched with deuterium oxide. The reduction product, benzene, was isolated via preparative vpc and the percentage of deuterium incorporation analyzed by mass spectrum.

When the reaction was quenched after 90 min, only 1.3% deuterium incorporation was found. However, when the reaction was quenched after only five min, the recovered benzene was 30% enriched in deuterium (d_1-

incorporation).

Similarly, the reaction of iodobenzene with trimethylsilylpotassium generated from hexamethyldisilane and $KOCD_3$ was quenched after two h with H_2O, and the benzene isolated and analyzed via mass spectrum. In this instance, the reduction product consisted of 64% benzene-d_1. These results are summarized in Scheme 19.

$$\mathrm{PhI} \xrightarrow[\mathrm{KOCH_3,\ HMPT}]{\mathrm{Me_3SiSiMe_3}} \xrightarrow{\mathrm{D_2O}} \mathrm{Ph\text{-}H} + \mathrm{Ph\text{-}D} + \mathrm{Ph\text{-}SiMe_3}$$

$$7 : 3$$

$$\mathrm{PhI} \xrightarrow[\mathrm{KOCD_3,\ HMPT}]{\mathrm{Me_3SiSiMe_3}} \xrightarrow{\mathrm{H_2O}} \mathrm{Ph\text{-}H} + \mathrm{Ph\text{-}D} + \mathrm{Ph\text{-}SiMe_3}$$

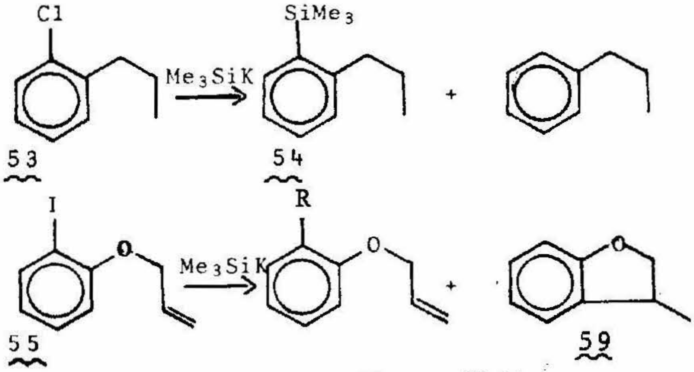
$$3.8 : 6.3$$

These results provide permissive evidence for the presence of two intermediates, phenyl radical (abstracting D· from CD_3O^-) and phenyl anion (quenched with D_2O). The implications in terms of the mechanism are discussed later.

G. Attempted Cyclization Reactions

A sample of o-chloropropylbenzene (53) was prepared and reacted with trimethylsilylpotassium according to Scheme 16. Two products were obtained, isolated by preparative vpc, and found to be the expected products of straightforward reduction (propylbenzene) and silylation (o-propylphenyltrimethylsilane, 54).

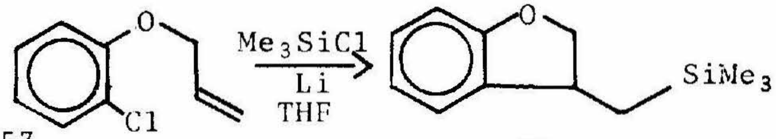
Likewise, o-iodophenyl allyl ether (55) was synthesized[74] and reacted with trimethylsilylpotassium.



R = SiMe$_3$ (56)

R = H

In this case, the three products found were o-allyloxyphenyltrimethylsilane (56), allyl phenyl ether, and 2,3-dihydro-3-methylbenzofuran (59). The cyclic product is suggestive of an intermediate o-allyloxyphenyl radical, which is known to readily cyclize to form (after hydrogen abstraction) 59.[74] We have observed a similar ring closure reation upon treatment of



57

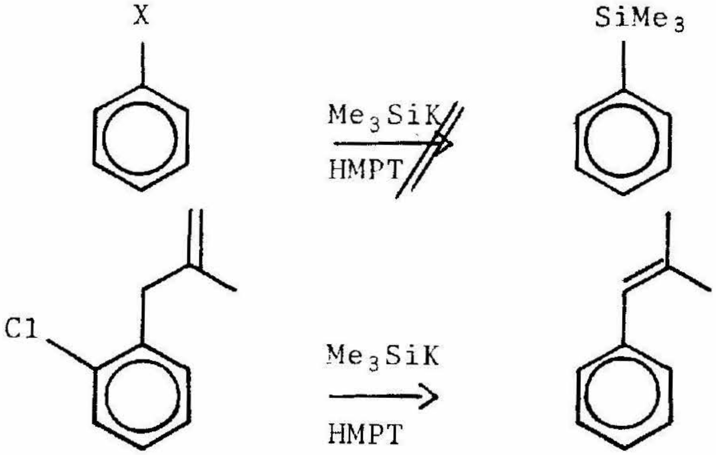
58

o-chlorophenyl allyl ether with lithium and chlorotrimethylsilane in THF. The observed product was 2,3-dihydro-3-(trimethylsilylmethyl)benzofuran.

H. Limitations

Fluorobenzene did not react with trimethylsilylpotassium in HMPT, even after 24 h at room temperature. Anisole was similarly inert, precluding any attempt at another catalytic reaction sequence. Phenyl mesylate gave products of nucleophilic attack at methyl, instead of aromatic substitution.

The basicity of trimethylsilyl anions should preclude the silylation of compounds with acidic protons. Isolated double bonds are not affected by trimethylsilyl anions; however, the attempted silylation of a β,γ-unsaturated aromatic halide resulted in isomerization of the double bond into conjugation with the aromatic ring, and concurrent reduction of the halide. Preliminary experiments showed that p- and o-halobenzoic esters could be silylated in fair yield.

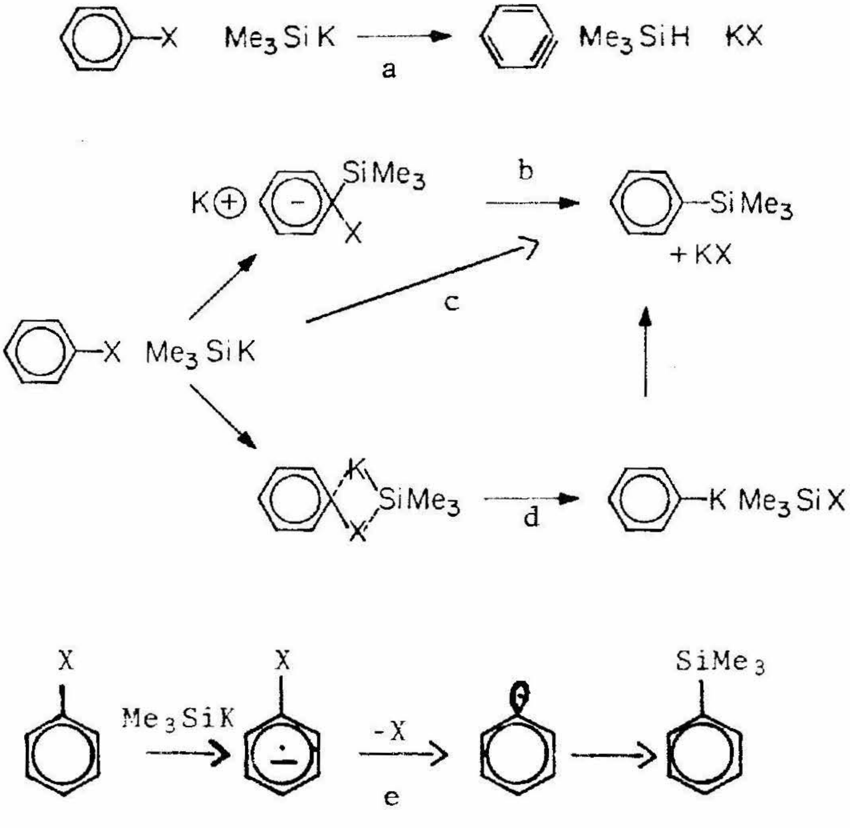


$X = OR, F, OSO_2Me$

p-Iodotoluene showed little or no reduction by potassium methoxide in HMPT in the absence of hexamethyldisilane. No methylanisole was found by vpc in this or any of the reactions in Table IV-VI. Bitolyl was similarly sought, but never observed.

I. Mechanism

Five possible mechanisms of nucleophilic aromatic silylation are depicted in Scheme 20. These are: (a) substitution via benzyne intermediates; (b) an addition-elimination mechanism; (c) direct, concerted substitution (d) halogen-metal exchange, followed by silylation of the carbanion intermediate; and (e) silylation via aryl radical intermediates.



Scheme 20

The mechanism of path a can be dismissed in view of the stereochemical results; no cine-substitution is observed. The direct substitution pathways (b and c) are more difficult to exclude. However, path b is usually followed only with aryl systems bearing electron-withdrawing groups (eg NO_2) which stabilize the anionic intermediate.[67] The concerted, four-center mechanism of path c, which was suggested by Brook for the reaction of triphenylsilylpotassium with bromobenzene,[63] does not involve an intermediate, but has as yet no precedent. Either pathway (b or c) requires the introduction of a second mechanism to account for the reduction product.

The phenyl anion intermediate (path d) was also suggested by Brook.[63] We found that, the quenching of the reaction of trimethylsilylpotassium and iodobenzene with D_2O (5 min after initiation) affords reduction product (benzene) with 30% d_1 incorporation, as determined by mass spectrometry. This suggests that at least a portion of the reaction may involve a phenylpotassium intermediate. Furthermore, the finding of only 1% deuterium incorporation in the reduction product when the reaction was quenched after 90 min indicates that (the presumed intermediate) phenylpotassium is highly reactive in this reaction medium. Hence, 30%

may be only a lower limit for the portion of the reaction proceeding via a phenyl anion intermediate.

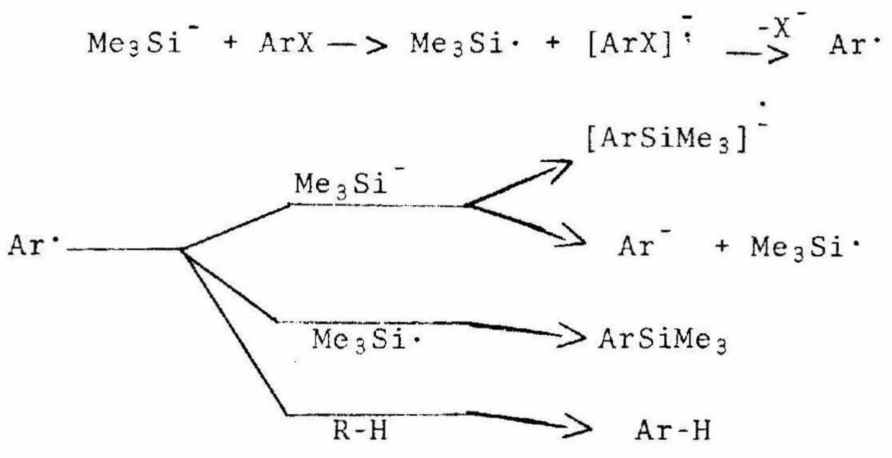
When the trimethylsilylpotassium used to silylate iodobenzene was generated from the reaction of hexamethyldisilane with CD_3OK, the reduction product obtained after quenching with H_2O had 64% d_1 incorporation. This is permissive evidence for the presence of a phenyl radical intermediate. While CD_3OK is a poor acid, it is a good hydrogen atom donor, as shown by Bunnett during his studies of the methoxide ion reduction or aryl iodides.[76] His proposed mechanism for this reaction is shown in Scheme 21.

$$\begin{aligned} R\cdot + CH_3O^- &\longrightarrow RH + \cdot CH_2O^- \\ CH_2O^- + ArI &\longrightarrow \cdot CH_2O + [ArI]^{\dot{-}} \\ [ArI]^{\dot{-}} &\longrightarrow Ar\cdot + I^- \\ Ar\cdot + CH_3O^- &\longrightarrow ArH + \cdot CH_2O^- \end{aligned}$$

Scheme 21

This mechanism in itself can explain the source of reduction product only. In fact, controls showed that potassium methoxide and iodobenzene in the absence of hexamethyldisilane do not react to give significant amounts of reduction product, in HMPT at 65°. Similarly, Bunnett found that the presence of a radical initiator was required to effect reduction (in methanol).[63]

A type of mechanism involving silyl anions as initial electron donors to the aryl halide to generate aryl radicals provides a fifth possibility. The intermediate aryl radicals in this mechanism could then choose from four further paths (Scheme 22): coupling with trimethylsilylpotassium ($S_{RN}1$)[75] (see Scheme 23) to give silylated product, one electron reduction to phenylpotassium, coupling with trimethylsilyl radical, or hydrogen abstraction to give reduction product. Radical anions of aryltrimethylsilanes (formed from the first route) are well characterized in other systems.[77]

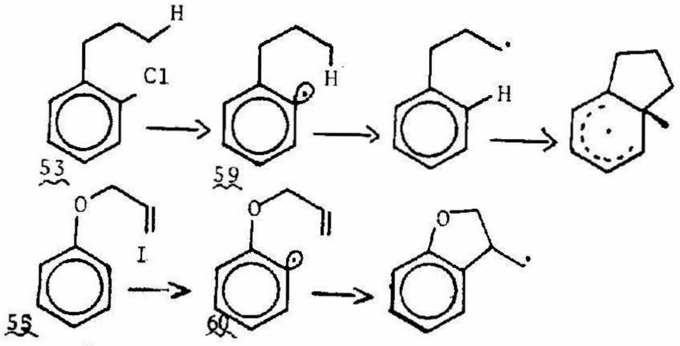


Scheme 22

$$\begin{array}{rcl}
Me_3Si^- + ArX & \longrightarrow & Me_3Si^{\cdot} + [ArX]^{\dot{-}} \\
[ArX]^{\dot{-}} & \longrightarrow & Ar^{\cdot} + X^- \\
Ar^{\cdot} + Me_3Si^- & \longrightarrow & [ArSiMe_3]^{\dot{-}} \\
[ArSiMe_3]^{\dot{-}} + ArX & \longrightarrow & ArSiMe_3 + ArX^{\dot{-}}
\end{array}$$

Scheme 23 $S_{RN}1$ Mechanism[75]

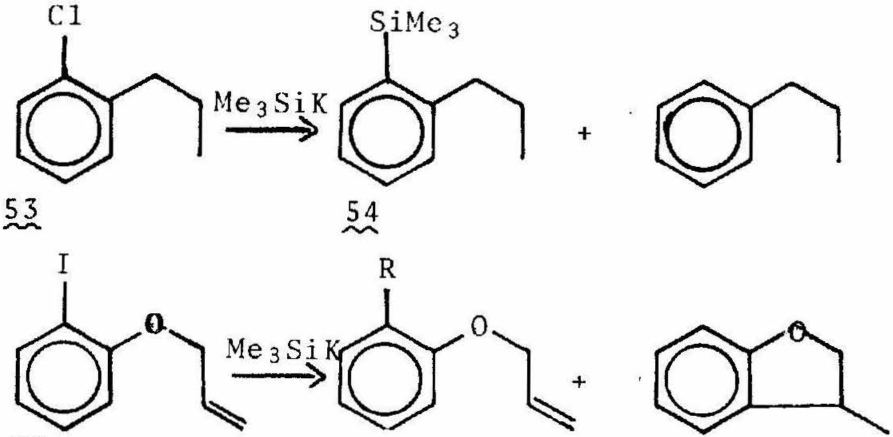
We sought to obtain further evidence for the intermediacy and lifetime of these aryl radicals. Two aryl radicals which might be expected to undergo intramolecular cyclization are o-propylphenyl (**59**)[78] and o-allyloxyphenyl (**60**).[74] In particular, the known cyclization of **60** is very rapid; the rate at 130° was recently



Scheme 24

determined[74b] to be 6 x 10^7 sec^{-1}.

By the mechanism of Scheme 22, the silylation of aryl halides **53** and **55** should generate the radical intermediates **59** and **60**, respectively. In fact, the reaction of **55** with trimethylsilylpotassium in HMPT resulted in cyclized as well as uncylized products. (No cyclized products were found in the silylation of **53**).



53 **54**

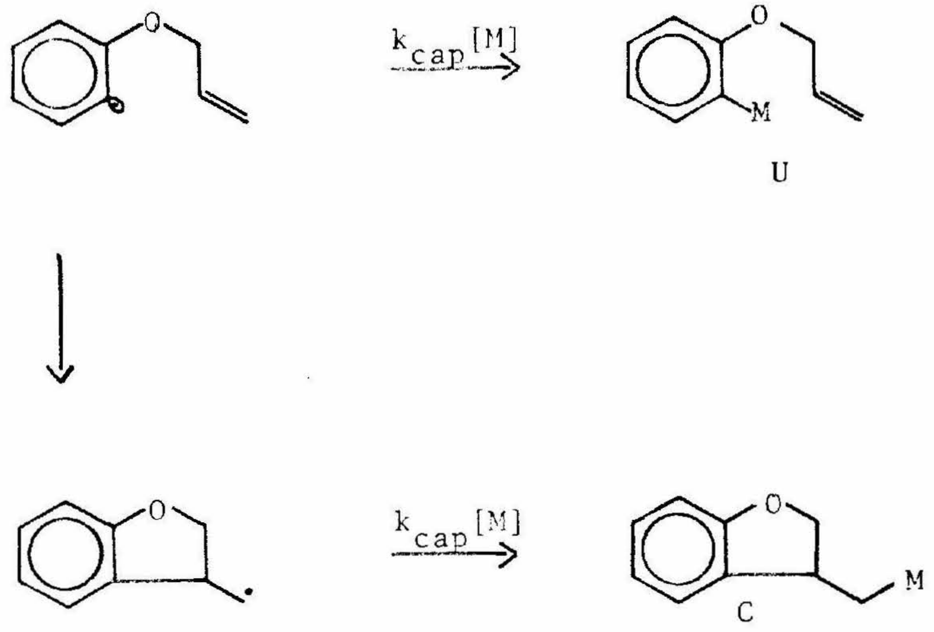
55 **59**

R = SiMe$_3$ (**56**)

R = H

Scheme 25

These results suggest the intermediacy of aryl radicals. A rough calculation of the rate of silylation (k_{cap}) can be carried out, using the relation $U/C = k_{cap}[M]/k_{cyc}$, by inserting appropriate values for k_{cyc}, the rate of unimolecular cyclization; [M], the concentration of silylating species and the observed ratio of products, uncyclized to cyclized where $U/C \simeq 0.17$. If [M] is taken to be 0.1 M,



Scheme 26

$$\frac{U}{C} = \frac{k_{cap}[M]}{k_{cyc}}$$

Scheme 26

the maximum concentration of trimethylsilyl anion, and k_{cyc} is assigned the reasonable[79] value of $\sim 10^6$ at 25°, then $k_{cap} \sim 2 \times 10^6$.

3. Conclusions

The reaction of aryl halides with trimethylsilyl anions in HMPT provides good yields of aryltrimethylsilanes, useful synthetic intermediates. The choice of alkali metal cation is unimportant, while the nature of the halide ion has a significant effect on the outcome of the reaction. Chlorides and bromides give high yields of silylated products, while iodides give somewhat lower yields, with correspondingly increased amounts of reduction products. In the halotoluenes, para isomers give better yields of silylation product than meta isomers, which in turn gives better yields than the ortho isomers. The reaction is regiospecific, with the trimethylsilyldehalogenation occurring at the carbon bearing the halide. Quarternary ammonium and phosphonium salts containing at least one aryl group also undergo nucleophilic aromatic silylation.

We have permissive evidence for the reaction proceeding via both aryl radical and aryl anion intermediates. The radical intermediates, if formed, must be captured to give noncyclized products at a rate approaching the diffusion-controlled limit, possibly via subsequent radical-radical recombination or electron transfer. A combination of competing mechanisms also accounts for the results.

It should be cautioned that the mechanism of the silylation may be different in THF and ether than in HMPT. The silylation to reduction ratios of the bromides and iodides are different in a different solvent. The reaction of an aryl chloride was shown in a competition study to proceed faster than epoxide reaction in HMPT, whereas in THF, the aryl chlorides react much more slowly. Thus, the extension of these conclusions to the reaction of trimethylsilyl and triphenylsilyl anions in other solvents is not warranted without further investigation.

4. Summary

The nucleophilic trimethylsilylation of unactivated aryl halides has been found to be a synthetically useful reaction. Limitations and extensions of the reaction were examined. Permissive evidence has been obtained for the presence of both aryl radical and aryl anion intermediates in the reaction.

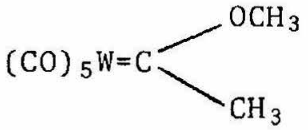
IV. TRIMETHYLSILYL- AND TRIMETHYLSTANNYL-SUBSTITUTED TRANSITION METAL CARBENES

1. Introduction

A. Synthesis of Transition Metal Carbenes by Reaction of Metal Carbonyls with Nucleophiles

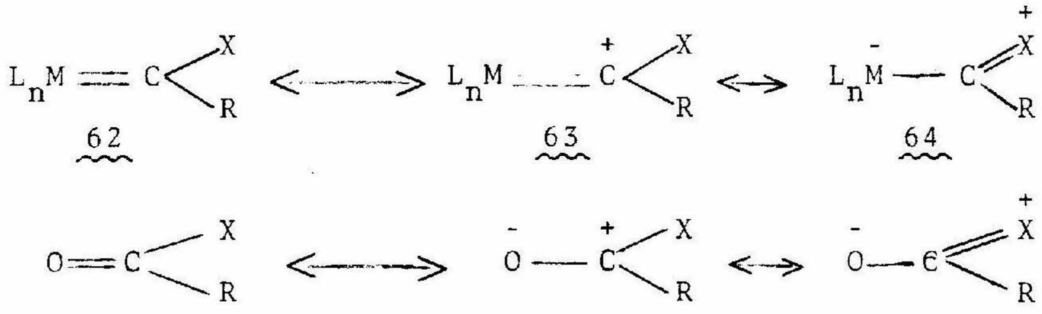
One of the most rapidly developing areas in the field of organometallic chemistry is that of transition metal carbene complexes. E. O. Fischer synthesized methylmethoxycarbene pentacarbonyltungsten, (61), the first example of this class of compound, in 1964.[80] Since that time, many more carbene complexes have been prepared,[81,82] involving every stable transition metal in Groups VI, VII, and VIII in both mononuclear and polynuclear complexes.

Complexes vary considerably in stability; the most stable share the following characteristics with 61: Group VI metal with carbonyl or other electron-accepting ligands, and at least one hetero-atom bonded to the carbene carbon.



61

The generally accepted explanation of these trends is that the resonance depicted in Scheme 27, placing negative charge on the metal, is an important contributor to the electronic structure of carbene complexes, in analogy with resonance in carboxylic acid derivatives.[83] Factors which minimize the importance of resonance structures 63 and 64 should destabilize the carbene complex.

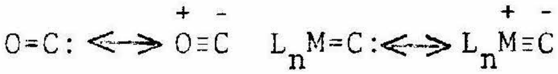


Scheme 27

Other observations support this view. Thus, 61 is thermally more stable than its O-trimethylsilyl analogue,[84] presumably because delocalization of the oxygen lone pairs into empty low-lying silicon d orbitals decreases the contribution of 64 to the resonance hybrid. Also, x-ray data show that X-$C_{carbene}$ bond to be shorter than expected for a single bond, in several complexes.[85] PMR spectral data suggest hindered rotation about this bond,[86] while there is believed to be little barrier to rotation about the C-M "double" bond.[87]

We felt that, since a large number of relatively stable transition metal analogous of carbonyl compounds are known, perhaps a similar analogue of the simplest such compound, carbon monoxide, could be prepared.

Such a derivative (65) would be a metal-bound carbon atom.[90]



$$O{=}C{:} \longleftrightarrow \overset{+}{O}{\equiv}\overset{-}{C} \qquad L_nM{=}C{:} \longleftrightarrow L_n\overset{+}{M}{\equiv}\overset{-}{C}$$

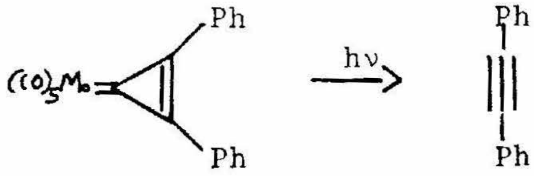
65 66

Scheme 28

The hypothetical molecule 65 is not as implausible a structure as it may first appear. A case can be made for significant stabilization via resonance delocalization in the manner of carbon monoxide (Scheme 28). The resonance form involving a triple bond between carbon and the metal is isoelectronic with transition metal carbyne complexes, well known from the work of Fischer.[91]

The triple bond between carbon and the metal in resonance form 66 involves placing positive charge on the metal, which suggests that the same ligands (such as CO) which are commonly incorporated into complexes like 61 will destabilize 65. Ligands such as phosphine, which can better stabilize positive charge at the metal, may prove to be better choices in the synthesis of 65.

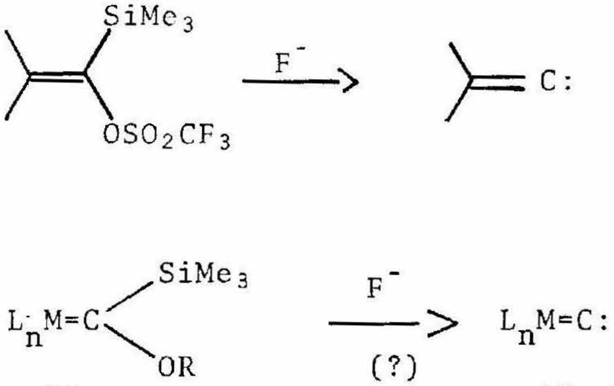
In addition to theoretical arguments, limited empirical evidence exists for the generation of this molecule. Rees and von Angerer[92] reported that the photolysis of the diphenylcyclopropylidene carbene complex 67 liberated diphenylacetylene. The fate of the metal was not reported. This transformation involves, at least formally, the generation of 65. Indeed, the repetition of this photolysis at low temperature represents an alternative approach to such generation, with trapping or spectral observation following.



Scheme 29

B. Alpha-elimination Reactions Involving Silicon

One potential route to 65 is the alpha-elimination of the nonmetal ligands from the carbene carbon in 68. Similar α-eliminations of trimethylsilylalkoxy moieties occur with facility, and have been used to thermally generate silylenes,[93] carbenes,[94] and nitrenes.[95] Most recently, vinyl carbenes have been produced by fluoride ion initiated α-desiloxations.[96] We wished to prepare trimethylsilyl- and trimethyltin (alkoxy) carbene complexes, with the hope of obtaining 65 via similar α-elimination reactions (Scheme 30).[89]



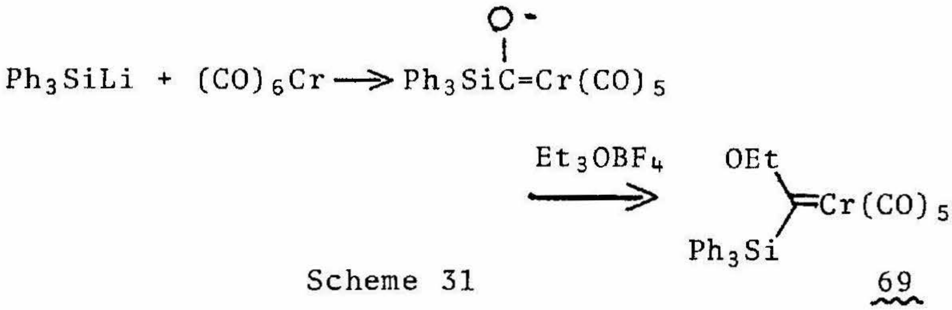
68 65

Scheme 30

While α-eliminations have not been observed in the tin series, reports of facile migrations from carbon to oxygen in other systems[97] suggest the possibility of utilizing trimethyltin carbene complexes in the above reaction.

C. Reaction of Metal Carbonyls with Silyl Anions

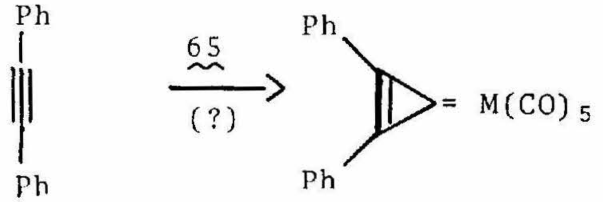
Prior to the beginning of our efforts in this area, only one report of similar silyl-substituted carbene complexes had appeared in the literature. Fischer prepared the complex 69 by a sequence analogous to his earlier preparation of 61 (Scheme 31).[98]



Scheme 31

69

We set out to prepare the corresponding trimethylsilyl and trimethyltin complexes by the same general route, and to attempt their α-eliminations. Since we feared that 65 might, even if formed, be quite unstable, we sought a suitable trapping agent. Simple olefins suffice to trap the vinylidene carbenes as cyclopropanes. For 65, a more suitable reagent appears: diphenylacetylene. The result of carbene-type addition of 65 would be the known (for M = chromium [99] or molybdenum[92]), very stable cyclopropenylidene complexes 67. This is simply the reverse of the reaction of Scheme 29.

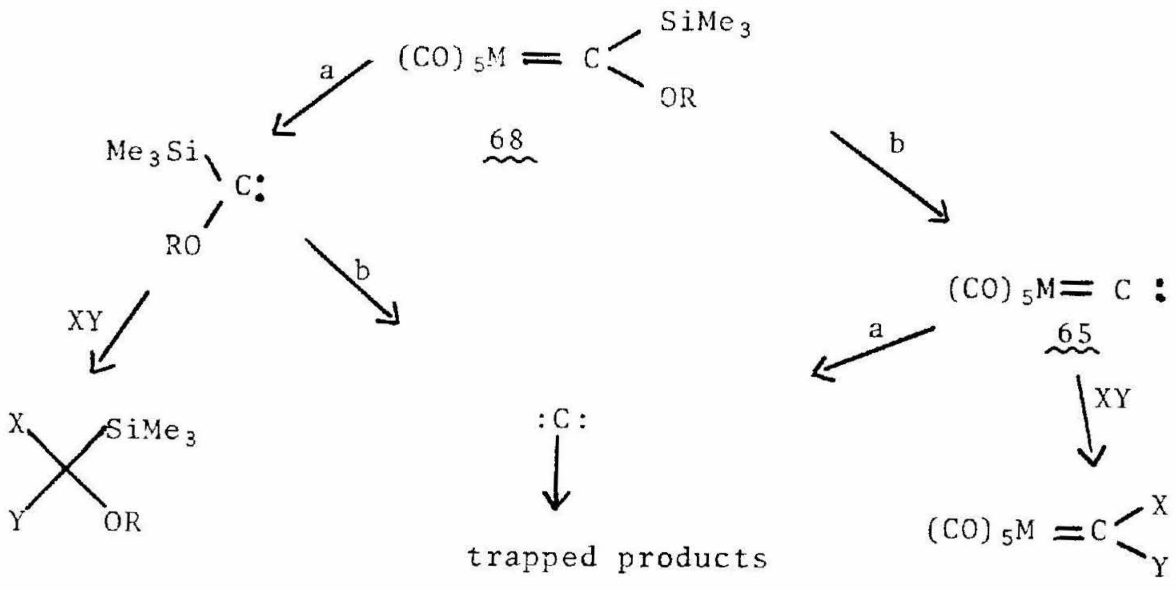


During the course of this work, Graham[100] reported the synthesis of cationic carbene complexes Re$(CO)_3$-(diphos)[CO(OEt)SiPh_2R] by similar routes (R = Ph, Me). His attempts to prepare the corresponding trimethylsilyl complex were abandoned due to the lability of the intermediate acylsilane complex.

2. Results and Discussion

A. Notion of Double Carbene Equivalent: A Transition Metal Carbene Complex Capable of Alpha-elimination

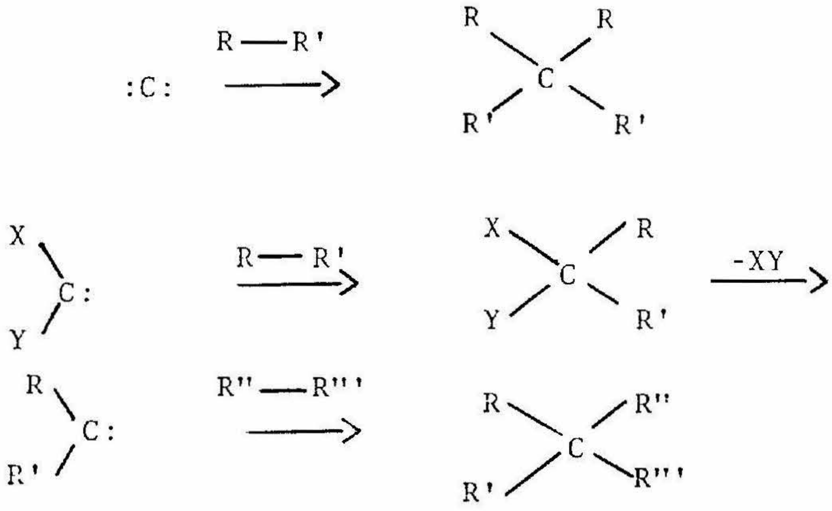
Our interest in trimethylsilyl(alkoxy)carbene complexes (**68**), emerged from our notion that these compounds might serve as double carbene (atomic carbon) equivalents. Since both α-alkoxytrimethylsilanes[94] and transition-metal carbene complexes[82] have been used as carbene or carbenoid precursors, compounds (**68**) which embody both of these functions might well undergo both sets of elimination reactions. This idea is presented in Scheme 32.



Scheme 32

The reagents and conditions in Scheme 32 are not specified, represented only by the letters a (for demetalation) and b (for desilyloxation). Ideally, a and b should differ, such that the reactions can be carried out sequentially, and the intermediates (or their trapped products) isolated. In addition, relatively mild conditions are desirable. We felt conditions could be found which satisfied these requirements; and, in fact, that 68 would prove to be an ideal precursor for the reactions of Scheme 32, if precedented means of accomplishing similar transformations in other systems proved effective. Such methods are (a) thermolysis at relatively low temperatures, in the range 55-130°, which effects carbene transfer from phenyl(methoxy)carbene transition metal complexes,[82] and (b) nucleophilic catalysis at 0° by fluoride ion, which results in disilyloxation of (α-trimethylsilyl)vinyl triflates.[96] These are among the mildest conditions known for carbene generation.

Of course, the carbene and atomic carbon intermediates in Scheme 32 are not expected to be stable, while the stability of 65 is unknown. Hence, they will be isolable only in the form of trapped derivatives (with the possible exception of 65). These derivatives may well be inaccessible by conventional means, signifying the synthetic possibilities involved, as shown in Scheme 33.



71

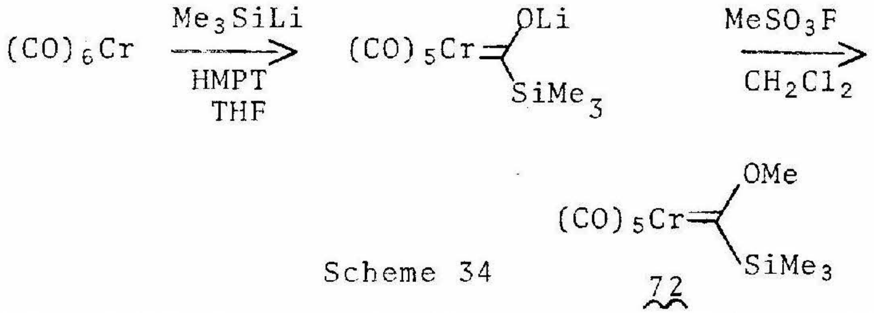
Scheme 33

Scheme 33 illustrates another advantage to the sequential generation of a double carbene equivalent, as opposed to its direct preparation. The direct method, including sequential generation in which the reaction cannot be stopped at the intermediate stage, results after trapping in the symmetrical product 70. In contrast, the sequential generation could allow the preparation of 71, with all four substituents different, or any number equivalent, and thus is more flexible than the direct method.

Our efforts to realize the above transformations have not been rewarded to date. We have concentrated on the right hand route of Scheme 32, attempting the nucleophilic desilyloxation of 68, which we have prepared for the first time. We have no evidence, however, for the generation of 65. The complexes 68 and their related trimethyltin derivatives undergo other reactions described below, which are not represented in Scheme 32.

B. Synthetic Approaches to Trimethylsilyl-Tungsten and Chromium Carbene Complexes

Initially, we were unsuccessful in our attempts to prepare $(CO)_5Cr[C(OCH_3)SiMe_3]$ (72) via the route of Scheme 34, utilizing Still's procedure for preparing trimethylsilyllithium[19] and methylating with methyl fluorosulfonate rather than trimethyloxonium tetrafluoroborate.[101]



Scheme 34

The difficulty lay in the presence of hexamethylphosphoric triamide (HMPT), which frustrated attempts at purification of 72. We next attempted to isolate the intermediate acylsilane anionic complex from an aqueous medium as its tetraethylammonium salt. This procedure has been used to free $[Ph_3SiW(CO)_5]^-$ from HMPT.[102] However, the trimethylsilylacyl anion complex does not survive treatment with water, decomposing to starting material and other metal-containing products lacking the trimethylsilyl group. Thus, we returned to the direct route.

It was finally discovered that, by the use of a jacketed chromatography column cooled to 10°, 72 could be chromatographed over Silica Gel as a yellow, very air-sensitive oil. The ir spectrum shows the expected three absorptions in the carbonyl region at 2010, 1980, and

1940 cm^{-1}. This compares with 2060, 1963, and 1946 reported for 69. The ^{13}C nmr spectrum provides very strong evidence, for transition-metal carbene carbons resonate farther downfield than any other type of carbon, including those of carbenium ions.[103] Compound 69 possesses the largest shift reported in the literature (431 ppm).[98] We determined a shift of 425 ppm for the carbene carbon of 72.

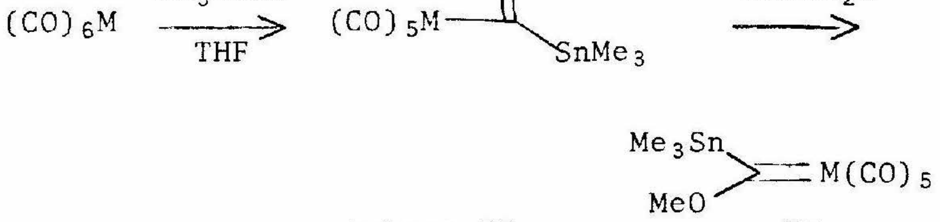
Having secured the trimethylsilyl carbene complex, we attempted its α-elimination (path b in Scheme 32) without success. Tetrabutylammonium fluoride, benzyltrimethylammonium fluoride, and potassium fluoride/18-crown-6 ether all failed to react with 72 in the presence of diphenylacetylene. Potassium methoxide resulted in the destruction of 72, but no trapping to form 67, as seen both from the ir (decay of carbonyl absorptions due to 72) and pmr (lack of new aromatic protons from 67).[104]

The failure of the α-elimination to proceed may be the fault of the poor leaving-group ability of methoxide, which is much worse than the extremely "hot" leaving group trifluoromethanesulfonate. Thus, we sought to prepare $(CO)_5Cr[C(OR)SiMe_3]$, R = tosylate or triflate. Unfortunately, these complexes, if formed, were extremely unstable. We were unable to characterize them as carbene complexes.

Metal carbene complexes have been convincingly shown to be intermediates in the metathesis of olefins.[105] Since the complex $(CO)_5W[C(OMe)Ph]$ is the only example of a "stabilized" carbene complex (bearing a heteroatom on the carbene carbon) which has yet been shown to initiate metathesis,[106] and this only with very reactive olefins, we sought to initiate olefin metathesis with **72**. Unfortunately, the complex again proved unreactive.

C. Synthetic Approaches to Trimethylstannyl-Tungsten and Chromium Carbene Complexes

We then turned to the preparation of the chromium and tungsten complexes $(CO)_5M[C(OMe)SnMe_3]$ (**73a** and **73b** respectively) via the route of Scheme 35.



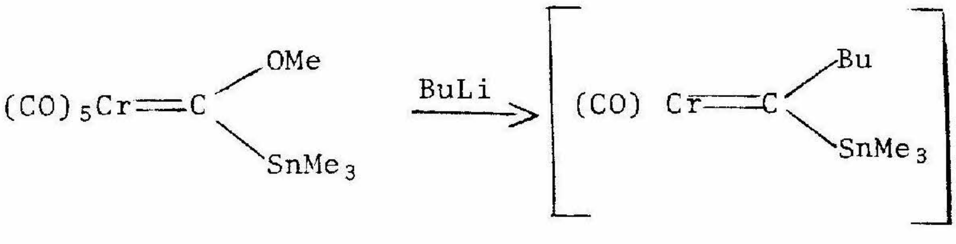
Scheme 35

73

a(m=Cr) b(M=W)

Fortunately, HMPT is not required for the production of trimethyltinlithium, and was absent from the product mixtures containing **73**. These complexes, in acetone solution, were filtered from inorganic salts and characterized or used in further reactions without further purification. (In fact, **73** is not stable on Silica Gel, decomposing to a gray, intractable sludge).

Both complexes **73** gave plausible ir and nmr spectra. The carbene carbons were seen in the ^{13}C nmr at about 100 ppm upfield of the silylcarbenes **69** and **72**. This is, however, still well downfield, and consistent with most carbene complexes.[102] The chromium derivative **73a** is an oil; the tungsten complex **73b** is a solid, which decomposes at 80°, but appears more stable to heat and oxygen, than **73a**. The same experimental conditions used to attempt α-elimination of **72** were tried with **73** resulting in a similar lack of success. In addition, **73** was reacted with butyllithium, resulting in a solid which by pmr appeared to be the result of attack on the carbene carbon, rather than tin:

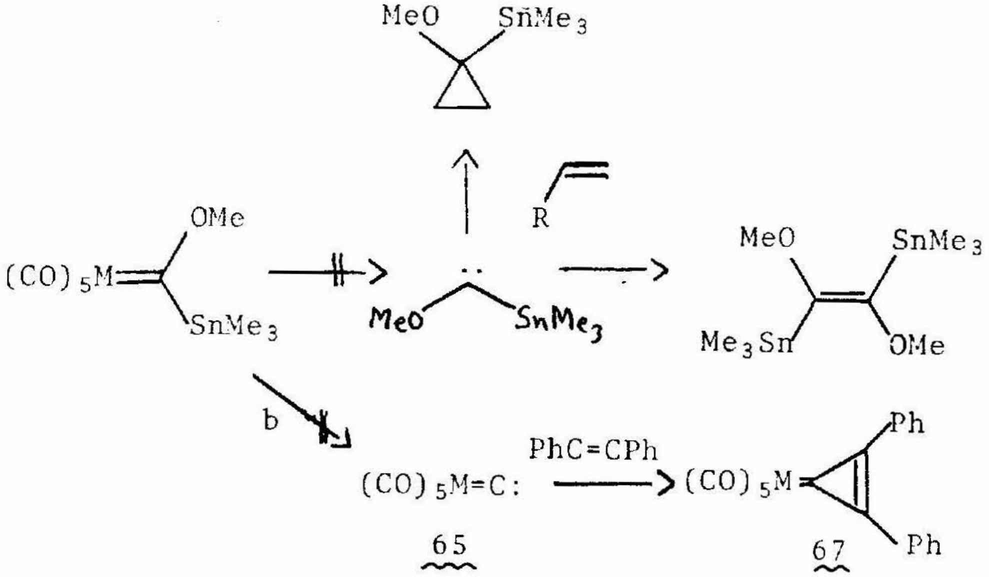


However, the resulting complex was too unstable to be fully characterized. Possibly, a larger alkoxy group would serve to hinder nucleophilic attack at the carbene carbon, thus promoting attack at tine

D. Reactivity of Trimethylstannylchromium and Tungsten Carbene Complexes. A Preliminary Report

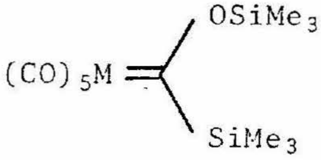
1. Alkenes

Repeated attempts to polymerize 1-hexene with trimethylsilyl- and trimethylstannyl carbene complexes resulted in no new olefins. However, when complex **73b** (M=W) was heated in the presence of norbornene (a reactive olefin toward metathesis) to 80° for 12 h, a polymer resulted which exhibited spectral characteristics in accord with the polymer reported to result from the metathesis of norbornene.[108] Thermolysis of **73a** and **73b** was examined for carbene or carbenoid formation. The products which might have been expected are trimethyltin cyclopropanes or bis(trimethyltin)olefins, or (in the case of destannyloxation) cyclopropenylidene complexes **67** (Scheme 36). Neither these nor any other products attributable to carbene intermediates were found.

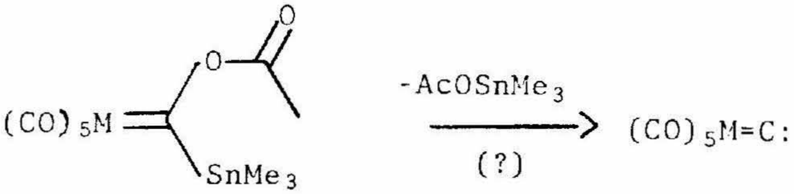


Scheme 36

Future modifications of the procedure of Schemes 34 and 35 (synthesis of the carbene complexes) may aid in the attempt to effect desilyloxation (path b in Scheme 32). The silylation, rather than methylation of the intermediate silyl acyl anion complex, would yield 74, which (as discussed above) should exhibit a weaker bond between oxygen and the carbene carbon - a bond which is broken during desilyoxation. The acylation of the tin acyl anion complex ought to provide 75. This carbene complex, in addition to possessing a weakened bond between oxygen and the carbene carbon (again due to resonance effects decreasing the electron density at the α-oxygen available for bonding to the carbene carbon), conceivably could undergo the desired elimination via a five-centered transition state (Scheme 37). Precedent exists in the literature for similar cyclic elimination processes of tin esters.[97] The synthesis of acyloxy-carbene complexes of chromium and tungsten has recently been described by Fischer.[109]



74



75

65

Scheme 37

2. Carbonyls

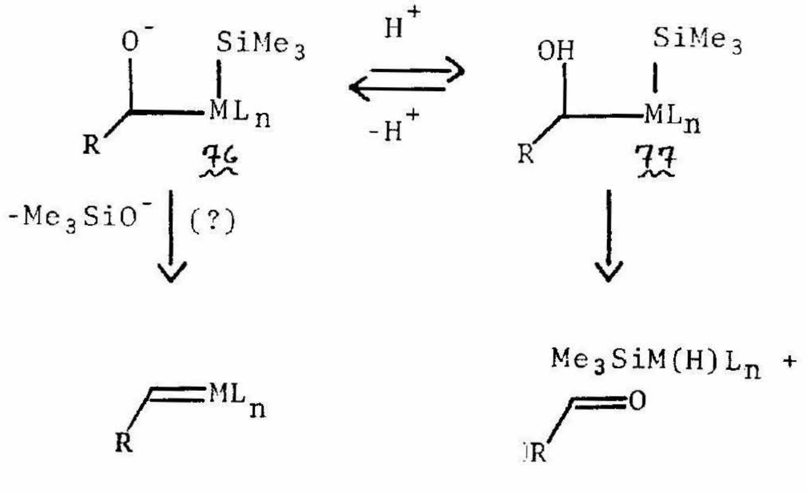
Although the polymerization of acetone has been shown via thermochemical estimates to be an energetically unfavorable process,[109a] several reports of its experimental realization have emerged.[109] Most of these were subsequently shown to actually involve the condensation of acetone under basic catalysis to give triacetone alcohol (2,6-dimethyl-2,6-dihydroxyheptan-4-one).[110] Thus, a true polymerization of acetone at present has little theoretical or experimental support.

While the gel obtained in our experiments is not triacetone alcohol on the basis of the pmr, the exact identity and constitution of the compound remains unclear. Further elucidation has been hampered by its instability, and the difficulty of separating acetone monomer. On one occasion, a slight excess of methyl lithium in the preparation of the carbene complex led to the formation of triacetone alcohol, as revealed by pmr. This process appears to be more favorable than gel formation, if excess base is present.

Initial observations of exothermic gas evolution in the reaction of **73b** with butanal led to further investigation. No polymer or gel was found. The pmr analysis of the trapped gas evolved showed only butanal; the ir showed the same, plus some carbon monoxide.

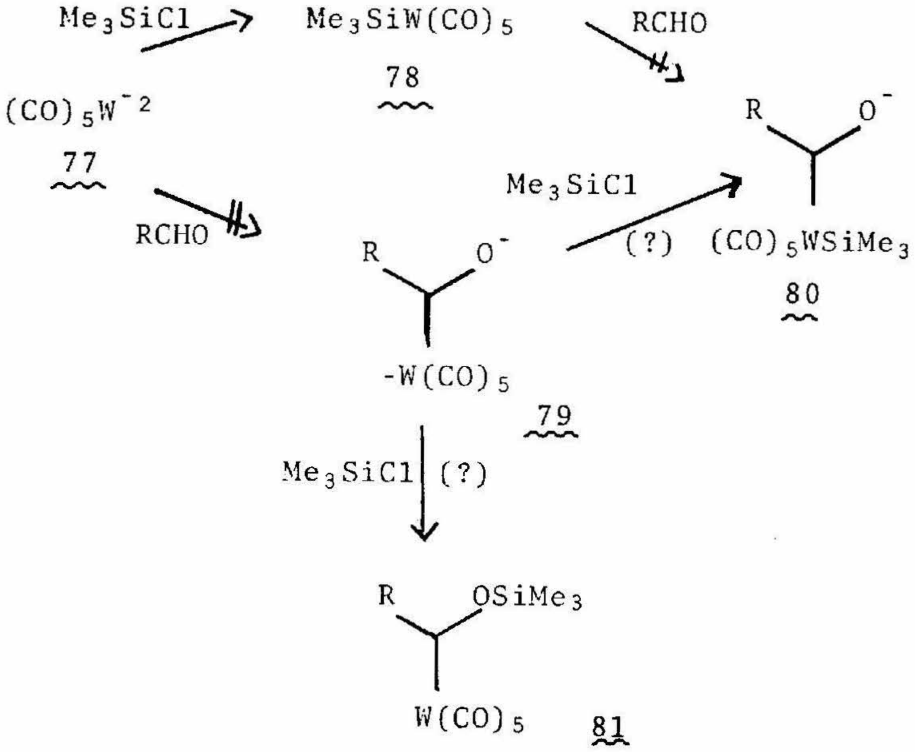
E. Attempted Generation of Carbene Complexes Via the β-hydroxysilane Anionic Elimination

In analogy with our work in epoxide deoxygenation via trimethylsilylpotassium, we investigated the feasibility of generating a transition-metal intermediate such as 76, similar to the anion of a β-hydroxysilane. Such an intermediate might well undergo β-elimination to give a metallocarbene. While the protonated, neutral form 77 would probably suffer rapid β-elimination in a different sense, 76 might not (Scheme 38).



Scheme 38

Our approaches to 76 consisted of sequential treatment of pentacarbonyltungsten dipotassium[111] with chlorotrimethylsilane and an aldehyde (Scheme 39).



Scheme 39

We attempted both sequences shown. The initial silylation resulted in the presumed silylated monanion 78, as expected on the basis of the work of Ellis.[110] Upon reaction of this mixture with gaseous formaldehyde or liquid butanal, no apparent reaction occurred. Vpc analysis revealed no ethylene or 4-octene, respectively, as should have been produced from the carbene complex.[112]

One possible drawback of this route is the fact that a seven-coordinate tungsten intermediate is required (80). While seven-coordination is known for tungsten complexes, it is rare, and probably destabilized by steric interactions.[113]

The reverse sequential route of initial aldehyde condensation followed by silylation appeared more promising. In this case, while the same intermediate 80 could be obtained, an attractive alternative route includes silylation on oxygen, rather than the metal, to yield 81. This intermediate would be just as likely to β-eliminate as would 80. This route avoids any seven-coordinate intermediate.

Unfortunately, this method also failed at the point of aldehyde condensation. The addition of formaldehyde resulted in its polymerization, presumably due to electron transfer from the metal dianion. In fact, the desired transformation of metal dianion to **79** may well be an endothermic process, given the stability of the carbonyl pi bond and the relatively weak nature of the metal-carbon bond formed.[114]

3. Conclusion

Trimethylsilyl and trimethylstannyl methoxycarbene complexes of chromium and tungsten, while unstable, can be prepared. For the most part, their reactivity parallels that of the more reactive types of transition metal carbene complexes (such as initiating olefin metathesis), rather than less reactive complexes (which can act as carbene transfer agents). Efforts to effect the α-elimination of the non-metallic carbene ligands have not been successful. Reactions of these carbene complexes with acetone have been investigated.

4. Summary

We have succeeded in the synthesis of trimethylsilyl- and trimethylstannyl-substituted carbene complexes of transition metals. Although our initial goal of effecting α-elimination reactions of these complexes has not been realized, the reactivity of these complexes has been investigated, and their successful initiation of olefin metathesis shown. We offer suggestions which may aid in future attempts at effecting the α-elimination reaction in these complexes.

V. EXPERIMENTAL

1. General

All reactions involving the generation and use of silyl anions were carried out under an argon atmosphere under anhydrous conditions using syringe techniques for transfer of liquids.

Elemental analyses were performed by the Caltech analytical facility. Melting points were obtained using a Thomas-Hoover capillary melting-point apparatus. Boiling points are uncorrected. Temperatures are given in degrees C.

Proton nuclear magnetic resonance (pmr) spectra were obtained on a Varian Associates A-60A or EM-390 Spectrometer. Chemical shifts are reported as parts per million downfield from tetramethylsilane in σ units and coupling constants in cycles per second (Hz). Spectra were obtained in deuteriochloroform or carbon tetrachloride, with tetramethylsilane, chloroform, or dichloromethane as internal reference. Proton magnetic resonance data are reported in the order: chemical shift; multiplicity, s = singlet, d = doublet, t = triplet, m - multiplet; number of protons; coupling constants; assignment.

Infrared spectra (ir) were recorded on a Perkin-Elmer 257 Grating Infrared Spectrophotometer as neat films, or in chloroform solvent. Mass spectra were recorded by the Caltech analytical facility on a Dupont 21-492B mass spectrometer.

Analytical vapor phase chromatogrphy (vpc) was performed on a Hewlett-Packard 5700 A Gas Chromatograph with flame ionization detector, equipped with a Hewlett-Packard 3370B digital integrator for quantitative analysis. Nitrogen was used as the carrier gas. Preparative vapor phase chromatography was carried out on a Varian Associates 920 Gas Chromatograph with thermal conductivity detector, using helium as the carrier gas. Analytical columns were packed in 0.125" stainless steel tubing, whereas preparative columns were packed in 0.375" aluminum columns. All columns of both types are listed in Table VII.

Peak assignments during analytical work were made by coinjection of authentic samples. Yields of olefins were determined after workup by comparison with an internal standard of known quantity. Ratios of detector response factors were measured, as given below, and taken into account.

Most reagent grade chemicals were used without further purification, as obtained from Chemical Samples Company (olefins); Orgmet, Inc., (metal carbonyls, hexa-

Table VII. Vpc Columns

Column Designation	Description
β,β	10' x 0.125", 10% β,β-oxypropriondinitrile on 100/120 Chromosorb P A/W
DBT	10' x 0.125", 10% dibutyl tetrachlorophthalate on 100/120 Chromosorb P A/W
DBT	20' x 0.125", 10% dibutyl tetrachlorophthalate on 100/120 Chromosorb P A/W DMCS
SE-30	10' x 0.125", 25% SE-30 on 100/120 Chromosorb P
SF-96	10' x 0.125", 10% SF-96 on 100/120 Chromosorb P A/W
TCP	22' x 0.125", 5% Tricresyl Phosphate on 100/120 Chromosorb P A/W DMCS
UCON	10' x 0.125", 10% UCON-550X on 100/120 Chromosorb W.

β,β	10' x 0.375", 25% β,β-oxypropriondinitrile on 60/80 Chromosorb P
Carbowax 20M	10' x 0.375", 25% Carbowax 20M on 60/80 Chromosorb W
DBT	10' x 0.375", 25% dibutyl tetrachlorophthalate on 45/60 Chromosorb A
QF-1	5' x 0.375", 25% QF-1 on 60/80 Chromosorb P A/W
SE-30	20' x 0.375", 25% SE-30 on 45/60 Chromosorb P
SF-96	10' x 0.375", 25% SF-96 on 45/60 Chromosorb A

methylditin); and Aldrich Chemical Company and MCB, Inc. (most other reagent chemicals). Hexamethyldisilane was initially obtained from Columbia Organics, and later prepared as described below.

HMPT was distilled in vacuo from lithium wire and redistilled from calcium hydride. Benzene and dichloromethane were distilled from P_2O_5 under nitrogen. Tetrahydrofuran and other solvents were distilled from the sodium ketyl of benzophenone, under nitrogen.

Sodium methoxide and potassium methoxide were transferred in a dry box from a freshly opened reagent bottle (Alfa) to a series of dry 50-ml widemouth bottles. Each bottle was half filled, sealed with screw cap and parafilm, and stored in a dessicator until needed. For reactions, quantities of methoxide were quickly transferred into dry reaction vessels. The amounts transferred were determined by weighing the bottle before and after transfer.

2. Epoxide Deoxygenations

A. Preparation of Epoxides and Reagents

Olefins were shown prior to their epoxidations to be greater than 96% isomerically pure by analytical vpc.

The relative retention times found on analytical vpc columns for each pair of olefin isomers used in the stereochemical studies were as follows: *trans*-2-butene = 1, *cis* = 1.1 (vs. hexane = 4.01), on 20 ft DBT, 25°; *trans*-3-hexene = 1, *cis* = 1.09 (benzene = 5.4), on 10 ft DBT, 80°; *trans*-4-octene = 1, *cis* = 1.08 (benzene = 0.85), on 10 ft DBT, 80°; *cis*-3-methyl-2-pentene (Z isomer) = 1,*trans* (E) = 1.16 (hexane = 0.55), on TCP, 25°; *cis*-2,5-dimethyl-3-hexene = 1.0, *trans* = 1.12 (hexane = 0.40), on TCP, 25°; *trans*-3,4-dimethyl-3-hexene = 1, *cis* = 1.09 (hexane = 0.19), on TCP, 25°.

2,3-Epoxybutane was obtained from Research Organic Chemicals Corporation as a mixture of isomers, which were separated via preparative vpc (Carbowax 20M, 80°). The relative retention times were: d,ℓ (**14**) = 1, meso (**15**) = 1.3. Each epoxide was shown to be isomerically pure (99%) by analytical vpc (β,β, 25°). The relative retention times were: *trans* = 1, *cis* = 1.36.

d,ℓ-4,5-Epoxyoctane (**8**).[115] To a stirred solution of 1.68g (15 mmol) of *trans*-4-octene in 50 ml of chloroform, cooled to 0°C, was added 3.45 (17 mmol) of 85% m-chloroperbenzoic acid. The reaction flask was fitted with a drying tube and allowed to stir overnight with gradual warming to ambient temperature. After 20 h, an aliquot from the reaction mixture was checked by analytical vpc (10 ft DBT, 80°) to ensure complete reaction. The heterogeneous mixture was filtered to remove m-chlorobenzoic acid, washed once with 10% aqueous sodium bicarbonate, water, and saturated sodium chloride solution, and dried (Na_2SO_4). The chloroform extract was concentrated at atmospheric pressure, and distilled, giving 0.8g (42%) of d,ℓ-4,5-epoxyoctane (8), b.p. 69-70° (26 torr). This was further purified via preparative vpc (β,β, 100°): ir (neat) 2960(s), 2870, 1470(s), 1380, 1120, 1070, 960, 910(s), 880, 740 cm^{-1}; pmr ($CDCl_3$) δ0.97 (t,6, J = 4.5Hz, CH_3), δ1.2-1.75 (m,8, CH_2), δ2.60 (t,2, J = 4.5Hz, epoxide H).

meso-4,5-Epoxyoctane (9)[115] was prepared in identical fashion to the d,ℓ isomer, and purified via preparative vpc (β,β, 100°): 2960(s), 2870, 1460, 1380, 1150, 1100, 950, 870, 850, 820, 780 cm^{-1}; pmr ($CDCl_3$) δ0.98 (t,6, J = 5Hz, CH_3), δ1.33-1.63 (m,8, CH_2), δ2.88 (s,2, epoxide H).

The rel. retention times on analytical vpc for the 4,5-epoxyoctanes: d,ℓ = 4.84, meso = 5.6 (trans-4-octene = 1) 10 ft DBT, 80°); d,ℓ = 1, meso = 1.16 (β,β, 70°).

1,2-Epoxyhexane (14)[116] was prepared in the same manner as the octane isomers, in dichloromethane. After washing, drying (Na_2SO_4), concentration, the epoxide was distilled at 118-120° (lit.[116] 117-119°) and purified via preparative vpc (β,β, 80°): pmr ($CDCl_3$) δ0.8-1.1 (m,3, CH_3), δ1.2-1.6 (m,6, CH_2), δ2.43 (d of d, 1, J_{trans} = 2.5Hz, J_{cis} = 5.0Hz, internal epoxide H), δ2.71 (t,1, J_{cis} = 4.5Hz, J_{gem} = 5.0Hz, terminal cis H), δ2.8-3.0 (m,1, terminal trans H). The rel. retention times on the analytical vpc were: 1-hexene = 1, 1,2-epoxyhexane = 6.09 (DBT, 80°).

d,ℓ-3,4-Epoxyhexane (6)[117] was prepared in the same fashion as was 1,2-epoxyhexane, and flash distilled at 106-110°, then further purified via preparative vpc (β,β, 60°): ir (neat) 2970(s), 1460(s), 1300, 1240, 1090, 1050, 1000, 920, 890(s), 810, 710 cm^{-1}; pmr δ0.97 (t,6, J = 7Hz, CH_3), δ1.3-1.7 (m,4, CH_2), δ2.63 (t,2, J = 4.5Hz, epoxide H).

meso-3,4-Epoxyhexane (7)[118] was prepared in the same fashion as 1,2-epoxyhexane, and flash distilled at 105-110°, then further purified via preparative vpc (β,β, 60°): ir (neat) 2980(s), 1510, 1380, 910, 800 cm^{-1}; pmr ($CDCl_3$) δ1.03 (t,6, J = 7Hz, CH_3), δ1.44 (q with fine structure, 4, J = 7Hz, CH_2), δ2.8 (m,2, epoxide H).

The rel. retention times on the analytical vpc were: d,ℓ-3,4-epoxyhexane = 3.60, meso = 4.53 (*trans*-3-hexene = 1) (DBT, 80°); d,ℓ-3,4-epoxyhexane = 1, meso = 1.31 (β,β, 25°).

d,ℓ-2,5-Dimethyl-3,4-epoxyhexane (10) was prepared in the same fashion as *trans*-4,5-epoxyoctane, and flash distilled at 69-70° (26 torr), then further purified via preparative vpc (β,β, 70°): ir (neat) 2980(s), 2935, 1470(s), 1385, 1365, 1275, 970, 930, 900(s), 850, 790 cm^{-1}; pmr ($CDCl_3$) δ0.92 and 0.96 (pair of unequal d, 12, J = 6Hz for each, CH_3), δ1.15-1.7 (m,2, $Me_2C\underline{H}$), δ2.48 (d,2, J = 6Hz, epoxide H).

Anal. Calculated for $C_8H_{16}O$: C, 74.94; H, 12.58. Found: C, 74.84; H, 12.35.

meso-2,5-Dimethyl-3,4-epoxyhexane (11) was prepared in the same fashion as *trans*-4,5-epoxyoctane, and flash distilled at 65-69° (25 torr), then further purified by preparative vpc (β,β, 70°): ir (neat) 2980(s), 2930, 1475, 1460, 1390, 1365, 1260, 1040, 970, 950, 940, 885, 800, 775 cm^{-1}; pmr ($CDCl_3$) δ1.01 (t,12, J = 6Hz, CH_3), δ1.2-1.7 (m,2, $Me_2C\underline{H}$), δ2.62 (d of d,2, J_1 = 7Hz, J_2 = 5Hz, epoxide H). The rel. retention times on the analytical vpc (β,β, 25°) were: meso-2,5-dimethyl-3,4-epoxyhexane = 1, d,ℓ = 1.14; on a different column

(10 ft DBT, 25°), meso = 4.53, d,ℓ = 5.8 (*trans*-2,5-dimethyl-3-hexene = 1).

Anal. Calculated for $C_8H_{16}O$: C, 74.96; H, 12.58. Found: C, 74.74; H, 12.18.

E-3-Methyl-2,3-epoxypentane (12)[118] was prepared in the same fashion as 1,2-epoxyhexane, and flash distilled at 95-99° (lit[118] 97-99°), and further purified via preparative vpc (DBT, 60°): ir (neat) 2980(s), 2960, 2940, 1460, 1380, 1260, 1150, 1100, 1020, 970, 860(s) cm^{-1}; pmr ($CDCl_3$), δ0.8-1.7 (m,11, CH_3 and CH_2), δ2.82 (q,1, J = 5.5Hz, epoxide H).

Z-3-Methyl-2,3-epoxypentane (13)[118] was prepared in the same fashion as 1,2-epoxyhexane, and further purified by preparative vpc (DBT, 60°): ir (neat) 2980(s), 2960, 2940, 1450, 1370, 1215, 1150, 1120, 1110, 1070, 1035, 915, 660(s), 755(s), 66 cm^{-1}; pmr ($CDCl_3$), δ0.8-1.8 (m,11, CH_3 and CH_2), δ2.83 (q,1, J = 5.5Hz, epoxide H). The rel. retention times on the analytical vpc DBT, 80°) were: E-3-methyl-2,3-epoxypentane = 2.88, Z-isomer = 2.94 (*trans*-3-methyl-2-pentene = 1).

d,ℓ-3,4-Dimethyl-3,4-epoxyhexane (14)[119] was prepared on a 500 mg (4 mmol) scale in the same manner as for *trans*-4,5-epoxyoctane, but was not distilled; instead, this compound was isolated directly from the preparative vpc (β,β, 100°): ir ($CDCl_3$) 2990(s), 2970, 2940, 1470(s), 1380(s), 1240, 1160, 1110, 1040, 1000, 970, 860(s) cm^{-1}; pmr ($CDCl_3$) δ0.88 (d of d, 6, J_1 = 5.5Hz, J_2 = 4.0Hz, $CH_2C\underline{H}_3$), δ1.28 (s, epoxide CH_3) amidst δ1.1-1.8 (m, CH_2) (total 10H).

6-Methyl-5-hepten-2-ol (22). To a mechanically stirred solution of 3g (83.7 mmol, 355 mequiv.) of sodium borohydride in 75m of ethanol, was added dropwise a solution of 35.33g (280 mmol) of 6-methyl-5-hepten-2-one in ethanol (75 ml), over the course of 30 min. After an additional 3 h, the reaction was quenched with aqueous 4% HCl solution, extracted with ether, washed, and dried (Na_2SO_4). The filtered solution was concentrated under reduced pressure, and the residue flash distilled to provide 27.9g (97%) of 6-methyl-5-hepten-2-ol, b.p. 38-40° (0.3 torr), which provided pmr and ir spectra identical with that of an authentic sample (Chem. Samples Co.).

5,6-Epoxy-6-methylheptan-2-one (30)[120] was prepared via the epoxidation of 6-methyl-5-hepten-2-one (Aldrich) using the procedure applied to the 4-octenes. The product was obtained in 81% yield, b.p. 50-53° at 0.2 torr (lit.[120] 68-70° at 10 torr). The product was further purified via preparative vpc (SF-96, 150°); ir (neat) 2960(s), 2930(s), 2860, 1715(s), 1460, 1370, 1250(s), 1140, 1050, 1000, 900, 835; pmr ($CDCl_3$) δ1.15 (s,3, CH_3), δ1.25 (s,3, CH_3) δ1.58 (s,3, CH_3) δ1.6-2.1 (m,4, CH_2), δ2.9 (m,1, epoxide H).

6-Methyl-5-hepten-2-yl-Acetate (28)[121] A solution of 13g (0.103 mole) of 6-methyl-5-hepten-2-ol (22) in 100 ml (1.06 mole) of acetic anhydride was heated to reflux in a 250-ml flask equipped with a reflux condenser. After 90 min 100 ml of water was added, and the mixture extracted with 100 ml of ether. The ether layer was washed with saturated aqueous sodium bicarbonate, water, and saturated sodium chloride solution, and dried ($MgSO_4$). The extract was then concentrated and distilled, giving 10g (58%) of 6-methyl-5-hepten-2-yl acetate (28), b.p. 82-85° (1 torr). This was further purified by preparative vpc (Carbowax 20M, 130°): pmr ($CDCl_3$) δ1.20 (d,3, J = 6Hz, $R_2CH\ C\underline{H}_3$), δ1.5-1.8 (m,8, gem-CH_3 and $AcO(Me)HC\ \underline{H}_2$), δ1.8-2.1 (m,5, allylic $C\underline{H}_2$ and $O_2CC\underline{H}_3$) δ4.7-5.3 (m,2, $OC\underline{H}$ and vinyl H).

5,6-Epoxy-6-methylheptan-2-yl acetate (29). A mixture of 3.1g (15.3 mmol) of m-chlorobenzoic acid and 2.44g (14.6 mmol) of the olefin (28) in 60 ml of chloroform in a 100 ml flask with drying tube was allowed to stir for five h. The mixture was then filtered, the filtrate was washed with saturated aqueous sodium bicarbonante, water, and saturated sodium chloride solution, dried (Na_2SO_4), concentrated, and distilled, giving 2.06g (84%) of the epoxide (29), b.p. 63-65° (0.2 mm), which was further purified via preparative vpc (Carbowax 20M, 175°); ir (neat) 2970, 1735(s), 1450, 1375, 1245(s), 1120, 1020, 950, 875 cm^{-1}; pmr ($CDCl_3$), δ1.18 (s,3, CH_3), δ1.24 (s,3, CH_3), δ1.29 (s,3, CH_3), δ1.4-.18 (m, 4, CH_2), δ2.0 (s,3, O_2CCH_3), δ2.9 (t,1, J = 5.5Hz, epoxide H), δ4.7-5.1 (m,1, OCH).

6-Methyl-5-hepten-2-ol tetrahydropyranyl ether (26). A solution of 12g (95 mmol) of 22 in 150 ml (1.64 mole) of redistilled dihydropyran, with a few crystals of p-toluenesulfonic acid as catalyst, was heated to reflux in a 250-ml flask fitted with a reflux condenser. After 3 h, the mixture was taken up in 150 ml of ether, washed with saturated aqueous sodium bicarbonate, water, and saturated sodium chloride, dried ($MgSO_4$), concentrated, and distilled, affording 15g (79%) of tetrahydropyranyl ether 26, b.p. 70-71° (0.2-torr); ir (neat) 2950(s), 2900, 1450, 1440, 1380, 1350, 1340, 1320, 1260, 1200, 1140(s), 1080(s), 1040, 1040(s), 1000, 970, 910, 870, 820 cm^{-1}; pmr ($CDCl_3$), δ1.0-2.2 (m,19, CH_2 and CH_3).

High-resolution mass spectrum: Calculated for $C_{13}H_{24}O_2$, 212.169. Found, 212.71. Base peak at m/e = 69. Other peaks at m/e = 170, 139, 128, 110, 100, 95, 85, 69, 57, and 53.

Anal. Calculated: C, 73.54; H, 11.39: Found: C, 73.14; H, 11.18.

5,6-Epoxy-6-methylheptan-2-ol tetrahydropyranyl ether (**27**) was prepared from **26** according to the procedure described for the epoxidation of *trans*-4-octene. After washing with saturated aqueous sodium bicarbonate, water, and saturated sodium chloride solution, drying (Na_2SO_4), and concentration, the product was distilled to give 5g (77%) of **27**, b.p. 77-80° (0.2 torr): ir (neat) 2940(s), 1375, 1200, 1120, 1075, 1030, 1020, 990, 965, 870 cm^{-1}; pmr ($CDCl_3$) δ1.07 (d,3, J = 6Hz, $CHC\underline{H}_3$), δ1.15 (s,3, CH_3), δ1.22 (s,3, CH_3), δ1.3-1.8 (m,10, CH_2), δ2.5-2.85 (m,1, epoxide H), δ3,3-4.0 (m,3, $ROCR_2\underline{H}$ and $ROCRC\underline{H}_2$), δ4.5-5.0 (m,1, $RC(OR)_2\underline{H}$).

tert-Butyl-(6-methyl-5-hepten-2-yloxy)dimethylsilane (**24**). Following the procedure of Corey,[122] 13.8g (108 mmol) of 6-methyl-5-hepten-2-ol was added to a stirred solution of 22.6g (150 mmol) of tert-butyldimethylsilyl chloride and 19.54g (287 mmol) of imidazole in 60 ml of N,N-dimethylformamide (previously distilled from BaO) in a 200-ml flask. The biphasic mixture was heated to 43° and allowed to stir for 10 h, during which time the reaction mixture attained homogeneity. The reaction mixture was then taken up in 150 ml of ether and washed with 4% aqueous HCl, saturated aqueous sodium bicarbonate, water, and saturated sodium chloride solution. After drying (Na_2SO_4), the extract was concentrated and distilled, giving 24.08g (92%) of **24**, b.p. 69-70° (0.2 torr); ir (neat) 2960(s), 2910(s), 2850, 1450, 1370, 1250(s), 1130, 1070, 1030, 830(s) cm^{-1}; pmr ($CDCl_3$) $\delta 0.13$ (s,6, $SiCH_3$), $\delta 0.98$ (s,9, $C(CH_3)_3$), $\delta 1.2$ (d,3, J = 6Hz, $CHCH_3$), $\delta 1.4$-1.8 (m,8, CH_2 and $C(CH_3)_2$), $\delta 1.85$-2.3 (m,2, allylic CH_2), $\delta 3.87$ (q,1, J = 6Hz, ROCH), $\delta 5.0$-5.3 (m,1, vinyl H).

Anal. Calculated for $C_{14}H_{30}OSi$: C, 69.35; H, 12.47 Found: C, 69.12; H, 12.08.

tert-Butyl-(5,6-epoxy-6-methylheptan-2-yloxy)-dimethylsilane (25). This epoxide was prepared from the olefin **24** according to the procedure described for the epoxidation of *trans*-4-octene. After washing and drying (Na_2SO_4), the product was concentrated, distilled, and a yield of 74% of epoxide **24** obtained, b.p. 80-81° (0.2 torr), and further purified via preparative vpc (QF-1, 150°); ir (neat) 2930(s), 2860, 1450, 1440, 1380, 1350, 1260, 1200, 1130(s), 1080(s), 1025(s), 990, 870, 815 cm^{-1}; pmr ($CDCl_3$) δ0.07 (s,6, $SiCH_3$), δ0.90 (s,9, $C(CH_3)_3$), δ1.17 (d,3, J = 6Hz, $CHC\underline{H}_3$), δ1.28 (s, 3, CH_3), δ1.5-1.7 (m,4, CH_2), δ2.6-2.9 (m,1, epoxide H), δ3.6-4.1 (m,1, $ROCR_2\underline{H}$).

Mass Spectrum: parent ion at m/e = 258 barely detectable. Base peak at m/e = 75 ($Me_2\overset{+}{Si}OH$). Other peaks at m/e = 243 ($M-CH_3$), 201 ($M-C(CH_3)_3$), 159, 145, 115, 109, 73, 59, 43, 28.

(4-Methyl-3-penten-2-yloxy)trimethylsilane (**32**). To a stirred solution of 2.70g (30 mmol) of 4-methyl-3-penten-2-ol (Chemical Samples Company) in 20 ml of THF under argon, was added via syringe 2.45g (15 mmol) of hexamethyldisilazane (Silar). The solution was stirred overnight at room temperature, then taken up in 100 ml of pentane, washed with ice water and saturated sodium chloride solution, and dried (Na_2SO_4). Filtration and distillation afforded 4.0g of material, b.p. 50-55° (14 torr), containing silyl ether **32** contaminated with some ROH. The silyl ether **32** was further purified by preparative vpc (SF-96, 120°). ir (neat) 2970(s), 2930, 1450, 1380, 1370, 1260(s), 1250(s), 1150, 1080(s), 1060, 1000(s), 910(s), 850(s), 760, 750 cm^{-1}; pmr

($CDCl_3$) δ0.10 (s,9, $SiCH_3$), δ1.17 (d,3, J = 6Hz, $CHC\underline{H}_3$), δ1.65 and δ1.67 (2,d,6, J = 2.5Hz for each, gem-CH_3), δ4.3-4.8 (m,1, SiOCH), δ5.0-5.3 (m,1, vinyl H).

Mass spectrum: No parent ion. Base peak at m/e = 73 (Me_3Si +). Other peaks at m/e = 129, 117, 75, 59, 43, 28.

3,4-Epoxy-4-methyl-2-pentanol (31)[123] To a mechanically stirred suspension of 20.02g (141 mmol) of anhydrous sodium hydrogen phosphate (Na_2HPO_4) and 26.1g (129 mmol) of technical (85%) m-chloroperbenzoic acid in 150 ml of chloroform at 0° (ice bath cooling) was added dropwise a solution of 13.0g (130 mmol) of 4-methyl-3-penten-2-ol in 100 ml of chloroform. Addition was complete after 30 min. After an addition four h of stirring at 0°, the filtered solution was washed with saturated sodium bicarbonate solution, then water and saturated sodium chloride solution, and dried (Na_2SO_4). The filtered solution was distilled giving 9.26g (62%) of 3,4-epoxy-4-methyl-2-pentanol (**31**), b.p. 30-31° (1 torr). This was further purified by preparative vpc (SF-96, 120°): ir: 4320 (s, broad), 2970(s), 2930, 1460, 1430, 1380(s), 1250, 1165, 1120, 1075(s), 1035, 945, 900, 875, 815 cm^{-1}; pmr ($CDCl_3$) δ1.18 (s,1.5, one component of a doublet corresponding to $CHC\underline{H}_3$, with J = 6Hz; remaining portion is lost under following peaks), δ1.29 and δ1.32 (two s, 7.5, second peak from $CHC\underline{H}_3$ and gem-CH_3), δ2.71 (d,1, J = 8Hz, epoxide H), δ3.05 (s,1, OH), δ3.42-3.88 (d of q,1, J_1 = 6.5Hz, J_2 = 8Hz, OCH). The signal assigned to OH disappeared upon shaking the sample with D_2O.

(3,4-Epoxy-4-methylpent-2-yloxy)trimethylsilane (33) was prepared via the silylation of 3,4-epoxy-4-methylpentan-2-ol (31) with hexamethyldisilazane in a procedure similar to the one described above. The product was obtained as a water-white liquid, b.p. 40-45° (25-27 torr), further purified via preparative vpc (SF-96, 100°). ir: 2970(s), 2920, 1450, 1430, 1380, 1250(s), 1165, 1110(s), 1090(s), 1050, 1000, 980, 920, 890, 850(s), 760, 700 cm^{-1}; pmr ($CDCl_3$) δ0.12 (s,9, $SiCH_3$), δ1.18 (d,3, J = 6Hz, $CHCH_3$), δ1.26 and δ1.28 (two s, 6, gem-CH_3), δ2.71 (d,1, J = 7.5Hz, epoxide H), δ3.4-3.75 (d of q,1, J_1 = 7.5Hz, J_2 = 6Hz, OCH).

High-resolution mass spectrum: Calculated for $C_7H_{14}O_2Si$, 158.113 Found, 158.112 (for M-C_2H_6). Other peaks at m/e = 173, 75, 67, 45, 41, 28. No parent ion found.

2-Methyl-3-penten-2-ol (**34**)[124] was prepared by three different methods:

1. Acid-catalyzed isomerization of 4-methyl-3-penten-2-ol: The treatment of 4-methyl-3-penten-2-ol (11g, 110 mmol) with 180 ml of a 2N sulfuric acid solution (with shaking over a five min period), affords, as previously reported,[124] an equilibrium mixture of 4-methyl-3-penten-2-ol and 2-methyl-3-penten-2-ol (in ratio 1:36 by vpc analysis on 10 ft DBT at 80°). A significant amount of diene products was also obtained. The isomeric alcohols were not easily separable except via preparative vpc. Relative retention times: 2-methyl-3- penten-3-ol = 1,4-methyl-3-penten-201 = 1.63 (10 ft DBT, 80°).

2. Catayltic semihydrogenation[125] of 2-methyl-3-pentyn-3-ol (**38**): One pellet of solid 85% potassium hydroxide (weighing < 0.1g) was powdered via mortar and pestle. This was combined with 0.1g of 5% palladium on charcoal catalyst with 10g (102 mmol) of 2-methyl-3-pentyn-2-ol (Chemical Samples Company) in 150 ml heptane (ethanol would have been preferable) in a one-liter Ehrlenmeyer flask with male ground-glass joint, and side-arm funnel with stopcock. A magnetic stirbar was added, the flask connected to an atmospheric hydrogenation ap-

paratus, and the atmosphere replaced by hydrogen. Stirring was begun, and hydrogen uptake monitored. After the first hour, hydrogen absorption continued at a steady rate of about 200 ml per hour for nine more h, after which time the rate decreased abruptly by a factor of ten. The reaction was then terminated, after 11 h and 2.035 liters of hydrogen absorbed. Since the vapor pressure of heptane is 45.9 torr at 300°K,[126] the theoretical volume of hydrogen required is given by: $2.45\ \text{l/mole} \cdot (1 - 45.9/760) \cdot 0.11\ \text{mole} = 2.35$ liters of hydrogen, or 1.1 times the observed uptake.

The product mixture was filtered via suction and subject to vpc analysis, which revealed Z-2-methyl-3-penten-2-ol, E-2-methyl-3-penten-2-ol, and 2-methyl-3-pentyn-2-ol present in ratio 92.5:7:0.5. (The latter two peaks were assigned by coinjection.) Relative retention times: E-2-methyl-3-penten-2-ol = 1, Z-2-methyl-3-penten-2-ol = 1.11g, 2-methyl-3-pentyn-2-ol = 1.29 (10 ft DBT, 80°). Separation of the allylic alcohol from excess heptane could not be profitably accomplished, either via fraction distillation, or using the method of Sharpless.[127]

3. Methyllithium reaction with methyl crotonate: Into a dry, argon-filled three-neck 500-ml flask equipped with overhead stirrer was placed 300 ml (0.57 mole) of a solution of methyllithium in diethylether. The flask was cooled to 0° with an ice bath. With stirring a solution of methyl crotonate (21.2 ml, 0.2 mole) in diethyl ether (50 ml) was added dropwise via addition funnel over the period of one h. Stirring was continued for another two h, with gradual warming to room temperature. Half of the reaction mixture was then transferred to another flask, cooled to 0°, and quenched via dropwise addition of saturated sodium bicarbonate solution. The biphasic mixture was separated, the aqueous layer reextracted with 200 ml diethyl ether, and the combined ether layers washed with water and saturated sodium chloride solution, and dried (Na_2SO_4). The solution was then filtered and distilled, resulting in 6.3g (56 mmol, 28%) of E-2-methyl-3-penten-2-ol, b.p. 52-53°/33 torr. This compound was further purified via preparative vpc (β,β, 80°), ir (neat) 3360 (broad), 3030, 2980(s), 2930, 1450, 1380, 1365, 1150(s), 995, 970(s), 900, 795, 770 cm^{-1}; pmr ($CDCl_3$) δ1.28 (s,6, gem-CH_3), δ1.63-1.71 (m,3, allylic $C\underline{H}_3$), δ1.87 (s,1, OH), δ5.5-5.8 (m,1, vinyl H). The proton assigned to OH was exchangeable with D_2O.

The second portion of the reaction mixture above was subjected to an attempted silylation with chlorotrimethylsilane. This was unsuccessful, for a trace of hydrochloric acid (present in chlorotrimethylsilane, even after distillation from calcium hydride) catalyzed extensive dehydration of the tertiary, allylic alcohol.

The diene fraction was distilled from the reaction mixture (b.p. 75-77°) and from the pmr spectrum, a mixture of the two expected dehydration products, 2-methyl-1,3-pentadiene and 4-methyl-1,3- pentadiene, was revealed in 3:1 ratio. pmr ($CDCl_3$) δ1.5-1.7 (m,6, allylic CH_3), δ4.6 (s,1.5, vinyl CH_2 of 2-methyl-1,3-pentadiene), δ4.8 (s,0.5, vinyl CH_2 of 4-methyl-1,3-pentadiene), δ5.1-6.6 (m,2, vinyl H).

(2-Methyl-3-penten-2-yloxy)trimethylsilane (**36**) could not be prepared via the silylation of 2-methyl-3-penten-2-ol with chlorotrimethylsilane or N,O-bis(trimethylsilyl)acetamide. The method finally utilized was the treatment of 3g (30 mmol) of the alcohol with 12.5 ml (60 mmol) of hexamethyldisilazane, in diethyl ether at room temperature for 24 h. The resulting mixture of silyl ether **36** and parent alcohol **34** was distilled without workup at 115-118°, and further purified via preparative vpc (DC-550, 100°). (The silyl ether was not stable on Carbowax 20M or β,β-oxyproprиondinitrile columns.) ir (neat) 2960(s), 1380, 1365, 1255(s), 1180(s), 935(s), 890, 845(s); pmr ($CDCl_3$) δ0.17 (s,9, $SiCH_3$), δ1.34 (s,6, gem-CH_3), δ1.72 (m,3, allylic CH_3), δ5.4-5.7 (m,2, vinyl H).

All of the above compounds could be separated by analytical vpc (10 ft DBT, 80°). Relative retention times: (benzene = 1); Z-2-methyl-3-penten-2-ol = 1.55; E-2-methyl-3-penten-2-ol = 1.4; its silyl ether (E-2-methyl-3-penten-2-yloxy)trimethylsilane = 2.6; 4-methyl-3-penten-2-ol = 2.4; its silyl ether (4-methyl-3-penten-2-yloxy)-trimethylsilane = 2.3; 3,4-epoxy-4-methylpentane-2-ol = 5.0, its silyl ether (3,4-epoxy-4-methylpent-2-yloxy)trimethylsilane = 5.4.

Reaction of (3,4-epoxy-4-methylpent-2-yloxy)-trimethylsilane (33) with trimethylsilylpotassium.

1. In situ generation with potassium hydride/ crown ether. Approximately one gram of potassium hydride (Alfa, 22% oil dispersion) in a dry, tared 25 ml rb flask with serum-capped sidearm and argon atmosphere was washed repeatedly with pentane (introduced and removed via syringe) to remove oil. After residual pen-

tane had been removed via evaporation at reduced pressure, the flask and contents were again weighed to determine the amount of potassium hydride present (0.2g, 500 mmol). This was suspended in a solution of 100 mg of benzene and about 10 mg of 18-crown-6 ether in 20 ml of THF, with magnetic stirring. 186 mg (1.6 mmol) of 3,4-epoxy-4-methyl-2-pentanol (31) was added dropwise via syringe to the reaction mixture resulting in hydrogen evolution and a color change to yellow. Stirring was continued for five min after gas evolution has ceased, prior to the addition of hexamethyldisilane (381 mg, 2.6 mmol) via syringe. The flask was fitted with a condenser, and the mixture allowed to reflux for 48 h. Aliquots were periodically withdrawn, quenched, and a pentane extract subject to vpc analysis. The analysis of the final aliquot, with retention times, assignments, and approximate area ratios (automatic integration gave unreliable results due to extensive tailing of the solvent peak) are given below: (retention times relative to benzene = 1): 1.4 (E-2-methyl-3-penten-2-ol, area = 1); 1.6 (Z-2-methyl-3-penten-2-ol, area = 5); 1.8 (unknown area = 0.5); 1.9 (unknown, area = 0.5); 2.2 (4-methyl-3-penten-2-yloxytrimethylsilane, area = 8); 2.6 (2-methyl-3-penten-2-yloxytrimethylsilane, area = 1); 3.0 (unknown, area = 2); 5.0 (3,4-epoxy-4-methylpentan-2-ol, area = 30); 5.5 (3,4-epoxy-4-methylpent-2-yloxytrimethylsilane, area = 32).

2. In situ generation with potassium hydride in HMPT. Potassium hydride (17.3g of 22% oil suspension, 86.5 mmol) was placed in a dry 300-ml flask with argon atmosphere and serum-capped sidearm, and washed repeatedly via syringe with 100-ml portions of pentane to remove oil. Residual pentane was removed with aspirator vacuum. With magnetic stirring, the cleaned potassium hydride was resuspended under argon in 75 ml of HMPT. The dropwise syringe addition of 3,4-epoxy-4-methylpentan-2-ol (4.26g, 36.7 mmol) followed, resulting in foaming, hydrogen evolution, and a color change of the reaction mixture to yellow. Five min after the cessation of gas evolution, 9.7g (66.3 mmol) of hexamethyldisilane was added via syringe. An immediate color change to dark orange (indicative of the formation of silyl anion) and slight gas evolution followed. After an additional five min, the stirred mixture was heated rapidly to 65°, with rapid gas evolution occurring. The mixture was stirred for 48 h at 65-70°, with periodic aliquots withdrawn, quenched, and subject to

vpc analysis (10 ft DBT, 80°). The final trace, with assignments: (retention times relative to benzene = 1): 1.1 (unknown, 33%); 1.2 (unknown, 14%); 1.4 (E-2-methyl-3-penten-2-ol, < 1%); 1.6 (Z-2- methyl-3-penten-2-ol, 8.5%); 1.7 (unknown, 4%); 2.4 (4-methyl-3- penten-2-yloxytrimethylsilane, 4%); 3.2 (unknown, 18%); 3.8 (unknown, 4%); 5.0 (3,4-epoxy-4-methyl-2-pentanol, 3%); 5.5 (3,4-epoxy-4-methylpent-2-yloxytrimethylsilane, 12%).

Synthesis of hexamethyldisilane. The following procedure is a modification of Gilman's.[128] Lithium wire (14.8g, 2.1 mole) was cut into pieces about 1-2 cm in length, and cleaned by successive immersion in hexane, absolute methanol, and dry THF. Immediately after the final rinse, each piece was place in a 1-ℓ three-neck flask with wire stirrer, overhead high-speed (5000 rpm max) stirring motor, and argon atmosphere. When the lithium addition was complete, 200 ml of THF was added, slow stirring begun, and 150 ml (1.18 mole) of chlorotrimethylsilane was added slowly via syringe. After addition was complete, high-speed stirring was initiated. The mixture was stirred at room temperature under argon for 65 h. The reaction could be followed by vpc by quenching an aliquot with water, thus hydrolyzing any silyl chloride remaining to hexamethyldisiloxane. The reaction mixture was then filtered thru Celite in a medium sintered-glass funnel and distilled at atmospheric pressure. After a low-boiling forerun, 50g of hexamethyldisilane was obtained, b.p. 112-114°, 99.9% pure by vpc. Redistillation of the forerun provided 15g of hexamethyldisilane (total yield, 74%). ir ($CHCl_3$) 2970(s), 2900, 1255(s), 840, 830 cm^{-1}; pmr ($CDCl_3$) δ0.067 (s,4.0Hz downfield of tetramethylsilane).

The anhydrous workup above minimizes hydrolysis of chlorotrimethylsilane (b.p. 57°) to hexamethyldisiloxane (b.p. 100°), which is more difficult to separate from hexamethyldisilane. This separation can be effected by shaking the mixture with conc. H_2SO_4, which removes the disiloxane. However, the yield of disilane suffers from such treatment.

The rel. retention times of these compounds on the analytical vpc (SE-30, 110°): hexamethyldisiloxane = 1, hexamethyldisilane = 1.35.

Preparation of Potassium Trimethylsilanolate (17)[129]

Using the method of Hyde,[129] about 100 ml of ammonia was condensed in a 300-ml 3-neck flask containing a gas inlet, overhead mechanical stirrer, and dry ice/isopropanol condenser with drying tube attached, held in a dry ice bath. With stirring, a few crystals of $Fe(NO)_3 \cdot 9H_2O$ were introduced into the liquid ammonia. Potassium (6.4g 164 mmol) was then added to the mixture in chunks, with stirring. Stirring was continued with dry ice cooling for 30 min after all of the potassium had reacted, as evidenced by the disappearance of the deep blue color associated with potassium dissolved in liquid ammonia. Stirring was halted, and the ammonia allowed to evaporate in a stream of argon over the course of two h. The condenser then was replaced with a 125 ml addition funnel, which was charged with a solution of 26.24g (161.6 mmol) of hexamethyldisiloxane in 25 ml of ether. The solid potassium amide was resuspended in 100 ml of ether, and the contents of the addition funnel added dropwise, with stirring. Stirring continued for two h. The pale gray supernatant was then decanted from the flask, suction filtered through a medium grain sintered-glass funnel, then subjected to vacuum (26 torr, then 0.1 torr) to remove volatile compounds. The potassium trimethylsilanolate (17) about 15g, or 74% based on hexamethyldisiloxane) residue, a fine white powder, was used as such in subsequent reactions without further purification.

Synthesis of 1,2-bis(2-chloroethoxy)ethane.[130] A mixture of 268 ml (2 moles) of triethylene glycol (dried over calcium chloride) and 350 ml (4.3 mole) of pyridine (distilled from potassium hydroxide) was dissolved in 200 ml of dichloromethane in a 2-ℓ three-neck flask equipped with overhead mechanical stirrer, 500 ml addition funnel, and reflux condenser with drying tube. As this stirred solution was heated to reflux, a solution of 300 ml (4.1 moles) of thionyl chloride in 200 ml of dichloromethane were added dropwise from the addition funnel. Addition was complete after one h, but stirring and refluxing continued for a total of five h. The reaction was then quenched with 500 ml of water. The organic portion was washed with 4% aqueous HCl, saturated sodium bicarbonate solution, water, and saturated sodium chloride solution and dried ($MgSO_4$). The solution was filtered, concentrated, and distilled to give about 200 ml of the dichloride, with no hydroxyl impurity; ir (neat) 2940, 2860, 1425, 1355, 1300, 1250, 1200, 1125(s), 1110(s), 1050, 915, 745, 665 cm^{-1}; pmr ($CDCl_3$) δ3.67 (s amid m).

Synthesis of 18-crown-6-ether.[130] Following the method of Cram et.al.,[130] a solution of 109g (1.94 moles) of potassium hydroxide (reagent, 85%) in 80 ml of water was carefully added to a mechanically stirred solution of 112.5g (100 ml, 0.749 mole) of triethylene glycol in 600 ml of THF in a 3-ℓ three-neck flask. The mixture was stirred for 15 min prior to the introduction of a solution of 140g (0.748 mole) of 1,2-bis(2-chloroethoxy) ethane in 100 ml of THF via addition funnel. After this very rapid addition was completed, the mixture was heated to gentle reflux via heating mantle and allowed to stir for 18 h. The mixture was then transferred to a 2-ℓ flask, and the solvent removed under reduced pressure. The resulting thick slurry was taken up in 500 ml of dichloromethane, then filtered through a Buchner funnel with suction. The filtrate was dried ($MgSO_4$), filtered, and concentrated. The product was distilled at 116-118° (0.15 torr). About 45g (39%) of 18-crown-6-ether was thus obtained. This was purified by the addition of 125 ml of acetonitrile, followed by heating to reflux, then gradual cooling to room temperature. Futher cooling to -78° afforded white crystals, which were filtered through alumina

(Woelm activity 1) to give pure 18-crown-6 ether. Crown ether which was not purified in this manner was not effective in catalyzing the potassium methoxide cleavage of hexamethyldisilane. ir (neat) 2990, 2870(s), 1465, 1450, 1350, 1290, 1220,1130(s), 980, 940, 850 pmr: $\delta 3.67$ (s, CH_2).

B. Epoxide Deoxygenations (General Procedures)

(i) THF/crown ether stoichiometric: To a stirred suspension of 273 mg (1.0 mmol) of 18-crown-6 ether and 158 mg (2.2 mmol) of potassium methoxide (9) in 10 ml THF was added a solution of 144 mg (1.1 mmol) of meso-4,5-epoxyoctane and 104 mg (1.3 mmol) of benzene as internal standard in 5 ml HMPT. To this was added 400 mg (2.7 mmol) of hexamethyldisilane via syringe, causing an immediate color change to gold. The reaction was allowed to stir at 25°C. After 75 min, saturated sodium chloride was added to the reaction mixture, the organic layer was separated and dried ($MgSO_4$). Analytical vpc analysis (10 ft DBT, 80°) indicated no epoxide and 91.7% yield of trans-4-octene (99% isomerically pure).

A 1.5g sample (10 mmol) of 1,2-epoxyhexane, subjected to the above conditions, gave after aqueous workup and distillation, a 75% yield of 1-hexene, which after purification via preparative vpc (10 ft DBT, 70°), gave 1-hexene which had pmr and ir spectra identical reagent (Aldrich) 1-hexene.

(ii) catalytic: To a stirred suspension of less than 10 mg each of potassium methoxide (0.14 mmol) and 18-crown-6 ether (0.03 mmol), and 142g (1.1 mmol) of d,ℓ-4,5-epoxyoctane (8), in 10 ml of THF at 25°C, was added 248 mg (1.7 mmol) of hexamethyldisilane in 10 ml THF. The reaction mixture was heated to reflux, and the rubber septum used for syringe entry was sealed off from the refluxing solvent by closing a Teflon stopcock in the sidearm of the reaction vessel.

The reaction was allowed to reflux for 24 h, quenched with saturated sodium chloride solution and taken up in 100 ml of pentane. This was washed with water and saturated sodium chloride solution. The internal standard (benzene, 155mg) was then added, and the final yield of 87% of *cis*-4-octene (> 99% isomerically pure) was determined by analytical vpc (10 ft DBT, 80°).

(iii) HMPT: To 14 mg (0.2 mmol) of potassium methoxide in 10 ml of HMPT at 65° was added 154 mg (1.2 mmol) of (8) followed by 270 mg (1.8 mmol) of hexamethyldisilane in 5 ml of HMPT. After stirring for 3 h, the reaction was quenched with saturated sodium chloride solution, and extracted with pentane. The pentane layers were combined, and dried (Na_2SO_4). After addition of benzene internal standard, a 96% yield of cis-4-octene (> 99% isomerically pure), was determined by analytical vpc (10 ft DBT, 80°).

The above procedure could also be carried out at room temperature with one full equivalent of potassium methoxide. The above reaction was run in this fashion on a larger scale (20 mmol), and the product cis-4-octene isolated and shown to be identical with reagent cis-4-octene.

Relative FID Response Factors. The detector response factor of each olefin was correlated to that of either benzene or hexane, which were the two compounds used as internal standards for vpc analysis during the epoxide deoxygenation reactions. Assignments of flame ionization detector response (FID) factors of: benzene = 1.12, and hexane = 1.03, were made in conformity with literature values relative to heptane.[131] Butenes were not measured, due to their volatility. 4-octenes = 1.01, 3-hexenes = 1.00, 1-hexene = 1.02 (relative to benzene = 1.12) (10 ft DBT, 80° for octenes, at ambient temperature for hexenes). 3-methyl-2-pentenes = 0.88, 2,5-diisopropyl-3-hexenes = 1.05 (vs. hexane = 1.03) (TCP, 25°). The trisubstituted olefins are broadened under these conditions (best for their separation and analysis), hence tend to detect low.

C. Controls and Modifications

(i) Potassium trimethylsilanolate (69 mg, 0.37 mmol) was reacted with 87 mg (0.68 mmol) of meso-4,5-epoxyoctane (9) and 176 mg (1.2 mmol) of hexamethyldisilane under the conditions of Procedure B(ii). A 78.8% yield of trans-4-octene, > 99% isomerically pure, as determined by analytical vpc (10 ft DBT, 80°), was obtained.

Other Controls: 2,5-dimethyl-cis-3-hexene was subjected to the conditions of procedure B(iii), at 65° for 3 h. About 3% isomerization to the trans olefin was found by vpc. The epoxides were shown to be stable to methoxide under the reaction conditions in the absence of hexamethyldisilane. Various solvents other than HMPT were tried and found ineffective in promoting the methoxide cleavage of hexamethyldisilane (including THF in the absence of crown ether), as assayed by the deoxygenation of d,ℓ-4,5-epoxyoctane (8). Conversely, 18-crown-ether was effective in other solvents (eg ether and benzene at reflux). Even HMPT (one equivalent) catalyzed the reaction, albeit slowly, in refluxing benzene. (The reaction with d,ℓ-4,5-epoxyoctane (8) had a half life of about 24 h.)

During the course of several experiments, gas evolution was noted immediately after hexamethyldisilane and potassium methoxide (one equivalent) came into contact. In an experiment designed to investigate the products of this reaction, 15.9 mmol of potassium methoxide and 16.8 mmol of hexamethyldisilane were combined in 60 ml of HMPT at 65°, and the evolved gases trapped at 77°K. Mass spectral analysis of the gases revealed the following major peaks (with assignments): m/e 146 ($Me_3SiSiMe_3^{+\cdot}$), 131 ($Me_3SiSiMe_2$), 89 (Me_2SiOMe), 73 (Me_3Si), and 59 (Me_2SiH). This is consistent with trimethylsilane as the evolved gas, with some methoxytrimethylsilane (the expected byproduct) and hexamethyldisilane carried along.

Cyclooctyltrimethylsilane. To a stirred suspension of 1.40866g (20.08 mmol) of potassium methoxide in 40 ml of HMPT under argon was added all at once via syringe a solution of 1.7008g (13.26 mmol) cis-1,2-epoxycyclooctane (Aldrich) and 5.0 ml (25 mmol) of hexamethyldisilane in 10 ml HMPT. An immediate color change to red occurred, indicative of the presence of trimethylsilylpotassium. The mixture was heated to 70°, and stirred for 14 h. The reaction was then quenched with water, and the organic products extracted with two 150 ml portions of an 80:20 (by volume) solution of pentane and ether. The combined organic layers were washed with saturated ammonium chloride solution, water and saturated sodium chloride solution, and dried (Na_2SO_4).

The filtered solution was subjected to distillation at one atmosphere to remove the solvent, and the pot residue (2.0g) shown by vpc to contain almost exclusively two components in about equal amounts, with relative retention times 1.0:1.5 (SF-96, 170°). The two peaks were isolated by preparative vpc on this column. Ths compound of shorter retention time was found to be the starting material, cis-1,2-epoxycyclooctane, as its ir spectrum and (when coinjected with authentic sample) vpc retention time were identical with that of a known sample. The second compound was identified as cyclooctyltrimethylsilane on the basis of the following spectral characteristics: ir ($CHCl_3$) 2920(s), 2850, 1460, 1440, 1260, 1250(s), 1160, 970 830(s); pmr ($CDCl_3$) δ0.10 (s,9, $SiCH_3$), δ0.26 (m,1,

$SiC\underline{H}R_2$), δ1.67 (s,14, CH_2).

High-resolution mass spectrum: Calculated m/e = 184.165 Found 184.169 for molecular ion. Base peak at m/e = 110 (loss of Me_3SiH). Other peaks at m/e = 169 (loss of methyl), 147, 82, 73, 59, 45, and 28.

Preparation of 1-hydroxycyclohexyl trimethylsilane (39).[132] Following the procedure of Still,[19] a solution of trimethylsilyllithium was prepared from the addition of 62 mmol of an ethereal methyllithium solution to 15 ml (75 mmol) of hexamethyldisilane in 30 ml of HMPT at 0°, in a 25-ml flask under argon. After 15 min, this solution was added slowly via syringe to a stirred solution, previously cooled to -78°, of 4.04g (48 mmol) of cyclohexanone in 55 ml of ether in a 200 ml flask with sidearm and argon atmosphere. The red color of trimethylsilyllithium was discharged upon addition. After stirring for two h at -78°, the solution was quenched with water, and the organic layer washed twice more with water, then saturated sodium chloride solution, dried (Na_2SO_4), and concentrated. The residue thus obtained (5.6g, 79%) proved to be nearly pure 1-hydroxycyclohexyltrimethylsilane (39). A sample was purified via preparative vpc (SF-96, 120°). ir (neat) 3350 (broad), 2940(s), 1500, 1300, 1245(s), 1205, 990, 900, 830(s), 745, 720, 690 cm^{-1}; pmr ($CDCl_3$) δ0.12 (s,9, $SiCH_3$); δ1.5-2.0 (m,11, CH_2 and OH).

Preparation of cyclohexen-1-yltrimethylsilane(40)[133] In a 50-ml flask, 3.5g (20.3 mmol) of the α-silyl alcohol (39), without vpc or other purification, was dissolved in dry pyridine (20 ml) and cooled with an ice bath to 0°. Thionyl chloride (2.0 ml, 27 mmol) was added, slowly, to avoid a violent exotherm. The nearly colorless solution turned red. The mixture was stirred at 0° for 30 minutes; the cooling bath removed and stirring continued two h longer. The reaction was then quenched by the addition of water, and taken up in 100 ml of ether. The aqueous layer was reextracted with 100 ml of ether, and the combined organic layers were washed with 4% aqueous hydrochloric acid, water and saturated sodium chloride and dried ($MgSO_4$). The filtered solution was concentrated and distilled at reduced pressure to yield 1.9g (61%) of cyclohexen-1-yltrimethylsilane (40), b.p. 70-72° (25-26 torr). pmr ($CDCl_3$) δ0.04 (s,9, $SiCH_3$); δ1.15-1.75 (m,4, remote CH_2); δ1.8-2.15 (m,4, allylic CH_2); δ5.85-6.1 (m,1, vinyl CH).

Preparation of 1,2-epoxycylohex-1-yltrimethylsilane (41).[134] In analogy to the method of Hudrlik,[134] a suspension of 0.392g (1.9 mmol) of m-chloroperbenzoic acid (tech, 85%) in 15 ml of dichloromethane was added dropwise a solution of 0.290g (1.88 mmol) of 40 in 10 ml of dichloromethane. The mixture was stirred at room temperature for three h, then filtered, washed with saturated sodium bicarbonate solution, water, and sodium chloride and dried (Na_2SO_4). The filtered solution was distilled at one atmosphere then at reduced pressure to yield 0.271g (84%) of the epoxide 41, b.p. 66-69°/20 torr (lit.[134] 106-107°/57 torr); pmr ($CDCl_3$) δ0.10 (s,9H, $SiCH_3$); δ1.2-1.6 (m,4H, remote CH_2); δ1.8-2.1 (m,4, near CH_2), δ3.1 (d of d,1H, J_1 = 3Hz, J_2 = 2Hz, epoxide H).

Reaction of α-halocarbonyl compounds with trimethylsilyl anions. a) 2-Chlorocyclohexanone (4.04g, 30.5 mmol) was combined with hexamethyldisilane (6.09g, 41.6 mmol) and potassium methoxide (3.06g, 43.6 mmol) in 100 ml of HMPT under argon. The mixture was stirred for three h, then quenched with cold saturated ammonium chloride solution and taken up in a solution of ether and pentane (50%). The organic extract was washed with water and saturated sodium chloride solution and dried

(Na_2SO_4).

This was filtered and concentrated under pressure. Vpc analysis (SF-95, 120°) of the residue revealed at least five products in comparable amounts. The ir spectrum of the mixture showed a hydroxyl group absorbing at 3500-3350 cm^{-1}, and at least three carbonyl stretching frequencies at 1755, 1730, and 1715 cm^{-1}, with a shoulder at 1705 cm^{-1}. Small amounts of three of the compounds were separated via preparative vpc (SF-96, 140°). One was shown to be the starting material, 2-chlorocyclohexanone. The second had pmr; δ0.17 (s,9H); δ0.9-1.5 (m,2H); δ1.7-2.1 (m,2H); δ2.63 (d,2H, J = 3Hz); δ2.78 (d,2H, J = 3H); δ2.7 (broad,s, 2H). Another compound had pmr: δ-0.18 (s,9H), δ-1.3-1.8 (m,4$^+$H), δ3.54 (apparent d), δ4.39 (s,2H). Trimethylsilyllithium in THF gave similar product mixtures.

b) Ethyl 2-bromoproprionate (3.0g, 16.6 mmol) was dissolved in 100 ml of THF under argon, and cooled to -78°. To this stirred solution was added a solution of trimethylsilyllithium prepared by adding 24 mmol of methyllithium solution to 5 ml (25 mmol) of hexamethyldisilane in 25 ml of HMPT at 0°. The mixture was stirred for two h at -78°, then warmed to room temperature, and worked up as in the above reaction. A pmr spectrum of the crude product (2.5g) was indicative of the presence of both silylated and reduced product (about 1:3): δ0.07 (s,4H, $SiCH_3$); δ1.16 (d, J = 4.5Hz); and δ1.24 (t, J = 7.5Hz), total 10H, δ2.7-3.0 (m,2H) δ4.16 (q,4H, J = 7Hz). Attempts to flash distill and vpc purify this material (SF-96, 150°) yielded only ethyl propionate.

3. Nucleophilic Aromatic Silylation

A. General Procedures for Silylation of Aryl Halides

i) HMPT/CH_3OM (M = Na,K): To 1.91g (0.027 mmol) of potassium methoxide suspended in 50 ml HMPT at 25° was added 3.12g (0.018 mmol) of p-bromotoluene followed by 4.38g (0.029 mmol) of hexamethyldisilane. The yellow reaction mixture was allowed to stir for 6 h. Aqueous 5% ammonium chloride solution was added to the reaction mixture, and this was extracted twice with 75 ml portions of pentane. The combined pentane layers were dried (Na_2SO_4). Distillation provided 2.46g (82% isolated yield) of p-tolytrimethylsilane (43);[135] 99.6% pure by analytical vpc (SE-30, 110°). b.p. 95-96°/30 torr (lit.[136] 192°/748); ir (neat) 2975(s), 1600, 1500, 1440, 1400, 1390, 1310, 1250(s), 1100(s) and 840(s) cm^{-1}; pmr ($CDCl_3$) δ0.25 (s,9,$SiCH_3$), δ2.34 (s,3, $ArCH_3$), δ7.17 (d,2, J = 9Hz, aromatic H), δ7.47 (d,2, J = 9Hz, aromatic H).

o-Chlorotoluene (18.2 mmol, 2.3g) by this method (in this case, the reaction was conducted at 65°) gave 69% of o-tolyltrimethylsilane (45),[135] b.p. 99-101°/ 30 torr, (lit.[136] 196°/748 mm); ir (neat) 2080(s), 1590, 1445, 1280, 1250(s), 1130, 1080, 830(s) cm^{-1}; pmr ($CDCl_3$) δ0.28 (s,9, $SiCH_3$); δ2.45 (s,3,$ArCH_3$); δ7.0-7.6 (m,4, aromatic H).

m-Tolytrimethylsilane (44) was obtained both by the above procedure, and the following method: To a suspension of 0.86g (12 mmol) of potassium methoxide and 0.168g (mmol) of 18-crown-6-ether in 50 ml of THF in a 100-ml flask, under argon was added 1.44g (8.4 mmol)of 3-bromotoluene, followed by 1.87g (12.8 mmol) of hexamethyldisilane. The reaction was allowed to stir for 24 h at room temperature. The reaction was then quenched with saturated aqueous sodium bicarbonate, extracted with 2 75-ml portions of pentane, washed with water and saturated sodium chloride solution, and dired (Na_2SO_4). The extract was then concentrated and distilled, giving 0.63g (45%) of 44,[135] b.p. 40-42°/ torr (lit.[136] 188°/748 torr); ir (neat) 2950(s), 1590, 1570, 1400, 1250(s), 1115, 870(s), 830(s) cm^{-1};

pmr ($CDCl_3$) δ0.25 (s,9, $SiCH_3$), δ2.33 (s,3, $ArCH_3$), δ7.1-7.4 (m,4, aromatic H).

The isomeric tolylsilanes were separable via analytical vpc (UCON, 110°). Rel. retention times were: 47 = 1, 46 = 1.07 and 48 = 1.37.

ii) HMPT/CH_3Li: To a stirred solution of 6.777g (46.3 mmol) of hexamethyldisilane in 100 ml HMPT near 0° was added 44.2 mmol of methyllithium solution in ether.[19] A dark red solution formed, with some gas ev evolution. Stirred at 0° for 20 min, then added rapidly a solution of 2.617g (17.8 mmol) of p-dichlorobenzene in 12 ml of HMPT. The mixture turned dark brown. Stirred overnight with gradual warming to 25°. The mixture was then quenched with water and extracted with two 100 ml portions of pentane. The combined pentane extracts were dried (Na_2SO_4). After filtration and concentration spontaneous crystals appeared which were recrystallized from benzene/ligroin, yielding 950 mg (24%) of 1,4-bis-(trimethylsilyl)benzene (49), m.p. 92-93° (lit.[137] 95°); ir ($CHCl_3$): 2960(s), 1400, 1380, 1265, 1250(s), 1135(s), 980, 830(s); pmr: ($CDCl_3$) δ0.25 (s,18, $SiCH_3$), δ7.67 (s,4, aromatic H).

iii) CH_3OK/18-crown-6: To a suspension of 0.25218g (3.6 mmol) of potassium methoxide and a trace (ca 10 mg) of 18-crown-6 ether in 10 ml THF was added a solution of 0.21050g (1.8 mmol) of o-bromotoluene and 0.512g (3.5 mmol) of hexamethyldisilane and 0.19830g of decane as internal standard in 10 ml of THF. The reaction mixture was heated to reflux and held at that temperature for 6 h. When the product ratios stabilized, a 0.5 ml portion of the reaction mixture was removed via syringe, quenched in 0.5 ml H_2O/0.5 ml pentane mixture, the entire sample mixed, and a 1.0μℓ aliquot from the organic layer analyzed affording 53.7% of o-tolyltrimethylsilane (45), 4% of o-bromotoluene (starting material), and 42% of toluene, by vpc analysis (UCON, 110°).

B. Procedure for vpc analyses.

Despite repeated attempts, the results of most runs of the crown ether + $KOCH_3$ silylations were much less satisfactory than the example above, for many did not a approach completion; significant (often 50-80%) amounts of starting material remained unreacted. Hence, subsequent runs for vpc analysis were carried out in HMPT solution, as described in procedure A(i) or (ii), using 1-2 mmol substrate for each experiment. Removal and workup of aliquots was performed as described in procedure A(iii).

The products of silylation of each halides were analyzed via vpc (UCON, 110°) to evaluate the regiospecificity of the reaction. Peak assignments were made on the basis of coinjection with authentic silane, prepared as described above. For yield determinations, it was sometime more convenient to utilize SE-30 at 110°. Yields were determined with respect to decane, added (usually after completion and workup) to the reaction. Response factor corrections were critical, as silanes are not detected efficiently by flame ionization detectors. These factors were measured by analysis of standard samples of tolylsilanes and decane, and were averaged over several measurements. Factors determined in this work:

Compound	Detector Response
Decane	(1.00)
o-tolyltrimethylsilane, **48**	0.864
m-tolyltrimethylsilane, **47**	0.766
p-tolyltrimethylsilane, **46**	0.757

These are *weight* correction factors. Thus, under these analytical conditions (UCON, 110°), 1 gram of p-tolyltrimethylsilane produces a peak of area equal to that caused by 757 mg of decane.

C. Competition Experiments

i) Intermolecular competition experiments were carried out following procedure A(iii), with 2 mmol of chlorobenzene or iodobenzene, 2 mmol of bromobenzene, 1 mmol each of hexamethyldisilane and potassium methoxide, a catalytic amount of 18-crown-6 ether, and a weighed amount of n-octane as internal standard. The relative rates of reaction of the halobenzenes were determined by analytical vpc (SE-30 at 110°).

ii) Intramolecular competition experiments consisted of subjecting the p-dihalobenzenes XC_6H_4Y to procedure A(i) with insufficient (0.7 equiv.) methoxide and hexamethyldisilane. Products and relative yields were shown by vpc analysis (SE-30, 110°) with respect to decalin as internal standard. Assignments were made on the basis of isolation (preparative vpc, SF-96) at 140° of individual peaks, and characterization by ir and mass spectra.

Major peaks observed in the mass spectra (with relative intensities): for p-chlorophenyltrimethylsilane, at m/e 186 (0.05), 1.84 (0.126), 171 (0.315), 169 (1), 141 (0.018), 139 (0.025), 91 (0.061), 73 (0.028), and 28 (0.075); for p-bromotrimethylsilane, at m/e 230 (0.15), 228 (0.15), 91 (0.0070), and 73

(0.006); for p-iodotrimethylsilane, at m/e 276 (0.227), 161 (1), 134 (0.075), 119 (0.064) and 73 (0.052).

The molecular ion is apparent in all three halophenylsilanes, as is Me_3Si^+. The major peak is due to loss of methyl from the molecular ion, with minor peaks from subsequent methyl detachment. Si^+ and $C_7H_7^+$ are also seen. Interestingly, the loss of halogen is not an observed process except in the iodide where I removed from the M-15 ion (with peaks due to subsequent fragmentation).

D. Deuterium Labelling Experiments

i) Deuterium oxide quenching. The silylation reaction described in procedure A(i) was performed on iodobenzene.[115]

Five min after initiation the reaction was quenched with D_2O. (Longer times afforded less deuterium incorporation.) After drying and filtration, the volatile components which distilled over at 75-90° were collected and the benzene therein isolated via preparative vpc (SE-30, 60°), and subjected to mass spectra analysis. The following peaks were found: m/e 78 (1), 79 (0.45), and 80 (0.03). Since the M + 1 peak in benzene was found to be 6.58% relative to the parent (m/e 78), it

✓

is enriched by a factor of 6.8, or (45.6-6.58) = 38.4% of the parent, due to deuterium incorporation. The actual percentage of overall deuterium incorporation is found by dividing this excess by the total aromatic species present. Thus, the actual percentage deuterium incorporation due to D_2O quench is 0.384/1.384 = 28%. A check exists, in that 6.58% of this should be present at M + 2. Calculated 0.0658 x 0.384 = 0.025, found 0.03 for m/e - 80. As a control, the same reaction was run on 1-iodonaphthalene with phenyltrimethylsilane added just prior to quenching. After workup, vpc analysis of the organic extracts revealed less than 0.04% of the phenyltrimethylsilane had been hydrolyzed to benzene.

ii) Perdeuteriomethoxide trapping. After preliminary experiments with methanol-h_4, the following experiment was carried out. A suspension of 6.5g of a potassium hydride (Alfa, 22.5%) oil dispersion (36 mmol) in 70 ml HMPT was stirred for 5 min, followed by the careful dropwise addition of 10.606g d_4-methanol (99%, Aldrich). Stirring continued for 2 h to ensure hydrogen evolution had ceased. Then, 4.08g (20 mmol) of iodobenzene were added, followed five min later by 6 ml (30 mmol) hexamethyldisilane. This mixture was stirred for 2 h prior to workup as in procedure A(i). The dried organic solution was filtered and distilled at one atmosphere. Again, the fraction with b.p. within 5 degrees of 80° was collected, and benzene recovered via preparative vpc as above, and analyzed via its mass spectrum. Peaks were found at m/e 80 (0.112), 79 (1), and 78 (0.592). By the derivation of procedure (1), the peak at M + 1 is too intense by a factor of 23.3 over natural abundance, resulting in a value of 62% overall deuterium incorporation from deuterio methoxide.

E. Intramolecular Cyclization Reactions

o-Chloropropylbenzene (53). Following the method of Gilman,[138] 10g (0.417 mole) of magnesium shavings were placed under argon in a 1-ℓ three-neck flask equipped with 500-ml addition funnel, overhead mechanical stirrer, and reflux condenser. A solution of 53.7g (0.33 mole) of o-chlorobenzyl chloride in 300 ml of ether was placed in the addition funnel. A 25-ml portion of this solution was added to the reaction flask, followed by a few crystals of iodine. Initial reaction was observed within minutes. The remainder of the organic solution was then added slowly, with stirring. When addition was complete, the dark brown reaction mixture was allowed to stir for 30 min at room temperature, then 30 min at reflux. A solution of 85 ml (0.65 mole) of diethyl sulfate in 100 ml of ether was then added dropwise to the mixture, over the course of 1 h. The reaction mixture was then poured over 500 ml of ice mixed with 50 ml of concentrated HCl. The ether layer was separated, the aqueous layer extracted with 200 ml of ether, and the combined layers concentrated. The residue was allowed to reflux with a solution of 20g (0.5 mole) of sodium hydroxide in 100 ml of water and 100 ml of ethanol, to decompose excess diethyl sulfate. The mixture was separated, the aqueous layer extracted with 100 ml of ether, and the combined organic layers washed with 4% aqueous HCl, saturated aqueous sodium bicarbonate, water, and saturated sodium chloride, and dried ($MgSO_4$). Concentration and distillation gave 31.23g (60.5%) of 53, b.p. 105-106°/28 torr (lit.[138] 71-72°/8.5 torr); ir (neat) 3040, 2960(s), 2920, 2860, 1570, 1470(s), 1440(s), 1380, 1070, 1050, 1025, 750(s), 680 cm^{-1}; pmr ($CDCl_3$) δ0.95 (t,3, J = 7Hz, CH_3), δ1.3-2.0 (m,2, $MeC\underline{H}_2CH_2$), δ2.65 (d of d, 2, J_1 = 7Hz, J_2 = 9Hz, $ArCH_2$), δ7.74 (m,4, aromatic H).

Nucelophilic silylation of o-(propylphenyl)-trimethylsilane (53). Potassium methoxide (2.04g, 29 mmol) and hexamethyldisilane (4.25g, 29 mmol) were combined with 3.1g (19.7 mmol) of 53 in 40 ml of HMPT under argon, and allowed to stir at 65° for 24 h. The reaction mixture was quenched with water and extracted with 100 ml of pentane. The pentane layer was washed with water and saturated sodium chloride solution, dried ($MgSO_4$), concentrated, and flash distilled at 106-110° (0.6 torr). About 3g of product were obtained, which could be separated by prepartive vpc (SF-96, 160°) into three components with rel. retention times 1, 2.4, and 4.8. These were isolated and shown to be, respectively, n-propyl benzene (reduced product), 53 (starting material), and 54 (silylated product). The first two were identified by comparison of spectra and vpc ret. times (upon coinjection) with those of authentic samples. Compound 54 exhibited the following spectra data: ir (CCl_3) 3050, 2955(s), 2870, 1590, 1465, 1435, 1380, 1265(s), 1250(s), 1130, 1090, 840(s), 685 cm^{-1}; pmr ($CDCl_3$) δ0.11 (s,9, $SiCH_3$), δ0.95 (t,3, J = 6.5Hz, CH_3) δ1.30-2 (m,2, CH_2CH_2Me), δ2.60 (d of d, 2, J = 8Hz, J_2 = 6Hz, $ArCH_2$), δ7.2 (m,4, aromatic H).

Anal. Calculated for $C_{12}H_{20}Si$; C, 74.92; H, 10.48, Found, C, 74.52; H, 10.43.

o-Iodophenyl allyl ether (55). Using the method of preparation of Beckwith,[74b] a mixture of 4.4g (20 mmol) of o-iodophenol, 2 ml (23 mmol) of 3-bromopropene, and 3.13g (22.6 mmol) of anhydrous potassium bicarbonate in 100 ml of acetone was allowed to reflux for 10 h, then combined with 100 ml of ether and washed with 10% aqueous potassium hydroxide, water, and saturated sodium chloride solution. The extract was dried ($MgSO_4$), concentrated, and distilled to give 3.686g (70.6%) of allyl o-iodophenyl ether,[74b] b.p. 75°/18 torr; ir (neat) 2920, 2970, 1590, 1475(s), 1440, 1295, 1280(s), 1255(s), 1235, 1055, 1020(s), 1000, 930, 755(s) cm^{-1}; pmr ($CDCl_3$) δ4.50 (d of d,2, J = 5Hz, J_2 - 1Hz, OCH_2), δ5.1-5.5 (m,2, vinyl CH_2), δ5.75-6.17 (m,1, vinyl CH), δ6.5-6.8 (m,2, aromatic H), δ7.03-7.28 (m,1, aromatic H), δ7.6-7.73 (m,1, aromatic H).

Nucleophilic silylation of 55. Silylation of 55 (2.21g, 8.5 mmol) with hexamethyldisilane (14 mmol) and potassium methoxide (1.1g, 16 mmol) was carried out in the manner described for the preparation of 54. The product mixture contained three products as determined by analytical vpc (10 ft x 0.125 in tris-cyanoethoxypropane, 170°), with rel. retention times 0.8:1:3.

2,3-dihydrobenzofuran (59) (independently prepared by the method of Beckwith[74]), and o-allyloxyphenyltrimethylsilane (57), in 1:6:1 ratio. Compound 57 was isolated (SF-96, 200°) as a water-white liquid: ir (neat) 2980(s), 2900, 1580(s), 1460, 1440(s), 1420, 1280, 1270, 1220(s), 1130, 1080, 1020, 990(s), 840(s) cm^{-1}; pmr (C_6D_6) $\delta 0.57$ (s,9, $SiCh_3$), $\delta 4.25$ (d of d,2 $J_1 = 5Hz$, $J_2 = 1Hz$, OCH_2), $\delta 5.0$-5.5 (m,2, vinyl CH_2), $\delta 5.7$-6.2 (m,1, vinyl CH), $\delta 6.7$ (d,1, J = 8Hz, aromatic H), $\delta 6.9$-7.6 (m,3, aromatic H).

High resolution mass spectrum: parent ion, calculated for $C_6H_{18}OSi$, m/e = 20.6166 Found 206.113. Base peak = M-15. Other peaks at m/e = 175, 163, 151, 149, 135, 91, 75, 73, and 28.

In an attempt to make an authentic sample of o-allyloxyphenyltrimethylsilane, a solution of 1.0g (6 mmol) of o-chlorophenyl allylether (prepared from o-chlorophenol and allyl bromide by the procedure described for the synthesis of 55)[139] in 50 ml of THF under argon was treated with 148 mg (21 mmol) of lithium wire and 1.5 ml (12 mmol) of chlorotrimethylsilane overnight at room temperature. The reaction was then filtered, washed quickly with water and saturated sodium chloride solution and dried (Na_2SO_4). The filtered solution was stripped of solvent, and the crude product, still containing a sizeable amount of unreacted starting halide, was purified via preparative vpc SF-95, 140°). (Rel. retention times: o-chlorophenyl allyl ether (57 = 1, the product - 1.7). Spectral characteristics of the product were consistent with a cyclized isomer of the expected compound o-allyloxyphenyltrimethylsilane, probably 2,3-dihydro-3-methylbenzofuran: ir ($CHCl_3$) 2950(s), 2880(s), 1610, 1600(s), 1485(s), 1460(s), 1400, 1320, 1250(s), 1150, 1100, 1040, 1015, 970(s), 850(s) cm^{-1}; pmr ($CDCl_3$); δ0.25 (s,9, $SiCH_3$); δ1.1-1.4 (m,2, CH_2); δ3.4-3.8 (m,1, CH); δ4.15 (t, 1, J = 7Hz, OCH); δ4.80 (t, 1, J=7Hz, OCH_3), δ6.8-7.4 (m,4, aromatic H).

High-resolution mass spectrum: Calculated $C_9H_{18}OSi$ = 206.113, Found 206.110. The base peak was at m/e = 118. Other peaks appeared at m/e = 191, 175, 163, 151, 149, 91, 73, 59 and 44.

Attempted Silylation of 3-(o-chlorophenyl)-2-methylpropene. A sample of this compound (o-methallylchlorobenzene, courtesy of Gil Johnson and Dr. R. G. Bergman) appeared only 80% pure by vpc analysis (UCON, 133°), but little contamination could be detected in its pmr spectrum in $CDCl_3$: δ1.07 (d,3, J = 1Hz, CH_3), δ3.47 (s,2, $PhCH_2$), δ4.6-4.7 (m,1, vinyl H), δ4.8-4.9 (m,1, vinyl H), δ7.1-7.5 (m,4, aromatic H). A solution of this compound (2.56g, 15.3 mmol) and hexamethyldisilane (3.36g, 23 mmol) in 5 ml of HMPT was added rapidly to a stirred suspension under argon of 1.86g (26.5 mmol) of potassium methoxide in 50 ml of HMPT. The visual phenomena associated with this reaction were unusual - an exotherm with rapid gas evolution, and a series of color changes, beginning with deep red, to yellow, then tan, ending in wine red. The mixture was stirred at ambient temperature for 2 h, then quenched (with discharge of color) with water, and taken up in 100 ml of a pentane/ether solution (80:20). The organic layer was washed with 4% aqueous HCl, then water, then saturated sodium chloride solution, and dried (Na_2SO_4). The solvent was removed from the filtered solution, and the residue (1.6g) shown to be the known[140] compound 1-phenyl-2-methylpropene (85%

of product, by vpc on UCON at 133°), with distinctive pmr in $CDCl_3$: δ1.74 (d,3, J = 1Hz, trans-CH_3), δ1.92 (d,3, J = 1.5Hz, cis-CH_3), δ6.25-6.4 (m,1, vinyl H); δ7.1-7.5 (m,5, aromatic H).

F. Controls and Limitations

Treatment of p-iodotoluene with an equivalent of potassium methoxide in HMPT, in the absence of hexamethyldisilane at 65° for 2 h resulted in less than 2% reduction. The reduction product is therefore not the product of direct reaction between methoxide and the aryl iodide, as discussed in the text. No products of methoxide substitution (anisole and methylanisoles) were ever detected via vpc in any of the methoxide-catalyzed reactions.

Several modifications of the silylation procedures were attempted, mostly without success. THF, diethyl ether, or 1,2-dimethoxyethane, with or without TMEDA (1,2-bis(dimethylamino)-ethane), failed to effect the methoxide cleavage of hexamethyldisilane, as assayed by aryl halide silylation.

G. Synthesis of Heteroaromatic Silanes

4-pyridyltrimethylsilane (48)[141] A solution of trimethylsilyllithium was prepared by the addition of 25 ml of 2.0M methyllithium solution in ether via syringe to a stirred solution of 10 ml (50 mmol) of hexamethyldisilane in 50 ml of HMPT, cooled to 0°, in a 250 ml flask under argon. After 20 min, a mixture of 2.119g (14 mmol) of 4-chloropyridine hydrochloride in 10 ml of HMPT was added cautiously, since an exothermic reaction ensued. The reaction was allowed to stir for 3 h, then quenched in water and taken up in two 100-ml portions of a pentane:ether solution (20:80), washed again with water, then saturated sodium chloride solution. After drying (Na_2SO_4) and concentration, the product was distilled to give 0.92g (43%) of 48, b.p. 85°/28 torr (lit.[141] 107°/48 torr), ir (neat) 2950(s), 2890, 1565, 1400, 1250(s), 1125, 1050(s), 900, 840(s), 750 cm^{-1}; pmr ($CDCl_3$) δ0.30 (s,9, $SiCH_3$); δ7.2-7.5 (m,2, aromatic H); δ8.5-8.7 (m,2, aromatic H α to N). No pyridine was detectable by analytical vpc (SF-96, 100°).

3-Pyridyltrimethylsilane (47).[141] A solution of trimethylsilyllithium was prepared in a manner identical to that described for the synthesis of **48**. To this solution (theoretically 50 mmol) at 0° under argon was added slowly via syringe 3.0 ml (26.8 mmol) of 3-chloropyridine. The mixture was allowed to stir for 3 h at room temperature, then extracted in two 100-ml portions of a pentane:ether solution (20:80), the combined organic layers washed with water and saturated sodium chloride solution, and dried (Na_2SO_4). Concentration and distillation gave 1.2g (30%) of **47**, b.p. 90-92°/28 torr (lit.[141] 94°/30 torr); ir (neat), 2950(s), 1585, 1400, 1250(s), 1125, 1050, 840(s), 800 750 cm^{-1}; pmr ($CDCl_3$) δ0.4 (s,9, $SiCH_3$); δ7.3-7.5 (m,2, aromatic H), δ8.5-8.7 (m,2, aromatic H).

The remainder of the product was nonvolatile tar. Pyridine was not observed in the product mixture after workup via analytical vpc (SF-96, 100°).

2-Pyridyltrimethylsilane (46).[141] To a stirred suspension of 1.56g (22 mmol) of potassium methoxide in 80 ml of HMPT under argon in a 200 ml flask was added via syringe a solution of 2.1g (13 mmol) of hexamethyldisilane in 20 ml of HMPT. The reaction mixture was allowed to stir for 4 h, then taken up in 100 ml of an ether/pentane (50%) mixture, quenched with cold saturated aqueous sodium bicarbonate, then wahed with saturated sodium chloride solution, and dried (Na_2SO_4). Concentration of 1 atmosphere and distillation gave 1.63g (80%) of 46, b.p. 79-80°/25 torr (lit.[144] 69°/14.5 torr); it (neat) 2950(s), 1575, 1555, 14,50, 1415, 1250(s), 1135, 1140, 985, 840(s), 750, 735 cm^{-1}; pmr ($CDCl_3$) δ0.28 (s,9, $SiCH_3$); δ6.9-7.2 (m, 1, aromatic H), δ7.3-7.6 (m,2, aromatic H), δ8.6-8.8 (m,1, aromatice H α to N). No pyridine could be detected via analytical vpc (SF-96, 100°). Rel. retention times under these conditions: pentane = 1, pyridine = 3.33.

Attempted silylation of 2-chlorothiophene: To a stirred solution of 5 ml (25 mmol) of hexamethyldisilane in 20 ml of HMPT at 0° under argon, was added slowly 12 ml of 2.20M ethereal solution of methyllithum. After 20 min, 1.8 ml (19.5 mmol) of 2-chlorothiophene was added a via syringe. The mixture was allowed to stir for 3 h, then quenched with water and extracted with two 50 ml portions of ether containing 20% of pentane. The combined organic layers were washed with saturated sodium bicarbonate solution and dried (Na_2SO_4).

The extract, upon vpc analysis (SE-30, 110°) revealed thiophene as the sole volatile product. The product was concentrated and distilled; thiophene (0.5g) was recovered, but none of the expected product of silylation 2-thienyltrimethylsilane[142] could be found in the distillate by pmr.

4. Transition Metal Carbenes

A. Synthesis

Trimethylsilylmethoxycarbenepentacarbonylchromium (72): To a stirred solution of 1.5 ml (7.5 mmol) of hexamethyldisilane in 5 ml of HMPT at 0° was added via syringe 3 ml of a 2M solution of methyllithium in ether (Et_2O). Fifteen min after addition was complete, the orange-red solution of trimethylsilyllithium in HMPT/Et_2O was added via double-ended needle to a second flask which held a suspension of 0.985g (4.5 mmol) of hexacarbonylchromium in 100 ml of THF, previously cooled to -78°. After addition was complete, this cherry-red solution was stirred for one h at -78° then concentrated under reduced pressure (∿ 0.5 torr) to remove solvent. Argon gas was admitted to the evacuated reaction flask and the mixture was taken up in 50 ml dichloromethane, and cooled to -50° (dry ice/diethylmalonate bath). To this was added 1.0 ml (12.4 mmol) of methyl fluorosulfonate by syringe. After 1 h at -50°, the reaction mixture was concentrated under vacuum. Argon gas was then admitted and the reaction mixture was chromatographed on Silica Gel 60, under argon, in a jacekted 40 cm x 4 cm column cooled to 10° ± 2, with diethyl ether as eluent. A broad yellow band, rf ≈ 0.5, was collected, the solvent removed, and the resultant oil (ca 500 mg, 34% theoretical) identified as $Me_3Si(OCH_3)C$ $Cr(CO)_5$ on the basis of the following spectra data (CD_3COCD_3): pmr (CD_3CO) $\delta 0.15$, s, with peaks at $\delta 1.9$ and $\delta 3.8$ due to THF. ir (carbonyl region 2010 cm^{-1} (sharp), 1980, 1940 (vs) C nmr: -2.6 ppm (CH_3-Si), 70.0 (CH_3-O), 219.5 (CO-cis), 223.5 (CO-trans), and 425 (C=Cr).

The same was invariably contaminated with some THF.

Trimethyltinmethoxycarbenepentacarbonylchromium **(73a)**: To a stirred solution of 3.4432g (10.5 mmol) of hexamethylditin in 15 ml of THF at -20° (dry ice/carbon tetrachloride bath) was added yellow solution of trimethyltinlithium, after 15 min stirring, was added via syringe to a stirred suspension of hexacarbonylchromium in 100 ml THF at -78°. The mixture was allowed to stir for 1 h at -78°. The solution was then decanted from a small amount of residue (presumably hexacarbonylchromium), transferred to another round-bottom flask, and concentrated under reduced pressure. Argon was admitted to the flask, and 50 ml of dichloromethane added. After cooling to -50°, 1 ml (12.4 mmol) of methyl fluorosulfonate was added via syringe. The mixture was stirred at -50° for 1 h, then subjected to vacuum rotary evaporation. Argon atmosphere was admitted, the mixture was taken up in the desired solvent (acetone-d_6 for spectra), and filtered through glass wool prior to use.

The complex evidence the following spectra characteristics: pmr, δ0.13 (s,9, $SnMe_3$) and δ3.83 (s, 4+, OCH_3) again, THF present in small amount. ir 2005 (sharp), 1940 and 1890 cm^{-1} ^{13}C nmr, -6.4 ppm (CH_3Sn), 69.2 (OCH_3) 222.2 (CO-cis), 227.1 (CO-trans), and 310 (C=Cr).

Trimethyltinmethoxypentacarbonyltungsten (73b) was obtained in similar fashion from hexacarbonyl tungsten, and identified on the basis of the following spectra data: pmr, δ0.15(s) plus m at δ1.9 and δ3.8 due to THF. ir, 2010 (sharp), 1910, 1890 (vs) cm^{-1} ^{13}C nmr, -6.0 (CH_3Sn), 6.72 (CH_3O), 2.2 (CO-cis), 216 (CO-trans) and 334 ppm (C=W). An extraneous peak at 294.8 ppm is assigned to the acyl anion complex.

B. Attempted Generation of Tungsten Carbene Complexes from Tungsten Pentacarbonyl Dianions.[102]

a) **With butanal** - A mixture of 11.2g (32 mmol) of hexacarbonyltungsten and 1.55g (67 mmol) of sodium metal was suspended in HMPT (50 ml) in a 200-ml rb flask with gas inlet and sidearm possessing a stopcock and second hose adapter. The mixture was magnetically stirred with a glass-coated stirbar, and evacuated via the sidearm. Gas evolution was noted. The mixture was stirred overnight at room temperature at a pressure diminishing to 0.1 torr.

After this period, the solution, now homogeneous and dark orange in appearance, had ceased evolution of gas (presumably CO). Argon at one atmosphere pressure was admitted to the flask. A serum cap replaced the hose connection on the sidearm, and 3 ml (34 mmol) of reagent grade n-butanal was added via syringe. Stirring was continued at room temperature under argon for four h. Chlorotrimethylsilane (4.0 ml, 32 mmol) was then added slowly via syringe. An immediate exotherm occurred. The mixture was stirred for eight h under argon, then analyzed via vpc (10 ft DBT, 80°)

for products. Butanal was the only product found. No 4-octenes or higher olefins were apparent.

b) With formaldehyde - Hexacarbonyltungsten (7.08g, 20 mmol) was suspended in 40 ml HMPT in a 200 ml rb flask with sidearm. Potassium metal (1.4g, 35 mmol) was added, and the flask evacuated to 1 torr. Gas evolution was noted. The mixture was magnetically stirred at room temperature for 14 h. The reaction mixture has ceased gas evolution and become a homogeneous orange solution. This flask, still evacuated, was then connected via double-ended needle to another 200-ml flask containing 0.68225g (44 mmol) of paraformaldehyde under argon. The paraformaldehyde was heated with a hot-air gun to generate gaseous formaldehyde which was allowed to bubble through the reaction mixture. A solid film formed on portions of the surface of HMPT. When no more gaseous formaldehyde was evolved, argon was admitted to the reaction vessel to one atmosphere pressure. After stirring for one h, the reaction mixture was treated with chlorotrimethylsilane (2.5 ml, 20 mmol), added via syringe. An immediate exotherm occurred, with a solid precipitate formed. A 2 ml aliquot of the atmosphere above the reaction mixture was removed via gas syringe and subjected to analytical vpc on a 10' x 1/8" Porapak N column. No ethylene or other volatile olefin was detected.

C. Attempted Generation and Trapping of 65:

a) with fluoride ion. Immediately after the preparation of a solution of trimethyltinmethoxycarbenepentacarbonylchromium (from 8 mmol of precursor) in 50 ml of dichloromethane, 20 ml of this solution was removed and placed in an argon-filled 50-ml round-bottom flask. The dichloromethane was removed via high vacuum, argon readmitted, and the residue redissolved in 30 ml of THF. To this was added 0.67208g (3.8 mmol) of diphenylacetylene and 0.5g (1.9 mmol) of anhydrous tetrabutylammonium fluoride (prepared by the neutralization of tetrabutylammonium hydroxide with 5% aqueous hydrofluoric acid, removal of water under vacuum, and drying in a drying pistol under high vacuum, at 100°). The resulting mixture (very nearly homogeneous) was stirred under argon for 24 h. At intermediate intervals, aliquots were removed and examined via pmr. The expected multiplet at $\delta 7.2$-7.6 due to diphenylacetylene was observed, as well as upfield peaks due to other reactants. No peaks were observed downfield of δ7.6. The reported[99] chemical shifts of δ7.74 and δ8.32 for the cyclopropenylidene complex (67b) were not observed.

b) via heat. A second 20 ml aliquot of the same dichloromethane solution of $(CO)_5CrC(OMe)SnMe_3$ was placed in a 100 ml flask, the solvent removed, and the residue resuspended with 0.72929g (4.1 mmol) of diphenylacetylene in benzene (50 ml) under argon. The mixture was heated at reflux overnight, incurring a color change from maize to dark navy. The colored material was a precipitate which coated the sides of the flask; a filtered aliquot was clear and colorless. The solvent was removed from this aliquot, and the white residue shown via pmr to consist solely of diphenylacetylene.

However, when the $(CO)_5WC(OMe)SnMe_3$ (73b) was heated in the presence of diphenylacetylene to 100° in decalin, the pmr revealed new peaks near diphenylacetylene: δ6.36 (s, ∿3H), δ7.67 (m, centered, ∿5H), δ8.1 (s, ∿2H). Diphenylacetylene was present in far greater amount (∿100H). The two peaks downfield correspond roughly to the expected chemical shifts for the cyclopropenylidene carbene complex sought; however, the area ratios are inconsistent with this assignment. The major portion of the carbene complex, as usual upon heating above 80°, was converted to a deep blue solid precipitate which has not been characterized.

These methods were also used in the attempted generation of **65** from $(CO)_5Cr(OMe)SiMe_3$. (Methoxide initiaion was also examined.) In these reactions, the silyl complex was collected directly off the chromatography column into a 500-ml argon-filled flask containing excess amounts of diphenylacetylene and fluoride (or methoxide) initiator. The resulting ether suspension was stirred for 24 h, or until the silyl carbene complex had decomposed, as evidenced by loss of yellow color and precipitation of the green decomposition product. At intervals during the process, aliquots were removed from the solution, the solvent removed, and the residue dissolved in deuterochloforom for pmr analysis. No peaks downfield of diphenylacetylene were ever found in these reactions.

c) Reaction with butyllithium. An estimated 2.0 mmol of $(CO)_5Cr(OMe)SnMe_3$, free from solvent, was redissolved with 0.4g (2.2 mol) of diphenylacetylene in THF (20 ml) under argon in a 50 ml flask. This solution, with stirring, was cooled to -78°, and 1 ml of a 2.0M solution of n-butyllithium in ether was added via syringe. After 1 h, the mixture was warmed to room temperature, and a portion removed. Subsequent evaporation of volatiles in vacuo, uptake of the residue in deuterochloroform, and pmr analysis of the filtered solution revealed mostly diphenylacetylene. In addition, a singlet at $\delta 0.11$ ($SnCH_3$) and two multiplets at $\delta 0.9$-1.2 and $\delta 1.4$-1.6 (possibly from an n-butyl residue) were present in small concentration. No peaks corresponding to olefinic protons were found, nor were any peaks found downfield of diphenylacetylene.

An identical sample of the carbene complex was treated with butyllithium as above, in the absence of diphenylacetylene. After solvent was removed, a pale yellow oil was produced. The infrared spectrum of this oil contained distinct absorbances at 3010, 2940, 1970, 1605(s), 1495(s), 1440(s), 1070, 1030, and 915 cm^{-1}. The peak at 1970 was weak; other broad, very weak absorbances were present in the region 1860-1910 cm^{-1}. The spectrum was not indicative of a metal carbonyl complex as present in high concentration, for the bands corresponding to carbonyls were not at all very strong.

Polymerization of acetone. This reaction was discovered during the attempts to secure carbon-13 nmr spectra of the trimethyltin-substituted carbene complexes of both chromium and tungsten. Thus, when about 7 mmol of $(CO)_5CrC(OMe)SnMe_3$, free from solvent, was placed in acetone-d_6 (4 ml) under argon in a stoppered nmr tube and kept at 0° overnight in the absence of light. The next day, the orange solution had solidified to a translucent orange gel. This could be dissolved in deuteriochloroform. The ir spectrum appeared to be no different from acetone-d_6, with peaks in the metal carbonyl region corresponding to the carbene complex. When allowed to stand at room temperature for a week, the gel reverted to liquid acetone-d_6 (and the decomposed metal complex).

Tests with nondeuterated acetone showed that only relatively small ratios of acetone to complex (estimated 10:1 or smaller) resulted in complete solidification. Even these gels retained significant quantities of monomer, or of structures with a singlet in the pmr at the identical chemical shift of acetone. Other peaks were found at $\delta 1.33$ and $\delta 1.38$ and at $\delta 1.50$, $\delta 2.60$, $\delta 2.77$, $\delta 2.94$ and $\delta 3.02$, in varying area ratio, although the first two are roughly equal, and larger than any of the others. A multiplet of $\delta 6.2$ was noted on one occasion. The same polymer and pmr spectrum was obtained with the corresponding tungsten complex, when allowed to stand in acetone solution.

That the solidification was not the result of catalysis by base (condensation chemistry) or methylfluorosulfonate was shown in separate experiments. A sample of carbene complex with methyllithium present in excess reacted with acetone to provide triacetone alcohol, the reported[112] product of condensation, as evidence via pmr: $\delta 1.16$ (s,12, $C(CH_3)_2$); $\delta 2.09$ (s, acetone monomer); $\delta 2.51$ (s,4, CH_2 next to carbonyl); $\delta 3.83$ (s,2, OH).

A 0.5 ml aliquot of methyl fluorosulfonate added to 4 ml of reagent acetone and a trace (about 0.1 ml) of THF at 0° provided an immediate reaction and color change to deep red, but no observable phase change and gel formation over the course of 24 h. The pmr spectrum of the product mixture revealed: δ1.56 and δ1.6 (two,s, ∼1), δ3.27 (s,∼2), δ4.0-4.6 (m,∼1), δ6.1-6.3 (m,∼2).

References

1. a) C.A. Kraus and H. Eatough, J. Am. Chem. Soc. 55, 5008 (1933); b) C.A. Kraus and W.K. Nelson, ibid., 56, 195 (1934).
2. a) D. Wittenberg and H. Gilman, Quart. Rev. 13, 116 (1959); b) H. Gilman and H.J.S. Winkler, in H. Zeiss, ed., "Organometallic Chemistry," Reinhold Publishing Co., New York, 1960, p. 270; c) D.D. Davis and C.E. Gray, Organometal. Chem. Rev. A, 6, 283 (1970); d) N.S. Vyazankin, G.A. Razuvaev, and O.A. Krugalaya, Organometal. Reactions 5, 101 (1975).
3. R.A. Benkeser and R.G. Severson, J. Am. Chem. Soc. 73, 1434 (1951).
4. H. Gilman and T.C. Wu, ibid., 4031.
5. R.A. Benkeser, et. al., ibid., 74, 648, 4200, 5699 (1952).
6. Indeed, this is a common method for the preparation of symmetrical disilanes: H. Gilman, et. al., J. Organometal. Chem. 13, 323 (1968).
7. J. Dunogues, R. Calas, M. Bolourtchain, C. Biran, and N. Duffuat, J. Organometal. Chem. 57, 55

(1973), and references cited therein.

8. J.-P. Picard, A. Ekouya, J. Dunogues, N. Duffuat, and R. Calas, ibid., 93, 51 (1975), and references cited therein.

9. a) N.S. Vyazankin, G.A. Razuvaev, E.N. Gladyshev, and S.P. Korneva, J. Organometal. Chem. 7, 353 (1967); b) E. Hengge and N. Holtschmidt, ibid., 12, P5 (1968).

10. Bis(trimethylsilyl)mercury is, however, commercially available from Petrarch Systems.

11. H. Gilman and C.W. Gerow, J. Am. Chem. Soc. 78, 5823 (1956).

12. H. Sakurai, A. Okada, M. Kira, and K. Yonezawa, Tetrahedron Lett., 1511 (1971).

13. H. Sakurai and F. Konda, J. Organometal. Chem. 92, C46 (1975).

14. P.B. Dervan and M.A. Shippey, J. Am. Chem. Soc. 98, 1265 (1976).

15. I.M.T. Davidson and A.B. Howard, J. Chem. Soc., Faraday I 71, 69 (1975).

16. For estimates of the basicity of silyl anions, see: a) H. Gilman, O.L. Marrs, W.J. Trepka, and

J.W. Diehl, J. Org. Chem. 27, 1260 (1962); b) A.G. Evans, M.A. Hamid, and N.H. Rees, J. Chem. Soc. B, 1110 (1971).

17. E.M. Arnett and L.E. Small, J. Am. Chem. Soc. 99, 808 (1977).

18. R. Walsh, private communication.

19. W.C. Still, J. Org. Chem. 41, 3063 (1976).

20. R. Walsh and J.M. Wells, J. Chem. Soc., Faraday I, 72, 100 (1976).

21. a) A. Wright and R. West, J. Am. Chem. Soc. 96, 3214 (1974); b) A.G. Brook, Accts. Chem. Res. 7, 77 (1974).

22. O.W. Steward, J.E. Dziedic, and J.S. Johnson, J. Org. Chem. 36, 3475 (1971).

23. a) H. Sakurai, A. Okada, H. Umino, and M. Kira, J. Am. Chem. Soc. 95, 955 (1973); b) H. Sakurai, H. Umino, and A. Okada, Chem. Lett., 671 (1973).

24. M.A. Shippey and P.B. Dervan, J. Org. Chem. 42, 2654 (1977).

25. H. Normant, Angew. Chem. Int. Ed. Engl. 6, 1046 (1967).

26. A. Streitweiser, Jr., et. al., J. Am. Chem. Soc. 93, 5096 (1971).

27. C. Eaborn and R.W. Bott, "The Synthesis and Reactions of the Silicon-Carbon Bond," in A.G. MacDiarmid, ed., "Organometallic Compounds of the Group IV Elements," Vol. 1, Pt. 1, Marcel Dekker, Inc., New York, 1968.

28. R.E. Dessy, et. al., J. Am. Chem. Soc. 88, 460 (1966).

29. F.C. Whitmore, L.H. Dommrt, J.R. Gold, and R.E. Van Strein, ibid., 69, 1551 (1947).

30. L.H. Sommer, D.L. Bailey, and F.C. Whitmore, ibid., 70, 2869 (1948).

31. P.N. Haszeldine, P.J. Robinson, and R.F. Simmons, J. Chem. Soc., 1890 (1964).

32. I.M.T. Davidson and C.J.L. Metcalfe, ibid., 2630 (1964).

33. a) A.W.P. Jarvie, A. Holt, and J. Thompson, J. Chem. Soc. B, 852 (1969); b) M.A. Cook, C. Eaborn, and D.R.M. Walton, J. Organometal. Chem. 24, 301 (1970).

34. For general reviews of these reactions, see: a) C. Eaborn, *J. Organometal. Chem.* *100*, 43 (1975); b) I. Fleming, *Chem. Ind.*, 449 (1975).

35. H. Gilman and R.A. Tomasi, *J. Org. Chem.* *27*, 3647 (1962).

36. H. Gilman, D. Aoki, and D. Wittenberg, *J. Am. Chem. Soc.* *81*, 1107 (1959).

37. P.F. Jones and M.F. Lappert, *J. Chem. Soc.*, *Chem. Commun.*, 526 (1972).

38. S.L. Hartzell and M.W. Rathke, *Tetrahedron Lett.*, 2737, 2757 (1976).

39. B.-T. Grobel and D. Seebach, *Angew. Chem. Int. Ed. Engl.* *13*, 83 (1974).

40. D.J. Peterson, *J. Org. Chem.* *33*, 780 (1968).

41. Inter alia: a) T.H. Chan, E. Chang, and E. Vinokur, *Tetrahedron Lett.*, 1137 (1970); b) H. Sakurai, K. Nishiwaki, and M. Kira, *ibid.*, 4193 (1973); c) Other works cited in reference 42b.

42. a) P.F. Hudrlik and D. Peterson, *Tetrahedron Lett.*, 1133 (1974); b) P.F. Hudrlik and D. Peterson, *J. Am. Chem. Soc.* *97*, 1464 (1975).

43. H.O. House, "Modern Synthetic Reactions," 2nd Ed., W.A. Benjamin, Inc., Menlo Park, 1972, p. 300.

44. P.F. Hudrlik, D. Peterson, and R.J. Rona, *J. Org. Chem.* *40*, 2263 (1975).

45. a) E. Vedejs and P.L. Fuchs, *J. Am. Chem. Soc.* *95*, 822 (1973); b) D.E. Bissing and A.J. Speziale, ibid., *87*, 2683 (1965).

46. D.J. Peterson, *J. Organometal. Chem.* *9*, 373 (1967).

47. For leading references to other methods of epoxide deoxygenation, see reference 48. See also references 49 and 50, respectively, for reports of olefin isomerization and stereoselective olefin synthesis.

48. a) M.T. Reetz and M. Plachy, *Synthesis*, 199 (1976); b) For a list of epoxide deoxygenations, see: J. March, "Advanced Organic Chemistry. Reactions, Mechanism, and Structure," 2nd Ed., McGraw-Hill Book Co., New York, 1977, p. 940; c) M. Rosenblum, M.R. Saidi, and M. Madhavarao, *Tetrahedron Lett.*, 4009 (1975).

49. D. Van Ende and A. Krief, *ibid.*, 2709 (1975) and references cited therein.

50. J. Reucroft and P.G. Sammes, Quart. Rev., Chem. Soc. 25, 135 (1971).

51. H. Gilman, R.K. Ingham, and A.G. Smith, J. Org. Chem. 18, 1743 (1953).

52. See also: H. Sakurai and A. Okada, J. Organometal. Chem. 35, C13 (1972).

53. a) C.J. Pedersen and H.K. Frensdorff, Angew. Chem. Int. Ed. Engl. 11, 16 (1972); b) G.W. Gokel, D.J. Cram, C.L. Liotta, H.P. Harris, and F.L. Coole, J. Org. Chem. 39, 2445 (1974).

54. M. Koreeda, N. Koizumi, and B.A. Teicher, J. Chem. Soc., Chem. Commun., 1035 (1976).

55. P.F. Hudrlik, in D. Seyferth, ed., "New Applications of Organometallic Reagents in Organic Synthesis," Journal of Organometallic Chemistry, Library 1, Elsevier Scientific Publishing Co., Amsterdam, 1976, Chapter 3.

56. J.F. Hyde, et. al., J. Am. Chem. Soc. 75, 5615 (1953).

57. C. Trindle, J.-T. Hwang, and F.A. Carey, J. Org. Chem. 38, 2664 (1973).

58. E. Vedejs and K.A.J. Snoble, J. Am. Chem. Soc. 95, 5778 (1973).

59. G.H. Birum and C.N. Matthews, J. Chem. Soc., Chem. Commun., 137 (1967).

60. J.W. Cornforth, R.H. Cornforth, and K.K. Mathew, J. Chem. Soc., 112 (1959).

61. a) T.J. Barton and J.A. Kilgour, J. Am. Chem. Soc. 96, 2278 (1974), and references contained therein; b) P.B. Valkovich and W.P. Weber, J. Organometal. Chem. 99, 231 (1975); c) cf. M. Ishikawa, T. Fuchikami, and M. Kumada, ibid., 133, 19 (1977).

62. For instance: E. Vedejs, K.A.J. Snoble, and P.L. Fuchs, J. Org. Chem. 38, 1178 (1973).

63. A.G. Brooke and S. Wolfe, J. Am. Chem. Soc. 79, 1431 (1957).

64. Although only 9% of benzene was recovered, subsequent experiments (reference 63) designed to trap phenylpotassium with benzophenone yielded 23% of triphenylmethanol, the product assigned to result from phenylpotassium. The 40% figure arises from the fact that 40% of the

silylated products appear to arise from bromotriphenylsilane, the other product of halogen-metal interconversion.

65. L. Friedman and J.F. Chlebowski, *J. Am. Chem. Soc.* **91**, 4864 (1969).

66. J.D. Roberts, H.E. Simmons, Jr., L.A. Carlsmith, C.W. Vaughan, *ibid.*, **75**, 3290 (1953).

67. J.F. Bunnett and R.E. Zahler, *Chem. Rev.* **49**, 273 (1951).

68. However, coupling between aryl halides and alkyllithium reagents has been reported: R.E. Merrill and E. Negishi, *J. Org. Chem.* **39**, 3452 (1974).

69. H.G. Kuivila, in J.J. Zuckerman, ed., "Organotin Compounds: New Chemistry and Applications," American Chemical Society, Washington, D.C., 1976, Chapter 3.

70. For a review, see: C. Eaborn, *J. Organometal. Chem.* 100, 43 (1975).

71. a) I. Fleming, *Chem. Ind.*, 449 (1975), and references contained therein; b) R.L. Funk and K.P.C.Vollhardt, *J. Am. Chem. Soc.* **99**, 5483

(1977), and references contained therein.

72. T.-L. Ho and G.A. Olah, Synthesis, 417 (1977).

73. Aryltrimethylsilanes are most commonly prepared from the reaction of chlorotrimethylsilane with Grignard or organolithium reagents. For other direct methods of synthesis, see: a) H. Matsumoto, S. Nagashima, K. Yoshikiro, and Y. Nagai, J. Organometal. Chem. 85, C1 (1975); b) G.L. Larson, Syn. React. Inorg. Metalorg. Chem. 6, 21 (1976).

74. a) A.L.J. Beckwith and W.B. Gara, J. Am. Chem. Soc. 91, 5691 (1969); b) A.L.J. Beckwith and W.B. Gara, J. Chem. Soc., Perkin II, 795 (1975).

75. J.K. Kim and J.F. Bunnett, J. Am. Chem. Soc, 92, 7463 (1970).

76. J.F. Bunnett and C.C. Wamser, ibid., 89, 6712 (1967).

77. Y.-P. Wan, D.H. O'Brien, and F.J. Smentowski, ibid., 94, 7680 (1972), and references cited therein.

78. M. Julia, Accts. Chem. Res. 4, 386 (1971).

79. The rate k_{cyc} has been experimentally determined (k_{cyc}= 6 x $10^7 sec^{-1}$) (reference 74b) only at 130°. To calculate the rate at 25° (the temp. at which the reaction involving trimethylsilylpotassium was conducted), either the A factor or the energy of activation must be given. These are known in the related 5-hexenyl radical cyclization: A = $10^{10.7}$, Ea = 7.8 kcal/mole. (D. Lal, D. Griller, S. Husband, and K.U. Ingold, J. Am. Chem. Soc. 96, 6355 (1974)). Assuming this value of the A factor, the calculated value of Ea = 5.4 kcal/mole, and k_{cyc}= 2 x 10^6 at 25°. Alternatively, given the above value for Ea, the calculated value of A = $10^{11.98}$, and k_{cyc}= 6 x 10^5 at 25°. Within the error limits of this calculation, these values of k_{cyc} are virtually identical; $k_{cyc} \approx 10^6$.

80. E.O. Fischer and A. Maasböl, Angew. Chem. Int. Ed. Engl. 3, 580 (1964).

81. For a general review of carbene complexes, see: a) D.J. Cardin, B. Cetinkaya, and M.F. Lapport, Chem. Rev. 72, 545 (1972); b) E.O. Fischer,

Pure Appl. Chem. *24*, 407 (1973).

82. E.O. Fischer, *Pure Appl. Chem.* *27*, 353 (1973).

83. J.E. Ellis, *J. Organometal. Chem.* *86*, 1 (1975).

84. E. Moser and E.O. Fischer, *J. Organometal. Chem.* *12*, P1 (1968).

85. E.O. Fischer, E. Winkler, C.G. Kreiter, G. Huttner, and B. Krieg, *Angew. Chem. Int. Ed. Engl.* *10*, 922 (1971).

86. E.g., several bis-dialkylaminocarbenes show different resonances in the pmr for the alkyl groups syn and anti to the metal atom. See reference 2.

87. Theoretical calculations *ab initio* by Goddard (reference 88) suggest the carbon-metal (nickel) "double" bond to be less than 5 kcal/mole stronger than the corresponding sigma bond.

88. A.K. Rappe and W.A. Goddard, III, *J. Am. Chem. Soc.* *99*, 3966 (1977).

89. W.A. Goddard, III, S.P. Walch, A.K. Rappe, T.H. Upton, and C.F. Melius, *J. Vac. Sci. Tech.* *14*, 416 (1977).

90. Such species are possible intermediates in the metal-catalyzed reduction of CO. Similar metal-bound carbon atoms have been the subject of theoretical studies (reference 89).

91. E.O. Fischer, H. Hollfelder, P. Friedrich, F.R. Kreissl, and G. Huttner, Angew. Chem. Int. Ed. Engl. 16, 401 (1977).

92. C.W. Rees and E. von Angerer, J. Chem. Soc., Chem. Commun., 420 (1972).

93. a) W.H. Atwell and D.R. Weyenberg, J. Am. Chem. Soc. 90, 3438 (1968); b) T.J. Barton and M. Juvet, Tetrahedron Lett., 3893 (1975).

94. a) W.H. Atwell, D.R. Weyenberg, and J.G. Uhlmann, J. Am. Chem. Soc. 91, 2025 (1969); b) A.G. Brook and P.J. Dillon, Can. J. Chem. 47, 4347 (1969).

95. F.P. Tsui, Y.H. Chang, T.M. Vogel, and G. Zon, J. Org. Chem. 41, 3381 (1976).

96. P.J. Stang and D.E. Fox, J. Org. Chem. 42, 1667 (1977).

97. D. Farcasiu, Tetrahedron Lett., 595 (1977), and references cited therein.

98. E.O. Fischer, H. Hollfelder, F.R. Kreissl, and W. Uedelhoven, *J. Organometal. Chem*. *113*, C31 (1976).

99. K. Ofele, *Angew. Chem. Int. Ed. Engl*. *7*, 950 (1968).

100. J.R. Anglin, H.P. Calhoun, and W.A. Graham, *Inorg. Chem*. *16*, 2281 (1977).

101. This mode of methylation is suggested by C.P. Casey, C.R. Cyr, and R.A. Boggs, *Syn. Org. Metal-Org. Chem*. *3*, 249 (1973).

102. a) J.E. Ellis, S.G. Hentges, D.G. Kalina, and G.P. Hagen, *J. Organometal. Chem*. *97*, 79 (1975); b) J.E. Ellis and G.P. Hagen, *Inorg. Chem*. *16*, 1357 (1977).

103. B.E. Mann, *Adv. Organometal. Chem*. *12*, 135 (1974).

104. The proton shift for the aromatic protons in **67b** is δ7.74 and δ8.32 (reference 97), as opposed to δ7.2-7.6 for diphenylacetylene.

105. a) T.J. Katz, S.J. Lee, and N. Acton, *Tetrahedron Lett*., 4247 (1976), and references cited therein; b) R.H. Grubbs and C.R. Hoppin, *J. Chem. Soc*., *Chem. Commun*., 634 (1977);

c) R.J. Haines and G.J. Leigh, Chem. Soc. Rev. 4, 155 (1975).

106. T.J. Katz and N. Acton, Tetrahedron Lett., 4251 (1976).

107. W.C. Still, J. Am. Chem. Soc. 99, 4836 (1977).

108. This polymer is well known: T.J. Katz, references 105a and 106, and works cited therein.

109. E.O. Fischer, T. Selmayr, and F.R. Kreissl, Chem. Ber. 110, 2947 (1977).

110. a) A. Kargin, V.A. Kabanov, V.P. Zubov, and I.M. Papisov, Dokl. Chem. (Engl. Trans.) 134, 1141 (1960); b) W. Kawai, Bull. Chem. Soc. Japan 35, 516 (1962); c) J. Furukawa, T. Saegusa, T. Tsuruta, S. Ohta, and G. Wasai, Makromol. Chem. 52, 230 (1962); d) H. Miyama and M. Kamachi, Polymer Lett. 3, 241 (1965).

111. V.C.E. Burnop, Polymer 6, 411 (1965).

112. B.A. Dolgoplosk, et. al., J. Organometal. Chem. 128, 339 (1977).

113. R. Hoffmann, B.F. Beier, E.L. Muetterties, and A.R. Rossi, Inorg. Chem. 16, 511 (1977).

114. We thank Dr. R.G. Bergman for this suggestion.

115. Initially, the deuterium oxide quenching experiment was carried out on p-iodotoluene, because benzene was more difficult to isolate by gas chromatography (due to silicon byproducts with similar retention times) than was toluene. However, the mass spectrum presented an insurmountable problem in the facile hydrogen loss from the parent radical cation of toluene to give the tropylium ion. Tropylium-d_1 is indistinguishable from the molecular ion of toluene-d_0.

116. D.J. Pasto and C.C. Cumbo, *J. Org. Chem*. *30*, 1271 (1965).

117. G.H. Posner and D.Z. Rogers, *J. Am. Chem. Soc*. *99*, 8208 (1977).

118. L. Spiegler and J.M. Tinker, *ibid*., *61*, 940 (1939).

119. R. Klein and M.D. Scheer, *J. Phys. Chem*. *74*, 613 (1970).

120. E. Klein and W. Rojahn, *Dragoco Rep. Ger. Ed*. *14*, 47 (1967); *Chem. Abstr*. *67*, 90705u (1967).

121. K.-H. Kubeczka, *J. Chrom*. *31*, 319 (1967).

122. E.J. Corey and N. Venkateswarlu, J. Am. Chem. Soc. 94, 6190 (1972).

123. J.L. Pierre, P. Chautemps, and P. Arnaud, Bull. Soc. Chim. Fr., 1317 (1969).

124. M.E. Cain, J. Chem. Soc., 3532 (1964).

125. R. Tedeschi and G. Clark, J. Org. Chem. 27, 4323 (1962).

126. R. Weast, ed., "Handbook of Chemistry and Physics," 55th ed., Chemical Rubber Company Press, Cleveland, 1974.

127. K.B. Sharpless, A.O. Chong, and J.A. Scott, J. Org. Chem. 40, 1252 (1975).

128. H. Gilman, et. al., J. Organometal. Chem. 13, 323 (1968).

129. J.F. Hyde, et. al., J. Am. Chem. Soc. 75, 5615 (1953).

130. G.W. Gokel, D.J. Cram, C.L. Liotta, H.P. Harris, and F.L. Coole, J. Org. Chem. 39, 2445 (1974).

131. W.A. Dietz, J. Gas Chrom. 5, 68 (1967).

132. W.K. Musker and G.L. Larson, Tetrahedron Lett., 3487 (1968).

133. A.D. Petrov, V.F. Mironov, and V.G. Glukhovtsev, Zh. Obshch. Khim. 27, 1535 (1957); Chem. Abstr. 52, 3668h (1958).

134. P.F. Hudrlik, et. al., Tetrahedron Lett., 1453 (1976).

135. R. West and P.C. Jones, J. Am. Chem. Soc. 90, 2656 (1968).

136. H.A. Clark, A.F. Gordon, C.W. Young, and M.J. Hunter, ibid., 73, 3798 (1951).

137. T.V. Molchanova, et. al., Tr. Inst. Khim., Akad Nauk SSSR, Ural. Filial 13, 17 (1966); Chem. Abstr. 68, 13069h (1968).

138. H. Gilman and O.L. Marrs, J. Org. Chem. 30, 1942 (1964).

139. F.M. Sonnenberg, J. Org. Chem. 35, 3166 (1970).

140. E.I. Snyder, J. Am. Chem. Soc. 85, 2624 (1963).

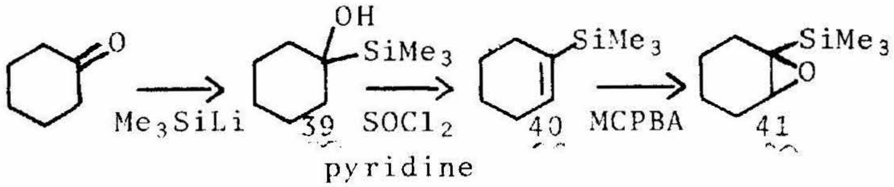
141. D.G. Anderson, M.A.M. Bradney, and D.E. Webster, J. Chem. Soc. B, 450 (1968).

142. C. Eaborn and J.A. Sperry, J. Chem. Soc., 4921 (1961).

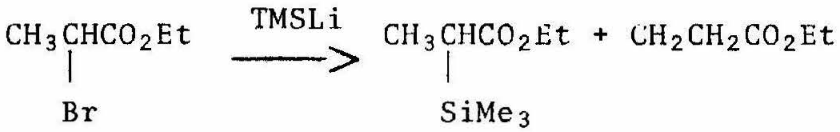
Appendix. Reaction of Alpha-halo Carbonyl Compounds with Trimethylsilyl Anions

In analogy with this work and that of Gilman,[36] trimethylsilyllithium should react with epoxides to give isolable β-hydroxysilanes without further elimination. These can then be treated with acid to promote anti-elimination,[42] or oxidized to β-ketosilanes, which are promising synthetic intermediates.[55]

Our attempts to prepare these same β-ketosilanes via the reaction of silyl anions in HMPT with α-chloroketones did not meet with success. We allowed 2-chlorocyclohexanone to react with trimethylsilyllithium and trimethylsilylpotassium under various conditions. In all cases dark mixtures comprised of several products were found. In particular, 1,2-epoxycyclohex-lyltrimethylsilane (41), which was independently synthesized by the route shown below, was shown to be absent from the product mixture. Preliminary experiments involving the reaction of ethyl 2-bromopropionate with trimethylsilyllithium were more promising, as the only two products re-



covered were the product of direct silylation, ethyl 2-trimethylsilylpropionate (42), and that of reduction, ethyl propionate.



$$\underset{\displaystyle\text{Br}}{CH_3\underset{|}{C}HCO_2Et} \xrightarrow{\text{TMSLi}} \underset{\displaystyle\text{SiMe}_3}{CH_3\underset{|}{C}HCO_2Et} + CH_2CH_2CO_2Et$$

ABSTRACTS OF PROPOSITIONS

Michael A. Shippey

1. A new synthetic approach to coumarins and annelated derivatives is outlined. This method should be particularly useful, both in terms of flexibility and efficiency, in the synthesis of psoralens, presently obtainable only with difficulty. Based on published mechanisms of photoactivation, rational approaches to new psoralen drugs are presented.

2. The preparation of stable derivatives of the theoretically interesting (but presently unknown) silaarenes is discussed.

3. A novel synthetic reagent is proposed as an "acyl anion equivalent" which can be converted to carbonyl compounds under a variety of conditions.

4. The study of simple means to achieve β-functionalization of organosilanes is suggested. Such methods could enable the transformation of organosilyl groups to a range of other functionality.

5. We propose to study the catalyzed metathesis of silicon-containing alkenes, from both synthetic and mechanistic viewpoints.