for the loss of stereospecificity in the product or racemization of the starting material, respectively.

Although the concerted mechanism of Scheme III is somewhat attractive, it is highly speculative, and must await further experimental tests. This type of three-centered mechanism involving *nucleophilic* attack by the metal at the carbon–halogen bond has been advocated, however, both for the oxidative addition of vinyl halides and aryl halides to the platinum group metals.

Alkene Synthesis via β-Functionalized Organosilicon Compounds

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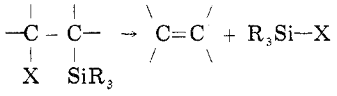
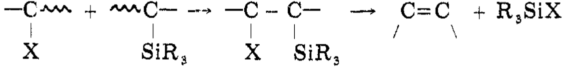
Reactions leading to the formation of carbon–carbon double bonds are of great importance to organic chemistry. Numerous named reactions (Hofmann, Saytzeff, Cope, Wittig, etc.) have been developed for that purpose. A new alkene synthesis, based on the propensity of β-functional alkylsilanes to undergo elimination,[1] has recently been introduced. In the late forties, a series of papers by Sommer, Whitmore, and their co-workers[2–5] established clearly that the general reaction with all these compounds is the formation of alkenes and the elimination of functionalized silyl compounds (reaction 1). Notwithstanding such important early observations and subsequent work on the β elimination of silicon compounds,[1] the recognition that reaction 1 can serve as a general method of alkene synthesis is a recent one. Much work in several laboratories, including our own, has demonstrated the usefulness of β-functionalized organosilicon compounds in alkene synthesis. This method, besides being generally competitive with other similar reactions such as the Wittig reaction, is particularly useful in the synthesis of heterosubstituted alkenes, α,β-unsaturated esters, aldehydes, and nitriles. The silicon method also enables the generation of strained alkenes such as allene oxides, cyclopropenes, and bridgehead alkenes which would have been difficult to prepare otherwise.



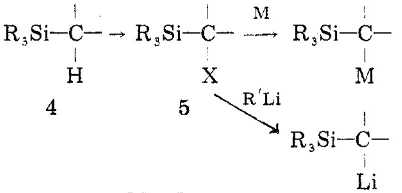
$$-\underset{X}{\overset{|}{C}}-\underset{SiR_3}{\overset{|}{C}}- \rightarrow \;\rangle C=C\langle\; + R_3Si{-}X \qquad (1)$$

The generality of the alkene synthesis can be expressed by eq 2. Simply stated, any formation of a carbon–carbon single bond which brings together the β relationship of the silyl group and the leaving group X can be considered as an alkene synthesis. The reactions which have been brought to bear to execute step a include the reaction of carbonyl compounds with α-silyl carbanions, carbene insertion into vinylsilanes, and the Diels–Alder reaction of vinylsilanes. So far, our experience has been that it is always possible to execute step b, even when the alkene to be generated is highly strained. There are, of course, problems still associated with this alkene synthesis, and these will be touched upon in the course of this Account.



$$-\underset{X}{\overset{|}{C}}\sim\sim + \sim\sim\underset{SiR_3}{\overset{|}{C}}- \xrightarrow{(a)} -\underset{X}{\overset{|}{C}}-\underset{SiR_3}{\overset{|}{C}}- \xrightarrow{(b)} \;\rangle C=C\langle\; + R_3SiX \qquad (2)$$

Scheme I



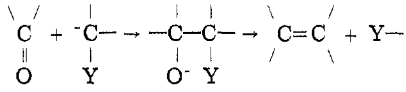
M = Li or Mg

$(CH_3)_3SiCH_2^-$ $(CH_3)_3Si\bar{C}{=}CH_2$

6 7

The Synthesis of Alkenes from Carbonyl Compounds and Carbanions α to Silicon

The most useful version of eq 2 involves the reaction of carbonyl compounds with carbanions α to silicon (eq 3, Y = SiR_3). This version bears obvious similarity to the Wittig reaction[6] (Y = PR_3^+) and its many modifications.[7] Indeed, in 1962, Gilman and Tomasi[8]



$$\underset{O}{\overset{\backslash\,/}{\underset{\|}{C}}} + {}^{-}\underset{Y}{\overset{|}{C}}- \rightarrow -\underset{O^-}{\overset{|}{C}}-\underset{Y}{\overset{|}{C}}- \rightarrow \;\rangle C=C\langle\; + Y{-}O^- \qquad (3)$$

T. H. Chan was born in China in 1941. He obtained his Ph.D. degree from Princeton University, with R. K. Hill, and then joined R. B. Woodward's research group as one of the 100 postdoctoral fellows who worked on the synthesis of vitamin B_{12}. He joined the faculty at McGill University, where he is associate professor of chemistry, in 1966. Dr. Chan's research interests concern the chemistry of organosilicon, phosphorus, and sulfur compounds and their application to organic synthesis; mechanistic studies; and the structural determination and chemical synthesis of natural products.

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(1) For review, see A. W. P. Jarvie, *Organometal. Chem. Rev., Sect. A*, 6, 153 (1970).

(2) L. H. Sommer and F. C. Whitmore, *J. Am. Chem. Soc.*, 68, 485 (1946).

(3) L. H. Sommer, D. L. Bailey, and F. C. Whitmore, *J. Am. Chem. Soc.*, 70, 2869 (1948).

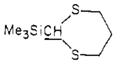
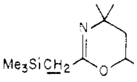
(4) L. H. Sommer, E. Dorfman, G. M. Goldberg, and F. C. Whitmore, *J. Am. Chem. Soc.*, 68, 488 (1946).

(5) L. H. Sommer, G. M. Goldberg, E. Dorfman, and F. C. Whitmore, *J. Am. Chem. Soc.*, 68, 1083 (1946).

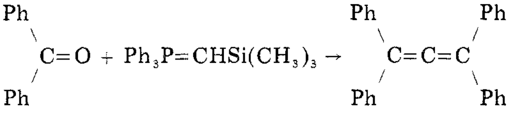
(6) G. Wittig and U. Schollkopf, *Ber.*, 87, 1318 (1954).

(7) For review, see S. Trippett, *Q. Rev., Chem. Soc.*, 17, 406 (1963).

Table I
Generation of α-Silyl Carbanions by Direct Metalation

Silicon compound	Base	Conditions	Ref
$Me_3Si\underline{CH}_2C_6H_5$	n-BuLi	TMEDA	9
$Me_3Si\underline{CH}_2C_6H_5$	n-BuLi	HMPA	15
$Me_3Si\underline{CH}_2SCH_3$	n-BuLi	THF	9
$Me_3Si\underline{CH}_2P(C_6H_5)_2$	n-BuLi	THF	9
$Me_3Si\underline{CH}_2P(S)(C_6H_5)_2$	n-BuLi	THF, 0 °C	9
$Me_3Si\underline{CH}_2CO_2C_2H_5$	$(C_6H_{11})_2NLi$	THF, −78 °C, 10 min	22
$Me_3Si\underline{CH}_2CO_2C(CH_3)_3$	$(i\text{-}Pr)_2NLi$	THF, −78 °C	23
$Me_2PhSi\underline{CH}(CH_3)CN$	$(i\text{-}Pr)_2NLi$	THF, −78 °C, 10 min	24
$Me_3Si\underline{CH}_2P(O)(OEt)_2$	n-BuLi	THF, 1.5 h	25
	n-BuLi	THF	26, 27, 28
$Me_3SiCH_2S(=O)Ph$	t-BuLi or n-BuLi	THF, −70 °C	29
$(Me_3Si)_3\underline{CH}$	MeLi	THF, reflux	30
$Me_3Si\underline{CH}(CH_3)CH=NC(CH_3)_3$	$(i\text{-}Pr)_2NLi$	THF, 0 °C	31
	n-BuLi	THF, −78 °C	62
$Me_3Si\underline{CH}_2C(=O)SR$	$(i\text{-}Pr)_2NLi$	THF, −78 °C	66

studied the reaction of trimethylsilylmethylenetriphenylphosphorane (**1**) with benzophenone (**2**) and



$$Ph_2C=O + Ph_3P=CHSi(CH_3)_3 \rightarrow Ph_2C=C=CPh_2$$

2 1 3

obtained tetraphenylallene (**3**) as the product. This may now be considered a special case of alkene synthesis via an α-silyl carbanion. In 1968, Peterson,[9] following his work on the study of α-silyl carbanions,[10] first proposed the alkene synthesis based on eq 3 ($Y = SiR_3$). At about the same time, we initiated our studies on the chemistry of silicon compounds, including extensive investigation of the olefination reaction using α-silyl carbanions.[11]

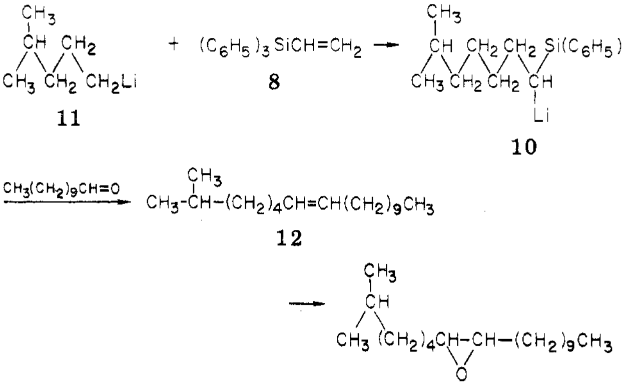
One of the easiest ways of preparing α-silyl carbanions is the reaction of α-halosilanes with magnesium[12,13] or lithium, or by halogen–metal exchange with alkyllithium.[14] The synthetic utility of this method is, however, limited by the availability of α-halosilanes, which are normally prepared by the halogenation of alkylsilanes[14] (Scheme I). The carbanions **6** and **7**, on the other hand, are quite useful because their precursor halides are readily available.[15,16]

An alternative method to generate α-silylalkyllithium compounds is by the addition of organolithium reagents to the double bond of triorganovinylsilanes[15,17,18] (eq 4).

$$RLi + R'_3SiCH=CH_2 \rightarrow R'_3SiCHLiCH_2R \qquad (4)$$

Both triphenylvinylsilane (**8**)[15] and trimethylvinylsilane (**9**)[19,20] have been used. It is easier to work with trimethylvinylsilane because in the product isolation step after olefination the hexamethyldisiloxane formed is readily removed by evaporation.

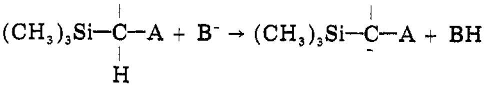
This method of generating α-silyl carbanions has certain advantages which are demonstrated in our synthesis of the sex pheromone of the Gypsy moth (disparlure, **13**)[15]. The carbanion **10**, readily generated



11 8 10 12 13

from triphenylvinylsilane and 4-methylpentyllithium (**11**), reacted with undecanal to give both geometric isomers of 2-methyl-7-octadecene (**12**, E:Z = 1:1) in one step. The synthesis of **12** by the Wittig reaction, on the other hand, required several steps to reach the corresponding phosphonium ylide.[21]

The most useful method of generating α-silylalkyllithium is by direct metalation of the parent compound; this is readily achieved when the alkyl group is further activated. In Table I (see ref 9, 15, 22–31) α-silyl



$$(CH_3)_3Si-\underset{H}{\overset{|}{\underset{|}{C}}}-A + B^- \rightarrow (CH_3)_3Si-\overset{|}{\underset{-}{C}}-A + BH$$

A = activating group, B = base

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

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

(10) D. J. Peterson, *J. Organometal. Chem.*, **8**, 199 (1967).

(11) T. H. Chan, E. Chang, and E. Vinokur, *Tetrahedron Lett.*, 1137 (1970).

(12) F. C. Whitmore and L. H. Sommer, *J. Am. Chem. Soc.*, **68**, 481 (1946).

(13) L. R. Hauser and C. R. Hance, *J. Am. Chem. Soc.*, **74**, 5091 (1952).

(14) A. G. Brook, J. M. Duff, and D. G. Anderson, *Can. J. Chem.*, **48**, 561 (1970).

(15) T. H. Chan and E. Chang, *J. Org. Chem.*, **39**, 3264 (1974).

(16) T. H. Chan and W. Mychajlowskij, *Tetrahedron Lett.*, 171 (1974).

(17) L. F. Cason and H. G. Brooks, *J. Org. Chem.*, **19**, 1278 (1954).

(18) L. F. Cason and H. G. Brooks, *J. Am. Chem. Soc.*, **74**, 4582 (1952).

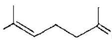
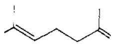
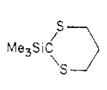
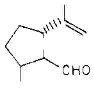
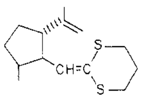
(19) P. F. Hudrlik and D. Peterson, *Tetrahedron Lett.*, 1133 (1974).

(20) T. H. Chan and N. Dawes, unpublished results.

(21) B. A. Bierl, M. Beroza, and C. W. Collier, *Science*, **170**, 87 (1970).

(22) K. Shimoji, H. Taguchi, K. Oshima, H. Yamamoto, and H. Nozaki, *J. Am. Chem. Soc.*, **96**, 1620 (1974).

Table II
Olefination of Carbonyl Compounds with α-Silyl Carbanions

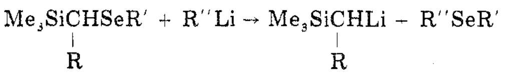
Carbanion	Carbonyl compound	Olefin (*E*/*Z*)	Yield, %[a]	Ref
Me_3SiCH_2			57	15
$Ph_3SiCH(CH_2)_4CH(CH_3)_2$	$CH_3(CH_2)_9CHO$	$(CH_3)_2CH(CH_2)_4CH{=}C_{10}H_{21}$ (1:1)	50	15
$Me_3SiCHCO_2Et$	$CH_3(CH_2)_7CHO$	$CH_3(CH_2)_7CH{=}CHCO_2Et$ (1:1)	81	22
$Me_3SiCHCO_2C(CH_3)_3$	C_6H_5CHO	$C_6H_5CH{=}CHCO_2C(CH_3)_3$[b]	75	23
$(CH_3)_2C_6H_5SiC(CH_3)CN$	$PhCOCH_3$	$PhCH_3C{=}C(CH_3)CN$ (ca. 1:1)	98[c]	24
$(Me_3Si)_2CH$	*t*-BuPhC=O	*t*-BuPhC=$CHSiMe_3$[d]	29	32
$Me_3SiCHP(O)(OEt)_2$	$(CH_3)_2CHCHO$	$(CH_3)_2CHCH{=}CHPO(OEt)_2$ (1:2:4)	92	25
			89	*e*
$Me_3SiCHS({=}O)Ph$	PhCHO	$PhCH{=}CHS({=}O)Ph$ (1:1)	87	29
$Me_3SiC(CH_3)CH{=}NC(CH_3)_3$	PhCHO	$PhCH{=}C(CH_3)CHO$ (1:1)	90	31

[a] Isolated yield unless otherwise stated. [b] No indication of isomer ratio. [c] GLC yields. [d] Only one isomer was obtained, Z. [e] N. H. Anderson, Y. Yamamoto, and A. D. Denniston, *Tetrahedron Lett.*, 4547 (1975).

carbanions obtained by direct metalation are listed. The variation in structures of the carbanions gives an indication of the synthetic utility of the olefination reaction.

Finally, cleavage of either the carbon–silicon bond in

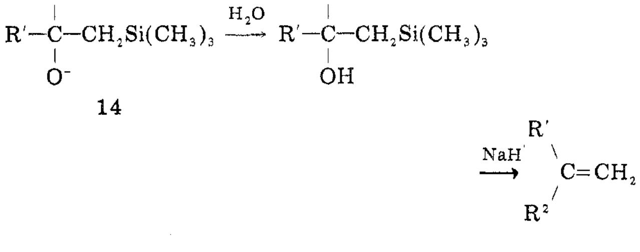
$$(\mathrm{Me_3Si})_n\mathrm{CH}_{4-n} + \mathrm{CH_3O^-} \rightarrow (\mathrm{Me_3Si})_{n-1}\bar{\mathrm{C}}\mathrm{H}_{4-n} + \mathrm{Me_3SiOCH_3}$$



$$\mathrm{Me_3Si}\underset{\displaystyle\mathrm{R}}{\mathrm{CH}}\mathrm{SeR'} + \mathrm{R''Li} \rightarrow \mathrm{Me_3Si}\underset{\displaystyle\mathrm{R}}{\mathrm{CH}}\mathrm{Li} - \mathrm{R''SeR'}$$

polysilylmethanes by methoxide or the carbon–selenium bond of α-silylalkyl selenides by alkyllithium can lead to α-silyl carbanions.[32]

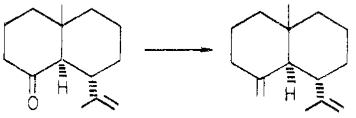
Both aldehydes and ketones react with α-silyl carbanions to give the adducts, which in most cases eliminate spontaneously to the olefins (eq 3). Some representative examples are given in Table II, together with the yields of the alkenes obtained. Several features of this olefination reaction are worthy of note. In the methylenation of carbonyl compounds with trimethylsilylmethyllithium, the adduct, β-oxyalkylsilane 14, does not eliminate under the reaction conditions.



$$\mathrm{R'}\!-\!\underset{\displaystyle\mathrm{O^-}}{\overset{\displaystyle\mathrm{R^2}}{\mathrm{C}}}\!-\!\mathrm{CH_2Si(CH_3)_3} \xrightarrow{\mathrm{H_2O}} \mathrm{R'}\!-\!\underset{\displaystyle\mathrm{OH}}{\overset{\displaystyle\mathrm{R^2}}{\mathrm{C}}}\!-\!\mathrm{CH_2Si(CH_3)_3} \xrightarrow{\mathrm{NaH}} \begin{matrix}\mathrm{R'}\\ \quad\backslash \\ \quad\mathrm{C{=}CH_2} \\ \quad/ \\ \mathrm{R^2}\end{matrix}$$

14

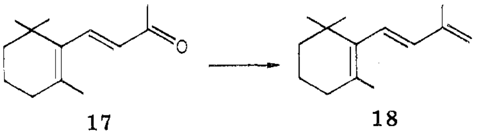
After being worked up, the β-silylcarbinol can be obtained in good yield. Peterson has achieved the conversion of 14 to alkene by refluxing the sodium salt of 14 in tetrahydrofuran.[9] Other satisfactory solutions to this problem are now available,[15,33] and the terminal alkene can in general be formed in good yield without contamination of the other double-bond isomer. This method of methylenation appears to be superior to the Wittig reaction in certain situations. In the synthesis of the sesquiterpene, β-gorgonene (**15**), it was found that **16** was unreactive upon treatment with $CH_2{=}PPh_3$.



16 **15**

However, treatment of **16** with $(CH_3)_3SiCH_2MgCl$ eventually led to the olefin **15**.[33]

The olefination reaction is particularly useful for the preparation of various heterosubstituted alkenes; vinyl sulfides,[9] vinyl phosphonates,[25] ketene thioacetals,[26-28] and vinylsilanes[30] can be prepared by this method. The olefination reaction has been applied to the synthesis of α,β-unsaturated esters,[22] nitriles,[24] and aldimines[31] (and thence aldehydes). The role of the silyl group, which stabilizes the carbanion sufficiently to suppress many of the side reactions due to condensation, is crucial in these cases. Yet the silyl group does not deactivate the carbanion to the extent that the addition of the carbanion to the carbonyl compound is diminished. This method of olefination is applicable to the conversion of α,β-unsaturated carbonyl compounds to the corresponding dienes. For example, β-ionone (**17**)



17 **18**

has been converted in reasonable yield to the methylene derivative **18**.[15]

When the alkene to be synthesized can display geometric isomerism, the product obtained has usually been found to be a mixture of *E* and *Z* isomers in nearly equal proportions (Table II). This lack of stereose-

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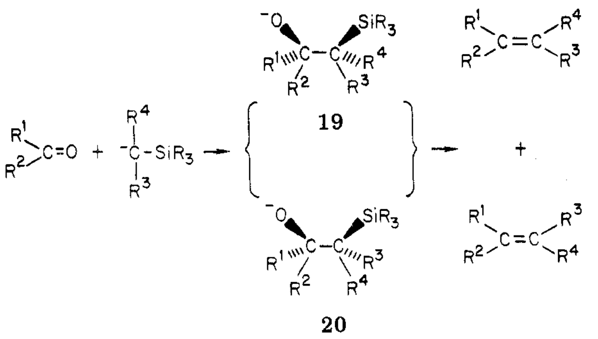
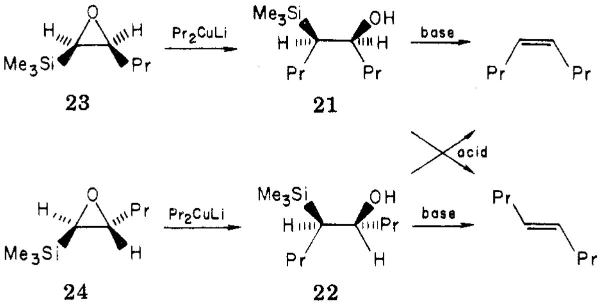
(23) S. L. Hartzell, D. F. Sullivan, and M. W. Rathke, *Tetrahedron Lett.*, 1403 (1974).
(24) I. Ojima and M. Kumegai, *Tetrahedron Lett.*, 4005 (1974).
(25) F. A. Carey and A. S. Court, *J. Org. Chem.*, 37, 939 (1972).
(26) F. A. Carey and A. S. Court, *J. Org. Chem.*, 37, 1926 (1972).
(27) D. Seebach, M. Kolb, and B.-Th. Gröbel, *Chem. Ber.*, 106, 2277 (1973).
(28) P. F. Jones and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, 526 (1972).
(29) F. A. Carey and O. Hernandez, *J. Org. Chem.*, 38, 2670 (1973).
(30) M. A. Cook, C. Eaborn, A. E. Jukes, and D. R. M. Walton, *J. Organometal. Chem.*, 24, 529 (1970).
(31) E. J. Corey, D. Enders, and M. G. Bock, *Tetrahedron Lett.*, 7 (1976).
(32) (a) H. Sakurai, K. Nishiwaki, and M. Kira, *Tetrahedron Lett.*, 4193 (1973); (b) W. Dumont and A. Krief, *Angew. Chem.*, 88, 184 (1976).
(33) R. K. Boeckman and S. M. Silver, *Tetrahedron Lett.*, 3497 (1973).

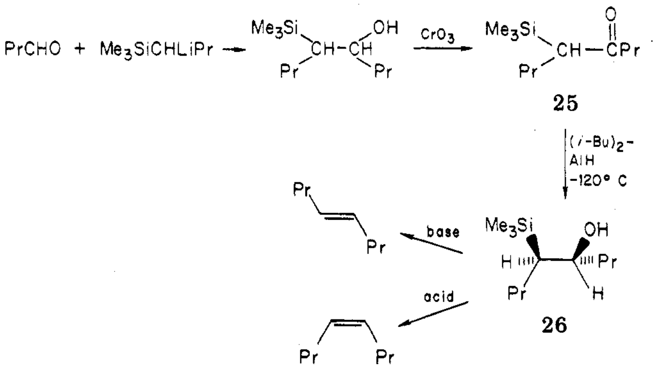
Scheme II



Scheme III



Scheme IV



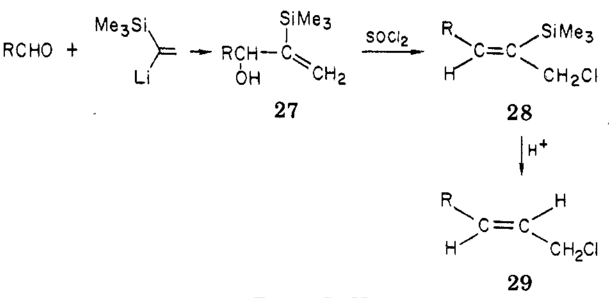
lectivity, in contrast to the Wittig reaction, where preference for the formation of one isomer can often be induced, diminishes the synthetic utility of the reaction.[34]

An explanation for this nonstereoselectivity is offered in Scheme II. In the addition of the α-silyl carbanion to the carbonyl compound, the reaction is believed to be irreversible, giving nearly equal amounts of the diastereomeric adducts **19** and **20**. Each diastereomer can eliminate stereospecifically to give only one isomer of the alkene.

An ingenious demonstration of the stereospecific nature of the adduct to alkene elimination was provided by Hudrlik, Peterson, and Rona (Scheme III).[35] Isomers **21** and **22** were generated independently by the reaction of lithium di-n-propylcuprate with the isomeric silyloxiranes **23** and **24**. Depending on the conditions of elimination, either (E)- or (Z)-4-octene could be obtained nearly to the exclusion of the other.

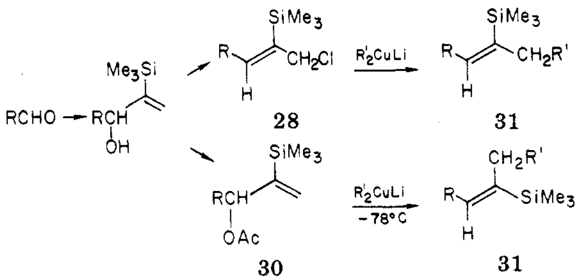
A solution to the stereoselective generation of disubstituted alkenes by the silicon method is thus

Scheme V



a, R = n-C$_{10}$H$_{21}$
b, R = c-C$_6$H$_{11}$
c, R = i-Pr
d, R = Ph

Scheme VI



possible. This has been demonstrated with 4-octene.[19,36] α-Trimethylsilylbutyllithium reacted with butanal to give the mixture of diastereomeric adducts which were oxidized to the β-ketosilane **25**. The β-ketosilane was then reduced stereoselectively back to only one diasteromer of the β-hydroxysilane **26**, which eliminated to give either isomer of 4-octene, depending on the reaction conditions (Scheme IV). A similar approach has been used for the stereoselective synthesis of trisubstituted alkenes. Stereospecific β elimination of diastereomerically pure β-oxysilane is also the basis of an interesting method of stereochemical inversion of olefins.

Our solution to the stereoselectivity problem takes a different approach. It was observed that compound **27**, obtained by the reaction of aldehydes with α-trimethylsilylvinyllithium, was converted stereoselectively on reaction with thionyl chloride to the chloride **28**. While the conversion of **27** to **28** can be understood in terms of the familiar allylic rearrangement, the presence of the silyl group appears to exert considerable influence on the stereochemistry of the process by giving predominantly the Z isomer. Since the silyl group of a vinylsilane can be replaced stereospecifically by a proton,[37,38] the sequence of reactions outlined in Scheme V constitute a method of stereoselectively transforming RCHO into (E)-RCH=CHCH$_2$Cl (**29**).[39] The presence of a reactive chloride in the resulting alkene is often desirable since it allows further elaboration into other functionalities.

A general method for the stereoselective conversion of aldehydes into di- and trisubstituted alkenes has been developed on the basis of a similar allylic rearrangement. Organocopper reagents, on reaction with

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(34) The lack of stereoselectivity may be desirable in certain limited cases: for example, see R. J. Anderson and C. A. Henrick, *J. Am. Chem. Soc.*, **97**, 4327 (1975).

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

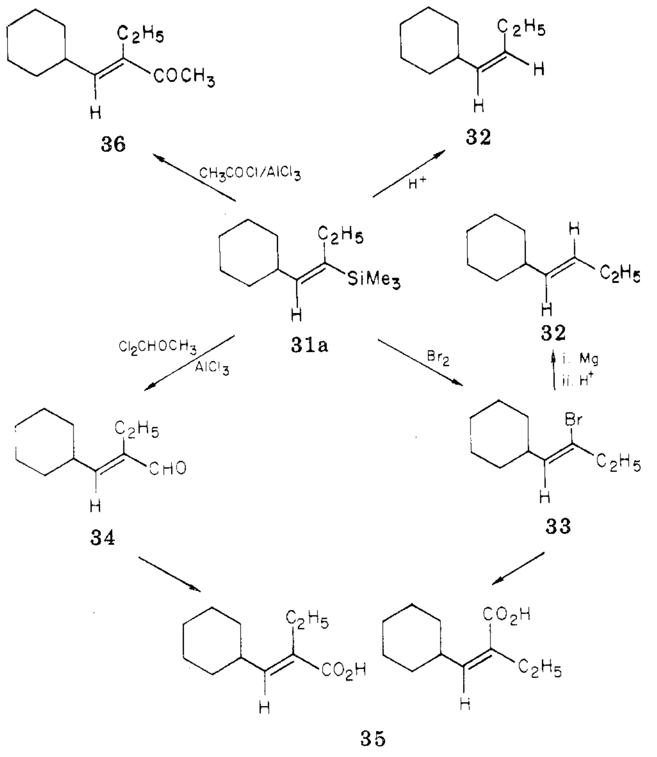
(36) P. F. Hudrlik and D. Peterson, *J. Am. Chem. Soc.*, **97**, 1464 (1975).

(37) K. E. Koenig and W. P. Weber, *J. Am. Chem. Soc.*, **95**, 3416 (1973).

(38) K. Utimoto, M. Katai, and H. Nozaki, *Tetrahedron Lett.*, 2825 (1975).

(39) T. H. Chan, W. Mychajlowskij, B. S. Ong, and D. N. Harpp, *J. Organometal. Chem.*, **107**, C1–C4 (1976).

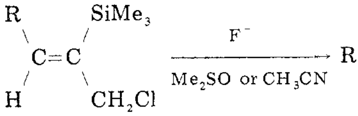
Scheme VII



the allylic acetate **30** at −78 °C, give stereoselectively the *E* isomers of substituted vinylsilane **31** (*E*:*Z* ~ 90:10) (Scheme VI).[40] On the other hand, the same lithium organocuprates, on reaction with (*Z*)-**28** at room temperature, give the *Z* isomers of substituted vinylsilanes **31** (*E*:*Z* ~ 10:90) by direct displacement (Scheme VI).

With the availability of both stereoisomeric vinylsilanes and the fact that the trimethylsilyl group in vinylsilanes can be replaced stereospecifically by a variety of electrophiles under electrophilic conditions,[38-42] we have at hand a convenient method for the stereoselective preparation of di- and trisubstituted alkenes. The following transformations with (*E*)-**31a** suffice as illustration (Scheme VII).[42c] Compound (*E*)-**31a** was converted to (*Z*)-**32** by acid. On the other hand, bromination of (*E*)-**31a** led to the *Z* isomer of vinyl bromide **33**. The inversion of stereochemistry in this reaction is likely due to a stereospecific trans addition of halogen to the double bond, followed by a trans elimination of trimethylbromosilane.[42] The stereochemistry of the vinyl bromide was shown by conversion to (*E*)-**32** via the vinylmagnesium bromide, a reaction known to proceed with retention of configuration. Friedel–Crafts reaction of (*E*)-**31a** with dichloromethyl methyl ether and aluminum chloride gave the aldehyde (*E*)-**34**. The stereochemistry of **34** was proven by oxidation to the corresponding acid, (*E*)-**35**, which is isomeric to the acid (*Z*)-**35** obtained by carbonation of the magnesium halide of (*Z*)-**33**. Similar Friedel–Crafts reaction of (*E*)-**31a** with acetyl chloride has led to the α,β-unsaturated ketone, (*E*)-**36**, of fixed stereochemistry.[42c] We have also prepared the sex pheromone of Gypsy moth (**13**) by this approach in 65% overall yield (from undecanal) with high stereoselectivity (*E*:*Z* = 13:87).[40]

The syntheses of allenes and allene oxides merit special discussion because they illustrate several features of the silicon method. α-Triphenyl- or trimethylsilylvinyllithium reacted with carbonyl compounds to give the alcohols **27** in good yield; efforts to convert **27** into allenes by β elimination under a variety of conditions proved to be futile. The exceptional resistance of **27** to β elimination is in dramatic contrast to the ease of elimination normally associated with other β-functionalized alkylsilanes. This difficulty, while frustrating at the time, has led to interesting dividends. The first was the recognition that **27** and its derivatives would undergo reactions expected of an allylic system. Some of our work described above is the outcome of such a realization. The second was that, when the solution finally came, it provided us with a mild and selective method of generating carbon–carbon double bonds. The solution is to take advantage of the known affinity of fluoride ion for silicon. The silicon–fluorine bond has the highest single-bond energy among elements. Thus, when the chloride **28** or the trifluoroacetate of **27** was treated with fluoride ion, the

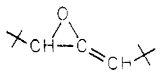


$$\mathrm{R(H)C{=}C(SiMe_3)(CH_2Cl)} \xrightarrow[\mathrm{Me_2SO\ or\ CH_3CN}]{\mathrm{F^-}} \mathrm{RCH{=}C{=}CH_2}$$

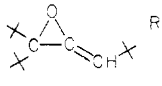
28 **37**

allene **37** was obtained in essentially quantitative yield.[16] The advantage of the present synthesis is that the product is devoid of contamination by isomeric alkynes which often occur in other methods of allene synthesis under strongly basic conditions.

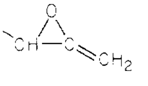
The synthesis of allene oxides is another good example to demonstrate the usefulness of the fluoride ion promoted β dehalosilylation. Allene oxides have been postulated as intermediates in the reaction of allenes with peracid[43] or with atomic oxygen.[44] Isolation of the allene oxides, except for the highly hindered ones such as **38**[45] and **39**,[46,47] has proved to be difficult however,



38



39



43

because of the ease with which the epoxide structure is opened under acidic conditions during peracid oxidation. The mode of preparation for the allene oxides has also precluded their use as useful synthetic intermediates. This is unfortunate because allene oxides possess unusual reactivities and are expected to undergo some interesting cycloaddition reactions (vide infra).

We have been able to prepare, isolate, and characterize a monosubstituted allene oxide (**40**) by the silicon method.[48,49] Epoxidation of **41** (as a mixture of *E* and

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[40] W. Mychajlowskij and T. H. Chan, *Tetrahedron Lett.*, 4439 (1976).

[41] I. Fleming and A. Pearce, *J. Chem. Soc., Chem. Commun.*, 633 (1975).

[42] (a) R. B. Miller and T. Reichenbach, *Tetrahedron Lett.*, 543 (1974); (b) A. G. Brook, J. M. Duff, and W. F. Reynolds, *J. Organomet. Chem.*, 121 293 (1976); (c) T. H. Chan, P. W. K. Lau, and W. Mychajlowskij, to be published.

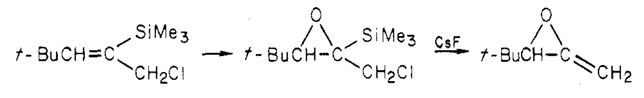
[43] J. K. Crandall, W. H. Macleden, and S. A. Sojka, *J. Org. Chem.*, **38**, 1149 (1973), and references therein.

[44] J. J. Havel, *J. Am. Chem. Soc.*, **95**, 530 (1973).

[45] R. L. Camp and F. D. Greene, *J. Am. Chem. Soc.*, **90**, 7349 (1968).

[46] J. K. Crandall and W. H. Macleder, *J. Heterocycl. Chem.*, **6**, 777 (1969).

[47] The generation of tetramethylallene oxide was claimed and later retracted. See H. M. R. Hoffman and R. H. Simthers, *Angew. Chem., Int. Ed. Engl.*, **9**, 71 (1970), and H. M. R. Hoffman, K. E. Clemens, E. A. Schmidt, and R. H. Smithers, *J. Am. Chem. Soc.*, **94**, 3201 (1972).



41 42 40

Z isomers) gave **42** as a distillable liquid. Reaction of **42** with cesium fluoride in triglyme generated **40**, which was transferred by passing nitrogen gas into a cold trap and characterized by standard spectroscopic means. Other allene oxides (**43**) have been similarly generated in situ and characterized by reaction with various nucleophiles and dienes.[50] A proper discussion of the chemistry of allene oxides is obviously beyond the scope of this review. Suffice it to say that by the silicon route allene oxides can indeed be prepared and used in a synthetically meaningful way for the construction of various cyclic structures (Scheme VIII).[49,50]

The Synthesis of Cyclopropenes from Carbene Addition to Vinylsilane

As we have mentioned in the introduction, any union of two fragments which brings together the β relationship of the silyl group and a good leaving group can be considered as an alkene synthesis. Addition of dihalocarbenes to vinylsilanes fulfills such a requirement.[51,52] The possibility that cyclopropanes such as **44** can serve as the precursors to cyclopropenes has not escaped the notice of other people.[52,53] Indeed, in 1968, Seyferth et al.[53] attempted the dehalosilylation of **45** with sodium ethoxide but obtained a product with acetylenic properties. Cyclopropene formation was postulated as the first step (Scheme IX).

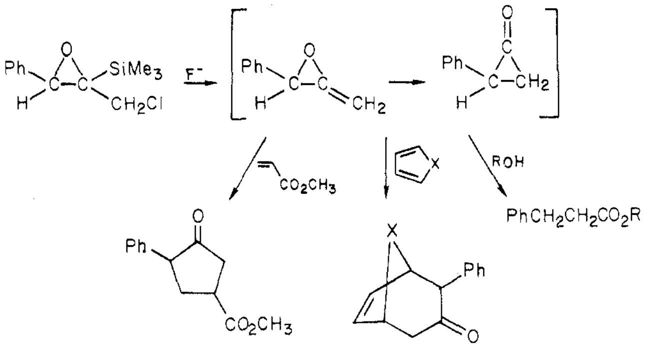
We have been able to achieve the synthesis and isolation of 1-chloro- and 1-bromocyclopropene by fluoride ion dehalosilylation from the appropriate precursors (Scheme X).[54] We have also used the fluoride ion promoted dehalosilylation to prepare a number of bicyclo[*n*.1.0]-(*n* + 3)-alk-(*n* + 3)-enes (**46**, *n* = 4 to 6). In all cases, the highly strained cyclopropenes have been trapped as the Diels–Alder adducts of 1,3-diphenylisobenzofuran (Scheme XI).[54-56]

The compounds **46** are of some interest of late. Because of their bicyclic structure, compounds **46** can be considered as *trans*-cycloalkenes with *n* + 3 carbons. Recently, it has been argued that these compounds can be used as a basis for statements regarding the range of validity of Bredt's rule.[57]

Generation of an Anti-Bredt Alkene

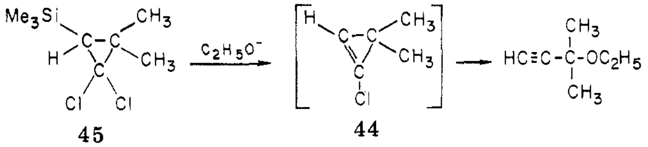
The study of bicyclic bridgehead alkenes which violate Bredt's rule has been a topic of much current interest.[58-61] A fundamental question in the study of these compounds is the nature of the double bond.

Scheme VIII



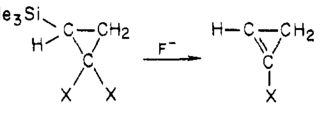
X = O, CH_2, or NCO_2CH_3

Scheme IX



45 44

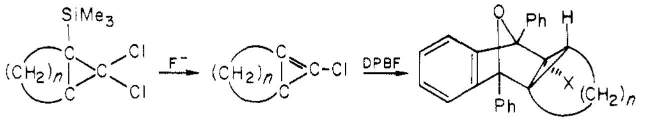
Scheme X



44

X = Cl or Br

Scheme XI



46

n = 4, 5, 6

We have prepared the bicyclo[2.2.2] compound **47** by the Diels–Alder reaction of 9,10-dibromoanthracene (**48**) with trimethylvinylsilane. The Diels–Alder reaction is, of course, one mode of carbon–carbon bond formation which can bring about the requisite β relationship of the silyl group and the leaving group represented in eq 2.

We have attempted the fluoride ion promoted elimination reaction on compound **47** under a variety of conditions, and, in all cases, debromosilylation occurred. From the products (**49–52**) formed (Scheme XII) there is little doubt that a carbene species (**53**) must have intervened. The carbene intermediate could have arisen from the rearrangement of the expected bridgehead alkene (**54**). Evidence for the formation of **54** has been adduced by trapping it with a 1,3-dipolar compound **55** to give the cycloadduct **56**. To account for the orientation of the 1,3-dipolar cycloaddition, as well as the rearrangement to carbene, it seems that the double bond in **54** must possess some polar character (Scheme XII).[61]

A full discussion of the implication of these results is not possible here.[61] What the reaction does illustrate

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(48) T. H. Chan, B. S. Ong, and W. Mychajlowskij, *Tetrahedron Lett.*, 3253 (1976).

(49) T. H. Chan, M. P. Li, W. Mychajlowskij, and D. N. Harpp, *Tetrahedron Lett.*, 3511 (1974).

(50) B. S. Ong and T. H. Chan, *Tetrahedron Lett.*, 3257 (1976).

(51) D. Seyferth, J. M. Burlitch, R. J. Minasz, J. Y. Min, H. D. Simmons, A. J. H. Treiber, and S. R. Dowd, *J. Am. Chem. Soc.*, 87, 4259 (1965).

(52) R. B. Miller, *Synth. Commun.*, 4, 341 (1974).

(53) D. Seyferth and T. F. Jula, *J. Organometal. Chem.*, 14, 109 (1968).

(54) T. H. Chan and D. Massuda, *Tetrahedron Lett.*, 3383 (1975).

(55) D. Massuda, Ph.D. Thesis, McGill University, 1977.

(56) Generation of the same bicyclic alkenes by alkoxide promoted dehydrohalogenation has been reported. See C. L. Osborn, T. C. Shields, B. A. Shoulders, J. F. Krause, H. V. Cortez, and P. D. Gardner, *J. Am. Chem. Soc.*, 87, 3158 (1965), and T. C. Shields and P. D. Gardner, *ibid.*, 89, 5425 (1967).

(57) G. Kobrich, *Angew. Chem., Int. Ed. Engl.*, 12, 464 (1973).

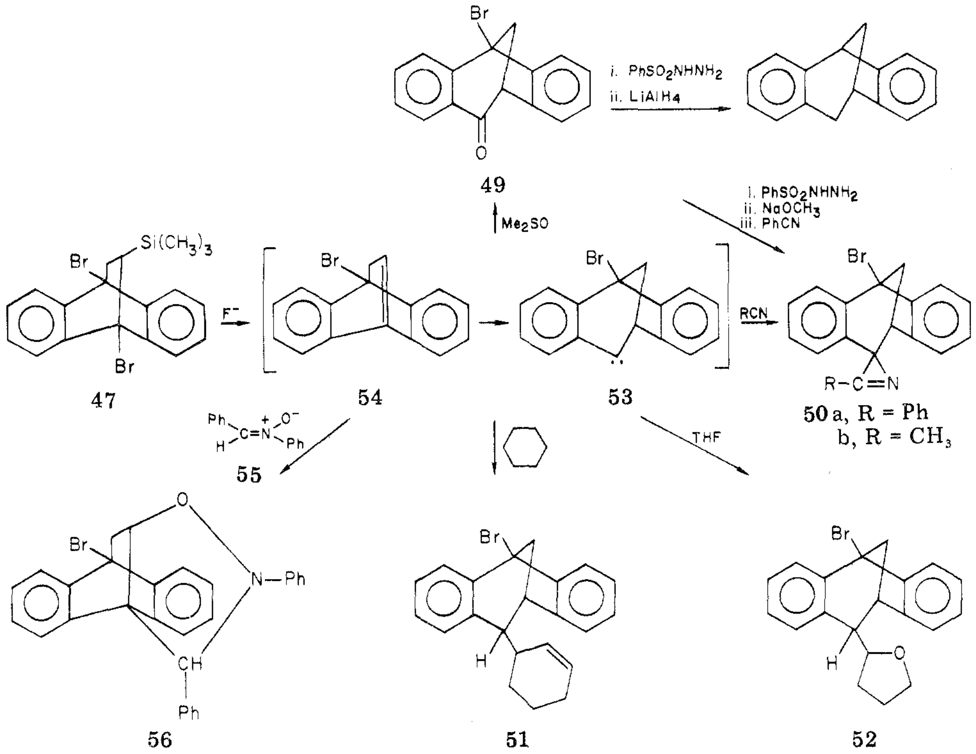
(58) G. L. Buchanan, *Chem. Soc. Rev.*, 3, 41 (1974).

(59) R. Keese, *Angew. Chem., Int. Ed. Engl.*, 14, 528 (1975).

(60) R. Keese and E.-P. Krebs, *Angew. Chem.*, 84, 540 (1972).

(61) T. H. Chan and D. Massuda, *J. Am. Chem. Soc.*, 99, 936 (1977).

Scheme XII



is that, by virtue of a different method of generating the bridgehead alkene, a new chemical pathway for these strained alkenes appears to have been revealed. This is only possible because fluoride ion itself, and the other product, trimethylfluorosilane, are unreactive toward the alkene **54**.

Conclusion

Examples cited in this Account have demonstrated convincingly that the silicon method is a useful alkene synthesis which complements in many ways other alkene syntheses. It is particularly attractive as a method to generate highly reactive alkenes. Further applications of the silicon route will undoubtedly be developed.[65]

The hard work of my graduate students, M. P. Li, W. Mychajlowskij, B. S. Ong, D. Massuda, E. Chang, and P. W. K. Lau, has made this work possible. Their dedication, even in time of diminishing encouragement about research from society, is an inspiration to me. Financial support from the National Research Council of Canada, Ministère de l'éducation, Gouvernement du Québec, and the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

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(62) K. Sachdev, *Tetrahedron Lett.*, 4041 (1976).

(63) K. Utimoto, M. Obayashi, and H. Nozaki, *J. Org. Chem.*, 41, 2941 (1976).

(64) P. B. Devan and M. A. Shippey, *J. Am. Chem. Soc.*, 98, 1265 (1976).

(65) For the important work by Cunico and his co-workers on the generation of alkynes by the elimination of β-halosilanes, see R. F. Cunico and E. M. Dexheimer, *J. Am. Chem. Soc.*, 94, 2868 (1972), and R. F. Cunico, *J. Organometal. Chem.*, 59, 153 (1973).

(66) D. H. Lucast and J. Wemple, *Tetrahedron Lett.*, 1103 (1977).