Ene and Retro-Ene Reactions in Group 14 Organometallic Chemistry

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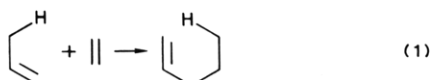
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Jacques Dubac was born in 1938 in Grenade-sur-Garonne, France. He received the diploma Licence ès Sciences Physiques from Université Paul-Sabatier in Toulouse, and the Doctorat d'Etat de Sciences Physiques (in 1969) from the same university under the direction of Professor Michel Lesbre and Dr. Pierre Mazerolles. His doctoral work involved the synthesis and reactivity of germacycloalcanes, particularly the germacyclobutanes. He became Professor at Université Paul-Sabatier in 1980. Dr. Dubac's principal research interest are the synthesis of main-group organometallics, especially silicon and germanium heterocyclics. His hobbies are cycling in the Pyrénées and the preparation of culinary delights based upon Gascogne duck.
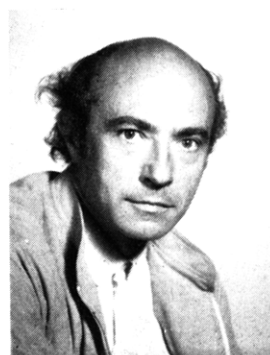
André Laporterie was born in 1944 in Caussade – Rivière, Hautes-Pyrénées, France. He obtained his Licence ès Sciences Physiques at Université Paul-Sabatier in 1965. In 1968, upon completion of research work on the synthesis of silyl and germylketenes in the laboratory of Professor M. Lesbre and under the supervision of Dr. P. Mazerolles, he obtained the Doctorat de 3eme Cycle. The same year, he joined Dr. J. Dubac's group, working on cycloaddition reaction of alkenyl derivatives of silicon and germanium, which led to the first ene syntheses in group 14 organometallic chemistry, and he obtained the Doctorat d'Etat degree in 1976. Subsequently, after studying the photooxygenation of group 14 allylic compounds, he prepared the first C-unsubstituted silole and germole. He is now Maître de Conférences in organic chemistry at Université Paul-Sabatier.

I. Introduction

The ene reaction, defined by Alder[1] as being an indirect substitutive addition, is the reaction of an olefin containing an allylic hydrogen (the ene) with a compound having a multiple bond (the enophile).
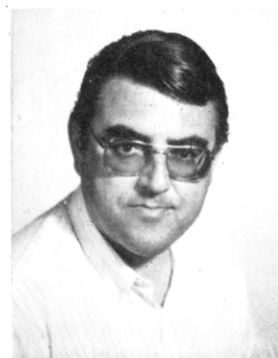
$$\text{(1)}$$

This reaction resembles other cycloadditions with a six-electron transfer such as the Diels–Alder reaction and the sigmatropic 1,5-migration of hydrogen:

$$\text{(2)}$$

The general synthetic and mechanistic aspects of the ene reaction of organic compounds have already been described.[2-5] Enophiles are π-bonded molecules, all having the characteristic of a low energy lowest unoccupied molecular orbital (LUMO).

Oppolzer and Snieckus[4a] classify the intramolecular ene reaction into three types (However, there are in principle six possibilities of intramolecular ene reactions,[4b] since the bridge can be attached at either of two positions X and Y on the enophile as well as at the three positions a, b, and c of the ene unit.) according to whether the atom X (eq 3) of the enophile group is bonded to the ene part of the molecule as at a (type I), at b (Type II), or at c (Type III). In this respect, the 1,5-migration of the hydrogen (eq 2) is an intramolec-

$$(3)$$

XY: $>C=C<$; $>C=O$; $>C=S$; $O=O$ ($^1O_2$); $-N=O$; $-N=N-$; $OS=N-$; $-C\equiv C-(C_6H_4)$.
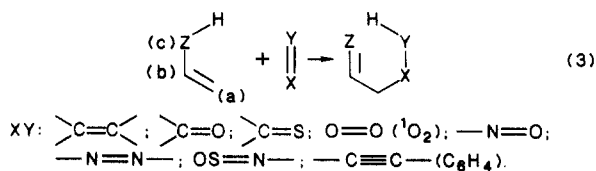
ular ene reaction of type I.

The prototropic migration of an allylic hydrogen provoked by a "σ enophile" has been far less studied than the traditional ene reaction ("π enophile"); it is known with chlorine oxide or *tert*-butyl hypochlorite, as in ene chlorination of olefins.[6-9]

The first applications of the ene reaction to organometallic chemistry were described as early as 1974.[10-13] They show the high reactivity of ethylenic derivatives (allylic and vinylic), both cyclic and noncyclic, of silicon and germanium toward electrophiles containing a C=C, N=N, C=O, or C≡C bond, and the possibility of a few of these having an enophile activity.

II. Group 14 Organometallic Enes

A. Allylsilanes and Allylgermanes

Maleic anhydride (MA) reacts with allyltrimethylsilane or -germane at 200 °C. Being better enophiles, ethyl azodicarboxylate (EAD) and especially 4-phenyl(or methyl)-1,2,4-triazoline-3,5-dione (PTD, MTD) react at 100 °C and room temperature, respectively (eq 4; Table I, entries 1-4, 73-77).[10,14]

$$(4)$$

M = Si, Ge
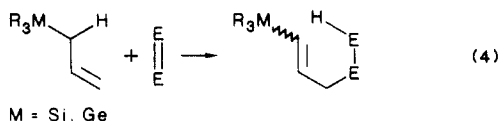
The interaction of allylsilanes with perhalogeno ketones in the absence of catalysts gives alcohols of the general type $R_3SiCH=CHCH_2C(CX_3)_2OH$ according to an ene reaction process (eq 5; Table I, entries 5, 6, 14,

$$(5)$$
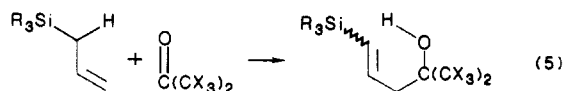
17, 25–33), but in the presence of aluminum chloride, significant yields of β-alkenyloxysilanes are also formed (cf. section IV.A).[15]

With allylsilanes having two reaction sites (e.g., methyl groups on the C=C bond), we have studied the regioselectivity of the ene reaction, and particularly the photooxygenation (eq 4, $E_2 = {}^1O_2$)[16] (Table I, entries 7-9, 11-21). The hydroperoxidation of allylsilanes by singlet oxygen proved to be an excellent means of functionalization of these compounds which give, after reduction, silicon-containing allylic alcohols (eq 6; cf. sections II.B, D, and E).

$$(6)$$

(R^1, R^2, R^3 = H or Me)
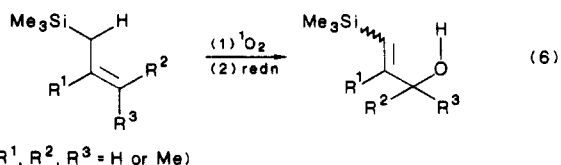
The formation of one of the products of the catalytic acetylation of prenyltrimethylsilane can be explained by an ene reaction mechanism (Table I, entry 10).[17]

B. Vinylsilanes

Ethylenic derivatives in which the double bond is in a vinylic position with respect to the silicon give the ene reaction (eq 7).[10]

$$(7)$$
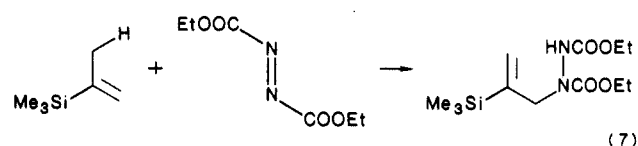
With singlet oxygen and sequential sodium borohydride reduction, 2-trimethylsilyl alcohols are produced in which the α position of the parent ketone has been regiospecifically oxygenated[18,19] (eq 8; Table I,

$$(8)$$
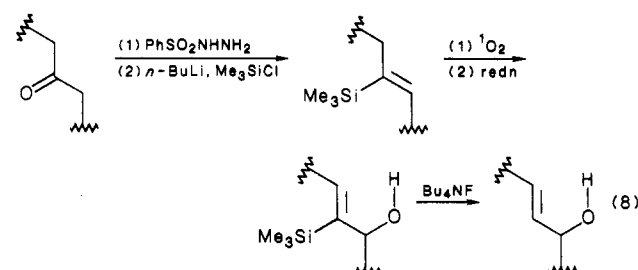
entries 39–44). Fluoride ion promoted desilylation (i.e., cleavage of the silicon–vinyl carbon bond) completes the conversion to the migrated allylic alcohol.[19]

As in the case of the prenyltrimethylsilane, the catalytic acetylation reaction of a vinylsilane involves an ene reaction mechanism (Table I, entry 45)[17] in part.

C. Allenylsilanes

Allenylsilanes are completely different from normal allenes in which the reaction occurs on an allylic hydrogen:[20] the trimethylsilyl group causes a reaction at the allenic hydrogen α to the silicon (eq 9; Table I, entries 46–49).[13]

$$(9)$$
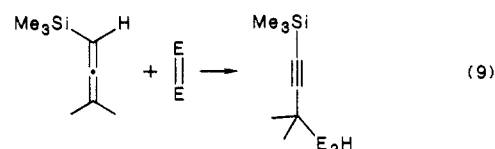
D. Silacycloalkenes and Germacycloalkenes (Table I, Entries 50–69, 78–87)

With group 14 noncyclic allylic derivatives, the ene reaction allows one to convert an Si(Ge)-allyl group to a Si(Ge)-vinyl group; this conversion becomes especially interesting in cyclic series. Indeed, while it was initially used only for the synthesis of metallacyclopent-2-enes,[10-13] the ene reaction, starting with a β-ethylenic organometallic cycloolefin, can produce an α-ethylenic cycloolefin (eq 10).

$$(10)$$
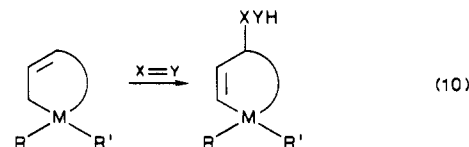
Thus, the ene synthesis allows one to obtain pure metallacyclopent-2-enes which are difficult to prepare otherwise.[21,22] Various enophiles have been used for this purpose (Table I, entries 50–67, 78–87): formaldehyde, benzyne, MA, EAD, PTD,[10-12] PhSO$_2$NSO,[13] and

$^1O_2$.[23-25] Certain adducts can be easily reduced, as is the case with those obtained from $PhSO_2NSO$ when treated with lithium aluminum hydride[13] (eq 11).
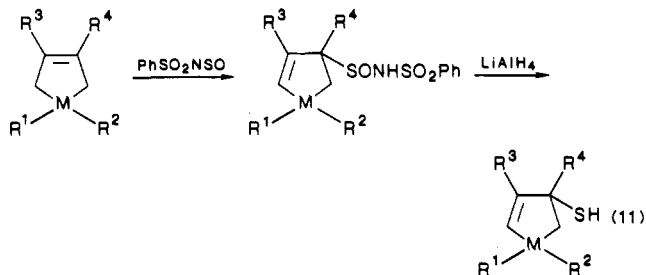
M = Si, Ge; R^1, R^2 = Me or Ph; R^3, R^4 = H or Me

Similarly, the hydroperoxidation by $^1O_2$, followed by reduction with sodium borohydride, produces corresponding metallacyclopentenols,[23-25] which are excellent precursors of group 14 metalloles (eq 12).[24-29,110]

M = Si, Ge; R^1, R^2 = alkyl, alkenyl, aryl group; R^3, R^4 = H or Me; Σ = OC(O)NHPh, OC(S)SMe

The same method of synthesis was also used to transform 1,2-disilacyclohex-4-ene into 1,2-disilacyclohexa-3,5-diene[30] (eq 13).

The ene reaction of mixed disubstituted metallacyclopentenes is stereoselective[10,11] (Table I, entries 61-63,84,85).

E. Enoxysilanes (Table I, Entries 70-72)

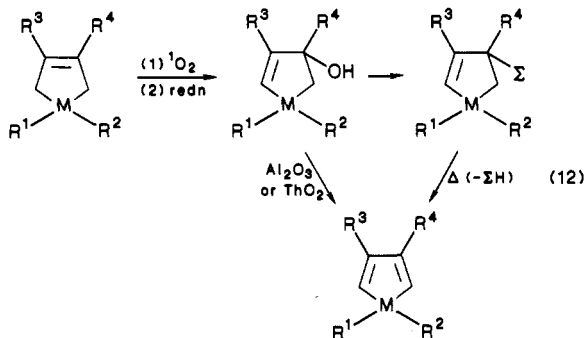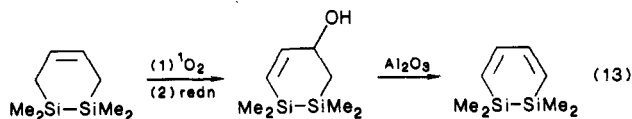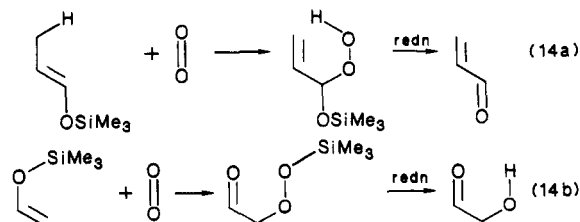Rubottom and Lopez-Nieves[31] have shown that with enoxysilanes the singlet oxygen causes both the classic ene reaction (prototropy, eq 14a) and a silatropic migration (eq 14b) leading to a silyl peroxide. The re-

duction of the photooxygenated adducts produces a desilylation which allows an interesting synthesis of ethylenic ketones[32] or ketols.[33]

F. Silenes

The behavior of group 14 derivatives having M=C bonds (M = Si,Ge) as organometallic enes has not yet

been throughly studied (eq 15).
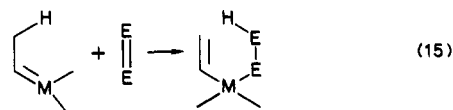
Irradiated phenyldisilanes or -trisilanes[114] react with alkenes or conjugated dienes to give adducts (eq 16)
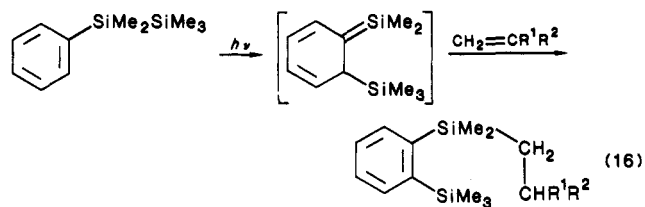
R^1 = H, R^2 = $SiMe_3$; R^1 = R^2 = Me; R^1 = Me, R^2 = C(Me)=CH_2

which can be explained in terms of photoisomerization of disilane (or trisilane) to an unstable silene, followed by an ene reaction of this intermediate to the olefin.

Unlike these reactions, the thermal generation of a silene or germene leads to a strongly enophilic species (cf. section III.B).

III. Group 14 Organometallic Enophiles

A. Vinylsilanes and Vinylgermanes (Table II, Entries 1-7)

Group 14 vinylic derivatives having an electron-deficient C=C bond react with an alkene behaving as an enophile.[10,34] The enophilic activity of these derivatives, just as their dienophile power,[34-37] is clearly greater than that of corresponding organic compounds (halogenopropenes), and the regiochemistry of the reaction, governed by orbital factors,[34] is specific (eq 17a).
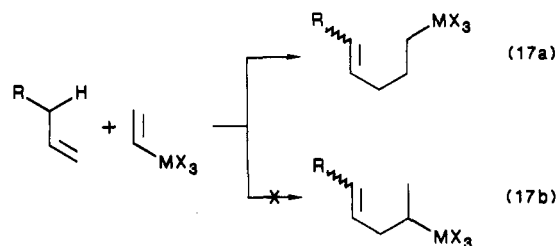
The formation of related isomers (eq 17b) was studied using various methods (e.g., reduction of the adducts at the C=C bond or at the silicon atom)[10] but never detected.

It is possible to use adducts of the vinyltrichlorosilane (a commercial product) to olefins for the formation of their γ-functional derivatives (eq 18). Thus, Kumada et al.[38] obtained the 4-octenylbromide from 1-hexene.

Σ: functional group
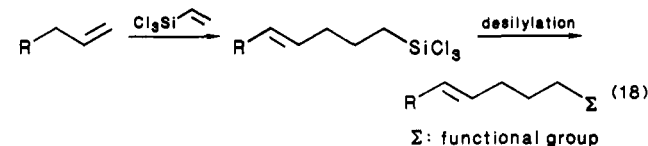
B. Derivatives Having a Multiple Bond to Silicon or Germanium

Group 14 derivatives with M=C bonds (M = Si, Ge) are excellent enophiles, reacting with alkenes (Z = C)

TABLE I. Ene Reactivity of Group 14 Alkenyl Derivatives toward Various Enophiles

entry	organometallic ene	enophile	products[a] (% isomers)	ref
1	Me₃Si— (allyl)	MA	c/t 50/50	10
2		EAD	c/t 60/40	10
3		PTD	cis	10, 14
4		MTD	b	14
5		CX₃COCX₃	b	15
6	Ph₃Si—	CX₃COCX₃		15
7	Me₃Si—	¹O₂	c/t 8/26 66	16
8		EAD	c/t 0/67 33	16
9		PTD	– 100	16
10		RCOCl/cat.	– c	17
11	Me₃Si—	¹O₂	c/t 0/55 45	16
12		EAD	c/t 0/55 45	16
13		PTD	c/t 0/73 27	16
14		CX₃COCX₃	b –	15
15	Me₃Si—	EAD	c/t 32/68	16
16		PTD	c/t 80/15 5	16
17		CX₃COCX₃	b –	15
18	Me₃Si—	¹O₂	c/t 10/10 80	16
19		EAD	trans	16
20		PTD	c/t 15/25 60	16
21	Me₃Si (cyclopentene)	¹O₂	74 26	16
22	Me₃Si (cyclopentadiene)	CX₃COCX₃	91 9	15
23	Me₃Si—···—SiMe₃ c/t 20/80	¹O₂	c/t 60/40	50
24	Me₂Si(—)₂	MTD	66[b] 34[b]	14
25		CX₃COCX₃	b	15
26		CX₃COCX₃	– b	15
27	MeSi(—)₃	CX₃COCX₃	(C₃H₅)₂MeSi—	15
28		CX₃COCX₃	(C₃H₅)MeSi(—)₂	15
29		CX₃COCX₃	MeSi(—)₃	15
30	Si(—)₄	CX₃COCX₃	(C₃H₅)₃Si—	15
31		CX₃COCX₃	(C₃H₅)₂Si(—)₂	15
32		CX₃COCX₃	(C₃H₅)Si(—)₃	15
33		CX₃COCX₃	Si(—)₄	15
34	Me₃Si (cyclohexylidene)	PTD		42
35	Me₃Si (adamantylidene)	PTD		42

TABLE I (Continued)

entry	organometallic ene	enophile	products[a] (% isomers)	ref
36		PTD		42
37		PTD		42
38		EAD		10
39		$^1O_2$		18, 19
40		$^1O_2$		18, 19
41		–	c/t 25/75	18, 19
42		$^1O_2$		18, 19
43		$^1O_2$	80 20	18, 19
44		$^1O_2$		18, 19
45		RCOCl		17
46		PTD		13
47		PhSO$_2$NSO		13
48		PTD		13
49		PhSO$_2$NSO		13
50		HCHO		10
51		C$_6$H$_4$		10
52		MA		10
53		EAD		10
54		PTD		10
55		PhSO$_2$NSO		13
56		$^1O_2$		23, 24
57		O=C(COOEt)$_2$		108

TABLE I (Continued)

entry	organometallic ene	enophile	products[a] (% isomers)	ref
58		PTD		10
59		PhSO$_2$NSO		13
60	MePhSi (cyclopentene)	$^1O_2$	MePhSi—Σ	50
61		EAD	c/t 30/70	10, 11
62	Me$_2$Si (methylcyclopentene)	PTD	c/t 30/70	10, 11
63		$^1O_2$	c/t 43/57	50
64		PhSO$_2$NSO	100 Me$_2$Si—Σ	—	13
65	Me$_2$Si (dimethylcyclopentene)	$^1O_2$	42	58 Me$_2$Si—Σ	25
66		PTD	100	—	10
67	Me$_2$Si (cyclopentene isomer)	$^1O_2$	80	—	20
68	Me$_2$Si / Me$_2$Si	$^1O_2$	Me$_2$Si / Me$_2$Si —OH		30
69	Me$_2$Si / Me$_2$Si (dimethyl)	$^1O_2$	Me$_2$Si / Me$_2$Si —OH 75	Me$_2$Si / Me$_2$Si —OH 25	30
70	Me$_3$SiO / Ph	$^1O_2$[d]	Me$_3$SiO Ph OOH 62	Ph O OOSiMe$_3$ 38	31
71	(norbornene OSiMe$_3$)	$^1O_2$	(OOSiMe$_3$ / O)	32
72	OSiMe$_3$ (cyclohexene *R*)	$^1O_2$[d]	HOO OSiMe$_3$ / *R (major) HO OSiMe$_3$ / *R Me$_3$SiOO O / *R (minor)	32
73	Me$_3$Ge— (allyl)	MA	Me$_3$Ge—Σ c/t 45/55	10
74		EAD	c/t 70/30	10
75		PTD	cis	111
76	Et$_3$Ge— (allyl)	EAD	Et$_3$Ge—Σ c/t 70/30	10
77		PTD	cis	10
78	Me$_2$Ge (cyclopentene)	EAD	Me$_2$Ge—Σ	10
79		PTD		10
80		PhSO$_2$NSO		13
81		$^1O_2$		23
82	Ph$_2$Ge (cyclopentene)	PTD	Ph$_2$Ge—Σ	10
83		PhSO$_2$NSO		13
84	MeBu-i-Ge (cyclopentene)	PTD	MeBu-i-Ge—Σ c/t 40/60	10, 11
85	MeBu-t-Ge (cyclopentene)	PTD	MeBu-t-Ge—Σ c/t 5/95	10, 11
86	Me$_2$Ge (methylcyclopentene)	$^1O_2$	Me$_2$Ge —OH 32	Me$_2$Ge —OH 68	25

TABLE I (Continued)

entry	organometallic ene	enophile	products[a] (% isomers)		ref
87	Me₂Ge (structure)	$^1O_2$	Me₂Ge (structure) OH **43**	Me₂Ge (structure) OH **57**	25
88	Ph₃Sn (structure)	$^1O_2$	Ph₃Sn (structure) HOO **—**	Ph₃Sn (structure) OOH	87

[a] With MA (maleic anhydride) Σ = $\overline{-CC(O)OC(O)CH}$, EAD (ethyl azodicarboxylate) Σ = $-N(COOEt)NHCOOEt$, PTD (4-phenyl-1,2,4-triazoline-3,5-dione) Σ = $\overline{-NC(O)NPhC(O)NH}$, MTD (4-methyl-1,2,4-triazoline-3,5-dione) Σ = $\overline{-NC(O)NMeC(O)NH}$, CX_3COCX_3 (X = F or Cl) Σ = $C(CX_3)_2OH$, RCOCl/cat. Σ = $C(O)R$, $PhSO_2NSO$ Σ = $-SONHSO_2Ph$; with $^1O_2$ the ene reaction adduct (Σ = OOH) is reduced and isolated in its alcohol form (Σ = OH). [b] Unidentified isomers. [c] Reaction with acid chlorides (furoyl, thienoyl, benzoyl) in presence of a catalyst ($AlCl_3$, $TiCl_4$); byproducts are also formed. [d] In this case, various reagents (H_2, Ph_3P) have been used to reduce peroxides, and the products obtained depend on whether or not desilylation occurs. [e] This compound has been prepared by heating reagents at 160 °C during 56 h; 80% yield; bp 117 °C/0.15 mmHg; NMR (^1H, CCl_4) SiMe 0.12 (s), 0.17 (s); $SiCH_2$ 0.63 (2 d); OH + CH 3.60 (m); CH_2–O 4.27 (q); CH_3–C–O 1.27 (t); ethylenic protons 6.00 and 6.52 (J_{AB} = 2 Hz, $J_{AX} \sim J_{BX}$ = 10 Hz).

TABLE II. Enophile Reactivity of Group 14 Vinyl Derivatives

entry	ene	organometallic enophile	product(s)	ref
1	R (structure)	$Cl_3SiCH=CH_2$	$RCH=CH(CH_2)_3SiCl_3$[a,b] (and $SiMe_3$ derivs)	10
2	(cyclopentene structure)	$Cl_3SiCH=CH_2$	(structure) $(CH_2)_3SiCl_3$ (and SiH_3 deriv)	10
3	(cyclohexene structure)	$Cl_3SiCH=CH_2$	(structure) $(CH_2)_3SiCl_3$ (and SiH_3 deriv)	10
4	Me₂Si (structure)	$Cl_3SiCH=CH_2$	Me₂Si (structure) $(CH_2)_3SiCl_3$ (and $SiMe_3$, SiH_3 derivs)	10
5	Me₂Si (structure)	$Cl_3SiCH=CH_2$	Me₂Si (structure) $(CH_2)_3SiCl_3$ **90** Me₂Si (structure) $(CH_2)_3SiCl_3$ **10**	109
6	Me₂Si (structure)	$(EtO)_3SiCH=CH_2$	Me₂Si (structure) $(CH_2)_3Si(OEt)_3$	10
7	Me₂Si (structure)	$Cl_3GeCH=CH_2$	Me₂Si (structure) $(CH_2)_3GeCl_3$	10

[a] R = n-C_3H_7, n-C_4H_9, n-C_5H_{11}, $SiMe_3$. [b] With R = $SiMe_3$, c/t = 40/60.

or carbonylated compounds (Z = O) according to a prototropic ene reaction (eq 19a).[39,40,107,115–119]

(structure) (19a)

(structure) (19b)
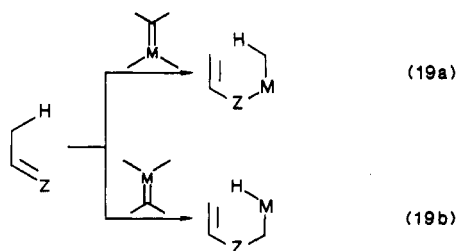
Their reactivity toward ketones is higher than toward alkenes, and their ene reactivity with ketones having a hydrogen atom α to the carbonyl group is greater than their reactivity with respect to this group (i.e., a pseudo-Wittig reaction). In the case of conjugated dienes, the ene reaction occurs in addition to the [2+4] cyclo-

addition,[39,40,115] but it can be exclusively ene.[40]

The sterically hindered silenes and germenes $Me_2M=C(SiMe_3)_2$ give, under mild conditions, the ene products with alkenes (propene, butenes, dienes), acetone, or ethyl acetate.[40] For example, a stable silene combines with acetone in an ene reaction.[116]

Thermolysis of pentamethyldisilanyldiazoacetate together with ketones having α-hydrogens gives, along with silylketenes, the corresponding silyl enol ethers which may be formed by a prototropic ene reaction between an intermediate silene and the ketone.[117]

Certain rearrangements of silenes, in particular during the thermolysis of phenoxyvinyldimethylsilane,[118] may also be explained by an intramolecular ene reaction similar to reaction 19a.

In 1-sila-1,3-butadienes[125] and 1-silacyclopenta-1,3-dienes[105,113] the 1,5-hydrogen migration is a good example of an intramolecular ene reaction involving silene,

giving a product with a silicon–hydrogen bond (eq 19b, 20, 36, 38).

(20)

trans-Me$_3$SiMe$_2$SiCH=CH—CMe=CH$_2$

(37%)

(21)

(22)
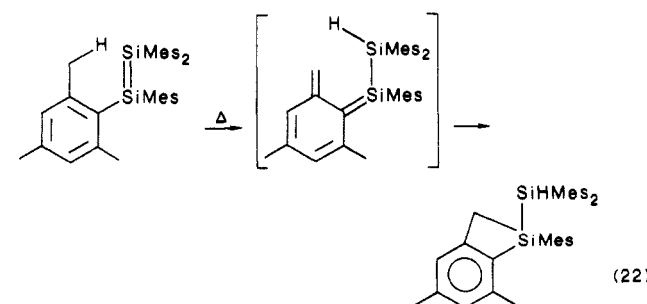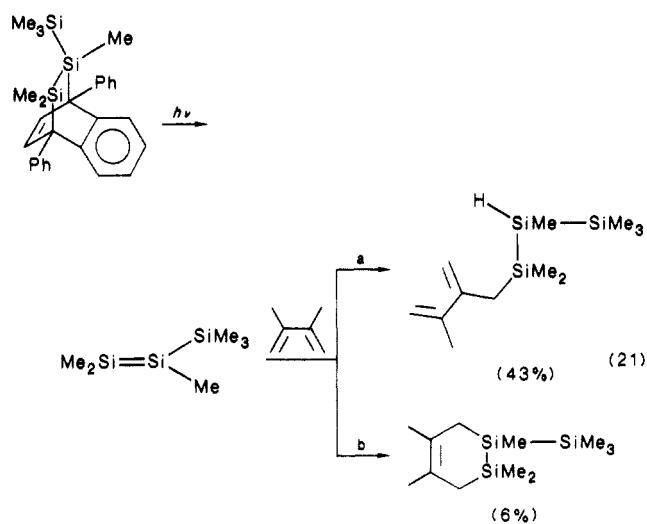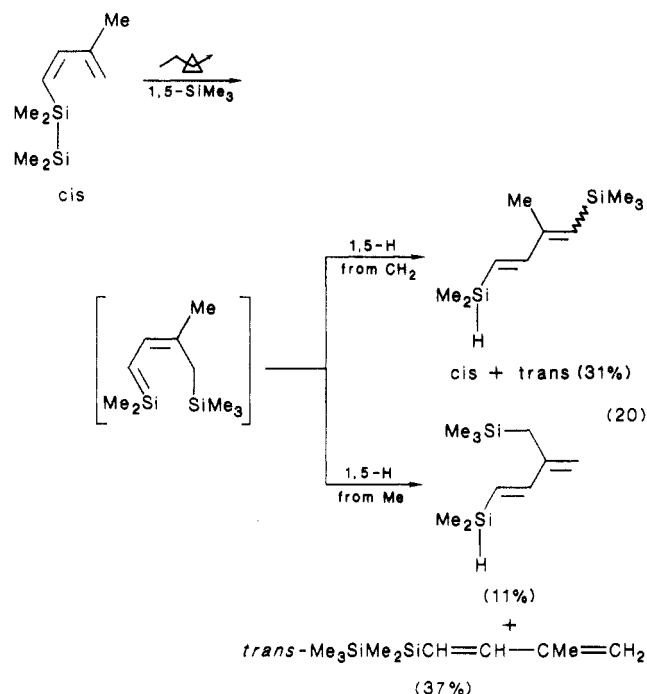
Disilenes produced photochemically react with 2,3-dimethylbutadiene mainly by an ene reaction[119] (eq 21a).

As in the case of silenes, disilenes give prototropic rearrangements which can be viewed as an ene reaction process. Indeed, thermal rearrangement of tetramesityldisilene yields a silabenzocyclobutene, whose formation has been suggested as proceeding via a [1,5]-prototropic shift followed by electrocyclic ring closure[121] (eq 22).

TABLE III. Solvent Effect on Relative Yields of Products in the Reaction^a between Allyltrimethylsilane and PTD[14]

solvent	relative yield, %		
	2	5	6
benzene	73	9	18
1,2-dichloroethane	71	17	11
dichloromethane	72	18	10
ethylacetate	71	20	9
acetone	44	48	7
acetone + H$_2$O^b	21	73	6
acetonitrile	28	67	6
acetonitrile + H$_2$O^b	12	84	4

^{a}[C$_3$H$_5$SiMe$_3$] = 0.12 mol/L; [PTD] = 0.11 mol/L; reaction temperature 25 °C. ^{b}3.3 vol %.

Whereas sila- (or germa-) imines react with carbonyl compounds by [2 + 2] cycloaddition,[120] Wiberg has recently reported that these derivatives prefer to give a prototropic ene reaction (eq 23, Z = O)[40,120] with

(23)

M = Si, Ge; R = SiMe$_{3-n}$-t-Bu$_n$
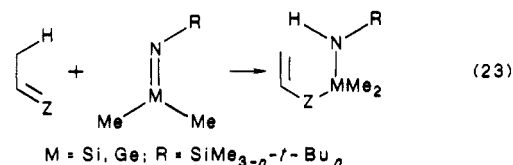
carbonyl compounds which have hydrogens in the α-position (e.g., acetone). An ene reaction also occurs with alkenes (Z = C).[40]

These reactions were discussed in recent reviews of unsaturated compounds of silicon[40,120] and germanium.[40]

IV. Mechanisms

The suprafacial attack of an enophile on an olefin, involving an interaction between three orbitals: (1) the HOMO of the π bond of the ene, (2) the LUMO of the π bond of the enophile, and (3) the LUMO of the C–H bond of the ene,[41] leads to a concerted mechanism or a reaction intermediate which can have zwitterionic or radical character.[2-5] The mechanism of the ene reaction (i.e., a Janus-faced reaction[2]) is often difficult to establish.

We shall examine the influence of the heteroatom (Si, Ge) on the reactivity of the ene and enophile molecules systematically.

A. Organometallic Enes: H–Ene and Metallo–Ene Reactions

1. General Data

In 1981, Butler et al.[14] studied the mechanism of the reaction of 1,2,4-triazoline-3,5-diones with two allylsilanes (Me$_3$SiC$_3$H$_5$ and Me$_2$Si(C$_3$H$_5$)$_2$) and analyzed the products of this reaction with respect to solvent and temperature. They concluded that there were two distinct reactions (Scheme I); the first (in nonpolar solvents and at high temperature) is the mechanism of the concerted H–ene reaction (Ia); the second, (Ib), involving a polar intermediate 3, corresponds to an electrophile addition of the enophile to the alkene.

The first mechanism yields the adduct 2 directly, whereas the intermediate 3 can produce both 4 and 6 which become abundant, and even predominant in certain polar solvents at low temperature (Table III).

The interpretation of the action of PTD on two other allylsilanes—capture of the allylic hydrogen (H⁻) as a

SCHEME I. Reaction of 4-Phenyl-1,2,4-triazoline-3,5-dione with Allyltrimethylsilane: Butler's Mechanism[14]
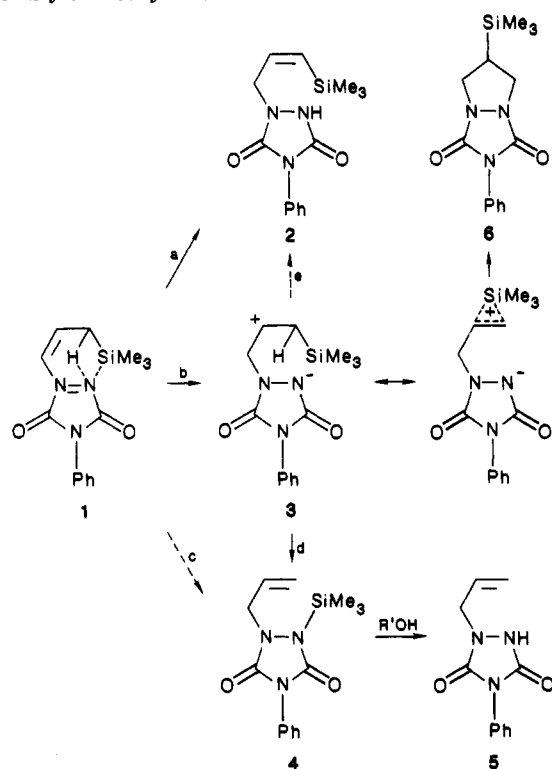
first step, and then a regioselective stabilization of the carbocation thus formed[42]—seems less probable in the light of recent studies regarding the enophile reactivity of the triazolinediones.[43-47] The results emphasize the analogy between the ene reaction and electrophilic addition to alkenes, at least as far as the first step is concerned.

In the case of carbonylated enophiles (CX_3COCX_3), Abel and Rowley[15] propose a mechanism involving a six-centre process in which there is a significant polar contribution transition state (eq 24).
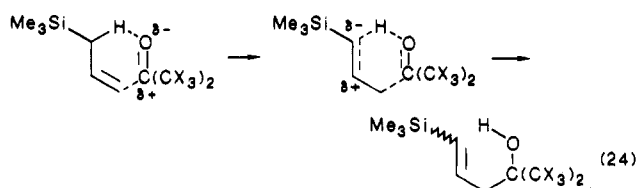
When this reaction is done at low temperatures, an oxetane is obtained in addition to the ene reaction product, and this oxetane fails to isomerize to the ene reaction product at higher temperatures (eq 25).
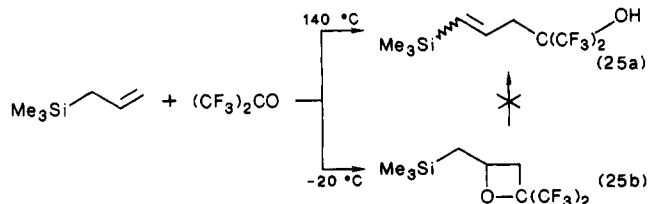

Moreover, in the presence of aluminum chloride, allyltrimethylsilane and hexafluoroacetone give two other products (eq 31), and the product distribution is consistent with the absence of a carbonium ion intermediate in the noncatalyzed reaction[15] (cf. section IV.A.4).

TABLE IV. Relative Reactivity of Allyl Compounds in the Reaction with PTD[14]

ene	rel reactivity
$Me_3SiCH_2CH=CH_2$	1
$Me(CH_2)_3CH=CH_2$	0.05
$MeCH_2CH_2OCH_2CH=CH_2$	0.01
$MeCOOCH_2CH=CH_2$	0.01
$NCCH_2CH=CH_2$	0.03
$BrCH_2CH=CH_2$	0.003
$PhCH_2CH=CH_2$	0.02

TABLE V. Relative Reactivity of Allylsilanes and Alkenes in the Reaction with EAD[10]

| ene	initiator or inhibitor	rel reactivity
$Me(CH_2)_3CH=CH_2$	no	1
$Me_3SiCH_2CH=CH_2$	no	3.7
	$(BzO)_2$	4.0
	galvinoxyl	4.0
$Me_3SiC(Me)=CH_2$	no	0.8
$Me_2Si\langle$	no	0.2
	$(BzO)_2$	3.8
	galvinoxyl	0.2
$\langle$	no	0.3
	$(BzO)_2$	5.3

2. Kinetic Aspects

From a kinetic point of view, the allyltrimethylsilane is more reactive toward the PTD than toward various substituted allylic compounds, particularly the alkenes (Table IV).[14] Toward EAD, allyltrimethylsilane is also more reactive than 1-hexene (Table V),[10b] but in cyclic series, 1,1-dimethylsilacyclopent-3-ene and cyclopentene have similar rate constants.

Whereas the presence of radical initiators or inhibitors has no effect on the rate of the reaction between EAD and allyltrimethylsilane, the same is not true for the silacyclopentenic series: the addition of a radical initiator multiplies their rate constant 17 times. The same effect is also observed for cyclopentene. The possibility of an evolution from the concerted mechanism of the ene synthesis toward a radical process has been suggested for reactions of EAD,[2,10,48] together with an approach parallel to the ethylenic bond,[43,49] which often leads to strong steric interactions, both in the case of the noncyclic allylsilanes[16] and that of silacyclopentenes.[10,11]

The energy level of the π-HOMO orbital of the alkenylsilanes seems to play an important role in the reactivity toward an enophile, and this is logical for an electrophile for two reasons. (i) Allylsilanes are more reactive than vinylsilanes. In the carbon series, the reactivity of an ene is increased by the presence of a methyl substituent on the 2-carbon: thus, isobutene is more reactive than 1-butene and 2-methyl-2-butene more reactive than 1-pentene toward EAD[2,48]. The opposite effect is observed in the silicon series where isopropenyltrimethylsilane is less reactive than allyltrimethylsilane[10] toward EAD (Table V). The difference in reactivity is even more obvious toward singlet oxygen, where vinylsilanes need reaction times of several hours[18,19] and allylsilanes require only a few minutes[16,23,25,30,50]. This is reasonable in the sense that the allylsilanes have a lower ionization potential than the vinylsilanes[51-54] and therefore a π-HOMO orbital of higher energy. (ii) The most reactive allylsilanes toward

TABLE VI. Relative Reactivity in the Reaction with Singlet Oxygen and Vertical Ionization Potentials of Silacyclopentenes and Disilacyclohexenes[50]

compd	rel reactivity[a]	IP, eV[53,54]
Me₂Si (ring)	1	9.10
MePhSi (ring)	1	9.10
Ph₂Si (ring)	1	9.10
Me₂Si (ring)	2	8.76
Me₂Si (ring)	3	8.40
Me₂Si / Me₂Si (ring)	1.5	8.20
Me₂Si / Me₂Si (ring)	4	7.70

[a] Approximate rates at beginning of reaction: the oxygen absorption for the single value corresponds to about 50 mL mn⁻¹ for a quantity of product of 0.02 mol in 500 mL of methanol. Photosensitizer: Rose Bengal.

SCHEME II. Regiochemistry of the Ene Reaction between a Symmetrical Enophile E₂ and an Allylic Organometallic Compound[16 a]

migration α-cis   migration α-trans   migration β   migration γ
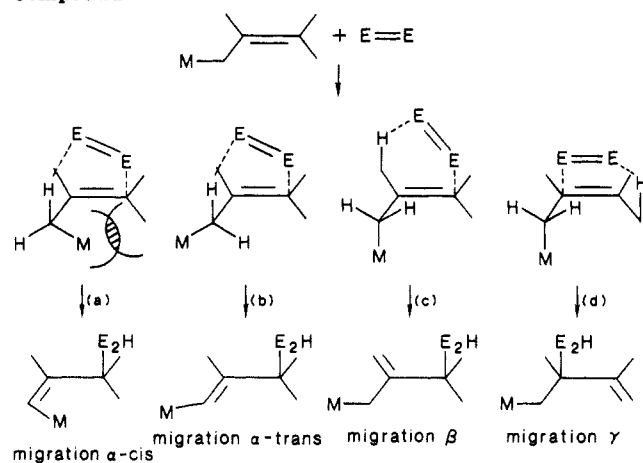
[a] M = organometallic group, e.g., SiMe₃.

$^1O_2$ are those whose ionization potential of the π-orbital is lowest. Indeed, in the cyclic allylsilane series, the ionization potential decreases as the double bond becomes more substituted,[53] or as the number of silicon atoms in the allylic position increases.[54] This interpretation is supported by our studies of relative reactivities toward $^1O_2$ (Table VI).[50]

3. Regiochemistry

The regiochemistry (Scheme II) of the ene reaction with various allylsilanes[16] has been examined recently. It seems that with EAD factors including: (i) preferential attack at the ethenylic carbon (C_1) having the highest coefficient of the π-HOMO of the allylsilane,[55]
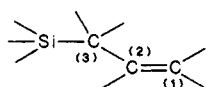
(ii) steric interactions with the SiMe₃ group, and (iii) approach of EAD parallel to the ethylenic bond plane,[43,49] all unite to produce the preferential (Table

SCHEME III

Table I, entry 7 (R = Me)   66%
Table I, entry 18 (R = H)   80%
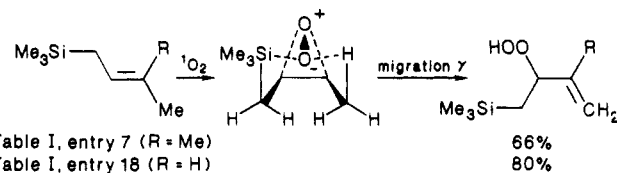
I, entries 8–12) and even regiospecific α-migration (Table I, entries 15, 19) products.

Recent results on the interpretation of the ene reaction with the triazolinediones[43-47] lead to mechanistic analogies with the singlet oxygen, particularly with respect to approach of the olefin perpendicular to the ethylenic bond plane. Comparative results[16] show that PTD yields, with the allylsilanes studied, the same regiochemistry as does the singlet oxygen, especially a preferential γ-migration on the prenyltrimethylsilane and the cis-crotyltrimethylsilane (Table I, entries 7,9,18,20). However, an increase in α-migration was noted with respect to the singlet oxygen reaction with the same allylsilanes, and also with respect to the reaction of PTD with olefines of similar structure,[44] perhaps because of steric interactions involving enophiles much larger than $^1O_2$ and preferential attack at the ethylenic carbon C_1, the furthest from the SiMe₃ groups. In both cases the regiochemistry does not behave as predicted by the frontier orbital theory for a concerted reaction.[16]

Consequently, the regiochemistry of the ene reaction of an allylsilane is determined mainly by (i) factors enabling a stabilization of the reaction intermediate which could be of an ionic (PTD, CX₃COCX₃)[14,15,42] or radical (EAD)[10b] nature depending on which enophile is used (see further), and (ii) conformational factors acting on the activation energy: cis effect with $^1O_2$[16,61,66-70] or by enophile–silicon interaction.[14,16] (For reviews on singlet oxygen see ref 56–65. The factors influencing the ene reaction with $^1O_2$ have been particularly well detailed by Gollnick and Kuhn.[61]) Thus, an oxygen–silicon interaction (Scheme III) would put the two α-hydrogens in an unfavorable position for the reaction with oxygen (the C–H bond has to be perpendicular to the double bond[61]) and would explain the increase in γ-migration observed in an allylsilane compared to its carbon analogue.[16] With the planar silacyclopentenes,[71-75] the impossibility of the endocyclic C–Si bonds being in the plane of the π orbital would prevent all possibilities of interaction, as reflected in the behavior of the silacyclopent-3-enes being very close to that of their carbon analogues.[16] Conformational factors would also explain the much greater reactivity of the 1,2-disilacyclohex-4-enes toward $^1O_2$ compared to that of the cyclohexenes.[30] The stereoselectivity of some ene reactions of linear allylsilanes (or germanes) (α-cis/α-trans, Scheme II)[16] or cyclic ones[10b] have been discussed.

4. H–Ene and Metallo–Ene Reactions

The term metallo–ene reaction was introduced in 1982 by Oppolzer et al.[76] to describe the addition of allylic organomagnesium and organozinc compounds to olefins,[76-80] particularly certain intramolecular rearrangements. One can agree with these authors that all reactions of the type 26 which involve a metallotropic migration of the element M, are indeed metallo-ene

reactions, e.g., the reactions of allylic Grignard reagents with aldehydes, ketones, or imines.[80b]

Reactions of unsaturated compounds with allyl-stannanes[81-85] are of this type (eq 26, M = Sn, Z = CH_2,CR_2), for example reactions of allyltins with car-

$$ \text{eq (26)} $$
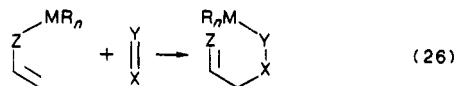
bonylated compounds[15,81-83] (XY = >C=O) and sulfur dioxide[84] (XY = OS=O), which take place with an allylic transposition of the hydrocarbonated chain, or the addition of organostannic enamines (Z = NR) to electrophilic alkenes.[86]

The allylgermanes also give the sulfination reaction (XY = OS=O; Z = CH_2; MRn = GeMe$_3$,GeEt$_3$) [Al-lyltrimethylgermane or allyltriethylgermane react in a sealed tube with excess of sulfur dioxide (50 °C; 2 days), 90% yield. Me$_3$GeOS(O)CH$_2$CH=CH$_2$: bp 75 °C/0.05 mmHg; IR 1635 (C=C), 1120 (S=O); NMR (^{1}H, CCl$_4$) 1.20 (s, GeMe) 3.20 (d, CH$_2$S) 5.40 (m, ethylenic protons). Et$_3$GeOS(O)CH$_2$CH=CH$_2$: bp 85 °C/0.04 mmHg; IR 1640 (C=C) 1120 (S=O); NMR (^{1}H, CCl$_4$) 1.0 (m, GeEt) 3.20 (d, CH$_2$S) 5.3 (m, ethylenic protons) (Dubac, J. Unpublished work)] but at higher temperatures than do the allylstannanes. They also undergo the sulfonation reaction (XY = O$_2$S=O).[90]

The sigmatropic migration of a silicon atom in the allylic position (eq 26, M = Si) induced by an enophile occurs less frequently than in the organostannic series. Singlet oxygen reacts with enoxysilanes according to the two types of ene reaction (eq 14),[31-33] the sila-ene reaction becoming specific (eq 14b) when prototropy (eq 14a) is impossible.[33] One of the adducts obtained by Butler[14] from the reaction of PTD with allyltri-methylsilane (Scheme I, adduct 4) also corresponds to the product of the sila-ene reaction, whether or not the mechanism involves an ionic intermediate (3).

Although allyltrimethylgermane (8) produces an ad-duct of the H-ene reaction (9) with PTD in benzene at 20 °C, it gives mainly the adduct of the germa-ene re-action (10) in acetonitrile at lower temperatures (Scheme IV).[111] However, two cyclic allylic derivatives, 1,1-dimethylsila(or germa)cyclopent-3-enes, give only the H-ene reaction adduct (12) regardless of the ex-perimental conditions (eq 28)[111]. The product of the metallo-ene reaction (13) has not been identified.

SCHEME IV
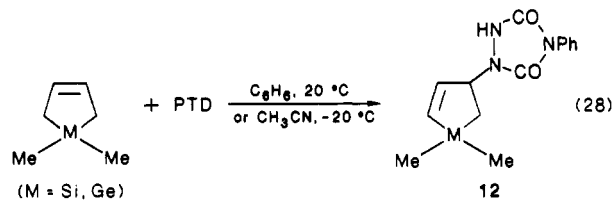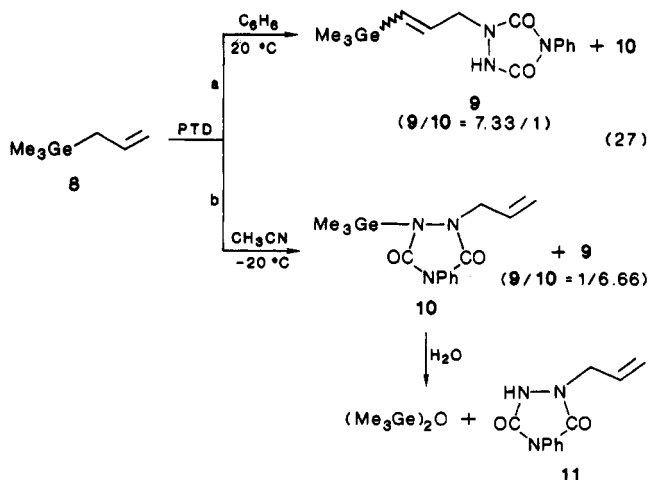
Products of this type (14) have been observed by Calas et al.[112] in the sulfonation by Me$_3$SiSO$_3$Cl of silacyclo-pent-3-enes. Even though the proposed mechanisms (Scheme V) do not correspond to H-ene and silia-ene reactions, they give the same products.
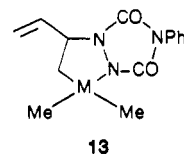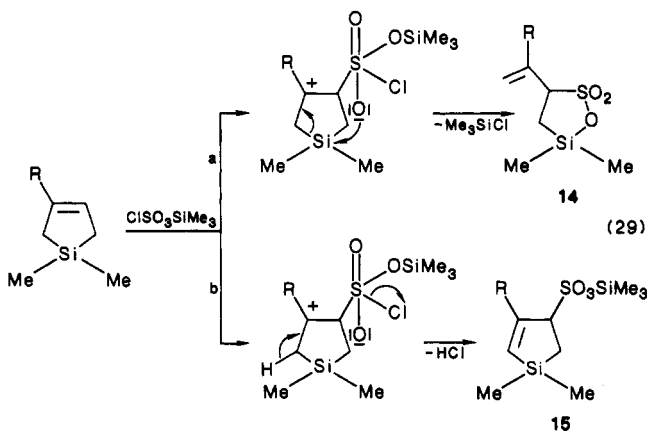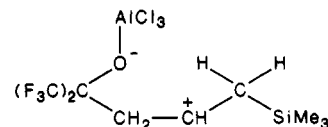

SCHEME V

CHART I

Only silyl migration is observed in the case of the addition of allylsilanes to aldehydes in the presence of a Lewis acid catalyst,[89] which gives, after hydrolysis, homoallylic alcohols.

The work of Abel and Rowley[15] on the reactivity of perhalogenoketones toward allylsilanes and allyl-stannanes provides a good example of the possibility of two sigmatropic migrations in organometallic group 14 compounds. In the absence of a catalyst, the allyl-silanes undergo the H-ene reaction (eq 24), whereas allylstannanes give the metallo-ene reaction (eq 30).
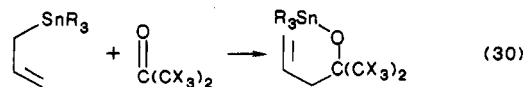
When allyltrimethylsilane is allowed to react with hexafluoroacetone, in the presence of aluminum chlo-ride, the metallo-ene product 16 is the main one (51%), together with the H-ene reaction product 7 (13%) and 17 (16%) (eq 31).[15] It has been suggested[15] that this reaction proceeds via an initial electrophilic attack of the HFA/AlCl$_3$ complex at the unsaturated site (Chart I). This intermediate can then rearrange by proton

$$Me_3SiCH_2CH=CH_2$$
$$+$$
$$(CF_3)_2CO$$
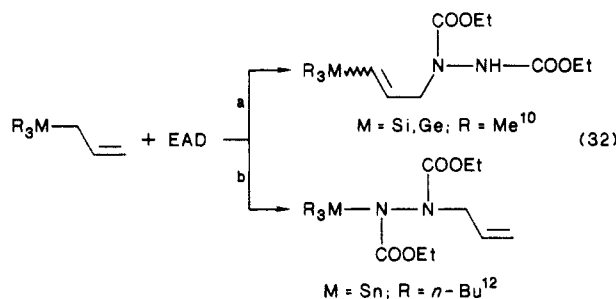
$\xrightarrow{AlCl_3}$

$\longrightarrow Me_3SiCH=CHCH_2C(CF_3)_2OH$

7 (13%)

$\longrightarrow Me_3SiOC(CF_3)_2CH_2CH=CH_2$ (31)

16 (51%)

$\longrightarrow Me_3SiCH_2CH=CHC(CF_3)_2OH$

17 (16%)
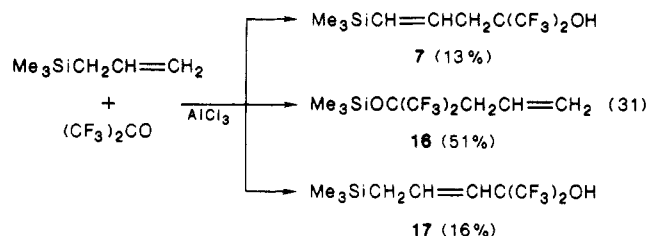
elimination of by trimethylsilyl migration to give the observed products. The noncatalyzed and the AlCl$_3$-catalyzed reaction of allyltrimethyltin and HFA give the same products (eq 30).

Similar differences in the reactivity between allylic silicon and germanium derivatives on the one hand (Table I, entries 2,74) and tin on the other hand (eq 32)[12] toward EAD (noncatalyzed reactions) have also

$$R_3M\text{---}\diagdown\diagup + EAD$$

a $\longrightarrow$ $R_3M\text{\small\char92\char92\char92\char92}\diagdown$ with COOEt, N---NH---COOEt

$$M = Si,Ge; R = Me^{10}$$

b $\longrightarrow$ $R_3M\text{---}N\text{---}N\text{---}\diagdown\diagup$ with COOEt groups

$$M = Sn; R = n\text{-}Bu^{12}$$

(32)

been observed.

To our knowledge, the only previously recorded H-ene reaction involving an allylstannane is the photooxygenation of prenyltriphenyltin[87] (Table I, entry 88), but the resulting hydroperoxides have neither been characterized by spectrometric analysis nor by reduction to alcohols. The effect of enophilic compounds on allylstannanes deserves a more detailed study.

In the reaction of tetracyanoethylene with allyltrimethylsilane, Hartman and Taylor[88] did not observe the H-ene reaction product, but 1,2-cycloaddition instead (similar to the oxetane of eq 25b), together with a demetallation product which could have resulted from an ionic intermediate similar to that of Chart I. The yield of this product is low (<5%) in benzene or in methylene chloride solution, and more abundant in polar solvents (33% in ethyl acetate, 87% in acetonitrile).

5. Conclusion

It seems, therefore, that the addition of an electrophilic π bond compound (X=Y) onto an allylic group 14 derivative can occur in three ways: (i) a H-ene reaction, (ii) a metallo-ene reaction, and (iii) a 1,2-cycloaddition.

With a strong electrophilic agent (e.g., sulfur oxides, α-halogenated carbonylated compounds, tetracyanoethylene) metallotropy is predominant. Such a reaction can be viewed as an electrophilic substitution[81-85,89,91,92] involving a six-centered concerted mechanism of the metallo-ene reaction type, or as involving an ionic intermediate (Chart IIa) stabilized in polar solvents or with the help of a catalyst (Chart I).

With weaker electrophiles known as enophiles (e.g., PTD, EAD, $^1O_2$), the classic H-ene reaction is generally observed, sometimes competing with the metallo-ene reaction (e.g. PTD in polar solvents or $^1O_2$ on the enoxysilanes). In this case, the resulting prototropic concerted reaction may have an ionic nature (Chart IIa)
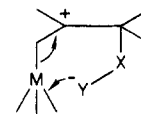
CHART II

a   b
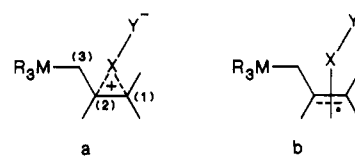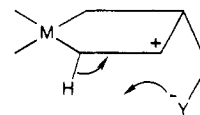
SCHEME VI

SCHEME VII

with a strong enophile (PTD), or a radical nature (Chart IIa) with a weaker enophile (EAD). An intermediate of the Chart IIb type is probable with EAD (Table V). Although the heteroatom M has a great influence on the direction of this electrophilic reaction (metallotropy: Sn $\gg$ Ge $\gtrsim$ Si), the structure of the allylic derivative is also very important (Schemes I, IV and eq 28), the sila- and germacyclopent-3-enes being less inclined toward the metallo-ene reaction. Apparently a conformational factor is involved due to the fact that endocyclic C-M bond in planar heterocycles cannot position themselves so as to give metallotropy, as opposed to the C-H bond (Scheme VI). With the noncyclic allylsilanes and -germanes in a polar solvent (eq. 27 and Scheme I), metallotropy is predominant (Scheme VII). The rarely observed 1,2-cycloaddition of the XY electrophile to the C=C bond could also involve intermediates of the type previously suggested in Chart II. Although singlet oxygen does not give dioxetanes with allylic organometallics, it often forms this type of adduct with alkenes.[61]

Furthermore, the sigmatropic reaction 26 (Z = MR$_2$) which involves a bimetallic vinylic derivative R$_3$M-R$_2$MCH=CH$_2$ and an alkene (XY = >C=C<) or another enophile (e.g., >C=O), can be viewed as a metallo-ene reaction. The 1,5-silyl migration as a route to 1-sila-1,3-butadienes[125] and 1-silacyclopenta-1,3-dienes[126] would be an intramolecular sila-ene reaction, while this migration in a disilylated enone is more complicated.[125]

B. Organometallic Enophiles

The influence of the heteroatom and its substituents is obvious from the behavior of vinylsilanes and -germanes $\Sigma_3MCH=CH_2$ during ene[10,34] and dienic[10,34-37] syntheses. For the Diels-Alder reactions between these molecules and dienes rich in electrons, the order of reactivity depends on the nature of Σ, with Cl > RO > H > Me. It is noteworthy that the replacement of a carbon atom by a silicon or germanium atom increases the dienophilic power of the αC=C bond.[10,34] Regarding the ene synthesis reaction, no adduct was obtained from vinylsilane (Σ = H), vinyltrimethylsilane (Σ = Me), and alkenes. The $\Sigma_3MCH=CH_2$ molecules have an enophilic activity when Σ = Cl, RO. As in Diels-Alder reactions, trichlorinated derivatives are more

CHART III
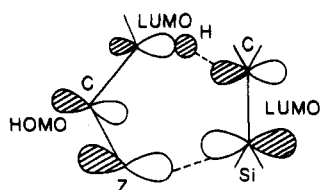
reactive than trialkoxylated derivatives.[10,34] Furthermore, these reactions (eq 17) yield only the linear adduct derived from the most sterically hindered transition state. The regiochemistry and the kinetics of these reactions are, therefore, under orbital control.[34] Since the highest HOMO coefficient of the ene is at its extreme end, just as is the highest LUMO coefficient of the enophile, reaction 17a occurs exclusively. The results obtained for dienophilic and enophilic activity of the vinylic derivatives $\Sigma_3MCH{=}CH_2$ (M = Si,Ge,Sn) when compared with those of corresponding carbon compounds (propene and derivatives) or boron (vinylboranes) can be interpreted in terms of a perturbation scheme involving the LUMO of the dienophile or the enophile and the HOMO of the diene. Thus, the increase in dienophilic or enophilic reactivity with increase in the electronegativity of substituents Σ going from carbon (M = C) to vinylsilanes or -germanes (M = Si,Ge) is related to an increase in electrophilic activity by a lowering of the LUMO.[34]

To our knowledge, there have been no studies of the mechanism of enophile activity of silenes or germenes, except for one report of kinetics.[40] Three observations are cited as a guide to further discussion: (i) as dissymetric enophiles, silenes and germenes give regiospecific bimolecular ene reactions, the hydrogen of the ene attaching itself to the carbon of the silene or germene (eq 19a); in the case of certain intramolecular rearrangements of silenes the formation of a silicon-hydrogen bond is possible (cf. section III.B);[105,107,113] (ii) the reactivity of alkenes toward the silene $Me_2Si{=}C\text{-}$ $(SiMe_3)_2$ increases with their nucleophilicity;[40] (iii) the silene $Me_2Si{=}C(SiMe_3)_2$ reacts with carbonyl compounds (e.g., acetone or ethyl acetate) much faster than with alkenes (e.g., isobutene).[40]

Apparently silenes and germenes react as enophiles in their singlet fundamental state (S_0), especially in the case of sterically hindered stable silenes.[40,116] The observed regiochemistry might then be explained by the scheme of orbital interaction of the ene reaction[41] (Chart III). In the silenes, the LUMO is usually concentrated at the electrophilic silicon atom,[120,122] which bonds itself to the Z atom of the ene (eq 19), bearer of the highest HOMO's coefficient, and the hydrogen atom migrates to the carbon of the silene. One cannot exclude the possible role of the triplet state (T_1)[120] in determining the ene reactivity of silenes, germenes, or disilenes, particularly when these species are produced photochemically,[119] and biradical intermediates are possible (cf., IV.A.1–3). In this respect, it is interesting to note that a silene produced photochemistry may play the ene role[114] (eq 16). In order to clarify this problem, it would be interesting to study the enophilic activity of silenes of reversed polarity,[102,122] and compare the results with those for silenes in which the silicon is the bearer of a positive charge. Effect of the solvent polarity should also be examined (cf. IV.4).

Finally, the competition between enophile and dienophile activities of silenes (or germenes) may be due to the small energy gap between the two frontier orbitals,[120,122] unlike alkenes which even with electron-withdrawing substituents, have only a weak enophile activity (e.g., maleic anhydride).

V. Retro-Ene Reactions

The retro-ene reaction corresponds to thermal decomposition of an olefin into its two alkenes (ene and enophile) which could formally produce it by an ene reaction.[2] Reactions of this type have not yet been studied extensively for group 14 organometallics.

Allyltrimethylsilane, the simplest organometallic molecule able to give such a reaction, decomposes at 600 °C. Under low pressure, propene elimination takes place, and transient 2-methyl-2-silapropene is produced (eq 33).[96–98]
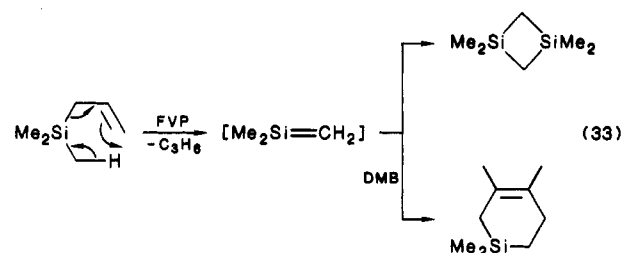
The original work of Bailey and Kaufmann[96] has been confirmed by kinetic and mechanistic studies of Barton, Davidson, et al.[98] who have shown that, under low pressure, the main decomposition involves a concerted retro-ene process. Under similar conditions the pyrolysis of diallyldimethylsilane occurs by the same mechanism.[99,123] The main products are propene and 1,1-dimethylsilacyclobutene, the latter resulting from the cyclization of the transient silabutadiene (eq 34).
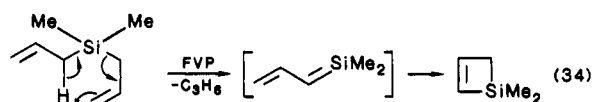
The pyrolysis method has been extended to cyclic molecules, giving access to new polyenes each having a Si=C bond such as silabenzenes[100–104] (eq 35), silacyclopentadienes (siloles)[105] (eq 36) and silafulvenes[106] (eq. 37)
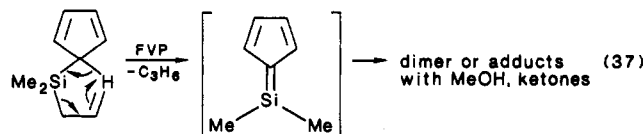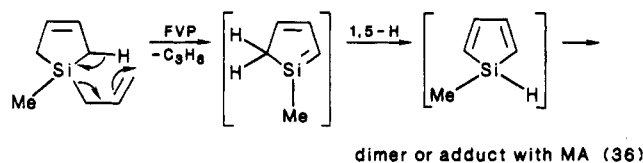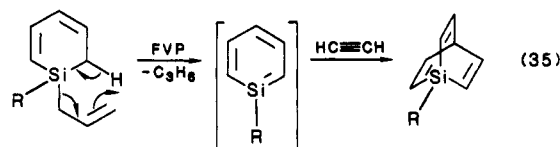
Recently, the flash vacuum pyrolysis of 1-allyl-1,3,4-trimethylsilacyclopent-3-ene (**18**) and 1-allyl-1-

phenyl-3,4-dimethylsilacyclopent-3-ene (19) has been studied.[113] Both 18 and 19 decompose by a retro-ene reaction (elimination of propene) to give 1,3,4-tri-methylsilole (20) and 1-phenyl-3,4-dimethylsilole (22) together with their transoid isomers (21, 23) (eq 38);
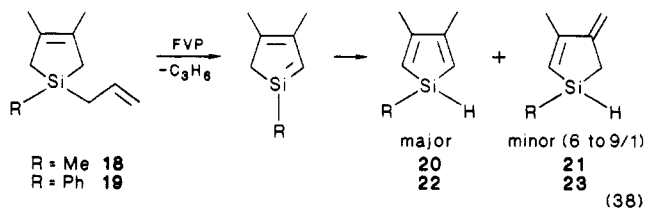

R = Me 18
R = Ph 19

major
20
22

minor (6 to 9/1)
21
23

(38)

these are the first stable monomeric C-methylated siloles having a Si–H bond. Thermolysis of 1-allyl-1,3,4-trimethylgermacyclopent-3-ene produces only 2,3-dimethylbutadiene by a cheleotropic elimination.[113]

Numerous examples of retro-ene synthesis involve molecules containing oxygen[2] as the heteroatom. To our knowledge, among group 14 organometallics the only work to date deals with the pyrolysis of acetylenic ethers which is an excellent method for obtaining ketenes having silicon or germanium substituents (eq 39).[10b,93-95,124] Since this decomposition occurs at 130–140 °C and atmospheric pressure, it is an example of retro-ene synthesis under milder condensed-phase conditions.

(39)
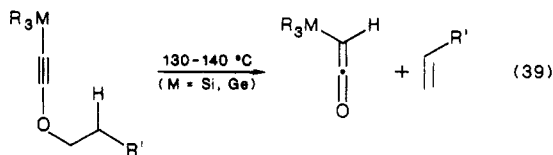
VI. Conclusions and Perspectives

Among the electrophilic reactions which organometallic compounds undergo the prototropic ene reaction appears at first as another example of the Alder reaction. Unquestionably, this reaction is extremely useful in a functionalization of organometallic compounds (e.g. photooxygenation), particularly for heterocyclics in which the introduction of a functional group is often difficult because of the fragility of metal–carbon endocyclic bonds. The realization of a competitive metallotropic reaction (i.e., a metallo-ene reaction), either predominant or exclusive, allows one to view electrophilic reactions of group 14 ethylenic derivatives with unusual clarity.

We believe that the potential of the ene reaction in organometallic or heteroatom chemistry, is still enormous. Applications of the ene reaction, i.e., the H–ene and metallo–ene or hetero–ene reaction, at first in group 14, to organic syntheses, especially of organosilicon compounds, has only just begun,[19,32,33,38] and the prototropic ene reaction is not yet known for organotin compounds. The functionalization of group 15 ethylenic derivatives, particularly those of phosphorus and arsenic, by ene reactions does not appear to have been studied. Noting the recent discovery of double-bonded group 14 enophilic compounds, such as silenes, germenes, sila- and germaimines, etc., we can envisage an extension of the ene reaction to low-valent compounds of this and other groups (e.g., borenes, borimines, etc.)

Recently, flash pyrolysis studies of organosilanes have shown that the retro-ene reaction, notably of allyl-

silanes, is the main process in thermal decompositions at low pressure. This method of synthesis has revealed the existence of unstable compounds having silicon-carbon double bonds (e.g., silabenzenes, silabutadienes, silafulvenes, 2H-siloles, etc.), which dimerize or isomerize. Thus the formation of 1H-siloles having silicon-hydrogen bond from intermediary 2H-siloles is at the moment the only way of synthesizing such compounds.[105,113] Obviously, these studies open up extremely interesting possibilities in the field of group 14 metalloles.

VII. Addendum

Electrophilic Reaction of Allyltrimethylsilane with Nitriles in the Presence of Boron Trichloride.[127]

Allyltrimethylsilane reacts with various nitriles in the presence of BCl_3 giving, after hydrolysis, β,γ-unsaturated ketones. In the case of prenyltrimethylsilane only the H–ene reaction takes place.

Enophilic Activity.[128]

Recent results in the enophilic activity of unsaturated silicon and germanium compounds are given in ref 128. (cf. section IIIB).

The Effect of the Trimethylsilyl Group on the Regiochemistry of the Ene Reaction.[129]

The Me_3Si group in a vinylsilane has been found to have a profound effect on the regiochemistry of the intramolecular ene reaction.

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