# Silylketenes. A bird's eye view

Agnès Pommier,[a,b] **Philip Kocienski**[b] **and Jean-Marc Pons**[a]

[a] *Laboratoire de Réactivité en Synthèse Organique (RéSo), UMR CNRS 6516, Faculté de St-Jérôme, boite D12, F-13397 Marseille Cedex 20, France*
[b] *Department of Chemistry, University of Glasgow, Glasgow, UK G12 8QQ*

Covering: up to the end of 1996

1   Introduction and history

Nearly a hundred years ago, in 1905, Staudinger reacted chlorodiphenylacetyl chloride with zinc:[1] he had discovered the first ketene, diphenylketene (**Scheme 1**).
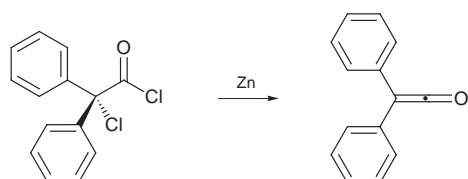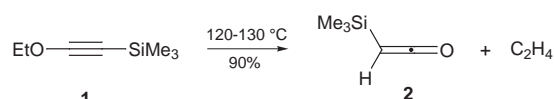

Scheme 1

The high synthetic value of such compounds was soon acknowledged, as these compounds are involved in a number of important reactions, the [2 + 2] cycloaddition with imines, leading to β-lactams, being one of the better known. The first review on the topic was Staudinger's book,[2] and the latest, Tidwell's,[3] was published three years ago. Meanwhile, a number of reviews have been published.[4–10]

Silylketenes are far more recent: the first one, trimethyl-silylketene **2**,[11] was discovered thirty years ago by Shchukov-skaya, who obtained it by pyrolysis of ethoxy(trimethyl-silyl)acetylene **1** (**Scheme 2**).[12]

Scheme 2

Since then, many different silylketenes have been prepared by various approaches and have been involved in a large number of reactions. However, to the best of our knowledge, with the exception of a chapter (ch. 4.5) in Tidwell's book,[3] only short reviews on silylketenes exist.[11,13–15] In this review, we will first examine the structure of these ketenes, then the methods of preparation, and lastly, their reactivity.

2   Structure—stability

2.1   Structure—spectroscopic studies

Trimethylsilylketene was first described as a 'tautomeric' mixture of trimethylsilylketene **2** and trimethylsilyloxyacetylene **3**.[12] However, spectroscopic studies soon established that the ketene structure was the only one involved (**Scheme 3**).[16,17]

Scheme 3

Indeed, the ^1H NMR spectrum of diethylsilylketene (Et_2-$HSiCH_a=C=O$) displays for proton H_a a doublet at δ 1.65. Such a chemical shift could fit with an acetylenic structure but the doublet multiplicity only accounts for the ketenic structure. **Table 1** collects a selection of ^1H and ^{13}C NMR and IR data for various silylketenes.

^{17}O and ^{29}Si NMR data of various silylketenes including tri-methylsilylketene (δ_O 255.0, δ_{Si} −0.2) were also recorded by Tidwell in a study devoted to the stability of this class of ketenes (*vide infra*).[23]

Two X-ray structures of silylketenes are known: EtS(Ph₃-Si)C=C=O[24] (**Fig. 1**) and [Cp₂Th(Cl)O][(Me₃Si)₃Si]C=C=O (*vide infra*).[25]

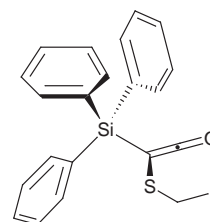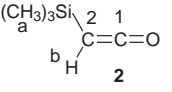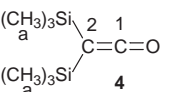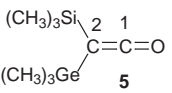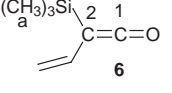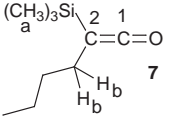**Fig. 1**

Table 1 Selected ^{1}H and ^{13}C NMR and IR data of silylketenes **2**, **4**–**6**

Ketene	ν_{max}/cm^{-1}	δ_H (ppm)	δ_C (ppm)
(CH₃)₃Si C=C=O, H **2**	2130[a]	H$_a$: 0.12 (s)[a] H$_b$: 1.65 (s)[a]	C1: 179.5[a] C2: −0.3[a]
(CH₃)₃Si C=C=O (CH₃)₃Si **4**	2085[b]	H$_a$: 0.25 (s)[b]	C1: 166.8[c] C2: 1.7[c]
(CH₃)₃Si C=C=O (CH₃)₃Ge **5**	2050[c]		C1: 166.2[c] C2: 0.5[c]
(CH₃)₃Si C=C=O **6**	2085[d]	H$_a$: 0.25 (s)[d]	C1: 183.7[d] C2: 22.3[d]
(CH₃)₃Si C=C=O, H$_b$ H$_b$ **7**	2010[e]	H$_a$: 0.00 (s)[e] H$_b$: 2.1–1.6 (m)[e]	C1: 182.6[e] C2: 13.0[e]

[a] Ref. 18. [b] Ref. 19. [c] Ref. 20. [d] Ref. 21. [e] Ref. 22.

Moreover, Tidwell recently described the crystal structure of a twisted tetraketene (*vide infra*).[26]
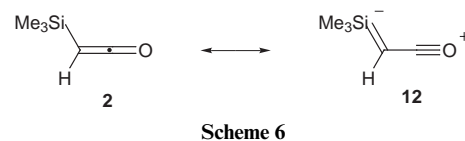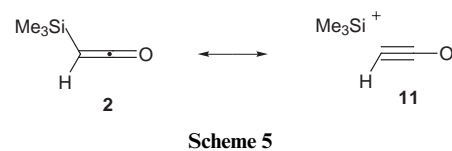
2.2 Stability

Silylketenes are remarkably stable compounds when compared to other ketenes. Particularly, they do not easily dimerize and therefore can be stored for a protracted period of time[12] (we have used successfully trimethylsilylketene which has been stored at −20 °C for over a year). Thus, triethylsilylketene **8**, when heated at 150–200 °C over 35 h, only led to 30–40% of allene **10** which most probably resulted from the decarboxylation of diketene **9** (**Scheme 4**).[27]

Scheme 4
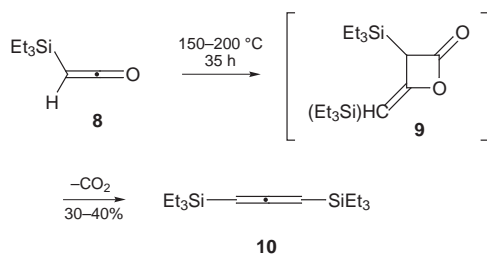
This stability towards dimerization is supported by semi-empirical AM1 calculations. Indeed, we have established that the calculated activation energy for silylketene dimerization is at least 10–15 kcal mol^{-1} higher than for chloro-, dichloro- or cyanochloro-ketenes.[28] Silylketenes are also stable towards hydration under neutral conditions (*vide infra*) and Tidwell reported *ab initio* calculations in good agreement with the experiments.[29,30]

Two explanations were originally made to account for the influence of silyl substituents on this dramatic stability. Brady proposed that it was due to hyperconjugative σ–π donation from the Si–C bond into the in-plane carbonyl π-orbital as shown in structure **11** (**Scheme 5**).[31]

By contrast, Runge, based on CNDO/S calculations, suggested that back-donation from the ketene π-system to the d-orbitals of the silicon occurred (*i.e.* silicon acted as a dπ–pπ electron acceptor) as shown by structure **12** (**Scheme 6**).[32]

Scheme 5

Scheme 6

Ab initio calculations devoted to substituent influence on ketene stability led Tidwell to propose that the stability of silylketenes resulted from the electropositivity of the silicon atom.[29,30] However, these studies failed to distinguish between the Brady–Runge proposals. A subsequent NMR study on ^{13}C, ^{17}O and ^{29}Si, performed by the same authors,[23] showed a decreased negative charge on the silicon and an increased negative charge on the carbonyl carbon and oxygen when compared to non-silylated ketenes and silylated alkenes, *i.e.* a charge distributed in favour of resonance structure **11** (Scheme 5).

3 Preparation

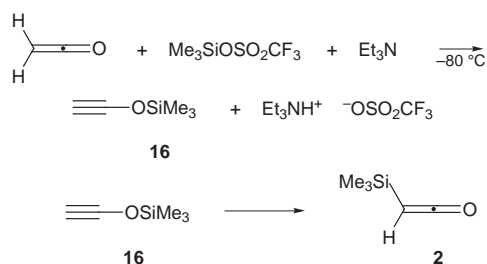### 3.1 Trialkylsilylketenes: R₃SiHC=C=O
3.1.1 Thermolysis
As already mentioned, the first synthesis of a silylketene is due to Shchukovskaya *et al.*, who reported in 1965 the preparation of trimethylsilylketene from ethoxytrimethylsilylacetylene under pyrolysis conditions (Scheme 2).[12] Trimethylsilylketene **2** or trialkylsilylketenes such as **15** can also be prepared from other alkoxy(trialkylsilyl)acetylenes such as isopropoxy- and *tert*-butoxy-(trialkylsilyl)acetylenes. Valenti *et al.* even established that the preparation of ketene **15** from *tert*-butoxy(*tert*-butyldiphenylsilyl)acetylene **13** only required a temperature of 80 °C instead of 130 °C for the ethoxy equivalent (**Scheme 7**).[18]

Scheme 7
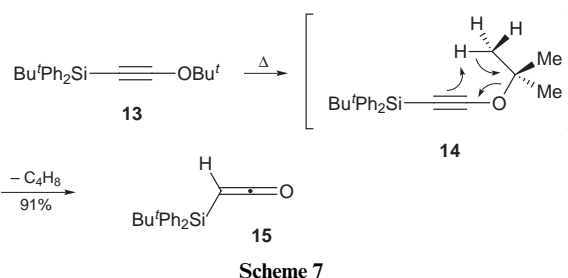
The same method has been used to prepare various other silylketenes, such as trichlorosilyl-, triethylsilyl- and diethylsilyl-ketenes.[16] Trimethylgermyl- and triethylgermyl-ketenes,[33] and (−)-methyl(1-naphthyl)phenylsilylketene,[34] the first optically active silylketene described, were also prepared following a similar procedure. Moreover, trialkylsilylalkoxyalkynes were also proposed as intermediates during the preparation of trialkylsilylketenes upon both retro-Diels–Alder reactions of silylethenoanthracene enol ethers[35] and thermolysis of 2-trimethylsilyl-4,5-dihydrofuran.[36]

The reaction is said to proceed *via* a six-membered ring transition state such as **14** (Scheme 7) which accounts for the H transfer and the formation of both the ketene and the alkene. Semi-empirical calculations on the parent non-silylated system were reported in 1987 by Moyano and Pericas.[37] More recently, we studied the same reaction at an *ab initio* level and found very similar results even for the formation of silylketene.[38] Calculations predict a rather synchronous concerted reaction path and were in good agreement with the substituent effect reported by Valenti.[18]
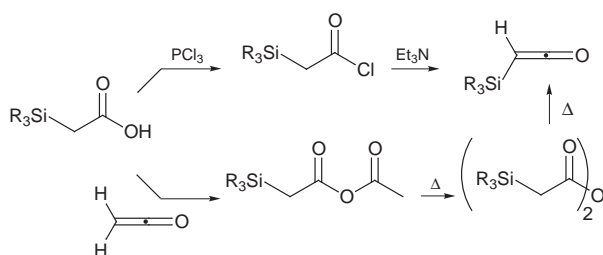
Finally, trimethylsilylketene **2** was also prepared from ketene, trimethylsilyl triflate and triethylamine in 63% yield, the last step being the rearrangement of trimethylsilyloxyacetylene **16** (**Scheme 8**).[39] This 1,3-silicon transfer has also been studied recently from a theoretical point of view (*ab initio* calculations) and the transfer is predicted to occur with retention of configuration rather than inversion.[40]

H₂C=C=O + Me₃SiOSO₂CF₃ + Et₃N →(−80 °C)

≡—OSiMe₃ + Et₃NH⁺ ⁻OSO₂CF₃
16

≡—OSiMe₃ → Me₃Si–CH=C=O (H)
**16** → **2**

Scheme 8

3.1.2 Other methods

More classical methods, such as the dehydrohalogenation of an acyl chloride promoted by triethylamine or the thermolysis of an anhydride, have also been used in silylketene preparation (**Scheme 9**).[41–43]

R₃Si–CH₂–CO₂H →(PCl₃) R₃Si–CH₂–COCl →(Et₃N) R₃Si–CH=C=O

+

H₂C=C=O + R₃Si–CH₂–CO–O–CO–CH₃ →(Δ) (R₃Si–CH₂–CO)₂O →(Δ) R₃Si–CH=C=O

Scheme 9

Photolysis (λ > 347 nm) of acylsilane **17** in absolute MeCN affords a 1:1 mixture of ketone **18** and *tert*-butyldimethylsilylketene **19** in 93% yield. Interestingly thermolysis of **17** leads to **18** and *tert*-butyldimethylsilyloxyacetylene but not to *tert*-butyldimethylsilylketene **19** (**Scheme 10**).[44]

17 →(hv, MeCN, 93%) **18** + **19**

18 : 19 = 1 : 1
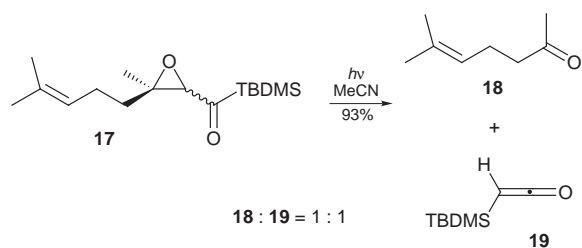
Scheme 10

Trimethylsilylacetic acid **20**, upon treatment with dicyclohexylcarbodiimide (DCC) and a catalytic amount of triethylamine, gives trimethylsilylketene **2** in 63% yield (**Scheme 11**).[45]

TMS–CH₂–CO₂H →(DCC, Et₃N, Et₂O, 0 °C, 63%) TMS–CH=C=O
20 → **2**
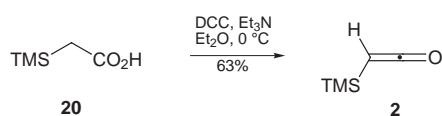
Scheme 11

Lastly, trimethylsilylketene was also prepared upon reaction between boron halides and trialkyltin(trialkylsilyl)acetic acids.[46]

### 3.2 Bis(trialkylmetal)ketenes: R₃M(R′₃M′)C=C=O

The first bis(trimethylmetal)ketenes were isolated as by-products of the preparation of trialkylsilylketenes or trialkyl-

germylketenes[33,47] and since then various others have been prepared on purpose with good yields. Indeed, upon treatment with trialkylmetal bromide in the presence of MgBr₂ alkoxy-(trialkylmetal)alkynes lead to a wide variety of dimetallated ketenes, either mixed or not (**Scheme 12**).[48,49] (Similarly, the reaction between sterically hindered ynol ethers and trialkylmetal halides leads to the corresponding ketenes.[50])

ER₃–C≡C–OR′ →(R₃E′Br, MgBr₂) R₃E(R₃E′)C=C=O

E = E′ = Si, Ge, Sn
E = Si; E′ = Ge, Sn
R = Me, Et, Pr; R′ = Et, Bu
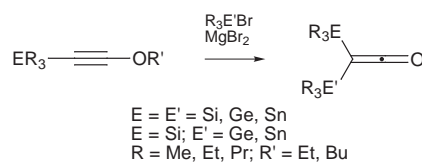
Scheme 12

Trimethylsilylethoxyacetylene reacts with boron halides at −50 °C to form (dihaloboryl)(trimethylsilyl)ketenes (**Scheme 13**). The same reaction can occur from bromobis(dimethylamino)borane to yield bis(dimethylamino)(trimethylsilyl)-ketene.[51] Dihaloboryl(trimethylsilyl)ketenes can further be transmetallated to tri-*n*-butylstannyl(trimethylsilyl)ketene under the action of an excess of methoxytri-*n*-butylstannane.[52]

TMS–C≡C–OEt →(BBr₃, pentane, −50 °C) [TMS(Br₂B)C=C(OEt)(Br)] →(67%) TMS(Br₂B)C=C=O + EtBr
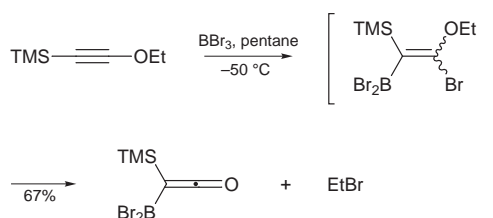
Scheme 13

Arsinosilylketenes are formed from silylmethoxacetylenes and chlorodiphenylarsine (**Scheme 14**).[53]

MePh₂Si–C≡C–OMe →(ClAsPh₂, MeCN, 81%) MePh₂Si(Ph₂As)C=C=O + MeCl
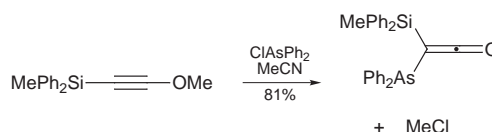
Scheme 14

An alternative method relies upon the trapping and further 1,3-silicon rearrangement of dilithio ynolate **22**, prepared either from 3,4-diphenylisoxazole[54] or 2,3-dihydrofuran **21**,[55] with a trialkylsilyl chloride. Thus bis(trimethylsilyl)ketene **4** was prepared in 65% yield from 2-phenyl-2,3-dihydrofuran **21** (**Scheme 15**). The same rearrangement was used to prepare bis(trimethylsilyl)ketene from trimethylsilylketene, trimethylsilyl triflate and triethylamine.[39]

21 →(BuLi / THF) H–C≡C–OLi + Ph–CH=CH₂ →(BuLi)

Li–C≡C–OLi →(Me₃SiCl, 65%) Me₃Si(Me₃Si)C=C=O
22 → **4**
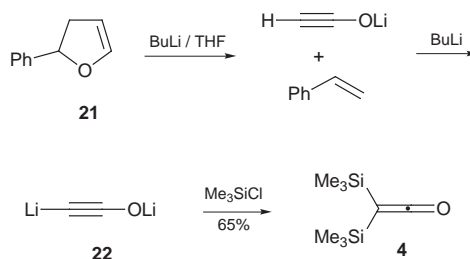
Scheme 15

Ethyl (trimethylsilyl)acetate **23** treated with LDA and chlorotrimethylgermane leads to ethyl (trimethylsilyl)(trimethylgermyl)acetate **24**, which can be transformed into trimethylgermyl(trimethylsilyl)ketene **5** (**Scheme 16**).[56]

Scheme 16

Me₃SiCH₂CO₂Et **23** → (i. LDA / Et₂O, ii. Me₃GeCl, 79%) → Me₃Si–C(Me₃Ge)–CO₂Et **24**

LDA / Et₂O, 63% → Me₃Si(Me₃Ge)C=C=O **5**
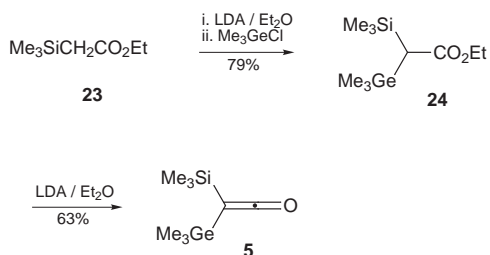
Bis(trialkylsilyl)ketenes were also prepared from trialkylsilylketenes upon treatment with BuⁿLi at low temperature and trialkylsilyl chlorides [19,57,58] and from *tert*-butyl bis(trimethylsilyl)acetate **25** upon treatment with LDA.[59] In the latter case, ester enolate **26** is formed primarily and then decomposes into bis(trimethylsilyl)ketene **4** (**Scheme 17**).
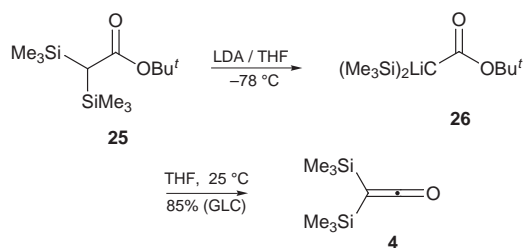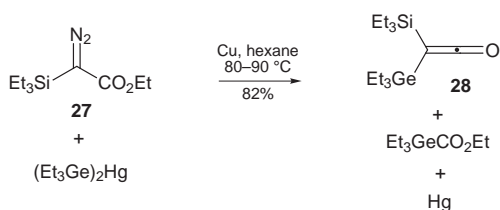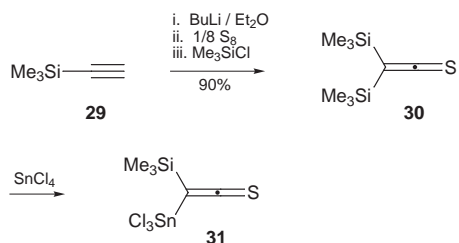
Scheme 17

Me₃Si–CH(SiMe₃)–C(=O)OBuᵗ **25** → (LDA / THF, −78 °C) → (Me₃Si)₂LiC–C(=O)OBuᵗ **26**

→ (THF, 25 °C, 85% (GLC)) → (Me₃Si)₂C=C=O **4**

Lastly, thermal or photochemical decomposition of α-diazo-α-silyl carbonyl compounds leads, depending on the reaction conditions, either to bis(trialkylsilyl)ketenes [60–64] or to mixed ketenes.[65,66] Copper catalyzed thermolysis of diazo compound **27** in the presence of bis(triethylgermyl)mercury leads to the formation of dimetallated ketene **28** (**Scheme 18**).[67]

Scheme 18

Et₃Si–C(N₂)–CO₂Et **27** + (Et₃Ge)₂Hg → (Cu, hexane, 80–90 °C, 82%) → Et₃Si(Et₃Ge)C=C=O **28** + Et₃GeCO₂Et + Hg

Trimethylsilylacetylene **29** can be converted in 90% yield into bis(trimethylsilyl)thioketene **30** *via* a three step sequence. Ketene **30** can then be transformed into trichlorostannyl(trimethylsilyl)thioketene **31** upon treatment with tetrachlorotin (**Scheme 19**).[68]
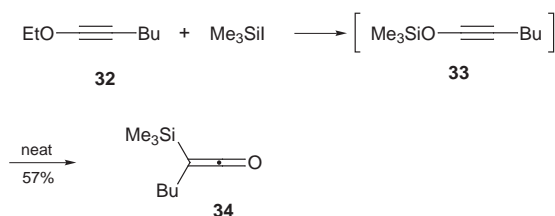
Scheme 19

Me₃Si–C≡CH **29** → (i. BuLi / Et₂O, ii. 1/8 S₈, iii. Me₃SiCl, 90%) → (Me₃Si)₂C=C=S **30**

→ (SnCl₄) → Me₃Si(Cl₃Sn)C=C=S **31**

3.3 Aryl-, alkyl- and alkoxy- and phosphorus-substituted (trialkylsilyl)ketenes: R₃Si(X)C=C=O

3.3.1 Thermolysis

Alkyl(trimethylsilyl)ketenes can be obtained through the thermal rearrangement of trialkylsilyloxyalkynes, the latter being prepared upon treatment of the corresponding alkoxyalkynes

with trimethylsilyl iodide.[69–71] Thus Sakurai prepared *n*-butyl(trimethylsilyl)ketene **34** in 57% yield from ethoxyhexyne **32** and trimethylsilyl iodide, probably *via* intermediate trimethylsilyloxyhexyne **33** (**Scheme 20**).[22]

Scheme 20

EtO–C≡C–Bu **32** + Me₃SiI → [Me₃SiO–C≡C–Bu **33**]
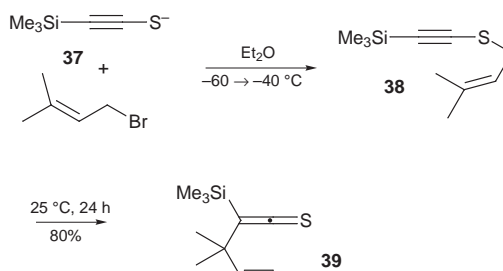
→ (neat, 57%) → Me₃Si(Bu)C=C=O **34**

This method was extended to various alkyl(trialkylmetal)ketenes.[50] Trialkylsilyloxyalkyne intermediates can also be generated, as already mentioned, by a Diels–Alder reaction of ethenoanthracene silyl enol ether,[35] or by the trapping of lithium ynolate by trimethylsilyl chloride.[54,72,73]

Similarly, diisopropylphosphino(trimethylsilyl)ketene **36** was prepared upon treatment of diisopropylphosphino(ethoxy)acetylene **35** with trimethylsilyl iodide (**Scheme 21**).[74] Further similar reactions were also reported by the same authors.[75,76]

Scheme 21

Prⁱ₂P–C≡C–OEt **35** → (Me₃SiI, CH₂Cl₂, Et₂O, 70%) → Prⁱ₂P(Me₃Si)C=C=O **36**
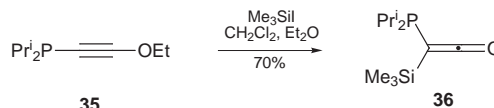
Alkenyl(trimethylsilyl)thioketene **39** was prepared through a thio-Claisen rearrangement of trimethylsilylalkynyl(allyl)sulfide **38** obtained from the reaction of trimethylsilyl alkynylthiolate **37** with dimethylallyl bromide (**Scheme 22**).[77] Trimethylsilyl(allyl)selenoketenes were also prepared following the same kind of procedure.[78]

Scheme 22

Me₃Si–C≡C–S⁻ **37** + (allyl bromide) → (Et₂O, −60 → −40 °C) → Me₃Si–C≡C–S–(allyl) **38**

→ (25 °C, 24 h, 80%) → **39**

3.3.2 Decomposition of diazo compounds

Thermal[79] or photochemical[60,63,80,81] decomposition of trialkylsilyldiazoacetates and trialkylsilyldiazoacetones leads to aryl-,[82] alkyl- and alkoxy-(trialkylsilyl)ketenes. Such a decomposition involves a Wolff rearrangement leading either to ketene **40** or to silene **41** which then isomerizes to ketene **42** (**Scheme 23**).
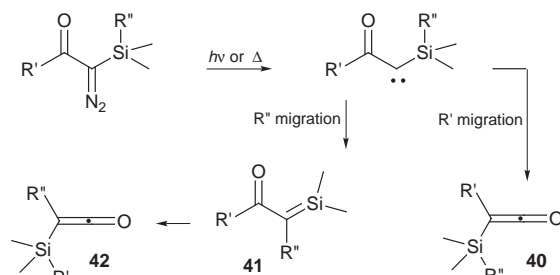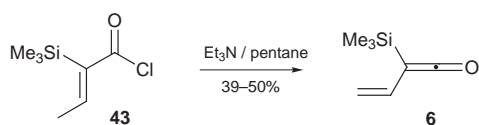
Scheme 23

This isomerization of silene into ketene was clearly established by Ando during a study dealing with the photolysis of pentamethyldisilanyldiazoacetate.[83,84] The photolysis of diazo-(pentamethyldisilanyl)methyl ketones in the presence of carbonyl compounds has been discussed by Maas.[62]

Monogermyl ketenes of formula R(Et$_3$Ge)C=C=O have also been prepared by the Wolff rearrangement of carbenoids Et$_3$GeCCOR, generated by the copper-catalyzed decomposition of the corresponding α-(triethylgermyl)diazo ketones in hexanes.[67]

3.3.3 Other methods

Dehydrohalogenation methods can also be used to prepare metalloketones. Thus phenyl(trimethylsilyl)acetyl chloride leads, in the presence of zinc, to phenyl(trimethylsilyl)ketene,[85] and (Z)-2-trimethylsilylbut-2-enoyl chloride **43** reacts with triethylamine to give vinyl(trimethylsilyl)ketene **6** (**Scheme 24**).[21,86] The same method was also used to prepare bromo(trimethylsilyl)-ketene.[87]

Scheme 24

Less classical methods are also reported. Thus vinyl(trimethylsilyl)ketenes were prepared by chromium complex-promoted olefination and carbonylation of alkynes[88,89] and ethoxy- and ethylthio-(triphenylsilyl)ketenes were obtained upon thermal decomposition of complexes (CO)$_5$WC(XEt)Si-Ph$_3$.[90,91] Thus ethylthio(triphenylsilyl)ketene **45** was obtained along with complex **44** in which the ketene is S-coordinated to a W(CO)$_5$ moiety. The structure of ketene **45** was established by X-ray diffraction (Fig. 1 and **Scheme 25**).[24]
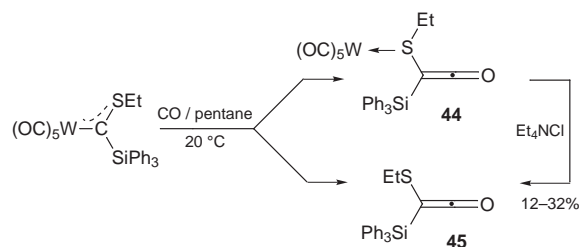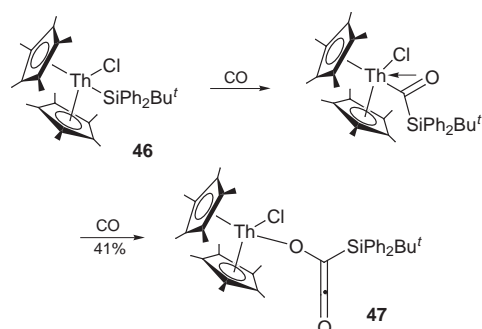
Scheme 25

Tilley describes the isolation of the first crystalline metalloxy ketene complex **47** obtained *via* 'double insertion' of carbon monoxide into the thorium–silicon bond of complex **46** (**Scheme 26**).[25] The same authors had previously worked on a tantalum analog, but without isolating it.[92]

2-Amidino silylketenes **50** were also proposed as intermediates during the reaction between N,N',N'-trimethyl-N-(trimethylsilylethynyl)hydrazine **48** with aryl isocyanates **49**[93] (**Scheme 27**) and a tetrakis(trimethylsilyl)allenylketene was detected in an argon matrix during the formation of tetrakis-(trimethylsilyl)butatriene.[94]

3.4 Bis(trialkylsilylketenes)

This particular class of compounds has been studied extensively by Tidwell, who recently published three reviews on the topic.[95–97] These compounds can be obtained by photolysis or thermolysis of silylated cyclobutenediones.[98] Thus 2,3-di(*tert*-butyldimethylsilyl)buta-1,3-diene-1,4-dione [or bis(*tert*-butyldimethylsilylketene)] **52** was prepared by photolysis in 92% yield from 3,4-disilylcyclobut-3-ene-1,2-dione **51** (**Scheme 28**).[99] More recently, Tidwell has carried out further studies on this

Scheme 26
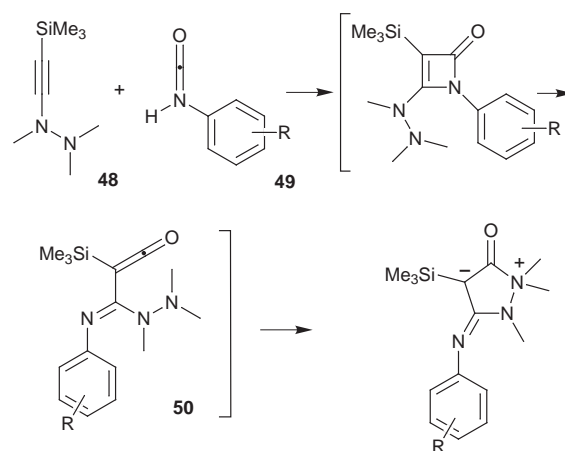
Scheme 27
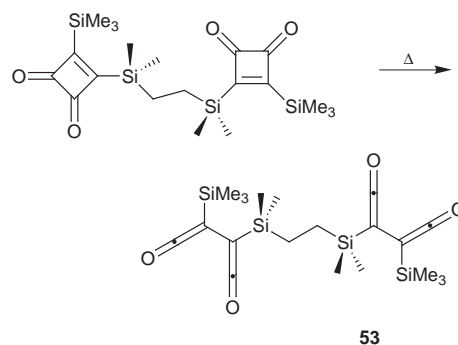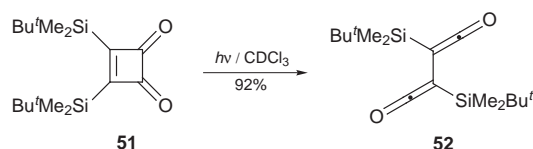
Scheme 28

class of silylketenes[100–108] and even extended them to 1,3-bis-ketene and trisketene,[109] and to tetraketenes **53**[26,110] (Scheme 28).

4 Reactivity

4.1 Nucleophilic addition

4.1.1 Heteroatomic nucleophiles

Hydration of silylketenes has been widely studied.[12,34,49,99] Under neutral conditions, hydration of trimethylsilylketene is slower than hydration of alkylketene;[29] however, under acidic or basic conditions, the reactivity of silylketene is significantly increased. Such behavior can be accounted for by the ability of silicon to stabilize an α negative charge (basic conditions) or a β positive charge (acidic conditions) in accord with calculations.[30] Silylketenes react with alcohols,[12,34,79,99,111–113] amines[12,112,114] or

hydroxylamines,[115] yielding the corresponding esters or amides. The condensation of *o*-acylphenols with trimethylsilylketene, followed by cyclization of the resultant α-silylcarboxylates, and a final elimination provides a one-pot preparation of various substituted coumarins.[116]

Recently Murai and Kato prepared aliphatic selenoamides from intermediate selenoketenes obtained by treatment of alkylselenoates with an acid and secondary amines.[117]

The use of Lewis acids such as BF$_3$–Et$_2$O,[112] ZnCl$_2$ or ZnI$_2$[118] results in a significant increase of the rate of addition of alcohols to silylketenes. Thus Kita prepared various α-silylacetates, such as **54**, with excellent yields (**Scheme 29**).[118] This kind of reaction was also catalyzed using a commercially available lipase isolated from *Rhizopus japonicus*.[119]
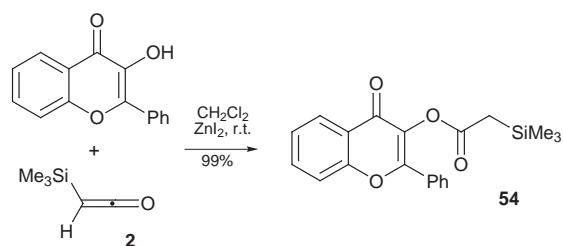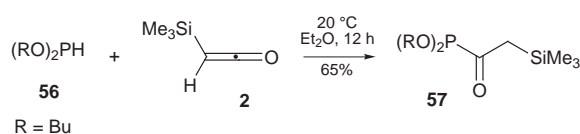

Scheme 29

Less common nucleophiles such as alkoxytributyltins,[120,121] phosphines and phosphites[122,123] and even silylphosphines[124] have also been added to silylketenes. The latter case is illustrated by the preparation of 2-phosphabuta-1,3-diene **55** (**Scheme 30**).[125]
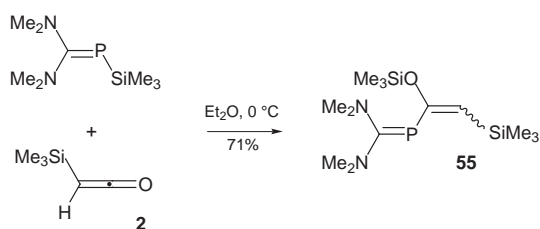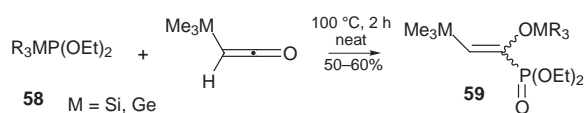

Scheme 30

Dibutoxyphosphine **56** reacts at room temperature with trimethylsilylketene **2** to yield dibutyl [(trimethylsilyl)acetyl]phosphonite **57** (**Scheme 31**).[126]
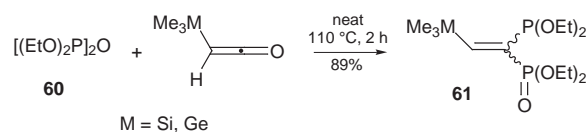

Scheme 31

Silyl and germyl diethyl phosphonites **58** react with metallated ketenes to yield the corresponding diethyl [2-(trialkylmetal)-1-(trialkylmetalloxy)vinyl]phosphonates **59** in 50–60% yields (**Scheme 32**).[127]
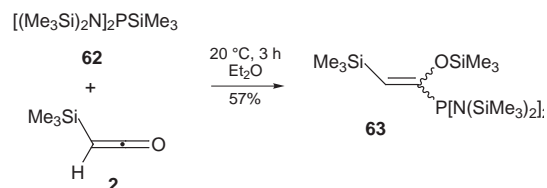

Scheme 32

Tetraethyl pyrophosphite **60** reacts with trimethylsilyl- or trimethylgermyl-ketene at 110 °C in the absence of solvent to yield adducts **61** in 89% yield[127] (**Scheme 33**) and bis[bis(trimethylsilyl)amino]trimethylsilylphosphine **62** reacts smoothly

Scheme 33

with trimethylsilylketene **2** to give vinyldiaminophosphine **63** in 57% yield (**Scheme 34**).[128]

Scheme 34

Lastly, addition of bromine to trimethylsilylketene leads to bromo(trimethylsilyl)acetyl bromide.[12]

4.1.2 Carbon nucleophiles

The reaction of trimethylsilylketenes with strong bases leads to ketones or to silyl enol ethers (depending on the reaction conditions). Thus, upon treatment with Bu^{n}Li, bis(trimethylsilyl)ketene leads after an acidic work-up to the corresponding ketone,[19] and so does bis(trimethylgermyl)ketene in the presence of MeLi.[129] However, treatment of ketene **64** with Bu^{n}Li, followed by an addition of trimethylsilyl chloride, leads to the formation of vinyl silyl ether **65** as a single (*Z*)-stereoisomer (**Scheme 35**).[130]
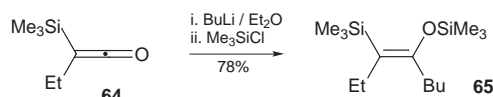
Scheme 35

Similarly, the addition of organocerium reagents to silylketene leads, depending on the electrophile involved, to various ketones such as **66** or **67** (**Scheme 36**).[131]
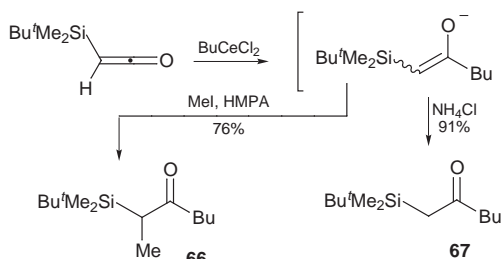
Scheme 36

Disilylketenes react with organolithiums to yield silylacetylene derivatives. The reaction proceeds through the formation of α,α-disilyl enolates which undergo Peterson-type elimination to yield the acetylene derivatives (**Scheme 37**).[132]
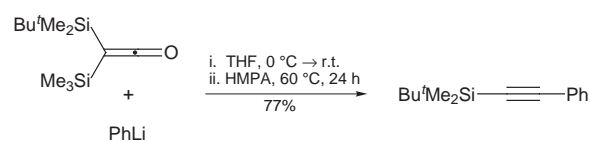
Scheme 37

Enamine **68** reacts with *tert*-butyldimethylsilylketene to yield 2-(*tert*-butyldimethylsilylacetyl)cyclohexanone **69** in 70% yield (**Scheme 38**).[133]
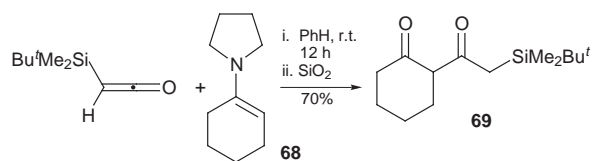
Scheme 38

Lastly, silylketene acetals,[134] cyanotrimethylsilane[135] and ynamines[136] also react with trialkylsilylketenes. Hence, ynamine **70** reacts with silylketene **71** to yield silylacetylene **73**, obtained through allene-acetylene rearrangement of **72** (**Scheme 39**).

Scheme 39

4.2 Addition-elimination

Stabilized phosphorus ylides react with trimethylsilylketene to give a Wittig olefination product. Thus, in the presence of ylide **74**, trimethylsilylketene **2** leads to the formation of allenic ester **75** in 85% yield (**Scheme 40**).[112]

Scheme 40

Kita later prepared various silylallenes from trimethylsilyl-ketene and stabilized ylides, and showed that less stable ylides such as **76** could also give reasonable yields of silylallenes like **78** when bis(trialkylsilyl)ketene **77** was used (**Scheme 41**).[137]

Scheme 41

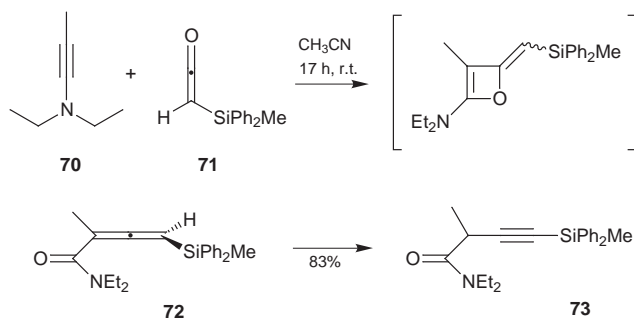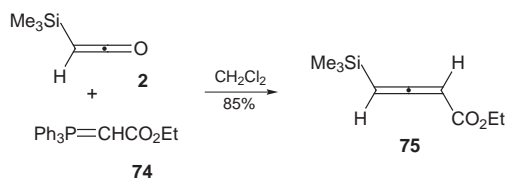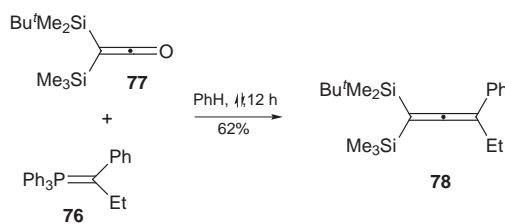In the presence of trimethylsilylketene, non-stabilized phosphorus ylides lead to complex mixtures of products, while stabilized sulfur ylides provide acylation products.[112]

N-[Bis(trimethylsilyl)methyl]-2-trimethylsilylethenimine **80** was prepared at room temperature from trimethylsilylketene and [bis(trimethylsilyl)methylimino]triphenylphosphorane **79** (**Scheme 42**).[138]

Trimethylsilylketene reacts with (*N*-aziridin-1-ylimino)tri-phenylphosphoranes **81** to give *N*-aziridin-1-yl-2-trimethyl-silylethenimines **82** (**Scheme 43**)[139] whilst silylphosphorane **83** and bis(trimethylsilyl)ketene **4** yield bis(trimethylsilyl)phospha-allene **84** with 40% yield (**Scheme 44**).[140] A similar aza-Wittig

CH(SiMe₃)₂ = BSM
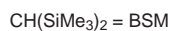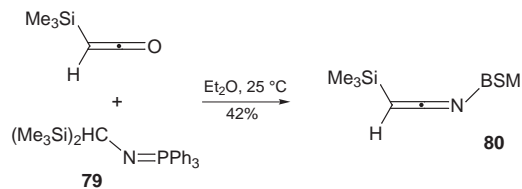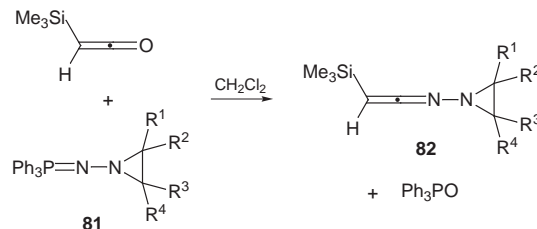
Scheme 42

Scheme 43
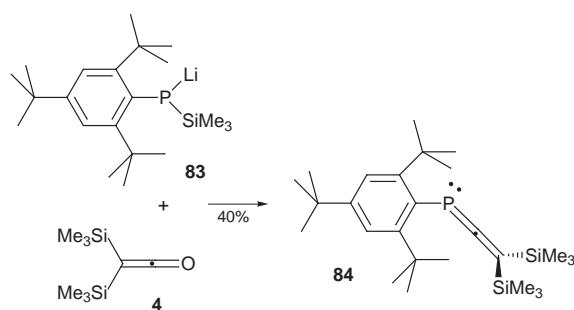
Scheme 44

reaction was recently used by Molina as a key-step in a synthesis of Aaptamine, an alkaloid of marine origin.[141]

4.3 Reactivity with diazo compounds

The reactivity of trialkylsilylketenes towards diazomethane has been extensively studied by Zaitseva and co-workers.[142–144] Thus trimethylsilylketene **2** reacts with diazomethane to give cyclo-propanone **85** or cyclobutanones **86** and **87** (depending on the stoichiometry), the former being formed as intermediates during the formation of the latter (**Scheme 45**).[145] However, when Brady applied this reaction to phenyl(trimethylsilyl)ketene, only cyclobutanones were isolated.[85]
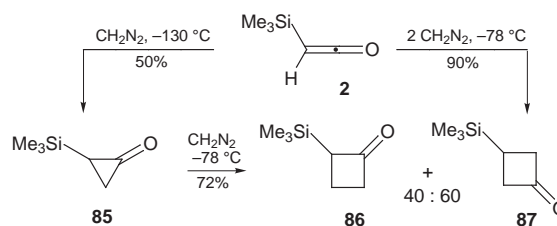
Scheme 45

Lastly, the condensation of silyldiazomethanes with silyl-ketenes[146–149] or germylketenes[149] stereoselectively leads to *cis*-dimetallated cyclopropanones as illustrated in **Scheme 46** by the preparation of *cis*-2,3-bis(diethylmethylsilyl)cyclopropanone **90**, from diethylmethylsilyldiazomethane **89** and diethylmethyl-silylketene **88**.[149] The decarbonylation of these *cis*-dimetallated cyclopropanones provides access to *Z*-dimetallated ethenes which then rearrange into the *E*-isomers (Scheme 46).[150]

It is noteworthy that thioketenes and selenoketenes do not react with diazo compounds in the same way. Indeed the initial [3 + 2] cycloaddition involves not the C=C bond of the
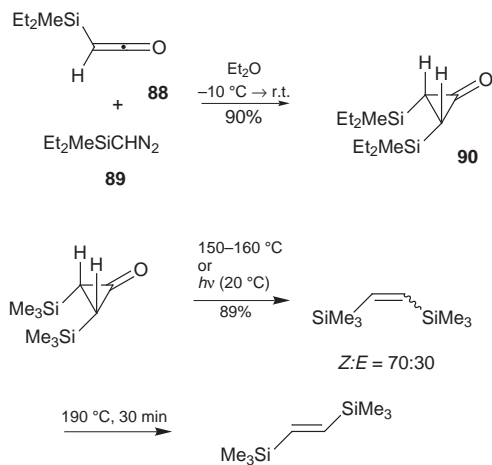
Scheme 46

Scheme 49

ketene but the C=X bond (X = S or Se). Thus, 2-alkylidene-1,3,4-thiadiazolines **93** and their selenium analogs **94** were obtained from thioketene **91** and selenoketene **92** respectively (**Scheme 47**).[151–153]

91 X = S   PhH, 13 h, 79%   93   *E* : *Z* = 10 : 1
92 X = Se Et$_2$O, 12 h, 60% 94
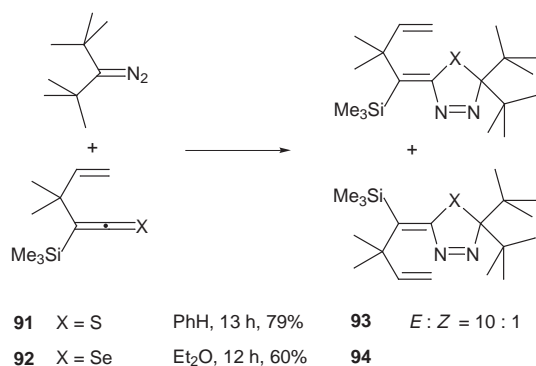
Scheme 47

Finally, Tidwell recently showed that silylated bisketene **95** and trimethylsilyl diazo compound **96** led to cyclopentene-1,3-dione **97** (**Scheme 48**).[106]
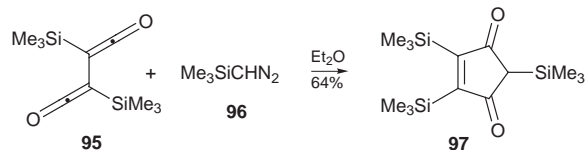
Scheme 48

4.4 [2 + 2] Cycloaddition reactions
4.4.1   Formation of β-lactones
The first [2 + 2] cycloaddition between a carbonyl compound and a silylketene was reported by Zaitseva and co-workers in 1975.[154] Thus in the presence of BF$_3$–Et$_2$O, trimethylsilylketene and benzaldehyde lead to a 2:1 mixture of *cis*- and *trans*-4-phenyl-3-trimethylsilyloxetan-2-one (**98** and **99**). After 6 h of heating at 50 °C the proportion of *trans*-isomer **99** diminishes. Distillation of the reaction mixture under reduced pressure leads to trimethyl(*trans*-styryl)silane **101** (13%) and *cis*-4-phenyl-3-trimethylsilyloxetan-2-one **98** (65%). The formation of trimethyl(*cis*-styryl)silane **100** requires heating of *cis*-oxetanone **98** up to 150–160 °C (**Scheme 49**).

Following these preliminary findings, Zaitseva,[155] and then Brady,[156] broadened the scope of the study to include cyclo-addition of silylketenes to various aldehydes and ketones. With trichloroacetaldehyde and tribromoacetaldehyde, the cyclo-addition leads predominantly, or even exclusively, to *trans*-

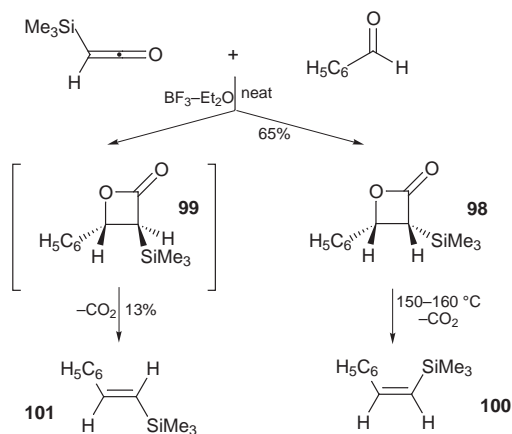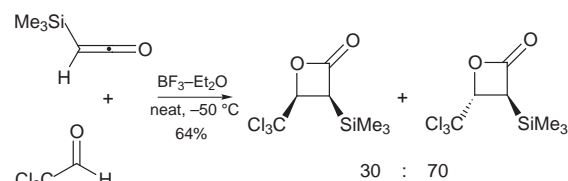isomers when chloromethyldimethylsilylketene is involved (**Schemes 50** and **51**).[155] With more common saturated aldehydes, the reaction yields a mixture in which the *cis*-β-lactone predominates; however, the stereoselectivity of the reaction is not very high (20% de), at least when BF$_3$–Et$_2$O is used (**Scheme 52**).[156]

Scheme 50
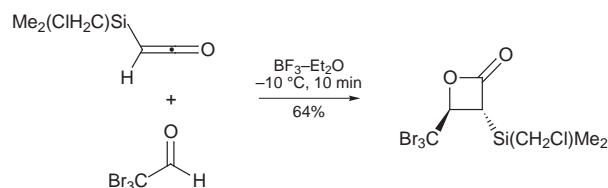
Scheme 51
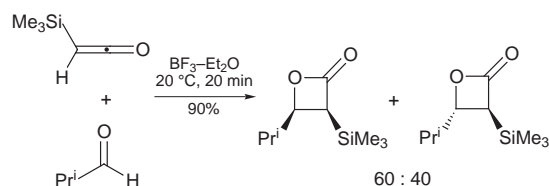
Scheme 52

More recently, Yamamoto and co-workers[157] showed that 100% de could be obtained in favor of the *cis*-isomer provided methylaluminium bis(4-bromo-2,6-di-*tert*-butylphenoxide) (MABR) was used instead of BF$_3$–Et$_2$O (**Scheme 53**).

Attempts to form and isolate β-lactones from α,β-unsaturated aldehydes and silylketenes have so far met with very little success. Brady showed that although β-lactones were formed and detected by IR, they underwent migration of the trimethylsilyl group from the carbon atom to the carbonyl oxygen atom followed by a ring opening of the β-lactone moiety, leading to the formation of the corresponding, α,β-unsaturated silyl esters. Thus trimethylsilyl β-styrylacrylates **103** and **104** were obtained from trimethylsilylketene and (*E*)-cinnamalde-hyde **102**[156] (**Scheme 54**). Similarly, Yamamoto obtained (*Z*)-alk-2-enoic acids from aromatic and α,β-unsaturated alde-hydes.[158] Finally, the formation of a β-hydroxy ester was reported from trimethylsilylketene and benzaldehyde in the presence of (EtO)$_2$Sn.[159]

Scheme 53
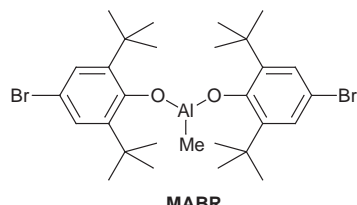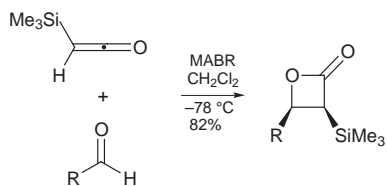
Scheme 54
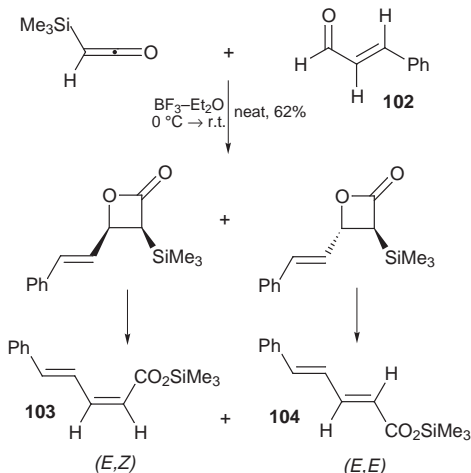
Scheme 56

Scheme 57

Scheme 58

Among the various ketones (acetone, butanone, cyclohexanone, pinacolone, acetophenone) tried, only acetone gave results. Thus, the IR spectrum of the reaction mixture after 10 h at 50 °C showed the presence of an oxetan-2-one (1830 cm^{-1}) along with an α,β-unsaturated ester (1700 and 1650 cm^{-1}). Distillation of the crude product led exclusively to trimethylsilyl but-2-enoate **105** in only 28% yield (**Scheme 55**).[155] Slightly better results were obtained with 1,1,1-trifluoroacetone **106** and trimethylsilylketene **2** in the presence of BF$_3$–Et$_2$O (**Scheme 56**).[160] However, trimethylsilylketene **2** reacts with hexafluoroacetone **107** even without Lewis acid catalysis, and leads after 15 d at 0 °C to 3-trimethylsilyl-4,4-bis(trifluoromethyl)oxetan-2-one **108** along with 3-trimethylsilyl-4-(3,3,3-trifluoro-2-trifluoromethyl-2-trimethylsilyloxypropylidene)oxetan-2-one **110**. The authors explain the formation of the latter by a mechanism involving the *in situ* formation of ketene **109** (**Scheme 57**).[160]

Scheme 55

This peculiar reactivity has initiated a study on the reactivity between silylketenes and various ketenes, such as bis(trifluoromethyl)ketene, diphenylketene and ethyl(trialkylsilyloxy) ketenes. In every case, the substituted diketenes were obtained
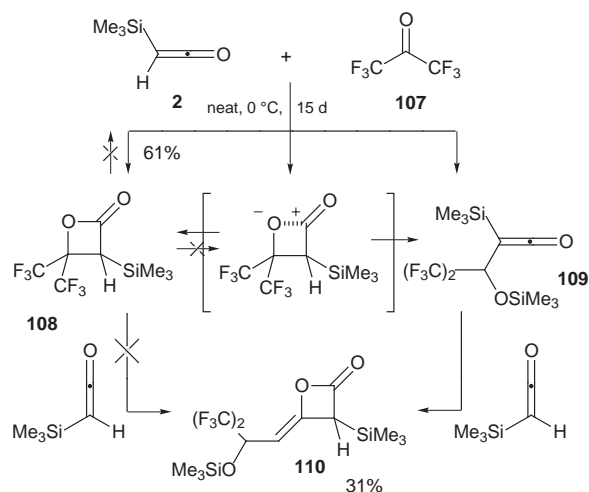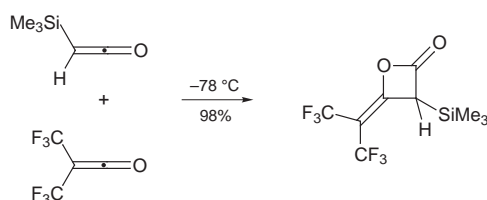
in excellent yields as shown in the example depicted in **Scheme 58**.[160]

β-Lactones prepared by [2 + 2] cycloaddition reactions between a silylketene and an aldehyde have also been used as intermediates, and in total synthesis. Thus, Mead prepared α-trimethylsilyl-β-lactones as precursors of tetrahydrofurans[161,162] (**Scheme 59**), Black used the same molecules for carbonyl homologation as a non-basic alternative to the Wittig reaction[163] and we reported total syntheses of lipstatin **114**[164,165] and its tetrahydro derivative,[166,167] both inhibitors of pancreatic lipase, based on the reaction between a chiral β-silyloxy aldehyde **112** and n-hexyl(trimethylsilyl)ketene **111**. A precursor β-lactone **113** of lipstatin **114** was obtained with over 80% de (1,3-diastereoselectivity) (**Scheme 60**).
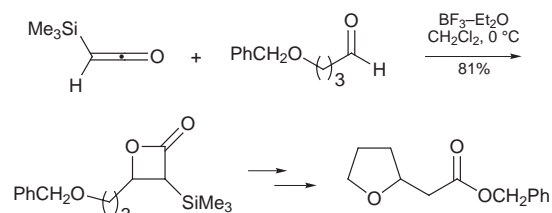
Scheme 59

Romo reported very high 1,2-diastereoselectivity for the reaction between benzyloxy aldehydes and trimethylsilylketene under magnesium bromide catalysis (**Scheme 61**).[168]

More recently, we obtained the β-lactone **117** with 83% ee from trimethylsilylketene and aldehyde **115** under the catalysis of 0.3 equiv. of chiral Lewis acid **116** (**Scheme 62**).[169]

Scheme 60
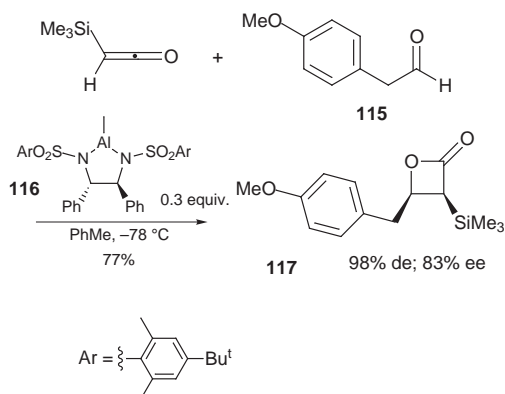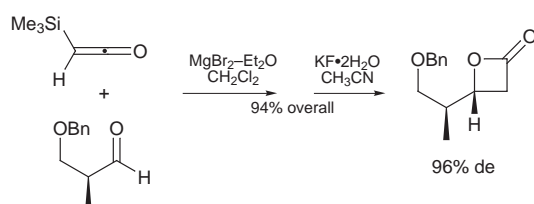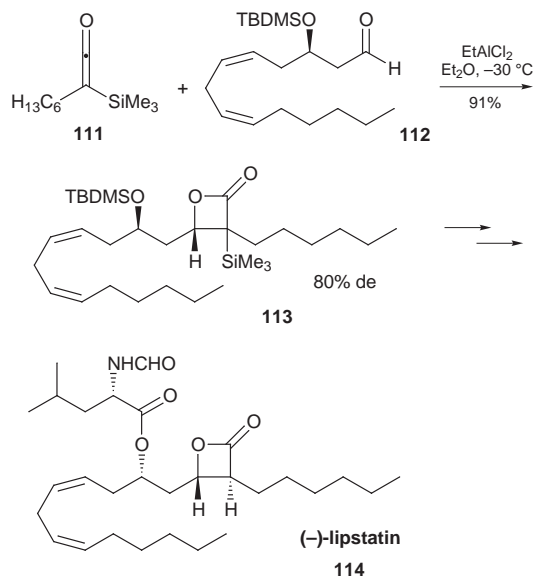
Scheme 61

Scheme 62

The mechanism of this Lewis acid-promoted [2 + 2] cyclo-addition is worth noting. We proposed in 1994,[167] based on experimental observations and on the work of Zaitseva[155,160] (Schemes 55–57) that the reaction could occur through the nucleophilic attack of the silylketene on the aldehyde–Lewis acid complex. Such a mechanism was also adopted by Romo to explain the very good diastereoselectivity he obtained[168] (Scheme 61) and found some theoretical support with independent *ab initio* studies.[170–172]

Lastly, a [2 + 2] cycloaddition between *N,N*-disubstituted amides and bis(trimethylsilyl)thioketene **118** was recently proposed to occur as the first step of a two-carbon extension process leading to *N*-disubstituted 3-oxothioamides **119** (**Scheme 63**).[173]

4.4.2 Formation of β-lactams

The [2 + 2] cycloaddition between a ketene and an imine, better known as the Staudinger reaction, has been known since the beginning of the century[174] and is nowadays one of the most useful routes to β-lactams.[175] However, examples with silyl-
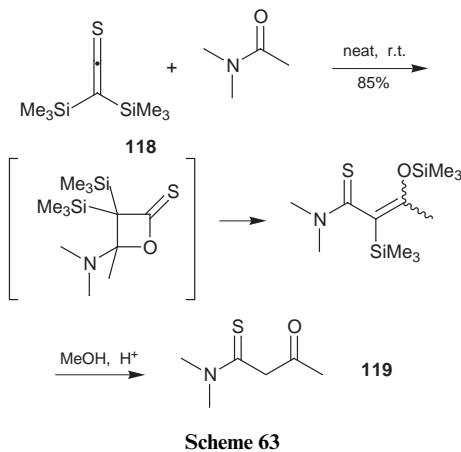
Scheme 63

ketenes are rather scarce, the first being described by Brady in 1976. He reacted bromo(trimethylsilyl)ketene **121** with *N-tert*-butylbenzylimine **120** and obtained in a fair yield of 56% *N*-(*tert*-butyl)silyl-β-lactam **122** (**Scheme 64**).[87]
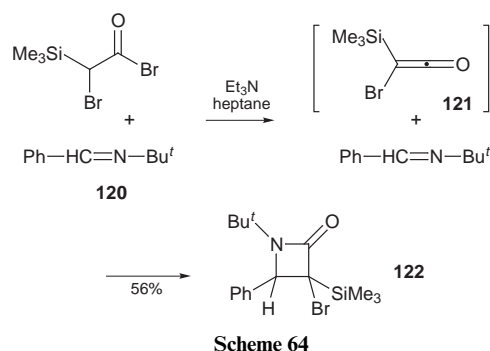
Scheme 64

Then 13 years elapsed before Schubert[176] described the cycloaddition between *N*-methylbenzylimine **124** and ethoxy-(triphenylsilyl)ketene **123** prepared *in situ*, as previously described from a metallic complex (**Scheme 65**).[91]
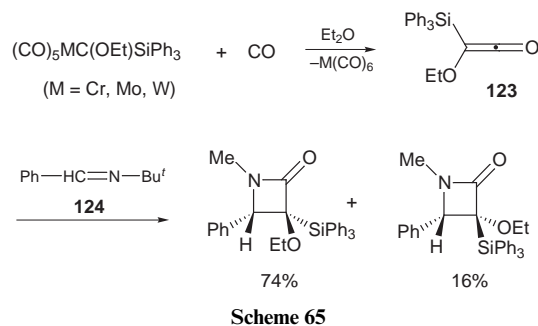
Scheme 65

Lastly, just about at the same time, Zaitseva *et al.* reported the reaction of trimethylsilylketene with *N*-alkylsulfonyl chloralimines (**Scheme 66**).[177,178]

Scheme 66
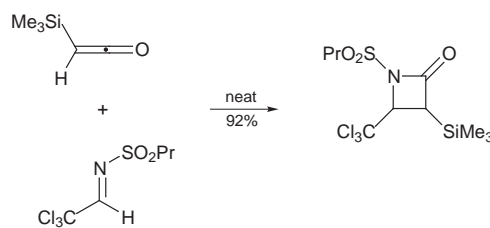
4.4.3 Formation of cyclobutanones

[2 + 2] Cycloaddition between olefins and silylketenes seldom

succeeds; indeed only the use of electron-rich alkenes allows the formation of cyclobutanones. The first examples reported are due to Zaitseva *et al.* who described, in 1974, the reaction between trialkylsilylketenes and ketene dialkyacetals (**Scheme 67**).[179] In a similar way Brady prepared cyclobutanones from trimethylsilylketene and tetraalkoxy olefins (**Scheme 68**).[180]
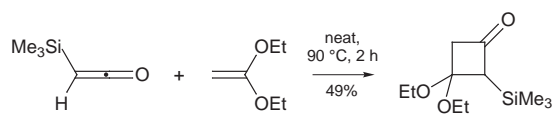
Scheme 67
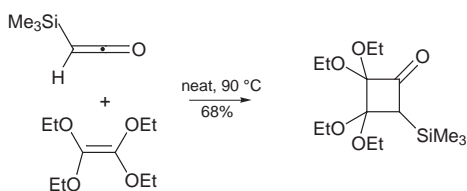
Scheme 68

Lastly, ethoxy- and ethylthio-(triphenylsilyl)ketene, prepared as previously described, react with various electron rich alkenes to yield cyclobutanones,[90,176] and ynamines can react with silylketenes to yield cyclobutenone derivatives.[136]

4.4.4 Reaction between silenes and trimethylsilylketene
Brook and Baumegger reported the formation of non-cyclic acylsilane **127** from silenes such as **125** and trimethylsilylketene. The formation of [2 + 2] cycloadduct **126** as the reaction intermediate is postulated (**Scheme 69**).[181]
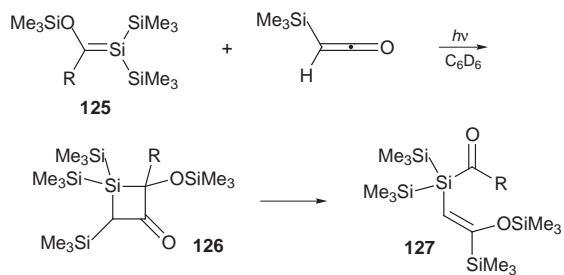
Scheme 69

4.5 [4 + 2] Cycloaddition reactions
In 1980, Danheiser and co-workers described the use of vinyl-(trimethylsilyl)ketene **6** as a diene in Diels–Alder reactions. For instance, in the presence of maleic anhydride, ketene **6** leads with a very good yield to cycloadduct **128** (**Scheme 70**).[21] Silylketenes can also serve as dienophiles in [4 + 2] cyclo-addition reactions. The first example of such a reaction describes the cycloaddition between trimethylsilylketene and acylketenes, generated *in situ* from 4-arylfuran-2,3-diones, to give 4-hydroxypyran-2-ones.[182]
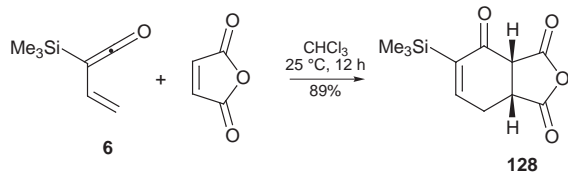
Scheme 70

More recently, the cycloaddition between trialkylsilylketene and electron-rich 1,3-dienes was also studied.[183] Experimental data clearly establish that the reaction is a stepwise process. In the first step, betaine intermediate **131** is formed through the attack of diene **130** on the central carbon atom of ketene **129**. If stopped at that stage, the reaction leads to acyclic ester **133**. However if the reaction time or temperature is increased, **131** undergoes cyclization to dihydropyranone **132** which then isomerizes to pyranone **134** (**Scheme 71**).
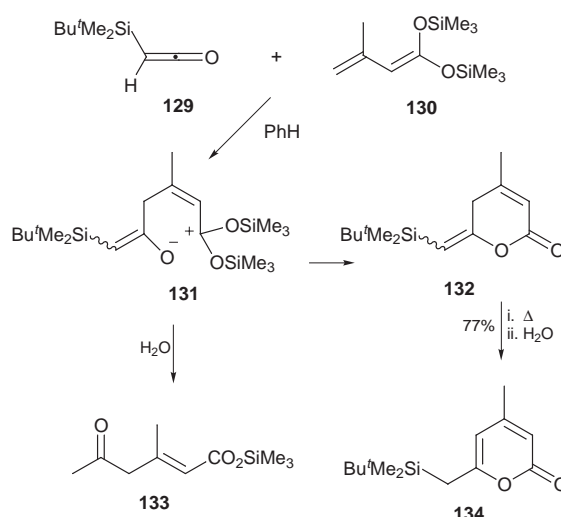
Scheme 71

Aoyama and Shioiri also showed that trimethylsilylketene undergoes [4 + 2] cycloaddition with acylisocyanates to yield a labile cycloadduct which could be trapped with dimethyl acetylenedicarboxylate or an enamine, providing a one pot synthesis of 2-pyridones (**Scheme 72**).[184,185]
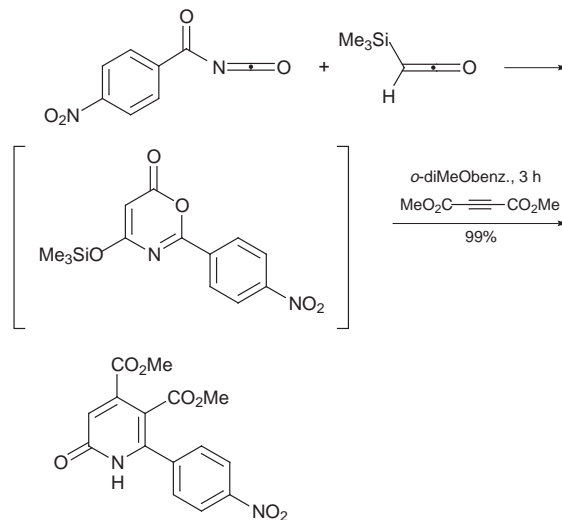
Scheme 72

Lastly, the same authors described a formal [2 + 2 + 2] cycloaddition involving two equivalents of trimethylsilylketene and enamine **68**. This cycloaddition led to resorcinol-type silyl ether **135** in 37% yield (**Scheme 73**).[133]

4.6 Miscellaneous
Trialkylsilylketenes undergo ozonolysis to give the corresponding trialkylsilyl formates (**Scheme 74**).[186]

Bis(ketenes) react with molecular oxygen and lead, with very low yield, to mono- or di-silylated maleic anhydrides.[98] *tert*-Butyldimethylsilylketene, treated with Bu"Li in THF at −100 °C, reacts with cyclohexanone to yield a spiro β-lactone in 52% yield (**Scheme 75**).[58]

Barton has established the thermal extrusion of dimethyl
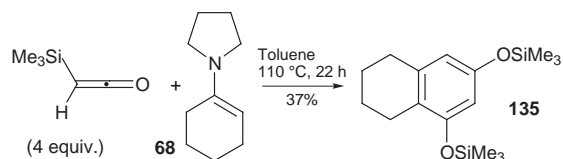
Scheme 73
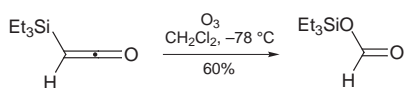
Scheme 74
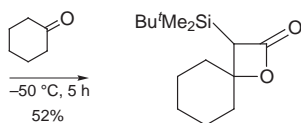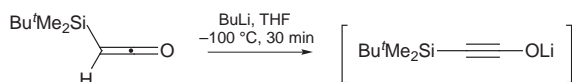
Scheme 75
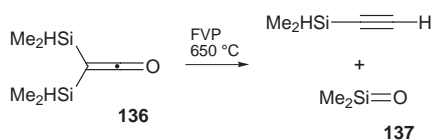
Scheme 76

silanone **137** from bis(dimethylsilyl)ketene **136** under flash vacuum pyrolysis (FVP) conditions (**Scheme 76**).[187]

5 Conclusion

Silylketenes are remarkable because of their stability. Moreover, a large variety of them can be prepared through various methods and their reactivity reveals interesting features. Indeed, although they behave as electrophiles in a number of reactions involving nucleophiles (heteroatom or carbon) and in cyclo-additions involving olefins or dienes, in the presence of an electrophile, such as an aldehyde, and a Lewis acid, silylketenes most probably behave as nucleophiles. This ambident reactivity is an interesting aspect of silylketenes which should in the future attract increasing attention from the chemical community.

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