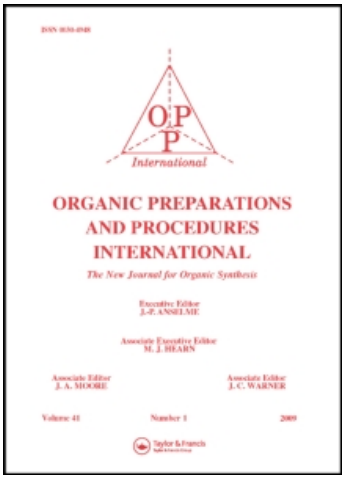

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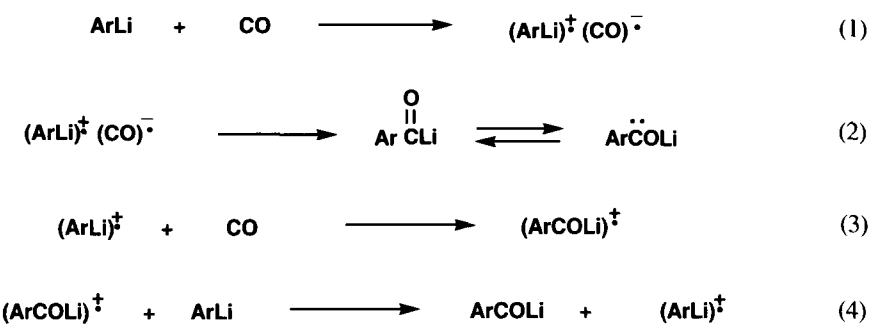
INTRODUCTION

This review will deal with acyl metal derivatives related to non-transition metal compounds, that is either main group metal or metalloid derivatives. The reason for this limited focus is that transition metal acyl systems are generally involved in catalytic processes in which carbon monoxide is used as one-carbon component, the so-called carbonylation and related reactions.[1] These types of intermediates are, in general, short-lived molecules, which are only isolated or spectroscopically characterised for mechanistic purposes. Some acyl metal compounds derived from transition elements are isolable and stable species and take part in stoichiometric processes in organic synthesis, particulary iron, cobalt, rhodium, nickel or palladium compounds either in neutral or *ate* form; however, they are adequately treated elsewhere.[1]

I. LITHIUM DERIVATIVES

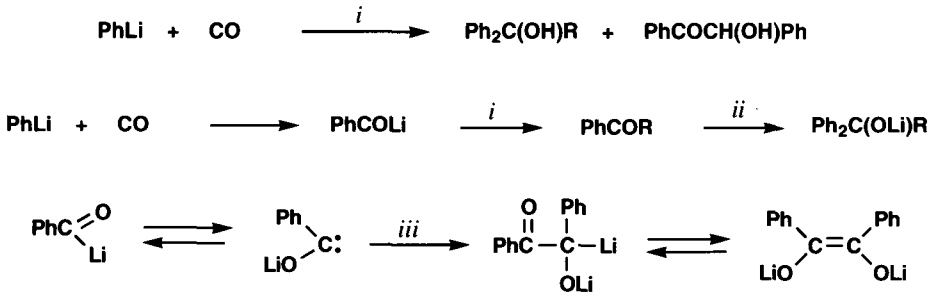
1. Acyllithium Reagents

The most interesting and extensively studied method for the preparation of an acyllithium intermediate is the reaction of an organolithium compound with carbon monoxide. In 1973 Whitesides *et al.* proposed the formation of an acyllithium reagent in the reaction of phenyllithium with carbon monoxide.[2] The synthetic usefulness of these reagents in organic synthesis has been widely studied.[3] These type of intermediates of the general class RC(O)Li are formed at low temperatures by reaction of the corresponding organolithium compounds with carbon monoxide, and they are usually trapped by electrophilic substrates. The carbonylation process takes place before the reaction with the electrophile, this chemoselective behaviour being explained by the proposal of an initial electron transfer mechanism.[4] The existence of radical anions has been demonstrated in the reaction of aryllithium compounds with carbon monoxide by use of ^{13}C NMR spectroscopy.[4] In the first step, an electron transfer from ArLi to CO produces a radical anion/radical cation pair (*Eq.* 1), which can be transformed into an acyllithium anion that is in equilibrium with the corresponding oxy-carbene structure (*Eq.* 2).[5] The observed inhibition of reaction by some radical inhibitors would imply the possibility of



a chain mechanism in which the radical cationic species shown in Eqs. 3 and 4 could be the chain carrying intermediates.[4c] *Ab initio* studies on formyllithium suggest a preference for an ionic η^2-bonding between the lithium atom and the carbonyl moiety.[5c]

The synthetic applications of acyl lithium reagents generated *in situ* from the ArLi/CO mixture are based on their reactivity as an α-acyl lithium anion. Thus, the first reaction studied was the carbonylation of phenyllithium in the presence of alkyl bromides to give alkyl diphenyl carbinols together with α-hydroxy-α-phenylacetophenone[5b] as by-product (*Scheme 1*). The mechanism

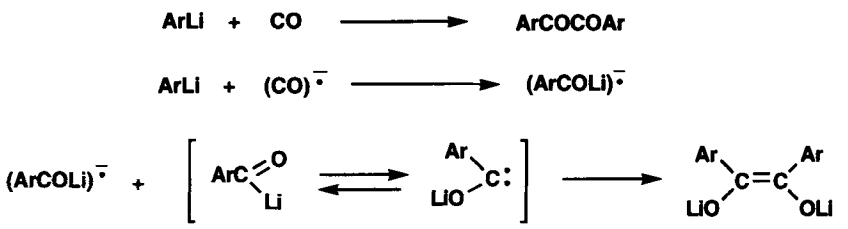


i) RBr; ii) PhLi; iii) PhCOLi

Scheme 1

proposed for the formation of both products involves the generation of benzoyllithium, which reacts with the alkyl bromide to give the corresponding phenone; the final reaction of this compound with a second equivalent of phenyllithium gives the carbinol. The by-product is formed by dimerization of benzoyllithium.

When the reaction of phenyllithium is carried out in the absence of electrophiles α,α-diphenylacetophenone is obtained (94%).[6] However, with 1-naphthyl- or 2,6-dimethylphenyl-lithium in a 1-4 HMPA/THF mixture at -78° a mixture of 1,2-diketones are formed,[7] due to the reaction of the corresponding aroyl anion radicals with aroyllithium followed by *in situ* oxidation of the corresponding aroins during the hydrolytic work-up (*Scheme 2*).

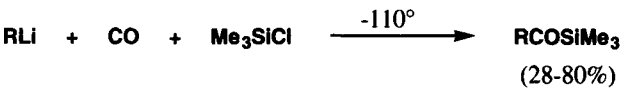


Scheme 2

One interesting reaction of alkyllithium compounds with carbon monoxide is carried out using mono- and dilithium derivatives to give symmetrical[8a] and cyclic ketones,[8b] respectively. The synthesis of cyclic ketones is performed under very dilute conditions in order to minimize the formation of polyketones (*Eq.* 5).

(5)

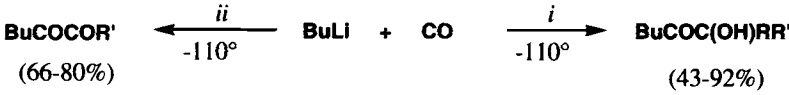
Seyferth *et al.* have developed high-yield acyl anion trapping reactions by carrying out this procedure at low temperatures (-135 to -110°) and atmospheric pressure in the presence of the electrophilic reagent. Thus, acyltrimethylsilanes have been prepared by slow controlled addition of the alkyllithium reagent to a solution of trimethylsilyl chloride saturated with carbon monoxide at -110° (*Eq.* 6).[9] The corresponding reaction of the acyllithium intermediate with trimethylsilyl chloride is faster than other irreversible processes such as dimerization.[2,10]



(6)

R = Pr^i, Bu^n, Bu^i, Bu^{sec}, Bu^t, $Pent^n$, $Pent^i$, Hex^n

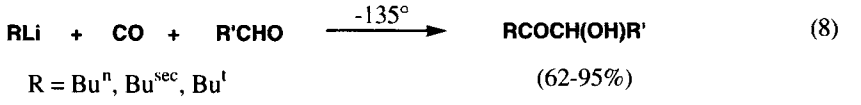
Acylation of ketones[10a,b,d] and esters[10a,c] with *n*-butyllithium and carbon monoxide at -110° yields α-hydroxy ketones and symmetrical or unsymmetrical 1,2-diketones, respectively (*Eq.* 7).



(7)

i) RCOR'; ii) RCO_2R'

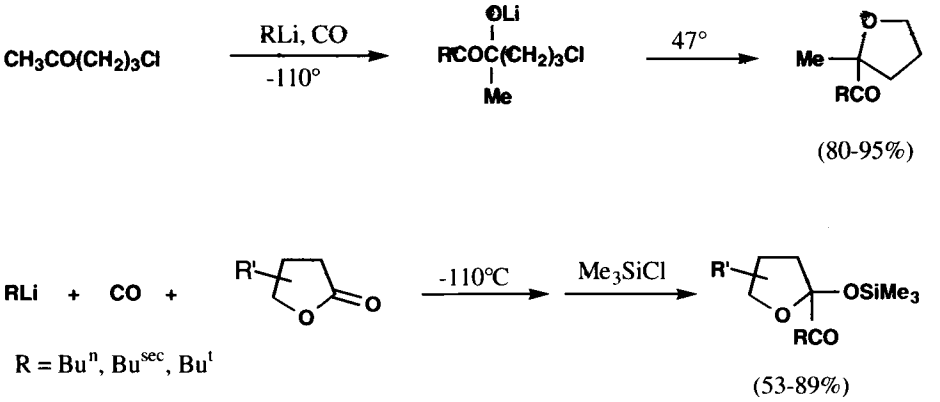
However, with aldehydes the addition of *n*-butyllithium to the carbonyl group is in general more rapid than the formation of Bu^nCOLi. This problem can be overcome by working with a 1-1 RLi/R'CHO stoichiometry and at lower temperatures (-135°); acyloins are obtained in good yields (*Eq.* 8).[11d,12]



(8)

The synthesis of acyloins and 1,2-diketones has been carried out by addition of alkanoyl reagents generated *in situ* to ketones and esters, respectively.[13] However, aryllithium compounds usually react with the electrophilic reagent rather than with CO which suggests that the electron-transfer process[4a,c] is slower for aryl than for alkyllithium compounds.

When 5-chloro-2-pentanone or γ-lactones are used as electrophiles, acyltetrahydro-furans are obtained.[14] In the first case, the resulting acyloin derivative is warmed to yield the corresponding cyclized product and in the second case, the lactol was silylated with Me_3SiCl (*Scheme 3*).

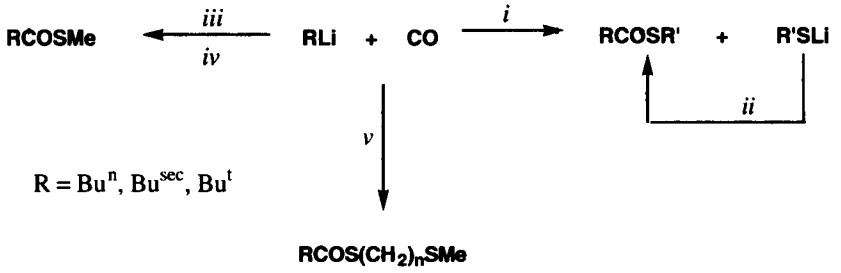


Scheme 3

Dialkyl disulfides are acylated using the alkyllithium/CO methodology at -110° to give *S*-alkyl thioesters and the corresponding thiolate; they can also be trapped with an acyl chloride and thus the yields of the thioester are increased considerably.[15] The reaction may be applied to *n*-, *sec*- and *tert*-butyllithium; in the last case, 1,2-di-*tert*-butyl-1,2-diketone is formed as a by-product, resulting from the addition of the acyllithium reagent generated *in situ* to the thioester. With cyclic disulfides, the reaction products after methylation with methyl iodide, are the corresponding methylthio thioesters. On the other hand, *S*-methyl thioesters are also prepared when elemental sulfur is treated with *sec*- or *tert*-butyllithium/CO at -78° followed by treatment with methyl iodide at -50° (57 and 51% yield, respectively); in the case of using *n*-butyllithium in the same process the reaction failed (<5% yield) (*Scheme 4*).

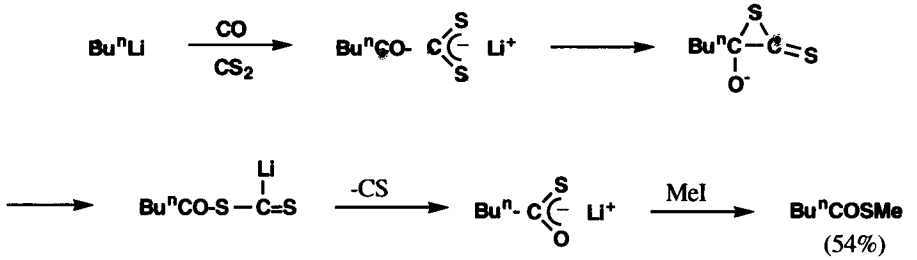
In situ generated acyllithium reagents react with carbon disulfide at temperatures ranging between -110 and -50° giving, after treatment with methyl iodide, the corresponding *S*-methyl thioesters.[16] These products are obtained by extrusion of carbon sulfide (CS) from the corresponding acyl carboxylate anion (*Scheme 5*). However, when COS is allowed to react with *tert*-butyllithium and CO at -110° the corresponding thioester Bu^{t}COCOSMe is isolated.

When isocyanates and isothiocyanates are used as electrophiles, with the RLi/CO combination, α-oxoamides and α-oxothioamides are obtained, respectively (*Scheme 6*).[17]

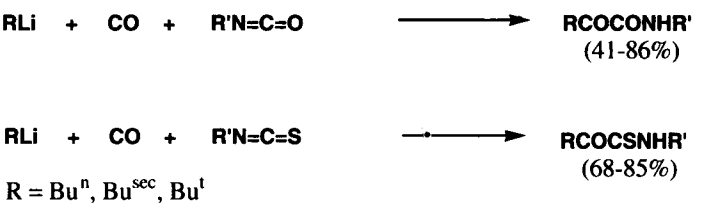


i) $(R'S)_2$; ii) RCOCl; iii) S_8; iv) MeI; v) $(CH_2)_nSS$

Scheme 4

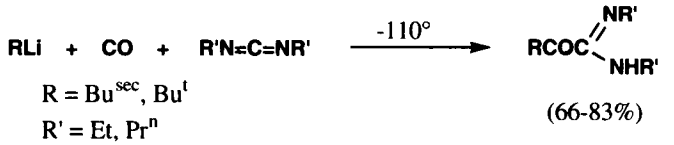


Scheme 5



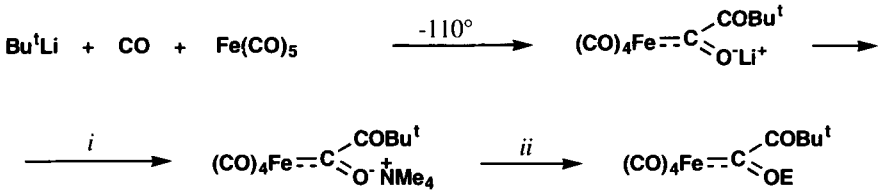
Scheme 6

The addition of acyllithium reagents to the C=N bond of carbodiimides takes place at -110° providing the corresponding α-oxoamidines (*Eq.* 9).[18] This reaction gives good results with *sec*- and *tert*-butyllithium. However, *n*-butyllithium does not add to carbodiimides under the same conditions. With diisopropyl- or di-*tert*-butylcarbodiimide, the reaction procceds in very low yields or not at all.



(9)

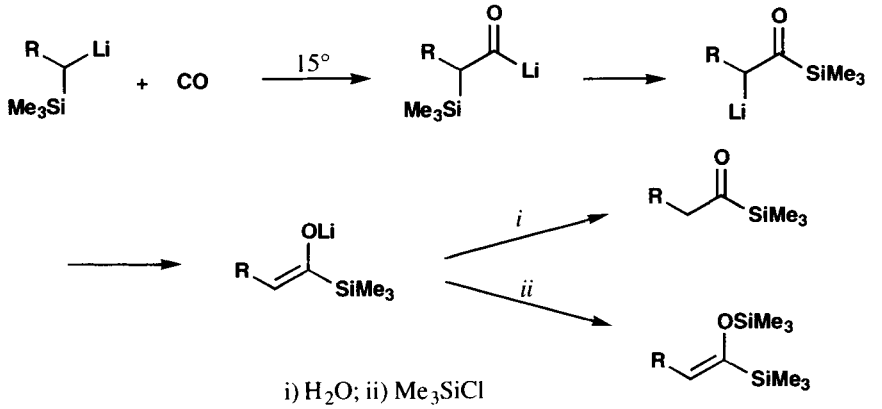
Pentacarbonyliron is also acylated by pivaloyllithium generated *in situ* at -110° to afford an unstable acylferrate complex, which is isolated as its tetramethylammonium salt (*Scheme 7*).[19] The tetramethylammonium salt obtained reacts with different electrophiles (ethyl fluorosulfonate, chlorotrimethylsilane or acetyl chloride) giving the corresponding thermolabile metal carbene



i) Me_4NBr; ii) $E^+ = FSO_3Et$, Me_3SiCl, MeCOCl

Scheme 7

complexes. Murai *et al.* have reported the addition of α-trimethylsilyl substituted alkyl and vinyl lithium compounds to carbon monoxide.[20a] The reaction of (trimethylsilyl)alkyllithium compounds with CO at -15° followed by quenching with water or chlorotrimethylsilane afforded acylsilanes or their enol silyl ethers, respectively (*Scheme 8*).[20b] The addition of the silylated alkyllithium to CO is followed by 1,2-silicon shift (Brook rearrangement[21]) to give stereoselectively *E*-enolates in an exclusive or predominant manner. The *E*-propionylsilane enolate gives a 93/7 *erythro/threo* mixture of aldols with benzaldehyde.

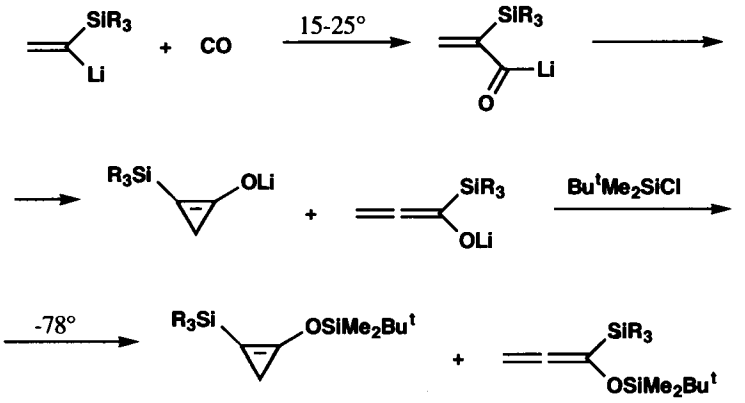


i) H_2O; ii) Me_3SiCl

Scheme 8

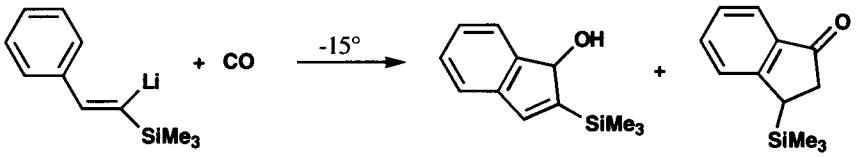
In the case of silylvinyllithium derivatives, the addition to carbon monoxide takes place also at 15° to give after quenching with *tert*-butyldimethylchlorosilane, silylated cyclopropanone enolates (*Scheme 9*).[22] The acyllithium intermediate suffers intramolecular nucleophilic 3-*exo* cyclization to give the corresponding cyclopropanolate. An alternative mechanism could be the intramolecular

double-bond addition of a lithium oxycarbene. As by-products silylated allenolates are also formed through a Brook rearrangement[21] of the acyllithium intermediate.



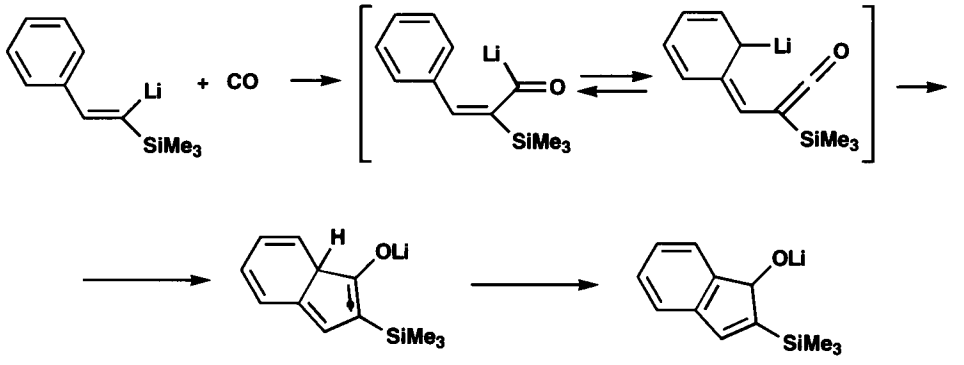
Scheme 9

Another intramolecular transformation of silylvinylacyllithium intermediates occurs in the reaction of 2-phenyl-1-(trimethylsilyl)vinyllithium with carbon monoxide at 15° giving, after hydrolysis, 2-(trimethylsilyl)-1-indenol (63%) and 3-(trimethylsilyl)indanone (10%) as byproduct (*Eq.* 10).[22]



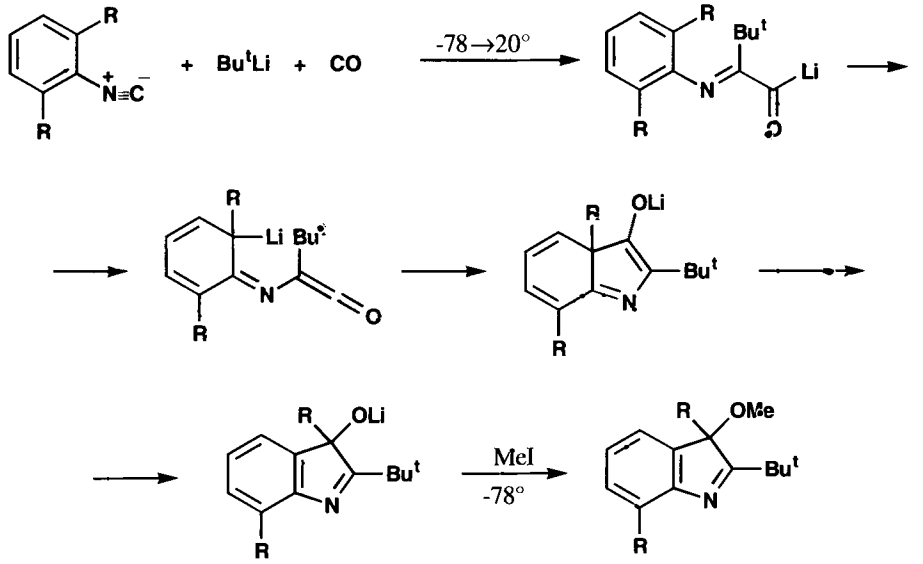
(10)

A plausible mechanism for this reaction could be the intramolecular transformation of the silylvinylacyllithium intermediate into the tautomeric ketene carbanion which then suffers internal nucleophilic attack followed by aromatization and 1,5-hydrogen shift to give the corresponding indenolate (*Scheme 10*). The 3-silylindanone is formed from the corresponding indenolate *via* 1,5-hydrogen and 1,5-silicon shifts.



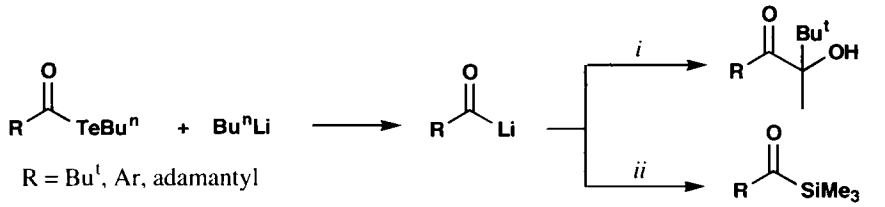
Scheme 10

A similar [4+1] cyclocoupling takes place when lithioaldimines are treated with carbon monoxide at room temperature.[23] The cyclization may proceed through an acyllithium intermediate as described in *Scheme 11* leading after quenching with methyl iodide, to the corresponding 3*H*-indole derivatives.



Scheme 11

A different method for the preparation of aliphatic and aromatic acyllithium intermediates is based on a tellurium-lithium exchange. Thus, the reaction of telluroesters (prepared by reaction of acyl chlorides with lithium or sodium butanetellurates;[24] see below) with *n*-butyllithium at -105° in the presence of pinacolone or chlorotrimethylsilane as electrophiles yields α-hydroxyketones or acylsilanes (*Scheme* 12).[25]



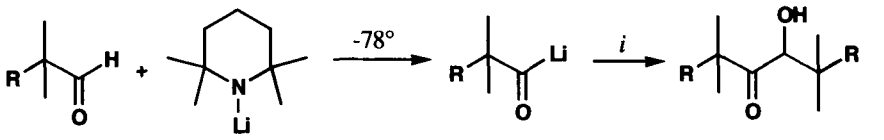
i) MeCOBut; ii) Me_3SiCl

Scheme 12

The same authors also studied the selenium-lithium and tin-lithium exchange with the corresponding acyl derivatives under the same conditions as shown in *Scheme 12* without success.

The most direct way to prepare acyllithium compounds is by the abstraction of a formyl hydrogen, which has been carried out with lithium tetramethylpiperidide using nonenolizable aldehydes

such as pivalaldehyde and α,α-dimethyl-α-cyclohexylacetaldehyde at -78° to afford the corresponding acyloins in 92 and 89% yield, respectively (*Eq.* 11).[26]



(11)

R = Me, Cy

i) $RCMe_2CHO$

2. Carbamoyllithium Reagents

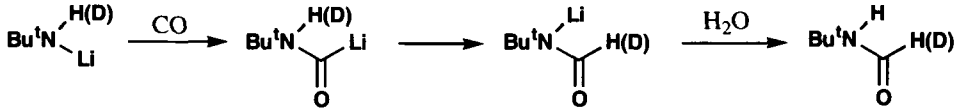
This type of intermediates are more stable and useful reagents in organic synthesis than the corresponding acyllithium ones (see above). The participation of carbamoyl metal derivatives as intermediates in the treatment of *N,N*-disubstituted formamides with alkaline metals (lithium, sodium or potassium) to give glyoxylic amides was first postulated in 1965.[27] Two years later, Schöllkopf and Gerhart described the preparation of diethylcarbamoyllithium at -78° by mercury-lithium transmetallation and studied its reactivity toward different electrophiles (*Eq.* 12).[28] Several other methods have

(12)

E^+ = MeOH, MeOD, PhCHO, PhCOMe, Ph_2CO, PhCOCl, $PhCO_2Et$, MeI, Hg_2Cl_2, Bu_3SnCl

been described in the literature for the preparation of carbamoyllithium compounds based on: (a) lithium amides carbonylation, (b) formamides direct deprotonation with alkyllithium reagents, and (c) tellurium-lithium or chlorine-lithium exchange.

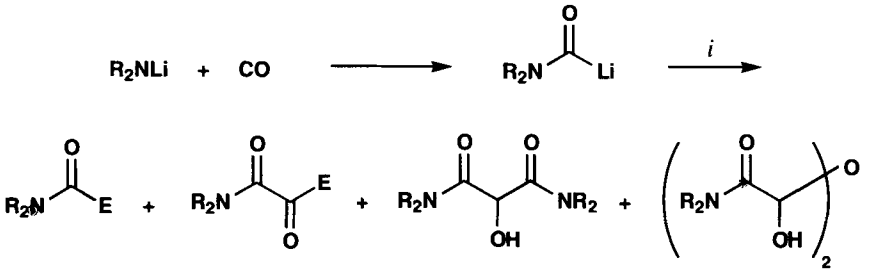
The reaction of lithium *tert*-butylamide with carbon monoxide[29] at 50° was formulated as proceeding through a very stable carbamoyllithium intermediate which reacts with trimethylelement chlorides derived from silicon, germanium, and tin as electrophiles.[30] However, a careful study of this reaction at low temperature demonstrated that this carbamoyllithium rearranges to the corresponding *N*-lithioformamide (*Scheme* 13).[31]



Scheme 13

The same authors studied the reaction of the lithium salts of piperidine and diisopropylamine with carbon monoxide and various electrophiles at -75°.[32] From the reaction of these carbamoyllithium derivatives with water, deuterium oxide, cyclohexanone, or methyl iodide as elec-

trophiles, the corresponding adducts are obtained together with glyoxyl derivatives and hydroxymalonamides as a result of a second insertion of carbon monoxide followed by final reaction of the carbamoyllithium formed with the initially generated adduct (*Scheme* 14).



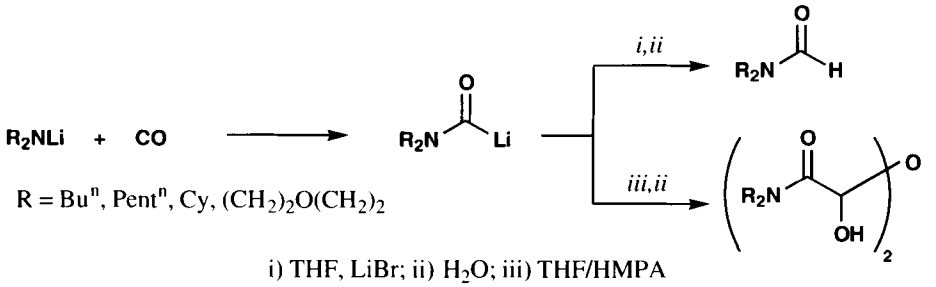
R = Pr^i, R-R=$(CH_2)_5$

i) $E^+ = H_2O, D_2O, (CH_2)_5CO$, MeI

Scheme 14

These side-reactions may be avoided if carbon monoxide is present in low concentration, as it was demonstrated using ^{11}C labelled carbon monoxide in the synthesis of piperidine derived amides by reaction of the corresponding labelled carbamoyllithium intermediate with alkyl iodides.[33]

Nudelman *et al.* have also suggested that the carbamoyl anion has some carbenoide character[34b] based in X-ray diffraction studies on carbamoyl derivatives of U and Th.[35] Based on their investigations about carbon monoxide insertion into organolithium reagents,[4-7] they studied the influence of the reaction conditions in the carbonylation of lithium amides, once the carbon monoxide flow ceased and the remaining carbon monoxide was evacuated, followed by hydrolysis.[34] At 0° in tetrahydrofuran and in the presence of lithium bromide, formamides are obtained. However, working with a 1:1 mixture of THF:HMPA, the corresponding glyoxylamides are formed in good yields (*Scheme 15*).

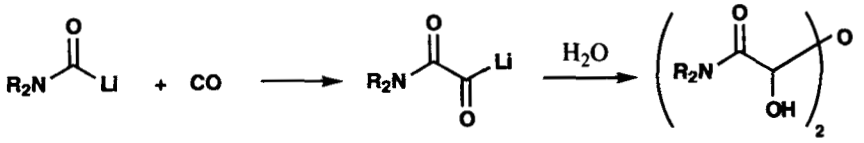


R = Bu^n, $Pent^n$, Cy, $(CH_2)_2O(CH_2)_2$

i) THF, LiBr; ii) H_2O; iii) THF/HMPA

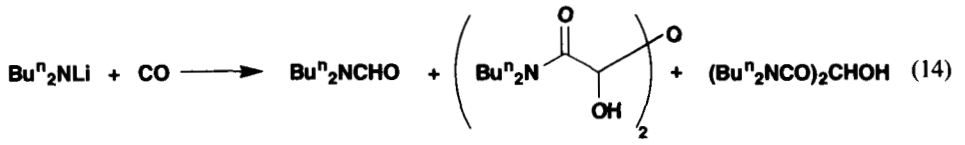
Scheme 15

The latter products are believe to arise by further reaction of the initially generated carbamoyllithium to a second carbon monoxide, followed by final hydrolysis (*Eq. 13*).



(13)

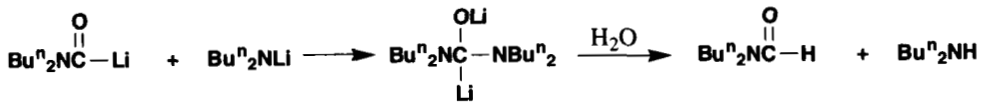
A more exhaustive study on the influence of the conditions in the reaction depicted in *Eq.* 14 led to the following conclusions:[34] (a) The ratio of amine/lithium amide influences the formation of



(14)

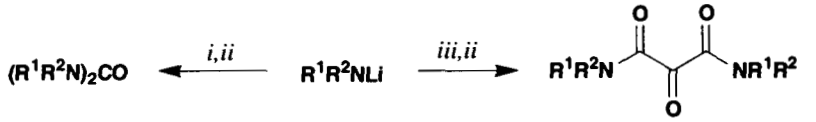
both glyoxylamide and tartronamide; very low concentration of the amine favors the formation of the tartronamide while high concentrations of the amide favors the formation of glyoxylamide. (b) At very low temperature (-95°) dibutylformamide is obtained mainly (82.7%), while at 50° the main product is dibutylglyoxylamide (83.3%). (c) Vigorous stirring increases the amount of glyoxylamide at expense of the corresponding formamide. (d) The carbonylation of lithium amides in a mixture of THF/HMPA at 0° constitutes an excellent method for the synthesis of glyoxylamides. (e) Some significant effects due to the presence of lithium salts have been noted in the glyoxylamide/tartronamide ratio. (f) The presence of a butyl halide leads to the formation of a small amount of *N,N*-dibutylvaleramide (Bu_2NCOBu; <5.3%).

These observations would mean that the carbamoyllithium intermediate is not stable under the mentioned reaction conditions and reacts with the lithium amide to give an α-alkoxyde organolithium compound, as shown in *Scheme 16*.



Scheme 16

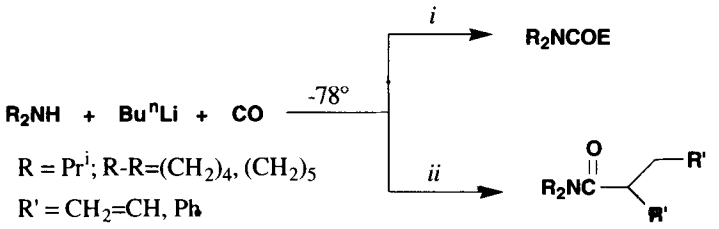
The mechanistic pathway shown in *Scheme 16* has been established by quenching the reaction with deuteriomethanol affording labelled dibutylamine and formamide in similar amounts. By treatment of the reaction mixture with oxygen prior to the aqueous work-up, either the corresponding urea or ketomalonamide are obtained depending on the proportion between the amide and the amine (*Scheme* 17).[34d]



i) R^1R^2NH/R^1R^2NLi:4/5; ii) CO, 0°; iii) R^1R^2NH/R^1R^2NLi:1/5

Scheme 17

When lithium amides are allowed to react with carbon monoxide at atmospheric pressure at -78° followed by ketones, alkyl halides or trialkyltin chlorides, the corresponding adducts are obtained.[36] In the case of allyl and benzyl bromide, dialkylation products are generated (*Scheme* 18). Carbamoylstannanes have been used in the synthesis of amides by palladium-catalyzed cross coupling reaction with organic halides (see below: carbamoylstannanes).



i) $E^+ = R^1COR^2$, R^1Hal, $R^1{}_3SnCl$; ii) $E^+ = CH_2{=}CHCH_2Br$, $PhCH_2Br$

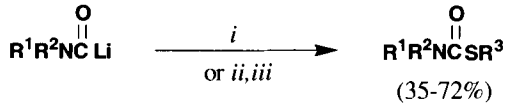
Scheme 18

Carbamoyllithium reagents have been trapped with elemental sulfur at -78° (as in the case of the corresponding acyllithium[15]) giving lithium thiocarbamates, which after *S*-alkylation at 0° yield *S*-alkyl thiocarbamates (*Scheme* 19).[37]

i) S_8; ii) R^3Hal

Scheme 19

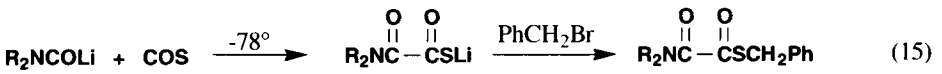
With other sulfur-containing electrophiles such as disulfides or carbon disulfide, thiocarbamates are also obtained (*Scheme* 20).[38]



i) $(R^3S)_2$; ii) CS_2; iii) R^3Hal

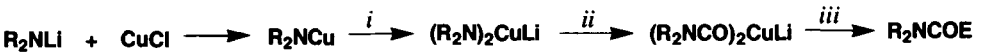
Scheme 20

With carbonyl sulfide, addition to the carbonyl group takes place affording lithium dialkyl thiooxamates, which by reaction with benzyl bromide provide the corresponding thiooxamates (*Eq.* 15).[38]



(15)

Lithium bis(*N,N*-dialkylcarbamoyl)cuprates[39] have been prepared by carbon monoxide insertion (under 50 Kg/cm^2 pressure) into the corresponding aminocuprates. These carbamoyl intermediates are thermally stable at 80° and react with alkyl and acyl halides to give the corresponding amides. The diethylcarbamoyl derivative undergoes conjugate addition to methyl vinyl ketone yielding *N,N*-diethyllevulinamide (*Scheme* 21).



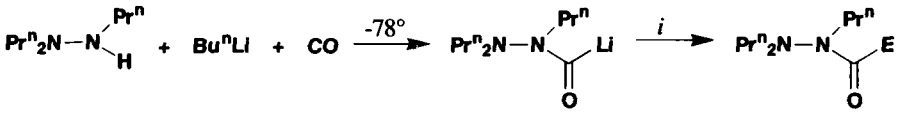
R = Et; R-R = $(CH_2)_2O(CH_2)_2$

i) R_2NLi; ii) CO; iii) E^+ = R'Hal, R'COCl, CH_2=CHCOMe

Scheme 21

The carbamoylation of β-bromostyrene takes place in the presence of 10 mol % of nickel diacetate affording *N,N*-diethylcinnamamide. On the other hand, the reaction with primary amines gives less satisfactory results than with secondary ones.

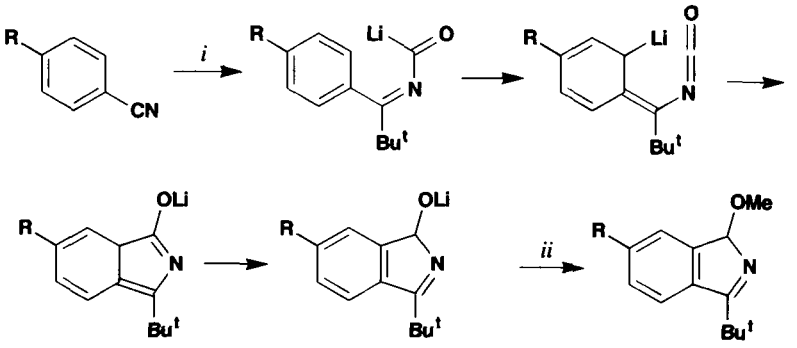
Tripropylcarbazolyllithium reacts with carbon monoxide in THF at -78° to give the corresponding intermediate, which can be trapped with water, deuterium oxide, aldehydes, ketones, esters and alkyl iodides (*Eq.* 16).[40]



(16)

i) E^+ = H_2O, D_2O, RCHO, RCOR', RCO_2Et, RI

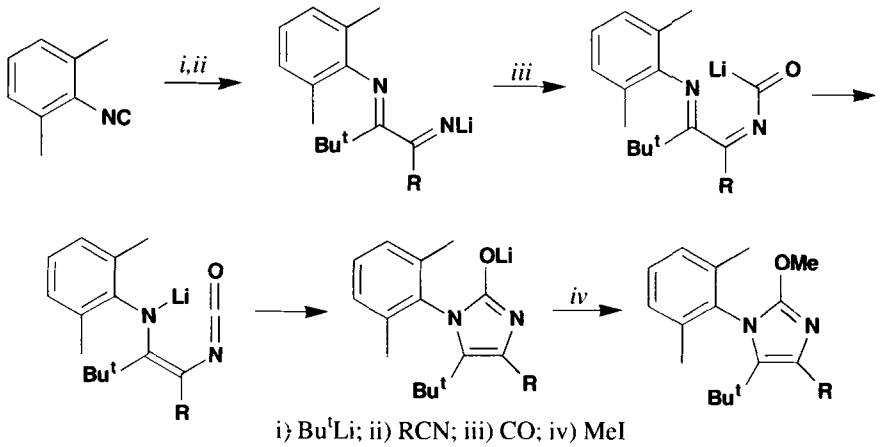
N-Lithioketinimines, obtained by addition of *tert*-butyllithium to *p*-alkyl substituted benzonitriles, reacted with carbon monoxide to give, after quenching with methyl iodide, 3*H*-indole derivatives. The acyllithium intermediate gave a [4+1] cyclocoupling through an isocyanate intermediate (*Scheme* 22).[24]



i) Bu^{t}Li, CO; ii) MeI

Scheme 22

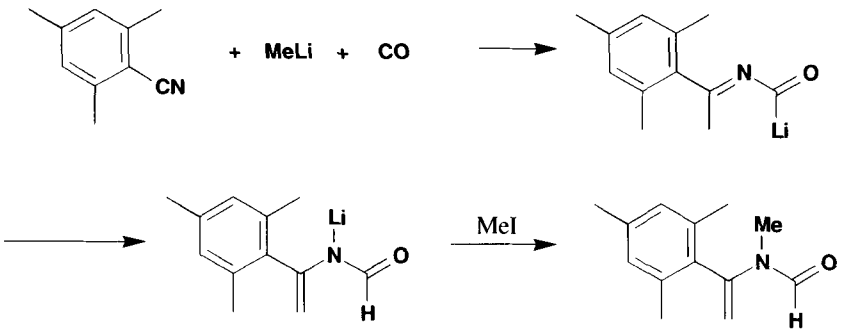
1,4-Diazabutadienyllithium, prepared by successive addition of *tert*-butyllithium and a nitrile to 2,6-dimethylphenyl isocyanide is also carbonylated and gives the same reaction as before (*Scheme* 22) providing, after quenching with methyl iodide, imidazole derivatives (*Scheme* 23).



i) Bu^{t}Li; ii) RCN; iii) CO; iv) MeI

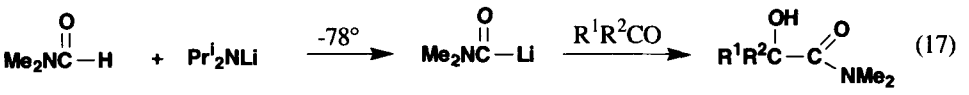
Scheme 23

In the case of 2,4,6-trimethylbenzonitrile the addition of methyllithium followed by carbonylation gives an acyl anion, which suffers intramolecular proton abstraction giving, after quenching with methyl iodide, *N*-1-(2,4,6-trimethylphenyl)vinyl-*N*-methylformamide (*Scheme* 24).

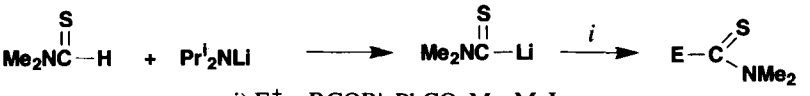


Scheme 24

The second general method for the preparation of carbamoyllithium compounds is the direct deprotonation of formamides. The first example was made using LDA at -78° in the presence of carbonyl compounds yielding α-hydroxyamides (*Eq.* 17).[41] The corresponding thiocarbamoyllithium has also been prepared by LDA deprotonation of *N,N*-dimethylthioformamide at -100° (*Eq.* 18).[42] *N*-Protected formamides have also been deprotonated with LDA affording the corresponding carbamoyllithium intermediates, which after addition to carbonyl compounds and final hydrolysis, yield deprotected α-hydroxyamides (*Eq.* 19).[43]

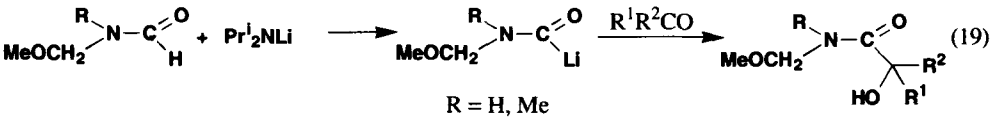


(17)



(18)

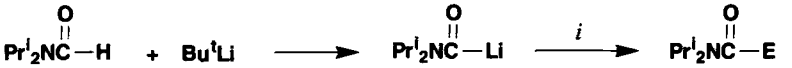
i) E^+ = RCOR', $PhCO_2Me$, MeI



(19)

R = H, Me

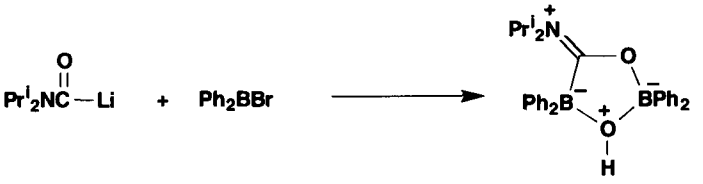
The above mentioned deprotonations are mobile equilibria that can be shifted to the right if an alkyllithium is used as a base.[44] Formamides react with *tert*-butyllithium at -95° in a Trapp's mixture (THF/ diethyl ether/pentane: 4-4-1) to give the corresponding carbamoyllithium compounds, which condense with electrophiles giving the expected reaction products in high yields (*Eq.* 20).[45]



(20)

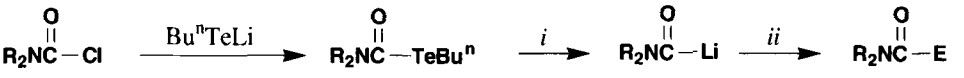
i) $E^+ = R^1R^2CO$, $PhCO_2Et$, D_2O, $PhCH_2Br$

When diphenylbromoborane is used as electrophile heterocyclic five-membered ring compounds are obtained instead of the corresponding acylborane (*Eq.* 21).[46]



(21)

More recently an efficient method for the preparation of carbamoyllithiums based on the tellurium-lithium exchange, which was already described for the preparation of acyllithium intermediates has been described.[26] Dialkylcarbamoyl chloride is allowed to react with *in situ* generated lithium butyltellurate providing carbamoyl butyltellurates, which react with *n*-butyllithium at -78°, *via* tellurium ate complexes, to afford the corresponding carbamoyl lithium reagents.[47] Final addition of electrophiles such as carbonyl compounds, esters or acyl chlorides, methyl vinyl ketone (conjugate addition) and methyl iodide led to the formation of the corresponding adducts (*Scheme* 25).[48]

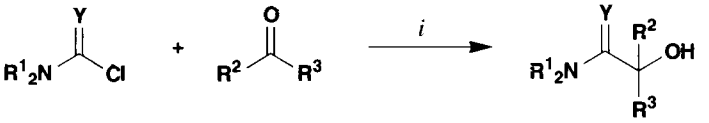


R = Me, Et, $(CH_2)_5$ (31-91%)

i) Bu^nLi; ii) $E^+ = R^1R^2CO, R^1CO_2R^2, R^1COCl, CH_2{=}CHCOMe, MeI$

Scheme 25

Carbamoyl and thiocarbamoyl chlorides have been directly metallated through a chlorine-lithium exchange reaction with lithium powder and a catalytic amount of naphthalene[49] in the presence of a carbonyl compound, yieding α-hydroxy amides and thioamides, carbamoyl- and thiocarbamoyllithium species being proposed as intermediates (*Eq.* 22).[50]



(22)

Y = O, S i) Li powder, $C_{10}H_8$ cat. (40-84%)

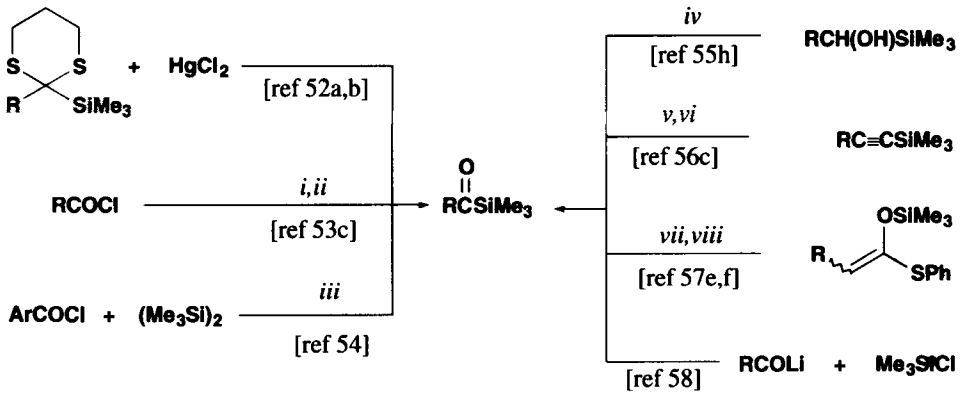
R^1 = Me, Pr^i

II. SILICON DERIVATIVES

Acylsilanes are probably the most versatile acyl metal reagents, their structure, prepararation and reactivity having been widely studied. They are, in general, sensitive to light and basic media, their behaviour being usually as typical ketones. Several reviews concerning the spectroscopic properties, X-ray diffraction studies, preparation and synthetic applications of acylsilanes have been published covering the literature up to 1992.[51] The present review covers the recent developements of acyl silanes in the last two years.

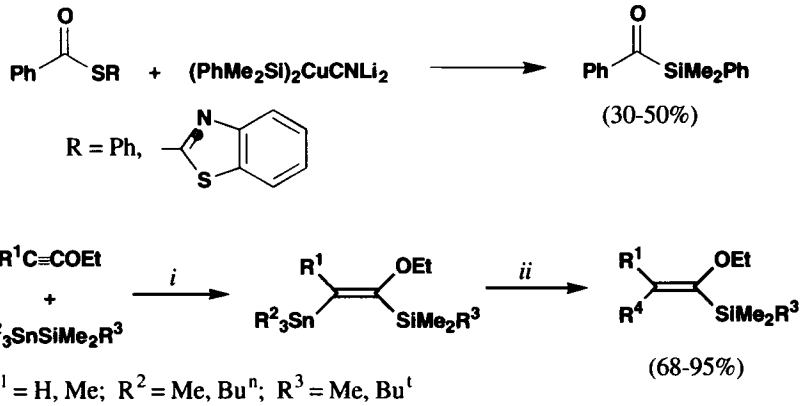
1. Preparation of Acyl- and Carbamoylsilanes

The general methods to prepare simple acylsilanes are: (a) hydrolysis of silylated thioketals;[52] (b) acylation of silylated metallic species;[53] (c) palladium-catalyzed coupling of aromatic derivatives;[54] (d) oxidation of α-silylated alcohols;[55] (e) hydroboration-oxidation of alkynylsilanes;[56] (f) enolate methodology;[57] and (g) silylation of acyllithium species.[58] Some representative examples have been outlined in *Scheme 26*. With regard to the acylation of silyl metallic species [method (b)[53d]], the preparation of benzoylsilane[59] by reaction of thioesters with Fleming's silylcupration reagent[60] has been recently described (*Eq.* 23). In relation to methods included in parts (e) and (f), the palladium-catalyzed silastannation of alkynes has been applied to 1-alkoxyalkynes employing palladium(II) acetate/1,1,3,3-tetramethylbutyl isocyanide to afford *syn* addition products.[61] 1-Ethoxy-1-silyl-2-stannyl-alkenes suffer cross-coupling reaction with organic halides using $PhCH_2PdCl(PPh_3)_2$ and copper(I) iodide as cocatalyst[62] giving 1-ethoxy-1-silylalkenes with retention of the stereochemistry (*Scheme* 27). Hydrolysis of the obtained silyl enol ethers furnishes the corresponding acylsilanes in good yields.



i) CuCN; ii) $LiAlMe(SiMe_3)_3$ or $LiAl(SiMe_3)_4$; iii) $[(\pi\text{-}C_3H_5)PdCl)]_2$, $P(OEt)_3$; iv) DMSO, $(COCl)_2$; v) $BH_3{\bullet}SMe_2$; vi) Me_3NO; vii) Na, Me_3SiCl; viii) H_2O

Scheme 26

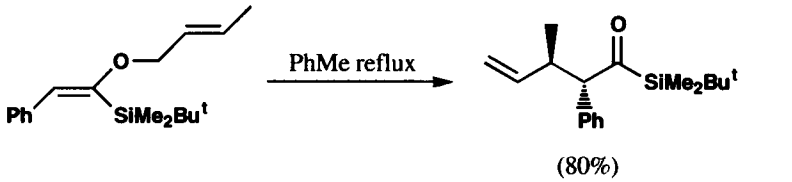


R^1 = H, Me; R^2 = Me, Bu^n; R^3 = Me, Bu^t

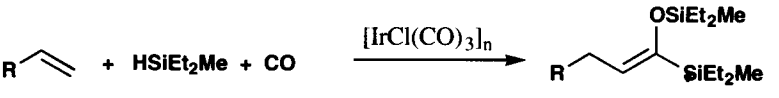
i) $Pd(OAc)_2$; ii) R_4Hal, $PhCH_2PdCl(PPh_3)_2$, CuI

Scheme 27

Ether exchange of 1-ethoxy-1-silylalkenes with allyl or crotyl alcohol gives with heating acylsilanes substituted by an allyl or crotyl unit at the α-position. The Claisen rearrangement,[63] in the case of crotyl alcohol, is stereospecific giving the corresponding *anti* β,γ-branched acylsilane (*Eq.* 24).



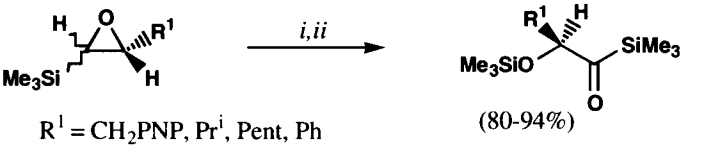
A new reaction to prepare silyl enol ethers, precursors of acylsilanes, is the iridium-catalysed reaction of alkenes with carbon monoxide and diethylmethylsilane at 140° under pressure (*Eq.* 25).[64]



(45-85%) (25)

The incorporation of the siloxylsilylmethylene unit into the terminal carbon atom of ethylene, norbornene and monosubstituted olefins affords 1-silylated silyl enol ethers as a *E/Z* diastereoisomers mixture. Dimethylphenylsilane and tetraethylsilane can also be used as silane reagents as well as $Ir_4(CO)_{12}$ as the catalyst.

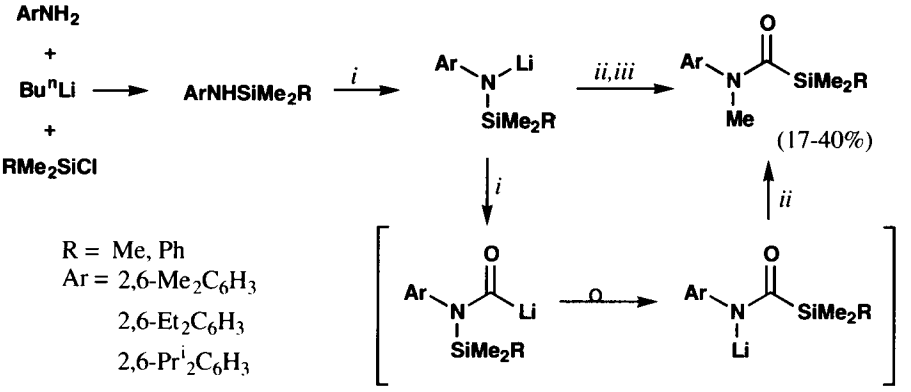
Another new synthetic methodology for homochiral α-hydroxy acylsilanes is based upon a Kornblum-type oxidation of homochiral (α,β-epoxyalkyl)silanes. The treatment of racemic or homochiral epoxides derived from 3-(trimethylsilyl) substituted allylic alcohols with dimethyl sulfoxide and trimethylsilyl trifluoromethanesulfonate followed by reaction with diisopropylethylamine affords the corresponding *O*-trimethylsilyl derivative of α-hydroxy acylsilanes (*Eq.* 26).[65]



$R^1 = CH_2PNP$, Pr^i, Pent, Ph (80-94%) (26)

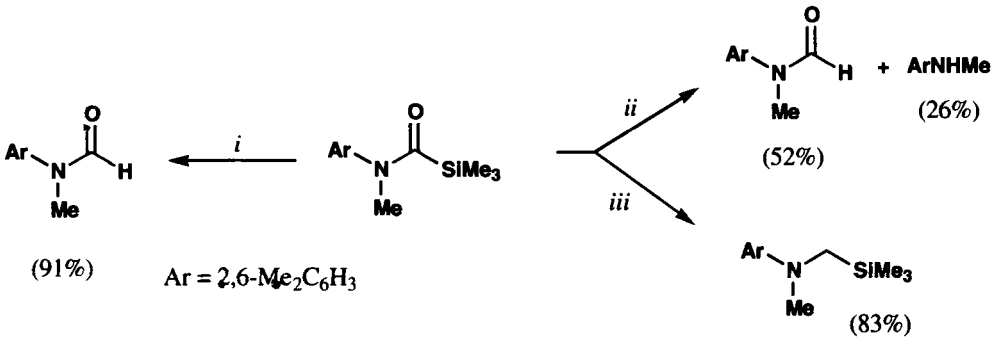
i) DMSO, $TfOSiMe_3$; ii) Pr^i_2NEt

Carbamoylsilanes, less known than the corresponding acyl derivatives,[66] have been prepared following method (g) above described for simple acylsilanes. The reaction of lithium silylamides with carbon monoxide (either at atmospheric pressure or at 30 atm) gives the corresponding carbamoyllithiums, which undergo anionic rearrangement to provide lithium (silylcarbamoyl)amides. After quenching with methyl iodide, the expected carbamoylsilanes are obtained (*Scheme* 28).[66]



i) Bu^nLi; ii) CO; iii) MeI

Scheme 28

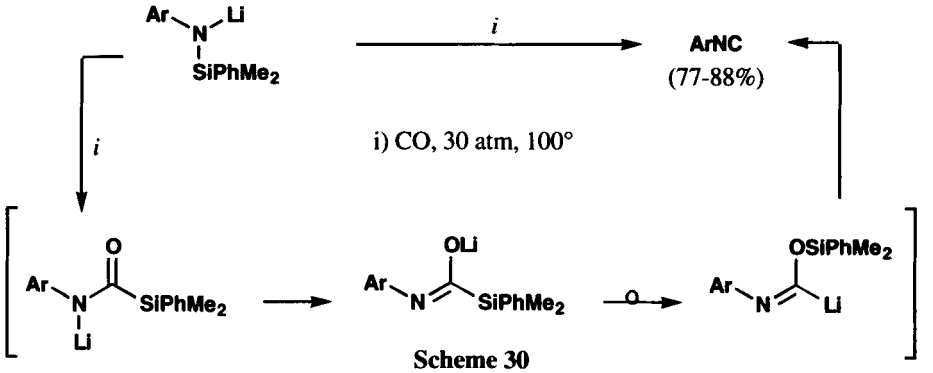


i) EtONa; ii) TBAF; iii) AlH_2Cl

Scheme 29

Some of the chemical properties of carbamoylsilanes have been studied. For example, the corresponding 2,6-dimethylphenyl derivative shown in *Scheme 29* is stable in the air and toward 10% sufuric acid. Treatment of this compound with 0.2 M EtONa/EtOH gives the corresponding formamide; the desilylation can also be carried out using fluoride anion. Clean reduction of the carbonyl moiety takes place with AlH_2Cl (*Scheme* 29).[67]

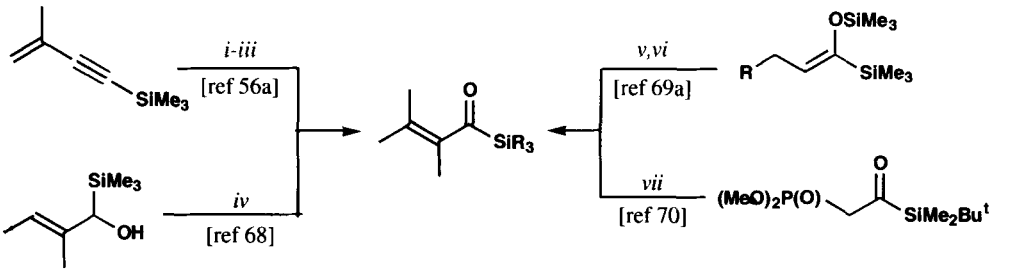
Lithium silylcarbonyl amides give the corresponding isocyanides under carbon monoxide pressure and with heating through the probable mechanism shown in *Scheme 30*.[67]



Scheme 30

The syntheses of α,β-unsaturated acylsilanes may be classified in four general methods: (a) hydroboration-oxidation of enynes;[56a] (b) oxidation of allylic alcohols;[68] (c) enolate-based methodology;[69] and (d) Horner-Emmons reaction.[70] Some representative examples are included in *Scheme 31*.

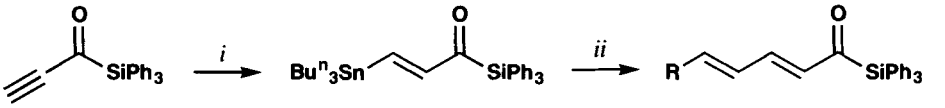
Unsaturated acylsilanes are prepared through a Michael-type addition of dialkyl cuprates to ethynyl triphenylsilyl ketone[69f,l,m] at low temperatures (*Eq.* 27). [71] When ethynyl triphenylsilyl ketone is treated with tributylstannyl cuprate as Michael reagent, the vinyl stannane derivative is obtained in a stereoselective manner (*Eq.* 27). [72] Further reaction of the β-stannyl α,β-unsaturated acylsilane with vinyl iodides under palladium catalysis gives polyunsaturated acylsilanes (*Eq.* 28).



i) $BHCl_2$; ii) MeOH, Me_3N; iii) Me_3NO; iv) Swern or Corey-Kim oxidations; v) PhSCl; vi) m-CPBA; vii) RCHO, LiCl, DBU

Scheme 31

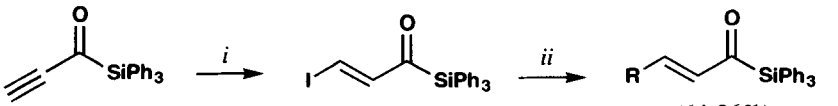
R = alkyl, vinyl, Ph (27)



R = Ph, $BocNHCH_2$ (28)

i) $Bu^n_3SnCu(CN)Li_2$; ii) RCH=CHI, $PdCl_2(MeCN)_2$

(*E*)-3-Iodopropenyl triphenylsilane, prepared by reaction of ethynyl triphenylsilyl ketone with trimethylsilyl iodide, undergoes stereospecific palladium-catalyzed coupling with tin compounds to yield unsaturated acylsilanes (*Eq.* 29).[73]



R = $Me_3SiC{\equiv}C$, $CH_2{=}C(OEt)$, $CH_2{=}CH$, 2-furyl, $BocNHCH_2CH{=}CH$, $Ph_3SiCOCH{=}CH$ (29)

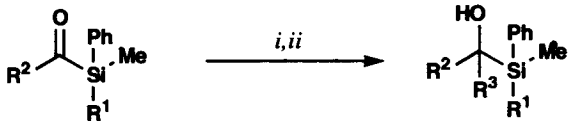
i) Me_3SiI; ii) $RSnBu^n_3$, $PdCl_2(MeCN)_2$

2. Reactivity of Acylsilanes

The reactivity of simple acylsilanes is similar that the corresponding carbonyl compounds. However, they exhibit abnormal behaviour involving rearrangements, which lead to the formation of silicon-oxygen bonds, especially in their reaction with nucleophilic reagents.[51b] In general they can be considered as synthetic equivalents of aldehydes.

(a) Reactions with Nucleophilic Reagents

The addition of organometallic reagents to acylsilanes bearing an α-chiral carbon atom gives α-hydroxysilanes, which are stereoselectively protodesilylated with retention of the configuration giving alcohols with very high diastereoselectivity.[74] The addition of Grignard reagents to acylsilanes, chiral at silicon has been also studied.[75] The diastereomeric ratio (9-79%) was first studied with racemic acylsilanes containing methyl, phenyl, *tert*-butyl and α-naphthyl silyl groups (*Eq.* 30).



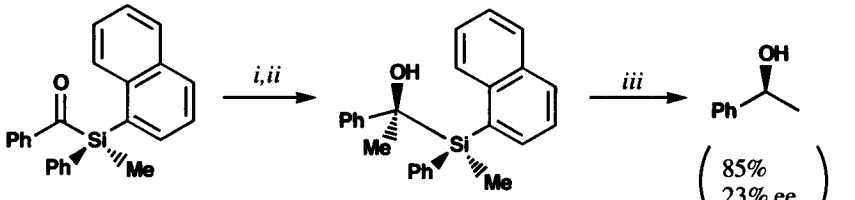
(30)

R^1 = Bu^t, α-naphthyl
R^2 = Me, Ph

(63-98%, 9-79% de)

i) R_3MgX; ii) NH_4Cl

The same reaction carried out with the enantiomerically pure starting material shown in *Eq. 31* and methylmagnesium bromide gave the corresponding α-silyl alcohol with 79% de. However, the protodesilylation with tetrabutylammonium chloride (TBAF) gives (*S*)-1-phenylethanol in 28% ee and with opposite configuration (*Eq.* 31); this suggests that in this case the protodesilylation is not a highly stereoselective process.[74]



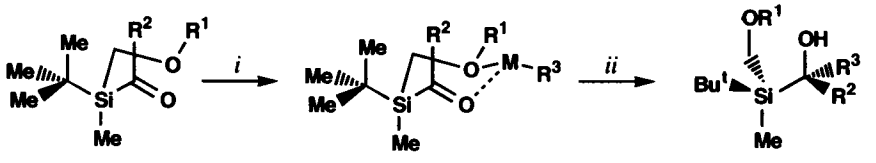
(31)

(79% de)

(85%, 23% ee)

i) MeMgBr; ii) NH_4Cl; iii) TBAF

The role of the solvent, the organometallic reagent and the substrate in the diastereoselectivity of 1,2-additions of organometallic reagents to racemic alkoxymethyl substituted acylsilanes chiral at silicon has also been studied.[76] For a given substrate, the best stereochemical results are obtained whith Grignard reagents (up to 99% de) by means of a 'chelate-controlled' reaction pathway (*Eq.* 32).[76]

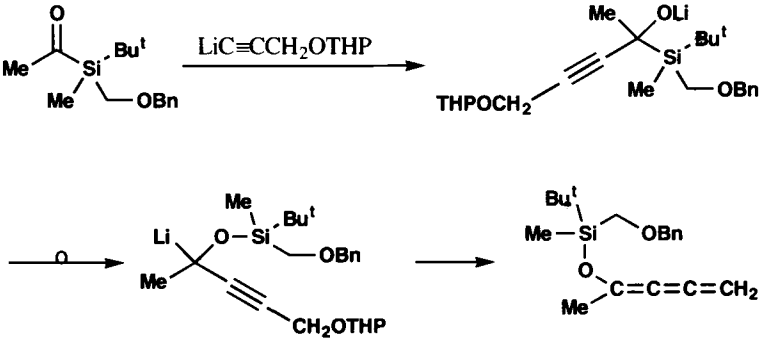


(32)

i) R^3M; ii) H_2O

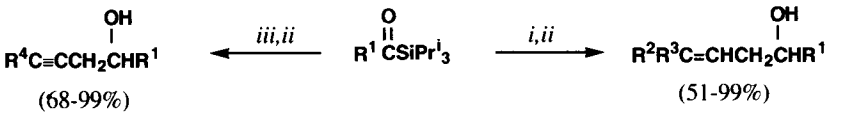
(30-98%, 9-99% de)

The addition of lithium acetylides to this type of acylsilanes has been applied to the synthesis of a silyloxy cumulene (*Scheme* 32).[77]



Scheme 32

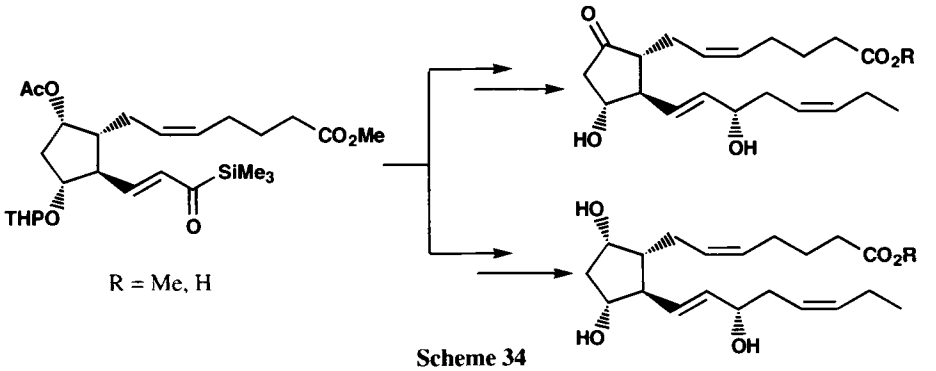
The use of acylsilanes as electrophiles in allylation and propargylation reactions has also been studied. The addition of allyl or propargyl magnesium and zinc halides to triisopropylsilyl derivatives giving the corresponding homo-allylic and propargylic alcohols takes place, in general, with high α/γ ratio (*Scheme* 33).[78]



i) $R^2R^3C{=}CHCH_2M$ (M=MgCl, ZnBr); ii) TBAF; iii) R^4CCCH_2M (M=MgBr, ZnBr)

Scheme 33

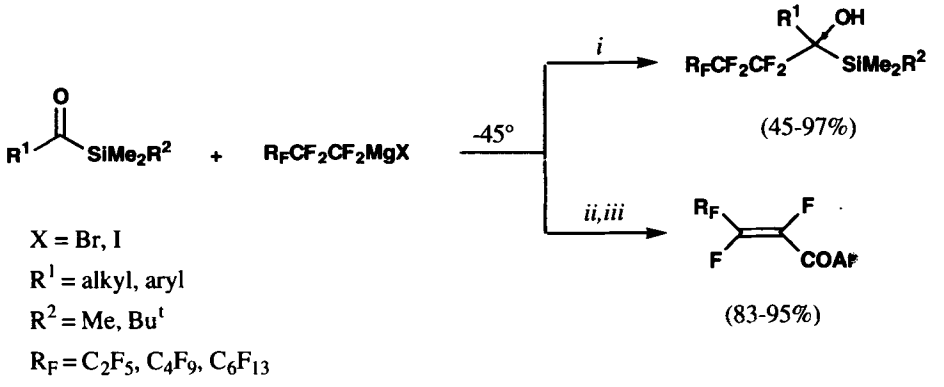
Different acylsilanes have been used in the reaction with allyl and propargyl organometallics in order to compare their reactivity with the corresponding aldehydes. This methodology, which gives better α/γ ratios, has been applied to the synthesis of the three series of prostaglandins (PGs) (*Scheme* 34).[78]



R = Me, H

Scheme 34

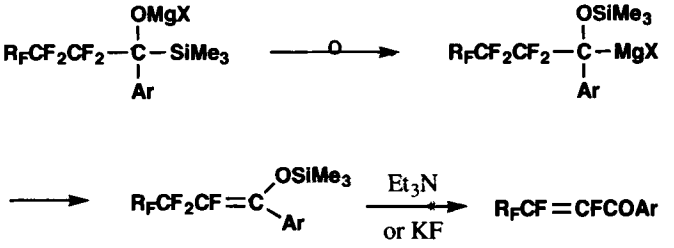
The addition of perfluoroorganomagnesium reagents[79] to acylsilanes gives, depending on the substituents and the reaction conditions, the corresponding 1-alkyl and 1-aryl 1-trialkylsilylperfluoroalkanols[79a,b] or perfluoroalk-1-enyl phenones (*Scheme* 35).[79a,c]



i) H_2O, -10 or -45°; ii) RT; iii) Et_3N

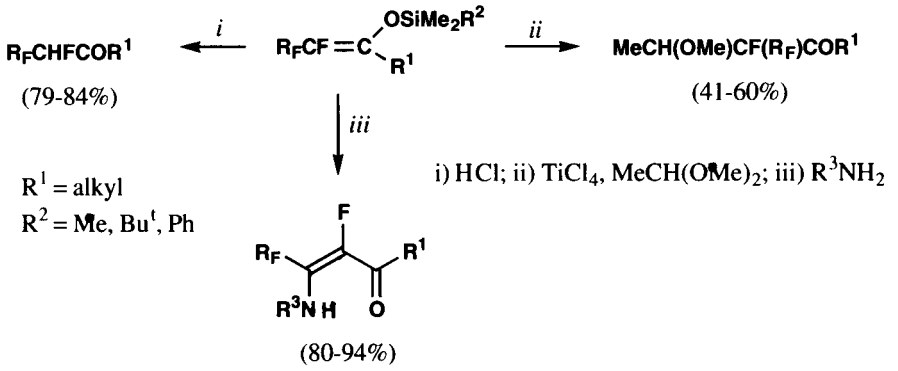
Scheme 35

The mechanism proposed for the formation of perfluoroalk-1-enyl phenones implies first a Brook rearrangement of the corresponding silyl ether followed by a β-elimination to give a silyl enol ether, which by means of triethylamine or potassium fluoride yields the corresponding enone (*Scheme* 36).[79c]



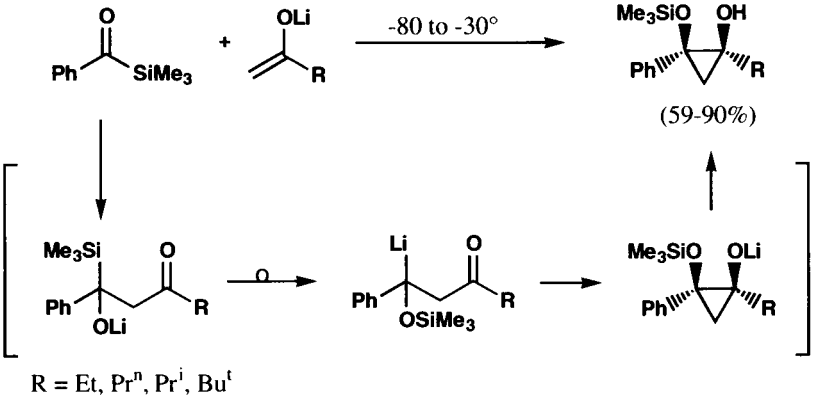
Scheme 36

The intermediate perfluoroendoxysilanes have been synthetized by addition of perfluoro organolithium and magnesium derivatives to aliphatic and aromatic acylsilanes, respectively.[80] These type of silyl enol ethers have been used as enolate equivalents leading either 2-hydroperfluoroalkyl ketones on hydrolysis or aldol products. By reaction with amines they react as electron-poor alkenes to give β-enamino ketones (*Scheme* 37).



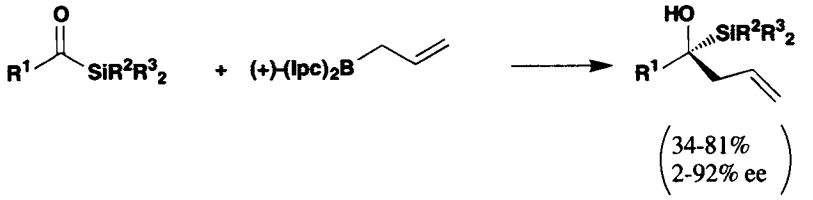
Scheme 37

The reaction of benzoylsilanes with lithium enolates derived from methyl ketones produces 1,2-cyclopropanediols (*Scheme* 38).[81] The initially formed 1,2-adducts suffer a Brook rearrangement to the corresponding β-hydroxy homoenolates,[82] which undergo typical intramolecular stereoselective cyclopropanation to give mainly cyclopropanediols. β-Hydroxy homoenolates have been trapped by reaction of the cyclopropanediols with sodium hexamethyldisilazane and benzaldehyde. The same methodology applied to crotonoylsilane gives mixtures of cyclopropanediols and Michael-type addition products.[81]



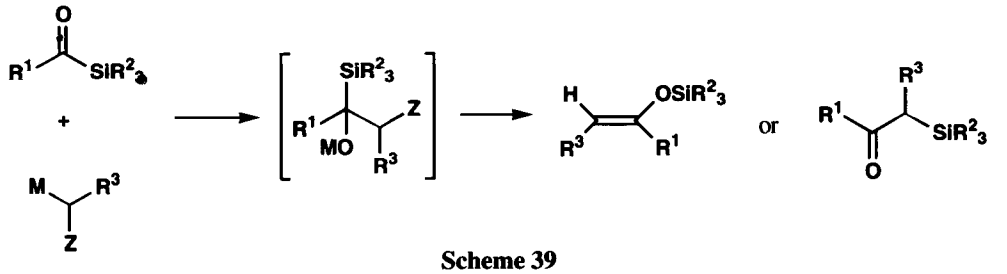
Scheme 38

In relation with the asymmetric reduction of acylsilanes to α-hydroxy silanes, three methods have been developed: (a) reduction with the Itsumo reagent,[83] (b) chromatographic resolution of the mandelate derivatives,[84] and (c) reduction with chloro(diisopinocampheyl)borane system.[85] Based on the last reagent, the asymmetric allylation of acylsilanes by means of *B*-allyl(diisopinocanpheyl)-borane has been reported (*Eq.* 33).[86]



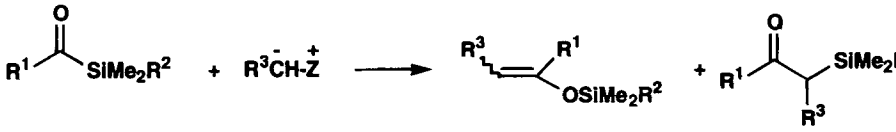
(33)

Alkylidenephosphoranes have also been used as carbon nucleophiles with arylacylsilanes to give silyl enol ethers[87] instead of the expected alkenes. However, alkylacylsilanes give the corresponding vinyl silanes[87] and with diazomethane give silyl enol ethers and the homologous β-ketosilanes.[88] The formation of silyl enol ethers in these reactions implies 1,2-migration of a silyl group (Brook rearrangement) as a cationic moiety ('cationotropy'). In contrast, in the case of the other reaction products, β-ketosilanes, a 1,2-migration of a silyl group as an anionic moiety ('anionotropy') from the same intermediate takes place (*Scheme* 39).



Scheme 39

When this type of reaction is applied to sulfur ylides, mixtures of silyl enol ethers and β-keto silanes are obtained (*Eq.* 34).[89] While silyl enol ethers are mainly formed under the salt-free ylide conditions, β-keto silanes are the major components obtained in the presence of soluble inorganic salts in THF, according to the cationotropic and anionotropic rearrangements of a silyl group, respectively.



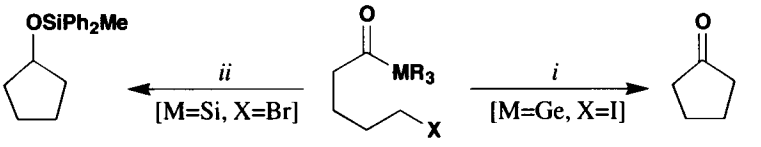
(34)

R^1 = Alkyl, cyclopropyl, aryl, R^2 = Me, Bu^t, Ph

R^3 = H, Me, Z = Me_2SO, *p*-$MeC_6H_4SONMe_2$, Ph_2S

(b) Reaction with Radicals

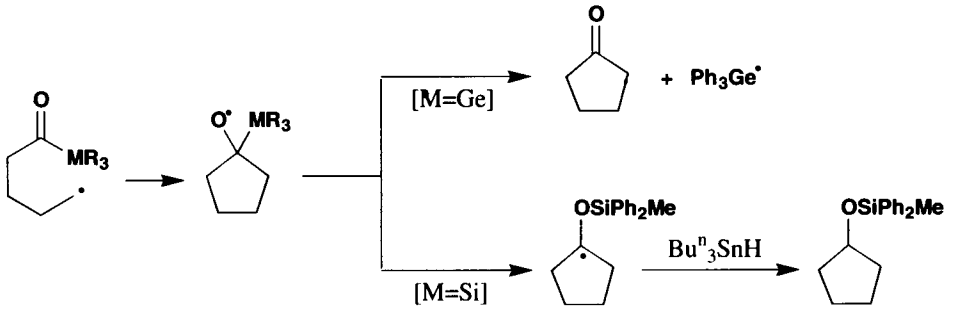
Acylsilanes, as well as the corresponding acylgermanes (see below), are excellent radicalophiles in intramolecular cyclizations.[90] The difference between these acyl metals is that acylsilanes give cycloalkanol derivatives whereas acylgermanes give cycloalkanones (*Eq.* 35). Curran *et al.*[91,92] have interpreted these results according to the different evolution of the cycloalkanol radical intermediate. The β-germyl alkoxy radical evolves by fragmentation to give cyclopentanone and



(35)

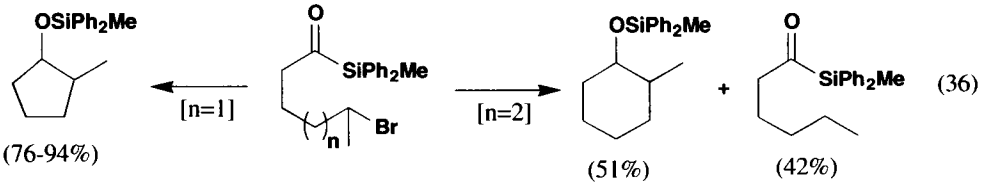
i) hν; ii) AIBN, Bu^n_3SnH

triphenylgermyl radical, which through a chain transfer step abstracts a halogen from another molecule of acylgermane. In contrast, the β-silylalkoxy radical evolves by a formal radical Brook rearrangement to the α-silyloxy substituted radical, which is reluctant to eliminate a silyl radical and abstracts a hydrogen from the tin hydride giving the corresponding *O*-silylated cyclopentanol (*Scheme* 40).



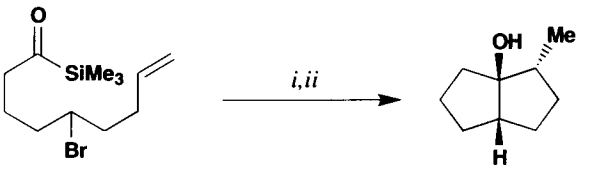
Scheme 40

The radical 1,5-*exo* cyclization of secondary radicals derived from bromoalkylacylsilanes is quite effective.[93] In contrast, 1,6-*exo* cyclizations are more sensitive toward steric effects: 1,5-hydrogen transfer is also observed (*Eq.* 36).



(36)

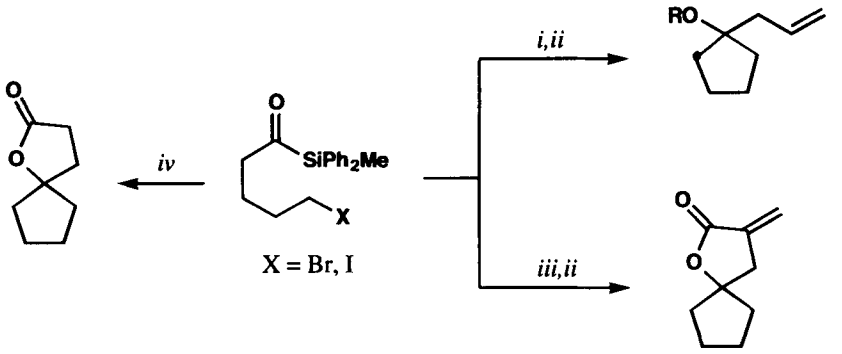
The tandem cyclization-addition reaction has been studied with the starting material shown in *Eq. 37*, which is stereoselectively transformed into the corresponding *endo* bycyclic alcohol.[93]



(37)

i) Bu^n_3SnH, AIBN; ii) TBAF (81%)

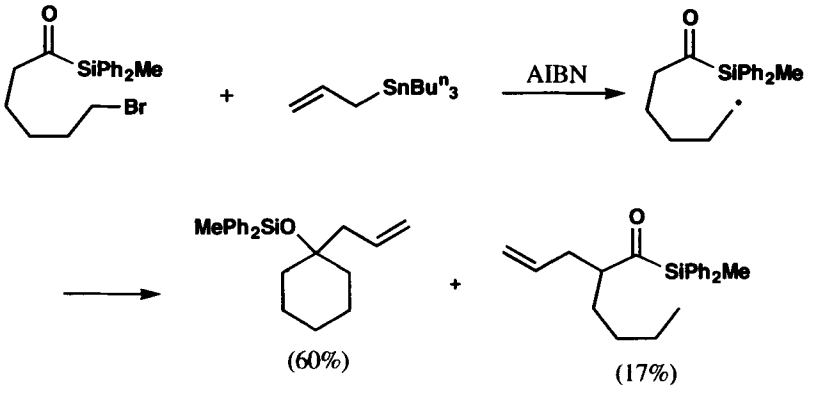
The reaction of 1-halo substituted acylsilanes with allyl stannanes[94] or methyl acrylate[95] and tributyltin hydride affords the corresponding products of tandem cyclization-addition reactions (*Scheme* 41).[96]



i) CH_2=$CHCH_2SnBu^n_3$, AIBN; ii) TBAF; iii) $CH_2C(CO_2Et)CH_2SnBu^n_3$, AIBN; iv) CH_2=$CHCO_2Me$, Bu^n_3SnH, AIBN

Scheme 41

When the reaction is carried out with a ω-bromo substituted acylsilane and allyltributylstannane, competition between 6-*exo* cyclization and 1,5-hydrogen transfer is observed (*Scheme* 42).[94]

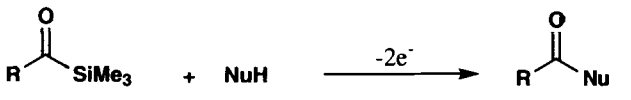


Scheme 42

(c) Oxidation Reactions

The oxidation of acylsilanes to carboxylic acids can be carried out with alkaline hydrogen peroxide.[97] Oxidation potentials of aliphatic acylsilanes are much lower than those of the corresponding ketones and aldehydes.[98] The silicon raises the HOMO level by interaction between the carbon-silicon σ orbital and the non-bonding p orbital of the carbonyl oxygen, which favors the electron-transfer process. Preparative electrochemical oxidation leads to the facile cleavage of the

carbon-silicon bond and the introduction of nucleophiles such as alcohols, water, carbamates and sulfonamides (*Eq.* 38).[98]

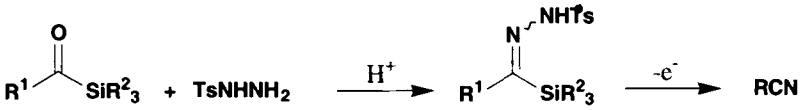


(38)

R = alkyl
NuH = ROH, H_2O, $MeNHCO_2Me$, MeNHTs

(69-92%)

Tosylhydrazones of acylsilanes also undergo smooth anodic oxidation in dichloromethane to give the corresponding nitriles (*Eq.* 39).[98] The transformation of acylsilanes to the corresponding nitriles has also been carried out by reaction of acylsilane phenylhydrazones with PCl_3[99] or by reaction of acyl silanes with acetic anhydride/pyridine.[100]

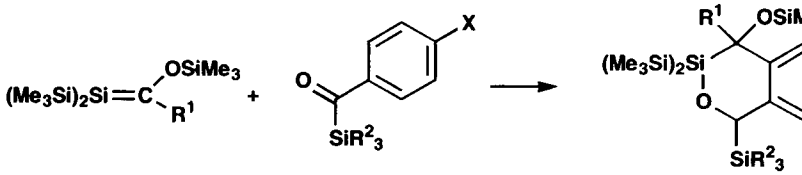


(39)

(55-84%)

(d) Cycloaddition Reactions

Silenes of the type shown in *Eq. 40* react with aroylsilanes in a [2+4] manner to afford bicyclic adducts.[101] This behavior has also been observed in the same reaction with phenones.[102] Reactions involving silenes are believe not to be concerted. Only the [2+2] adduct is formed in the case shown in *Eq. 40*. However, as in the case of carbonyl compounds, no isomerisation of [2+4] to [2+2] adducts is observed.[102]

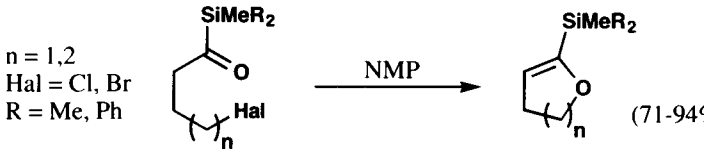


(40)

R^1 = Bu^t, adamantyl, R^2 = Me, Ph, X = H, F, Cl, Br, OMe (40-56%)

(e) Other Reactions

The first example in which the carbonyl oxygen of an acylsilane participates as nucleophile is the intramolecular cyclization of γ- and δ-halo substituted acylsilanes to give, by heating in the presence of *N*-methyl-2-pyrrolidinone (NMP), the corresponding 2-silyldihydrofurans or pyrans, respectively (*Eq.* 41).[103]

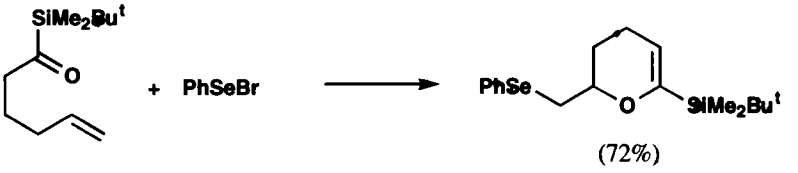


(41)

n = 1,2
Hal = Cl, Br
R = Me, Ph

(71-94%)

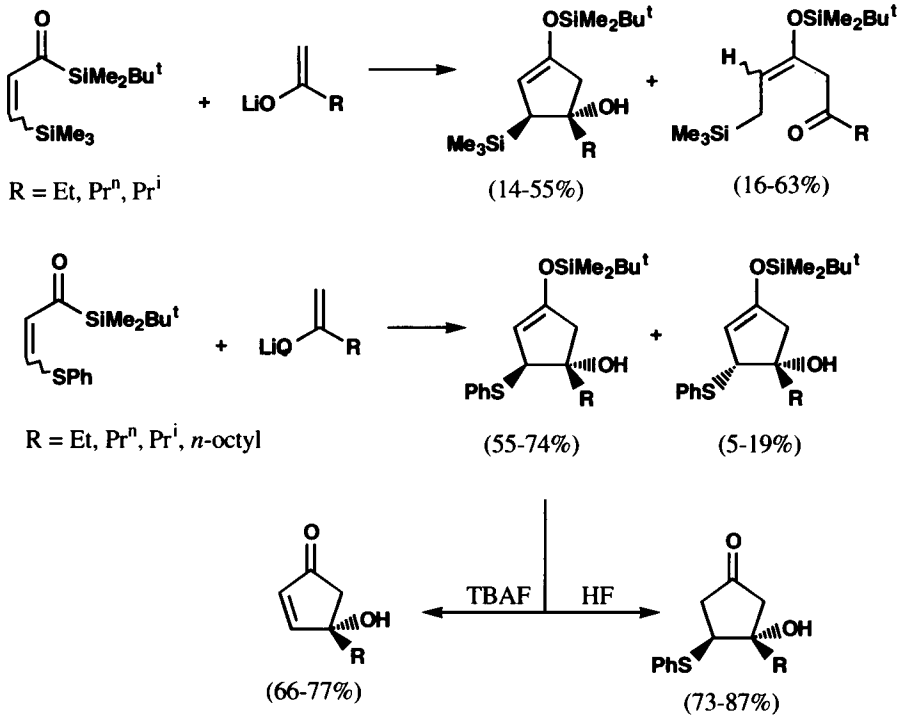
The carbonyl oxygen of an acylsilane also acts as a nucleophile in the intramolecular addition to olefins promoted by phenylselenyl bromide (*Eq.* 42).[103]



(72%) (42)

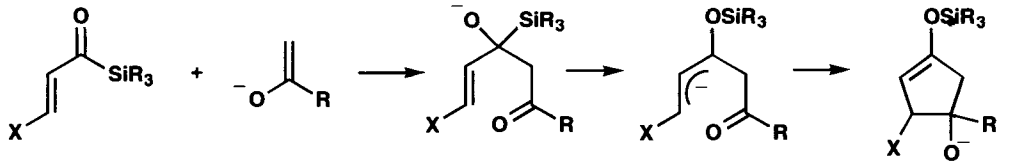
α,β-Unsaturated acylsilanes are valuable building blocks for the synthesis of complex organic compounds. Thus, this class of compounds undergo (a) conjugate additions,[69f] (b) titanium tetrachloride-promoted conjugated allylations,[104] (c) Diels-Alder reactions,[69f] (d) 1,3-dipolar cycloadditions[103], and (e) [3+2] and [3+3] annulation reactions.[70,105,106]

In relation with [3+2] annulation reactions, a new strategy has been developed employing β-substituted α,β-unsaturated acylsilanes and ketone enolates as three- and two-carbon components, respectively (*Scheme* 43).[107] The (*Z*)-β-silyl substituted derivatives give mainly cyclic products and the corresponding (*E*)-isomer acyclic compounds. The *Z/E* mixture of β-(phenylthio)acryloylsilane affords diastereomeric cyclopentenols, the corresponding final ratio being unafected by the *E/Z* ratio of the starting acylsilane. These results suggest that the annulation reaction could follow the mechanism shown in *Scheme 44*, in which a Brook rearrangement is the key step of the process. This



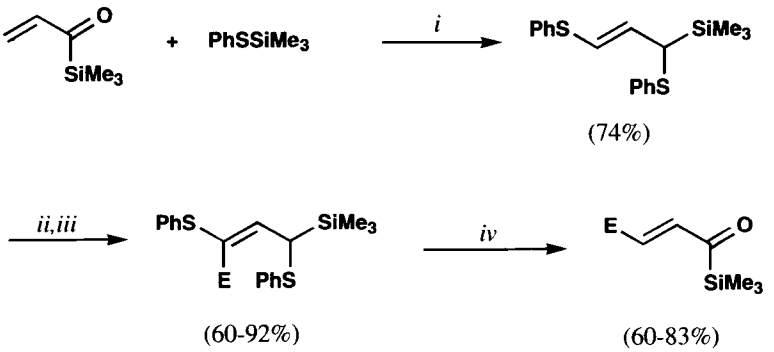
Scheme 43

methodology has been applied to the synthesis of chromomoric acid D-II methyl ester,[107] an analogue of the antitumor marine prostanoid clavulones.



Scheme 44

Acryloyl trimethylsilane is transformed into (*Z*)-trimethylsilyl-1,3-bis(phenylthio)-propene[108] by reaction with (phenylthio)trimethylsilane in the presence of boron trifluoride (*Scheme* 45), acting this material as an useful β-acylvinyl anion equivalent.[109] The deprotonation of silylated bis(phenylthio)propene with *tert*-butyllithium at -40° followed by reaction with electrophiles (benzaldehyde, methyl chloroformate, allyl bromide and methyloxirane) leads to the regio- and stereoselective functionalization at the C-3 carbon. These products afford, after treatment with mercury(II) chloride, the corresponding β-functionalized α,β-unsaturated acylsilanes (*Scheme* 45).[109]



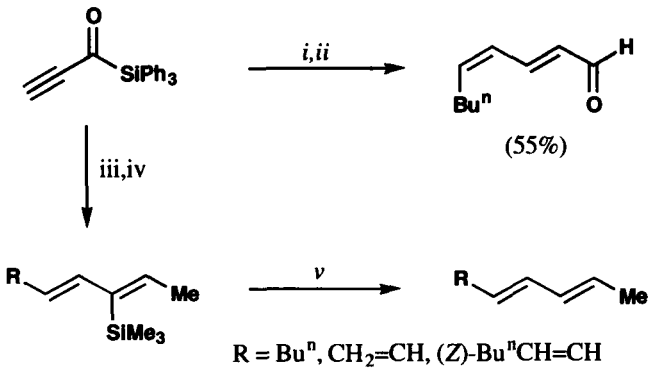
E = PhCHOH, CO_2Me, CH_2=$CHCH_2$, $MeCH(OH)CH_2$

i) BF_3•OEt_2; ii) Bu^tLi; iii) E^+; iv) $HgCl_2$

Scheme 45

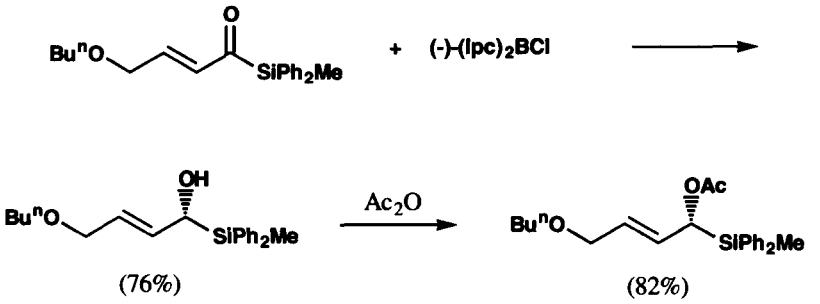
The carbocupration of ethynyl triphenylsilyl ketone (see *Eq.* 27) with the vinyl cuprate shown in *Scheme 46* gives a polyunsaturated acylsilane, which was conveniently desilylated with TBAF giving the corresponding dienal.[71] When this acylsilane is treated with different vinyl cuprates and then with ethylidenetriphenylphosphorane the corresponding polyunsaturated silanes are obtained, which after desilylation afford polyenes in a stereoselective manner (*Scheme* 46).

The asymmetric reduction of the α,β-unsaturated acylsilane shown in *Scheme 47* with (-)-chloro(diisopinocampheyl)borane[85] gives (*R*)-(*E*)-4-(benzyloxy)-1-[(dimethylphenyl)silyl]-2-buten-1-yl acetate, which has been used as homochiral building block in the synthesis of the AB-ring system of (+)-sesbanimide A (*Scheme* 47).[110]



i) $[(Z)\text{-}Bu^nCH{=}CH]_2CuLi$; ii) TBAF; iii) R_2CuLi
iv) $CH_3CH{=}PPh_3$; v) TBAF, NaOH

Scheme 46



Scheme 47

III. GERMANIUM DERIVATIVES

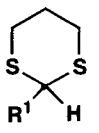
Acylgermane compounds are more stable than the corresponding silane and stannane derivatives. They do not suffer appreciable hydrolysis in 10% hydrochloric acid or 10% sodium hydroxyde and are nearly inert toward lithium diisopropylamide and Lewis acids.[111] Their spectroscopic properties (IR and UV spectroscopy) and X-ray diffraction studies are similar than those of acylsilanes and stannanes,[51b] showing that the carbonyl group is very polar.[112]

1. Preparation of Acylgermanes

The first four methods described for the synthesis of these compounds are based on the hydrolysis of α,α-dibromobenzylgermanes,[112] the hydrolysis of 2-germyl substituted 1,3-dithianes,[52a,b] the oxidation of α-germyl alcohols,[113] and the acylation of triphenylgermyllithium.[113] The most useful procedures are based on the last three methods.

Concerning the germylation of masked acyl anions, organolithium compounds derived from 1,3-dithianes react with chlorotrialkyl or aryl germanes to give the corresponding 2-germyl substituted derivatives, which after treatment with mercury(II) chloride afford the expected α-germyl ketones[52a,b]

(*Eq.* 43). A related methodology based on 1,3-dioxan derivatives has been applied to the synthesis of silyl, germyl and stannyl alk-1-ynyl ketones (*Eq.* 44).[69l,m]

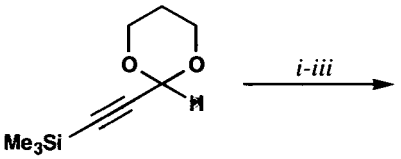


$$\xrightarrow{i\text{-}iii} \quad R^1COGeR^2{}_3 \qquad (43)$$

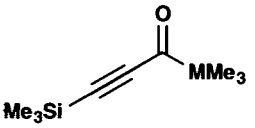
R^1 = Me, Ph, Me_3Si, Et_3Ge; R^2 = Et, Ph

i) Bu^nLi; ii) $R^2{}_3GeBr$; iii) $HgCl_2$

Following the same procedure described for acylsilanes, the reaction of acyl anion equivalents such as lithiated vinyl ethers with chlorotrimethylgermane affords the corresponding acylgermanes.[114]



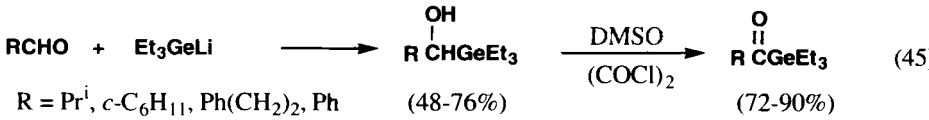
$$\xrightarrow{i\text{-}iii} \qquad (44)$$



i) Bu^nLi; ii) Me_3MCl; iii) 0.01 M H_2SO_4

(M = Si, 84%; M = Ge, 68%; M = Sn, 70%)

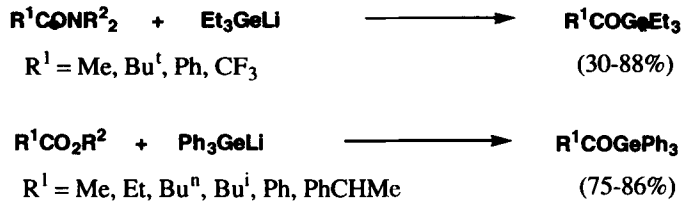
The addition of trialkyl- or arylgermyllithium to aldehydes gives good yields of α-hydroxygermanes which afford the corresponding acylgermanes upon oxidation. This procedure was studied in the case of triphenylgermillithium and acetaldehyde[113] using the Jones oxidation (chromium trioxide and sulfuric acid)[111] giving acetyltriphenylgermane in 23% yield. Very recently this methodology has been improved using the Swern oxidation[114] in the synthesis of acyltriethylgermanes (*Eq.* 45).[115]



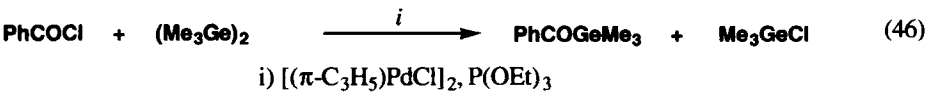
RCHO + Et_3GeLi → R CHGeEt$_3$ (OH) —DMSO, $(COCl)_2$→ R CGeEt$_3$ (O) (45)

R = Pr^i, *c*-C_6H_{11}, $Ph(CH_2)_2$, Ph (48-76%) (72-90%)

With regard to the acylation of trialkylgermyllithium compounds, the addition of the phenyl derivative to acetyl chloride at -78° gives very low yield of the corresponding acyltriethylgermane (1.2%).[113] When *N,N*-dialkylamides are allowed to react with triethylgermyllithium, acyltriethylgermanes are obtained.[118] Acylgermanes are obtained in good yields using esters as acylating agents and triphenylgermyllithium (*Scheme* 48).[111,119] Another methodology is based on the palladium-catalyzed acylation of hexamethyldigermane[120] (see below in preparation of acylstannanes). Thus, the reaction with benzoyl chloride catalyzed by dichlorodi(π-allyl)dipalladium(II) and triethyl phosphite affords benzoyltrimethylgermane in 62-78% yield, depending on the reaction conditions (temperature and reaction time) (*Eq.* 46).[118]



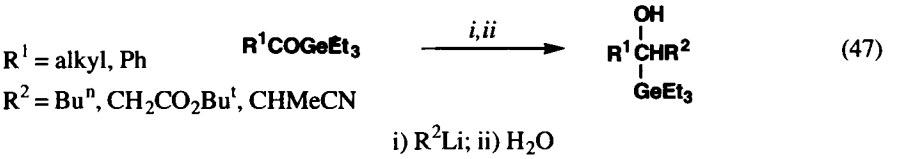
Scheme 48



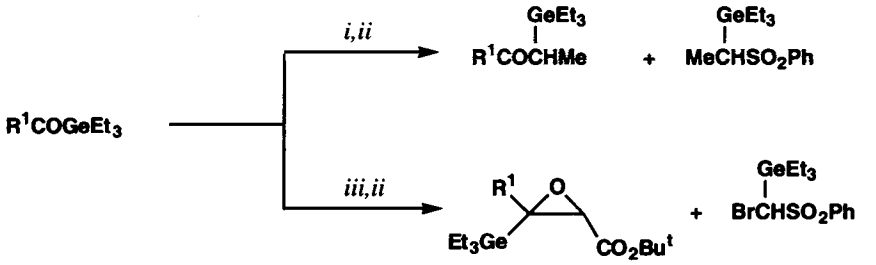
2. Reactivity of Acylgermanes

The acylgermyl moiety can be transformed into a carboxylic acid or an aldehyde by hydrolysis or photolysis, respectively.[121] Thus, nucleophilic addition to the carbon-oxygen double bond and photolysis are the two basic reactions of these compounds.

The nucleophilic addition of lithium aluminium hydride[112] or phenylmagnesium bromide[113] to acylgermanes gives the corresponding α-germyl alcohols. More recently, the addition of organolithium compounds to the same substrates has been widely studied.[117] Butyllithium and lithium enolates derived from *tert*-butyl acetate and propionitrile give the corresponding α-germyl alcohols (*Eq.* 47). Trialkylgermyl groups tend to link with carbon rather than oxygen, in contrast to trialkylsilyl groups, which have a high affinity to oxygen.[122]



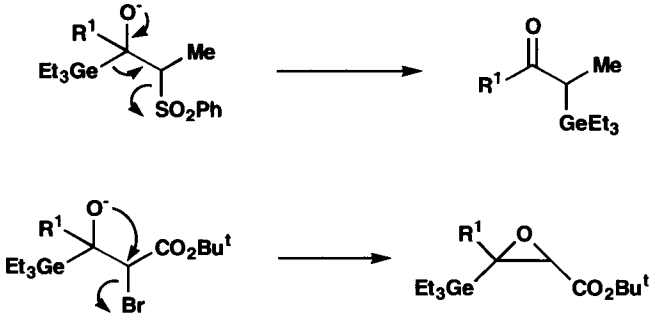
The reaction of acylgermanes with 1-lithioethyl phenylsulfone gives a mixture of α-germyl ethylsulfones. In the case of lithium enolate derived from *tert*-butyl bromoacetate, a mixture of *cis/trans* isomeric oxiranes and α-bromo-α-germyl acetate is obtained (*Scheme* 49).[117]



i) MeCH(Li)SO_2Ph; ii) H_2O; iii) BrCH(Li)CO_2Bu^t

Scheme 49

α-Germyl ketones and oxiranes are formed by elimination of the arylsulfinate and bromide, respectively, from the 1,2-addition products (*Scheme* 50).[117]



Scheme 50

The other by-products are formed by nucleophilic attack to the germanium moiety and elmination of an organolithium compound and carbon monoxide (*Eq.* 48).[117] Acylgermanes react also with Wittig reagents to give vinylgermanes.[123]

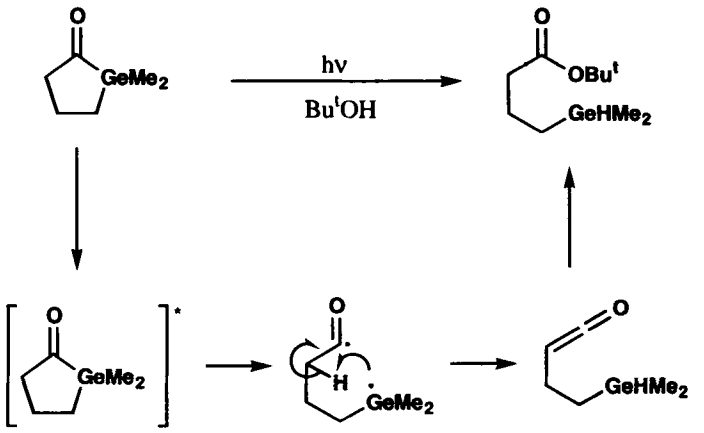
(48)

(Triphenylgermylacetyl)triphenylgermane, prepared by reaction of triphenylgermyllithium with ethyl bromoacetate (66%), reacts with aldehydes in the presence of boron trifluoride to give aldols in a fashion similar to its silylated congeners (α-trimethylsilyl ketones) (*Eq.* 49).[124] The acylgermyl moiety is stable under the Lewis acid conditions and is inert toward ketones and acetals. In addition, these aldol reactions do not take place using lithium diisopropylamide.

(49)

Photolysis of acylgermanes leads to a Norrish type I cleavage. The mechanism of the photodecomposition of benzoyltriphenylgermane was first studied by Brook *et al.* in carbon tetrachloride as solvent and benzoyl chloride (91%) and chlorotriphenylgermane (94%) were the main products.[125] Photolysis of germacyclopentanone in *tert*-butanol leads to *tert*-butyl 2-methyl-2-germa-6-hexanoate in 40% yield.[126] The mechanism proposed to explain the formation of this ester implies the homolytic cleavage of the carbon-germanium bond to give a ketene intermediate (*Scheme* 51). This pathway has been established by deuterium incorporation only in the α-position of the ester functionality when the reaction was carrried out in Bu^{t}OD.

Germyl radicals derived from benzoyltriphenylgermane and benzoylphenyldimethylgermane have been detected by laser-photolysis.[127]

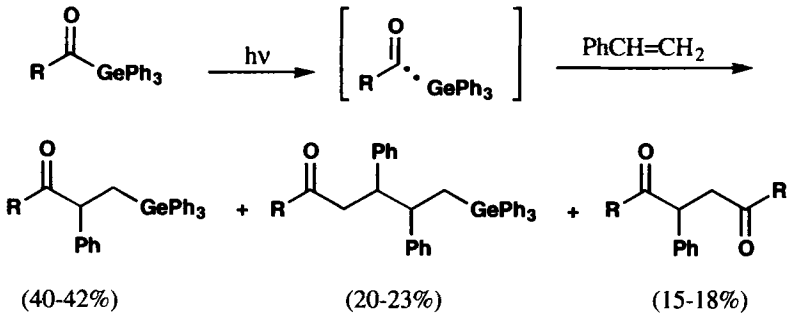


Scheme 51

The study of the photolysis of benzoyltriethylgermane in various media using the chemically induced dynamic nuclear polarization method (^{1}H CIDNP) shows that the triplet radical pair of Et_3Ge• and PhCO• are formed initially.[128] Propionyl- and benzoyltriphenylgermane upon irradiation are degradated to a complex mixture of products such as carboxylic and hexaphenylgermane.[111] In contrast, α-arylacylgermanes suffer quantitatively photochemical decarbonylation to give α-arylalkylgermanes (*Eq.* 50).[111]

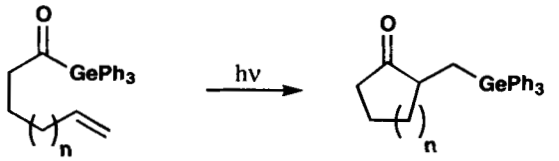
$$\mathbf{ArCHRCOGePh_3} \xrightarrow{h\nu} \mathbf{ArCHRGePh_3} + \mathbf{CO} \qquad (50)$$

The formation of the triplet radical pair in the solvent is also proposed in the intermolecular addition of acylgermanes to styrene (*Scheme* 52).[129] The same authors describe the efficient photochemical intramolecular cyclization reactions of acylgermanes[130] to give cycloalkanones through a 5-*exo-trig* and 6-*exo-trig* process (*Eq.* 51).



R = Me, $PhCH_2CH_2$

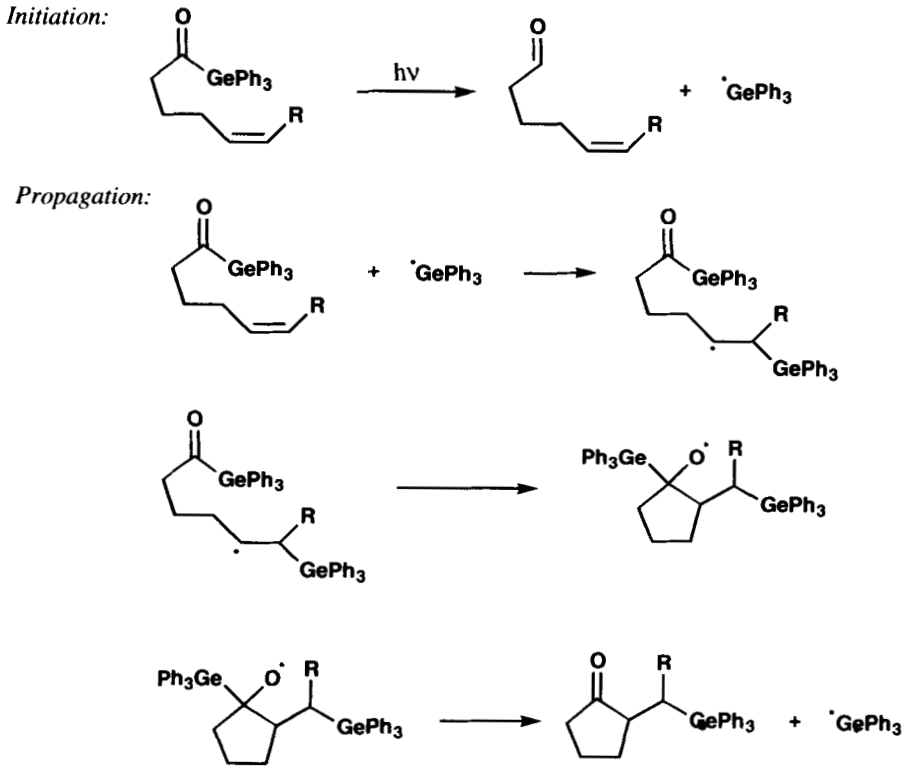
Scheme 52



(65-97%) (51)

Experimental evidence[91] indicates that unsaturated acylgermanes react through a radical mechanism, which involves: (a) addition of the germyl radical, (b) 5-*exo* cyclization of this radical to give a β-germyl alkoxy radical, and (c) fragmentation to form the corresponding cyclopentanone and regeneration of the chain-carrying germyl radical (*Scheme* 53). Internal olefins do not react[129] because the corresponding adducts revert rapidly to give the starting material.

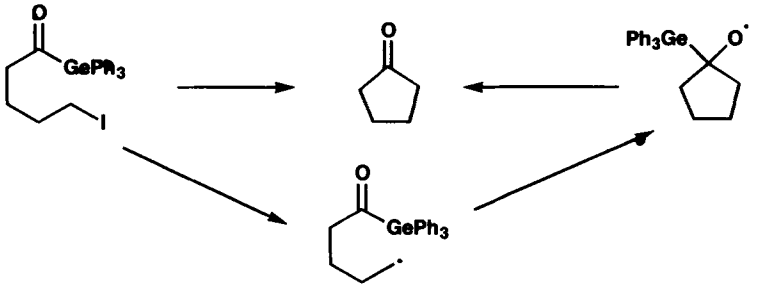
According to the proposed mechanism, acylgermanes should be good aceptors for radicals. This view has been demonstrated by photolysis or thermolysis of δ-iodoacyltriphenylgermane in the presence of AIBN and triphenylgermanium hydride, which is converted into cyclopentanone (*Scheme* 54).[91]



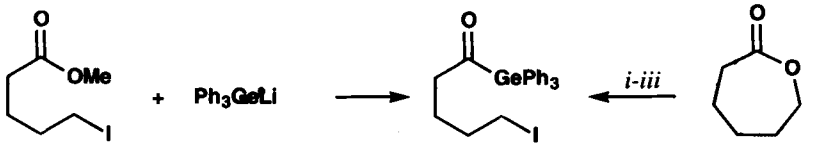
Scheme 53

This type of reactions has also been described for acylsilanes[87] and also as well as the tandem cyclization-addition reactions,[90] which does not occur in the case of acylgermanes. Rate

measurements of 5- and 6-iodo substituted acyltriphenylgermanes, prepared by the method of Kiyooka (*Eq.* 52),[130] are surprisingly high.[92] The 5-*exo*-cyclization of the δ-radical intermediate is



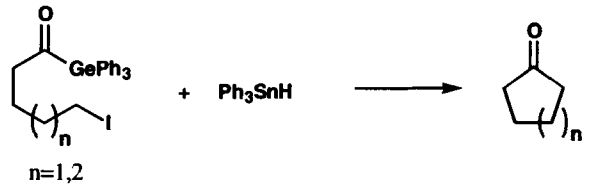
Scheme 54



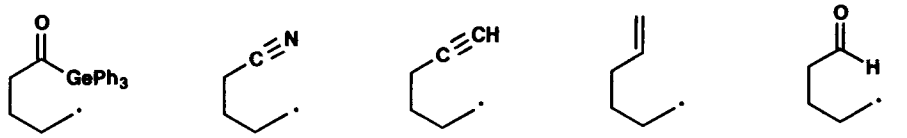
(52)

i) Ph_3GeLi; ii) MsCl; iii) NaI

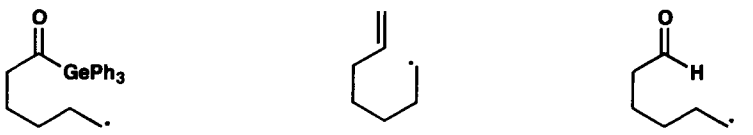
faster than the corresponding one for the related nitrile, alkyne, alkene or aldehyde. The rate of the 6-*exo*-cyclization of the ω-radical is about the same for the analogous aldehyde and considerably faster than for the corresponding heptenyl radical (*Scheme* 55).



n=1,2



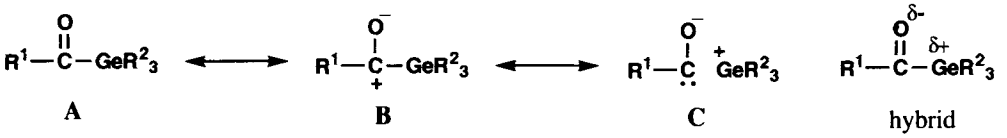
$7x10^6\ s^{-1}$ $4x10^4\ s^{-1}$ $3x10^5\ s^{-1}$ $1x10^6\ s^{-1}$ $9x10^5\ s^{-1}$



$2x10^6\ s^{-1}$ $5x10^3\ s^{-1}$ $1x10^6\ s^{-1}$

Scheme 55

The properties and reactivity of acyl germanes (as well as those of related silanes and stannanes) have been rationalized by the resonance theory.[131] Resonance structure C becomes important because germanium is more electropositive than carbon (*Scheme* 56). The carbonyl carbon is



Scheme 56

electron-poor; this fact should accelerate cyclization of nucleophilic radicals.[132] In general, acylgermanes can be considered reagent equivalents of the carbonyl radical aceptor synthon, according to Curran's notations.[92] The reactivity of carbamoylgermanes, which have been prepared by reaction of carbamoyllithium with chlorotrimethylgermane[10] remains unexplored.

IV. TIN DERIVATIVES

As a consequence of the greater reactivity of the tin-carbon bond, acylstannanes are the least explored acyl metallic compounds derived from group 14 elements, despite of their theoretical and practical interest in synthetic organic chemistry.[134] In general, they are very unstable to light and toward molecular oxygen, especially trialkylacylstannanes. Their spectroscopic properties have been studied together with silicon and germanium derivatives.[51b]

1. Preparation of Acylstannanes

The most general strategies for the synthesis of acylstannanes are either the acylation of trialkylstannyl metal or palladium-catalysed coupling of acyl chlorides and distannanes.

(a) Acylation of Stannyl Metals

The first preparation of acyltin compounds was based on the reaction of triphenyltinlithium with acyl chlorides at -70° (*Eq.* 53).[111]

$$Ph_3SnLi + RCOCl \xrightarrow{-78^\circ} Ph_3SnCOR \quad (53)$$

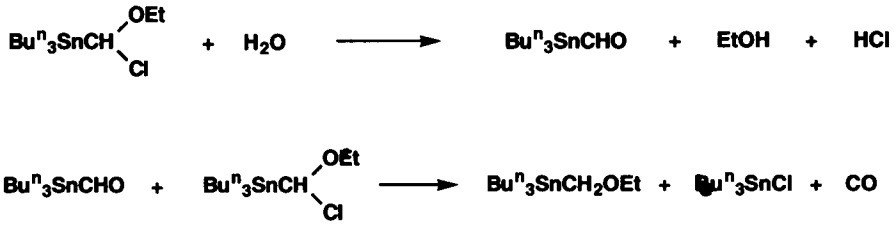
R = Me, Ph

The corresponding tributylacylstannanes have been prepared starting from tributylstannylmagnesium chloride and an aldehyde (*Eq.* 54).[135] This process is a kind of Cannizzaro reaction, requiring an excess of aldehyde.

$$Bu^n_3SnMgCl + 2\,RCHO \longrightarrow Bu^n_3SnCOR + RCH_2OMgCl \quad (54)$$

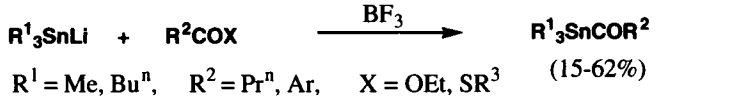
R = Me, Et, Pr^i, Ph (59-82%)

Quintard *et al.* studied the hydrolysis of α-chloro(α-ethoxymethyl)tributyltin with water to give carbon monoxide, chlorotributyltin and (ethoxymethyl)tributyltin. They detected the formation of formyltributyltin as intermediate by UV spectroscopy (*Scheme* 57).[135a]



Scheme 57

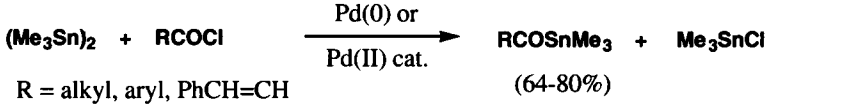
A general route to acylstannanes based on the acylation of trialkylstannyllithium with esters and thioesters has recently been described.[136] This methodology is especially suited for the preparation of aroyltrialkylstannanes, which can not be prepared by Quintard's method.[137] The reaction can be carried out with trimethyl- and tributylstannyllithium and esters, or better with thioesters, in the presence of boron trifluoride etherate (*Eq.* 55).



(55)

(b) Acylation of Distannanes

Palladium-catalyzed acylation of hexamethylditin is a general procedure for the preparation of acyltrimethyltin compounds from acyl chlorides (*Eq.* 56).[138] This procedure is based on the previously described synthesis of α-diketones via cross-coupling of hexaethylditin[139a] and hexabutylditin[139b] with acyl halides under palladium catalysis (see above). The reaction can be carried out with tetrakis(triphenylphosphine)palladium(0) as the catalyst and is suitable for large-scale use. However, the reaction with hexabutylditin failed.

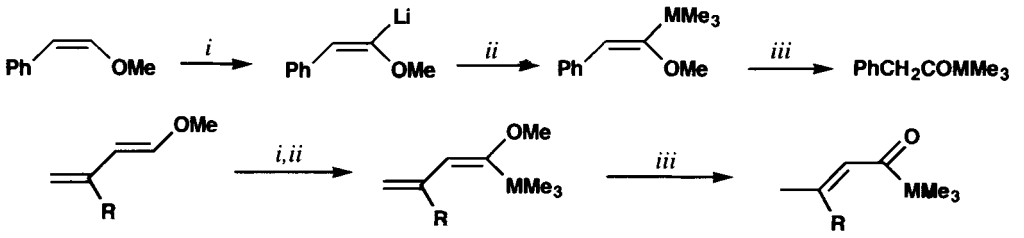


(56)

(c) Stannylation of Acyl Anions

A common access to acyl metals (Si, Ge and Sn derivatives) is the hydrolysis of the corresponding metallovinyl ethers.[112] These vinyl derivatives are prepared by α-deprotonation of *cis*-β-methoxystyrene with *tert*-butyllithium[140] followed by reaction with chlorotrimethyl metal derivatives as electrophiles. The hydrolysis of vinyl derivatives in acetone-water gives the corresponding acyl metals (*Scheme* 58). The same methodology has been studied with conjugated vinyl ethers to give finally α,β-unsaturated acyl metals (*Scheme* 58).

As was described above for acylsilanes and germanes, organolithium derived from 1,3-dithianes can be stannylated. However, the final deprotection of the dithioketal formed does not take



M = Si, Ge, Sn, R = H, Me

i) Bu^tLi; ii) Me_3MCl; iii) H_2O

Scheme 58

place.[52a] Alk-1-ynyl stannyl ketones have been prepared by the same procedure described for silyl and germyl derivatives (see *Eq.* 44).[69l,m]

(d) Oxidation of α-Hydroxystannanes

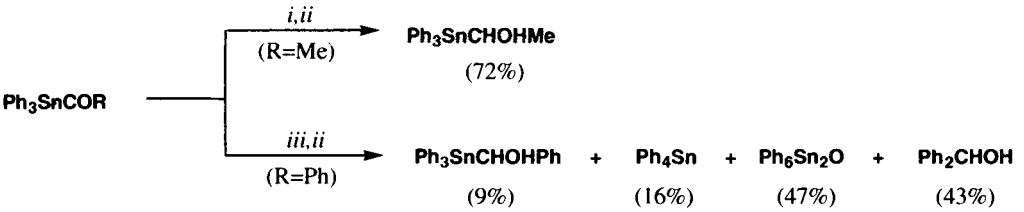
α-Hydroxystannanes, prepared by addition of trialkylstannanes to aldehydes,[141] can be oxidized *in situ* by the Mukaiyama procedure[142] employing azodicarbonyldipiperidine (ADD) or diisopropyl azodicarboxylate as a hydride acceptors to afford acylstannanes (*Eq.* 57). [143] This methodology has also been applied to the synthesis of α,β-unsaturated acylstannanes.[62,72]

$$RCHO \xrightarrow{i,ii} RCOSnBu^n_3 \qquad (57)$$

i) Bu^n_3SnLi; ii) ADD

2. Reactivity of Acylstannanes

Nucleophilic addition to the carbonyl group of acylstannanes is one of the most studied reactions of these compounds. Acetyl triphenyltin is readily reduced by lithium aluminum hydride, whereas the reaction of the corresponding benzoyl derivative with phenylmagnesium bromide gives the alcohol in low yield, hexaphenyltin oxide and benzydrol being the main products (*Scheme* 59).[111]

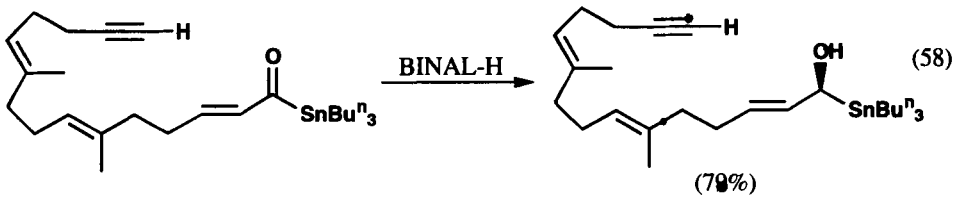


i) LAH; ii) H_3O^+; iii) PhMgBr

Scheme 59

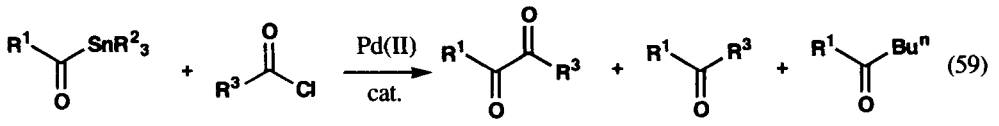
The asymmetric reduction of acylstannanes to give enantiomerically enriched α-alkoxy stannanes[143] has been carried out with Noyori's reagent [(*R*)-(+)-BINAL-H].[144] These compounds have

been used, for instance, in the synthesis of cembranolide precursors (*Eq.* 58).[143b] α-Alkoxy stannanes are valuable precursors for racemic[145] and scalemic[146] α-alkoxy organolithium reagents by tin-lithium transmetallation.[147]



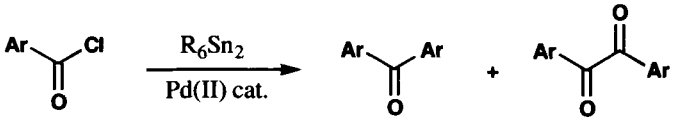
(58)

The possibility of using acyltin compounds as acyl anion equivalents has been studied only in their coupling with aromatic acyl halides under palladium catalysis, affording unsymmetrical α-diketones (*Eq.* 59).[139b] These diketones were obtained together with the decarbonylation product as well as the corresponding alkyl butyl ketone.



(59)

Reaction of acyltin reagents generated *in situ* starting from hexaethylditin[139a] or hexabutylditin[139b] with acyl chlorides gave symmetrical diaryl ketones and/or α-diketones (*Eq.* 60). The



(60)

R = Et, Bu^n

chemical behavior of acyltrialkyltin compounds toward oxygen is similar to that observed for ketones giving the corresponding trialkyltin carboxylates.[135b,136,143b] However, benzoyltriphenyltin is inert to photochemical oxidation.[111]

The preparation of carbamoylstannanes has only been carried out by reaction of the corresponding carbamoyllithium intermediates[28,30,36] with chlorotrialkylstannanes as electrophiles (see section I.2). Lindsay and Widdowson studied the synthesis of different carbamoylstannanes and their coupling with vinyl and aryl halides under palladium catalyzed conditions to give amides (*Eq.* 61). The palladium catalyzed acylation of hexamethylditin failed in the case of diphenylcarbamoyl chloride.[138]

(61)

R^1 = Pr^i, $(CH_2)_4$, $(CH_2)_5$, R^2 = Me, Bu^n, Ph, R^3 = vinyl, aryl

V. SELENIUM DERIVATIVES

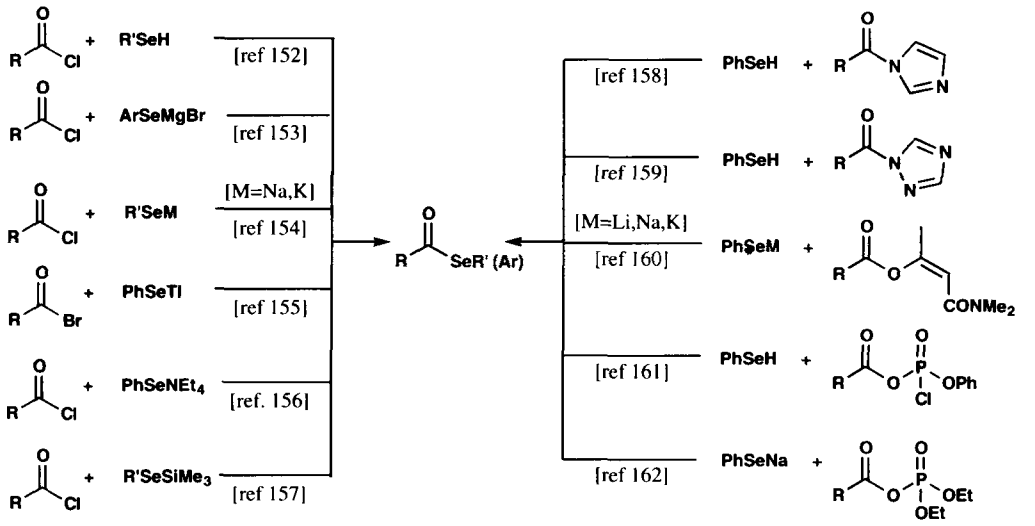
Selenol esters[148] are stable and accessible compounds, which are prepared from carboxylic acid or their derivatives. The high reactivity toward nucleophiles makes selenol esters **I** very useful acyl transfer agents specially for acyl radicals. However, selenol carboxylic acids **II** are unstable[149a] and are transformed into diacyl selenides **III**, which are also thermally labile.[150] Compounds **III** react with sodium methoxide giving the more stable sodium selenol carboxylates[149] **IV**. The spectroscopic properties of selenol esters have been studied together with sulfur and tellurium derivatives[151] and indicate the presence of a "normal" carbonyl functionality.

1. Preparation of Acyl Selenides

The general methods for the preparation of selenol esters have been recently reviewed[148g] and can be classified into five type of reactions according to the starting selenium-containing materials.

(a) Acylation of Selenols and their Salts

Acyl chlorides or bromides, imidazolides or triazolides, vinyl esters and mixed anhydrides or carboxylic acids and phosphorochloridates can act as acylating compounds. Selenols as well as magnesium, alkali metals, thalium(I), tetraethylammonium salts of selenium and trimethylsilyl selenides can be used as selenium compounds (*Scheme* 60).[152-162]

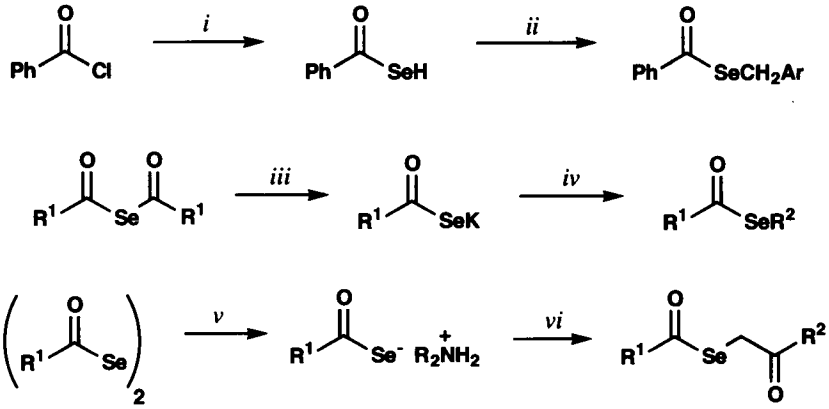


Scheme 60

(b) Alkylation of Selenocarboxylates

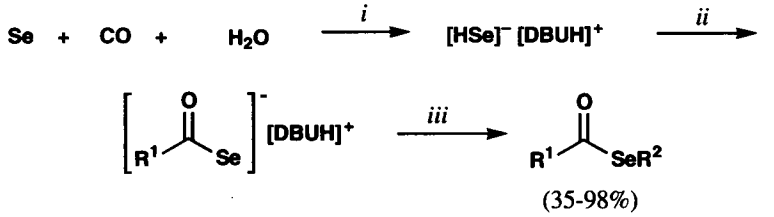
Due to the difficulty of preparation of selenocarboxylates, this method has been used only rarely. Selenobenzoic acid is formed by reaction of benzoyl chloride with hydrogen selenide followed by alkylation *in situ* (*Scheme* 61).[149] Diacyl selenides can be transformed into potassium selenocarboxylates by treatment with methanolic potassium hydroxide.[163] On the other hand, diacyl selenides can be converted into piperidinium carboxylates by reaction with piperidine (*Scheme* 61).[150,164]

The reduction of elemental selenium with carbon monoxide and water in the presence of tertiary amines can be controled to provide amine salts of hydrogen selenide [HSe^-] [R_3NH^+] or of hydrogen diselenide [HSe_2^-] [R_3NH^+]. Subsequent acylation of the hydrogen selenide generated *in situ* by using a stoichiometric amount of water, followed by alkylation of the intermediate acyl selenoate ammonium salt led to the formation of *Se*-alkyl seleno- carboxylates (*Scheme* 62).[165]



i) H_2Se, Py; ii) $ArCH_2Br$, $NaHCO_3$; iii) KOH; iv) R^2X; v) $(CH_2)_5NH$; vi) R^2COCH_2Br

Scheme 61



i) DBU; ii) R^1COCl; iii) R^2Hal

Scheme 62

The preparation of lithium selenocarboxylates by direct reaction of acyl chlorides with lithium selenide has recently been described by Kato *et al.* The corresponding *Se*-methyl esters have been prepared by reaction of lithium selenocarboxylates with methyl iodide (*Eq.* 62).[166]

$$2\,Li + Se \xrightarrow{i} Li_2Se \xrightarrow{ii} \underset{(35\text{-}98\%)}{RCOSeLi} \xrightarrow{iii} \underset{(71\text{-}97\%)}{RCOSeMe} \qquad (62)$$

i) NH_3(l); ii) RCOCl; iii) MeI

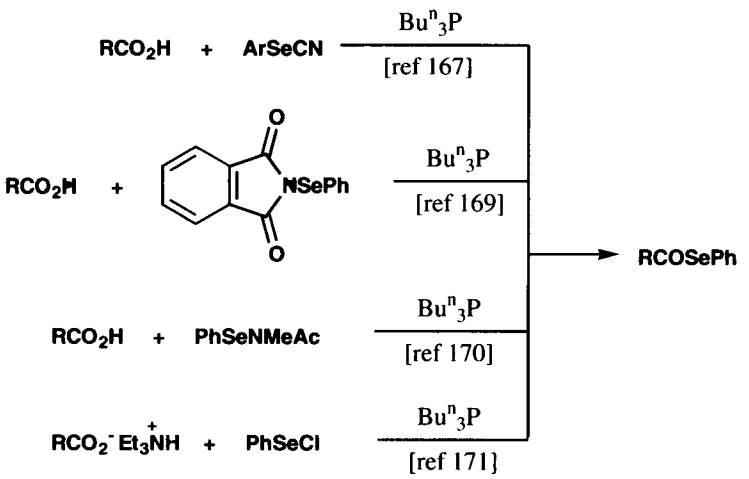
(c) Reaction of Esters with Aluminium Selenolate

This method is appropiate for the mild transformation of esters into methylselenol esters by means of dimethylaluminium methylselenolate (*Eq.* 63).[167]

$$R^1CO_2R^2 + Me_2AlSeMe \longrightarrow R^1COSeMe \qquad (63)$$

(d) Reaction of Carboxylic Acids with Tributylphosphine

Phenylselenocyanate,[168] *N*-phenylselenophthalimide[169] or *N*-acetylselenamide[170] react with carboxylic acids in the presence of tri-n-butylphosphine to provide acyl phenyl selenides (*Scheme* 63). A recent procedure, that avoids malodorous phenylselenocyanate and the expensive and difficultly purified *N*-phenylselenophthalimide, is based on the reaction of carboxylic acids with triethylamine followed by treatment with benzeneselenenyl chloride and tri-n-butylphosphine (*Scheme* 63).[171]



Scheme 63

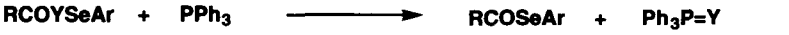
(e) Other Methods

The reaction of hydrazides with benzeneseleninic acid (or the corresponding anhydride) in the presence of triphenylphosphine affords an acyldiimide, which reacts with another equivalent of benzeneseleninic acid to give selenol esters (*Eq.* 64).[172]

(64)

i) $PhSeO_2H$, PPh_3; ii) $PhSeO_2H$

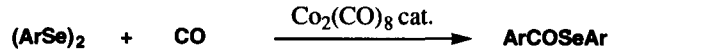
Sulfur or selenium can be removed from arylselenylthio or seleno carboxylates to give selenol esters with triphenylphosphine (*Eq.* 65).[173]



(65)

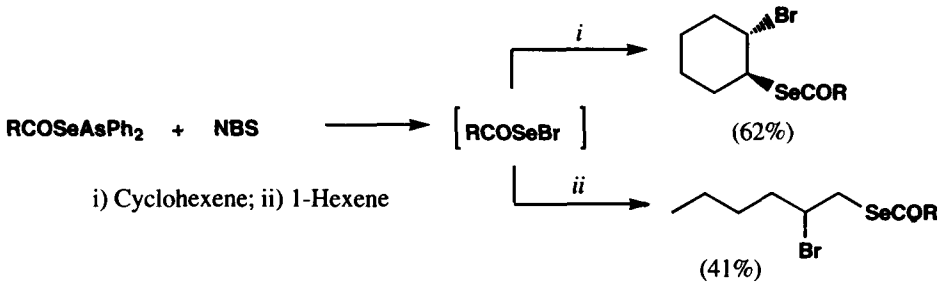
Y = S, Se

Carbon monoxide insertion into diaryl diselenides under high pressure at 100-200° can be performed in the presence of octacarbonyldicobalt as catalyst affording selenol esters (Eq 66).[174]



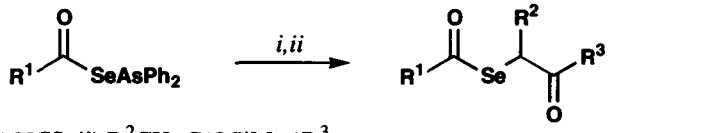
(66)

The use of an electrophilic selenocarboxylating agent for the synthesis of selenoesters has been recently described by Kato *et al.* When acylselenenyl bromides, prepared *in situ* by reaction of *Se*-arsanylselenoesters with *N*-bromosuccinimide, are allowed to react with cyclohexene or 1-hexene at -70°, β-bromo selenoesters are obtained (*Scheme* 64).[175]



Scheme 64

Attempts to isolate acyl selenenyl chlorides or bromides failed and gave diacyl diselenides. When enol silyl ethers are treated with acyl or dimethylcarbamoyl selenenyl chlorides at room temperature, *Se*-β-oxoalkyl selenoesters are obtained (*Eq.* 67).[175]



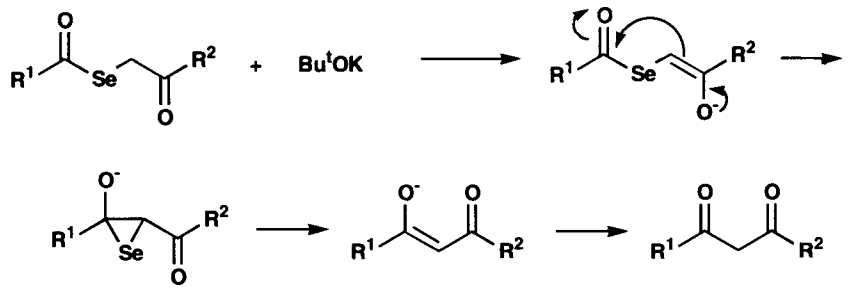
(67)

i) NCS; ii) $R^2CH=C(OSiMe_3)R^3$

(50-67%)

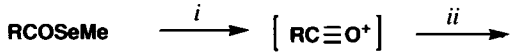
2. Reactivity of Acyl Selenides

The weak bonding between carbon and selenium allows selenol esters to act as acyl transfer agent in nucleophilic substitutions as well as in acyl radical transfer reactions. They can be transformed into the corresponding carboxylic acids, esters or amides in the presence of mercury(II)[167a,176] and copper(I) or copper(II)[167a,b] salts. By means of *N*-phenylseleno-phtalimide/tri-n-butylphosphine, carboxylic acids can be converted directly into amides.[169] *Se*-Acylmethyl selenocarboxylates react with potassium *tert*-butoxide to yield 1,3-diketones (*Scheme* 65).[163b]



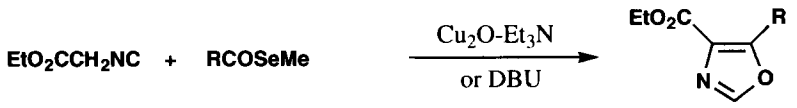
Scheme 65

Aromatic compounds can be acylated inter or intramolecularly with selenoesters[167b,177] in the presence of the copper(I) triflate-benzene complex through the corresponding acylium cations (*Eq.* 68).



i) $(CuOTf)_2$-PhH; ii) ArH (23-100%) (68)

Oxazoles may be prepared by reaction of selenol esters and activated isocyanides under activation by cuprous oxide (*Eq.* 69).[167b,177]

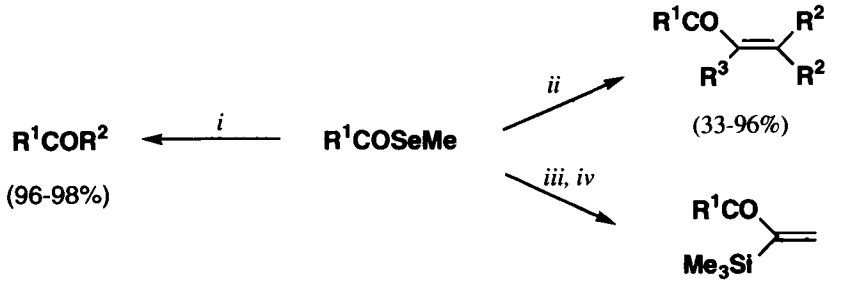


(40-92%) (69)

The reaction of selenoesters with lithium organocuprates provides ketones,[167c] conjugated enones,[178] and α-trimethylsilyl enones from esters in a two-step process[167c] (*Scheme* 66). This methodology has been applied to the synthesis of (*Z*)-12-nonadecen-9-one and (*Z*)-13-eicosen-10-one, components of the pheromone of peach fruit moth *Carposia niponensis*.

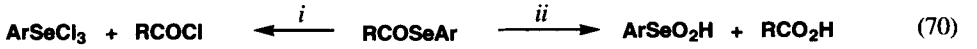
The reaction of selenoesters with diazomethane produces methylene insertion to give α-selenyl ketones together with methyl ketones, diphenyl diselenide and di(phenylseleno)methane as by-products.[179] The α-selenoketones are converted into methyl ketones by treatment with aqueous hydrobromic acid.

Se-Aryl selenoesters are oxidized by chlorine or hydrogen peroxide to afford areneselenenyl trichloride or areneseleninic acids, respectively (*Eq.* 70).[157]



i) $R^2{}_2CuLi$; ii) $R^2{}_2C{=}CR^3Cu{\bullet}MgBr_2$, Me_2S, HMPA; iii) $Me_2AlSeMe$; iv) $CH_2{=}C(SiMe_3)Cu$

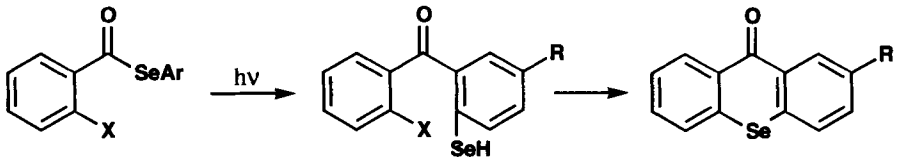
Scheme 66



(70)

i) Cl_2; ii) H_2O_2

The photostimulated reaction of *Se*-aryl selenol esters derived from *ortho*-substituted aromatic and heteroaromatic acids gives cyclization by intramolecular substitution.[180] It has been proposed that a photochemical Fries rearrangement of the selenoester to the corresponding selenoketone takes place, followed by intramolecular nucleophilic photosubstitution (*Eq.* 71).



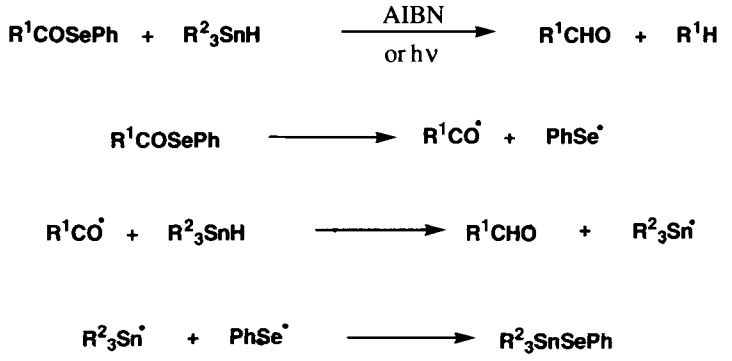
(71)

X = Hal, MeSO, *p*-TolSe, R = H, Me

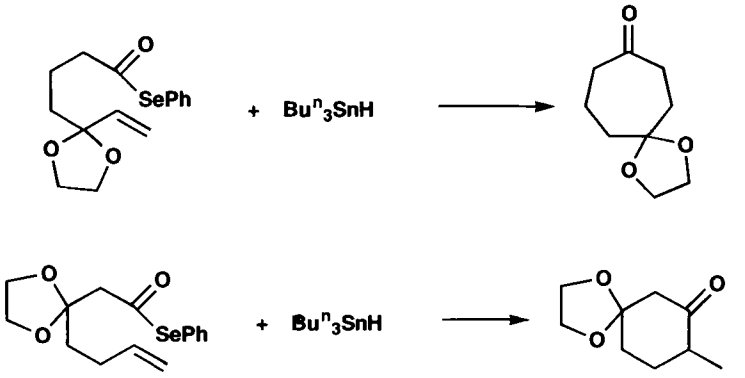
The reduction of *Se*-phenyl selenoesters with trialkyltin hydrides to yield aldehydes or alkanes through a radical process is one of the most studied reaction of these compounds. The acyl radical intermediates give aldehydes by reaction with a hydrogen atom or decarbonylate at higher temperatures to yield the corresponding hydrocarbon (*Scheme* 67).[181] This reduction has been applied to the synthesis of α,β-unsaturated aldehydes[181a] in the synthesis of natural products.[161,180,181]

Primary alkyl, vinyl and aryl substituted acyl radicals, generated by tri-*n*-butyltin hydride treatment of the corresponding phenyl selenoesters, participate in inter and intramolecular alkene and alkyne addition reactions. These radicals exhibit nucleophilic character and react better with alkenes bearing electron-withdrawing or radical stabilising groups. These reactions have been widely studied by Boger, Crich and other groups.[183-193]

Initial studies of intramolecular acylation of a variety of ε-unsaturated *Se*-phenylseleno-esters show that cyclohexanones or cycloheptanones can be obtained, depending on the functionality present in the hydrocarbon chain, together with the corresponding aldehydes (*Scheme* 68).[183]

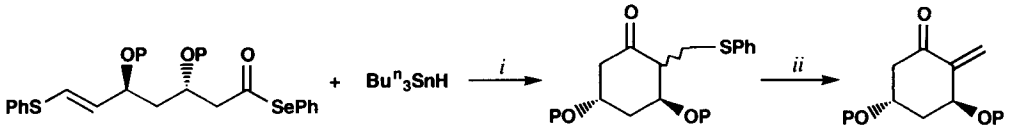


Scheme 67



Scheme 68

This methodology has been applied to the synthesis of the methylenecyclohexanone shown in *Scheme* 69, which is an A ring model for 1α,25-dihydroxy vitamin D_3.[184]



P = Me_2Bu^tSi

i) AIBN; ii) MMPP

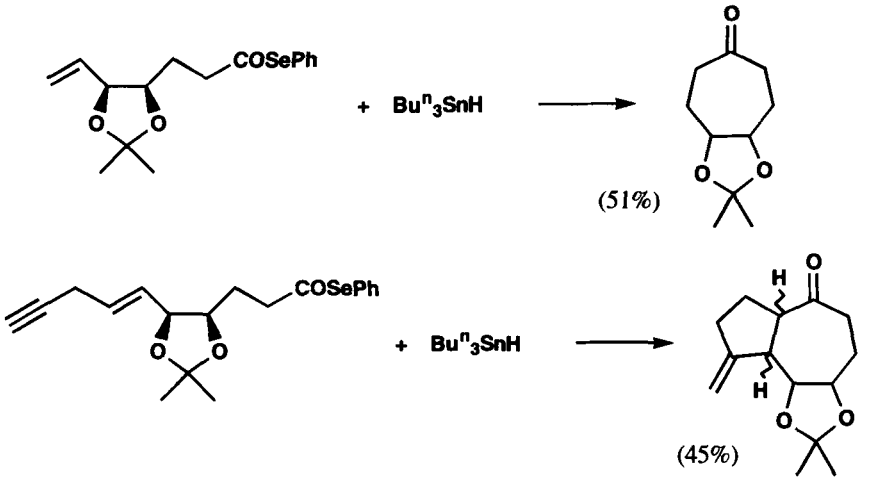
Scheme 69

However, several attemps to induce cyclization of 6-heptynoyl radicals to the corresponding α-methylenecycloalkanones failed.[183a, 184b] The studies of the cyclizations of 6-heptenoyl radicals indicate the reversibility of these reactions.[185] 6-Heptenoyl radicals bearing ether-type functionality at the

δ-position (allylic position) undergo cyclization inefficiently under the *endo* mode ring closure giving cycloheptanones. When the ether functionality is at the β-position the *exo* mode ring closure predominates to give cyclohexanones. Substitution at both 3- and 5-positions gives efficient cyclization of *exo* and *endo* mode ring closure products (*ca.* 3:1 mixture). The presence of a phenylthio group at the terminal 7-position gives efficiently the *exo* mode cyclization.

Enantiomerically pure cycloheptanones and bicyclo[5.3.0]decan-2-ones (perhydroazulenones) have also been prepared in a tandem process by an *endo* mode acyl radical cyclization of 6-heptenoic derivatives.[186] Unsaturated *Se*-phenyl selenoesters, prepared from 2,3-*O*-isopropylidene-*L*-*erythro*-furanose, react with tri-*n*-butyltin hydride affording mainly cycloheptanone derivatives (*Scheme* 70).

The above described intramolecular addition has been carried out efficiently with several *Se*-phenyl selenoesters using activated[187a] and unactivated[187] π-systems and has been applied to the synthesis of chromanones.[187b] The mode of cyclization with simple carbon-carbon double bonds is: 5-*exo-trig*>6-*exo-trig*, 5-*exo-trig*>6-*endo-trig*, 6-*endo-trig*>7-*endo-trig*, 7-*exo-trig*>8*endo-trig* (*Eq.* 72).

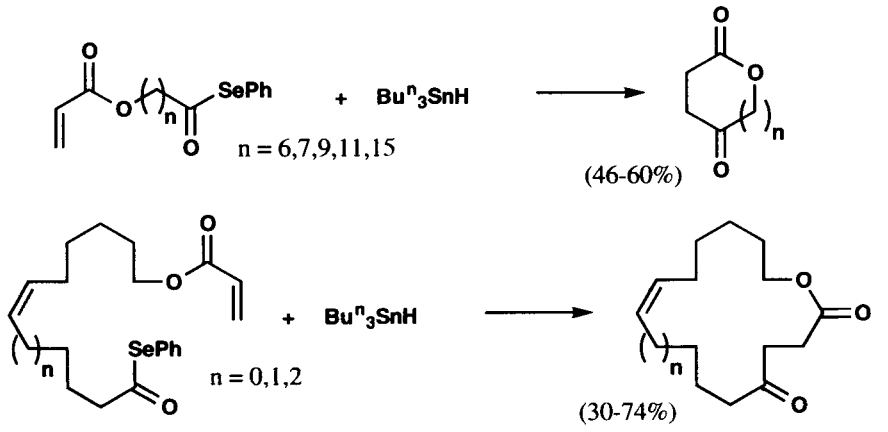


Scheme 70

(72)

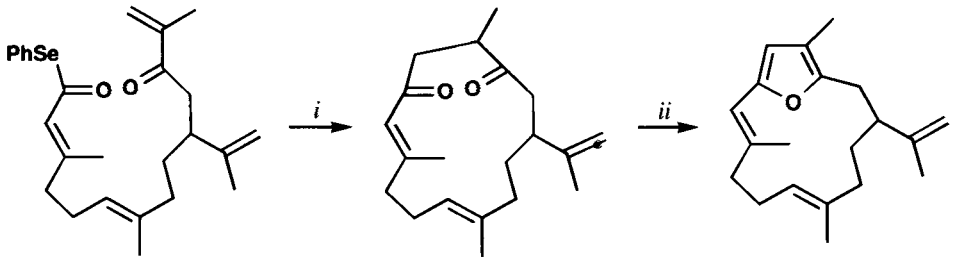
Se-Phenyl selenoesters have also been used for the generation of acyl radicals as intermediates in macrocyclization free-radical alkene addition reactions.[162] Reactions are carried out under

high-dilution conditions and with slow addition of tributyltin hydride, giving only the corresponding macrolides (*Scheme* 71).



Scheme 71

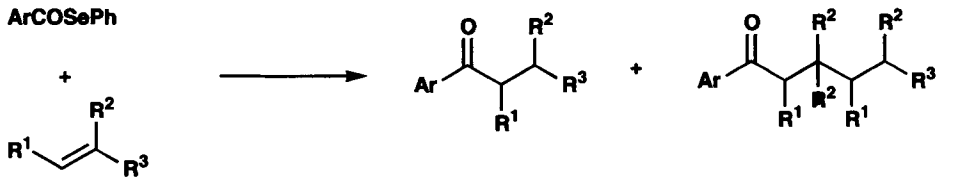
When the substrate bears additional unsaturation, the macrocyclization rate competes with those of 5-*exo-trig* cyclization of 5-hexenoyl radicals and exceeds those of 6-*exo* or 7-*endo-trig* cyclization of 6-heptenoyl radicals. The above mentioned macrocyclization has also been applied by Astley and Pattenden to the synthesis of the furanocembrane unit in lophotoxin and pukalide *via* a 14-*endo-trig* cyclization (*Scheme* 72).[188]



i) Bu$^n_3$SnH, AIBN; ii) *p*-TSA

Scheme 72

The intermolecular reaction has been successfully studied with *Se*-phenyl selenoesters and substituted alkenes.[189] With electron-deficient olefins, the addition takes place giving only bis-addition products in high yield (*Eq.* 73). Neither competitive reduction (less than 5%) nor decarbonylation are observed. However, with electron-rich alkenes, low yields of addition products together with substantial amounts of reduction products (61-80%) are obtained. Phenyl selenoesters derived from aliphatic carboxylic acids give addition products in moderate yields (29-55%) with no evidence of reduction, decarbonylation and subsequent reduction being important competing processes.

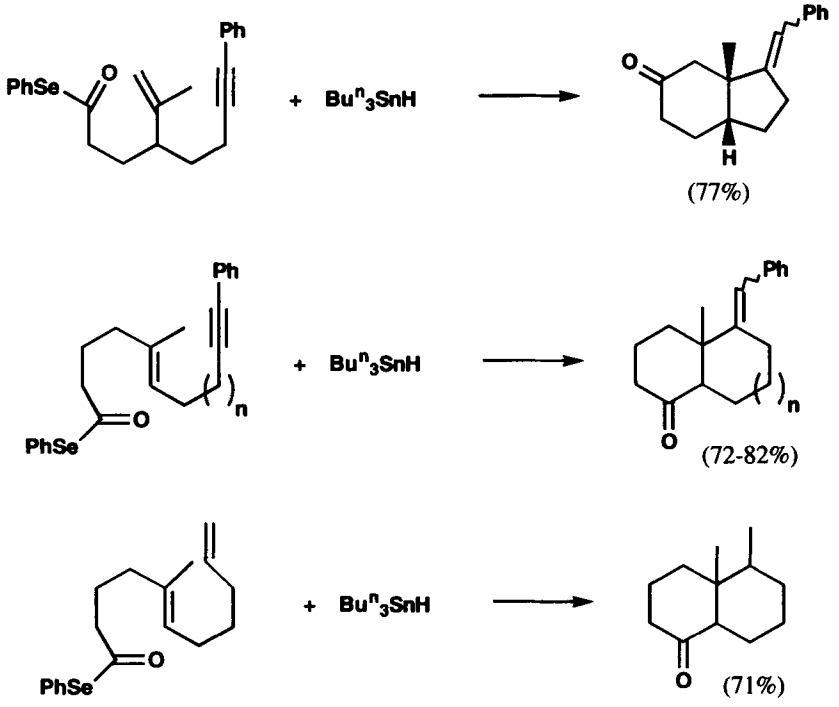


(73)

R^1 = H, Me; R^2 = CN, CO_2Me, Ph; R^3 = H, Me, $OSiMe_3$

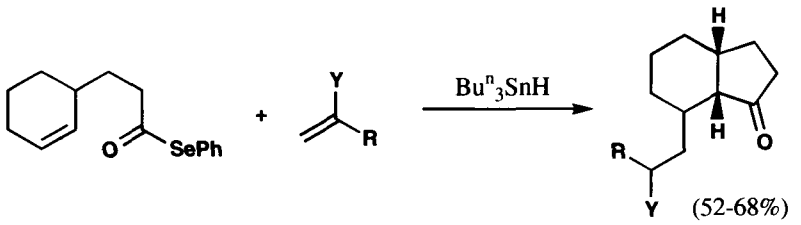
A detailed study of the use of Se-phenyl selenoesters in inter- and intramolecular alkene addition reactions has been carried out by Boger and Nathviuk.[190] Primary alkyl, vinyl and aryl substituted acyl radicals participate in inter- and intramolecular addition reactions with alkenes at rates that exceed those of the potentially competitive decarbonylation or reduction.

Tandem polycyclization reactions can be initiated by acyl radicals derived from *Se*-phenyl selenoesters followed by sequential intramolecular free-radical addition to an alkyne or alkene (*Scheme* 73).[191] In each case, the polycyclization reaction is initiated with a 6-*endo-trig* free-radical



Scheme 73

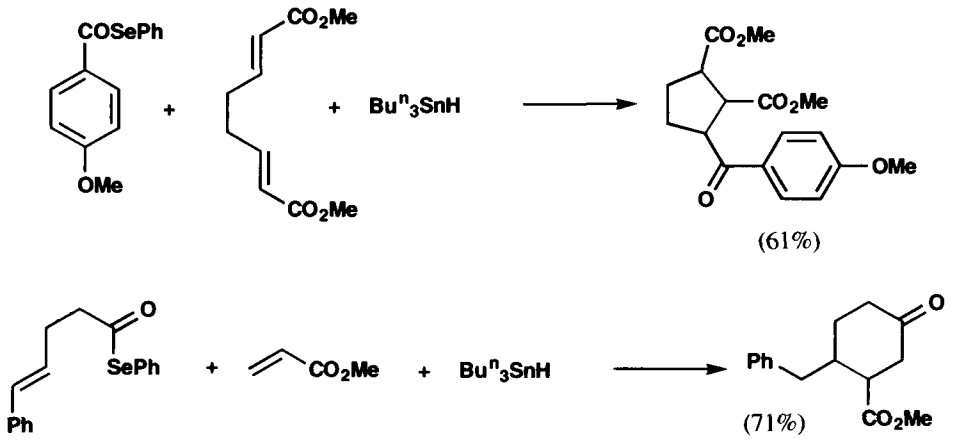
addition followed by subsequent 5-*exo-dig*, 6-*exo-dig*, or 6-*exo-trig* cyclization. Tandem cyclization-intermolecular addition reactions afford stereoselectively 7-substituted *cis*-1-hydrindanones by initial 5-*exo-trig* acyl radical alkene cyclization (*Eq.* 74).[191] Tandem intermolecular addition-cyclization



(74)

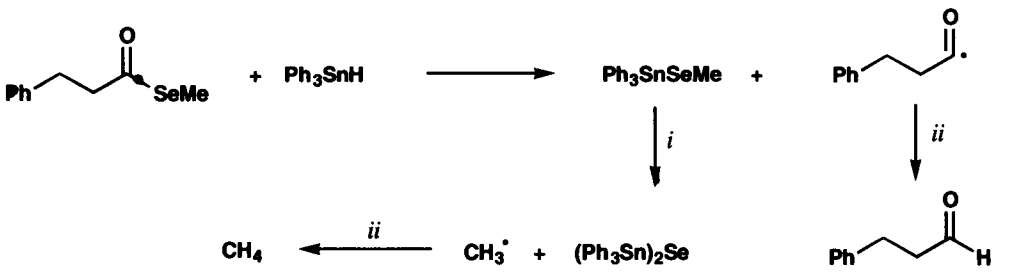
reactions have also been studied with aryl phenyl and alkyl *Se*-phenyl selenoesters and acceptor alkenes (*Scheme* 74).[191]

Schwartz and Curran have found that methyl selenoesters, prepared by reaction of esters with dimethylaluminium methaneselenolate,[167a] also generate acyl radicals by means of two equivalents of tri-*n*-butyltin hydride; these acyl radicals participate in inter- and intramolecular alkene addition reactions.[192] While phenyl selenolesters require only one equivalent of the hydride, methyl derivatives require two due to the formation of a stannyl selenide; the last compound has been detected in the reduction of *Se*-methyl 3-phenylpropionate with triphenyltin hydride (*Scheme* 75).



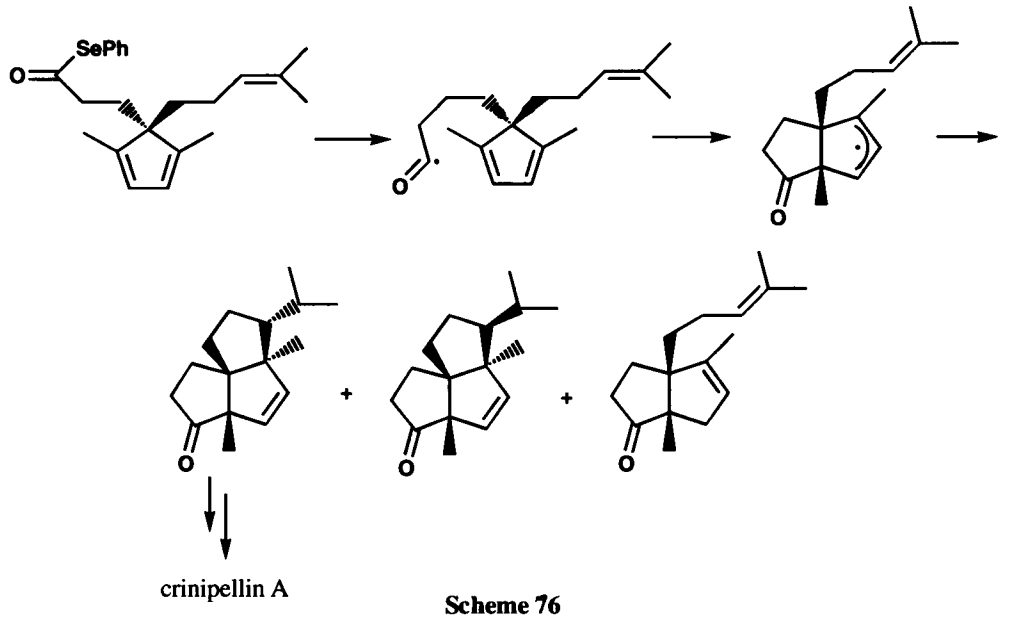
Scheme 74

The same authors have applied the tandem polycyclization reaction of a methyl selenol ester to the construction of the triquinane portion of the antibiotic crinipellin A (*Scheme* 76).[192] Polyolefin cyclization processes initiated by radicals derived from phenyl selenol esters leading to steroid ring synthesis have recently been described.[193] The tandem 6-*endo-trig* cyclizations of dienic, trienic and tetraenic substituted acyl radical intermediates produced from *Se*-phenyl selenoesters are stereospecific (*Eq.* 75).



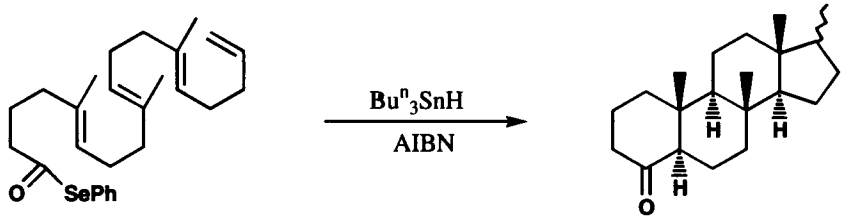
i) $Ph_3Sn^{\bullet}$; ii) Ph_3SnH

Scheme 75



crinipellin A

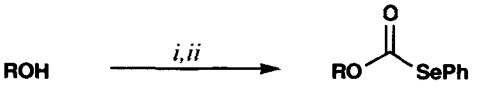
Scheme 76



(75)

3. Alkoxycarbonyl Selenides

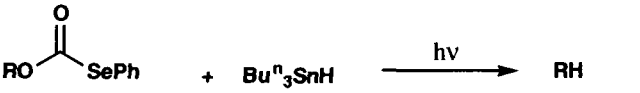
Se-Phenyl selenocarbonates are prepared by reaction of the corresponding alcohols with phosgene and triethylamine followed, by reaction with selenophenol and pyridine (*Eq.* 76).[180c]



(76)

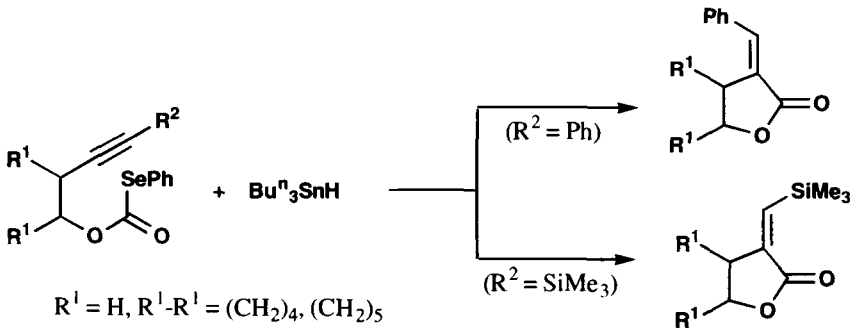
i) $COCl_2$, Et_3N; ii) PhSeH, Py

The reduction of selenocarbonates with tri-n-butyltin hydride to the corresponding hydrocarbons is a good method for the deoxygenation of alcohols (*Eq.* 77).[180c] At low temperatures, the corresponding formates are obtained and isolated as by-products. This reaction has been applied to the preparation of steroids.



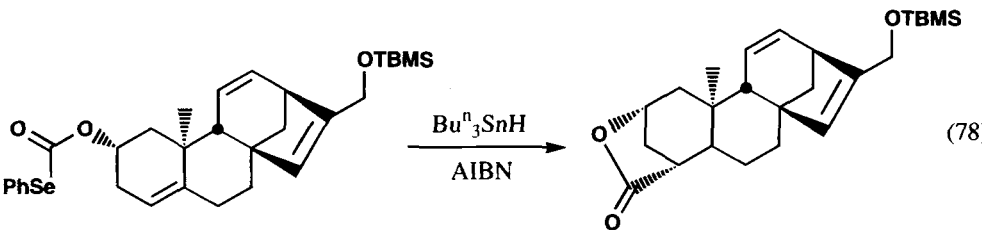
(77)

As in the case of acyl selenides, the mechanism of this reaction involves alkoxycarbonyl radicals as intermediates, which have been trapped in an intramolecular addition process using alkynes[194] and olefins.[195,196] In the case of alkynes, the cyclization of homopropargylic alcohols gives α-alkylidene-γ-lactones stereoselectively (*Scheme* 77).[194]



Scheme 77

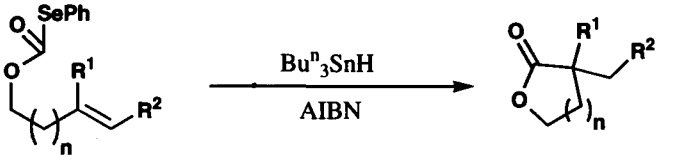
The first intramolecular radical addition of selenocarbonates to olefins to give δ-lactones was carried out by Corey *et al.* in the synthesis of (±)-atractyligenin (*Eq.* 78).[195]



(78)

(73%)

In the case of *O*-alk-3-enyl and *O*-alk-4-enyl *Se*-phenyl selenocarbonates, they undergo regiospecific *exo*-cyclization to the corresponding γ- and δ-lactones upon treatment with tri-*n*-butylstannane and AIBN (*Eq.* 79).[196]

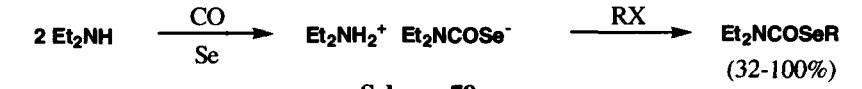


R^1 = H, Me, R^2 = H, Ph, n = 1,2 (80-99%)

However, the intermolecular addition of alkoxycarbonyl radicals, generated from selenocarbonates, failed; only addition of tri-*n*-butyltin hydride to the olefinic component is observed.[187,188]

4. Carbamoyl Selenides

The first synthesis of *Se*-alkyl selenol carbonates was based on the reaction of diethyl amine with carbon monoxide and elemental selenium to give the corresponding diethylammonium salt of selenol carbamic acid. This compound is alkylated *in situ* to provide generally good yields of the corresponding selenol carbamates (*Scheme* 78).[197]



Scheme 78

The reaction of diethylcarbamoyl chloride with lithium *n*-butylselenide gives *Se*-*n*-butyl *N,N*-diethyl selenocarbamate in 65% yield (*Eq.* 80).[197]

(80)

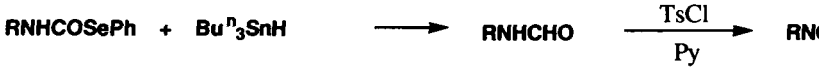
Se-Phenyl selenocarbamates have been prepared by addition of benzeneselenol to isocyanates in the presence of a catalytic amount of potassium *tert*-butoxide (*Eq.* 81).[197]

(81)

R = Ph, PhCH=CH, *n*-C_7H_{15}, Me_2C=CH (65-82%)

i) PhMe, reflux; ii)PhSeH, Bu^tOK cat.

The only reduction of selenol carbamates described uses tri-*n*-butyltin hydride and yields formamides, which are then transformed into isonitriles (*Eq.* 82).[198]



(82)

Biscarbamoyl diselenides, prepared by reaction of secondary amines with carbon monoxide

and selenium in the presence of oxygen,[199] react with aromatic compounds to give Lewis acid promoted carbamoylation (*Eq.* 83).[200] The same reaction can be carried out with diacyl diselenides as acylating electrophilic agents.

$$R_2NCOSeSeCONR_2 + ArH \xrightarrow[\text{or } SnCl_4]{HgBr_2} ArCONR_2 \qquad (83)$$

VI. TELLURIUM DERIVATIVES

The structure of an alkali metal tellurocarboxylates is the same as that of the corresponding seleno derivative, the negative charge being located on the more electropositive alkali metal atom.[149b] These types of compounds have been prepared by reaction of diacyl tellurides with sodium ethoxide (*Eq.* 84).[149b]

$$(RCO)_2Te + NaOEt \longrightarrow RCOTeNa \qquad (84)$$

Tellurol esters are easily accessible from the corresponding acid chlorides or anhydrides and lithium or sodium tellurolates,[201] yields being moderate because of partial decomposition during the work-up (*Eq.* 85).

$$R^1COCl + R^2TeM \longrightarrow R^1COTeR^2 \qquad (85)$$

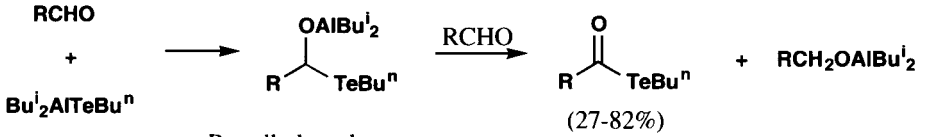
R^1, R^2 = alkyl, aryl, M = Li, Na (20-71%)

Starting from (phenyltelluro)trimethylsilane[202] the reaction with acyl chlorides leads to the corresponding tellurol esters with higher yields (*Eq.* 86).[203]

$$RCOCl + PhTeSiMe_3 \longrightarrow RCOTePh + Me_3SiCl \qquad (86)$$

(62-91%)

Very recently, a new method based on the reaction of aldehydes with diisobutylaluminium tellurate has been described (*Scheme* 79).[204] This procedure can also be applied to the synthesis of selenol esters and thioesters. The reaction presumably procceds by addition of the aluminum component to the aldehyde followed by intramolecular hydride shift to give the corresponding tellurol ester.



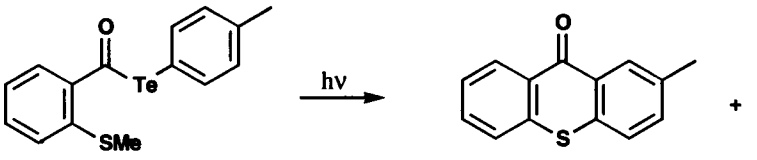
(27-82%)

R = alkyl, aryl

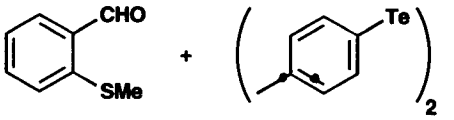
Scheme 79

Tellurol esters are thermally stable but should be stored under nitrogen. They have been much less studied than the corresponding selenium compounds. The photolysis with ultraviolet light of*Te-p*-tolyl telluroesters gives aldehydes and bis(*p*-tolyltelluride);[205] they do not undergo photochem-

ical cyclization as the corresponding selenoesters.[178] In the case of the methylthio substituted telluroester shown in *Eq. 87*, a 22% of thioxanthone is also formed unexpectedly.[205b] White light

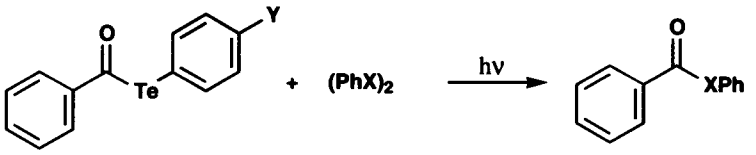


(22%) (87)



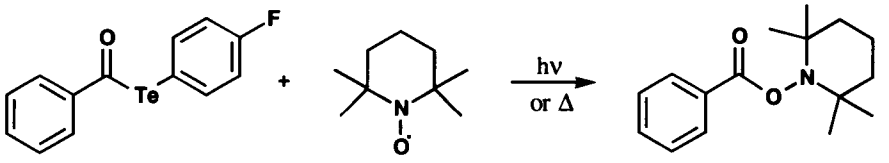
(13%) (33%)

photolysis of different aromatic acyl tellurides has been studied in the presence of radical traps.[206] In the presence of diphenyl diselenide or disulfide, the corresponding selenoesters or thioesters are obtained, respectively (*Eq.* 88). Irradiation or thermal reaction of the starting material shown in *Eq. 89* in the presence of a nitroxyl, yields a benzoyloxyamine derivative in high yield.[206]



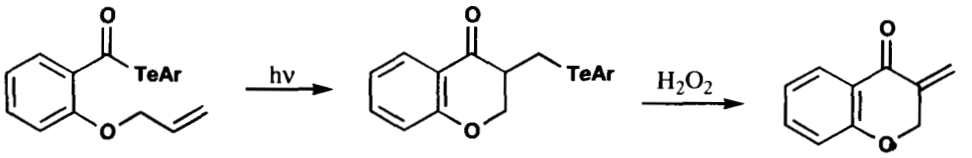
(88)

X = S, Se
Y = F, OMe



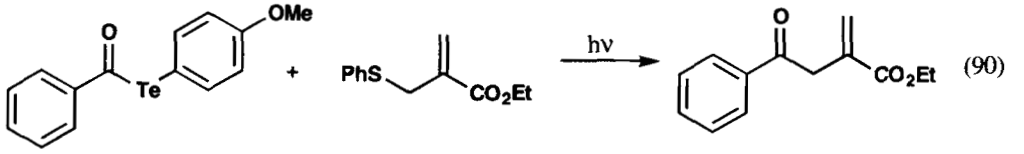
(89)

These reactions ilustrate the homolytic cleavage of the acyl-tellurium bond and the possible intervention of a chain mechanism in the case of the disulfide and diselenide. Irradiation of *ortho*-allyl ether derivatives to give products resulting from an intramolecular acylation of the olefin demonstrates very clearly that the two propagation steps are: cyclization of the acyl radical and chain transfer by abstraction of an aryltelluryl group from an additional molecule of acyl telluride (*Scheme* 80).



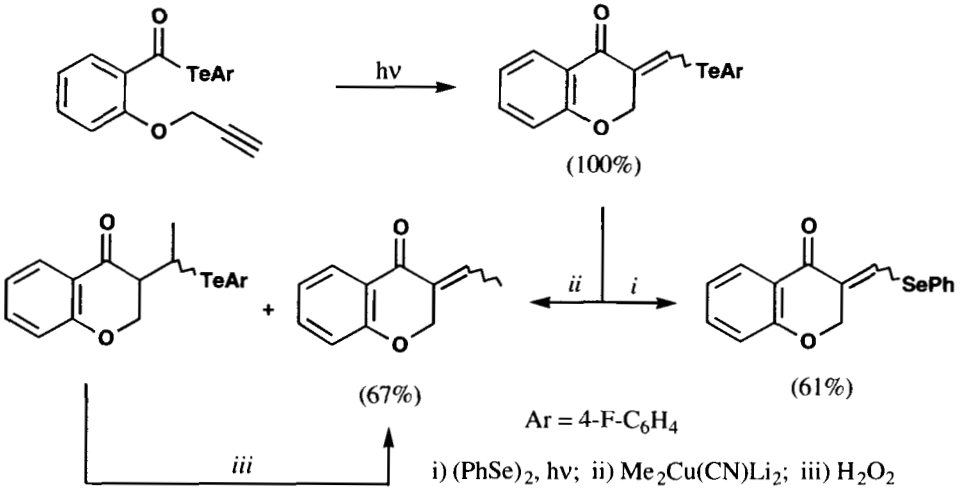
Scheme 80

Intermolecular carbon-carbon formation is achieved by photolysis of an acyl telluride with an allyl sulfide (*Eq.* 90).[206]



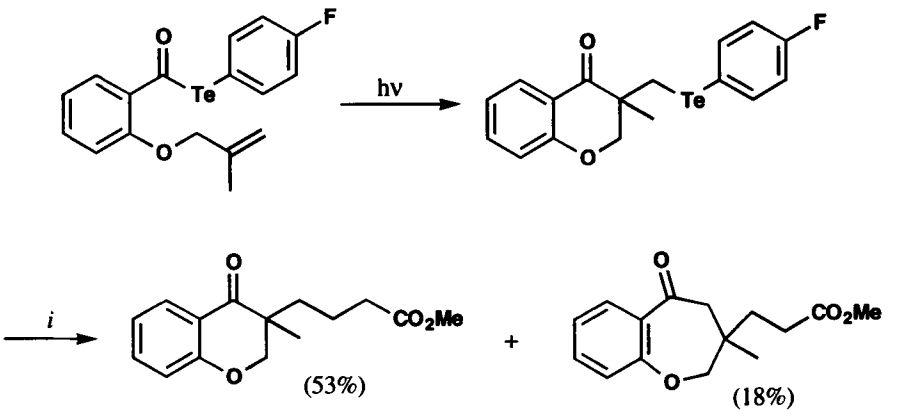
(90)

Intramolecular addition to alkynes by a radical chain process takes place by photolysis of an alkynyl acyl telluride to provide the corresponding vinyl telluride in quantitative yield as a 2:1 diastereoisomeric mixture (*Scheme* 81).[207] Photolysis of the vinyl telluride obtained in the presence of diphenyl diselenide gives the corresponding vinyl selenide by conjugate addition of the phenylselenenyl radical with subsequent expulsion of the aryltelluryl radical. Conjugate addition of higher order cuprates affords 2:1 mixture of the addition product that resulting from a subsequent elimination of the aryltelluro group. By oxidation of this reaction mixture with 30% hydrogen peroxide the corresponding ethylidene chromanone is obtained (*Scheme* 81).[205]



Scheme 81

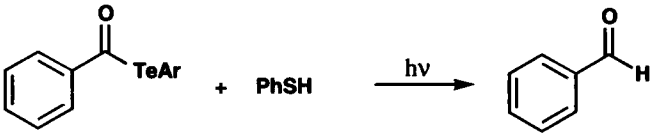
The chromanone shown in *Scheme 82* resulting from photolysis of acyl telluride did not undergo elimination; treatment with tri-*n*-butyltin hydride, methyl acrylate and AIBN gave 53% yield



i) CH_2=$CHCO_2Me$, $Bu^n{}_3SnH$, AIBN

Scheme 82

of the product resulting from the radical addition and 18% of the product resulting from ring expansion[208] of the intermediate radical followed by trapping with methyl acrylate. When the photolysis of acyl aryl tellurides is carried out in the presence of thiophenol, aldehydes are formed as a further evidence that acyl radicals are formed (*Eq.* 91).[207]



(80%) (91)

The simple photochemistry of acyl tellurides contrasts with those of acylgermanes, whose main mode of reaction involves chain reactions in which the carbonyl carbon atom is attacked by nucleophilic radicals with subsequent expulsion of the triarylgermyl radical. However, acyl tellurides derived from aliphatic carboxylic acids are unable to undergo radical chemistry by thermal, photochemical or AIBN initiation.

Acyl tellurides are also excellent precursors for acyllithium compounds by tellurium lithium exchange (see above).[25] Carbamoyl tellurides can also been prepared by reaction of diethylcarbamoyl chloride with lithium *n*-butyltellurate[46,47] and have been used as starting materials for diethylcarbamoyllithium (see above).

The reaction of acyl tellurides with lithium organocuprates affords ketones[203] as in the case of acyl selenides (*Eq.* 92).[167c]

(92)

CONCLUSION

From the chemistry described in this review we conclude that acyl metal compounds derived from main group metals and metalloids are versatile intermediates in organic synthesis, mainly acting either as carbanion or radical reagents, for the transfer of the acyl moiety to different organic substrates.

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