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ACTIVATION OF SILICON–HYDROGEN, SILICON–OXYGEN, SILICON–NITROGEN BONDS IN HETEROGENEOUS PHASE

SOME NEW METHODS IN ORGANIC SYNTHESIS

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Abstract—Anionic activation of Si–H, Si–O and Si–N bonds by fluoride ions under heterogeneous conditions is reported: Si–H activated by KF or CsF is a very powerful and selective reducing reagent; the carbonyl group of aldehydes, ketones or esters can be reduced without reduction of other functional groups (C=C, NO_2, Br, amido). Furthermore, selective reductions of aldehydes in the presence of ketones and ketones in the presence of carboxylic esters are also possible. CsF in the presence of $Si(OR)_4$ is found to be very efficient in promoting Michael additions of monoketones and arylacetonitriles on different kinds of Michael acceptors such as α, β unsaturated ketones, esters, nitriles and even amides. This constitutes an extension of Michael reaction since the addition occurs even with crowded ketones. N, N bis(silyl)enamines activated by fluoride ions react with carbonyl compounds and provide an interesting route to 2-aza-1, 3 dienes.

The present paper highlights the various methods we investigated to activate Si–H, Si–O and Si–N bonds. We have developed an anionic activation in heterogeneous conditions especially with fluoride ions.

We started into this field through a mechanistic study of the hydrolysis and the alcoholysis of Si–Cl bonds. This study provided both a kinetic and a stereochemical proof of the existence of nucleophilic activation at a Si atom.[1] The results of these studies showed that hydrolysis and alcoholysis of $R_1R_2R_3SiCl$, activated by nucleophiles such as HMPA were entropy controlled ($\Delta S\ddagger \sim -60$ cal mol^{-1} K^{-1}, $-3 < \Delta H\ddagger < 3$ kcal mole^{-1}) and that the rate equation was found to be:

$$v = k(R_1R_2R_3SiCl)(ROH)(Nu)$$

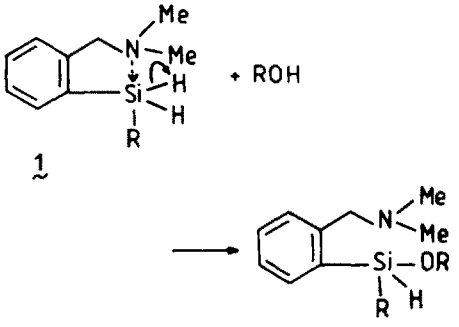
$$Nu = HMPA \gg DMSO > DMF.$$

Furthermore, the stereochemistry observed was retention of configuration while inversion was normally found in the absence of the nucleophilic catalyst. These observations were explained by the reversible formation of a pentacoordinate intermediate followed by a rate determining nucleophilic attack of water (or alcohol) on the pentacoordinated silicon atom (Reaction I).

The increase in rate between the unactivated and the activated hydrolysis was in the range of 10^3.

Illustrations of such nucleophilic enhanced reactivity are demonstrated in the following cases. For instance, a N atom in a suitable intramolecular position, as shown in **1**, activates the Si–H bond and a rapid reaction with alcohols occurs[2] (Reaction II). No such reaction occurs with $PhSiH_2R$ under identical conditions.

(II)



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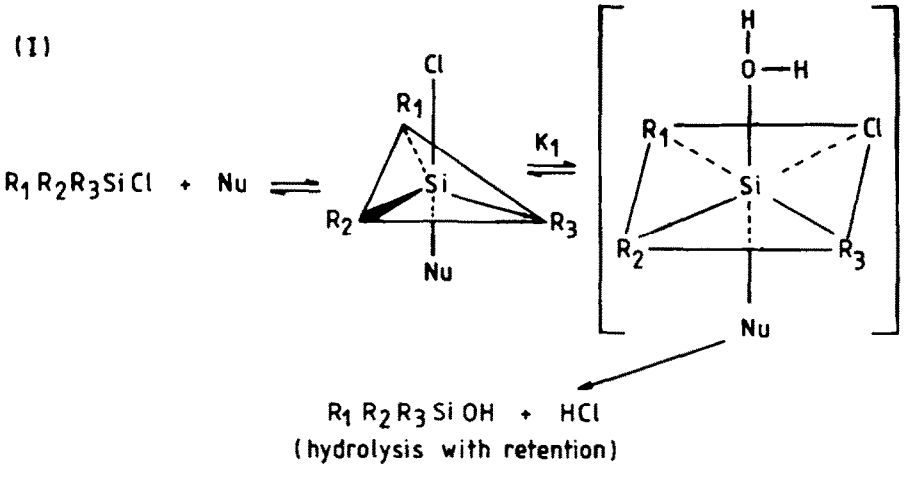
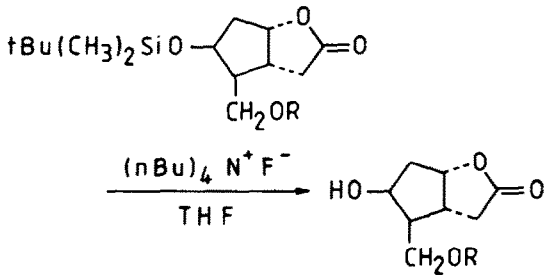
Several examples exist in the literature which demonstrate the efficency of fluoride ion in the activation of various Si-element bonds. The activation of the Si–O

(I)



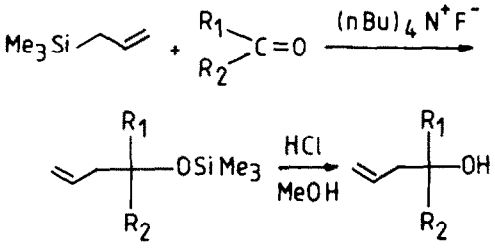
bond is, for instance, illustrated in the deprotection of an alcohol[3] (Reaction III).

(III)



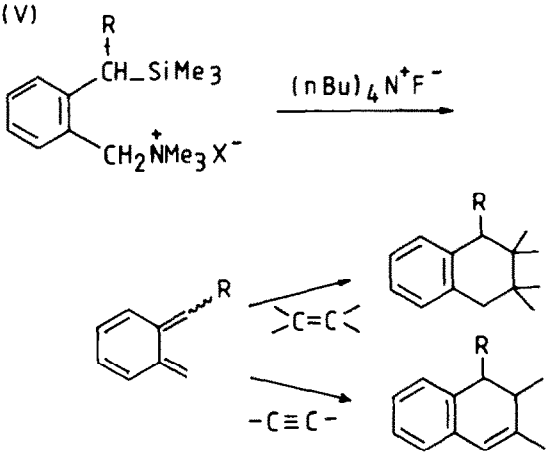
The activation of the Si–C bond is illustrated by the cleavage of the Si–allyl bond giving the homoallyl alcohol by reaction with a carbonyl compound[4] (Reaction IV).

(IV)

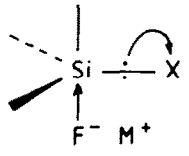


Another report demonstrates the formation of *o*-xylylène, an intermediate in formation of polycyclic compounds[5,6] (Reaction V).

(V)

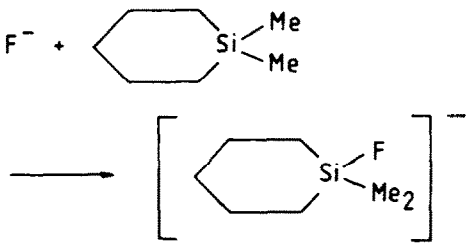


It is probable that in these cases the cleavage of the Si–X bonds occur through anionic activation. The coordination of fluoride ion stretches the Si–X bond producing an increased negative charge on the leaving group.



This mechanism is supported by experiments performed in the gas-phase. Organic pentavalent silyl anions are generated by reaction of fluoride ion with tetrasubstituted silanes[7] (Reaction VI).

(VI)



We report now some applications of activated Si–H, Si–O and Si–N bonds in organic synthesis. The activation of the Si functional reagent was carried out at the surface of a variety of salts as a tool for the alcoholysis of silanes, reductions of carbonyl compounds, Michael condensations and formation of heterodienes.

Activation of silicon–hydrogen bonds

Synthesis of alkoxysilanes. Alcoholysis of silanes has been widely studied and several catalysts have been employed: metal alkoxides,[8] amines,[9] metal halides[10,11] and transition metals either in heterogeneous catalysis by Cu[12], Pd or Ni[13] or in homogeneous catalysis by metal complexes.[14–17]

Our first attempts were activation of the Si–H bond in order to perform the alcoholysis of the dihydro- and trihydrosilanes, $\alpha NpSiH_3$, $\alpha NpPhSiH_2$, Ph_2SiH_2 and $PhCH_3SiH_2$. The reactions were carried out with different kinds of alcohols or phenols (*m*-cresol, *n*-heptanol, menthol, undecenol) at the surface of various types of commercially available salts (potassium tartrate, potassium phthalate, KSCN, $KHCO_2$, KF, CsF, $CsCH_3CO_2$) in absence of solvent. Mono or poly-alkoxysilanes were obtained (Reaction VII). Some of the results are shown in Table 1.

(VII) $R_1R_2SiH_2 + ROH \xrightarrow{salt} R_1R_2SiHOR,\ R_1R_2Si(OR)_2, (H_2)$

$R_1SiH_3 + ROH \xrightarrow{salt} R_1SiH_2(OR), R_1SiH(OR)_2, R_1Si(OR)_3, (H_2)$

The results show that the extent of alcoholysis of silanes in the presence of salts is dependent upon several factors including the nature of both reagents, the nature of the salt, the temperature and the value of the ratio (silane)/(alcohol). In particular, this reaction allowed the classification of the different salts for the activation of Si–H bonds. The reactivity sequences were found to be:

Silanes:

$$\alpha NpSiH_3 > Ph_2SiH_2 > PhMeSiH_2 > \alpha NpPhSiH_2$$

Salts:

$$CsF > KF > \text{potassium phthalate} > KHCO_2 > KSCN > \text{potassium tartrate.}$$

For synthetic purposes, this new method appears to be more selective than heterogeneous catalysis. For in-

Table 1. Alcoholysis of silanes

Silane	Salt	ROH	Conditions time (h)	Conditions temp.(°C)	Products (yield %)	
					$\alpha NpSiH(OR)_2$	$\alpha NpSi(OR)_3$
$\alpha NpSiH_3$	KSCN	Heptanol (3 eq.)	5	180	80	0
	$KHCO_2$	"	1	180	0	100
					$Ph_2SiH(OR)$	$Ph_2Si(OR)_2$
Ph_2SiH_2	KSCN	Heptanol (2 eq.)	0.5	180	100	0
	Potassium Phthalate	" (3 eq.)	0.3	180	0	100
	$KHCO_2$	Menthol (3 eq.)	5	180	0	100
	"	" (1 eq.)	5	180	90	0
					$\alpha NpPhSiH(OR)$	$\alpha NpPhSi(OR)_2$
$\alpha NpPhSiH_2$	CsF	Menthol (1 eq.)	1	25	100	0
	CsF	" (1 eq.)	1	180	0	100
					$PhCH_3SiH(OR)$	$PhCH_3Si(OR)_2$
$PhCH_3SiH_2$	$KHCO_2$	Heptanol (2 eq.)	0.3	180	0	90
	KSCN	Cresol (2 eq.)	2	180	5	95

stance, it is always possible to obtain either mono-, di- or trialkoxysilanes exclusively from any alcohol and silane by changing the salt or the temperature and/or (silane)/(alcohol) ratio. Selectivity is even more significant when ethylenic alcohols were used. The C=C double bond was not affected (Reaction VIII). A similar reaction catalyzed by $(PPh_3)_3RhCl$ leads to the formation of $Ph_2Si\langle O \rangle (CH_2)_{11}$.[17]

(VIII) $CH_2=CH\_(CH_2)_9OH + Ph_2SiH_2 \xrightarrow{CsF} (CH_2=CH\_(CH_2)_9O)_2SiPh_2$

The results, in Table 1, demonstrate the convenience of the method and the possibility of the activation of the Si–H bonds at the surface of salts. We studied the extension of this method to the reduction of carbonyl compounds.

Reductions of carbonyl compounds. We now wish to report two practical methods for the reduction of carbonyl compounds (aldehydes, ketones, esters) as generalized in Scheme 1:

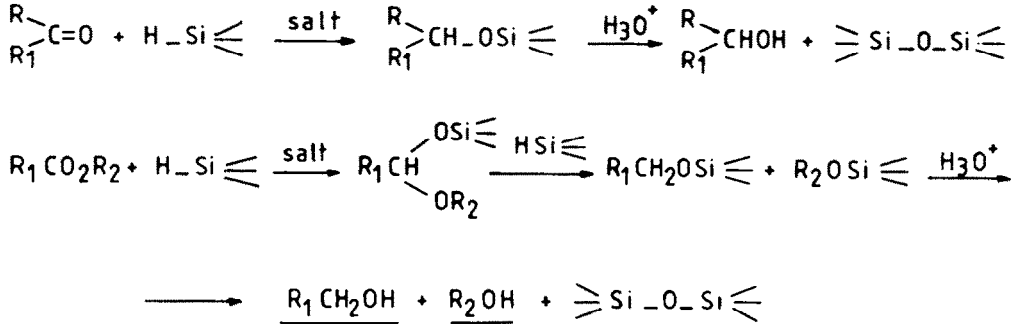
The di- or trihydrogenosilanes previously used (Table 1) were efficient reducing agents, in particular αN_pSiH_3 which, in the presence of CsF at 50°, converts PhCOPh to $\alpha NpSi(OCHPh_2)_3$ in 100% yield. However, these silanes are not readily available and monohydrogenosilanes are not useful except when alkoxy groups are also bound to the silicon atom. Furthermore, $(EtO)_3SiH$ and $(EtO)_2Si(Me)H$ can be easily prepared from the industrial chlorohydrogenosilanes.

With these monohydrogenosilanes and the most efficient salts (KF and CsF), we carried out the reduction reactions in the following manners:

(1) The first method involved the use of $(EtO)_3SiH$ and $(EtO)_2Si(Me)H$ which were found to be excellent reducing agents when activated by KF or CsF in the absence of solvent.[19]

(2) The second method involved the use of a solvent (DMF, DMSO) in the presence of $(EtO)_2Si(Me)H$ or $Me_3SiO(HSiMeO)_nSiMe_3$ (PMHS), an industrially available polymer.[20] Selected results are shown in Table 2 (without solvent) and Table 3 (in the presence of solvent).

The reduction results depend upon three factors: the nature of the silanes and the carbonyl compounds, the



Scheme 1.

Table 2. Reduction of carbonyl compounds (without solvent)

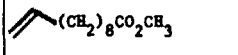
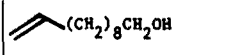
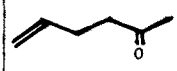
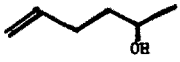
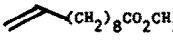
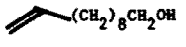
Carbonyl Compound	Silane	Salt	Conditions time (h)	Conditions temp.(°C)	Alcohol isolated	(yield %)
PhCHO	$(EtO)_3SiH$	KF	6	25	$PhCH_2OH$	(90)
PhCH=CHCHO	$(EtO)_2Si(Me)H$	CsF	2	25	$PhCH=CHCH_2OH$	(95)
"	$(EtO)_3SiH$	KF	24	25	"	"
$C_6H_{13}CHO$	$(EtO)_3SiH$	KF	4	25	$C_6H_{13}CH_2OH$	(70)
$PhCOCH_3$	$(EtO)_2Si(Me)H$	CsF	2.5	100	$PhCHOHCH_3$	(70)
"	$(EtO)_3SiH$	CsF	0.5	0	"	(80)
PhCOPh	$(EtO)_3SiH$	CsF	0.08	25	PhCHOHPh	(95)
	$(EtO)_3SiH$	CsF	0.25	0		(90)
$PhCO_2C_2H_5$	$(EtO)_3SiH$	CsF	0.5	60	$PhCH_2OH$	(90)
	$(EtO)_3SiH$	CsF	0.5	60		(70)
$nC_8H_{17}CH=CH(CH_2)_7CO_2Ment$	$(EtO)_3SiH$	CsF	72	25	$nC_8H_{17}CH=CH(CH_2)_7CH_2OH$	(80)

Table 3. Reduction of carbonyl compounds (with solvent)

Carbonyl compound	Reducing System	Solvent	Conditions time (h)	Conditions temp.(°C)	Alcohol isolated	(Yield %)
PhCHO	A	DMF	0.25	20	$PhCH_2OH$	(90)
$C_6H_{13}CHO$	A	DMF	1.75	10	$C_6H_{13}CH_2OH$	(85)
$PhCOCH_3$	C	DMF	2.5	30	$PhCHOHCH_3$	(80)
PhCOPh	A	DMF	0.5	20	PhCHOHPh	(90)
	A	DMF	5	60		(85)
$PhCO_2C_2H_5$	B	DMSO	6.5	80	$PhCH_2OH$	(80)
	B	DMSO	6	80		(70)

Reducing system : A = $HSiMe(OEt)_2/KF$
B = $PMHS/KF-2H_2O$
C = PMHS/KF

nature of the salts and the temperature. The observed silane reactivity sequence was:

$$(EtO)_3SiH > (EtO)_2Si(Me)H.$$

For instance, $PhCOCH_3$ requires 2.5 hr and 100° to be reduced with $(EtO)_2Si(Me)H$ while 0.5 hr at 0° is necessary with $(EtO)_3SiH$. The observed order of reactivity of the carbonyl derivative was: aldehyde > ketone > ester. Without solvent, aldehydes are reduced at room temperature with KF while ketones require the use of CsF. Reduction of esters was more difficult and required CsF at high temperatures.

When a solvent was added (Table 3), the rate of the process was accelerated and even KF can be used for the reduction of esters. With these results and the high observed selectivity, the selective reductions of aldehydes in the presence of ketones and of ketones in the presence of esters were attempted. The results are shown in Table 4.

It was always possible to selectively reduce aldehydes or ketones by changing the temperature or the nature of the salt. Compared to other methods,[21-32] this system is as least as selective and essentially more convenient. The reduction of bifunctional compounds illustrates the practical utility of the reducing ability of $Si-H/F^-$.

Table 4. Selective reduction of carbonyl compounds

Carbonyl compound	Silane or Reducing system	Salt or Solvent	Conditions time (h)	(temp.(°C)	Alcohol obtained	(Yield %)
PhCHO PhCOMe	$(EtO)_3SiH$	KF	36	25	$PhCH_2OH$ $PhCHOHMe$	(100) (0)
//	D[b]	DMF	2.5	60	idem	
$Me(CH_2)_5CHO$ $PhCH_2COCH_2Ph$	$(EtO)_3SiH$	KF	20	25	$Me(CH_2)_5CH_2OH$ $PhCH_2CHOHCH_2Ph$	(100) (0)
PhCOMe $PhCO_2Et$	$(EtO)_3SiH$	CsF	0.016	25	PhCHOHMe $PhCH_2OH$	(100) (0)
//	A[a]	DMF	4	40	idem	
$PhCH_2COMe$ $Me(CH_2)_{10}CO_2Et$	$(EtO)_2SiMeH$	CsF	5	25	$PhCH_2CHOHMe$ $Me(CH_2)_{10}CH_2OH$	(100) (0)

a : see Table III

b : D = PMHS/$KHCO_2$

Table 5. Reduction of bifunctionnal compounds

Carbonyl compound	Silane	Salt	Conditions time (h)	temp.(°C)	Isolated compound	(Yield)
$pNO_2C_6H_4CHO$	$(EtO)_3SiH$	KF	2	100	$pNO_2C_6H_4CH_2OH$	(80)
PhCOCHBrMe	$(EtO)_3SiH$	CsF	0.5	25	PhCHOHCHBrMe	(70)
$PhCO(CH_2)_2CO_2Me$	$(EtO)_2Si(Me)H$	CsF	2.5	25	4-Phenylbutyrolactone	(85)
$MeCOCH_2CONHPh$	$(EtO)_3SiH$	CsF	10	25	$MeCHOHCH_2CONHPh$	(90)
$CH_2{=}CH(CH_2)_2COMe$	$(EtO)_3SiH$	CsF	0.25	0	$CH_2{=}CH(CH_2)_2CHOHMe$	(90)

We studied the reduction of aldehydes and ketones having another functional group such as a C=C double bond or a bromo, nitro, amido or ester group and selected results are shown in Table 5.

It was found possible to reduce the CO group in a selective manner. The C=C double bond and the bromo, nitro, amido or ester groups were not affected. Additionally, α,β-unsaturated aldehydes and ketones were reduced selectively (1, 2 reduction) in the presence of CsF (Reaction IX).

(IX)

$$Ph_2SiH_2 + R_1R_2C{=}CHCOR_3 \xrightarrow{CsF} (R_1R_2C{=}CH\underset{R_3}{\underset{|}{C}}HO)_2SiPh_2 \xrightarrow{H_2O} R_1R_2C{=}CH\underset{R_3}{\underset{|}{C}}HOH$$

The results are shown in Table 6.

Table 6. CsF-promoted reduction of α,β-ethylenic carbonyl compounds

Carbonyl compound	Conditions time (h)	temp.(°C)	Products (Yield %) 1,2 reduction (%)	1,4 reduction (%)	Total reduction
$PhCH{=}CH{-}\overset{\overset{O}{\|}}{C}{-}H$	1/20	25	100	0	0
$PhCH{=}CH\underset{\underset{O}{\|}}{C}CH_3$	0.5	25	100	0	0
$PhCH{=}CH\underset{\underset{O}{\|}}{C}Ph$	1	0	95	5	0

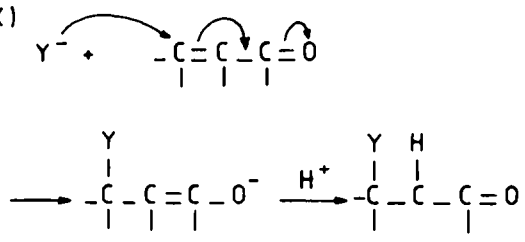
These observations are interesting in view of the fact that dihydrogenosilanes in the presence of $(PPh_3)_3RhCl$ reduce α, β-unsaturated compounds to a mixture of 1, 2- and 1, 4-products (33) and PhCH=CHCOPh undergoes 1, 4-reduction even with $(iBu)_2AlH$ which is very efficient for 1, 2-reductions.[34]

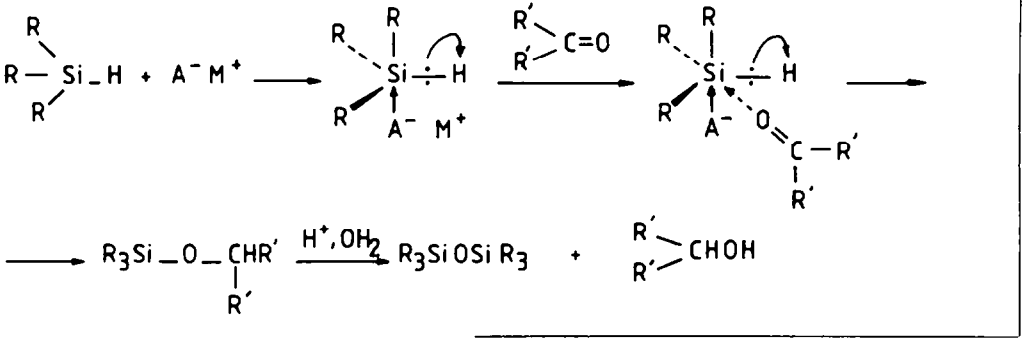
Our reduction method is selective, convenient and inexpensive (silanes are obtained from industrial products and salts can be recovered and reused).

It is probable that the role of the salt is to activate the Si atom by anionic coordination to give a pentacoordinate Si in which the Si–H bond is weakened. The efficiency of the salts increases when the cation-anion interaction decreases: we observed the following reactivity sequence $LiF \ll KF < CsF$, in which CsF is the most efficient.

The great utility of this method is to eliminate the preparation of the silyl enol ether. Selected results are indicated in Table 7. The reactions were carried out without solvent and in presence of a stoichiometric amount of CsF and $Si(OR)_4$. The 1, 4-addition product was obtained (Reaction X).

(X)





Activation of silicon–oxygen bond

Michael type additions. In a previous work,[35] the reaction of silyl enol ethers with aldehydes has been studied in presence of CsF. Under heterogeneous conditions, this reaction gives an α, β-unsaturated product. On the other hand, $FN(nBu)_4$[36] promotes the aldol reaction without dehydration. The procedure is very simple: use of solvent is unnecessary, the reaction temperatures are in a convenient range (between 0° and 100°), and salt may be recovered and recycled.

Furthermore under the same conditions the reaction of silyl enol ethers with α, β-unsaturated compounds was also investigated and an interesting Michael type reaction was observed with α, β-unsaturated ketones and esters.

The Michael reaction is an important synthetic tool in organic chemistry. Generally these reactions are catalysed by bases[37] such as alkali metal alkoxides and undesirable side reactions occur often under these basic conditions. Because of its widespread use in organic synthesis, numerous methods have been developed to carry out Michael type reactions under mild conditions.[38–41] We report here a new procedure allowing direct Michael type addition of monoketones and arylacetonitriles to unsaturated ketones, esters and even amides.

When the $CsF/Si(OR)_4$ system is compared to the others published in the literature which employ other sources of fluoride for the Michael type addition[42–44] only $CsF/Si(OR)_4$ is effective in promoting all the reactions which were carried out[45] and (Table 7).

The chief advantages are the following:

(1) The method is unequivocal: only the 1, 4-addition product is obtained

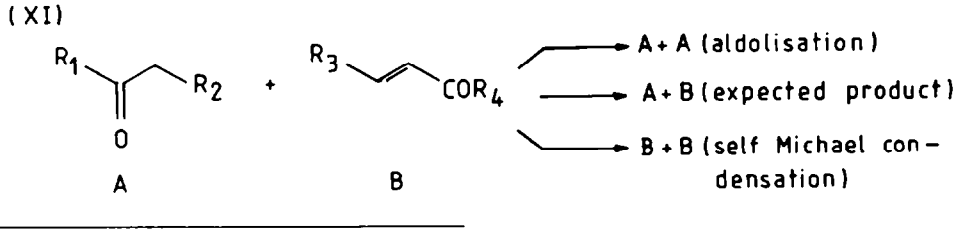
(2) The reaction is regioselective with 2-methyl cyclohexanone: there is only one reaction product from the kinetic enolate.

(3) Direct addition of monoketones to fairly hindered acceptors such as pulegone or 3-methyl 2-butene nitrile occurs and is an interesting extension of Michael type reaction.

(4) Michael type addition is also possible even with α, β-unsaturated amides which is unusual.

The main limitation of this method stems from the possibility of self-condensation of reagents (Reaction XI).

(XI)



Self condensation of one of the two starting reagents usually predominates:

(1) When A is an aldehyde, then the chief reaction is aldolisation (A + A).

(2) When A gives an enolate more slowly than B, the

Table 7. Michael additions in presence of $Si(OEt)_4$[a]/CsF or $Si(OMe)_4$[b]/CsF

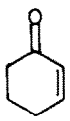
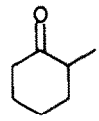
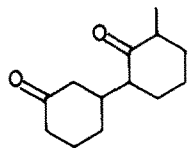
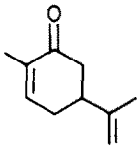
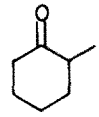
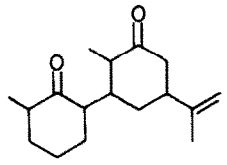
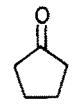
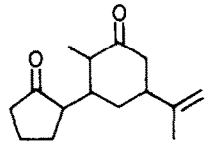
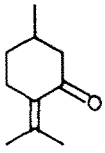
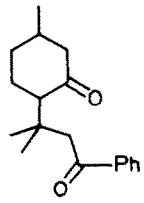
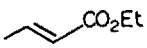
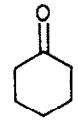
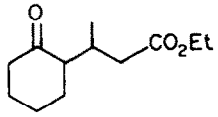
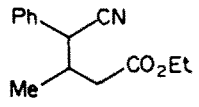
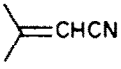
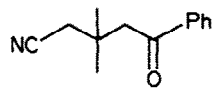
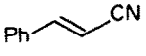
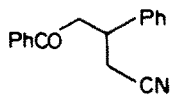
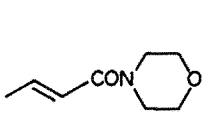
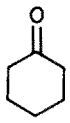
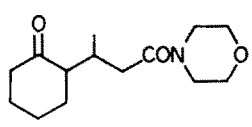
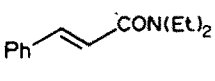
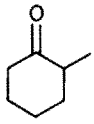
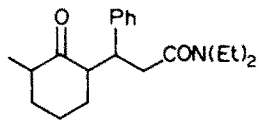
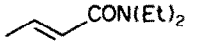
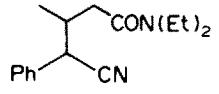
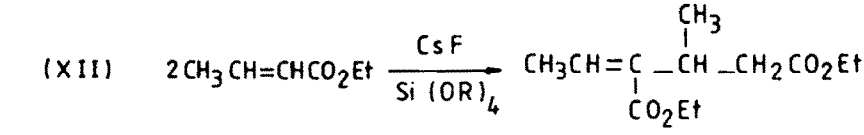
Electrophile	Michael donor	Reaction conditions t(h)	T(°C)	Reaction products yield (%)
		(a) 6	25	
		(b) 4	25	 (70)
		(b) 3	80	 (60)
	PhCOMe	(b) 6	80	 (65)
		(a) 2	100	 (55)
	$PhCH_2CN$	(a) 1	25	 (85)
	PhCOMe	(b) 3	80	 (55)
	PhCOMe	(b) 1	90	 (55)

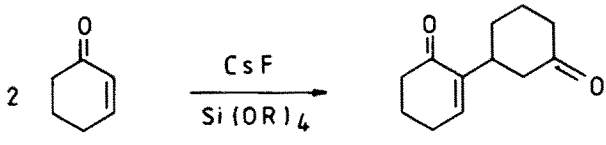
Table 7. *Contd*

Electrophile	Michael donor	Reaction conditions t(h)	T(°C)	Reaction products yield (%)
		(b) 3	65	 (50)
		(b) 5	80	 (86)
	$PhCH_2CN$	(b) 0.75	65	 (79)

main reaction is the Michael condensation product of B(B + B). For example this occurs when A is t-butyl methyl ketone or diisobutylketone and B is ethyl crotonate or cyclohexene-2-one (Reactions XII and XIII).

bon enamines: N, N-dialkylenamines are nucleophilic reagents and react with a large variety of electrophiles with C–C bond formation.[47] In contrast N, N-bis(silyl)enamines do not react with electrophiles under

(XII) 

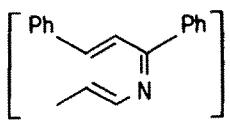
(XIII) 

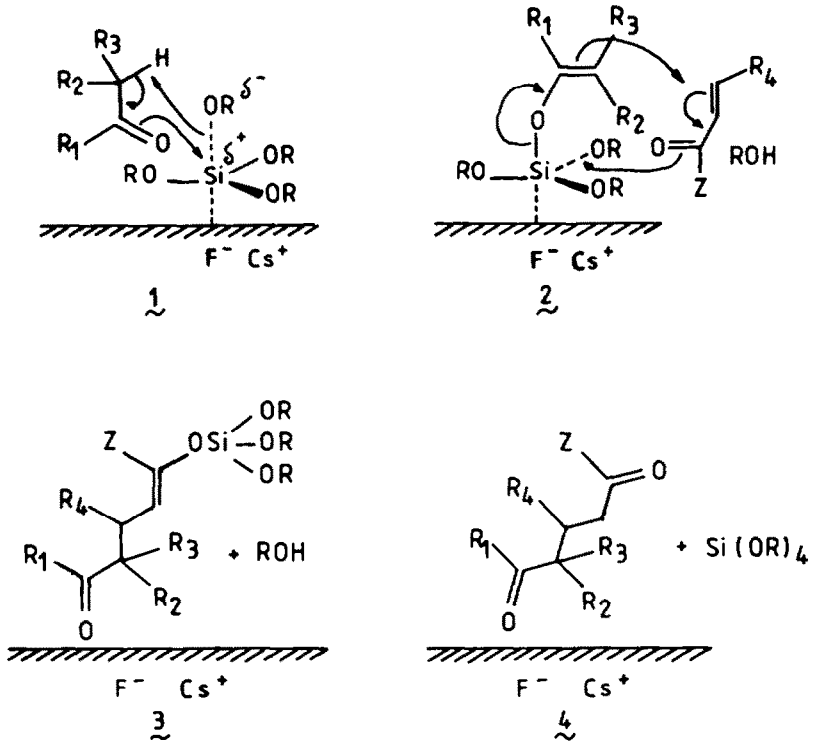
To explain the results, the following mechanism is proposed: the first step is nucleophilic activation of $Si(OR)_4$ by the fluoride to give a basic species able to promote enolate formation. This enolate is silylated very quickly giving the corresponding silyl enol ether. The salt activated silyl enol ether promotes the 1, 4-adduct from the α, β-unsaturated compound. This adduct reacts *in situ* with the alcohol obtained during the formation of the silyl enol ether (Scheme 2, step 2) to give the 1, 5-difunctional compound. We have checked that the hydrolysis is not necessary to give this 1, 5-difunctional product.

Activation of silicon–nitrogen bond

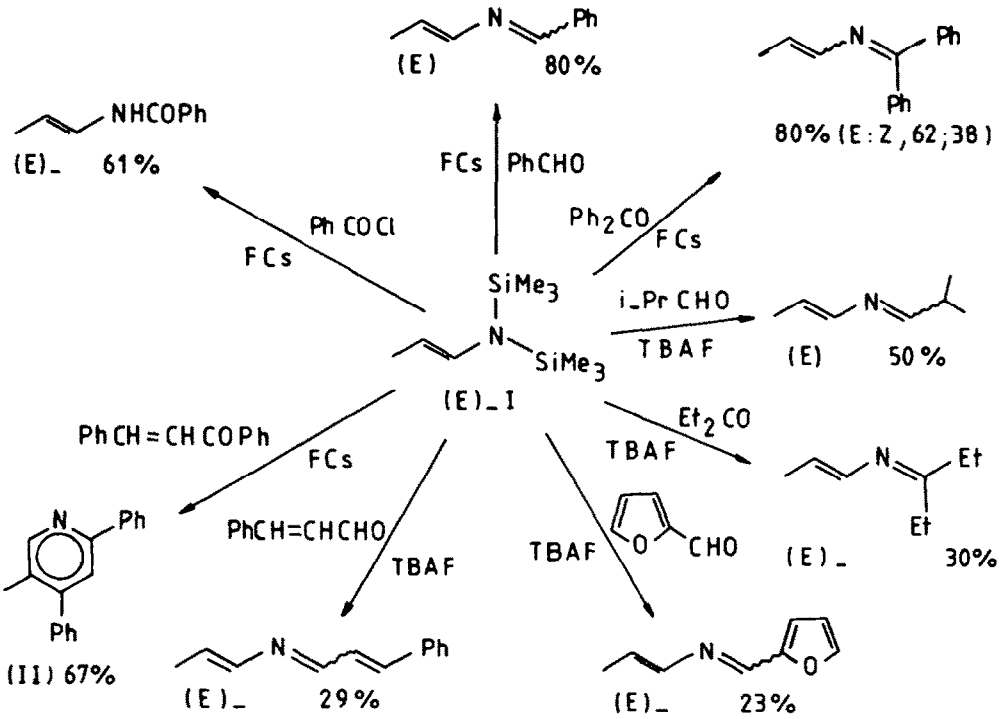
Synthetic uses of N, N-bis(silyl)enamines. Recently easy routes to synthesize N, N-bis(silyl)enamines have been reported.[46] They appear as a new functional group since they exhibit different reactivity compared to carusual reaction conditions.[46a] We have extended to these compounds the activation by fluoride ions and we observe the formation of N=C bonds(Scheme 3).[48]

The reactions of enamine I with electrophiles lead to the C–N bond. In these reactions, with the exception of benzophenone, the configuration of the C–C bond is retained. Reactions of carbonyl compounds constitute a simple route to 2-aza-1, 3 dienes[49] which are synthons of 6-membered N-heterocycles.[50] It is worth noting the reaction of I with chalcone giving the substituted pyridine II probably through cyclization of an intermediate azatriene:





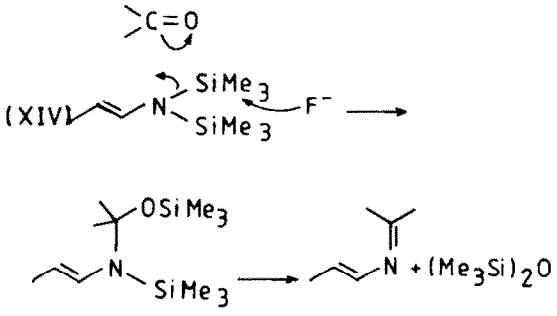
Scheme 2.



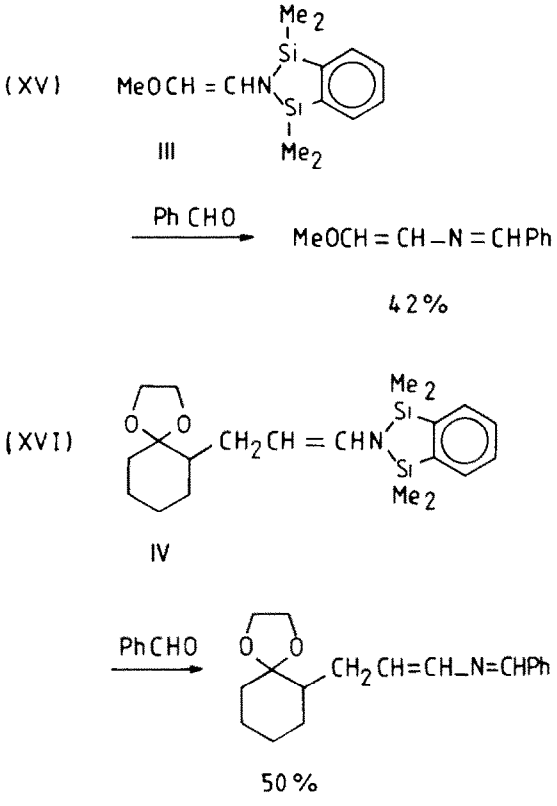
Scheme 3. Fluoride-ion catalyzed reaction of (E)-$CH_3CH{=}CHN(SiMe_3)_2$ with electrophiles[a]

[a]Reactions were carried out using 5% CsF in DMF (N, N-dimethylformamide) at 80° or 5% TBAF in THF at room temperature.

The formation of these hetero-dienes can be explained via a nucleophilic attack of the N atom in I on the CO group followed by a β-elimination of hexamethyldisiloxane, which was identified in the reaction mixture (Reaction XIV).



The synthetic possibilities are illustrated by the reactions of functional bis(silyl) enamines III and IV (Reactions XV and XVI).



N, N-bis(silyl) enamines appear to react with carbonyl compounds as protected primary vinylamines providing an easy access to a variety of heterodienes.

CONCLUSION

Heterogeneous anionic activation of Si–H, Si–O and Si–N bonds provides new possibilities in organic synthesis: selective reduction, extension of Michael type reaction to the case of fairly crowded ketones as well as extension to new acceptors (esters and amides) and access to unusual heterodienes. Furthermore the techniques required are very simple. This work is a continuation of studies in the general area of anionic activation of Si center.[1–6] The activation is postulated to proceed through a pentacoordinated Si intermediate and appears to open a large variety of possibilities for the use of Si in organic synthesis.

EXPERIMENTAL

General procedures

Synthesis of alkoxysilanes. All the alcoholysis reactions were carried out under N_2. The following is given as an example: 2.76 g Ph_2SiH_2 (0.015 mol) and 3.56 g *m*-cresol (0.030 mol) were added together with 3 g of KSCN to the reaction flask under N_2. The temp was maintained at 180° by use of an oil bath. The mixture was stirred until the evolution of gas stopped (7 min). The salt was filtered off from the organic layer, and the latter was analysed by gas chromatography. $Ph_2Si(OCr)_2$ (m.p. 81°) was recrystallized from pentane and identified by its NMR and IR spectra, and by elemental analysis. The yields were determined by GLC and were based upon reacted silane.

Reduction of carbonyl compounds. All the reactions were carried out under N_2 and after hydrolysis (NaOMe/MeOH or HCl/Me_2CO), the alcohols obtained were purified by distillation or preparative layer chromatography and identified by ^{1}H-NMR, IR, mass spectrometry and by comparison with authentic samples. For instance, a mixture of ethyl dodecanoate (2.18 g, 10.0 mmol) and triethoxysilane (3.77 g, 23.0 mmol) was added to CsF (1.52 g, 10.0 mmol) under N_2. The reaction was followed by IR spectroscopy. After 30 min at 60°, 12 N HCl (1 ml) in acetone (5 ml) was added. After 30 min, the mixture was extracted with ether (2 × 150 ml). The combined extracts were dried with $MgSO_4$ and ether was removed using a rotatory evaporator. The residue was distilled *in vacuo* to give 1-dodecanol; yield: 1.8 g (90%); b.p. 145°C/15 torr. The GLC retention time was identical with that of an authentic sample.

Michael reaction procedure. The reaction of acetophenone with ethyl crotonate illustrates the standard procedure: to 2.75 g of CsF (0.0179 mol) were added 2.14 g acetophenone (0.0179 mol), 2.04 g ethyl crotonate (0.0179 mol) and 3.72 g tetraalkoxysilane. The well stirred mixture was heated at 60° for 3 hr and then poured into 20 ml 10% HCl. The product was extracted with ether and dried on $MgSO_4$ but, during the extraction, filtration on Hyflo-supercel was always necessary. The 3-methyl 5-phenyl 5-oxo-ethyl pentanoate was isolated by distillation (3.35 g, 80%, b.p. 145/1 mm).

Reactions with N, N-*bis(silyl)enamines.* The reaction with benzaldehyde illustrates the standard procedure: to a mixture of 6 g (3×10^{-2} mol) of (E)-$CH_3CH{=}CHN(SiMe_3)_2$ and 0.22 g (5%) of CsF in 10 ml of dry degassed DMF (N, N-dimethylformamide) was added 3.1 g (3×10^{-2} mol) of benzaldehyde. The well stirred mixture was heated at 80° for 2 hr and then poured into 50 ml water. After extraction with ether and drying, the 2-aza-1, 3-diene (3.5 g; 80%) was isolated by distillation (b.p. 128/20 mm). IR (CCl_4): 1660, 1650 cm^{-1}. NMR (CCl_4) δ(ppm): 1.8 (3H, d, J = 7 Hz), 6.1 (1H, dq), 6.8 (1H, d, J = 14 Hz), 7.5 (5H, m), 8.0 (1H, s).

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REFERENCES

[1]R. J. P. Corriu, G. Dabosi and M. Martineau, *J. Organometal. Chem.* **154**, 33 (1978).
[2]R. J. P. Corriu, G. Royo and A. de Saxce, Unpublished results.
[3]E. J. Corey and A. Venkateswarlu, *J. Am. Chem. Soc.* **94**, 6190 (1972).
[4]A. Hosomi, A. Shirahata and H. Sakurai, *Tetrahedron Letters* 3043 (1978).
[5]Y. Ito, M. Nakatsuka and T. Saegusa, *J. Am. Chem. Soc.* **102**, 863 (1980).
[6]S. Djuric, T. Sarkar and P. Magnus, *Ibid.* **102**, 6885 (1980).
[7]S. A. Sullivan, C. H. De Puy and R. Damrauer, *Ibid.* **103**, 480 (1981).
[8]W. H. Nebergall, *Ibid.* **72**, 4702 (1950); H. Gilman and G. N. R.

Smart, *J. Org. Chem.* **19**, 441 (1954); B. N. Dolgov, N. P. Kharitonov and M. G. Vorontov, *Zh. Obsh. Khim.* **24**, 1178 (1954); B. N. Dolgov, N. P. Kharitonov and T. V. Tsukshverdt, *Ibid.* **28**, 2714 (1958).
[9]H. Gilman, G. E. Dunn, H. Hartzfeld and A. G. Smith, *J. Am. Chem. Soc.* **77**, 1287 (1955).
[10]I. S. Akhrem, M. Deneux and M. E. Volpin, *Izvest Akad. Nauk. SSSR*, 932 (1973); K. A. Andrianov and L. M. Tartakovskaya, *Ibid.* 2631 (1972); M. Deneux, I. C. Akhrem, D. V. Avetissian, E. I. Myssof and M. E. Volpin, *Bull. Soc. Chim. Fr* 2638 (1973).
[11]B. N. Dolgov, Y. I. Khudobin and N. P. Kharitonov, *Izvest Akad. Nauk. SSSR*, 113 (1958) *and* 1238 (1959); B. N. Dolgov, N. P. Kharitonov, N. L. Glushkova and Y. I. Khudobin, *Zh. Obsh. Khim.* **28**, 2710 (1958).
[12]W. S. Miller, J. S. Peake and W. H. Nebergall, *J. Am. Chem. Soc.* **79**, 5604 (1957); B. Sternbach and A. G. Mac Diarmid, *Ibid.* **81**, 5109 (1959); V. O. Reikhsfel'd and V. A. Prokhorova, *Zh. Obsh. Khim.* **31**, 2613 (1961).
[13]L. H. Sommer and J. E. Lyons, *J. Am. Chem. Soc.* **89**, 1521 (1967); *Ibid.* **91**, 7061 (1969).
[14]I. Ojima, T. Kogure, M. Nihonyanagi, H. Kono and S. Inaba, *Chem. Letters* 501 (1973).
[15]A. J. Chalk, *J. Chem. Soc. Chem. Commun.* 847 (1970).
[16]N. J. Archer, R. N. Haszeldine and R. V. Parish, *Ibid.* 524 (1971).
[17]R. J. P. Corriu and J. J. E. Moreau, *J. Organometal. Chem.* **114**, 135 (1976); **127**, 7 (1977).
[18]J. Boyer, R. J. P. Corriu, R. Perz and C. Reye, *Ibid.* **157**, 153 (1978).
[19]J. Boyer, R. J. P. Corriu, R. Perz and C. Reye, *Tetrahedron* **37**, 2165 (1981); J. Boyer, R. J. P. Corriu, R. Perz, M. Poirier and C. Reye, *Synthesis* **7**, 558 (1981).
[20]C. Chuit, R. J. P. Corriu, R. Perz and C. Reye, *Ibid.* **11**, 981 (1982).
[21]J. M. Lalancette, A. Freche, J. R. Brindle and M. Laliberte, *Ibid*, 526 (1972).
[22]G. W. Gribble and D. Ferguson, *J. Chem. Soc. Chem. Commun.* 535 (1975).
[23]Y. Maki, K. Kikuchi, H. Sugiyama and S. Seto, *Tetrahedron Letters* 263 (1977).
[24]Y. Yamamoto, H. T. A. Sonoda and S. I. Murahashi, *J. Am. Chem. Soc.* **98**, 1965 (1976).
[25]M. M. Midland and A. Tramontano, *J. Org. Chem.* **43**, 1470 (1978).
[26]G. C. Andrew, *Tetrahedron Letters* 697 (1980).
[27]H. C. Brown and S. U. Kilkani, *J. Org. Chem.* **42**, 4169 (1977).
[28]R. O. Hutchins and D. Kandasamy, *J. Am. Chem. Soc.* **95**, 6131 (1973).
[29]N. Y. M. Fung, P. de Mayo, J. H. Schauble and A. C. Weedoh, *J. Org. Chem.* **43**, 3977 (1978).
[30]C. S. Sell, *Aust. J. Chem.* **28**, 1383 (1975).
[31]J. L. Namy, P. Girard and H. B. Kagan, *Nouveau J. de Chimie Fr* 5 (1977).
[32]G. H. Posner, A. W. Runquist and M. J. Chapdeleine, *J. Org. Chem.* **42**, 1202 (1977).
[33]I. Ojima, M. Nihonyanagi, T. Kogure, M. Kumagai, S. Horiuchi and K. Nkatsugawa, *J. Organometal. Chem.* **94**, 449 (1975).
[34]R. J. P. Corriu and C. Guerin, *Ibid.* **144**, 165 (1978).
[35]J. Boyer, R. J. P. Corriu, R. Perz and C. Reye, *Ibid.* **184**, 157–166 (1980).
[36]R. Noyori, K. Yokoyama, J. Sakata, I. Kuwajima, E. Nakamura and M. Shimizu, *J. Am. Chem. Soc.* **99**, 1265 (1977).
[37]E. D. Bergman, D. Ginsberg and R. Rappo, *Org. React.* **10**, 179 (1959).
[38]T. Saegusa, Y. Ito, S. Tomita and H. Kinoshita, *Bull. Chem. Soc. Jpn.* **45**, 496 (1972).
[39]B. M. Trost, P. E. Strege, L. Weber, T. J. Fullerton and T. J. Dietsche, *J. Am. Chem. Soc.* **100**, 3407 (1978).
[40]J. H. Nelson, P. N. Howells, G. C. Delullo and G. L. Lauden, *J. Org. Chem.* **45**, 1246 (1980).
[41]G. V. Kryshtal, V. V. Kulganek, V. F. Kucherov and L. A. Yanovskaya, *Synthesis* 107 (1979).
[42]I. Belsky, *J. Chem. Soc. Chem. Comm.* 237 (1977).
[43]J. H. Clark, *Ibid.* 789 (1978).
[44]L. A. Carpino and A. C. Sau, *Ibid.* 514 (1979).
[45]J. Boyer, R. J. P. Corriu, R. Perz and C. Reye, *Tetrahedron* in press (1982).
[46a]R. J. P. Corriu, J. J. E. Moreau and M. Pataud-Sat, *J. Org. Chem.* **46**, 3372 (1981); [b]*J. Organometal. Chem.* **228**, 301 (1982); [c]R. J. P. Corriu, V. Huynh and J. J. E. Moreau, to be published.
[47]A. G. Cook *Enamines: Synthesis, Structure and Reactions* (Edited by Marcel Dekker) New York (1969).
[48]R. J. P. Corriu, V. Huynh, J. J. E. Moreau and M. Pataud-Sat, *Tetrahedron Letters* 3257 (1982).
[49]T. Kauffmann, E. Koppelmann and M. Berg, *Angew. Chem. Int. Ed. Engl.* **9**, 163 (1970); A. Dehnel, J. P. Finet and G. Lavielle, *Synthesis* 474 (1977); Yu. S. Dol'Skaya, G. Ya, Kondrat'eva and N. I. Golovina, *Izv. Akad. Nauk.. SSSR, Ser. Khim.* Engl. Transl. 550 (1978); S. D. Worley, K. G. Taylor, B. Veneugopalan and M. S. Clark, Jr. *Tetrahedron* **34**, 833 (1978).
[50]A. Desmoulin, H. Gorissen, A. M. Hesbain-Frisque and L. Ghosez, *J. Am. Chem. Soc.* **97**, 4409 (1975); R. Gompper and U. Heinemann, *Angew. Chem. Int., Ed. Engl.* **20**, 196 (1981) and refs therein.