

Some aspects of the reactivity of hypervalent species of silicon in organic synthesis

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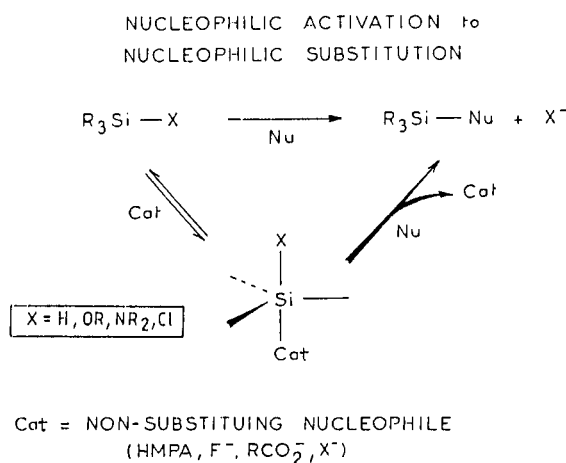
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Abstract

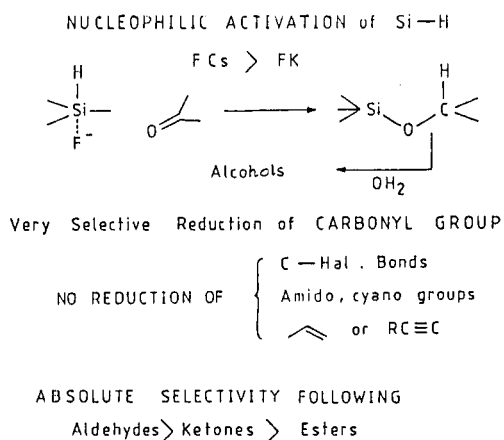
The nucleophilic activation for nucleophilic displacements at silicon is extensively used in organic synthesis. This process involves pentacoordinated intermediates. The reactivity of pentacoordinated organosilanes, silicates and siliconates (neutral or anionic) is studied. All the examples reported here illustrate the great reactivity of hypervalent species. These species react faster than the corresponding tetracoordinated silanes.

The nucleophilic activation for nucleophilic displacements is a process extensively used at silicon mainly in the uses of organosilanes in synthesis: cleavage and activation of Si-O bonds (ref.1), activation of Si-H (ref.2), Si-C (ref.3), Si-N (ref.4) bonds, all processes performed using F⁻ or HMPA or more generally using nucleophiles having a high affinity towards silicon, as catalysts. The same process was also observed at Phosphorus (ref.5). Since such a process is not known in carbon chemistry, we have proposed a mechanism involving the formation, in a preequilibrium, of a pentacoordinated intermediate formed with the nucleophilic catalyst. This step is followed by the nucleophilic attack of the incoming nucleophile in the rate determining step (Scheme 1).

Scheme 1



Scheme 2

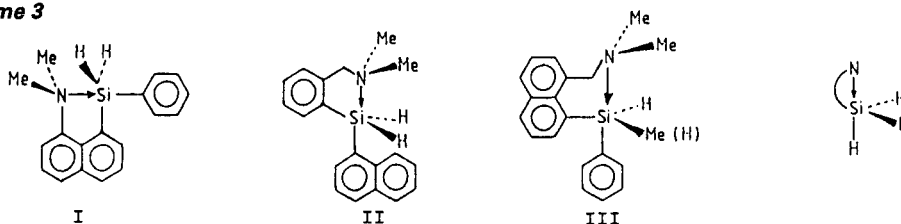


Some examples of this mechanism will be given in the following reduction reactions. The activation of Si-H bond by F⁻ is a very efficient and very selective way for the reduction of carbonyl groups. It is possible to reduce a >C=O group without reduction of NO₂, >C=C<, -C≡C-, halo, CN, and -CONH₂ groups. There is also a very selective reduction of 2-Enones in 1-2 position, even with the chalcone (ref.6) (Scheme 2).

The mechanism involves a nucleophilic activation of Si-H bond at the surface of F^- in heterogeneous conditions, or by coordination of F^- in homogeneous conditions, and the attack of carbonyl group with hydride transfer in the rate determining step.

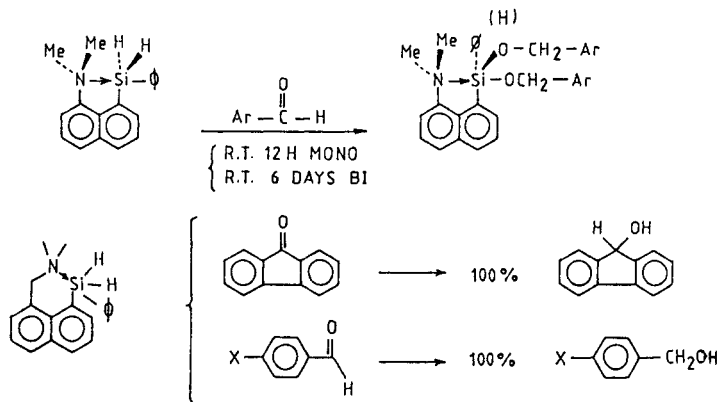
In order to support this mechanism we have studied the reactivity of pentacoordinated hydrogenosilanes we have prepared. The Si-H bond is a very interesting one for comparison since we have obtained a very good evidence for the formation of pentacoordinated structures in solid state (XR) (ref.7) and in solution (Si^{29} NMR)(ref.8). The Si-H bond has a good ability to form pentacoordinated structures and the hydrogen was always in equatorial position (Scheme 3).

Scheme 3



It is well known that the tetravalent dihydrogenosilanes do not react with alcohols or carboxylic acids, or carbonyl groups. On the other hand the same reagents are able to substitute the Si-H bond when the silicon is in a pentacoordinated state. We have even found the possible hydrosilylation of carbonyl groups (ref.9) (Scheme 4).

Scheme 4

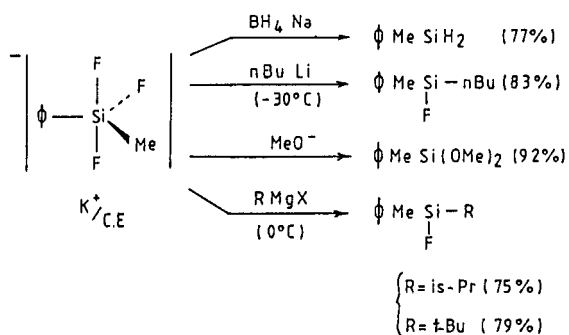


The reactivity of pentacoordinated hydrogenosilanes support very well the mechanism we have proposed for the hydrosilylation of alcohol and carbonyl groups. More generally it was interesting to consider the reactivity of hypervalent species of silicon towards nucleophiles. Since recently Damrauer (ref.10) reported a very good method for the preparation of hypervalent fluorosilanes, it was possible to perform a direct study. We have observed a very high reactivity for the trifluorosilicates (Scheme 5) and a faster reactivity of the pentacoordinated towards the tetracoordinated ones (Scheme 6).

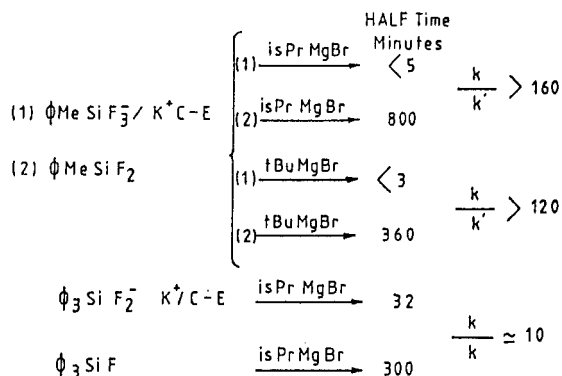
The same increase of reactivity was also observed in the case of neutral pentacoordinated species. The case of (IV) is particularly illustrative since the tri, bi, and monofluorosilanes are pentacoordinated. The tri-substitution takes place much faster than in the case of trifluoronaphthylsilane (Scheme 7).

We have extended successfully the Damrauer procedures to the preparation of hypervalent methoxysilanes. These compounds are very reactive. For instance the pentamethoxysilicate is hydrolysed very quickly giving a gel (Scheme 8).

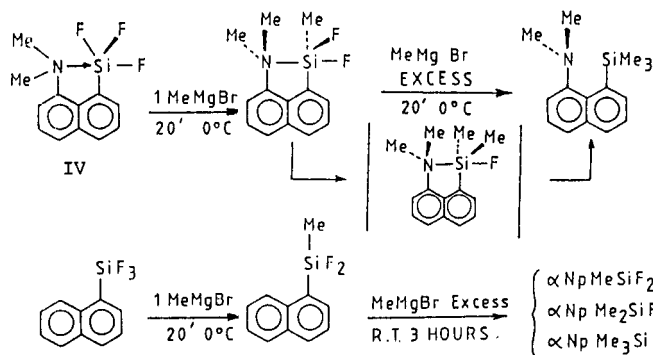
Scheme 5



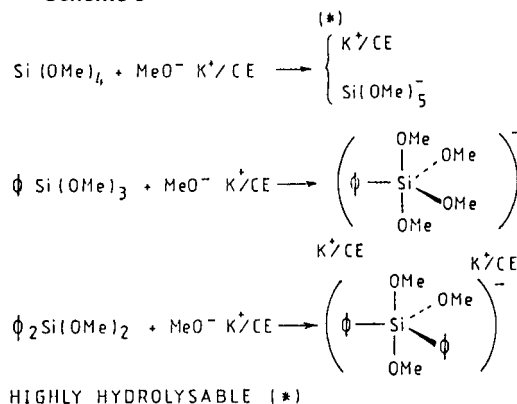
Scheme 6



Scheme 7



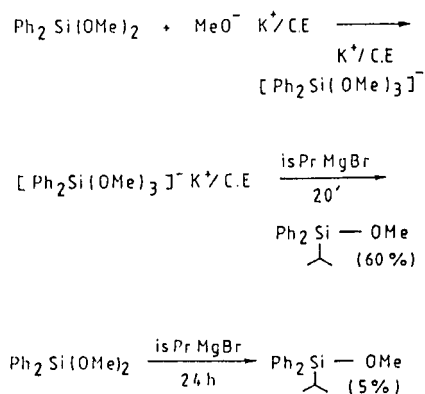
Scheme 8



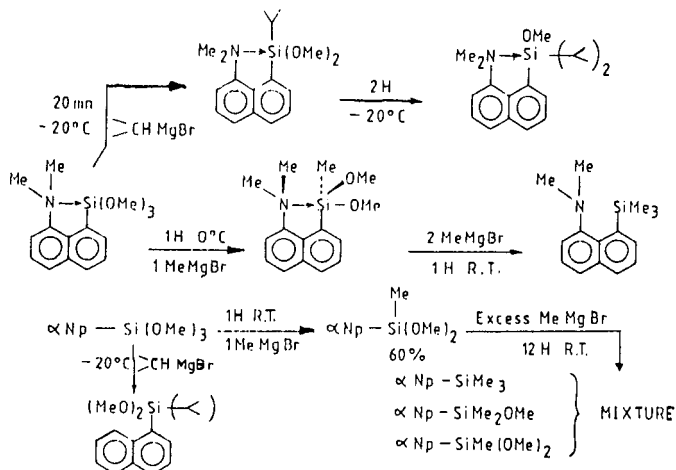
We have observed once again a higher reactivity for the pentacoordinated silicon (Scheme 9).

The comparison was also performed in the case of neutral species and the reactivity was found always in favour of pentacoordinated silicon (Scheme 10).

Scheme 9



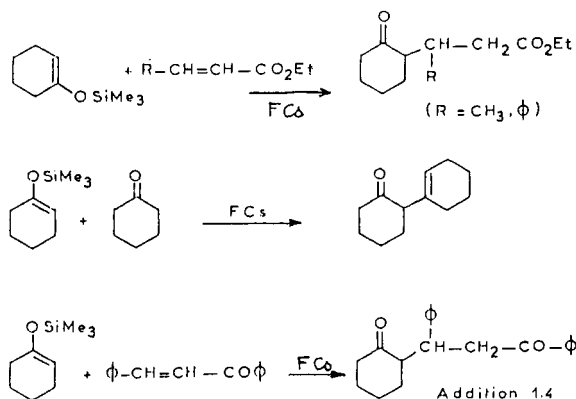
Scheme 10



The very high reactivity of hypervalent species containing Si-O bonds confirms the possible formation of pentacoordinated silicon in the course of the nucleophilic activation of Si-O bond (activation of enoxysilanes) (ref.1a) (Scheme 11-12).

The formation of hypervalent species was also demonstrated in the case of the polymerisation of the acrylate through the group transfer polymerisation (ref.7). In this case the activating nucleophile activates the Si-O bond and the transfer takes place through an hexacoordinate intermediate (ref.11) (Scheme 13).

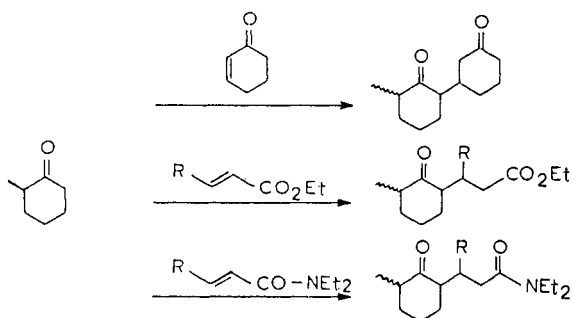
Scheme 11



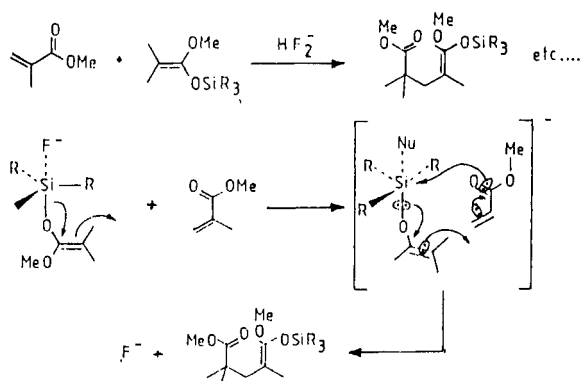
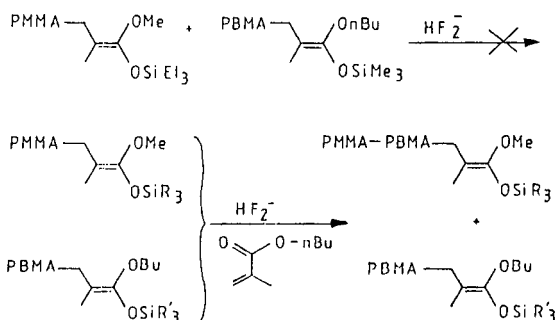
MICHAEL REACTION EXTENSION

FCs / Si(OR)₄ System

in HETEROGENEOUS CONDITIONS

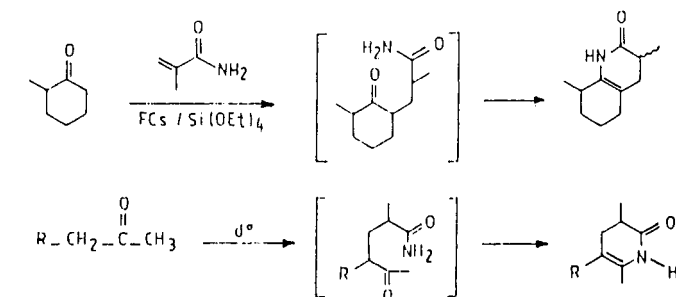
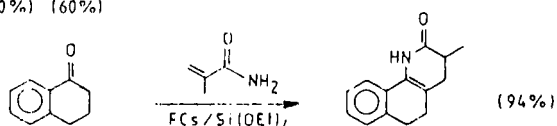


Scheme 13

POLYMERISATION with TRANSFER of SiMe₃SOGAH - WEBSTER - FARNHAM JACS (83) 5706
DUPONT de NEMOURSR₃ = Me R'₃ = Et or R₃ = Me₂Tol R'₃ = Me₂φ

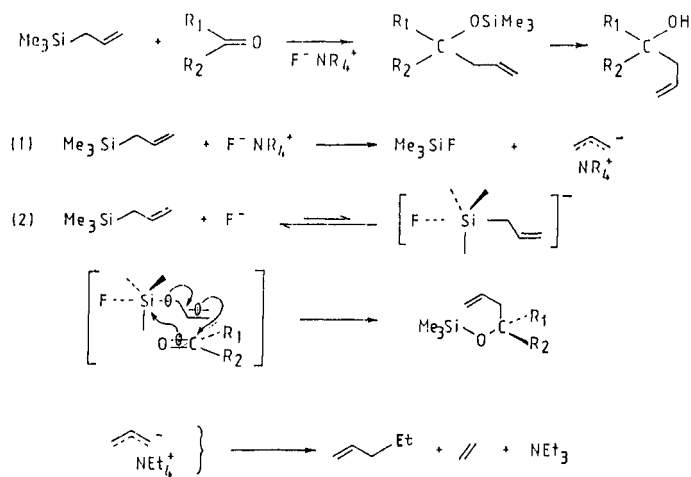
SOGAH - FARNHAM - WEBSTER

Scheme 12

(R = σ, nCH₂, Et)
(94%) (60%) (60%)

The activation of Si-C bond by F^- was reported in the case of the transfer of the allyl group (ref.12). The mechanism can be either an heterolytic cleavage of Si-O bond or a nucleophilic activation through hyper-coordinated silicon intermediate (Scheme 14).

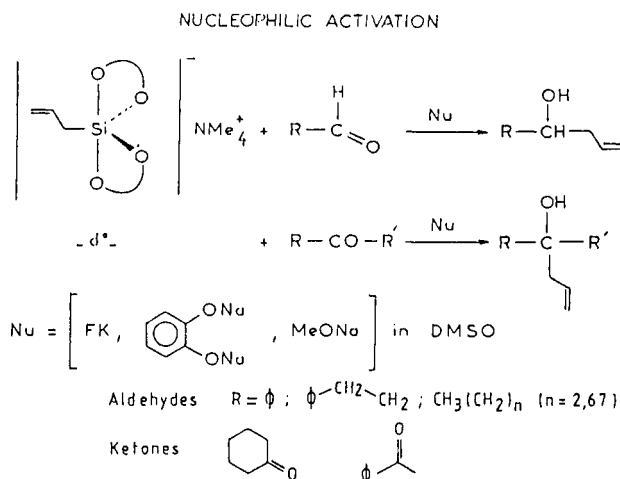
Scheme 14



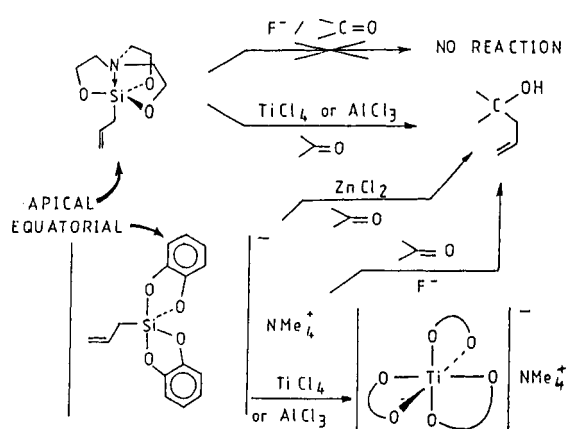
In order to check the possible reaction with pentacoordinate silicon, the reactivity of the allyl siliconates having an anionic pentacoordinated structure has been studied. These species react with carbonyl groups. It is possible to perform the reaction in different conditions (ref.13) : without any activation, with electrophilic activation using Zn X_2 , and also with nucleophilic activation (Scheme 15-16).

All these results are in good agreement with the activation of Si-C bond taking place through a nucleophilic activation instead of an heterolytic cleavage of Si-C bond.

Scheme 15

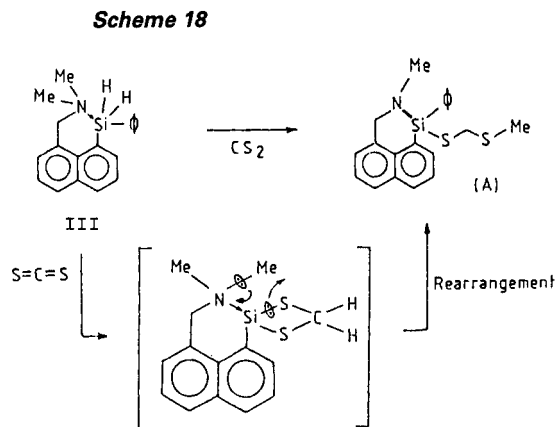
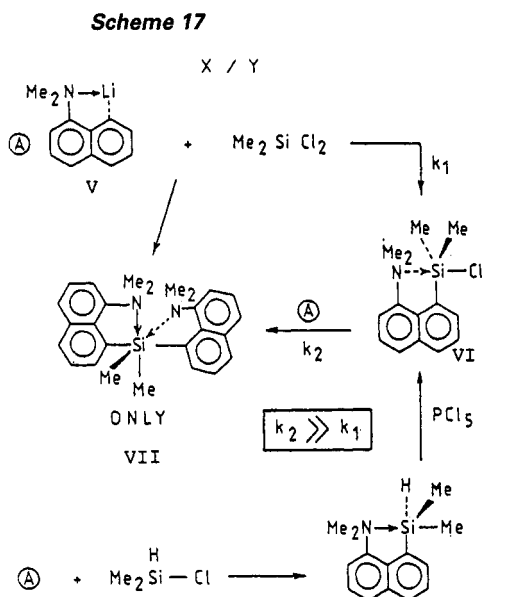


Scheme 16



The higher reactivity of pentacoordinated Si-Cl bond was also observed in the reaction of the organolithium (V) towards Me_2SiCl_2 . This reaction gives the exclusive formation of disubstituted product (VII) whatever is the ratio between V and Me_2SiCl_2 (even with a fixed time excess of Me_2SiCl_2). The conclusion is that the mono-substituted pentacoordinated chlorosilanes VI reacts faster with (V) than Me_2SiCl_2 . This high reactivity of VI was checked by separated preparation and reaction (Scheme 17).

All these experiments illustrate very well the great reactivity of hypervalent species. They confirm the possibility of pentacoordinated intermediate in the nucleophilic activation, of nucleophilic substitution at silicon. This possibility cannot be ruled out only on the basis of the argumentation of a more crowded and less electrophilic species than tetracoordinated silicon. Furthermore after these results, it becomes interesting to understand why these hypercoordinated species react faster than the tetracoordinated ones. The two possible explanations are one part the increase of the length of Si-X bonds which corresponds to an higher lability and other part the increase of the electrophilicity of the central Si atom (14). The illustration of that is the reactivity observed between dihydrogénosilanes (III) and CS_2 which gives a rearrangement never reported in silicon chemistry. Interestingly the process started with a double hydrosilylation of CS_2 (Scheme 18).



In order to explain the reaction of (III) with CS_2 we have treated it with molecular S and we have obtained a product (VIII) identified as a silathione stabilized by intramolecular coordination with the NMe_2 group. This product is highly oxydable; it is stable in anaerobic conditions and reacts instantaneously with air, with formation of the trisiloxane (IX) (Scheme 19).

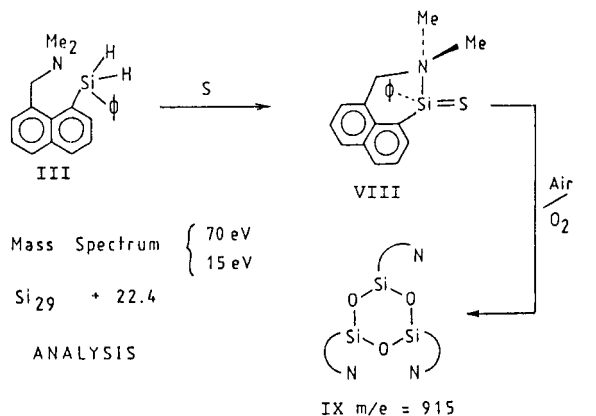
Besides the microanalysis, the spectroscopic arguments supporting the structure of the silathione are :

- 1) the mass spectrum obtained at two different electronic impacts
- 2) the H^1 NMR showing a clean diastereotopism of $-\text{CH}_2-$ and NMe_2 groups due to the strong coordination of the nitrogen atom to silicon
- 3) the Si^{29} chemical shift which is just between the low-valent and hypervalent species chemical shifts (Scheme 20).

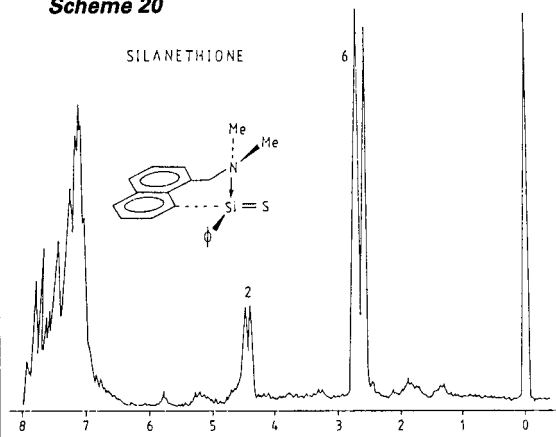
The reaction of CO_2 is a very interesting one, we have observed the elimination of $\text{H}_2\text{C}=\text{O}$ and formation of trisiloxane when the reaction is performed in vacuum line, using dry and degassed solvents; the mechanism of this reaction is illustrated below (Scheme 21).

The silyl ester of formic acid was obtained by an independent route and its pyrolysis at 120° gives elimination of H₂C=O and silanone which can be trapped by (Me₂SiO)₃ giving the compound (X). We have extended this reactivity to the case of carboxylic acids. The hydrogenosilanes react very well with formation of aldehydes and trisiloxane (ref.15) (Scheme 22). Schemes 23-24-25 report the results obtained and the selectivity of the reaction.

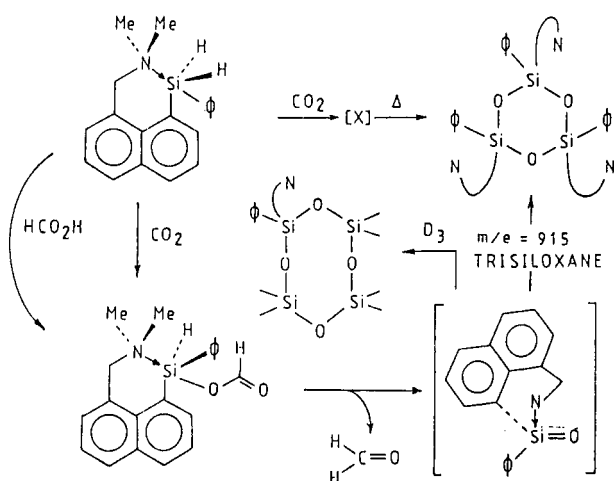
Scheme 19



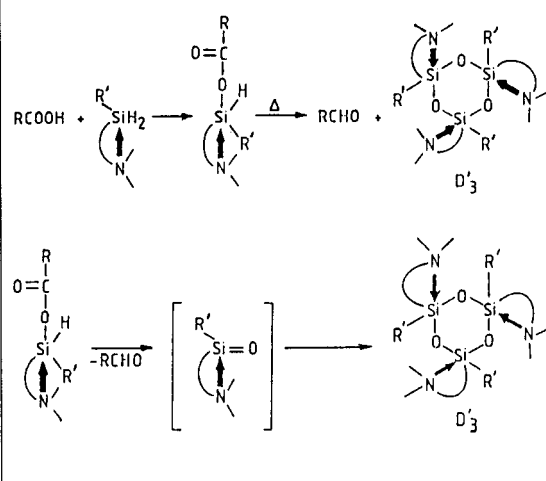
Scheme 20



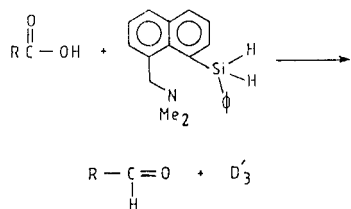
Scheme 21



Scheme 22

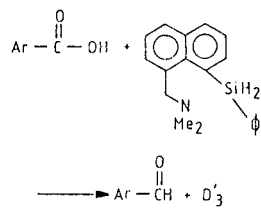


Scheme 23



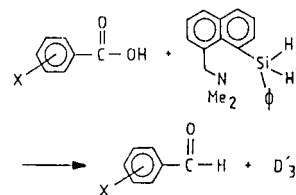
ACID	ALDEHYDE	YIELD %
CH ₃ CH ₂ COOH	CH ₃ CH ₂ CHO	85
CH ₃ (CH ₂) ₆ COOH	CH ₃ (CH ₂) ₆ CHO	50
C ₆ H ₁₁ COOH	C ₆ H ₁₁ CHO	68
(CH ₃) ₃ CCOOH	(CH ₃) ₃ CCHO	50
Ph-CH=CH-COOH	Ph-CH=CH-CHO	71
(CH ₃) ₂ CHCOOH	(CH ₃) ₂ CHCHO	80

Scheme 24



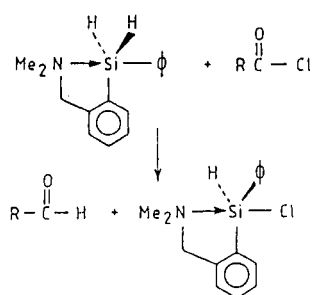
Acid	Aldehyde	Yield %
		90
		76
		88

Scheme 25

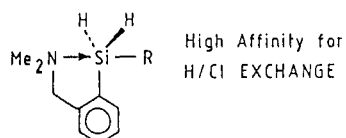


ACID	ALDEHYDE	YIELD %
PhCOOH	PhCHO	83
pF C ₆ H ₄ COOH	pF C ₆ H ₄ CHO	94
oF C ₆ H ₄ COOH	oF C ₆ H ₄ CHO	96
pMeO C ₆ H ₄ COOH	pMeO C ₆ H ₄ CHO	76
pNO ₂ C ₆ H ₄ COOH	pNO ₂ C ₆ H ₄ CHO	60
mNO ₂ C ₆ H ₄ COOH	mNO ₂ C ₆ H ₄ CHO	60
oNO ₂ C ₆ H ₄ COOH	oNO ₂ C ₆ H ₄ CHO	50
mNC C ₆ H ₄ COOH	mNC C ₆ H ₄ CHO	60

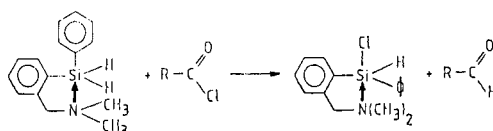
Scheme 26



HYDROGEN - CHLORINE EXCHANGE
SELECTIVE ROSENMUND REACTION



Scheme 27



Acid chloride	Aldehyde	Yield %	Acid chloride	Aldehyde	Yield %
		90			90
		78			85
		86			87
		86			84

Another unexpected reaction of pentacoordinated hydrogenosilanes is the very clean hydrogen-halogen exchange; this exchange takes place in very mild conditions (ref. 15) (Scheme 26). We have used this reaction for obtaining a very simple and useful synthesis of aldehydes from acyl chlorides. Scheme 27 reports the main results obtained and the selectivity of the reaction.

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