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SOME PRACTICAL USES OF THE DISILANE RESIDUE FROM THE DIRECT SYNTHESIS OF METHYLCHLOROSILANES *

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Summary

Some practical uses for the disilane residue from the direct synthesis of methylchlorosilanes have been proposed. This residue can be converted into organochloro- (Me_2SiCl_2, $MeSiCl_3$, Me_3SiCl) or organohydrochloro-monosilanes ($HMeSiCl_2$, HMe_2SiCl). These disilanes can also be used for the synthesis of alkyl (haloalkyl, alkenyl, aryl, etc.) methyldichlorosilanes or alkyl (haloalkyl, alkenyl, aryl, etc.) trichlorosilanes. The reductive properties of the Si—Si bond of these species have been utilized (e.g. in the reduction of phosphine oxides into the corresponding phosphines). Polysilanes resulting from the disproportionation of this residue are precursors of polycarbosilanes.

Introduction

The direct synthesis of methylchlorosilanes (Rochow synthesis) affords a high boiling residue mainly containing 1,1,2-trimethyltrichlorodisilane (ca. 30%), *sym*-dimethyltetrachlorodisilane (ca. 60%) along with other methylchlorodisilanes, -polysilanes, -siloxanes, -disilylmethanes, etc. The present state of development of the silicone industry involves an average annual production of disilane residue in the order of 12,000 metric tons, an amount which represents four percent of the total Me_2SiCl_2 formed. The ratio and the composition of the disilane residue depends on the silicon purity, catalyst nature and reaction conditions.

This residue in itself has not of yet found any industrial application, thus explaining why many conversions of these species have been studied. We wish

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* In honor of Professor Henry Gilman for his many years of outstanding research and teaching in the field of organometallic chemistry and in remembrance of the 2nd International Symposium on Organosilicon Chemistry, Bordeaux, 1968.

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here to report the contribution of our Laboratories to the conversion of the disilane residue into compounds of practical value. These investigations were performed with the collaboration of Rhône-Poulenc Industries (Marcel Lefort and coworkers).

Consequently we will not approach the problem of the synthesis of these or other disilanes to which Gilman [1] has made substantial contributions. Moreover, we make no mention of alkylations (arylations), alkoxylations, reductions or other reactions involving Si—Cl bonds not involving Si—Si cleavage, as these are for the most part reviewed by Kumada [2] and Hengge [3]. Therefore we shall not discuss the chemical properties of hexamethyldisilane or of 1,2-dimethyltetraalkoxydisilanes (precursor of silylenes [4]), for instance, nor the hydrolysis or amination [5] of *sym*-dimethyltetrachlorodisilane.

Likewise, we shall not discuss the chemical behavior of the other methylchlorodisilanes nor of the Si_2Cl_6 which are formed in non-appreciable amounts in the direct synthesis of dimethyldichlorosilane.

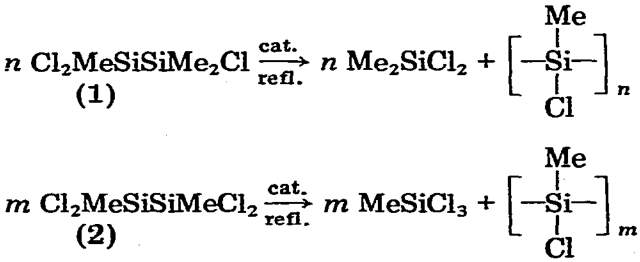
We only report reactions concerning:

1. Disproportionation.
2. Cleavage in the presence of HCl.
3. Cleavage in the presence of hydrogen.
4. Cleavage in the presence of metal or metalloid halides.
5. Cleavage in the presence of halo derivatives.
6. Cleavage in the presence of acetylenics.
7. Miscellaneous reactions.

Discussion

1. Disproportionation

1,1,2-Trimethyltrichlorodisilane 1 and *sym*-dimethyltetrachlorodisilane 2 undergo a facile disproportionation according to the scheme:



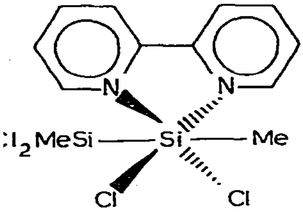
$$n\ \underset{(1)}{\mathrm{Cl_2MeSiSiMe_2Cl}} \xrightarrow[\text{refl.}]{\text{cat.}} n\ \mathrm{Me_2SiCl_2} + \left[-\overset{\mathrm{Me}}{\underset{\mathrm{Cl}}{\mathrm{Si}}}- \right]_n$$

$$m\ \underset{(2)}{\mathrm{Cl_2MeSiSiMeCl_2}} \xrightarrow[\text{refl.}]{\text{cat.}} m\ \mathrm{MeSiCl_3} + \left[-\overset{\mathrm{Me}}{\underset{\mathrm{Cl}}{\mathrm{Si}}}- \right]_m$$

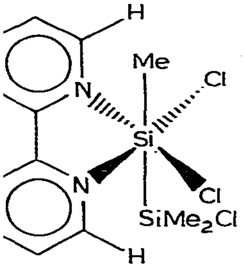
Although the presence of a catalyst was not necessary to observe the reaction at above 200°C [6], convenient yields were obtained using catalysts such as Bu_3N [7,8], Me_4NCl [7—9], Bu_4PCl [7], Et_4PI [7,8], Bu_4NF [10], Me_3N [11], $(Ph_3P)_2NiCl_2$ [12], PO_4H_3 [13], and $P(O)(OMe)_3$ [13]. However, $P(O)(NMe_2)_3$ [13,14] (HMPA) seems to be the most efficient catalyst, both with the disilane fraction or with the crude residue. As an example [14] the dismutation of a disilane fraction (b.p. 120—160°C), 800 g, with HMPA, 8 g, gave a mixture (636 g) of Me_3SiCl (2.5% weight) Me_2SiCl_2 (36.4%), $MeSiCl_3$ (61%) and a residue (170 g). The formation of Me_3SiCl was due to the presence of $SiMe_3$ units. These esults can be compared to those observed during the course of Si_2Cl_6 disproportionation.

The Si—Si bond in disilanes is well known to be easily cleaved by bases [2,3, 2]. Moreover, the formation of complexes of amines with Si_2Cl_6 [18—21,23,24] s well as $Si_2Me_2Cl_4$ [25,26] has been described.

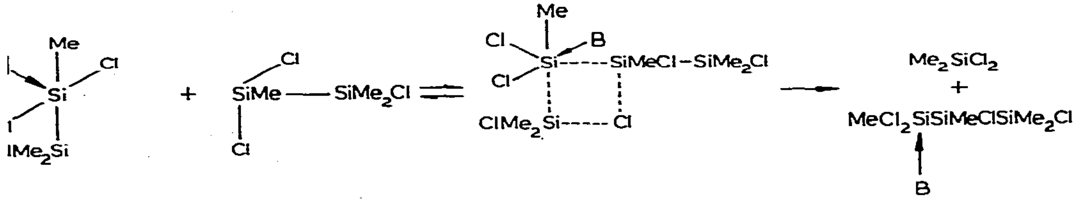
Thus for instance, 2,2′-bipyridyl gives a complex with $Cl_2MeSiSiMeCl_2$ [25,26] hich is stable up to room temperature:



he X-ray structure analysis of this complex has been carried out [27]. A comlex was also obtained with trimethylamine at —80°C. A similar complex etween 2,2′-bipyridyl and $Cl_2MeSiSiMe_2Cl$ was observed in THF and identified y ^1H NMR spectroscopy (position of both Hα) [26]:



The complexation occurs on the more chlorinated silicon atom. This observaion and results observed in the redistribution of $Cl_2MeSiSiMe_2Cl$ suggest a echanism different from that previously proposed [21]:



This interpretation also permits the rationalization of other reactions of these pecies, particularly the cleavage by HCl given below. It is noteworthy that the eactivity decreases in the order $Cl_3Si > MeCl_2Si > Me_2ClSi$. So $Me_3SiSiMeCl_2$ eacts giving Me_3SiCl whereas we have verified that $ClMe_2SiSiMe_2Cl$ does not ndergo disproportionation when refluxed with HMPA.

To illustrate this mechanism the following products were isolated: $(Cl_2MeSi)_3$-iMe by warming $MeCl_2SiSiMeCl_2$ in the presence of Me_3N and $(Cl_3Si)_3SiSiCl_2Me$ rom Cl_5Si_2Me treated under similar conditions [11].

The disproportionation of the corresponding alkoxydisilanes was studied largely in the presence of MeOLi [26] or under thermal conditions [27]. The proposed mechanism is in complete accord with our interpretation for the chlorodisilane dismutation.

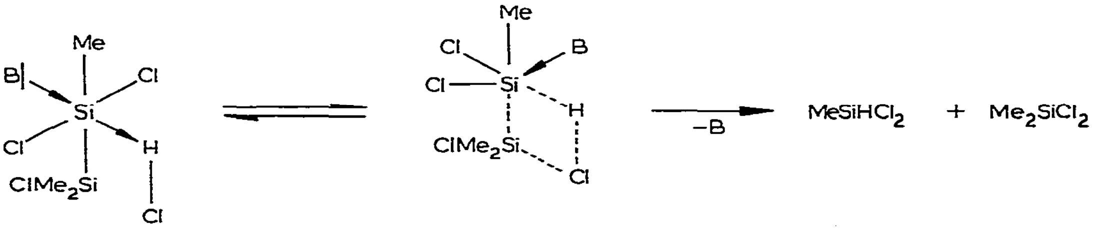
2. *Cleavage by HCl*

Tertiary organic amines such as Bu_3N [30] or $PhNMe_2$ [32], $HCONMe_2$, *N*-methyl-2-pyrrolidone or poly(vinyl pyrrolidone) [31] or suitable salts thereof are known to catalyze the HCl cleavage of the disilane fraction. Thus for instance 640 g of this fraction heated with 10% weight $HCONMe_2$ as a catalyst gave 644 g of monosilanes containing (% weight) $MeSiHCl_2$ 40.6, Me_3SiCl, 2, $MeSiCl_3$ 30.6, Me_2SiCl_2 20.8 [31]. Similarly, $Cl_2MeSiSiMeCl_2$ and $Cl_2MeSiSiMe_2Cl$ were cleaved as follows:

$$Cl_2MeSiSiMeCl_2 \xrightarrow[\text{cat.}]{\text{HCl}} HMeSiCl_2 + MeSiCl_3$$

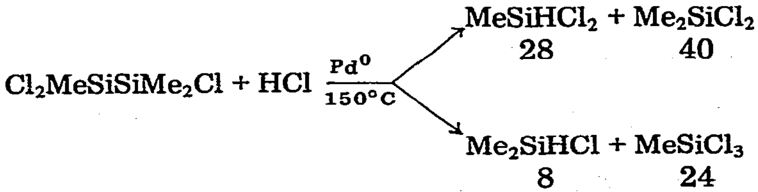
$$Cl_2MeSiSiMe_2Cl \xrightarrow[\text{cat.}]{\text{HCl}} HMeSiCl_2 + Me_2SiCl_2$$

In these reactions hydrogen goes on the more chlorinated silicon atom and HMe_2SiCl is not formed in appreciable amounts. As observed in the previous chapter, the scission occurs only if there are at least two chlorines on one of the silicon atoms and consequently $ClMe_2SiSiMe_2Cl$ does not react. Such behaviour can be once again rationalized by the mechanism previously proposed in the absence of HCl, i.e. with $Cl_2MeSiSiMe_2Cl$:



We must specify that uncatalyzed reaction has been observed [39], for instance, with $Me_3SiSiMe_2Cl$ but requires drastic thermal conditions (500°C) [34]. Moreover, transition metal complexes such as $(Me_2PhP)_2PdCl_2$ [51] catalyze the cleavage of the disilane fraction by HCl at 150°C, giving a mixture of Me_2SiHCl (1.3%), $MeSiHCl_2$ (24%), $MeSiCl_3$ (54%) and Me_2SiCl_2 (15%). Similarly, $(Ph_3P)_2NiCl_2$ catalyzes the selective cleavage of $Cl_2MeSiSiMe_2Cl$ by HCl in a mixture of $Cl_2MeSiSiMe_2Cl$ and $ClMe_2SiSiMe_2Cl$ resulting from a disilane fraction methylation [35].

In addition a partial reverse cleavage has been observed by Nagai et al. [36] when tetrakis(triphenylphosphine)palladium(0) was used:



$$Cl_2MeSiSiMe_2Cl + HCl \xrightarrow[150°C]{Pd^0} \begin{cases} \underset{28}{MeSiHCl_2} + \underset{40}{Me_2SiCl_2} \\ \underset{8}{Me_2SiHCl} + \underset{24}{MeSiCl_3} \end{cases}$$

In the presence of $\mathrm{AlCl_3}$, HCl induces the cleavage of $\mathrm{Si{-}CH_3}$ bonds in suffi- ntly methylated di- or polysilanes [37] (as observed with $\mathrm{H_2SO_4}$) [38] and, instance methylchlorodisilanes contained in the disilane fraction are con- rted to *sym*-dimethyltetrachlorodisilane so easily prepared in a pure state:

$$_n\mathrm{Cl}_{3-n}\mathrm{SiSiMe}_m\mathrm{Cl}_{3-m} \xrightarrow[\mathrm{AlCl_3}\ \Delta]{\mathrm{HCl}} \mathrm{MeCl_2SiSiMeCl_2}$$

$\leqslant m, n \leqslant 3$.

Similarly $\mathrm{Cl_2MeSiSiMe_2Cl}$ can be isolated in good yields starting from $\mathrm{Me_2SiSiMe_2Cl}$ [35].

Cleavage in the presence of hydrogen

Usually $\mathrm{HMe_2SiCl}$ is not formed when disilanes are cleaved by HCl. Since s compound is useful as a linking unit in silicones it was interesting to pre- re it from the disilane residue. This is the reason why hydrogenolysis of the ilane fraction was investigated as well as that of $\mathrm{Cl_2MeSiSiMeCl_2}$ and $\mathrm{MeSiSiMe_2Cl}$ studied separately.

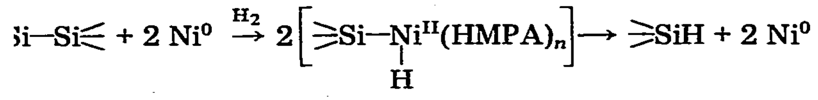
Several types of catalysts have been used for that purpose, namely Pd, Rh or /C [39], Pd [39] complexes, Cu metal, Cu chlorides or Cu complexes [40], kelocene or reduced nickel with HMPA [41,42] as a cocatalyst. Some results given in Table 1.

These results require the following comments:

Reduced nickel was prepared by reduction of anhydrous nickel chloride by ethylsilane [43,44].

Whatever Ni catalyst was used, in the absence of HMPA, $\mathrm{Cl_2MeSiSiMe_2Cl}$ was re reactive than $\mathrm{Cl_2MeSiSiMeCl_2}$ [41,42] as observed with Pd or Pt catalysts 8] and the reaction was slow. In contrast, using HMPA as the catalyst, the ction rate increased and the tetrachloro derivatives became more reactive.

We suggest that the active moiety is a [$\mathrm{Ni^0}$] species coming from reduction of her $\mathrm{NiCl_2}$ by $\mathrm{Et_3SiH}$ or $\mathrm{NiCp_2}$ by disilanes in situ [42] (the reductive proper- s of these disilanes are discussed below):



$$\mathrm{i{-}Si}\lessgtr + 2\,\mathrm{Ni^0} \xrightarrow{\mathrm{H_2}} 2\left[\gtrless\mathrm{Si{-}}\underset{\mathrm{H}}{\mathrm{Ni}}{}^{\mathrm{II}}(\mathrm{HMPA})_n\right] \longrightarrow \gtrless\mathrm{SiH} + 2\,\mathrm{Ni^0}$$

As already seen for acidic cleavage, hydrogenolysis can occur under thermal nditions [45].

Cleavage in the presence of metal and metalloid halides

Whereas the reductive properties of alkylated di- [46—48] or polysilanes [49], dialkoxytetraalkyldisilanes [46,48] have been used in the reduction of metal metalloid halides and related compounds, the disilane fraction has not been uch used for that purpose.

However, because of the reactivity of these methylchlorodisilanes towards lides, the redistribution between the disilane residue and $\mathrm{Me_3SiCl}$ or $\mathrm{Me_2SiCl_2}$ 5,50] can be used to increase the ratio of $\mathrm{Cl_2MeSiSiMe_2Cl}$:

$$\text{silane residue} + \mathrm{Me_3SiCl} \xrightarrow{\mathrm{AlCl_3}} \mathrm{Cl_2MeSiSiMe_2Cl}$$

TABLE 1

HYDROGENOLYSIS OF $Cl_2MeSiSiMeCl_2$, $Cl_2MeSiSiMe_2Cl$ OR DISILANE FRACTION

Starting material	Reaction conditions		Catalyst	Products (% weight)						Ref.
	Pressure (kg/cm^2)	Temp. (°C)		Me_2SiHCl	$MeSiHCl_2$	$MeSiCl_3$	Me_2SiCl_2	Other products	Unreacted disilanes	
$Cl_2MeSiSiMeCl_2$	210.9	120	$(Ph_3P)_2PdCl_2$	—	69	24.4	3.5			39
$Cl_2MeSiSiMe_2Cl$			$(Ph_3P)_2PdCl_2$	33.2	29.8	2.0	8.9	26	26	39
Disilane fraction	172.2	200	$(Ph_3P)_2PdCl_2$	2.8	39.7	28.3	6.5	11.5 ($MeSiH_2Cl$: 6.3)	11.2	39
Disilane fraction	25	100 (25 mn)	$NiCp_2$/HMPA	2.9	41.3	23.5	21.8	$HSiCl_3$ 7.9 Me_3SiCl 2.2		42
Disilane fraction	25	100 (25 mn)	$NiCp_2$/HMPA	2.8	40.2	25.0	24.9	$HSiCl_3$ 4.9 Me_3SiCl 2.2		42
Disilane fraction	25	100 (25 mn)	Red. Ni/HMPA (3%)	1.6	36.1	32.9	23.5	$HSiCl_3$ 3.4 Me_3SiCl 2.4		42
Disilane fraction	135	150 (85 h)	Red. Ni/HMPA (3%)	8.7	52.8	10.6	10.9	$MeSiH_2Cl$ 15.3 Me_3SiCl 10.7		42

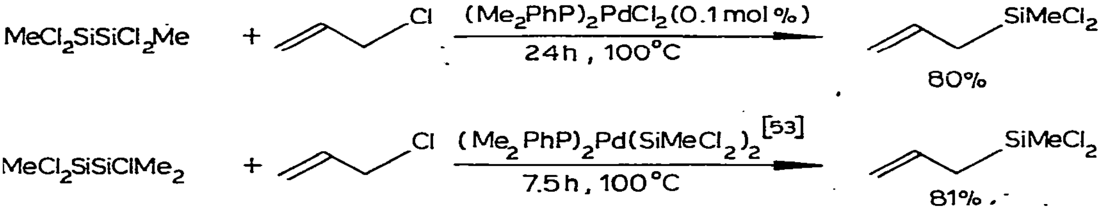
5. Cleavage in the presence of an organic halide

This field was investigated because of the possibility of synthesizing organochlorosilanes having substituents other than methyl groups via an economical route. First results were observed by Barry et al. [51] who obtained $RSiCl_3$ from RCl and Si_2Cl_6 with CuCl, $SbCl_3$ or $MgCl_2$ as the catalyst. More recently Atwell and Bokerman [52,53] generalized the reaction to methylchlorodisilanes and effected the reaction:

$$R{-}Cl + {\geq}Si{-}Si{\leq} \xrightarrow{\text{Pd (Pt or Ni) cat.}} {\geq}Si{-}R + {\geq}Si{-}Cl$$

R = H, sat. alkyl, allyl, phenyl, benzyl.

However, starting from the constituents of the disilane fraction, examples were given with HCl (previously mentioned), Me_2CHCl, $PhCH_2CH_2Cl$, PhCl, $PhCH_2Cl$ and especially $CH_2{=}CH{-}CH_2Cl$, e.g.:

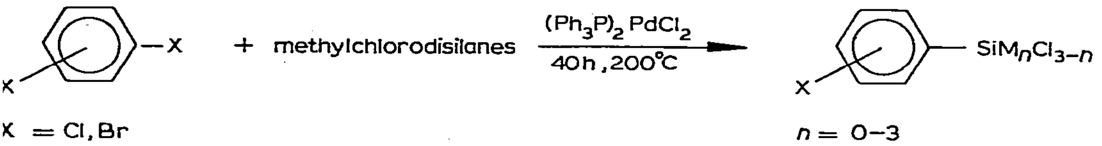


Furthermore, allylsilanes also were synthesized using $(Ph_3P)_4Pd^0$ [54], or $(Bu_3P)_4Pd^0$ [55] as the catalyst and the reactivity was higher when the number of chlorine atoms on the Si—Si linkage was increased [54] *. Otherwise catalysts such as Bu_3N, HCl, Bu_4NCl or Bu_4PCl [56] permitted to perform the reaction alone or as claimed in a recent patent along with Cu^I, Cu^{II} or Ni^{II} salts [57]. In the last case only allyl chloride and hexachlorodisilane are exemplified.

Concerning haloaromatic derivatives, besides the results mentioned above in the case of PhCl and Si_2Cl_6 [51] or constituents of the disilane fraction [52,53], $PhMeSiCl_2$ and $PhSiCl_3$ were formed by thermal cleavage (520°C) of disilane residue in the presence of PhCl [58]. Moreover, Nagai et al. [59—63] in the context of their studies of the silylation of halobenzenes by disilanes investigated the behaviour of the constituents of disilane residue towards halobenzenes in the presence of Pd^0 or Pd^{II} catalysts, e.g.:

$$PhBr + MeCl_2SiSiCl_2Me \xrightarrow[\text{25h, 145°C}]{(Ph_3P)_4Pd^0} PhSiMeCl_2$$

X = Cl, Br



X = Cl, Br $\qquad n = 0{-}3$

Bromobenzene afforded $PhSiMeCl_2$ in about 60% yield (regarding the involved bromobenzene) after 25 h at 145°C, whereas the formation of the C_{Ar}—Si bond was observed with PhCl in low yields (10%) only when using Me_6Si_2 as the disilane [62]. These results differ notably from those previously given by Atwell

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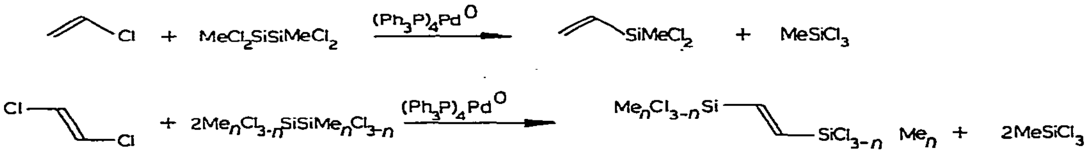
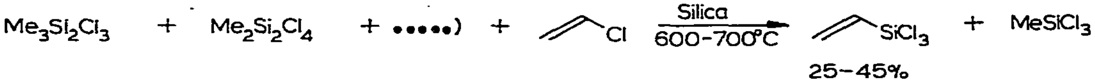
* In contrast, in the presence of Pd/Cl as the catalyst, $(Me_3Si)_2$ was the most reactive.

and Bokerman [52,53], who claimed to have obtained $PhSiMeCl_2$ in satisfactory yields (60%) from chlorobenzene and $MeCl_2SiSiCl_2Me$ in the presence of Pd/C (1 mol.%) during 24 h at 200°C.

Nagai et al. [55,60,64] also investigated the cleavage of methylchlorodisilanes in the presence of vinyl chlorides and succeeded in the synthesis of vinylchlorosilanes, i.e. [64]:



These results should be compared with those of Mironov dealing with the thermal reactions of vinylchloride with disilane residue [65].



As previously mentioned, alkyl chlorides can be used to form R—Si bonds even from methylchlorodisilanes contained in the disilane fraction [52,53]. We only add here the reaction observed in the presence of CCl_4 [66]:

$$MeCl_2SiSiCl_2Me + CCl_4 \xrightarrow[\text{refl. 2 h}]{Ph_3P(3\%)} \underset{62\%}{Cl_3CSiMeCl_2} \xrightarrow[Me_2SiCl_2]{Ph_3P(5\%)} \underset{95\%}{Cl_3CSiMe_2Cl}$$

In contrast, the redistribution of chloromethyldisilanes (reviewed in refs. [2, 3 and 67]) and the reaction of disilanes on acyl chlorides will not be discussed; hexamethyldisilane undergoes $\equiv$Si—Si$\equiv$ cleavage by ArCOCl in the presence of Pd^{II} complexes [68], and many previous reactions reported the cleavage of $\equiv$Si—Me bonds in the presence of $AlCl_3$ when the disilane has less than four chlorine atoms [48,69—72]. As already seen with HCl, reaction of the disilane fraction with $RCOCl/AlCl_3$ provided a source of pure $MeCl_2SiSiCl_2Me$.

These results highlight that, except for the thermal reactions without synthetic applicability, the synthesis of organotrichlorosilanes from disilanes requires hexachlorodisilane, which is not formed in appreciable amounts during the course of the direct synthesis of Me_2SiCl_2. For example, in contrast to allylmethyldichlorosilane, allyltrichlorosilane has found industrial application (fiberglass adhesives etc.).

We considered that the disilane fraction should be active as a reducing agent to obtain organotrichlorosilanes rather than a silylating agent in a catalytic process between organic halides and silicon tetrachloride. So we proposed a route involving the $NiCp_2$ catalyst/HMPA cocatalyst system [41,42] as an efficient one for hydrogenolysis of disilane residues:

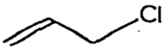
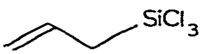
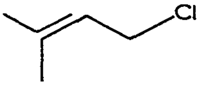
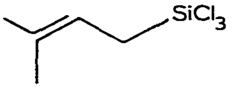
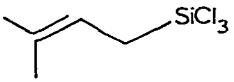
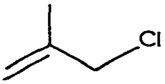
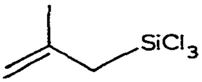
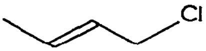
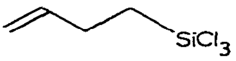
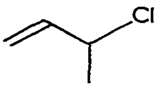
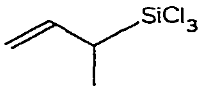
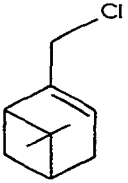
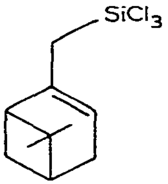
$$\begin{array}{lcl} R\text{—}Cl + SiCl_4 + Cl_2MeSiSiMeCl_2 & \xrightarrow{NiCp_2/HMPA} & RSiCl_3 + 2\ MeSiCl_3 \\ \quad(\text{and/or} & & (\text{and/or} \\ \quad Cl_2MeSiSiMe_2Cl) & & Me_2SiCl_2 + MeSiCl_3)\,. \end{array}$$

The results are summarized in Table 2.

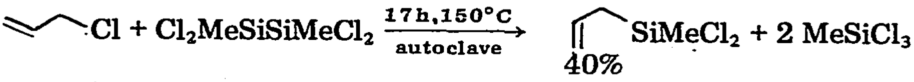
If $SiCl_4$ is not used, the reaction proceeds less readily. This can be seen in the case of allyl chloride and the results are then comparable to those of Atwell and

TABLE 2

SYNTHESES OF ALLYLTRICHLOROSILANES FROM ALLYL HALIDES, DISILANE RESIDUES AND $SiCl_4$

	RCl	Reaction time	$R'SiCl_3$		Yield (%) (isolated product)
A		15h (90°C) (autoclave)		1	35
B		3.5 h (reflux)		2	80
C		20h (reflux)		2	50
D		15 h (reflux)		3	100
E		15 h (reflux)		4	72
F		20 h (reflux)		4	30
G		100 h (reflux)		5	85

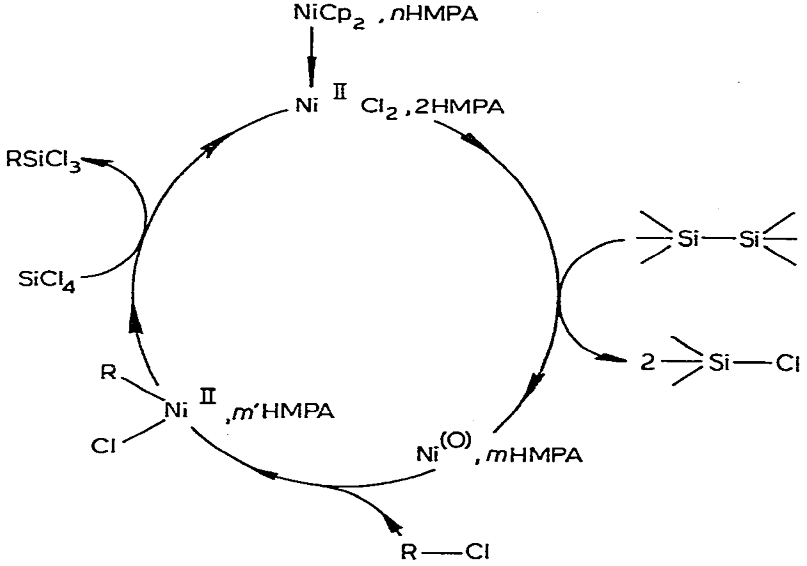
Bokerman [52,53]:



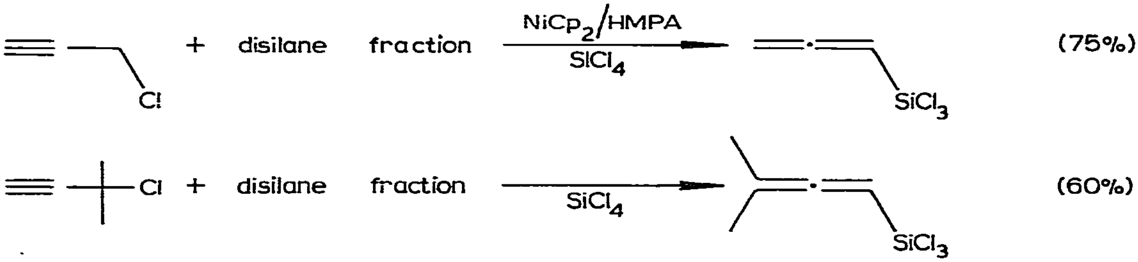
Silylation always appears to be regiospecific and yields the thermodynamically more stable isomer. Thus, in the case of *trans*-crotyl chloride, we obtained *trans*-crotyltrichlorosilane 4 (72%), exclusive of the *cis* and methallyl isomers. The previously proposed route of Seyferth et al. [8] posed more difficulties in execution but also resulted in a mixture of *cis*- and *trans*-crotyltrimethylsilanes (40/60, 52% global yield). With the chlorides (C) and (F) we observe a prior rearrangement of the starting halo compounds into prenyl and crotyl chlorides, respectively.

Similar behaviour was noted with benzyl chlorides and bromobenzene whereas chlorobenzene remained inert under the same conditions. Results are given in Table 3.

We propose the following catalytic cycle as an aid in the explanation of our results and as a possible mechanism [74]:



Recently we extended this work to the synthesis of allenyltrichlorosilanes from propargyl chlorides [75,78], e.g.:



This constitutes the first practical route to such species.

6. *Addition to unsaturated hydrocarbons*

Following the addition reactions of disilanes to 1,3-dienes [79,80], Nagai et al. [81] reported a similar reaction with methylchlorodisilanes according to:

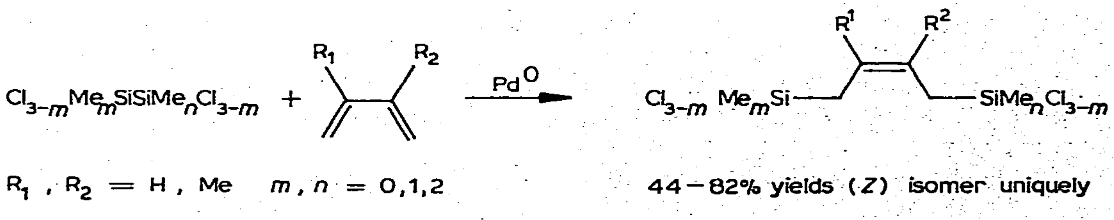
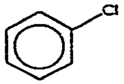
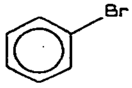
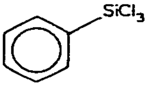
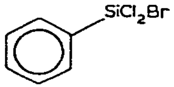
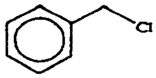
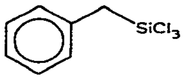
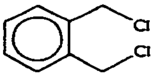
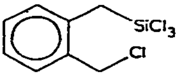
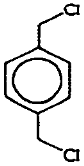
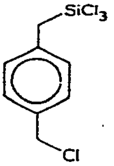
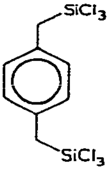
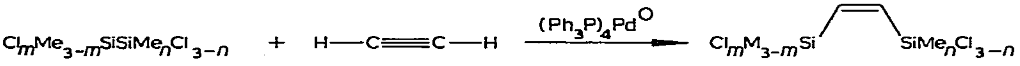


TABLE 3

SYNTHESES OF ARYL- AND BENZYL-TRIHALOSILANES FROM THE CORRESPONDING HALIDES, THE DISILANE FRACTION AND $SiCl_4$

	RCl	Reaction time	$R'SiCl_3$	Yield (%) (isolated product)
H		24 h (reflux)		0
I		24 h (reflux)	 6 +  7 6/7 = 20/80	90
J		24 h (reflux)	 8	40
K		6 h (reflux)	 9	50
L		15 h (reflux)	 10 +  11 10/11 = 70/30	100

Acetylenic hydrocarbons also lead to 1 : 1 adduct with disilanes [87]:



m = 1, 2 ; n = 0, 1, 2 (containing 7–21% (E) isomer)

Phenylacetylene also underwent a *cis* addition *.

7. *Miscellaneous reactions*

As specified first, cyclisation reactions for instance with diamines, diols, dithiols, dilithio derivatives, etc., are considered beyond the scope of this article although many original polyheterocyclic derivatives have been synthesized by this route.

7.1. Halogenation. Whereas hexaalkyldisilanes and alkylchlorodisilanes of lower chlorine content are easily cleaved by halogens giving halomonosilanes

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* Recently, the first results concerning 1,2-disilylation of allenes were published (see H. Watanabe, M. Saito, N. Sutou and Y. Nagai, J. Chem. Soc. Chem. Commun., (1981) 617 and 6th Intern. Symp. Organosilicon Chem., Budapest, 1981, Abstr. p. 44).

[2,3], the main constituents of the disilane fraction give the corresponding halomethyl- or dihalomethyldisilanes by substitution of one or two hydrogens of a methyl group, especially under photochemical conditions [23,88].

7.2. Reductive properties of disilane fraction. As mentioned above it is well known that the $\equiv$Si—Si$\equiv$ bond exhibits powerful reductive properties. However, only a few studies concerning the disilane fraction have been performed. Since the reduction of halo-derivatives was developed in Section 4, we only mention here reduction of triphenylphosphine oxide by the disilane fraction. To our knowledge the other reduction reactions involved hexaalkyl(aryl)disilanes, alkoxysilanes or hexachlorodisilane.

We reduced triphenylphosphine oxide according to [89]:

$$\mathrm{Ph_3PO} + \begin{array}{c}\text{disilane fraction}\\ \text{or}\\ \text{disilane residue}\end{array} \rightarrow \underset{\sim 95\%}{\mathrm{Ph_3P}} + \text{methylchlorosiloxanes}$$

The reaction was accompanied by the formation of $MeSiCl_3$ and Me_2SiCl_2 resulting from the disproportionation of methylchlorodisilanes already described (Section 1). These results can be compared to those observed in the reduction of Ph_3PO [90,91], Ph_3PS [92], R_2SO [90,91], R_3NO [90,91,93,94] by Si_2Cl_6 or non-industrial disilanes.

8. Conclusions

This article deals with trends for the conversion of the industrial disilane residue into valuable products. This disilane residue constitutes an important by-product in the dimethyldichlorosilane synthesis.

At the present time the main applications of these disilanes are as follows.

In the Laboratory. The synthesis of hexaalkyl-, alkylaryl- or alkylalkoxydisilanes as well as Me_6Si_2 a versatile organosilicon reagent, and the synthesis of allyl- and vinyl-silanes, versatile synthons in organic synthesis.

In Industry. The main application consists of the acidic cleavage in the presence of base giving, as major products $MeSiHCl_2$ and $MeSiCl_3$ without significant amounts of final residue. Another application which is found increasingly often is the synthesis of Si—C materials by the pyrolysis of polysilanes resulting from the disilane fraction disproportionation [95,96].

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