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REACTIONS OF ACETALS, ORTHOESTERS AND THEIR ANALOGUES WITH HALOGENOSILANES

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SUMMARY

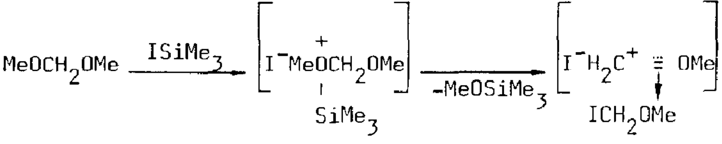
The reactions of cyclic and acyclic acetals and orthoesters and their analogues with halogenosilanes, leading to halogenoalkoxysilanes, carbonyl compounds and esters are reviewed. General conditions of reaction procedure - the use of the dissolvent, low (in some cases) temperatures - are established. The influence of the initial reagents structure and synthesis conditions on the direction and reaction products yields are described.

The chemistry of acetals is a flourishing branch of organic chemistry [1]. Acetals, orthoesters and their analogues are convenient precursors in the synthesis of ethers and esters, diols, unsaturated alcohols, dihydropyrans and other mono- and polyfunctional compounds. These applications are summarized in several reviews [2,3] and books [1,4], but the use of these reagents in the selective preparation of organosilicon compounds has received less attention. These reactions are important theoretically as well as in synthesis, and although the few data on their mechanism are contradictory, they do indicate the considerable diversity of these reactions.

REACTION OF HALOGENOSILANES WITH ACYCLIC ACETALS AND THEIR HETEROANALOGUES

The reaction of acyclic acetals with halogenosilanes usually leads to a complex mixture of products, consisting mainly of halogenomethyl esters [5], carbonyl compounds [6-9], trimethylsilyl esters [10] and unsaturated compounds [10-14].

Dichloromethane [7,14-16], chloroform [6,7], carbon tetrachloride [15], acetonitrile [8,9] and tetrahydrofuran [17] are usually used as solvents. The reaction takes place in two hours, and in some cases in 10-20 min. [6,7,14], at 45°C [7-17]. Dimethoxymethane was treated with iodotrimethylsilane at room temperature to form iodomethyl methyl ether in 93% yield [18]. This product is used to introduce the methoxymethyl [19] or iodomethyl [20] group into various organic compounds. The suggested mechanism is shown in equation (1) [13]:



$$\mathrm{MeOCH_2OMe} \xrightarrow{\mathrm{ISiMe_3}} \left[\mathrm{I^-} \underset{\mathrm{SiMe_3}}{\overset{+}{\mathrm{MeOCH_2OMe}}} \right] \xrightarrow[\mathrm{-MeOSiMe_3}]{} \left[\mathrm{I^-H_2C^+} \underset{\mathrm{ICH_2OMe}}{\overset{\cdot\cdot}{=}} \mathrm{OMe} \right] \qquad (1)$$

At 25°C acyclic ketals give the keton or aldehyde together with the trimethyl silyl ester and alkyliodide in 84-97% yields [6,21]:

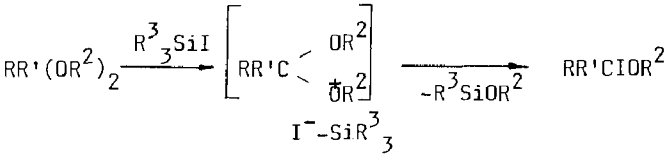
$$\mathrm{RR'C(OR^2)_2 + Me_3SiI \longrightarrow RR'CO + R^2OSiMe_3 + R^2I}$$

$$\mathrm{R = Alk \qquad R'R^2 = Alk,\ Ph} \qquad (2)$$

The reaction is carried out in methylene chloride saturated with propene to scavenge hydrogen iodide which is always present in iodotrimethylsilane because of adventitious hydrolysis. The course of the main reaction is not affected, and the 2-iodopropane is easily removed at low pressure.

If propene is not used, the yield decreases because of the competing acid-catalyzed aldol condensation [6].

The reaction is suggested to proceed via an intermediate complex [22], then an α-iodoalkyl alkyl ether which dissociates into carbonyl compound and alkyl iodide:



$$\mathrm{RR'(OR^2)_2} \xrightarrow{\mathrm{R^3{}_3SiI}} \left[\mathrm{RR'C} \begin{matrix} \nearrow \mathrm{OR^2} \\ \searrow \overset{+}{\mathrm{O}}\mathrm{R^2} \end{matrix} \right] \xrightarrow[\mathrm{-R^3SiOR^2}]{} \mathrm{RR'ClOR^2} \qquad (3)$$
$$\mathrm{I^- \text{-} SiR^3{}_3}$$

$$\mathrm{RR'ClOR^2 \longrightarrow RR'CO + R^2I} \qquad \mathrm{R,R' = H,Alk;\ R^3 = Me,Et}$$

The formation of α-iodoalkyl ethers from acyclic acetals and iodotriethylsilane has been confirmed by NMR and UV-spectroscopy [22].

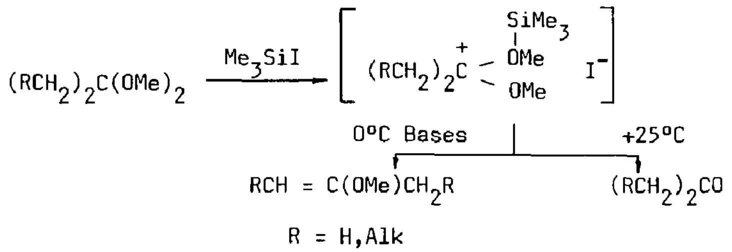
Acetals can be converted into carbonyl compounds by means of systems generating iodomethylsilane in the reaction mixture directly. For example, the use of trimethylchlorosilane and metallic iodides (or quaternary ammonium iodide) gives ketons in 95-100% yields [8.9]:

$$\mathrm{RR'C(OR^2)_2 \xrightarrow{ClSiMe_3/XI} RR'CO + R^2OSiMe_3 + R^2I}$$

$$\mathrm{R = C_6H_{13},\ -(CH_2)_5-;\ Ph,\ 4\text{-}MeOPh} \qquad (4)$$

$$\mathrm{X = Li,Na,K,Cu,Me_4N,\ Bu_4N,Me_3PhN}$$

In presence of the bases such as 2,6-diterbutyl-4-methylpyridine or hexamethyldisilazane, iodotrialkylsilanes react with acyclic acetals to give methyl vinyl ethers in 71-86% yields [15,23].



$$(RCH_2)_2C(OMe)_2 \xrightarrow{Me_3SiI} \left[(RCH_2)_2\overset{+}{C} < \begin{matrix} \overset{SiMe_3}{\overset{|}{OMe}} \\ OMe \end{matrix} \quad I^- \right] \qquad (5)$$

$$\begin{tikzcd} & \left[(RCH_2)_2\overset{+}{C}(\overset{+}{O}(SiMe_3)Me)(OMe)\; I^- \right] \arrow[dl, "0^\circ C\ Bases"'] \arrow[dr, "+25^\circ C"] & \\ RCH = C(OMe)CH_2R & & (RCH_2)_2CO \end{tikzcd}$$

$R = H,Alk$

The products are easily separated [24] unless the reaction is carried out at 25°C when carbonyl compounds are formed [6,7]. Acetals of unsymmetric ketones generate two alkene isomers in equal amount [15]. The rate of the reaction is very dependent on the nature of the solvent: it is higher in methylene chloride and chloroform (2.5-4 h) than in pentane or carbon tetrachloride (6-47 h) [15].

Dimethylvinylideneacetal reacts with iodotrimethylsilane exothermically with C-O bond breaking to give alkyl iodide and methyl trialkylsilylacetate in quantitative yield [10,11]:

$$CH_2 = C(OMe)_2 \xrightarrow[-MeI]{R_3SiI} R_3SiCH_2COOMe \qquad (6)$$

$R = Me,Et$

Methyltrichlorogermane reacts with diethylvinylideneacetal (molar ratio 1:2) to form O,O-diethyl(methylchlorogermyl)vinylidenacetal in 38% yield [10], the HCl which is formed being scavenged by the excess acetal.

At low temperatures (-78°C) the acetal fragment is preserved in the product:

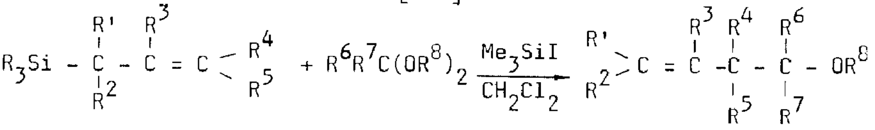
$$2CH_2 = C(OEt)_2 \xrightarrow[-EtCl,MeCOOEt]{MeGeCl_3} MeCl_2GeCH = C(OEt)_2 \qquad (7)$$

There are some data on the reaction of acyclic acetals with chlorosilanes by a radical-chain mechanism [12]. For example, dialkyl esters are formed in high yield (93%) when a mixture of acetal and chlorosilane is treated by -radiation in presence of 2% ditertbutyl peroxide [12]:

$$\begin{aligned} &MeCH(OMe)_2 + HSiCl_3 \longrightarrow MeCHClOMe + HCl_2OSiMe \\ &MeCHClOMe + HSiCl_3 \longrightarrow MeCH_2OMe + SiCl_4 \end{aligned} \qquad (8)$$

Acyclic acetals react with trichlorosilane very rapidly to form the α-chloroether in quantitative yield, which transforms into ethyl methyl ether.

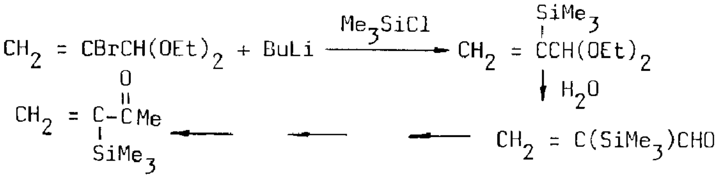
In reactions involving acetals, iodotrimethylsilane behaves not only as a co-reagent but also as a catalyst. For example, under the influence of iodotrimethylsilane, dealkoxylation of the acetal occurs with the addition of an alkoxycarbenium ion to a double bond [13]:



$$R_3Si-\overset{R'}{\underset{R^2}{C}}-\overset{R^3}{C}=C{<}^{R^4}_{R^5} + R^6R^7C(OR^8)_2 \xrightarrow[CH_2Cl_2]{Me_3SiI} {}^{R'}_{R^2}{>}C=\overset{R^3}{C}-\overset{R^4}{\underset{R^5}{C}}-\overset{R^6}{\underset{R^7}{C}}-OR^8 \qquad (9)$$

R'...R^8 = Alk

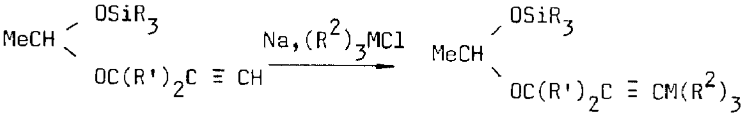
The reaction of unsaturated acetals with butyl-lithium in tetrahydrofuran at low temperature (-78°C), followed by treatment with trimethylchlorosilane leads to (trimethylsilyl) acetal which is hydrolysed by aqueous acetone in presence of catalytic ammounts of paratoluenesulphonic acid to form α-trimethylsilylpropenal in 73% yield [12]:



$$\begin{array}{l} CH_2=CBrCH(OEt)_2 + BuLi \xrightarrow{Me_3SiCl} CH_2=\overset{SiMe_3}{C}CH(OEt)_2 \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow H_2O \\ CH_2=\underset{SiMe_3}{C}-\overset{O}{\overset{\|}{C}}Me \longleftarrow \longleftarrow \longleftarrow CH_2=C(SiMe_3)CHO \end{array} \qquad (10)$$

The reaction is preparatively valuable because it provides a route to unsaturated silyl-substituted ketones in good yields.

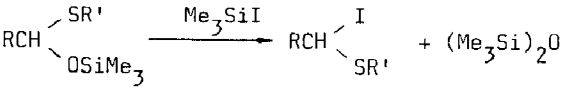
Acetylenic organosilicon acetals react with sodium, and then readily with organochlorosilanes or organotin chlorides by reaction (II) [25]:



$$MeCH{<}^{OSiR_3}_{OC(R')_2C\equiv CH} \xrightarrow{Na,(R^2)_3MCl} MeCH{<}^{OSiR_3}_{OC(R')_2C\equiv CM(R^2)_3} \qquad (11)$$

R,R',R^2 = Me,Et M = Si, Sn

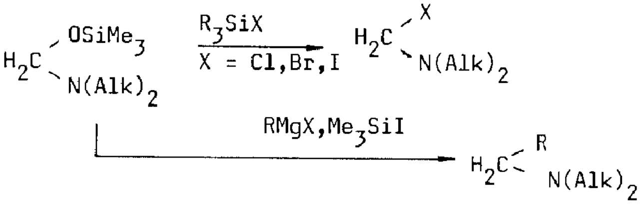
1-Alkylthio-1-(trimethylsiloxy)alkanes react with iodomethylsilane with C-O bond breaking giving α-iodosulphides in 90% and higher yields [26]:



$$RCH{<}^{SR'}_{OSiMe_3} \xrightarrow{Me_3SiI} RCH{<}^{I}_{SR'} + (Me_3Si)_2O \qquad (12)$$

R = R' = H,Me

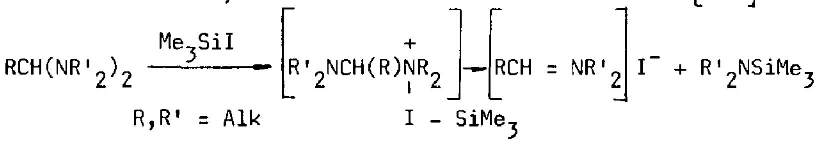
Heteroanalogues of acyclic acetals react with halosilanes to form trimethylsilyl ethers of methylamines, methylamides, etc. [27]:



$$\begin{array}{l} H_2C{<}^{OSiMe_3}_{N(Alk)_2} \xrightarrow[X\,=\,Cl,Br,I]{R_3SiX} H_2C{<}^{X}_{N(Alk)_2} \\ \quad \llcorner\!\!\xrightarrow{\qquad\qquad RMgX,Me_3SiI \qquad\qquad} H_2C{<}^{R}_{N(Alk)_2} \end{array} \qquad (13)$$

In these reactions acyclic heterosubstituted unsymmetric acetals can be regarded as the effective amino- and amido-methylating reagents at C, O or N-atoms leading to Mannich type Condensations under neutral anhydrous conditions [27]. Their reactivity is in some cases higher than that of such traditional aminomethylating reagents as methylenamides and α-aminoethers [28,29].

In contrast to unsymmetric heterosubstituted acyclic acetals, the aminals react with iodomethylsilane to form a salt and silazane [30]:



$$RCH(NR'_2)_2 \xrightarrow{Me_3SiI} \left[R'_2NCH(R)\overset{+}{\underset{\text{I - SiMe}_3}{N}}R_2 \right] \rightarrow \left[RCH = NR'_2 \right] I^- + R'_2NSiMe_3 \qquad (14)$$

R,R' = Alk

Phosphorus acetals react with two molar proportions of iodotrimethylsilane at 0°C to give bis(trimethylsilyl)dialkoxymethylphosphonates and thence stable phosphonium salts [31]:

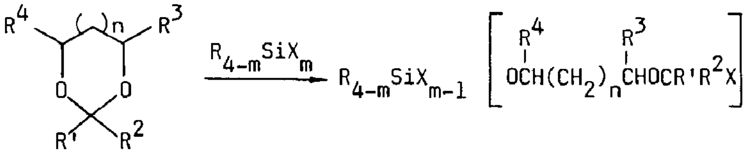
$$(RO)_2P(O)CH(OR)_2 \xrightarrow{Me_3SiI} (Me_3SiO)_2P(O)CH(OR) \underset{(Me_3Si)_2NNa}{\overset{Me_3SiI}{\rightleftarrows}} \left[(MeSiO)_3\overset{+}{P}CH(OR)_2 \right] I^- \qquad (15)$$

R = Alk

It is interesting to note that phosphonium salts can be transformed into initial phosphonates by treatment with sodium bis(trimethylsilyl)amide [31].

REACTIONS OF HALOGENOSILANES WITH CYCLIC ACETALS

Halogenosilanes react with cyclic acetals with ring opening giving halogenosilyl ethers and acyclic dihaloethers [32,33]:



(16)

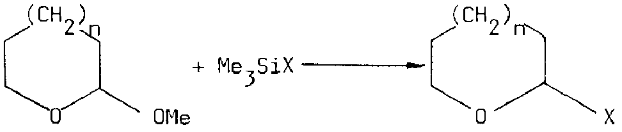
R',R^2 = H,Alk
R^3,R^4 = Me,Et,Ph
n = 0,1,2

m = 1...4 h = 0,1,2
R = Alk,Ph
X = Cl,Br,I

The reaction with cyclic acetals proceeds under more severe conditions than the reaction with acyclic acetals (see Table).

Halogen-containing solvents (dichloromethan, chloroform, carbon tetrachloride), as well as high-boiling amines such as quinoline (to act as solvent and HCl acceptor) have been used (see Table).

Monomethoxyderivatives of tetrahydrofuran and tetrahydropyran under the influence of halogenotrimethylsilanes transform into the corresponding halogenoderivatives in 86-100% yields [32]. In this case the exocyclic bond C-O reacts:

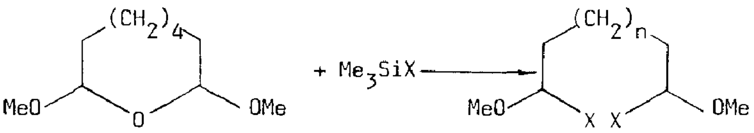


(17)

n = 0,1 X = Cl, Br

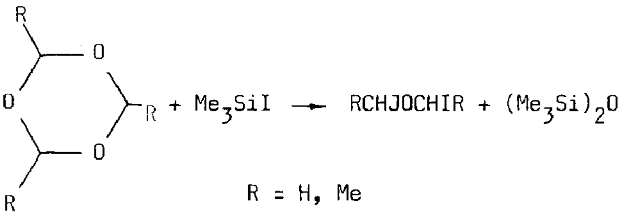
The yield of the final product increases to 86% when a trichlorosilane is used but the reaction proceeds slowly [27].

2,5-Dimethoxytetrahydrofuran reacts with trimethylhalosilanes to form 1,4-dibromo-1,4-dimethoxybutan rather than 2,5-dibromotetrahydrofuran as was expected. 1,6-Dimethoxytetrahydropyran behaves in the same way being converted into 1,5-bromo-1,5-dimethoxypentane:



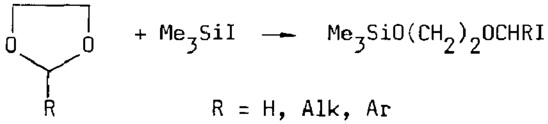
(18)

Under the influence of iodotrimethylsilane, bis(iodomethyl) and bis- α-iodoalkyl ethers are formed from trioxanes in quantitative yield [34]:



(19)

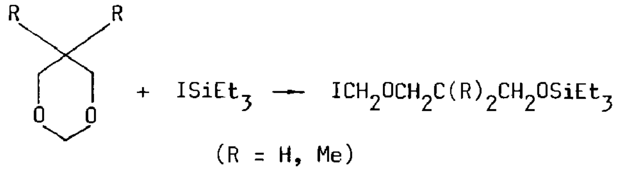
The reaction of iodotrimethylsilane with 1,3-dioxolanes proceeds rapidly in mild conditions (at -78°C, 10 min) (see Table) [32-35]:



(20)

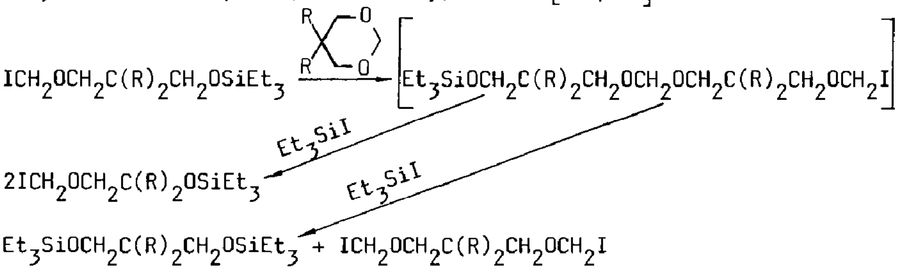
The α-iodoethers show characteristic signals in the NMR spectra of the reaction mixture.

The reaction of 1,3-dioxanes with iodotriethylsilane proceeds in the same way [22, 36]:



(21)

The NMR-spectra of the reaction mixture (-70° - -10°C) suggest that the initial α-iodoether reacts with the dioxolane to form an acyclic acetal which, like 1,1-dialkoxyalkanes, reacts rapidly with iodotrimethylsilane in two senses: either it transforms into two α-iodoether molecules or into 1,3-di(triethylsiloxy)alkane and 1,3-di(iodomethoxy)alkane [22,36] :



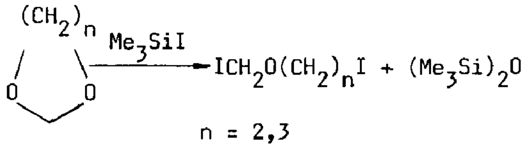
(22)

Raising the temperature (to 20°C) leads to the appearance in NMR spectrum of the signals which indicate the formation of CH_2I groups by the dissociation of α-iodoethers:

$$ICH_2OCH_2C(R)_2CH_2OSiEt_3 \xrightarrow[-CH_2O]{} ICH_2C(R)_2CH_2OSiEt_3$$

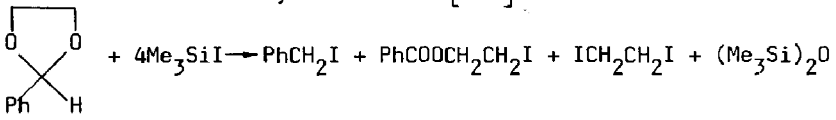
$$ICH_2OCH_2C(R)_2CH_2OCH_2I \xrightarrow[-CH_2O]{} ICH_2C(R)_2CH_2I \qquad (23)$$

At higher temperatures (0...+15°C) iodomethylsilane splits cyclic formals to form iodomethyl-ω-iodoalkyl ethers [37]:



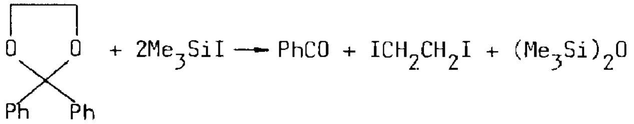
(24)

The size of the ring controls the reactivity[37]. With a phenyl group at position 2 in 1,3-dioxolane, the main products are α-iodoethyl benzoate, diiodoethane and hexamethyldisiloxane [37] :



(25)

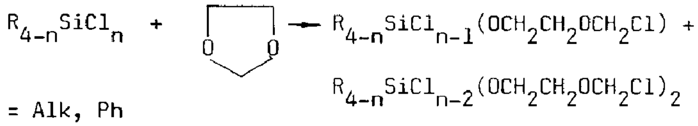
Again 2,2-diphenyl-1,3-dioxolane with iodotrimethylsilane forms three main products: diphenylketone, diiodoethane, and hexamethyldisiloxane[37] :



(26)

Unlike acyclic dimethyl- and diethyl ketals which fully transform into the corresponding ketones, 1,4-dioxoaspiro[4,5]decane under the action of iodotrimethylsilane gives a mixture containing only 20% of ketone, other products were not identified [6].

The reaction of 1,3-dioxolane with equimolecular ammounts of tetrachlorosilane and other organochlorosilanes (methyltrichlorosilane, phenyltrichlorosilane, dimethyldichlorosilane, trimethylchlorosilane) has been studied. This reaction proceeds without catalysts under pressure at 175°C [38]:



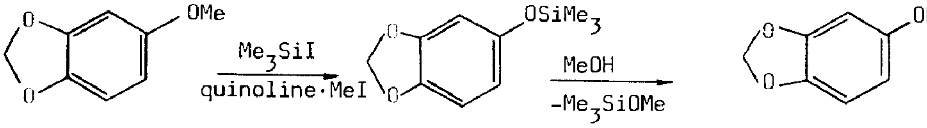
(27)

R = Alk, Ph

n = 1,2,3

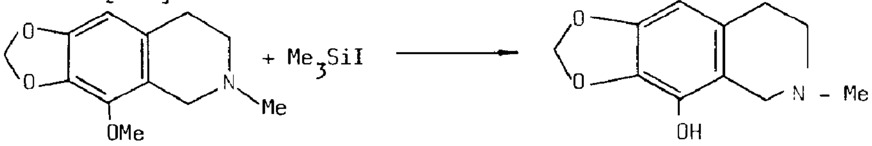
The reactivity of organosilanes depends on their structure: tetrachlorosilane reacts with 1,3-dioxolane in 20 h with 71.3% conversion, but trimethylchlorosilane is almost unreactive under the same conditions. The reactivity of the silane decreases with increase in the size of the substituents at the silicon atom [38].

Experiments on substituted benzodioxolanes[39] and 1,2-methylenedioxy-3-methoxybenzene [40] show that dissociation is impossible under the reaction conditions recommended for simple aromatic ethers[41,7]. Reaction proceeds when chlorinated dissolvents (dichlorometane, chloroform) are replaced by aromatic amines (especially quinoline)[42,7]. In substituted benzodioxolanes the reaction proceeds with halogenosilanes involving the methoxy-group of the aromatic ring but not the acetal group:



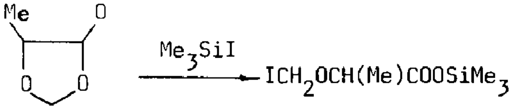
(28)

The methoxy-group in the substituted isoquinoline in equation 29 is selectively abstracted in presence of 1,4-diazobicyclo[2,2,2] octane to form the hydroxyisoquinoline [43]:



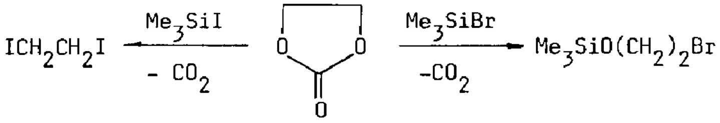
(29)

5-Methyl-1,3-dioxolane-4-on reacted with iodotrimethylsilane to break the C(2)-O bond and form a trimethylsilyl iodoether [16] , i.e. the carbonyl group was unchanged:



(30)

At the same time reaction of ethylenecarbonate with bromotrimethylsilane involves decarboxylation leading to β-bromethyl trimethylsilyl ether. Reaction with iodotrimethylsilane leads to 1,2-diiodoethane formation [44] :

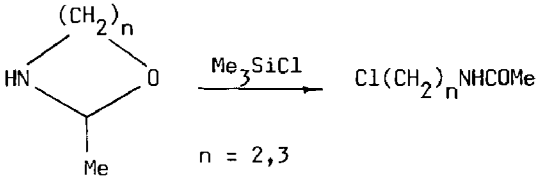


(31)

REACTION OF HALOGENOSILANES WITH HETEROANALOGUES OF CYCLIC ACETALS

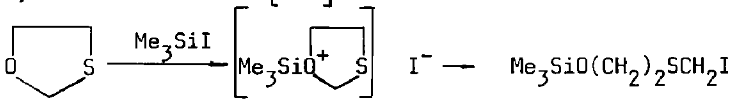
Only a few papers on nitrogen- and sulfur bearing acetal analogues with halogenosilanes have been published. In most cases reaction proceeds with ring opening and the corresponding halogenosilyl derivatives are formed. The reactions are usually carried out in cyclohexane, dimethylsulfoxide, dimethylformamid (see the Table).

For example, 2-methyl-1,3-oxazolidine and 2-methyl-4,5-dihydro-1,3-oxazine react with trimethylchlorosilane to form compounds containing an amido group in 87% yield [45] :



(32)

1,3-Oxathiolane reacts with iodotrimethylsilane and transforms into an iodomethylthioether at 0°C [32] :

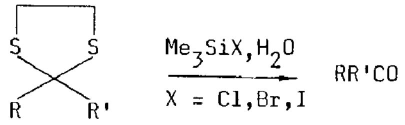


(33)

It is supposed that oxonium ion is formed electorally because the second product trimethylsilylthioester was not indentified in the mixture [32] .

Thioketals react differently with halogenomethylsilanes. 1,4-Dithiospiro [4,5] decane does not react with iodotrimethylsilane in boiling carbon tetrachloride [6,7] during 24 h.

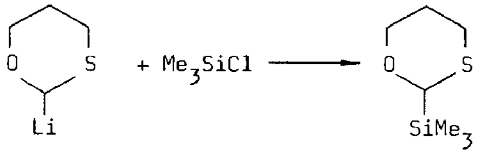
On the other hand, 1,3-dithiolanes react with iodo- or bromtrimethylsilane in dimethylsulfoxide giving ketones in 6-24% yield [48] :



(34)

Di(2-phenyl-1,3-dioxolane)-2-yl and 2,2-ethylendithioadamantane give di(phenylketone) and adamantane in 6 and 28% yield respectively [48] .

A new route to 2-substituted-1,3-oxathiolanes by trimethylsilyldelithiation has been suggested:



(35)

The reaction proceeds in tetrahydrofurane under nitrogen at low temperatures. The yield of 2-substituted-1,3-oxathianes is about 60-76% [17] .

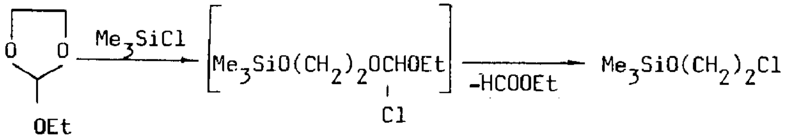
REACTION OF HALOGENOSILANES WITH ORTHOESTERS AND THEIR ANALOGUES

Trialkylorthoformate reacts with equimolar quantities of trimethylsilane [17] or bromtrimethylsilane [49-54] to form the corresponding alkylformates in high yields:

$$HC(OR)_3 + Me_3SiX \xrightarrow[25°C]{CHCl_3} HCOOR + Me_3SiOR + RX \qquad (36)$$

$R = Alk \qquad X = Cl,Br,F$

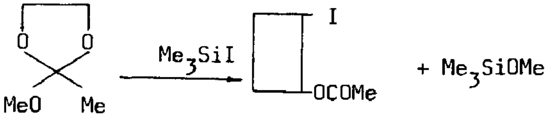
It is interesting that chlorosilanes are more active than fluorinesilanes. Cyclic orthoesters are less reactive than acyclic ones. 2-Ethoxy-1,3-dioxolane does not react with trimethylchlorosilane at room temperature. After heating at 50°C for 10 h β-chloroethoxytrimethylsilane and ethylformate are formed in 70 and 78% yields [52] :



(37)

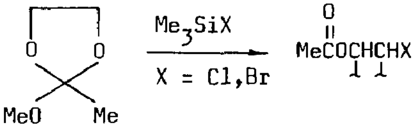
The reaction is supposed to proceed by fission of an exocyclic C-O bond with the intermediate formation of a chloroacetal [52] .

Trans-1,2-iodo(methoxycarbonyl)cyclobutane is formed in 82% yield by the reaction of orthoesters of cis-cyclobutane -1,2-diol with iodotrimethylsilane:



(38)

The use of iodo- and bromotrimethylsilanes in reactions with saccharides to transform the cycloacetal fragment into an ester is possible [45] :



(39)

The two main reactions of halogenosilanes with acetals lead either to ester or to carbonyl compound.

At the same time it is possible to preserve the acetal group when there is another active functional group in the molecule.

Thus the reaction of halogenosilanes with acetals reveals a wide potential for the synthesis of compounds carrying halogeno, silyl or ester substituents.

Table

CONDITIONS AND RESULTS OF ACETALS REACTION WITH HALOIDS AND HALOGENOSILANES

Reagents		Reaction conditions	Products	References	
Acetal	Haloid (halogenosilane)				
1	2	3	4	5	
1. $CH_2(OMe)_2$	Me_3SiI	$t = 25°C$ $\tau = 0.5$ h	ICH_2OMe	75-93	[5]
2. $R_2C\langle^{OR^1}_{OR^2}$	Me_3SiI	hexamethyldisilazane CH_2Cl_2, $CHCl_3$, CCl_4 N_2, $t = 0°C$ $\tau = 2$ h	$RCH = C\langle^{OMe}_{CH_2R}$	57-89	[15]
R,R^1 = Me, Et R^2 = Ph, Alk					
$R^1R^2C(OR^3)_2$	Me_3SiI	$CHCl_3$ / C_3H_6	$R^1R^2C = O$	84-97	[6,7]
$R^1R^2 = (CH_2)_4$, $(CH_2)_5$		CH_2Cl_2, CCL_4			
H, Me, Alk		$t = 25°C$ $\tau = 0.25$ h			
R^3 = Me, Et	Me_3SiCl/MI	CH_3CN			
	M = Li, Na, K, Cu	$t = 45°C$ $\tau = 0.5\text{-}2.5$ h	$R^1R^2C = O$	30-95	[8,9]
3. $CH_2 = C(OR)_2$	R_3SiI	-	R_3SiCH_2COOR	98	[10]
R = Alk	R = Me, Et			-	[11]
$CH_2 = CBrCH(OEt)_2$	BuLi,Me_3SiCl THF	$t = -78°C$ $\tau = 1.5\text{-}2$ h	$CH_2 = \underset{SiMe_3}{C}\text{-}CH(OEt)_2$	-	[12]
$CH_2 = C(OEt)_2$	$MeGeCl_3$				

Table cont.

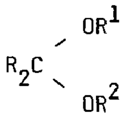
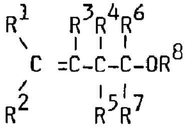
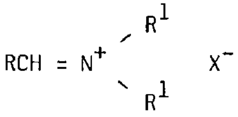
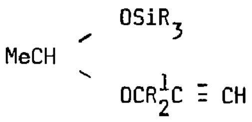
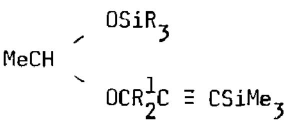
1	2	3	4	5	
4.  $R_2C(OR^1)OR^2$ $R,R^1 = Me, Et$ $R^2 = Ph, Alk$	$HSiCl_3$	γ-radiation $\tau = 1$ h	$R_2CHOR^1 = C(OEt)_2$ R_2CHOR^2	35-93	[13]
5. $R_3SiC(R^1R^2)CR^3 = CR^4R^5$ $R^1 + R^5 = Me, Alk$	$R^6R^7C(OR^8)_2$ $R^6R^7 = Me, Alk$ $R^8 = Me, Et$	CH_2Cl_2 Me_3SiI $t = -40°C - -78°C$ $\tau = 0.3-8$ h	 $R^1R^2C{=}C(R^3)-C(R^4R^5)-C(R^6R^7)-OR^8$	65-90	[14]
6. $RCH\ (NR^1_2)_2$ $R = iPr, Et$ $R^1 = n\text{-}Bu, -(CH_2)_5-$	Me_3SiX $X = I, Cl$ $OCOCCF_3$	Et_2O, THF, N_2 $t = 0°C$, $\tau = 0.34$ h	 $RCH = N^+R^1_2\ X^-$	96	[30]
7.  $MeCH(OSiR_3)OCR^1_2C \equiv CH$ $R = Alk$	Na, Me_3SiCl		 $MeCH(OSiR_3)OCR^1_2C \equiv CSiMe_3$	-	[25]

Table cont.

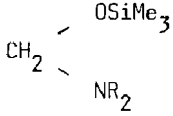
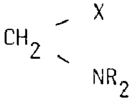
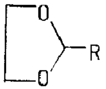
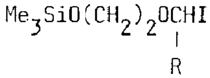
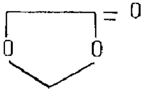
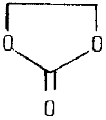
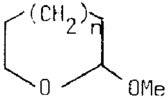
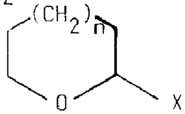
1	2	3	4	5	
 $CH_2(OSiMe_3)(NR_2)$ R = Alk	R^1_3SiX X = Cl, Br, I R^1 = Alk		 $CH_2(X)(NR_2)$	-	[27]
8. $(RO)_2P(O)CH(OR)_2$	Me_3SiI		$(Me_3SiO)_2P(O)CH(OR)_2$	-	[31]
9. 	$R_{4-n}SiCl_n$, n = 1-4 R = Me, Et, Ph	t = 100-150°C τ = 8 h	$R_{4-n}SiCl_{n-1}(OCH_2-CH_2-OCH_2Cl)$ $R_{4-n}SiCl_{n-2}(OCH_2CH_2-OCH_2Cl)_2$	60-71	[38]
 R = H, Me, Ar	Me_3SiI	cyclohexane N_2 t = -78°C τ = 0.1-0.5 h	 $Me_3SiO(CH_2)_2OCH(R)I$	50-70	[35]
10. 	Me_3SiI	CH_2Cl_2 t = 0°C τ = 1 h	$Me_3SiOCOCH(Me)OCH_2I$	-	[16,7]
	Me_3SiBr Me_3SiI	-	$Me_3SiOCH_2CH_2Br$ ICH_2CH_2I	- -	[7] [7]
11.  n = 0.1	Me_3SiX X = Cl, Br, I	-		84-100 NMR	[33]

Table cont.

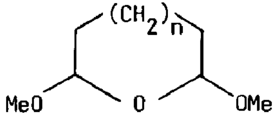
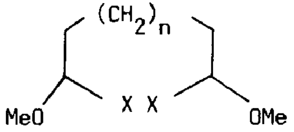
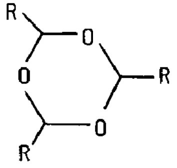
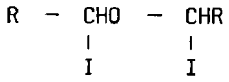
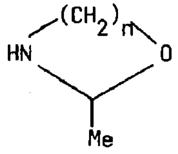
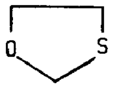
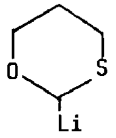
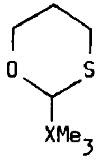
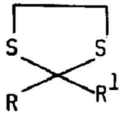
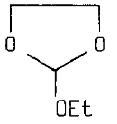
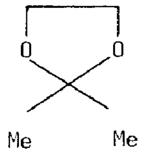
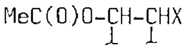
1	2	3	4	5
 $n = 0.1$	Me_3SiX X = Cl, Br, I	-		84-100 [33] NMR
 R = H, Me	Me_3SiI	t = 40°C τ = 3 h	 $R-\underset{I}{CHO}-\underset{I}{CHR}$	93-96 [34]
12.  $n = 2.3$	Me_3SiX or HX X = Cl, N_3, SPh	MeOH, DMFA t = 20-90°C τ = 3-60 h	$X(CH_2)_nN$ HCOMe	60-99 [40]
13. 	Me_3SiI	cyclohexane, N_2 t = -78°C τ = 0.2 h	$Me_3SiO(CH_2)_2S\ CH_2I$	- [32]
	Me_3XCl X = Ge, Sn, Si	THF, hexane, N_2 t = -78°C		60-76 [17]
	Me_3SiX X = Br, I	τ = 6-24 h	$RR^1C = O$	65-98 [48]

Table cont.

1	2	3	4	5	
14. $HC(OR)_3$ R = Me, Et	Me_3SiBr	t = 25°C τ = 0.2 h	HCOOR	-	[49]
	R^1_3SiX X = Cl, F R^1= Me, Et	t = 46°C-50°C τ = 0.5-10 h	HCOOR	53	[32]
15. 	Me_3SiCl	t = 50°C τ = 10 h	$Me_3SiO(CH_2)Cl$	70	[52]
16. 	Me_3SiX X = Cl, Br	CH_2Cl_2 t = 40°C τ = 1.5 h MeCN τ = 0.11 h	 $MeC(O)O\text{-}\underset{\perp}{C}H\text{-}\underset{\perp}{C}HX$	42-70	[45]

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