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Reactions of trimethyliodosilane with mono-, di-, and trioxacycloalkanes

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Abstract

The reactions of Me_3SiI with mono-, di-, and trioxacycloalkanes have been studied first. Preparative methods for the synthesis of some promising synthones, namely α,ω-diiodoalkanes, α,ω-alkanediols, and iodomethyl ω-iodoalkyl ethers, have been developed based on these reactions. The effect of the cycle size and the nature of the substituent on the course of the reactions is demonstrated. Schemes for the mechanism of the reactions are suggested.

Introduction

Over three decades ago one of us proposed a very simple and convenient method for the synthesis of trialkyliodosilanes based on the splitting of hexaalkyldisiloxanes with aluminium iodide [1] or with a mixture of aluminium and iodine [2].

The investigation of the chemical properties of trialkyliodosilanes thus obtained has shown that they readily split C–O–C and Si–O–C fragments in the absence of catalysts [3].

Developing our investigations in 1975 we demonstrated the use of trimethyliodosilane for splitting these fragments in both organic and organosilicon compounds [4,5]. In the same year our results were presented at two international conferences (the cleavage of oxygen-containing organic and organosilicon compounds with trialkyliodosilanes, 4th International Symposium on Organosilicon Chemistry, Moscow, 1975 [6]; the interaction of trimethyliodosilane with oxygen-containing organosilicon compounds, 7th International Conference on Organometallic Chemistry, Venice, 1975 [7]).

Within 2 years two groups of American workers added to these investigations [8,9]. We cannot help being astonished at their claim to priority of using Me_3SiI to cleave the C–O–C fragments in oxygen-containing organic compounds.

More recently still Me_3SiI has found wide application in organic synthesis [10–15].

Here we report the synthetic possibilities of the reactions (first studied by us) of

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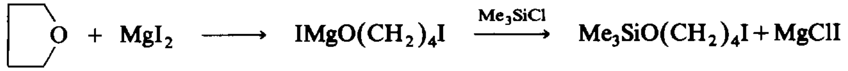
Me_3SiI with mono-, di-, and trioxacycloalkanes supplemented with the results of other authors.

Our results have previously been published in Russian as well as presented at a number of international symposia.

I. Reactions with monooxacycloalkanes

In 1959 the splitting of tetrahydrofuran (THF) with magnesium iodide in the presence of magnesium and Me_3SiCl was reported by Anderson and Sprung [16]. The mechanism proposed included the initial splitting of the cyclic ether with MgI_2 accompanied with the reaction of the Grignard reagent formed with Me_3SiCl.

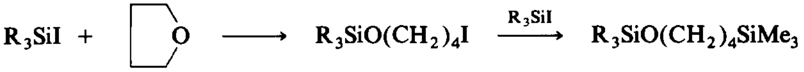


$$Me_3SiO(CH_2)_4I + Mg \longrightarrow Me_3SiO(CH_2)_4MgI \xrightarrow{Me_3SiCl} Me_3SiO(CH_2)_4SiMe_3 + MgClI \quad (1)$$

The preparative formation of $Me_3SiO(CH_2)_4SiMe_3$ in the reaction of THF with Me_3SiCl in the presence of Mg and MgI_2 has been reported by Gilman [17].

However, a more convincing mechanism for this reaction, in our opinion, was suggested by Krüerke [18]. This included the initial substitution of the chlorine atom in Me_3SiCl by iodine and the subsequent cleavage of THF with Me_3SiI thus formed.

$$MgI_2 + 2\,R_3SiCl \longrightarrow R_3SiI + MgClI$$



(2)

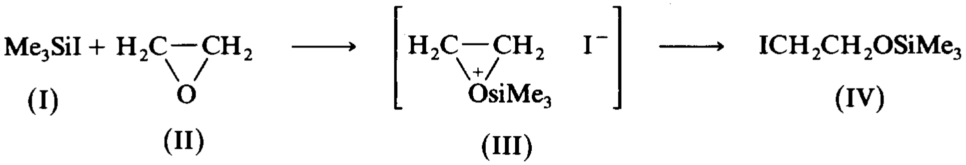
Mechanism 2 is supported by the fact of formation of Me_3SiI in 60% yield from Me_3SiCl and MgI_2 [18] as well as by our results.

In the reaction of THF with Me_3SiCl, MgI_2, and Mg along with $Me_3SiO(CH_2)_4SiMe_3$ the by-product bis(trimethylsiloxy)octane has been isolated in 6% yield [19].

$$2\,Me_3SiO(CH_2)_4I + Mg \longrightarrow Me_3SiO(CH_2)_8OSiMe_3 + MgI_2 \quad (3)$$

I.a. Reactions with oxiranes

The reaction of Me_3SiI with ethylene oxide was first studied by us. The reaction proceeds readily at ambient temperature with quantitative formation of trimethyl (β-iodoethoxy)silane, probably via the intermediate formation of trimethylsiloxonium iodide [20]:

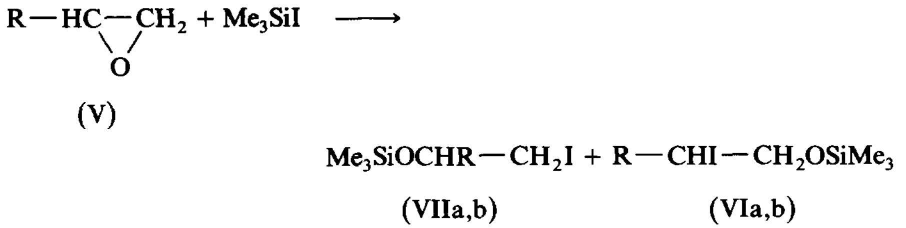


(4)

The direction of the oxirane ring cleavage is governed by the nature of the substituent.

The data in the literature on the splitting of substituted oxiranes with organyl chlorosilanes are contradictory [21,22].

We have found that monosubstituted oxiranes with electron-donating substituents react with Me_3SiI with splitting of both C–O bonds, the splitting of the $O–CH_2$ bond being predominant.



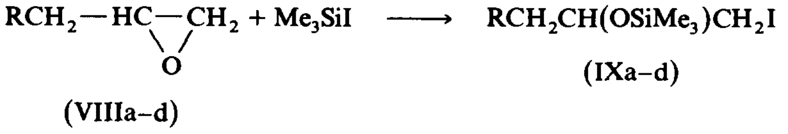
$$\mathrm{R{-}\underset{\diagdown\, O\, \diagup}{HC{-}CH_2}} + \mathrm{Me_3SiI} \longrightarrow \underset{\text{(VIIa,b)}}{\mathrm{Me_3SiOCHR{-}CH_2I}} + \underset{\text{(VIa,b)}}{\mathrm{R{-}CHI{-}CH_2OSiMe_3}} \quad (5)$$

(V)

$(R = CH_3$ (a); C_2H_5 (b))

According to ^1H NMR spectra, the isomer ratio is VIIa : VIa = 2.5 : 1 and VIIb : VIb = 2 : 1 for $R = CH_3$ and C_2H_5, respectively. Compounds VIa,b and VIIa,b can be stored in the dark for at least two years.

Electron-withdrawing substituents in the oxirane ring promote its selective cleavage [23] in accordance with the Krasusky rule [24].



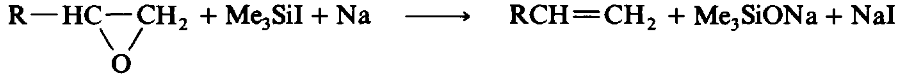
$$\mathrm{RCH_2{-}\underset{\diagdown\, O\, \diagup}{HC{-}CH_2}} + \mathrm{Me_3SiI} \longrightarrow \mathrm{RCH_2CH(OSiMe_3)CH_2I} \quad (6)$$

(VIIIa–d) (IXa–d)

$(R = Cl$ (a); CF_3 (b); C_3F_7 (c); C_4F_9 (d))

The yield of adducts (IXa–d) is 94–95% in all cases.

The reaction of oxirane and its derivatives with Me_3SiI in the presence of sodium metal results in formation of the corresponding olefins and sodium trimethylsilanolate:



$$\mathrm{R{-}\underset{\diagdown\, O\, \diagup}{HC{-}CH_2}} + \mathrm{Me_3SiI} + \mathrm{Na} \longrightarrow \mathrm{RCH{=}CH_2} + \mathrm{Me_3SiONa} + \mathrm{NaI} \quad (7)$$

$(R = H, CH_3, C_2H_5)$

This pathway results from the reaction of sodium with the products (VI, VII, and IX) which are intermediates of the Me_3SiI-induced splitting of the oxirane ring. The reaction scheme is that typical for all species containing the $-O-CH_2-CH_2X$ fragment (X = Hal) [25]. This has been convincingly proven for the reaction of sodium metal with trimethyl (β-iodoalkoxy) silanes as an example:

$$\mathrm{Me_3SiOCH_2CHIR} + 2\,\mathrm{Na} \longrightarrow \mathrm{RCH{=}CH_2} + \mathrm{Me_3SiONa} + \mathrm{NaI} \quad (8)$$

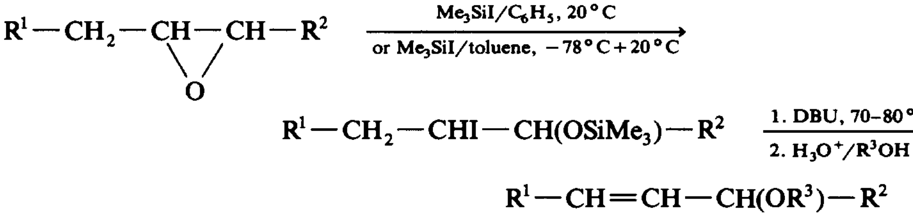
(IV; VIa,b; VIIa,b)

$(R = H$ (IV); CH_3 (VIa,b); C_2H_5 (VIIa,b))

The olefins formed were trapped in a solution of bromine in CCl_4 yielding the corresponding 1,2-dibromoalkanes; the sodium trimethyl silanolate gave hexamethyldisiloxane when treated with diluted HCl.

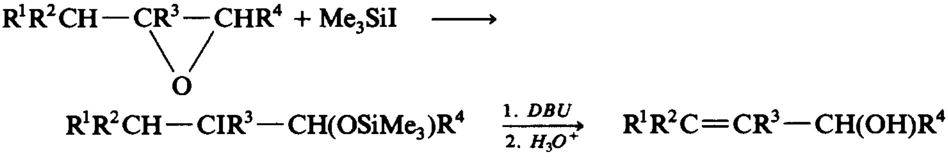
Physico-chemical characteristics, elemental analysis data and the ^1H NMR spectra of the products of the reaction of Me_3SiI with oxirane and its derivatives are given in Tables 1 and 2.

Recently, Japanese authors [26] followed the Me_3SiI-induced oxirane splitting with treatment with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) for the synthesis of unsaturated alcohols and ethers.



(9)

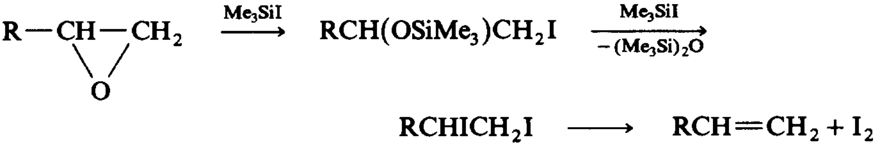
($R^1 = CH_3$; $R^2 = H, CH_3$; $R^1R^2 = -(CH_2)_3-$; $-(CH_2)_5-$; $-(CH_2)_9-$)



(10)

The authors did not consider the possibility of isomeric products resulting from oxirane splitting.

Oxiranes, when treated with an excess of Me_3SiI produce the corresponding diiodides which, further, readily eliminate the iodine molecule yielding the corresponding olefins [27].



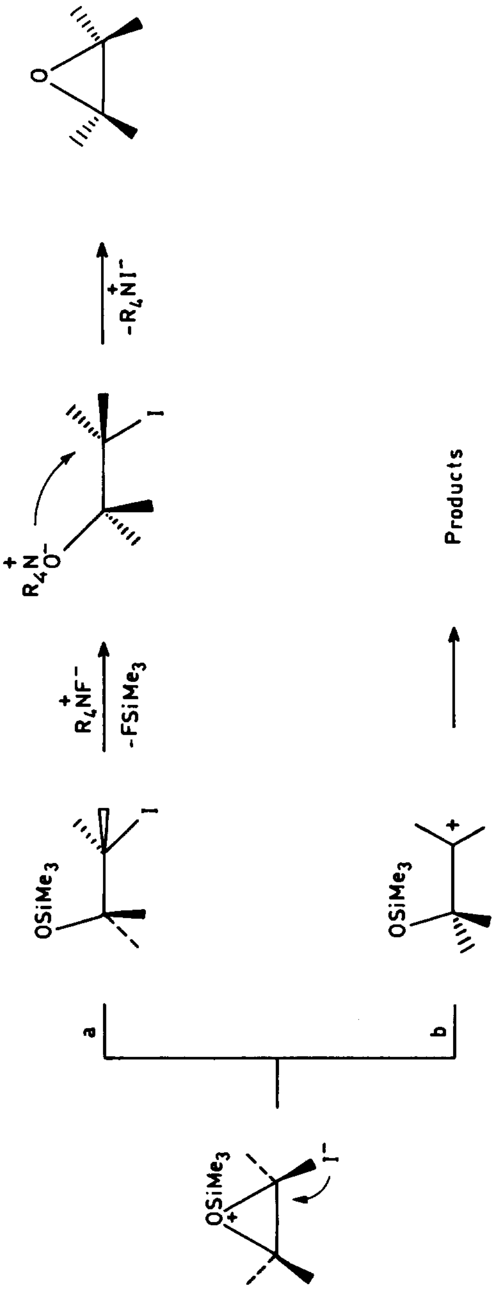
(11)

The stereochemistry of the oxirane ring opening in response to Me_3SiI has been established by treatment with tetrabutyl ammonium fluoride in THF of the trimethyl(2-iodoalkoxy)silanes formed, which results in the recovery of the initial oxirane (path a, eq. 12). An alternative scheme for the splitting of the oxirane cycle with Me_3SiI to give rise to a tertiary carbenium ion has also been suggested (path b, eq. 13) [28].

I.b. Reaction with tetrahydrofuran and tetrahydropyran

The reaction of Me_3SiCl with THF and THP only proceeds under rigid conditions—at high temperatures and pressures in the presence of catalysts [29,30].

We have shown that the splitting of THF and THP with Me_3SiI proceeds readily


OSiMe$_3$
+
I$^-$
a
b
OSiMe$_3$
I
R$_4\overset{+}{N}$F$^-$
-FSiMe$_3$
R$_4\overset{+}{N}$
O$^-$
I
-R$_4\overset{+}{N}$I$^-$
O
OSiMe$_3$
+
Products

(12)

(13)

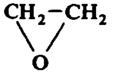
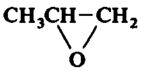
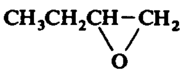
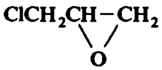
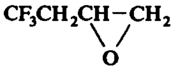
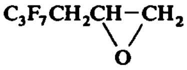
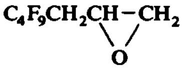
Table 1

Physicochemical constants and analytical data for products of the reaction of Me_3SiI with oxiranes

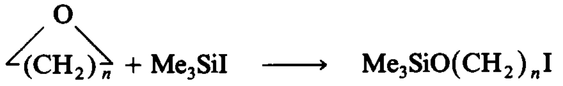
Compound	Product	n_D^{20}	d_4^{20}	Molecular formula	Found (calcd.) (%)					
					C	H	Cl	I	F	Si
IV	$ICH_2CH_2OSiMe_3$	1.4738	1.4230	$C_5H_{13}OSiI$	25.05 (24.59)	5.70 (5.30)		51.84 (51.97)		11.50 (11.50)
VIa	$CH_3CHICH_2OSiMe_3$	–	–	$C_6H_{15}OSiI$	27.84 (27.92)	5.73 (5.85)		49.08 (49.15)		10.78 (10.87)
VIb	$CH_3CH_2CHICH_2OSiMe_3$			$C_7H_{17}OSiI$	31.47 (30.89)	6.31 (6.30)		46.92 (47.12)		10.32 (10.11)
VIIa	$CH_3CH(OSiMe_3)CH_2I$			$C_6H_{15}OSiI$	27.84 (27.92)	5.73 (5.85)		49.08 (49.15)		10.78 (10.87)
VIIb	$CH_3CH_2CH(OSiMe_3)CH_2I$			$C_7H_{17}OSiI$	31.47 (30.89)	6.31 (6.30)		46.92 (47.12)		10.32 (10.11)
IXa	$ClCH_2CH(OSiMe_3)CH_2I$	1.4920	1.4510	$C_6H_{14}OSiClI$	24.50 (24.96)	5.09 (4.89)	12.04 (12.29)	43.72 (43.96)		9.45 (9.97)
IXb	$CF_3CH_2CH(OSiMe_3)CH_2I$	1.4360	1.5120	$C_7H_{14}OSiIF_3$						
IXc	$C_3F_7CH_2CH(OSiMe_3)CH_2I$	1.4210	1.5309	$C_9H_{14}OSiF_7I$						
IXd	$C_4F_9CH_2CH(OSiMe_3)CH_2I$	1.3930	1.5834	$C_{10}H_{14}OSiIF_9$	25.70 (25.22)	3.13 (2.96)		26.95 (26.65)	36.13 (35.91)	

Table 2

^1H NMR data of the products of reaction of Me_3SiI with oxiranes

Compound	Oxirane	Product	^1H NMR (TMS)				
			1	2	3	4	5
II		$\mathrm{I\overset{1}{C}H_2\overset{2}{C}H_2OSi(\overset{3}{C}H_3)_3}$	3.13 t	3.78 t	0.05 s		
Va		$\mathrm{\overset{1}{C}H_3\overset{2}{C}HI\overset{3}{C}H_2OSi(\overset{4}{C}H_3)_3}$	1.90 d	3.68–3.98 m	3.79 d	0.04 s	
		$\mathrm{\overset{1}{C}H_3\overset{2}{C}H[OSi(\overset{4}{C}H_3)_3]\overset{3}{C}H_2I}$	1.28 d	3.68–3.98 m	3.05 d	0.04 s	
Vb		$\mathrm{\overset{1}{C}H_3\overset{2}{C}H_2\overset{3}{C}HI\overset{4}{C}H_2OSi(\overset{5}{C}H_3)_3}$	0.99 t	1.55 m	3.54 m	3.79 d	0.12.s
		$\mathrm{\overset{1}{C}H_3\overset{2}{C}H_2\overset{3}{C}H[OSi(\overset{5}{C}H_3)_3]\overset{4}{C}H_2I}$	0.85 t	1.55 m	3.54 m	3.19 d	0.09 s
VIIIa		$\mathrm{Cl\overset{1}{C}H_2\overset{2}{C}H[OSi(\overset{4}{C}H_3)_3]\overset{3}{C}H_2I}$	3.53 d	3.71 m	3.28 d	0.17 s	
VIIIb		$\mathrm{CF_3\overset{1}{C}H_2\overset{2}{C}H[OSi(\overset{4}{C}H_3)_3]\overset{3}{C}H_2I}$	2.35 m	3.94 m	3.19 d	0.12 s	
VIIIc		$\mathrm{C_3F_7\overset{1}{C}H_2\overset{2}{C}H[OSi(\overset{4}{C}H_3)_3]\overset{3}{C}H_2I}$	2.38 m	4.06 m	3.22 d	0.08 s	
VIIId		$\mathrm{C_4F_9\overset{1}{C}H_2\overset{2}{C}H[OSi(\overset{4}{C}H_3)_3]\overset{3}{C}H_2I}$	2.41 m	4.09 m	3.24 d	0.13 s	

in the absence of catalysts (60 ° C, reagents molar ratio 1 : 1) quantitatively resulting in the unstable trimethyl(4-iodobutoxy)silane [31,32].



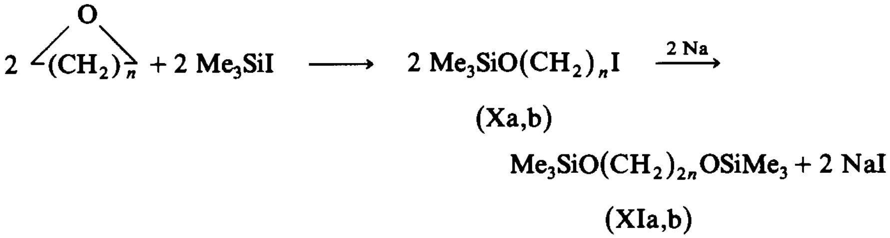
(14)

(Xa,b)

($n = 4$ (a); $n = 5$ (b))

In the presence of sodium metal Me_3SiI reacts with THF to give 1,8-bis(trimethylsiloxy)octane (XIa) in 50% yield.

Along with compound (XIa) about 10% of 1-trimethylsilyl(4-methylsiloxy)butane (XIIa) has been isolated.



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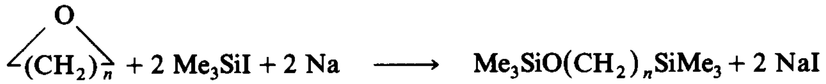


(16)

(XIIa,b)

Compound XIa was also directly obtained in 42% yield in the reaction of X with sodium in THF solution which confirms its formation by eq. 15.

$$2\ Me_3SiO(CH_2)_4I + 2\ Na \longrightarrow \underset{(XIa)}{Me_3SiO(CH_2)_8OSiMe_3} + 2\ NaI \qquad (17)$$

The formation of product XIIa (eq. 16) seems to be explicable by eq. 18:

$$Me_3SiO(CH_2)_nI + 2\ M + Me_3SiI \not\longleftrightarrow Me_3SiO(CH_2)_nSiMe_3 + 2\ MI \qquad (18)$$

Under the experimental conditions sodium metal did not react with trimethyl(iodobutoxy)silane (Xa). Nevertheless, the conversion of Xa into 1,4-diiodobutane (XIIIa) in 85% yield and hexamethyldisiloxane was observed.

$$Me_3SiO(CH_2)_nI + Me_3SiI \longrightarrow \underset{(XIIIa,b)}{I(CH_2)_nI} + (Me_3Si)_2O \qquad (19)$$

Similarly to THF, THP reacts with Me_3SiI at 90 ° C with the 1 : 1 reagent molar ratio with the formation of trimethyl(5-iodopentoxy)silane (Xb) (eq. 14) in high yield. In the presence of sodium metal the reaction of Me_3SiI with THP leads to 1,10-bis(trimethylsiloxy)decane (XIb) in 33% yield. Treatment of THP with a two-fold excess of Me_3SiI (molar ratio 1 : 2) leads to 1,5-diiodopentane (XIIIb) in quantitative yield by eq. 19. Physico-chemical characteristics and the data of elemental analysis of the products of reactions 14–19 are given in Tables 3 and 4.

Table 3

Physicochemical constants and analytical data for products of the reaction of Me_3SiI with oxacyclanes

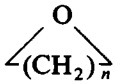
Compound	Product	n_D^{20}	d_4^{20}	Molecular formula	Found (calcd.) (%)			
					C	H	Si	I
Xa	$I(CH_2)_4OSiMe_3$	1.4772	1.3352	$C_7H_{17}SiOI$	30.78	6.24	9.34	47.13
					(30.88)	(6.29)	(10.31)	(46.62)
XIa	$Me_3SiO(CH_2)_8OSiMe_3$	1.4243	0.8486	$C_{14}H_{34}Si_2O_2$	57.98	11.73	19.48	
					(57.86)	(11.72)	(19.32)	
XIIa	$Me_3SiO(CH_2)_4SiMe_3$	1.4200	0.8310	$C_{10}H_{26}Si_2O$	54.14	11.81	23.96	
					(54.97)	(11.97)	(25.70)	
XIIIa	$I(CH_2)_4I$	1.6380	2.3816	$C_4H_8I_2$	15.39	2.48		81.34
					(15.50)	(2.60)		(81.93)
Xb	$I(CH_2)_5OSiMe_3$	1.4812	1.3351	$C_8H_{19}SiOI$	34.15	6.68	9.15	44.42
					(33.58)	(6.65)	(9.76)	(44.50)
XIb	$Me_3SiO(CH_2)_{10}OSiMe_3$	1.4252	0.8489	$C_{16}H_{38}Si_2O_2$	60.00	11.54	18.15	
					(60.03)	(12.03)	(17.63)	
XIIb	$Me_3SiO(CH_2)_5SiMe_3$	1.4162	0.8360	$C_{11}H_{28}Si_2O$	55.38	11.63	23.44	
					(56.82)	(12.13)	(24.15)	
XIIIb	$I(CH_2)_5I$	1.6041	2.1925	$C_5H_{10}I_2$	18.60	3.18		77.80
					(18.54)	(3.15)		(78.34)

Table 4

^{1}H NMR data of the products of reaction of Me_3SiI with THF and THP

Compound	Product	^{1}H NMR (TMS)			
		1	2	3	4
Xa	$IC\overset{1}{H}_2(C\overset{2}{H}_2)_2C\overset{3}{H}_2OSi(C\overset{4}{H}_3)_3$	3.21 t	1.74 m	3.56 t	0.12 s
XIa	$(C\overset{1}{H}_3)_3SiOC\overset{2}{H}_2(C\overset{3}{H}_2)_6C\overset{2}{H}_2OSi(C\overset{1}{H}_3)_3$	0.68 s	3.52 t	1.33 m	
XIIa	$(C\overset{1}{H}_3)_3SiOC\overset{2}{H}_2(C\overset{3}{H}_2)_2C\overset{4}{H}_2Si(CH_3)_3$	0.45–0.09 m	3.51 t	1.43 m	
XIIIa	$IC\overset{1}{H}_2(C\overset{2}{H}_2)_2C\overset{1}{H}_2I$	3.19 t	1.94 m		
Xb	$IC\overset{1}{H}_2(C\overset{2}{H}_2)_3C\overset{3}{H}_2OSi(C\overset{4}{H}_3)_3$	3.24 t	1.76 m	3.59 t	0.14 s
XIb	$(C\overset{1}{H}_3)_3SiOC\overset{2}{H}_2(C\overset{3}{H}_2)_8CH_2OSi(CH_3)_3$	0.67 s	3.52 t	1.31 m	
XIIb	$(C\overset{1}{H}_3)_3SiOC\overset{2}{H}_2(C\overset{3}{H}_2)_3CH_2Si(CH_3)_3$	0.04–0.02 s	3.49 t	1.38 m	
XIIIb	$IC\overset{1}{H}_2(C\overset{2}{H}_2)_3CH_2I$	3.16 t	1.84 m		

Reaction of Me_3SiI with THF and THP leads to the formation of the corresponding α,ω-bis(trimethylsiloxy)alkanes and this represents a simple and convenient synthetic approach to the otherwise hardly accessible 1,8- and 1,10-alkanediols XIV which are smoothly formed by hydrolysis and alcoholysis of α,ω-bis(trimethylsiloxy)alkanes:



$$+ 2\,Me_3SiI \xrightarrow{M} Me_3SiO(CH_2)_{2n}OSiMe_3 + 2\,MI \qquad (20)$$

(XIa,b)

($M = Li, Na, K, 1/2\ Mg$; $n = 4$ (a), 5 (b))

$$Me_3SiO(CH_2)_{2n}OSiMe_3 \xrightarrow{H_2O} HO(CH_2)_{2n}OH + (Me_3Si)_2O \qquad (21)$$

(XIVa,b)

Table 5

Reaction of Me_3SiI with THF and THP in presence of alkali metals

Cycloalkane	Yield of α,ω-bis(trimethylsiloxy)alkanes (%)		
	Potassium	Sodium	Lithium
THF	72	50	30
THP	38	33	21

Table 6

Reaction of trimethyl(ω-iodoalkoxy)silanes with alkali metals

Trimethyl(ω-iodoalkoxy)silane	Yield of α,ω-bis(trimethylsiloxy)alkanes (%)		
	Potassium	Sodium	Lithium
$I(CH_2)_4OSiMe_3$	68	42	22
$I(CH_2)_5OSiMe_3$	75	60	27

The yield of compounds XIa,b in reaction 20 substantially depends on the metal and the size of the heterocycle. In the reaction of Me_3SiI with THF the yield of XIa increases with increasing atomic number of the alkali metal. With THP the yield of (XIb) is much lower but the same dependence on the metal is observed (cf. Table 5). Individual trimethyl(iodoalkoxy)silanes (Xa,b) also react with alkali metals being converted into the corresponding α,ω-bis(trimethylsiloxy)alkanes (XIa,b).

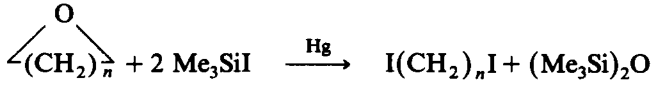
$$2\,Me_3SiO(CH_2)_nI + 2\,M \longrightarrow Me_3SiO(CH_2)_{2n}OSiMe_3 + 2\,MI \qquad (22)$$

(Xa,b) (XIa,b)

($M = Li, Na, K$; $n = 4$ (a), 5 (b))

The yield of compounds XIa,b increases sharply on going from lithium to potassium (Table 6). As was mentioned earlier [19] the 1,8-bis(trimethylsiloxy)octane is formed after heating THF with Me_3SiCl for six days in the presence of magnesium metal, with a very low yield (6%). The replacement of Me_3SiCl by Me_3SiI in this reaction produces 1,8-bis(trimethylsiloxy)octane (XIa) in 50% yield. This compound has also been obtained by us in the reaction of magnesium with trimethyl(4-iodobutoxy)silane (Xa) although in a lower yield (25%). In this reaction THP leads to a similar product in 21% yield.

Unlike alkali metals and magnesium, mercury metal displays specific behaviour in the above reactions. Cleavage of THF and THP with Me_3SiI in the presence of mercury leads exclusively to the corresponding α,ω-diiodoalkanes (XIIIa,b).



$$+ 2\,Me_3SiI \xrightarrow{Hg} I(CH_2)_nI + (Me_3Si)_2O \qquad (23)$$

(XIIIa,b)

($n = 4$ (a), 5 (b))

The same results have been obtained for the reaction of compounds Xa,b with mercury metal.

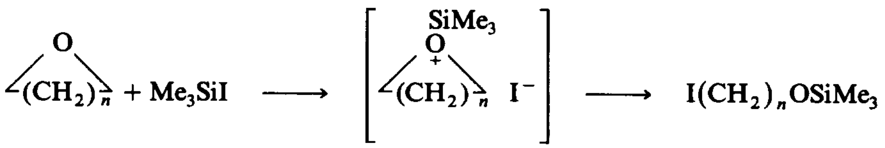
$$2\,Me_3SiO(CH_2)_nI \xrightarrow{Hg} 2\,I(CH_2)_nI + (Me_3Si)_2O \qquad (24)$$

(Xa,b) (XIIIa,b)

Mercury(II) iodide affects the direction of the reaction of Me_3SiI with THF and THP in the same way as mercury metal.

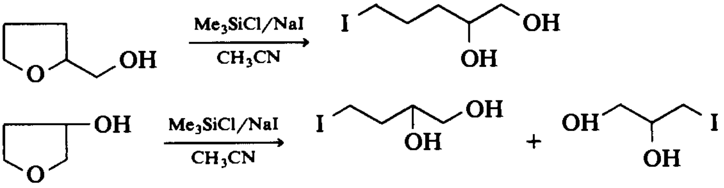
The size of the cycle has a decisive effect on the reaction of Me_3SiI with oxacycloalkanes. Thus, ethylene oxide, propylene oxide, tetrahydrofuran, and tetrahydropyran are cleaved at 20, 30, 60, and 90 °C, respectively.

The initial stage of the reaction of Me_3SiI with all oxacycloalkanes seems to be the formation of the intermediate trimethylsiloxonium iodide, which is followed by nucleophilic attack of the iodide anion on the carbon atom adjacent to the oxygen atom:



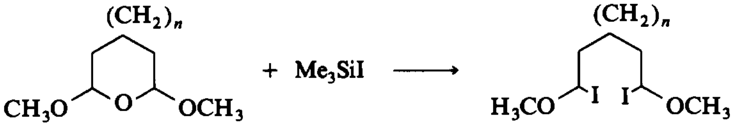
$$+ Me_3SiI \longrightarrow [\,I^-\,] \longrightarrow I(CH_2)_nOSiMe_3 \qquad (25)$$

Recently it has been shown that the hydroxy substituted tetrahydrofurans when treated in acetonitrile with the system Me_3SiCl/NaI (equivalent to Me_3SiI) form the corresponding polyfunctional compounds [33].



(26)

1,3-Dialkoxy-2-oxacycloalkanes in the reaction with Me_3SiI form α,ω-dialkoxy diiodoalkanes [34].



$(n = 0, 1)$

(27)

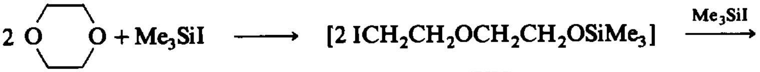
II. Reactions with di- and trioxacycloalkanes

II.a. Reaction with 1,4-dioxane

In contrast to THF and THP, 1,4-dioxane cannot be cleaved with chloro- and bromosilanes even under severe conditions [35].

We have found that the highly electrophilic Me_3SiI readily splits 1,4-dioxane at a temperature as low as 40 °C in the absence of catalysts [36].

In the reaction of Me_3SiI with 1,4-dioxane, with molar ratio 1 : 2, 1,2-bis(trimethylsiloxy)ethane (XVI), 1,2-diiodoethane (XVII) and HMDS are formed:



$$2\ \text{dioxane} + Me_3SiI \longrightarrow [2\ ICH_2CH_2OCH_2CH_2OSiMe_3] \xrightarrow{Me_3SiI}$$

(XV)

$$Me_3SiO(CH_2)_2OSiMe_3 + I(CH_2)_2I + (Me_3Si)_2O \quad (28)$$

(XVI) (XVII)

We assume that the reaction proceeds via intermediate formation of 1-trimethylsiloxy 2-iodoethoxyethane (XV). The data of Table 7 are indicative of a decrease of the 1,2-bis(trimethylsiloxy)ethane yield as the 1,4-dioxane : Me_3SiI molar ratio changes from 1 : 1 to 1 : 4. With the molar ratio 1 : 4 the yield is negligible, and the only products of the reaction were found to be 1,2-diiodoethane (XVII) and HMDS. The formation of 1,2-diiodoethane from 1,2-bis(trimethylsiloxy)ethane has been proven experimentally:

$$\underset{(XVI)}{Me_3SiOCH_2CH_2OSiMe_3} + 2\ Me_3SiI \longrightarrow \underset{(XVII)}{ICH_2CH_2I} + 2(Me_3Si)_2O \quad (29)$$

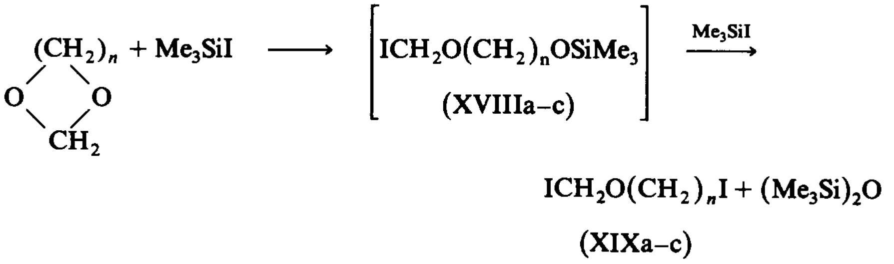
Reaction 29 proceeds with quantitative yield. Thus, the reaction of Me_3SiI with 1,4-dioxane is a simple preparative method for synthesis of 1,2-diiodoethane in quantitative yield.

II.b. Reaction with 1,3-dioxacycloalkanes

The reaction of Me_3SiI with 1,3-dioxacycloalkanes and their derivatives at low temperatures has found application in synthesis of acyclic analogues of nucleosides possessing antiviral activity [37]. It should be noted that 1-iodomethoxy(2-trimethylsiloxy)ethane (XVIIIa) which is formed in the reaction of Me_3SiI with 1,3-dioxolane at −78 °C has not yet been isolated, only identified by ^1H NMR spectroscopy.

We have shown that the reaction of Me_3SiI with 1,3-dioxolane leads at 20 °C to iodomethyl 2-iodoethyl ether (XIX) in quantitative yield [38].

In a similar manner iodomethyl 3-iodopropyl ether (XIXb) and iodomethyl 4-iodobutyl ether (XIXc) are formed in high yields in the reaction of Me_3SiI with 1,3-dioxane and 1,3-dioxepane, respectively.



(30)

(n = 2 (a), 3 (b), 4 (c))

Reaction 30 is a convenient synthetic method for the preparation of iodomethyl, ω-iodoalkyl ethers which are of interest as synthons in fine organic synthesis. The rate of reaction 30 decreases with increasing size of the cycle, i.e. as n increases from 2 to 4. For example, 1,3-dioxolane, 1,3-dioxane, and 1,3-dioxepane are split with Me_3SiI at 20, 80, and 105 °C, respectively.

The investigation using ^1H NMR technique of the mechanism of reaction of triethyliodosilane with 1,3-dioxane in the temperature range −70 to 10 °C led the authors to the suggestion that the initially formed 1-iodomethoxy 3-triethylsiloxy propane reacts further with the starting dioxane resulting in acyclic formal. The latter, in turn, is split with Et_3SiI with either recovery of 1-iodomethoxy 3-ethylsiloxy propane or formation of 1,3-bis(triethylsiloxy)propane and 1,3-bis(iodomethoxy)propane [39].

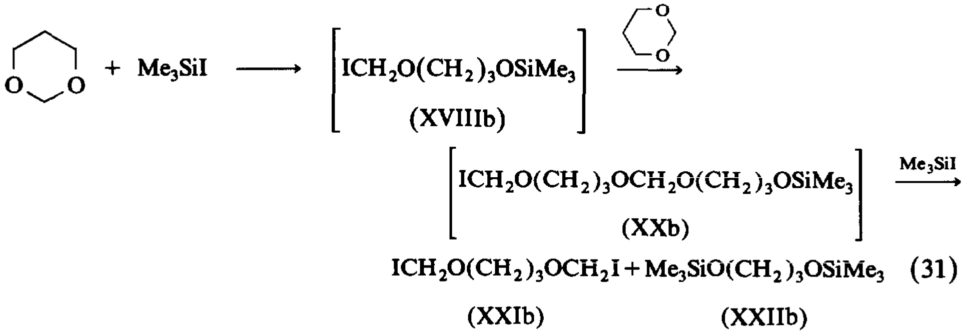
However, the analysis of ^1H NMR spectra did not allow an unequivocal assignment of the triplets of the CH_2I group (3.22 and 3.27 ppm) so the exact composition of the reaction mixture has not been determined. Moreover, the reaction products have neither been isolated nor characterized.

Table 7

Reaction of Me_3SiI with 1,4-dioxane

Molar ratio 1,4-dioxane : Me_3SiI	Yield of products (%)		
	1,2-diiodoethane	1,2-bis(trimethylsiloxy)ethane	hexamethyldisiloxane
1:1	96	53	32
1:2	96	34	30
1:3	96	19	62
1:4	98	–	98

Using the ^{1}H NMR technique we have shown that the reaction of Me_3SiI with 1,3-dioxane at 20°C results in an equimolar mixture of 1,3-bis(iodomethoxy)propane (XXIb) and 1,3-bis(trimethylsiloxy)propane (XXIIb) which were isolated in 82 and 12% yield, respectively. Their formation can be represented by the scheme which includes the cleavage of 1,3-dioxane with intermediate (XVIIIb) and further reaction of Me_3SiI with the resulting formal (XXb).



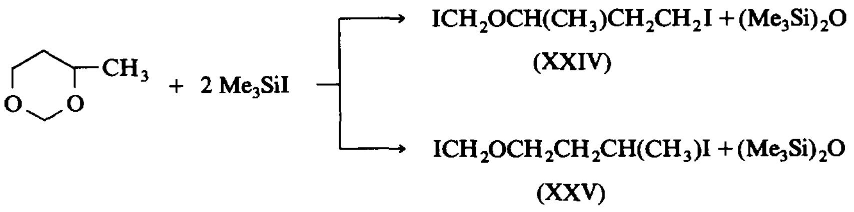
(31)

At the same time, the process which occurs at 80°C is represented by reaction 30. This is caused by the fact that the rate of the reaction of Me_3SiI with compound XVIII considerably exceeds the rate of its reaction with 1,3-dioxane. Besides, there is one more product in the reaction of 1,3-dioxane with Me_3SiI at 80°C which was found to be bis(iodomethyl) ether (XXIIIb). Its formation with that of HMDS is represented by the following scheme:

$$\underset{\text{(XXIb)}}{ICH_2O(CH_2)_3OCH_2I} + Me_3SiI \longrightarrow \underset{\text{(XIXb)}}{ICH_2OCH_2CH_2CH_2I} + ICH_2OSiMe_3 \quad (32)$$

$$2\ ICH_2OSiMe_3 \longrightarrow \underset{\text{(XXIIIb)}}{ICH_2OCH_2I} + (Me_3Si)_2O \quad (33)$$

When treating 4-methyl-1,3-dioxane with Me_3SiI the bond-breaking reactions of C(2)–O(1) and C(2)–O(3) compete, the first being predominant. According to ^{1}H NMR the ratio of isomers XXIV and XXV formed is 2 : 1.

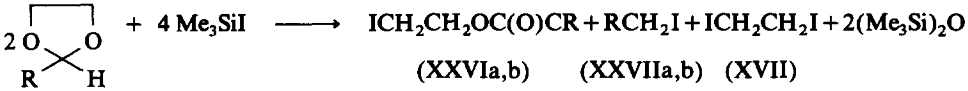


(34)

This probably could be explained by the fact that the inductive effect of the methyl group in the 4 position of the heterocycle increases the electron density on the oxygen atom O(3) which stabilizes the trimethylsiloxy carbenium ion formed, resulting in the rupture of the C(2)–O(1) bond predominating.

In the presence of a hydrocarbon substituent attached to the acetal carbon atom C(2) the reaction course is dramatically changed. Thus, in the 2-substituted 1,3-dioxolane the C(2)–O(1), C(2)–O(3), C(5)–O(1), C(4)–O(3), and C(2)–H bonds are split.

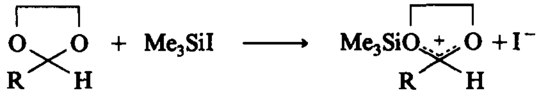
The reaction of the 2-substituted 1,3-dioxolanes with Me_3SiI leads to a mixture of three compounds (XXVI, XXVII, XVII) and HMDS [40].



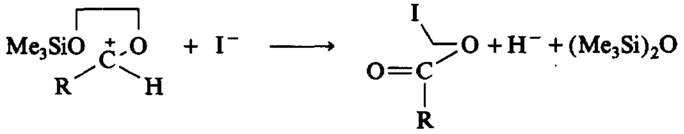
(35)

($R = CH_3$ (a); C_6H_5 (b))

This at first glance unexpected direction of the reaction might be explained by typical formation of the dioxolenium ion from the 2-substituted 1,3-dioxolanes followed by hydride transfer with the participation of the second dioxolenium ion [41]. The action of the weakly nucleophilic iodide ion on the dioxolenium ion results in the cycle opening with the formation of the iodoethyl ester of the corresponding carboxylic acid. The second dioxolenium ion acts here as a hydride ion acceptor which, splitting in turn, forms the compound XXVII.

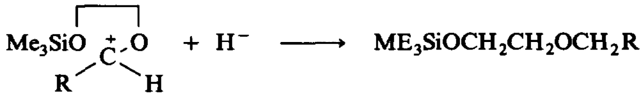


(36)



(37)

(XXVI)



(38)

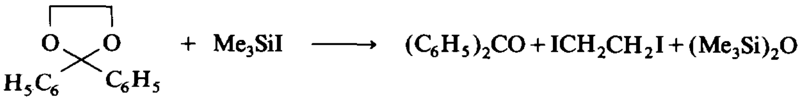
$$Me_3SiOCH_2CH_2OCH_2R \xrightarrow{Me_3SiI} Me_3SiOCH_2CH_2OSiMe_3 + \underset{(XXVII)}{RCH_2I} \quad (39)$$

$$Me_3SiOCH_2CH_2OSiMe_3 \xrightarrow{2\,Me_3SiI} 2(Me_3Si)_2O + \underset{(XVII)}{ICH_2CH_2I} \quad (40)$$

The ^1H NMR data for the mixture of Me_3SiI with 2-substituted 1,3-dioxolane at −60 °C are indicative of the presence of 1-iodoorganyl methoxy(2-trimethylsiloxy)ethane $RCHIOCH_2CH_2OSiMe_3$ (XXVIII). Raising the temperature leads to the formation of the products represented by eq. 35. However, an attempt to detect ethyl iodide in the reaction with 2-methyl-1,3-dioxolane failed.

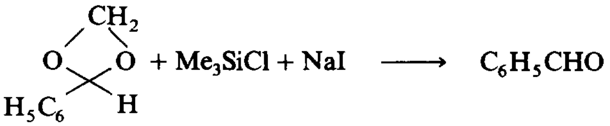
On account of the foregoing arguments the mechanism suggested earlier for the reaction of trimethylchlorosilane with the 2-substituted 1,3-dioxolanes seems to be incorrect [42]. Apparently, that is why the authors do not mention it in their review [43].

The reaction mechanism that we propose is proven by the fact that the reaction of Me_3SiI with 2,2-diphenyl 1,3-dioxolane proceeds much more simply because the hydride transfer does not occur:


(41)

The benzophenone formed does not react with Me_3SiI even at 150 °C. The physico-chemical constants of the synthesized compounds, their elemental analysis as well as the ^1H NMR spectra parameters are given in Tables 8 and 9.

However, when 2-phenyl-1,3-dioxocyclobutane is split with the system Me_3SiCl/NaI in CH_3CN at 45 °C (which is equivalent to Me_3SiI) Japanese authors observed only formation of benzaldehyde in 30% yield [44].


(42)

Therefore, reactions of Me_3SiI with 1,3-dioxacycloalkanes and their derivatives can be used as convenient synthetic methods for obtaining novel iodomethyl ω-iodoalkyl ethers which have promise as synthons for organic chemistry.

III. Reactions with trioxacycloalkanes

The splitting of C–O bonds in 1,3,5-trioxacyclohexane and in 2,4,6-trimethyl 1,3,5-trioxacyclohexane with Me_3SiI proceeds under mild conditions with quantita-

Table 8

Physicochemical constants and analytical data for products of the reaction of Me_3SiI with 1,3-dioxacycloalkanes

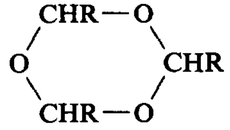
Compound	Product	B.p. (mmHg)	n_D^{20}	d_4^{20}	Molecular formula	Found (calcd.) (%)		
						C	H	I
XIXa	$ICH_2OCH_2CH_2I$	93 (3)	1.6405	2.5704	$C_3H_6I_2O$	11.58 (11.55)	1.95 (1.93)	81.09 (81.38)
XIXb	$ICH_2O(CH_2)_3I$	82 (0.06)	1.6150	2.3299	$C_4H_8I_2O$	15.04 (14.74)	2.40 (2.47)	77.73 (77.78)
XIXc	$ICH_2O(CH_2)_4I$	85 (0.01)	1.5690	2.1678	$C_5H_{10}I_2O$	16.96 (17.66)	3.08 (2.97)	75.22 (74.66)
XXIb	$ICH_2O(CH_2)_3OCH_2I$	102 (0.015)	1.6080	2.2358	$C_5H_8I_2O_2$	16.41 (16.87)	2.85 (2.83)	72.00 (71.31)
XXIV	$ICH_2OCH(CH_3)CH_2CH_2I$				$C_5H_{10}I_2O$	17.60 (17.66)	3.03 (2.96)	74.57 (74.66)
XXV	$ICH_2OCH_2CH_2CH(CH_3)I$	82 (0.07)	–	–	$C_5H_{10}I_2O$	17.60 (17.66)	3.03 (2.96)	74.57 (74.66)

Table 9

^1H NMR data of the products of reaction of Me_3SiI with 1,3-dioxacycloalkanes

Compound	Product	^1H NMR (TMS)				
		1	2	3	4	5
XIXa	$IC\overset{1}{H}_2OC\overset{2}{H}_2C\overset{3}{H}_2I$	5.72 s	3.71 t	3.22 t		
XIXb	$IC\overset{1}{H}_2OC\overset{2}{H}_2C\overset{3}{H}_2C\overset{4}{H}_2I$	5.72 s	3.49 s	2.09 m	3.18 m	
XIXc	$IC\overset{1}{H}_2OC\overset{2}{H}_2C\overset{2}{H}_2C\overset{3}{H}_2C\overset{4}{H}_2I$	5.74 s	3.46 t	1.82 m	3.18 m	
XXIb	$IC\overset{1}{H}_2OC\overset{2}{H}_2C\overset{3}{H}_2C\overset{2}{H}_2OC\overset{1}{H}_2I$	5.74 s	3.51 t	2.13 m		
XXIc	$IC\overset{1}{H}_2OC\overset{2}{H}_2C\overset{3}{H}_2C\overset{3}{H}_2C\overset{2}{H}_2OC\overset{1}{H}_2I$	5.74 s	3.44 s	1.69 m		
XXIIb	$(C\overset{1}{H})_3SiOC\overset{2}{H}_2C\overset{3}{H}_2C\overset{2}{H}_2OSi(C\overset{1}{H}_3)_3$	0.08 s	3.52 t	2.09 m		
XXIIc	$(C\overset{1}{H}_3)_3SiOC\overset{2}{H}_2C\overset{3}{H}_2C\overset{3}{H}_2C\overset{2}{H}_2OSi(C\overset{1}{H}_3)_3$	0.05 s	3.46 m	1.55 m		
XXIIIb	ICH_2OCH_2I	5.72 s				
XVII	ICH_2CH_2I	3.58 s				
XXIV	$IC\overset{1}{H}_2OC\overset{2}{H}(C\overset{5}{H}_3)C\overset{3}{h}_2C\overset{4}{H}_2I$	5.85 s	4.24 m	2.00 m	3.14 t	1.25 d
XXV	$IC\overset{1}{H}_2OC\overset{2}{H}_2C\overset{3}{H}_2C\overset{4}{H}IC\overset{5}{H}_3$	5.61 s	3.59 m	2.00 m	3.59	2.00 d
XXVIa	$C\overset{1}{H}_3COOC\overset{2}{H}_2C\overset{3}{H}_2I$	2.08 s	4.32 t	3.28 t		
XXVIb	$C_6\overset{1}{H}_5COOC\overset{2}{H}_2C\overset{3}{H}_2I$	8.05–7.25 m	4.50 t	3.36 t		
XXVIIb	$C_6\overset{1}{H}_5C\overset{2}{H}_2I$	7.23 m	4.44 s			

tive formation of bis(iodomethyl) ether or bis(α-iodoethyl) ether, respectively [45].



$$2\ \ldots + 6\,Me_3SiI \longrightarrow 3\,RCHIOCHIR + 3(Me_3Si)_2O \quad (43)$$

(XXVIIIa,b)

(R = H (a), CH_3 (b))

Reaction 43 is a convenient method of synthesis of the otherwise difficult to obtain α,α'-diiodoalkyl ethers, which are effective alkylating agents. Bis(iodomethyl) ether (XXVIIIa) is thermally rather stable even when heated in a sealed tube at 100 °C for 10 h. Neither, under the same conditions, does it react with Me_3SiI. However, bis(iodomethyl) ether is gradually decomposed by light. On the contrary, bis(α-iodoethyl) ether (XXVIIIb) undergoes complete resinification after 10 h when stored in a sealed tube with copper powder.

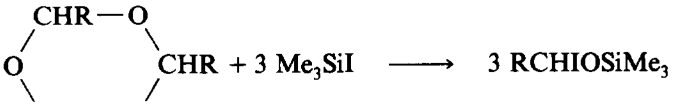
In a similar way to 1,3,5-trioxacyclohexane, the easily available polyformaldehyde reacts with Me_3SiI resulting in bis(iodomethyl) ether in quantitative yield [46].

$$(CH_2O)_n + 2n\ Me_3SiI \longrightarrow n\ ICH_2OSiMe_3$$

$$2\ ICH_2OSiMe_3 \longrightarrow \underset{\text{(XXVIIIa)}}{ICH_2OCH_2I} + (Me_3Si)_2O \qquad (44)$$

The formation of highly unstable trimethyl(iodomethoxy)silane has been established by ^1H NMR spectroscopy. Reaction 44 is of indubitable synthetic interest.

Therefore, the primary product in the reaction of Me_3SiI with 1,3,5-trioxacyclohexanes is $RCHIOSiMe_3$, disproportionation of which results in the final product:



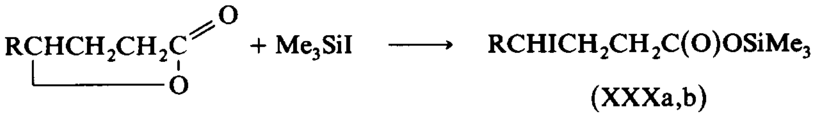
(XXIXa,b)

$$2\ RCHIOSiMe_3 \longrightarrow IRHCOCHRI + (Me_3Si)_2O \quad (45)$$

(XXVIIIa,b)

IV. Reaction with lactones

We have established that γ-lactones (butyrolactone, valerolactone) are readily cleaved by Me_3SiI with the formation of trimethylsilyl esters of the corresponding iodoalkane carboxylic acids [47].



(46)

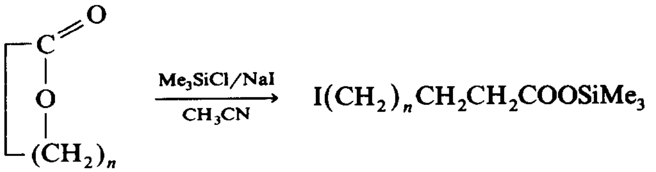
(XXXa,b)

(R = H (a), CH_3 (b))

The composition and the structure of the reaction products have been proved by elemental analysis and IR and ^1H NMR spectroscopy.

The reaction of Me_3SiI with lactones opens a way to synthesis of ω-iodoalkane carboxylic acids which are difficult to obtain and, nowadays, widely used in synthesis of biologically active compounds. The preparative value of this method has lately been proven by other authors [48].

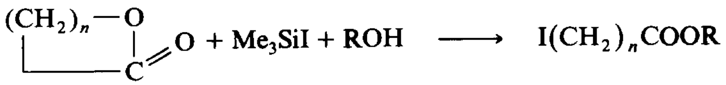
Cleavage of β-, γ-, and σ-lactones with Me_3SiI *in situ* (with system $Me_3SiCl/NaI/CH_3CN$) proceeds more slowly, the β-butyrolactone reacts somewhat faster than its γ-isomer due to a greater steric strain of the ring [49].



(47)

This system was used for the splitting of lactones in a series of studies [50,51], although the yield of trimethylsilyl ester of ω-iodobutyric acid was considerably lower and did not exceed 50% and γ-valerolactone does not react with this system at all. A further reason for using Me_3SiI is the fact that the reaction mixture does not contain CH_3CN, Me_3SiCl, NaI, and NaCl which complicate the isolation of the final product.

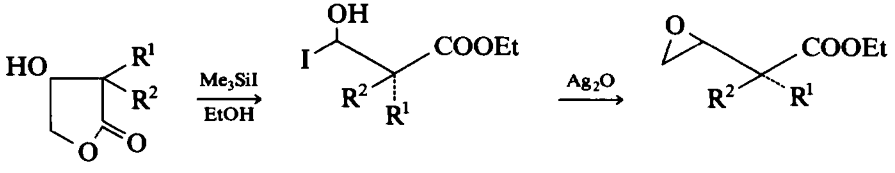
Treatment of lactones with Me_3SiI and alcohol results in the formation of esters of the corresponding ω-iodoalkane carboxylic acids [52].



(48)

(R = CH_3, C_2H_5, i-C_3H_7, i-C_4H_9, $C_6H_5CH_2$; n = 2, 3, 4, 7)

The reaction of Me_3SiI with cyclic oxylactones in ethyl alcohol with subsequent treatment with silver oxide results in optically pure β,γ-epoxy esters [53].



(49)

Relevant experimental data can be found in the publications cited.

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