Generation and capture of alkylchlorosilanones

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Alkyltrichlorosilanes react with DMSO (molar ratio 1 : 1, 0 °C) to give cyclic oligoalkylchlorosiloxanes of the general formula $[R(Cl)SiO]_n$ (where R = Me or Et; n = 3—6). With an excess of alkyltrichlorosilane (2 : 1), linear oligoalkylchlorosiloxanes $Cl[R(Cl)SiO]_mSiCl_2R$ (where R = Me or Et; m = 1—5) are also formed. In the presence of hexamethyldisiloxane (molar ratio Cl_3SiR : DMSO : $(Me_3Si)_2O$ = 1 : 1 : 2, 20 °C), the reaction products are both cyclic and linear oligoalkyl(trimethylsilyloxy)siloxanes $[R(Me_3SiO)SiO]_n$ (n = 3—5) and $Me_3Si[OSi(OSiMe_3)R]_mOSiMe_3$ (m = 1—3), respectively. The reaction of DMSO with trichloro(vinyl)silane and hexamethyldisiloxane occurs in a similar manner. A plausible scheme of formation of the final products via intermediate alkylchlorosilanones RClSi=O and alkyl(trimethylsilyloxy)silanones is discussed.

Key words: alkyltrichlorosilanes, dimethyl sulfoxide, chlorosilanones, silanones, oligosiloxanes.

Earlier, we showed that the reaction of dialkyldichlorosilanes with dimethyl sulfoxide is a convenient method for the generation of dialkylsilanones,[1,2] which was confirmed in later investigations.[3] In a continuation of these studies, we found that alkyltrichlorosilanes react with DMSO in the molar ratio 1 : 1 at 0 °C to give chloromethyl methyl sulfide and oligochlorocyclosiloxanes $(RClSiO)_n$ in up to 80% overall yield (Tables 1

Table 1. Characteristic peaks in the mass spectra of oligosiloxanes **1—3** and **8—10**

Ion	m/z^* (I_{rel} (%))					
	1	**2**	**3**	**8**	**9**	**10**
$[M - Me]^+$	267(100)	361(100)	455(60)	227(100)	321(100)	415(61)
$[M - Cl]^+$	247(12)	341(16)	435(33)	207(10)	301(16)	395(22)
$[M - Me - Me(Cl)SiO]^+$	173(8)	267(13)	361(27)	133(4)	227(10)	321(6)
$[M - Me - 2\ Me(Cl)SiO]^+$	79(12)	173(6)	267(100)	—	133(3)	227(6)
$[MeSiCl_2]^+$	113(15)	113(13)	113(27)	113(8)	113(29)	113(33)
$[Me_2SiCl]^+$	93(4)	93(23)	93(93)	—	93(45)	93(100)

* For ^{35}Cl. The intensity ratio for isotopic peaks corresponds to the calculated one.

Table 2. Characteristic peaks in the mass spectra of oligosiloxanes **4—7** and **11—15**

Ion	m/z^a (I_{rel} (%))								
	4	**5**	**6**	**7**	**11**	**12**	**13**	**14**	**15**
$[M - Et]^+$	295(100)	403(100)	511(100)	619(43)	241(100)	349(100)	457(100)	565(100)	673(2.5)
$[M - 2\ Et + H]^+$	267(38)	375(35)	483(8)	591(15)	213(56)	321(50)	429(16)	537(4)	—
$[M - Et - Et(Cl)SiO]^+$	187(1)	295(32)	403(7)	511(68)	133(6)	241(4)	349(3)	457(5)	565(56)
$[M - Et - 2\ Et(Cl)SiO]^+$	—	187(4)	295(8)	403(100)[b]	—	—	241(8)	349(7)[c]	455(84)
$[EtSiCl_2]^+$	127(1)	127(6)	127(7)	127(25)	127(2)	127(12)	127(23)	127(8)	127(32)
$[Et_2SiCl]^+$	121(1)	121(8)	121(56)	121(60)	121(1)	121(12)	121(30)	121(28)	121(76)
$[EtSiClH]^+$	93(1)	93(4)	93(29)	93(48)	93(1)	93(8)	93(18)	93(19)	93(52)
$[C_2H_4Cl]^+$	63(2)	63(4)	63(6)	63(23)	63(4)	63(26)	63(12)	63(3)	63(28)

[a] For ^{35}Cl. The intensity ratio for isotopic peaks corresponds to the calculated one. [b] 295 $[M - Et - 3\ Et(Cl)SiO]^+$ (73). [c] 241 $[M - Et - 3\ Et(Cl)SiO]^+$ (3).

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Table 3. Characteristic peaks in the mass spectra of oligosiloxanes **16**—**21**

Ion	*m/z* (I_{rel} (%))					
	16	**17**	**18**	**19**	**20**	**21**
$[M - Me]^+$	465(77)	471(34)	577(9)	625(41)	633(16)	785(8)
$[M - R]^+$	453(2)	457(17)	577(9)	613(2)	619(15)	—
$[M - Me - Me_2SiO + H]^+$	377(13)	383(11)	489(3)	537(8)	547(3)	—
$[M - R - Me_2SiO + H]^+$	365(45)	369(25)	489(3)*	525(20)	533(5)	**
$[Me_2SiOSiR_2]^+$	171(6)	175(6)	147(30)	171(8)	175(8)	171(8)
$[Me_2SiOSiR(OH)]^+$	159(9)	161(23)	149(3)	159(11)	161(16)	159(18)
$[Me_2SiOSiMe_2]^+$	147(15)	147(23)	147(30)	147(12)	147(15)	147(16)
$[Me_2SiOSiH(OH)]^+$	133(5)	133(12)	133(2)	133(4)	133(13)	133(6)
$[R_2Si]^+$	109(15)	115(1)	73(100)	109(30)	115(1)	109(22)
$[MeR_2Si]^+$	97(52)	101(14)	73(100)	97(93)	101(30)	97(70)
$[Me_2RSi]^+$	85(96)	87(51)	73(100)	85(95)	87(59)	85(94)
$[Me_3Si]^+$	73(100)	73(100)	73(100)	73(100)	73(100)	73(100)
$[Me_2SiH]^+$	59(46)	59(50)	59(3)	59(37)	59(53)	59(31)

* 429 $[M - Me - Me(Me_2SiO)SiO]^+$ (4), 281 $[M - Me - 2\ Me(Me_2SiO)SiO]^+$ (11).
** 625 $[M - Me - CH_2{=}CH(Me_2SiO)SiO]^+$ (8).

and 2). Apparently, the corresponding labile short-lived alkylchlorosilanones are the reaction intermediates.

$$MeSOMe + Cl_3SiR \longrightarrow$$

$$\longrightarrow MeSiCH_2Cl + [RClSi{=}O] + HCl. \quad (1)$$

$$n\,[RClSi{=}O] \longrightarrow \underset{\mathbf{1-7}}{(RClSiO)_n} \quad (2)$$

R = Me, n = 3 (**1**), 4 (**2**), 5 (**3**);
Et, n = 3 (**4**), 4 (**5**), 5 (**6**), 6 (**7**)

With an excess of alkyltrichlorosilane (2 : 1), the reaction affords, along with compounds **1**—**7**, linear oligoalkylchlorosiloxanes $Cl(RClSiO)_mSiCl_2R$ (**8**—**15**) in up to 27% yield (see Tables 1 and 2).

$$Cl_3SiR + m\,(RClSi{=}O) \longrightarrow \underset{\mathbf{8-15}}{Cl(RClSiO)_mSiCl_2R} \quad (3)$$

R = Me, m = 1 (**8**), 2 (**9**), 3 (**10**);
Et, m = 1 (**11**), 2 (**12**), 3 (**13**), 4 (**14**), 5 (**15**)

Oligomers **8**—**15** were also obtained in small amounts (<10%) in the equimolar ratio of the reagents.

The reaction of DMSO with alkyltrichlorosilanes in the presence of HMDS (as a scavenger for dialkylsilanones[1]) in the molar ratio 1 : 1 : 2 at 20 °C did not yield the expected linear siloxanes $Me_3Si(OSiRCl)_nOSiMe_3$ (R = Me or Et) under the conditions studied. The major reaction products were cyclic and linear oligoalkyl(trimethylsilyloxy)siloxanes $[R(Me_3SiO)SiO]_n$ (**16**—**21**), where n = 3—5 (Table 3), and $Me_3Si[OSi(OSiMe_3)R]_mOSiMe_3$ (**22**—**26**), where m = 1—3 (Table 4).

Table 4. Characteristic peaks in the mass spectra of oligosiloxanes **22**—**26**

Ion	*m/z* (I_{rel} (%))				
	22	**23**	**24**	**25**	**26**
$[M - Me]^+$	295(30)	443(3)	591(9)	471(18)	633(5)
$[M - R]^+$	295(30)	443(3)	591(9)	457(9)	619(4)
$[M - 2\ Me + H]^+$	—	429(18)	577(9)	457(9)	619(4)
$[M - Me - Me_3SiO + H]^+$	207(90)	355(4)	489(4)	383(8)	547(3)
$[M - R - Me_3SiO + H]^+$	207(90)	355(4)	489(4)	369(13)	533(1)
$[Me_3SiOSiEt(OH)]^+$	—	—	—	161(28)	161(11)
$[Me_3SiOSiR_2]^+$	147(3)	147(23)	147(30)	175(6)	175(6)
$[Me_3SiOSiMe_2]^+$	147(3)	147(23)	147(30)	147(26)	147(10)
$[Me_3SiOSiH(OH)]^+$	133(3)	133(2)	133(2)	133(13)	133(9)
$[R_3Si]^+$	73(100)	73(100)	73(100)	115(1)	115(5)
$[R_2MeSi]^+$	73(100)	73(100)	73(100)	101(13)	101(32)
$[RMe_2Si]^+$	73(100)	73(100)	73(100)	87(46)	87(57)
$[Me_3Si]^+$	73(100)	73(100)	73(100)	73(100)	73(100)
$[Me_2SiH]^+$	59(5)	59(4)	59(3)	59(46)	59(58)

Table 5. Characteristic peaks in the mass spectra of oligosiloxanes **27**–**32**

Ion	m/z^* (I_{rel} (%))					
	27	**28**	**29**	**30**	**31**	**32**
$[M - Me]^+$	241(100)	281(71)	417(22)	579(6)	741(7)	525(10)
$[M - 29]^+$	227(21)	267(33)	403(7)	565(4)	727(12)	511(7)
$[M - Me - Me_3SiO + H]^+$	153(5)	193(4)	329(11)	491(5)	653(2)	437(4)
$[M - Et - Me_3SiO + H]^+$	—	—	315(13)	477(3)	—	423(4)
$[M - Me - Et(Cl)SiO]^+$	—	—	309(72)	471(8)	633(8)	417(22)
$[M - Et - Et(Cl)SiO]^+$	—	—	295(96)	457(23)	619(23)	403(45)
$[Me_3SiOSiEt_2]^+$	—	—	175(7)	175(4)	175(9)	175(3)
$[Me_3SiOSiEt(OH)]^+$	—	—	161(35)	161(9)	161(16)	161(9)
$[Me_3SiOSiMe_2]^+$	147(2)	147(1)	147(27)	147(8)	147(15)	147(7)
$[Me_3SiOSiH(OH)]^+$	133(5)	133(13)	133(15)	133(7)	133(11)	133(6)
$[Et_3Si]^+$	—	—	—	115(2)	115(7)	115(3)
$[MeEt_2Si]^+$	—	—	101(5)	101(26)	101(39)	101(33)
$[Me_2EtSi]^+$	—	—	87(35)	87(55)	87(68)	87(63)
$[Me_3Si]^+$	73(23)	73(100)	73(100)	73(100)	73(100)	73(100)
$[Me_2SiH]^+$	59(2)	59(5)	59(42)	59(62)	59(50)	59(61)

* For ^{35}Cl. The intensity ratio for isotopic peaks corresponds to the calculated one.

Presumably, they are formed owing to the insertion of alkylchlorosilanones RClSi=O generated in the initial stage (reaction 1) into a molecule of hexamethyldisiloxane to give 3-R-3-chlorohexamethyltrisiloxane (**27**), whose geminal dissociation[4,5] results in chlorotrimethylsilane and alkyl(trimethylsilyloxy)silanone, the latter undergoing cyclization or insertion into a molecule of the starting hexamethyldisiloxane to form oligomers **22**–**26**.

$$[RClSi{=}O] + Me_3SiOSiMe_3 \longrightarrow [Me_3Si(OSiRCl)OSiMe_3] \longrightarrow \mathbf{27}$$

$$\longrightarrow Me_3SiCl + [R(Me_3SiO)Si{=}O], \quad (4)$$

$$n\,[R(Me_3SiO)Si{=}O] \longrightarrow [R(Me_3SiO)SiO]_n \quad (5)$$

16–**21**

R = $CH_2{=}CH$, n = 3 (**16**); Et, n = 3 (**17**), 4 (**20**); Me, n = 4 (**18**); $CH_2{=}CH$, n = 4 (**19**), 5 (**21**)

$$[R(Me_3SiO)Si{=}O] + Me_3SiOSiMe_3 \longrightarrow Me_3Si[OSi(OSiMe_3)R]_mOSiMe_3 \quad (6)$$

22–**26**

R = Me, m = 1 (**22**), 2 (**23**), 3 (**24**); Et, m = 2 (**25**), 3 (**26**)

It is not improbable that alkylchlorosilanone [RClSi=O] generated in the initial stage (reaction (1)) further splits HMDS to give methyl(trimethylsilyloxy)silanone.[6]

$$[R(Cl)Si{=}O] + Me_3SiOSiMe_3 \longrightarrow [R(Me_3SiO)Si{=}O] + Me_3SiCl \quad (7)$$

The reaction of DMSO with alkyltrichlorosilanes in the presence of HMDS in the ratio 1 : 1 : 1 at 20 °C yields a mixture of oligomers that were also formed in the absence of HMDS (reactions (1)–(6)), as well as 3-chloro-1,1,1,3,5,5,5-heptamethyltrisiloxane (**28**) (for R = Me) (Table 5), $Me_3Si[OSi(Cl)Et][OSi(OSiMe_3)Et]_nOSiMe_3$, where n = 1 (**29**), 2 (**30**), and 3 (**31**), and $Me_3Si[OSi(Cl)Et]_2[OSi(OSiMe_3)Et]OSiMe_3$ (**32**) (for R = Et) (see Table 5). Their identification is strong evidence in favor of reaction (4).

The reaction with trichloro(vinyl)silane yields only oligo(trimethylsilyloxy)vinylcyclosiloxanes (**16**, **19**, and **21**) (see Table 3).

Mixed-type oligochloro(trimethylsilyloxy)cyclosiloxanes $[R(Me_3SiO)SiO]_n[RClSiO]_{m-n}$ (n = 1–2 and m = 3–5) were not detected upon the reaction of $RSiCl_3$ with DMSO in the presence of HMDS, which also confirms the proposed scheme of the process (see reactions (4) and (7)).

Experimental

GLC-MS analysis was performed on an LKB-2091 chromatomass-spectrometer (ionizing voltage 60 V, capillary column 38 m long (phase SE-54)). The temperature was programmed to 270 °C at a rate of 16 deg min^{-1}; accelerating voltage 2 kV.

Dimethyl sulfoxide was kept over fused KOH, decanted, purified by freezing–thawing, and distilled *in vacuo*.

Reaction of DMSO with trichloromethylsilane. Trichloromethylsilane (15.0 g, 0.1 mol) was placed in a 50-ml flask equipped with a high Vigreux distilling column and cooled to 0 °C. DMSO (7.8 g, 0.1 mol) was added dropwise. Vigorous evolution of hydrogen chloride was observed. The reaction

mixture was slowly heated to boiling to give chloromethyl methyl sulfide, yield 8.6 g (87%), b.p. 109—110 °C, n_D^{20} 1.4960 (Ref. 7: b.p. 110—112 °C). Found (%): C, 25.02; H, 5.25; Cl, 36.82; S, 33.0. C_2H_5ClS. Calculated (%): C, 24.87; H, 5.22; Cl, 36.71; S, 33.20. The residue was distilled *in vacuo* to give a fraction with b.p. 30—170 °C (2 Torr), yield 7.2 g. GLC-MS data are presented in Tables 1 and 2.

Reaction of DMSO with trichloromethylsilane in the presence of HMDS. The reaction of trichloromethylsilane with DMSO in the presence of an equimolar amount of HMDS was carried out in a similar manner to yield chloromethyl methyl sulfide (7.3 g, 74%). The residue was distilled *in vacuo* to give a fraction with b.p. 70—200 °C (6 Torr), yield 5.2 g. GLC-MS data are presented in Tables 1 and 2.

Reactions of Me_2SO with $EtSiCl_3$ and CH_2=$CHSiCl_3$ in the presence of $(Me_3Si)_2O$ (molar ratios 1 : 1 : 1 and 1 : 1 : 2) were carried out as above. In the presence of $(Me_3Si)_2O$, the reaction products are chloromethyl methyl sulfide and dimethyl sulfide.

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References

1. S. V. Basenko and M. G. Voronkov, *Dokl. Akad. Nauk*, 1994, **339**, 486 [*Dokl. Chem.*, 1994 (Engl. Transl.)].
2. M. G. Voronkov and S. V. Basenko, *J. Organomet. Chem.*, 1995, **500**, 325.
3. P. Lu, J. K. Paulasaari, and W. P. Weber, *Organometallics*, 1996, **15**, 4649.
4. M. G. Voronkov, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 824 [*Russ. Chem. Bull.*, 1998, **47**, 795 (Engl. Transl.)].
5. M. G. Voronkov, *J. Organomet. Chem.*, 1998, **557**, 143.
6. M. G. Voronkov, S. V. Basenko, I. A. Gebel, and R. G. Mirskov, *Abstrs. XI Int. Symp. on Organosilicon Chemistry*, Montpellier, 1996, PA32.
7. H. Bohme, H. Fisher, and R. Frank, *Lieb. Ann.*, 1949, **563**, 54.

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