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INSERTION REACTIONS OF ORGANOCHLOROSILANES WITH CYCLIC ETHERS

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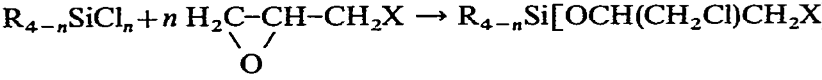
SUMMARY

Phenyl glycidyl ether and allyl glycidyl ether (3-phenoxy- and 3-allyloxy-1,2-epoxypropane) cause fission of the silicon–chlorine bonds in a number of alkylchlorosilanes to form chloro-substituted alkoxysilanes. Relative reactivities of cyclic ethers with chlorosilanes have been discussed. Structures of the adducts are suggested on the basis of their IR and proton magnetic resonance spectra.

Recently insertion reactions of alkylchlorosilanes with cyclic ethers[1] have been reported and it has been assumed that such reactions proceed through the normal mode of ring fission[2,3]. These studies have now been extended to addition reactions of alkylchlorosilanes with phenyl glycidyl ether and allyl glycidyl ether:



$$R_{4-n}SiCl_n + n\ \underset{\quad\ \diagdown\ \diagup}{H_2C{-}CH}{-}CH_2X \rightarrow R_{4-n}Si[OCH(CH_2Cl)CH_2X]_n$$
$$\qquad\qquad O$$

$R{=}CH_3$; $n{=}1, 2$ or 3; $X{=}OC_6H_5$ or $OCH_2CH{=}CH_2$

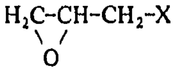
The reaction of methyltrichlorosilane with allyl glycidyl ether is highly exothermic and the reaction mixture starts boiling immediately after the addition of the chlorosilane to the cyclic ether. However, the tris derivatives $MeSi[OCH(CH_2Cl)CH_2OCH_2CH{=}CH_2]_3$ could be obtained only after refluxing for about 30 h at 85–90° bath temperature.

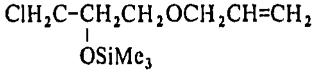
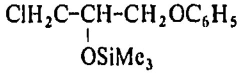
Conversely, the reaction of methyltrichlorosilane with phenyl glycidyl ether in 1/3 molar ratio could not be completed even after 90 h refluxing, despite the exothermic nature of the reaction. This difference in the reactivities of allyl and phenyl glycidyl ethers may be due to steric factors or this may arise from the ease in the opening of the ring due to increase in the negative charge on the epoxy oxygen brought about by the allyl group.

All the alkoxides, except $MeSi[OCH(CH_2Cl)CH_2OCH_2CH{=}CH_2]_3$ obtained in these reactions were volatile under reduced pressure (Table 1). The tris derivative which separated out as a highly viscous liquid turned into a brownish foamy solid on attempted distillation under 0.3 mmHg at 260° bath temperature.

TABLE 1

REACTION OF CHLOROSILANES WITH CYCLIC ETHERS,



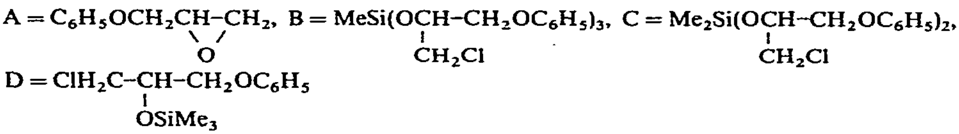
No.	Chlorosilane (g)	X (g)	Molar ratio	Reaction conditions	Product formed b.p. (°C/mmHg) Yield (%)	Analyses found (calcd.) (%)		Mol.wt. found (calcd.)
						Si	Cl	
1	Me_3SiCl 3.14	$OCH_2CH{=}CH_2$ 3.13	1/1	Slightly exothermic, refluxed for about 36 h.	 $ClH_2C{-}\underset{OSiMe_3}{C}H_2CH_2OCH_2CH{=}CH_2$ 58–60/0.5 (62)	12.50 (12.64)	15.99 (15.96)	223 (222)
2	Me_3SiCl 3.59	OC_6H_5 5.0	1/1	Refluxed for 84–85 h.	 $ClH_2C{-}\underset{OSiMe_3}{CH}{-}CH_2OC_6H_5$ 88–90/0.5 (75)	10.60 (10.85)	13.52 (13.70)	255 (258)
3	Me_2SiCl_2 5.66	$OCH_2CH{=}CH_2$ 10.3	1/2	Exothermic, refluxed for 6–7 h.	$Me_2Si[OCH(CH_2Cl)\text{-}CH_2OCH_2CH{=}CH_2]_2$ 138/0.5 (75)	7.83 (7.85)	19.72 (19.84)	354 (357)
4	Me_2SiCl_2 1.54	OC_6H_5 4.02	1/2	Refluxed for about 60 h.	$Me_2Si[OCH(CH_2Cl)\text{-}CH_2OC_6H_5]_2$ 190–195/0.7 (65)	6.30 (6.52)	16.38 (16.46)	457 (430)
5	$MeSiCl_3$ 2.26	OC_6H_5 5.67	1/3	Slightly exothermic, refluxed for about 90 h.	$MeSiCl[OCH(CH_2Cl)\text{-}CH_2OC_6H_5]_2$ 223–228/0.1 (55)	5.97	22.85[a] 7.35[b]	
					$MeSi[OCH(CH_2Cl)CH_2OC_6H_5]_3$ 260–270/0.1 (32)	4.78 bis (6.22) tris (4.66)	18.12[a] (23.55)[a] (7.85)[b] (17.64)[a]	

6	$MeSiCl_3$	$OCH_2CH=CH_2$	1/3	Highly exothermic,	$MeSi[OCH(CH_2Cl)$-	Crude		Crude
	2.10	4.31		refluxed for 30 h	$CH_2OCH_2CH=CH_2]_3$	5.66	21.67	(844)
					Highly viscous liquid	Residue		
					turned into brownish	7.40	20.61	(492)
					foamy solid on attempted			
					distillation at 0.3 mmHg	(5.71)	(21.62)	
7	$MeSiCl_3$	$OCH_2CH=CH_2$	1/2	Highly exothermic	$MeSiCl[OCH(CH_2Cl)$-	7.42	28.05^a	
	3.36	4.88		refluxed for 6 h	$H_2COCH_2CH=CH_2]_2$		9.29^b	507
					115–120/0.6	(7.43)	(28.16)^a	(377)
					(40)		(9.38)^b	
8	$MeSiCl_3$	$OCH_2CH=CH_2$	1/1	Highly exothermic,	$MeSiCl_2[OCH(CH_2Cl)$-	10.77	39.44^a	
	4.21	2.98		refluxed for 4 h	$CH_2OCH_2CH=CH_2]$		27.95^b	312
							(40.34)^a	(263)
						(10.66)	(26.89)^b	

[a] Total chlorine. [b] Ionic chlorine.

TABLE 2

IR ABSORPTION BANDS OF PHENYL GLYCIDYL ETHER AND ITS CHLOROSUBSTITUTED ALKOXYSILANES



$A = C_6H_5OCH_2\underset{\setminus\;O\;/}{CH-CH_2}$, $B = MeSi(O\underset{CH_2Cl}{CH}-CH_2OC_6H_5)_3$, $C = Me_2Si(O\underset{CH_2Cl}{CH}-CH_2OC_6H_5)_2$,
$D = ClH_2C-\underset{OSiMe_3}{CH}-CH_2OC_6H_5$

A	*B*	*C*	*D*	*Tentative assignment*
	470 w	465 vw		
512 m	510 s	520 m	520 m	
	565 w			
592 m	592 m	590 w	590 w	
		595 w		
620 w	610 (sh)	615 w	615 w	ν(Si–C)
635 vw	645 w	650 w		
700 s	700 s	700 s	700 s	π[CH(aryl)]
		725 w		
765 vs	778 s	775 s	778 s	ν(C–Cl)
795 (sh)	795 (sh)			+
815 s	812 vs	815 (sh)		ν(Si–O)
835 w				
850 w	855 (sh)	845 s		ρ (CH_3) of MeSi group
*875 m		865 (sh)	870 s	* $-HC-CH_2$ ring
895 w	898 s	890 m	890 w	\ /
*915 s				O
980 w	965 (sh)	955 m	955 m	ν(C–C) or ν(C–O)
1005 w	1010 s	1002 s	1000 s	
1045 s				
	1065 s	1070 s	1065 s	
1090 m	1085 vs	1090 (sh)	1085 (sh)	(Si–O–C)
	1100 vs	1105 vs	1100 s	+
1135 m	1130 vs	1130 vs	1130 vs	(C–O)
1160 m				
1185 s	1185 m	1188 (sh)	1185 (sh)	Planar aryl ring vibrations
*1252 vs	1250 vs	1275 vs	1275 vs	$\delta_s(CH_3)$ of MeSi group
	1275 (sh)			
1300 s				* $-HC-CH_2$ ring \ / O
1355 s	1370 w	1365 w	1365 vs	(C–C) skeletal vibration
	1440 vw	1425 w	1425 w	δ(C–H) aryl, CH_2
1425 w	1480 (sh)	1478 m	1472 m	$\delta_{as}(CH_3)$ of MeSi group
1500 vs	1510 s	1510 s	1510 s	
1545 (sh)				
1595 w				ν(C=C)
1602 vs	1610 s	1612 s	1610 s	
2880 w	2890 (sh)	2892 (sh)	2885 (sh)	
2940 m	2950–2970 s(br)	2945 m		ν(C–H)
		2980 s	2978 s	
3012 m	3055 m	3055 w	3060–3070 w(br)	ν(C–H) aryl
3070 w	3075 m	3075 w		

TABLE 3

IR ABSORPTION BANDS OF ALLYL GLYCIDYL ETHER AND ITS CHLORO-SUBSTITUTED ALKOXYSILANES

$\underset{\diagdown O \diagup}{H_2C{-}CH}{-}CH_2OCH_2CH{=}CH_2$	$Me_2Si(O\underset{CH_2Cl}{CH}CH_2OCH_2CH{=}CH_2)_2$	$ClH_2C\underset{OSiMe_3}{C}HCH_2OCH_2CH{=}CH_2$	*Tentative assignment*
470 vw			
500 w	510–515 m (br)		δ_{as}(Si–O–C) or
560 m	560 m	560 w	Si–O–C torsion
620 w		620 w	ν(Si–C)
640–650 m (br)	640 m		
	700 s	690 m	
	735 m		ν_s(Si–O)
	765 m		
780 s	780 (sh)	775 s	ν(C–Cl) + ν_{as}(Si–O)
810 m	810 (sh)		
	845 s		
	855 s		ρ (CH_3) of MeSi group
875 s[a]	885 m	880 s	
930 vs[a]	930 s	930 m	π-CH_2 (allyl group) + ν(C–C)
1005 s	1000 s	1000 (sh)	
1095–1105 vs	1090–1130 vs (br)	1100–1120 vs (br)	ν_{as}(Si–O–C) + ν(C–O)
1130 (sh)			
1170 (sh)			δ(CH_2)
1275 m[a]	1280 s	1275 s	δ_s(CH_3) of MeSi group
1365 s	1370 m	1360 w	
1390 w	1410 vw	1410–1425 w	δ_{as}(CH_3) + CH_2 scissoring
1425 s	1428 s		
1465 w	1482 vw	1470 w	
1660 m	1655 m	1635–1645 w	ν(C=C)
2875 s	2880 s	2885 s	
2945 m	2920 m	2915–2940 w (br)	ν(C–H)
3010–3020 s (br)	2980 m	2980 s	
3075 m	3090 m	3090 w	ν(=CH)

[a] $\underset{\diagdown O \diagup}{-HC{-}CH_2}$ ring.

All the products were monomeric in refluxing benzene except $MeSi[OCH(CH_2Cl)CH_2OCH_2CH{=}CH_2]_3$ which appears to be dimeric in nature. On ageing, it turned into an insoluble transparent gel.

Infrared absorption spectra

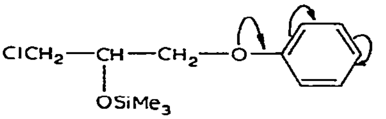
The characteristic IR absorption bands of the oxirane ring at 875, 915–930 and 1250–1275 cm^{-1} shown in the spectra of phenyl and allyl glycidyl ethers should disappear with the formation of chloro-substituted alkoxides. Absorption frequencies of these alkoxides (Tables 2 and 3) indicate the absence of 915–930 cm^{-1} bands. However, absorption bands in the range of 850–880 and 1250–1275 cm^{-1} due to methyl rocking and $\delta_s(CH_3)$ respectively have been observed in these derivatives.

Addition products of phenyl glycidyl ether gave characteristic absorption bands at 3055–3075 cm^{-1} due to =CH stretching and at 1510 and 1610 cm^{-1} for C=C skeletal in-plane vibrations. However, CH out-of-plane deformations of the aromatic ring in the range of 700–1000 cm^{-1} are probably overlapped with other fundamental modes of the molecules. The characteristic bands of the allyl group have been observed in the region of 3090 cm^{-1} and at 1635–1660 cm^{-1} due to =CH stretching and ν(C=C) modes[4] respectively.

Proton magnetic resonance spectral studies

PMR spectra of chloro-substituted alkoxysilanes, *e.g.* $Me_{4-n}Si[OCH(CH_2Cl)CH_2OR]_n$ where $R = C_2H_5$*, C_4H_9*, C_6H_5 or $CH_2CH{=}CH_2$ and $HSi[OCH(CH_2Cl)CH_2X]_3$* ($X = OC_2H_5$ or Cl) revealed the following:

(*i*). *Methyl protons* ($Me_{4-n}Si$). All the compounds showed a sharp singlet at τ 9.72–9.86 (Table 4) due to methyl protons of the silylmethyl group. A slight downfield shift of methyl protons signals in the compounds, (where $R = C_6H_5$), may be expected on the basis of the following electron displacements:



(I)

(*ii*). *Methylene protons* (CH_2Cl *and* CH_2OR). Methylene protons adjacent to oxygen (CH_2OR) and chlorine (CH_2Cl) are chemically nonequivalent, yet they appear to give signals in the same range. Even a quartet due to methylene protons of ethyl group, *i.e.* OCH_2CH_3 seems to overlap the doublets of CH_2Cl and CH_2O protons; this results in a complex multiplet between τ 6.38–6.52 in the spectra of $MeSi[OCH(CH_2Cl)CH_2OC_2H_5]_3$ and τ 6.4–6.58 in $Me_2Si[OCH(CH_2Cl)CH_2OC_2H_5]_2$.

An attempt has been made to ascertain the tentative positions of CH_2Cl and CH_2O protons by spin decoupling of the methyl protons of ethyl group; this gave a singlet due to methylene protons of OCH_2CH_3 group.

On the basis of Paulings' electronegativity scale, the change in the chemical shift of methyl protons in compounds like $X(CH_3)_n$ where $X = F$, Cl, Br, I, O, N and S) appears to be governed by the electronegativity of the atom[5]. Likewise, CH_2O

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* Syntheses of these derivatives are reported in previous communication.

TABLE 4

PROTON CHEMICAL SHIFTS OF CHLOROSUBSTITUTED ALKOXYSILANES AND CHLOROHYDRIN ETHERS

Compound	*Chemical shifts, τ*[a]			
	MeSi	*CH_2Cl and CH_2O*	*OCH*	*Other protons*
$ClH_2C\underset{\substack{\vert \\ OSiMe_3}}{C}HCH_2OC_4H_9$	9.86	6.42–6.62, m	5.96–6.3, m	8.5 and 9.05, complex m, C_3H_7
$ClH_2C\underset{\substack{\vert \\ OSiMe_3}}{C}HCH_2OC_6H_5$	9.82	6.40 and 6.0	5.70–5.85, m	2.55–3.18, complex m, C_6H_5
$ClH_2C\underset{\substack{\vert \\ OSiMe_3}}{C}HCH_2OCH_2CH=CH_2$	9.84	6.42–6.62, m	6.08–6.32, m	5.92–6.02, $OCH_2CH=CH_2$ 3.8–4.9, m, $CH=CH_2$
$Me_2Si[OCH(CH_2Cl)CH_2OC_2H_5]_2$	9.80	6.40–6.58, m[b]	5.75–6.02, m	8.78, t, CH_3C
$Me_2Si[OCH(CH_2Cl)CH_2OC_6H_5]_2$	9.72	6.32 and 5.98	5.52–5.82, m	2.58–3.20, complex m, C_6H_5
$Me_2Si[OCH(CH_2Cl)CH_2OCH_2CH=CH_2]_2$	9.80	6.38–6.56, m	5.62–5.82, m	5.92, $OCH_2CH=CH_2$ 3.82–4.90, complex m, $CH=CH_2$
$MeSi[OCH(CH_2Cl)CH_2OC_2H_5]_3$[c]	9.78	6.38–6.52, m	5.52–5.88, m	8.80, t, CH_3C
$HSi[OCH(CH_2Cl)CH_2OC_2H_5]_3$		6.30–6.50, m	5.60–5.78, m	5.52, HSi 8.80, t, CH_3CO
$HSi[OCH(CH_2Cl)_2]_3$		6.28	5.45–5.70, m	5.32, HSi
$ClH_2CCHOHCH_2OC_2H_5$		6.35–6.50, m[b]	5.90–6.15, m	6.20, OH 8.85, t, CH_3CO
$ClH_2CCHOHCH_2OC_4H_9$		6.37–6.55, m[b]	5.90–6.25, m	6.05, OH $\left.\begin{array}{l}9.05\\8.5\text{–}8.55\end{array}\right\}$ m, C_3H_7CO

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[a] m = multiplet, t = triplet. [b] Quartet due to OCH_2 group overlaps the doublets of CH_2Cl and CH_2O protons. [c] After spin-decoupling of OCH_2CH_3, signals due to CH_2Cl and CH_2O are observed at 6.52 and 6.40 respectively.

protons should give signals at a lower field relative to CH_2Cl proton signals. Thus, the doublets at τ 6.40 and 6.52 may be tentatively ascribed to CH_2O and CH_2Cl protons respectively in the spectrum of $MeSi[OCH(CH_2Cl)CH_2OC_2H_5]_3$.

The positions of CH_2Cl and CH_2O proton signals have been further revealed from the spectra of $Me_3SiOCH(CH_2Cl)CH_2OC_6H_5$ and $Me_2Si[OCH(CH_2Cl)CH_2$-$OC_6H_5]_2$ which gave two distinct signals at τ 6.32 and 5.98 due to CH_2Cl and CH_2O protons respectively, in the latter compound. The downfield shift of the vicinal methylene protons in these phenyl derivatives as compared with those of $Me_{4-n}Si$-$[OCH(CH_2Cl)CH_2OC_2H_5]_n$, *i.e.*: $-CH_2OC_6H_5$, τ 5.98; $-CH_2OC_2H_5$, τ 6.40, may be due to the deshielding effect of the ring current associated with the conjugated system. A similar observation has been made in certain organic molecules[6] also, *e.g.*, $-CH_2OPh$, τ 6.10; $-CH_2O$alkyl, τ 6.60.

(*iii*). *Methine protons* (*OCH*). All the chloro-substituted alkoxides showed a multiplet due to OCH protons in the range of τ 5.52–6.32. In this case a downfield shift of the methine proton in phenyl derivatives may be explained on similar lines as mentioned for the corresponding methylene protons, $(CH_2OC_6H_5)$: Me_3SiOCH-$(CH_2Cl)CH_2OC_6H_5$, τ 5.70–5.85; $Me_3SiOCH(CH_2Cl)CH_2OC_4H_9$, τ 5.96–6.30. A complex multiplet at τ 2.55–3.20 for aromatic protons has been observed in the phenyl compounds. Allyl compounds showed a complex multiplet at τ 3.8–4.9 due to $CH{=}CH_2$ protons. The position of downfield $CH{=}CH_2$ signals may be attributed to the circulation of electrons in the plane containing sp^2 carbon orbitals, which tend to deshield the nuclei lying in that plane. The deshielding effect has also been shown in the chemical shift of vicinal methylene protons, *i.e.*, $CH_2CH{=}CH_2$ (*cf.* ref. 7).

A singlet at τ 5.32 and 5.52 in the spectra of $HSi[OCH(CH_2Cl)]_3$ and HSi-$[OCH(CH_2Cl)CH_2OC_2H_5]_3$ respectively may be ascribed to the H–Si proton. Voronkov[8] has reported an H–Si signal at τ 5.74 in the spectrum of $HSi(OEt)_3$.

Apart from the identification of the chlorosilanes, PMR spectra also provide evidence for the normal mode of ring fission during the course of such reactions, as the positions of methylene and methine protons in these derivatives are in almost the same range as in the corresponding chlorohydrin ethers, *i.e.*, $ClH_2C{-}CH(OH){-}CH_2OR$. Ishii and coworkers[9] have arrived at similar conclusions from PMR spectra of the insertion products obtained from (trimethylsilyl)dialkylamine with epoxides.

EXPERIMENTAL

Alkylchlorosilanes and glycidyl ethers were fractionally distilled before use. The compounds were analysed by previously described methods[1]. IR spectra of the neat compounds were recorded on a UR-10 double beam IR spectrophotometer having KBr and NaCl prisms. PMR spectra were recorded with Japan Electron Optics C-60H spectrometer in CCl_4 at 20°.

Interaction of methyltrichlorosilane and allyl glycidyl ether (1/3 *molar ratio*)

Allyl glycidyl ether (4.13 g) was added gradually to cooled methyltrichlorosilane (2.10 g). The reaction being highly exothermic, contents started boiling on the addition of glycidyl ether and turned into yellowish liquid. The mixture was then heated at 85–90° for about 30 h. Absence of ionisable chlorine in the reaction mixture indicated the completion of the reaction.

The highly viscous liquid obtained was subjected to vacuum distillation. It turned into a brownish foamy solid at 0.3 mmHg at a bath temp. of 180°. (Found in crude product: Cl, 21.67; Si, 5.66; mol.wt., 844. Found in residue: Cl, 20.61; Si, 7.40. Cl_3Si calcd.: Cl, 21.62; Si, 5.71%; mol.wt., 492.)

Details of other similar reactions are given in Table 1.

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