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SYNTHESIS OF ALKOXYSILANES BY INSERTION REACTIONS OF HALOSILANES WITH CYCLIC ETHERS

R. C. MEHROTRA AND P. BAJAJ
The Chemical Laboratories, University of Rajasthan, Jaipur (India)

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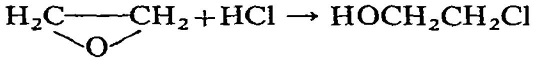
SUMMARY

A number of new chloro-substituted alkoxysilanes have been synthesised by the interaction of R_nSiCl_{4-n} ($R = H$, CH_3, C_2H_5, C_6H_5 and $CH{=}CH_2$ and $n = 1, 2, 3$) with epichlorohydrin (2,3-epoxypropyl chloride) and ethyl and butyl glycidyl ether (ethyl and butyl 2,3-epoxypropyl ether). The silicon atom becomes attached through oxygen to the secondary carbon atom.

INTRODUCTION

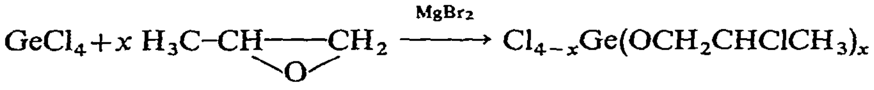
Reactions of silicon halides with ethylene oxide have been reported by Sauer and Patnode[1] and it has been suggested that these may occur through an intermediate step (1) initiated by traces of hydrogen chloride present in the system:



$$\underset{\diagdown O \diagup}{H_2C\text{——}CH_2} + HCl \rightarrow HOCH_2CH_2Cl \qquad (1)$$

$$SiCl_4 + 4\,HOCH_2CH_2Cl \rightarrow Si[OCH_2CH_2Cl]_4 + 4\,HCl \qquad (2)$$

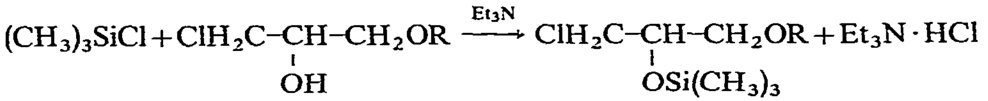
In recent publications, Lavigne and coworkers[2-4] have studied the reactions of halogermanes on cyclic ethers in the presence of magnesium bromide:



$$GeCl_4 + x\,H_3C\text{–}\underset{\diagdown O \diagup}{CH\text{——}CH_2} \xrightarrow{MgBr_2} Cl_{4-x}Ge(OCH_2CHClCH_3)_x$$

($x = 1, 2, 3$ or 4)

In these, as well as other insertion reactions carried out with germanium halides in our laboratories, the formation of alkoxy germanium derivatives cannot occur through the initial formation of the alcohol in view of the well known non-reactivity of alcohols with germanium halides in the absence of a base[5]. The reactivity of silicon halides also decreases with alkyl substitutions and it has been observed during the course of the present investigations that the reaction of trimethylchlorosilane with 3-chloro-2-hydroxy-n-propyl ethyl or butyl ether could not be taken to completion even after long refluxing unless a base was present:

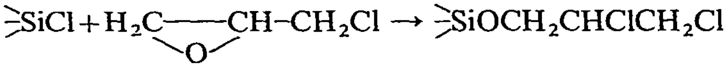


$$(CH_3)_3SiCl + ClH_2C\text{-}\underset{\displaystyle OH}{CH}\text{-}CH_2OR \xrightarrow{Et_3N} ClH_2C\text{-}\underset{\displaystyle OSi(CH_3)_3}{CH}\text{-}CH_2OR + Et_3N\cdot HCl$$

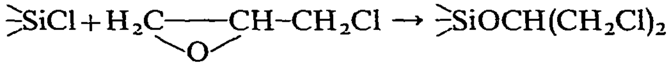
($R = C_2H_5$ or C_4H_9)

Titanium and zirconium tetraalkoxides have also been synthesised by the reactions of their halides with cyclic ethers[6]. In addition to metal halides, reactants possessing M–S, M–O or M–N bonds have also been utilised in such reactions; Abel and Walker[7] obtained the alkoxy silanes from the condensation of linear and cyclic thiosilanes and disilthianes with ethylene, propene and cyclohexene oxides. Some reactions of alkoxytriorganostannanes[8] and (trimethylsilyl)dialkylamine[9] with epoxides have also been attempted.

Reactions of epichlorohydrin (2,3-epoxypropyl chloride) with organochlorosilanes have been studied by Andrianov and coworkers[10], who reported that the silicon moiety becomes attached through oxygen to the primary carbon atom:



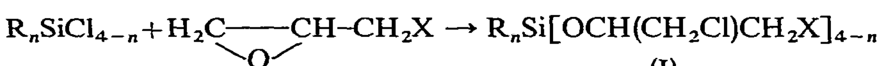
Later, Shostakovskii[11] and Malinovskii *et al.*[12] concluded that silicon atom actually becomes attached through oxygen to the secondary carbon atom as represented below:



The main evidence in support of their conclusions was that aqueous chromate oxidation gave $CO(CH_2Cl)_2$ only.

RESULTS AND DISCUSSION

We now report a detailed study of the reactions of chlorosilanes with cyclic ethers:



(I)

($R = H, CH_3, C_2H_5, C_6H_5$ or $CH{=}CH_2$; $n = 1, 2, 3$; $X = Cl, OC_2H_5$ or OC_4H_9)

The identity of the products (I) was confirmed by unambiguous synthesis involving reaction of the corresponding alcohols with the appropriate chlorosilanes.

The halosilane was refluxed with the cyclic ether in benzene at a bath temperature of 60–100° for 4–40 h. In spite of the exothermic nature of the reactions they required a long reflux time for completion. Diphenyldichlorosilane with glycidyl ether (2,3-epoxypropyl ethyl ether) failed to give a bis-compound, and yielded only the mono-substituted product even after refluxing for 120–130 h.

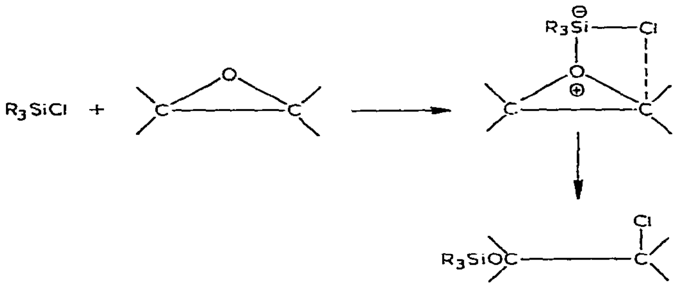
The reactivity of chlorosilanes tends to decrease with the increase in the number of alkyl groups attached to silicon, and the complete reactivity sequence observed was:

$$HSi > CH_3Si > (CH_3)_2Si > (CH_3)_3Si \gg (Ph)_2Si$$

All the alkoxides obtained in the above reactions are volatile under reduced pressure and are monomeric in benzene.

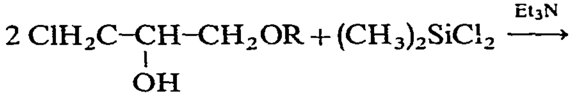
In general, the reactivity of the epoxide is determined by the accessibility of the epoxy group and the electron density around the epoxy oxygen. Substituents such as methylene and vinyl groups increase the reactivity towards acidic, electrophilic reagents. Propylene oxide, for example, is more reactive towards acid than is a glycidyl ether or epichlorohydrin[13]. In the present investigations it was observed that silicochloroform reacts more readily with glycidyl ether than with epichlorohydrin.

Since aluminium trichloride, and the tetrachlorides of silicon, tin or titanium behave as Lewis acids[13], it is reasonable to assume that the halosilane coordinates with the epoxy oxygen to assist in the transfer of a proton and the formation of an ether link:



Chlorosubstituted alkoxide

We have confirmed that the reaction proceeds through the normal fission of the epoxy ring in which the silicon moiety becomes attached through oxygen only to the secondary carbon atom[11]. This is shown by the nature of the products from the reactions of halosilanes with ethyl or butyl 3-chloro-2-hydroxy-n-propyl ether:



$$2\ ClH_2C\text{-}\underset{\displaystyle OH}{\underset{|}{C}H}\text{-}CH_2OR + (CH_3)_2SiCl_2 \xrightarrow{Et_3N}$$

$$\longrightarrow (CH_3)_2Si[OCH(CH_2Cl)CH_2OR]_2 + Et_3N \cdot HCl$$

$(R = C_2H_5 \text{ or } C_4H_9)$

The characteristic IR bands of the oxirane ring at 840, 912 and 1255 cm^{-1} (ref. 14) present in glycidyl ether spectra disappear on the formation of the alkoxide. Similarly with chlorohydrin ethers in which the reaction proceeds through the secondary alcoholic group, characteristic absorption bands at 1300 cm^{-1} and 3410 cm^{-1} [ν(O–H) bonded] disappear as the alkoxide is formed.

The alkoxysilanes prepared by the two different methods indicated showed identical IR spectra. For example, both the samples of $(CH_3)_2Si[OCH(CH_2Cl)\text{-}CH_2OC_4H_9]_2$ showed sharp bands at 832 cm^{-1} ν_s(Si–O), 936 cm^{-1} ν(C–C) and a split band (1090 cm^{-1} along with 1120 cm^{-1}) due to ν_{as}(Si–O–C) + ν(C–O) characteristic of the structural fragment (Si–O–C–C) in confirmation of the assignments made earlier by Voronkov[15] and other workers[16–19]. Bands at 688 cm^{-1} due to

TABLE 1. REACTIONS OF HALOSILANES WITH EPOXIDES

No.	Halosilane (g)	X in $\underbrace{H_2C\text{—}CH}_{O}CH_2X$ (g)	Molar ratio	Reaction conditions	B.p. of the product (°C/mm)	Yield (%)	Analysis (calcd.) Found (%) Si	Cl	Mol. wt. found (calcd.)	n_D^{35}
1	$HSiCl_3$ 3.79	Cl 7.76	1/3	Exothermic refluxed for 7 h at 70° bath temp.	182–185/3	86	6.9 (6.81)	51.3 (51.6)	405 (412)	1.4850
2	$HSiCl_3$ 0.76	OC_2H_5 1.74	1/3	Refluxed for 4 h at 60–65°	126–130/1	80	6.39 (6.37)	24.19 (24.12)	437 (441)	1.4455
3	$HSiCl_3$ 1.75	OC_4H_9 4.48	1/3	Refluxed for 5 h at 60–70°	195–198/0.5	77	5.52 (5.34)	20.4 (20.24)	534 (525)	1.4475
4	CH_3SiCl_3 1.35	OC_2H_5 2.76	1/3	Exothermic; refluxed for 22 h at 90–95°	155–158/2	75	6.24 (6.16)	23.22 (23.30)	466 (455)	1.4485
5	$C_2H_5SiCl_3$ 2.08	OC_2H_5 3.74	1/3	Refluxed for 30 h at 90–100°	170–172/0.4	77	6.07 (5.98)	22.4 (22.50)	466 (469)	1.4405
6	$C_2H_5SiCl_3$ 1.64	OC_4H_9 3.94	1/3	Refluxed for 33 h	195–200/0.4	75	5.12 (5.078)	19.3 (19.21)	553 (553)	1.4425
7	$(CH_3)_2SiCl_2$ 1.83	OC_2H_5 2.89	1/2	Slightly exothermic, refluxed for 22 h	115–118/2	75	8.21 (8.4)	21.29 (21.28)	338 (333)	1.4320
8	$(CH_3)_2SiCl_2$ 1.84	OC_4H_9 3.72	1/2	Refluxed for 26 h	152–155/2	72	7.19 (7.21)	18.1 (18.23)	389 (389)	1.4365
9	$(CH_3)_3SiCl$ 3.05	OC_2H_5 2.9	1/1	Refluxed for 40 h	108–110/60	89	13.25 (13.37)	16.9 (16.9)	211 (210)	1.4140
10	$(CH_3)_3SiCl$ 2.6	OC_4H_9 3.12	1/1	Refluxed for 45 h	124/40	85	11.58 (11.78)	14.9 (14.89)	237 (238)	1.4225
11	$C_6H_5SiCl_3$ 4.1	OC_2H_5 5.89	1/3	Refluxed for 35 h	120–124/0.3	64	5.45 (5.43)	20.8 (20.5)	508 (517)	1.4725
12	$C_6H_5SiCl_3$ 1.63	OC_4H_9 3.0	1/3	Refluxed for 38 h	192–195/0.5	56	4.69 (4.66)	17.6 (17.66)	607 (601)	1.4735
13	$H_2C{=}CHSiCl_3$ 2.49	OC_2H_5 4.82	1/3	Refluxed for 22 h	170–174/5	75	6.03 (6.0)	22.79 (22.74)	462 (467)	1.4470
14	$H_2C{=}CHSiCl_3$ 3.27	OC_4H_9 7.9	1/3	Refluxed for 30 h	145–148/2	73	5.1 (5.08)	18.95 (19.2)	556 (551)	1.4485

ν_s(Si–C); 855 cm^{-1} due to CH_3 rocking (sym); 1260 cm^{-1} due to $\delta_s(CH_3)$; 1450 cm^{-1} for $\delta_{as}(CH_3)$ and 740 cm^{-1} due to ν(C–Cl) have also been observed.

EXPERIMENTAL

Moisture was rigorously excluded. Chlorohydrin ethers and their corresponding glycidyl ethers were synthesised by Kuwamura's method[14], 1,3-dichloro-2-propanol was prepared from epichlorohydrin and hydrochloric acid. These reagents were dried over anhydrous sodium sulphate and vacuum-distilled before use. Freshly distilled halosilanes and anhydrous benzene were used.

Molecular weights were determined ebullioscopically in benzene and refractive indices with an Abbe refractometer. IR spectra were recorded in carbon tetrachloride on a Perkin–Elmer grating spectrophotometer model 337 with KBr optics.

Silicon

(*i*). In the case of monoalkyl, vinyl and phenyl compounds, silicon was estimated by decomposing the compound with a few drops of H_2SO_4 (concd. AR) and HNO_3 (concd. AR) in a platinum crucible and igniting to silica.

(*ii*). In dimethyl- and trimethylsilicon compounds, the following method for silicon estimation was adopted because of the higher volatility and the comparatively stable nature of carbon–silicon bond: 0.1–0.3 g of the compound was added to 30 ml H_2SO_4 (AR) in a 250 ml conical flask. The flask was cooled and 5 g each of solid ammonium sulphate (AR) and ammonium nitrate (AR) was added and kept overnight at room temperature and finally digested for 4 h. The solution was then cooled and diluted with water. The precipitate was filtered, dried and ignited to silica.

Chlorine

About 0.2–0.3 g sample was treated with 10 ml of ethanolamine (free of halogen) and then refluxed for 20 min with small amount of sodium. The system was then neutralised with nitric acid, cooled and analysed gravimetrically.

Reaction between trichlorosilane and epichlorohydrin

Epichlorohydrin (7.76 g) was added to trichlorosilane (3.79 g) during 6 h in benzene (20 ml) with cooling and gradual heating. Absence of ionizable chlorine in the reaction mixture indicated the completion of the reaction. After removal of the volatile fractions the residue was distilled under reduced pressure to give a colourless viscous liquid (86%); b.p. 182–185°/3 mm. (Found: Cl, 51.3; Si, 7.0. $C_9H_{16}Cl_6O_3Si$ calcd.: Cl, 51.5; Si, 6.8%.)

Details of other similar reactions are given in Table 1.

Reaction between diphenyldichlorosilane and ethyl glycidyl ether

Ethyl glycidyl ether (3.37 g) was added to diphenyldichlorosilane (4.17 g) in benzene (20 ml) and the mixture was refluxed for 120–125 h. Volatile fractions were removed under reduced pressure and the residue was vacuum distilled to give a colourless viscous liquid (67%); b.p. 158–162°/0.4 mm. (Found: ionic chlorine, 9.48; total chlorine, 19.2; Si, 7.96. $C_{17}H_{20}Cl_2O_2Si$ calcd.: ionic chlorine, 9.98; total chlorine, 19.96; Si, 7.9%.)

TABLE 2. REACTIONS OF HALOSILANES WITH CHLOROHYDRIN ETHERS AND 1,3-DICHLORO-2-PROPANOL

No.	Halosilane (g)	X in $ClCH_2CH(OH)CH_2X$ (g)	Et_3N (g)	Molar ratio	Reaction conditions	B.p. of the product formed (°C/mm)	Yield (%)	Analysis found (calcd.) (%)		Mol. wt. found (calcd.)	n_D^{35}
								Si	Cl		
1	$(CH_3)_3SiCl$ 1.67	OC_4H_9 2.54	1.69	1/1	Exothermic refluxed for 3 h	124–125/40	85	11.61 (11.78)	14.91 (14.89)	236 (238)	1.4225
2	$(CH_3)_3SiCl$ 3.88	OC_2H_5 4.87	3.56	1/1	Refluxed for 2 h	108–110/60	91	13.21 (13.37)	16.9 (16.9)	211 (210)	1.4140
3	$(CH_3)_2SiCl_2$ 2.14	OC_2H_5 5.52	2.98	1/2	Refluxed for 1–2 h	124–126/4	74	8.4 (8.43)	21.4 (21.28)	335 (333)	1.4319
4	$(CH_3)_2SiCl_2$ 2.1	OC_4H_9 5.17	3.2	1/2	Refluxed for 3 h	150–152/2	70	7.10 (7.21)	18.28 (18.23)	392 (389)	1.4425
5	CH_3SiCl_3 2.1	OC_2H_5 5.4	4.36	1/3	Refluxed for 4 h	158–160/2	73	6.11 (6.16)	23.42 (23.33)	455 (455)	1.4485
6	$C_6H_5SiCl_3$ 1.77	OC_2H_5 3.42	2.75	1/3	Refluxed for 7 h	124–126/0.4	65	5.48 (5.43)	21.07 (20.5)	534 (517)	1.4725
7	$HSiCl_3$ 5.77	Cl 16.7		1/3	Highly exothermic refluxed to remove HCl	182–185/3	93	6.84 (6.81)	51.1 (51.6)	415 (412)	1.4855
8	$C_2H_5SiCl_3$ 2.2	OC_2H_5 5.29	4.24	1/3	Refluxed for 4 h	176–178/0.8	70	6.05 (5.98)	22.45 (22.5)	467 (469)	1.4410
9	$C_2H_5SiCl_3$ 1.44	OC_4H_9 4.29	2.89	1/3	Refluxed for 4–5 h	192–195/0.1	70	5.09 (5.07)	19.3 (19.21)	554 (553)	1.4425
10	$C_6H_5SiCl_3$ 1.96	OC_4H_9 4.14		1/3	Refluxed for 34 h to remove the HCl liberated	195–198/0.7	66	4.7 (4.66)	17.9 (17.6)	620 (601)	1.473
11	$(C_6H_5)_2SiCl_2$ 2.91	OC_2H_5 3.13	2.52	1/2	Refluxed for 8 h	170–172/0.4	70	6.17 (6.14)	15.5 (15.51)	443 (457)	1.5045
12	$(C_6H_5)_2SiCl_2$ 2.79	OC_4H_9 3.67	2.44	1/2	Refluxed for 8–9 h	182–185/1.5	53	5.49 (5.47)	13.56 (13.81)	495 (512)	

Reaction between trimethylchlorosilane and 3-chloro-2-hydroxy-n-propyl butyl ether in presence of a base

Trimethylchlorosilane (1.67 g) was added gradually to a cooled mixture of 3-chloro-2-hydroxy-n-propyl butyl ether (2.54 g) and triethylamine (1.69 g) in benzene (20 ml). Reaction was exothermic, and triethylamine hydrochloride was precipitated immediately. The mixture was refluxed at 90–95° for 2 h. The $Et_3N \cdot HCl$ was filtered off, the solvent was removed under reduced pressure, and the residue distilled at 124°/40 mm (85%). (Found: Cl, 14.91; Si, 11.61. $C_{10}H_{23}ClO_2Si$ calcd.: Cl, 14.86; Si, 11.77%.)

The details of other reactions are given in Table 2.

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