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Preparation and Synthetic Applications of Alkyl Chlorosilicates

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Alkyl chlorosilicates of the type, $\text{Si}(\text{OR})_n\text{-Cl}_{4-n}$, obtainable by the action of silicon tetrachloride on an alcohol^{2,3} find some application in the synthesis of mixed silicate esters by further reaction with another alcohol,^{3,4} and in the synthesis of polysilicate esters by controlled hydrolysis.³

This paper presents the results of a study made to determine the most suitable conditions for synthesis of various types of silicate esters utilizing the alkyl chlorosilicates as intermediates.

Experimental

To avoid repetition of experimental details, the data pertaining to new compounds are presented in tabular form and, except as otherwise noted, the experiments described hereunder may be considered as typical.

Alkyl Chlorosilicates (*cf.* Table I).—The reaction was carried out in a 3-liter three-necked flask fitted with a

the flask was added, with cooling and over a period of two and one-half hours, 523 g. (9.0 moles) of allyl alcohol. The mixture was then transferred to the boiling flask of an all-glass fractionating column and heated rapidly to free it of dissolved hydrogen chloride. Fractionation of the remaining liquid at 32 mm. yielded, in one such experiment, the following: allyl trichlorosilicate, 6.1 g.; diallyl dichlorosilicate, 130.2 g.; triallyl chlorosilicate, 449.0 g.; allyl orthosilicate, 112.0 g.

If diallyl dichlorosilicate is desired as the major product, a 1.8:1 mole ratio of allyl alcohol to silicon tetrachloride is taken; and if allyl trichlorosilicate is desired the ratio should be 1.1:1.

The reverse order of addition, *i. e.* the addition of silicon tetrachloride to the alcohol, is unsatisfactory because relatively larger amounts of orthoester are formed and a considerable portion of the silicon tetrachloride is recovered.

Stability of Alkyl Chlorosilicates—Effect of Hydrogen Chloride and of Aluminum Chloride.—On attempting the synthesis of mixed esters by reaction of a pure alkyl chlorosilicate with an alcohol, it was observed in certain instances that the product consisted of a mixture of all

TABLE I^a

Formula	Name	B. p., °C. (mm.) ^b	Cl Analyses			
			Calcd.		Found	
$\text{Si}(\text{OCH}_3)_3\text{Cl}$	Methyl trichlorosilicate	79.0–79.5			82–86	
$\text{Si}(\text{OCH}_3)_2\text{Cl}_2$	Dimethyl dichlorosilicate	100.0–100.5			98–103	
$\text{Si}(\text{OCH}_3)_3\text{Cl}$	Trimethyl chlorosilicate	112.0–112.5			114.5–115.5	
$\text{Si}(\text{OC}_2\text{H}_5)_3\text{Cl}$	Ethyl trichlorosilicate	101.5–102.0			103–105	
$\text{Si}(\text{OC}_2\text{H}_5)_2\text{Cl}_2$	Diethyl dichlorosilicate	136.0–136.5			136–138	
		51.5–51.7 (32)				
$\text{Si}(\text{OC}_2\text{H}_5)_3\text{Cl}$	Triethyl chlorosilicate	156.0–156.5			155–157	
		68.5–69.0 (32)				
$\text{Si}(\text{OC}_3\text{H}_7)_3\text{Cl}$	Allyl trichlorosilicate	112.0–122.5 (atm.)	55.54	55.31	55.36	55.28
		35.5–36.0 (32)				
$\text{Si}(\text{OC}_3\text{H}_7)_2\text{Cl}_2$	Diallyl dichlorosilicate	80.5–81.0 (32)	33.28	33.48	33.42	33.40
$\text{Si}(\text{OC}_3\text{H}_7)_3\text{Cl}$	Triallyl chlorosilicate	114.2–114.8 (32)	15.11	14.95	15.06	15.10
$\text{Si}(\text{OC}_4\text{H}_7)_3\text{Cl}$	Methallyl trichlorosilicate	141.0–141.5	51.75	51.59	51.64	51.60
		53.0–53.5 (32)				
$\text{Si}(\text{OC}_4\text{H}_7)_2\text{Cl}_2$	Dimethallyl dichlorosilicate	88.5–89.0 (20)	29.40	29.26	29.28	
$\text{Si}(\text{OC}_4\text{H}_7)_3\text{Cl}$	Trimethallyl chlorosilicate	122.0–123.0 (20)	12.81	12.77	12.80	12.78
$\text{Si}(\text{OC}_2\text{H}_5)(\text{OC}_3\text{H}_7)_2\text{Cl}_2$	Ethyl allyl dichlorosilicate	66.0–66.5 (32)	35.26	35.19	35.10	
$\text{Si}(\text{OC}_2\text{H}_5)_2(\text{OC}_3\text{H}_7)\text{Cl}$	Diethyl allyl chlorosilicate	85.5–86.0 (32)	16.83	16.72	16.69	16.76
$\text{Si}(\text{OC}_2\text{H}_5)(\text{OC}_3\text{H}_7)_2\text{Cl}$	Ethyl diallyl chlorosilicate	98.0–99.0 (32)	15.92	15.82	15.79	17.86
$\text{Si}(\text{OC}_3\text{H}_7)(\text{OC}_6\text{H}_{11})_2\text{Cl}_2$	Allyl cyclohexyl dichlorosilicate	127.0–127.5 (32)	27.79	27.65	27.78	
$\text{Si}(\text{OC}_3\text{H}_7)_2(\text{OC}_6\text{H}_{11})\text{Cl}$	Diallyl cyclohexyl chlorosilicate	143.0–144.0 (32)	12.81	13.02	13.08	
$\text{Si}(\text{OC}_3\text{H}_7)(\text{OC}_6\text{H}_{11})_2\text{Cl}$	Allyl dicyclohexyl chlorosilicate	148.0–148.5 (2)	11.12	11.20	11.20	

^a The compounds of the methyl and ethyl series are not new, but are listed here because the boiling points given are believed to be more reliable than those given in the literature. ^b Boiling points are given for atmospheric pressure unless otherwise indicated. ^c See ref. 2.

mercury-sealed stirrer, dropping funnel and gas exit tube, all openings being protected by calcium chloride tubes. To 612 g. (3.6 moles) of silicon tetrachloride contained in

possible esters. Since it had been found that in both the hydrolysis and alcoholysis reactions of silicate esters acids have the effect of labilizing the alkoxy groups, it was thought that the disproportionation accompanying the reaction of the chlorosilicate with an alcohol was caused by the hydrogen chloride liberated.

No direct evidence in support of this interpretation was adduced. On the contrary, the great stability of a pure alkyl chlorosilicate and the absence of any effect of dry hydrogen chloride are shown by the following experiments.

(1) Pittsburgh Plate Glass Company Fellow, 1941–1943. Present address: Lindsay Light and Chemical Company, West Chicago, Illinois.

(2) Friedel and Crafts, *Ann. chim. phys.*, [4] 9, 5 (1866).

(3) Signer and Gross, *Ann.*, 485, 56 (1931).

(4) German Patent 625,077, May 24, 1938 (*C. A.*, 32, 7678 (1938)).

A sample of diethyl dichlorosilicate was heated under reflux for 118 hours without change, the entire sample distilling at 136.5–137.0°. Another sample was heated under reflux for 25 hours while dry hydrogen chloride was slowly bubbled through and was thereafter recovered unchanged. It is concluded that disproportionation requires the presence of a hydroxylic component in addition to the free acid.

Anhydrous aluminum chloride was found to cause extensive decomposition. A mixture of 56.7 g. of diethyl dichlorosilicate and 1.3 g. of aluminum chloride was heated under reflux and then distilled. The pot contents decomposed during the distillation, setting to a porous white solid which became brown on further heating. The distillate consisted chiefly of diethyl ether and none of the starting compound was recovered. Tri-*n*-amyl chlorosilicate under the same treatment behaved similarly, except that the distillate consisted chiefly of *n*-amylene and *n*-amyl alcohol in approximately equal amounts.

Preparation of Mixed Alkyl Chlorosilicates $[\text{Si}(\text{OR})_m(\text{OR}')_n\text{Cl}_{4-m-n}]$.—The action of silicon tetrachloride on a mixture of two alcohols leads to a complex mixture of compounds (15 possible components, *cf.* Fig. 1) which cannot be resolved by fractional distillation unless the boiling point relationships happen to be unusually favorable. Individual mixed alkyl chlorosilicates may be prepared in fair yields by treating a pure alkyl chlorosilicate with the calculated amount of alcohol under conditions such that disproportionation is minimized. This means generally that the reaction is carried out in the presence of a base such as isoquinoline, as in the example below.

Ethyl allyl dichlorosilicate was prepared in 26 mole per cent. yield by adding a cold solution of 1 mole of allyl alcohol in 150 ml. of benzene to a cold solution containing 1 mole of ethyl trichlorosilicate and 1.3 moles of isoquinoline in 200 ml. of benzene, using the apparatus previously described. The mixture is warmed to coagulate the isoquinoline hydrochloride and filtered, and the filtrate is subjected to fractional distillation at reduced pressure.

It is to be noted that the cyclohexyl radical shows a relatively low degree of lability in the silicate esters and quite satisfactory yields of mixed cyclohexyl allyl chlorosilicates were obtained without using a base. Thus, allyl trichlorosilicate treated with 1 mole of cyclohexanol yielded 50 mole per cent. cyclohexyl allyl dichlorosilicate and 13 mole per cent. dicyclohexyl allyl chlorosilicate.

The boiling points of the mixed chlorosilicates exhibit quite striking regularities. This is shown in Fig. 1 for the allyl-ethyl family of compounds.

Preparation of Mixed Orthoesters $\text{Si}(\text{OR})_n(\text{OR}')_{4-n}$ (*cf.* Table II).—Diethyl diallyl orthosilicate was prepared by adding 383 g. (0.66 mole) of cold dry allyl alcohol to a cold mixture of 56.7 g. (0.30 mole) of diethyl dichlorosilicate and 52.2 g. (0.66 mole) of dry pyridine. The reaction is strongly exothermic and during the addition the mixture is agitated in an ice-bath. The product is washed with several 50-ml. portions of cold water (ether is added if necessary to secure a clean separation of layers), dried over calcium chloride, and distilled under reduced pressure. The yields were 72–80% of theoretical. Equally satisfactory results are obtained by starting with diallyl dichlorosilicate and ethanol.

The preparation of mixed allyl-methyl esters by this procedure was unsatisfactory, possibly because of the higher susceptibility of the methyl esters to hydrolysis. A large quantity of gelatinous solid is formed, and the desired ester is obtained in 5–15% yield.

The preparation of the mixed esters containing glycol residues shown in Table II was carried out by the above-described procedure with the substitution of glycol for alcohol. Distillation of the glycol esters was not attempted in most instances.

Preparation of Disilicate Esters $(\text{RO})_2\text{SiOSi}(\text{OR})_2$.—Hexaethyl disilicate was prepared by adding 20 ml. of cold water to a cold mixture of 19.9 g. (0.1 mole) of triethyl chlorosilicate and 12.0 g. (0.13 mole) of pyridine. The two layers which formed were easily separated and the upper layer was washed several times with 20-ml. portions of 15% sodium chloride solution, then dried over calcium

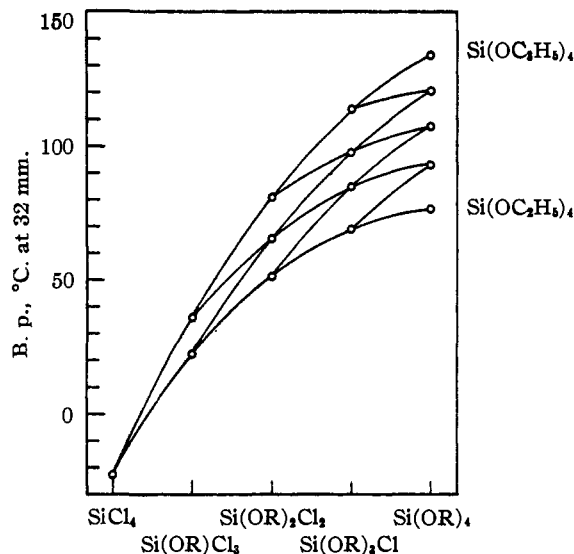


Fig. 1.—Boiling point relationships (at 32 mm. pressure) for the family of ethyl-allyl chlorosilicates.

chloride for eighteen hours. The product was then fractionally distilled at 3 mm. pressure, yielding 10.2 g. (60%) hexaethyl disilicate, b. p. 95.0–96.0 (3 mm.). This ester has previously been prepared by the action of silicon tetrachloride on ethanol⁶ and by the action of Si_2OCl_6 on ethanol.⁷ In this Laboratory it has also been prepared in 30% yield by the partial hydrolysis of ethyl orthosilicate.

Hexa-allyl disilicate and hexamethylalyl disilicate were prepared from the corresponding trialkyl chlorosilicates in 52 and 78% yields, respectively, following the above procedure but with the addition of some ether to the mixture to facilitate separation of layers. The procedure has also been applied successfully to the preparation of the symmetrical mixed esters shown in Table II, starting with the appropriate mixed trialkyl chlorosilicate.

Hydrolysis of Dialkyl Dichlorosilicates.—The hydrolysis of dialkyl dichlorosilicates in the presence of pyridine likewise results in the replacement of halogen without simultaneous replacement of alkoxy groups. The products are clear, viscous, non-volatile liquids having very nearly the correct analysis for a polymeric metasilicate, $[\text{Si}(\text{OR})_2]_n$. In the example below the preparation of such a product from a mixed dialkyl dichlorosilicate is described. In the absence of base, and with excess water, the hydrolysis proceeds to completion with the eventual separation of silica gel. When treated with 1 mole of water, in the absence of base, the hydrolysis is accompanied by disproportionation reactions with the formation of orthoester and silica.

The mixed metasilicate ester from allyl cyclohexyl dichlorosilicate was prepared by adding 150 ml. of ether saturated with water to a mixture of 34.4 g. (0.135 mole) of the dichlorosilicate and 25.6 g. (0.32 mole) of pyridine. Ice water was then added, the ether layer was separated and washed with several portions of water. After drying over calcium chloride, the ether was evaporated and other volatile materials were removed by heating at 100° under 2 mm. pressure. There remained 25.4 g. of a nearly colorless viscous liquid. *Anal.* Calcd. for $\text{Si}(\text{O}(\text{C}_2\text{H}_5)(\text{OC}_6\text{H}_{11}))_2$: Si, 14.01. Found: Si, 13.72, 13.67.

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(5) Friedel and Crafts, *Bull. soc. chim.*, [1] 5, 238 (1863).

(6) Friedel and Ladenburg, *Ann.*, 147, 362 (1868).

(7) Schumb and Holloway, *This Journal*, 63, 2753 (1941).

TABLE II
 SILICATE ESTERS PREPARED FROM CHLOROSILICATES

Formula	Name	°C.	B. p. Mm.	n_D^{20}	Silicon, %		
					Calcd.	Found	
$\text{Si}(\text{OC}_3\text{H}_7)_2(\text{OCH}_3)$	Methyl triallyl orthosilicate	116.0-116.3	34	1.4252	12.18	12.21	12.20
$\text{Si}(\text{OC}_3\text{H}_7)_2(\text{OCH}_2)_2$	Dimethyl diallyl orthosilicate	94.7-95.0	34	1.4110	13.73	13.82	13.85
$\text{Si}(\text{OC}_3\text{H}_7)(\text{OCH}_2)_3$	Trimethyl allyl orthosilicate	70.5-70.8	34	1.3919	15.74	15.89	15.89
$\text{Si}(\text{OC}_3\text{H}_7)_3(\text{OC}_2\text{H}_5)$	Ethyl triallyl orthosilicate	121.0-121.5	34	1.4230	11.49	11.50	11.51
$\text{Si}(\text{OC}_3\text{H}_7)_2(\text{OC}_2\text{H}_5)_2$	Diethyl diallyl orthosilicate	107.5-108.0	34	1.4098	12.08	12.12	12.16
$\text{Si}(\text{OC}_3\text{H}_7)(\text{OC}_2\text{H}_5)_3$	Triethyl allyl orthosilicate	93.5-94.0	34	1.3973	12.74	12.89	12.91
$\text{Si}(\text{OC}_3\text{H}_7)_4(\text{OC}_3\text{H}_7)$	Isopropyl triallyl orthosilicate	74.5-75.0	2	1.4204	10.86	10.92	10.95
$\text{Si}(\text{OC}_3\text{H}_7)_2(\text{OC}_3\text{H}_7)_2$	Diisopropyl diallyl orthosilicate	57.5-58.0	2	1.4075	10.78	10.82	10.85
$\text{Si}(\text{OC}_3\text{H}_7)_3(\text{OC}_4\text{H}_9)$	Isobutyl triallyl orthosilicate	85.5-86.5	3	10.30	10.31	10.30
$\text{Si}(\text{OC}_3\text{H}_7)_2(\text{OC}_4\text{H}_9)_2$	Diisobutyl diallyl orthosilicate	91.0-91.5	3	9.73	9.70	9.71
$\text{Si}(\text{OC}_3\text{H}_7)_3(\text{OC}_4\text{H}_9)$	<i>s</i> -Butyl triallyl orthosilicate	74.5-75.0	2	1.4242	10.30	10.36	10.33
$\text{Si}(\text{OC}_3\text{H}_7)_2(\text{OC}_4\text{H}_9)_2$	<i>t</i> -Butyl triallyl orthosilicate	73.0-73.5	2	1.4212	10.30	10.33	10.30
$\text{Si}(\text{OC}_3\text{H}_7)_3(\text{OC}_4\text{H}_9)_2$	Di- <i>t</i> -butyl diallyl orthosilicate	61.5-62.0	2	1.4121	9.73	9.70	9.78
$\text{Si}(\text{OC}_3\text{H}_7)_4(\text{OC}_6\text{H}_{11})$	Cyclohexyl triallyl orthosilicate	104.5-105.5	3	9.40	9.33	9.38
$\text{Si}(\text{OC}_3\text{H}_7)_2(\text{OC}_6\text{H}_{11})_2$	Dicyclohexyl diallyl orthosilicate	128.0-129.0	3	8.24	8.31	8.28
$\text{Si}(\text{OC}_3\text{H}_7)_3(\text{OC}_6\text{H}_{11})_2$	Cetyl triallyl orthosilicate	225.0-228.0	2	1.4440	6.38	6.38	6.33
$\text{Si}(\text{OC}_4\text{H}_7)_2(\text{OCH}_3)$	Methyl trimethallyl orthosilicate	128.0-128.5	18	1.4320	10.30	10.38	10.31
$\text{Si}(\text{OC}_4\text{H}_7)_2(\text{OCH}_2)_2$	Dimethyl dimethallyl orthosilicate	114.5-115.0	34	1.4156	12.08	12.16	12.12
$\text{Si}(\text{OC}_4\text{H}_7)(\text{OCH}_2)_3$	Trimethyl methallyl orthosilicate	83.0-83.5	34	1.4003	14.60	14.68	14.63
$\text{Si}(\text{OC}_4\text{H}_7)_3(\text{OC}_2\text{H}_5)$	Ethyl trimethallyl orthosilicate	133.0-133.5	18	1.4275	9.80	9.84	9.83
$\text{Si}(\text{OC}_4\text{H}_7)_2(\text{OC}_2\text{H}_5)_2$	Diethyl dimethallyl orthosilicate	115.5-116.0	18	1.4200	10.78	10.86	10.82
$\text{Si}(\text{OC}_4\text{H}_7)(\text{OC}_2\text{H}_5)_3$	Triethyl methallyl orthosilicate	92.5-93.0	18	1.4051	11.97	12.02	12.06
$\text{Si}(\text{OC}_4\text{H}_7)_3(\text{OC}_3\text{H}_7)$	Isobutyl trimethallyl orthosilicate	117.0-118.0	3	1.4306	8.92	8.91	8.93
$\text{Si}(\text{OC}_4\text{H}_7)_2(\text{OC}_3\text{H}_7)_2$	Diisobutyl dimethallyl orthosilicate	114.0-115.0	3	1.4216	8.87	8.85	8.83
$\text{Si}(\text{OC}_4\text{H}_7)(\text{OC}_3\text{H}_7)_3$	Triisobutyl methallyl orthosilicate	106.5-107.5	3	1.4135	8.81	8.86	8.80
$\text{Si}(\text{OC}_4\text{H}_7)_2(\text{OC}_3\text{H}_7)_2$	Di- <i>t</i> -butyl dimethallyl orthosilicate	82.0-83.0	2	1.4219	8.87	8.83	8.81
$\text{Si}(\text{OC}_5\text{H}_9)_2(\text{OC}_2\text{H}_5)_2$	Diethyl difurfuryl orthosilicate	112.5-123.5	3	8.98	9.05	9.05
$\text{Si}(\text{OC}_5\text{H}_9)(\text{OC}_2\text{H}_5)_3$	Triethyl furfuryl orthosilicate	85.5-86.5	3	10.78	10.83	10.81
$[(\text{C}_2\text{H}_5\text{O})_2\text{SiO}]_2(\text{C}_2\text{H}_4)$	Ethylene glycol bis-(triallyl silicate)	1.4391	12.24	12.19	12.22
$[(\text{C}_2\text{H}_5\text{O})_2\text{SiO}]_2(\text{C}_2\text{H}_4)_2\text{O}$	Diethylene glycol bis-(triallyl silicate)	1.4442	11.17	11.29	11.30
$[(\text{C}_4\text{H}_7\text{O})_2\text{SiO}]_2(\text{C}_2\text{H}_4)$	Ethylene glycol bis-(trimethallyl silicate)	1.4487	10.34	10.21	10.16
$[(\text{C}_4\text{H}_7\text{O})_2\text{SiO}]_2(\text{C}_2\text{H}_4)_2\text{O}$	Diethylene glycol bis-(trimethallyl silicate)	1.4510	9.56	9.34	9.33
$[(\text{C}_2\text{H}_5\text{O})_3\text{Si}]_2\text{O}$	Hexaethyl disilicate	95.5-96.5	3	16.39	16.50	16.47
$[(\text{C}_3\text{H}_7\text{O})_3\text{Si}]_2\text{O}$	Hexaallyl disilicate	160.0-161.0	10	1.4394	13.54	13.38	13.34
$[(\text{C}_4\text{H}_7\text{O})_3\text{Si}]_2\text{O}$	Hexamethallyl disilicate	176.0-178.0	4	1.4414	11.25	11.19	11.16
$[(\text{C}_3\text{H}_7\text{O})_2(\text{C}_2\text{H}_5\text{O})_2\text{Si}]_2\text{O}$	<i>sym</i> -(Tetraethyl diallyl disilicate)	149.0-151.0	18	1.4080	15.31	15.27	15.25
$[(\text{C}_3\text{H}_7\text{O})(\text{C}_6\text{H}_{11}\text{O})_2\text{Si}]_2\text{O}$	<i>sym</i> -(Tetracyclohexyl diallyl disilicate)	9.63	9.76	9.79

Summary

1. The preparation of some new series of alkyl chlorosilicates, including mixed types, is reported.

2. It is shown that the halogens may be replaced by alkoxy or oxy groups without affecting

the original alkoxy groups on treatment with an alcohol or with water in the presence of a tertiary amine. This technique has been used to prepare various mixed orthosilicate, disilicate and polysilicatesilicate esters.

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