[Contribution from the Research Laboratory of the General Electric Co.]

Chlorinated Aromatic Silicates and Related Compounds

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Twelve chlorinated aromatic silicates were synthesized from phenols with either chlorosilanes or ethyl orthosilicate, and from sodium phenates and silicon tetrachloride. Phenol and di-*t*-butoxydiaminosilane formed diphenoxydi-*t*-butoxysilane. All the compounds were white solids or colorless liquids having a wide liquid range, and they all had a strong phenolic odor even when highly purified. The hydrolytic stability of the chlorinated aromatic silicates, even those in which all *ortho* positions were blocked, was no better than that of unchlorinated aromatic silicates. The intrinsic thermal stability of 2-chlorophenyl orthosilicate was about the same as that of cresyl silicate, but was decidedly inferior to cresyl silicate in the presence of metals at 400°.

Although aromatic orthosilicates have been known since 1885[1] and have recently been offered commercially,[2] little has been reported about chlorinated aromatic silicates.[3-5] We have synthesized a variety of chlorinated aromatic silicates, including some with both *ortho* positions blocked, with the thought that these compounds might have enhanced hydrolytic stability.

The compounds prepared are listed in Table I together with their physical properties, analyses and methods of synthesis. All the materials were white solids or colorless liquids having a wide liquid range, and they all had a strong phenolic odor even when highly purified.

We applied conventional methods of synthesis to the preparation of these compounds, *i.e.*, reaction of: A) phenols with chlorosilanes[1,6]; B) sodium phenates with silicon tetrachloride[7]; C) phenols with ethyl orthosilicate; and D) one phenol with an aminosilane. The application of these methods to the preparation of analogous compounds has recently been described.[3]

The method of synthesis involving the reaction of silicon tetrachloride with chlorophenols proved quite satisfactory with those having no more than one *ortho* substituent. With 2,4,6-trichlorophenol, no reaction occurred with boiling silicon tetrachloride. The sodium salts of both 2,4,6-trichlorophenol and pentachlorophenol reacted satisfactorily with silicon tetrachloride to give the corresponding orthosilicates. The acid-catalyzed reaction of phenols with ethyl orthosilicate gave both chlorophenoxysilanes and chlorophenoxyethoxysilanes, depending on the molar proportions of the reactants.

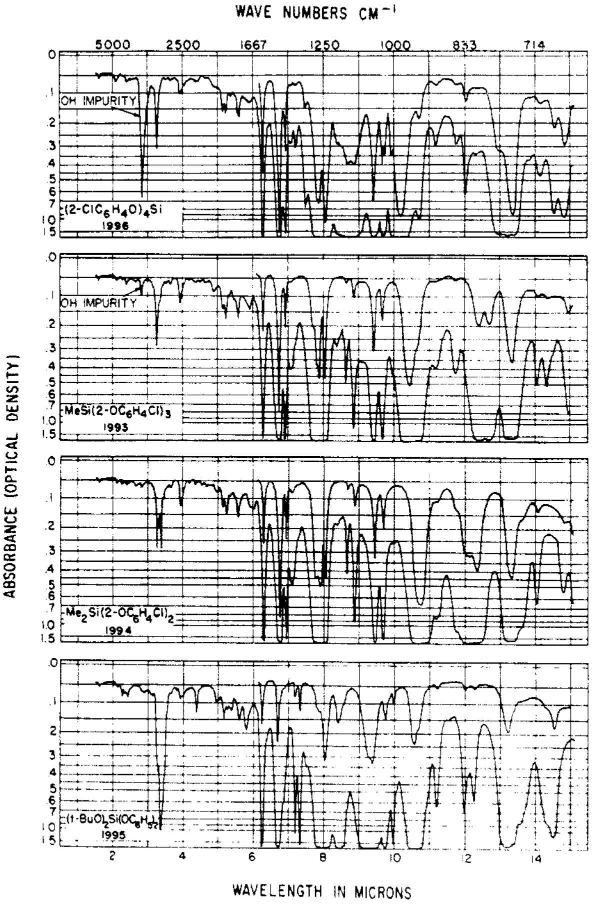

Fig. 1. Infrared spectra of representative compounds. Perkin Elmer Model 21 spectrometer with rock salt prism. Sample thickness: Upper curve a capillary layer; lower curve 0.030 mm.

The chlorinated aromatic silicates were no more resistant to hydrolysis than unsubstituted aromatic silicates. Extensive hydrolysis in boiling water occurred even with 2,4,6-trichlorophenyl orthosilicate, in which all *ortho* positions are blocked; the analogous borate appeared to be even more sensitive toward hydrolysis.[11] On the other hand, di-*t*-butoxydiphenoxysilane did exhibit improved hydrolytic stability; it was unaffected by boiling water,

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(1) J. Hertkorn, *Ber.*, **18**, 1679 (1885).

(2) Notably by Monsanto Chemical Co., Oronite Chemical Co., Dow Corning Corp. and Kay-Fries Chemicals Inc. in the United States. Tonnage amounts are also said to be produced in Europe.

(3) J. L. Speier, Jr., *J. Am. Chem. Soc.*, **74**, 1003 (1952); U. S. Patent **2,611,778**, September 23, 1952.

(4) R. Schwarz and W. Kuchen, *Ber.*, **86**, 1144 (1953).

(5) H. Jorg and J. Stetter, *J. fur Prakt. Chem.*, **117**, 305 (1927), have reported the synthesis of a number of bromophenoxy silicon compounds.

(6) L. H. Johnston, U. S. Patent **2,335,012**, November 23, 1943.

(7) R. A. Thomson and F. S. Kipping, *J. Chem. Soc.*, 1176 (1929).

TABLE I

PROPERTIES OF AROMATIC SILICATES

Compound	Method	Yield, %	M.P.	B.P., 1 mm.	n_D^{20}	d^{20}	Analyses Calcd.	Analyses Found
$(2\text{-}ClC_6H_4O)_4Si$[a]	A	74	−40[b]	287–290	1.5378	1.364[c]	R$_D$, 0.2447 Cl, 26.3	0.2467 25.9, 26.0
$(4\text{-}ClC_6H_4O)_4Si$[d]	A	76	74–75				Si, 5.21 Cl, 26.3	5.3, 5.4 26.0
$(2\text{-}ClC_6H_4O)_2(4\text{-}ClC_6H_4O)_2Si$[e]	A	89	−55[b,f]	280–293	1.5860	1.356	R$_D$, 0.2447	0.2475
$(2,4\text{-}Cl_2C_6H_3O)_4Si$	A[g]	59	198–199				Si, 4.16 Cl, 42.0	3.9, 4.2 40.1, 43.2
$(2,4,6\text{-}Cl_3C_6H_2O)_4Si$	B[h]	30	192–193	340–360			Si, 3.45 Cl, 52.4	3.6, 3.7 52.4, 52.4
$(Cl_5C_6O)_4Si$	B	30	285–286				Cl, 64.8	64.1, 60.2, 59.7[i]
$(2,4\text{-}Cl_2C_6H_3O)_2Si(OC_2H_5)_2$	C	23		[j]	1.5327		Cl, 31.8	31.0
$(2,4\text{-}Cl_2C_6H_3O)_3SiOC_2H_5$	C	11		273–275	1.5718		Cl, 37.8	36.5
$(2,4,6\text{-}Cl_3C_6H_2O)_2Si(OC_2H_5)_2$	C	26	68–69[k]	230–242			Si, 5.48 Cl, 41.6	5.4, 5.6 41.4, 41.5
$(2,4,6\text{-}Cl_3C_6H_2O)_3SiOC_2H_5$	C	24	81–82	288–293			Si, 4.22 Cl, 48.1	4.1 47.0, 47.2
$(2\text{-}ClC_6H_4O)_2Si(CH_3)_2$	A	32	2	127[l]	1.5482	1.227	R$_D$, 0.2586 C and H, 53.7, 4.5 Cl, 22.6	0.2588 53.1, 4.6 22.2
$(2\text{-}ClC_6H_4O)_3SiCH_3$	A	42		183	1.5742	1.318	R$_D$, 0.2498 C and H, 53.6, 3.6 Cl, 25.0	0.2504 53.9, 3.4 24.3
$(C_6H_5O)_2Si(OCMe_3)_2$	D	77		160	1.4905	1.029	R$_D$, 0.2791 C and H, 66.6, 7.8	0.2812 66.9, 8.0

[a] η(100°F) 21.6 cstks.; η(210°F) 3.8 cstks. ASTM flash point 276°; fire point 312°. [b] ASTM pour point. [c] Coefficient of expansion (25° to 350°): 0.00085 ml./g./°. [d] ASTM flash point 280°; fire point 312°. The synthesis of this compound was recently reported in references (3) and (4). [e] Made by the reaction of an equimolar mixture of 2-chlorophenol and 4-chlorophenol with silicon tetrachloride. η(100°F) 20.2 cstks.; η(210°F) 3.6 cstks. ASTM flash point 276°; fire point 314°. Probably a mixture of various *o*- and *p*-chlorophenoxysilanes. [f] Another sample had ASTM pour point −30°. [g] Also prepared by Method C in 25% yield, m.p. and mixed m.p. 198°–199°. [h] 2,4,6-Trichlorophenol did not react with silicon tetrachloride at reflux temperature. Refluxing with ethyl orthosilicate gave 90% of the theoretical amount of alcohol, but no effort was made to isolate the product. [i] A test with alcoholic silver nitrate proved the absence of hydrolyzable chlorine. The presence of silicon was qualitatively demonstrated. [j] Boiling point 227° to 231° at 5 mm. [k] This product depressed the melting point of 2,4,6-trichlorophenol. [l] Boiling point 269° to 270° at 149 mm.

but was hydrolyzed by boiling 10% sulfuric acid. Thus, the presence of *t*-alkoxy groups enhanced the hydrolytic stability of the neighboring phenoxy groups, just as it has been reported to stabilize alkoxy groups.[8] It seems probable that *t*-alkoxy groups would similarly impart enhanced hydrolytic stability to neighboring chlorophenoxy groups.

The thermal stability of 2-chlorophenyl orthosilicate was evaluated both in the presence and absence of air and metals. This compound proved to be superior to cresyl silicate and methyl silicone oil at 250° in the presence of air, and it was comparable to cresyl silicate in being superior to methyl silicone oil at 350° in the absence of air. However, 2-chlorophenyl silicate proved to be decidedly inferior to cresyl silicate in the presence of common metals at 350° to 400° in the absence of air.

EXPERIMENTAL

Starting materials. The chlorophenols used in this investigation were commercial materials whose properties after purification was as follows: 2-chlorophenol, redistilled b.p. 80° at 28 mm., m.p. 7°, n_D^{20} 1.5590; 4-chlorophenol, m.p. 42°; 2,4-dichlorophenol, m.p. 45° from heptane; 2,4,6-trichlorophenol, m.p. 69° after steam distillation and recrystallization from heptane; pentachlorophenol, m.p. 188° after decolorizing and recrystallization from benzene-heptane. Silicon tetrachloride from Stauffer Chemical Co. and ethyl orthosilicate from Carbide and Carbon Chemicals Corp. were used as received. The methylchlorosilanes were supplied by the Silicone Products Department of the General Electric Company. Di-*t*-butoxydiaminosilane was obtained from the Minnesota Mining and Manufacturing Co.

Methods of synthesis. The following are illustrative of the four methods used.[9] Specific details related to the various phenoxysilanes and chlorophenoxysilanes may be found in Table I.

A. *Chlorosilanes with phenols.* The simple apparatus con-

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(8) C. S. Miner, Jr., L. A. Bryan, R. P. Holysz, Jr., and G. W. Pedlow, Jr., *Ind. Eng. Chem.*, **39**, 1368 (1947).

(9) Direct chlorination of phenyl orthosilicate also appeared feasible, but we did not use this method extensively because of the isomeric mixtures likely to be obtained. Bubbling chlorine through a carbon tetrachloride solution of phenyl orthosilicate for 10 hr. in the presence of ferric chloride gave dichloro derivatives, b.p. 230° to 237° at 1 mm., as a major product. *Anal.* Calcd. for $C_{24}H_{18}O_4Cl_2Si$: Cl, 15.1. Found: Cl, 14.3.

sisted of a round bottom flask fitted with a dropping funnel thermometer well, and tap-water cooled reflux condenser surmounted by a Dry Ice–trichloroethylene cold finger, from which an exit line led through a drying tube and a water scrubber to the atmosphere. The cold finger was necessary to prevent serious loss of volatile chlorosilane starting materials by entrainment with evolved hydrogen chloride.

The chlorosilanes were added gradually to the stoichiometric amount of molten phenol, and the temperature of the reaction mixture was raised to 200° to 300° over a period of 7 to 20 hr. as permitted by the rate of refluxing and hydrogen chloride evolution. The shorter reaction times were realized in syntheses involving *p*-chlorophenol. The presence of a single *ortho*-chloro substituent retarded the reaction considerably, and 2,4,6-trichlorophenol did not react with boiling silicon tetrachloride.

The reactions of phenols with chlorosilanes were considered complete when the evolution of hydrogen chloride ceased and the theoretical weight loss had been attained. Completeness of reaction was found to be essential; otherwise the products were contaminated with difficultly removable by-products containing hydrolyzable chlorine. Use of excess phenol would probably be of value in this connection. While we used stoichiometric amounts of reactants, an excess of phenol actually prevailed, because of slight losses of chlorosilane by entrainment with hydrogen chloride. Too large an excess, particularly of the more volatile phenols, might unduly restrict the final reaction temperature and thus lead to incomplete reaction.

Distillation and/or recrystallization from hexane or chlorobenzene produced, on a 0.5- to 5.0-kg. scale, yields of 60 to 90% of purified product.

B. *Silicon tetrachloride with sodium phenates.* The sodium phenate was prepared by portion-wise addition of the theoretical amount of freshly cut sodium to a stirred, refluxing solution of the phenol in xylene. The preparation usually required about 0.5 hr. per mole, and 500 ml. to 1000 ml. of xylene was used per 100 g. of phenol.

The theoretical amount of silicon tetrachloride was then added to the cold, stirred sodium phenate suspension, and the reaction mixture was refluxed for 6 hr. Negative halogen tests on the reflux indicated the absence of unreacted silicon tetrachloride.

The precipitated salt was removed by filtration, and xylene was removed by distillation. Vacuum distillation and/or recrystallization from heptane or chlorobenzene produced, on a 100-g. scale, yields of 30% of purified product.

C. *Ethyl orthosilicate with phenols.* The acid-catalyzed reaction of phenols with ethyl orthosilicate gave both tetra(chlorophenoxy)silanes and chlorophenoxyethoxysilanes, depending upon the molar ratio of reactants. The reactions were carried out on a 200-g. scale by heating a mixture of ethyl orthosilicate, chlorophenol, and a few tenths of a gram of *p*-toluenesulfonic acid. At pot temperatures of 170–320°, the theoretical amount of ethanol was removed by distillation over a period of 10 hr. The crude products were purified by distillation and/or recrystallization from heptane.[10]

D. *Di-t-butoxydiphenoxysilane* was prepared from 110 g., (0.53 mole) of di-*t*-butoxydiaminosilane refluxed for 4 hr. with 99.6 g., 1.06 moles, of phenol. The theoretical weight of ammonia was evolved. Distillation gave 1.46 g. (0.41 mole) 77% yield of di-*t*-butoxydiphenoxysilane, b.p. 158–165° at 1 mm., n_D^{20} 1.4899. A yellow color and amine odor were removed by a quick wash with $1N$ hydrochloric acid, drying over anhydrous potassium carbonate, and redistillation. The final product was a colorless liquid having a mild phenolic odor, b.p. 160° at 1 mm., n_D^{20} 1.4905, d^{20} 1.029.

Hydrolysis. The chlorinated aromatic silicates showed hydrolytic stability comparable to that of unsubstituted aromatic silicates.[11] Two gram samples of diethoxydi(2,4,6-trichlorophenoxy)silane and ethoxytri(2,4,6-trichlorophenoxy)silane were boiled with distilled water for 2 hr. and steam distilled. The steam distillate contained appreciable amounts of 2,4,6-trichlorophenol, m.p. and mixed m.p. 68–69°. The residue from the steam distillation contained silica, a white solid which was solvent-insoluble and did not fuse on being heated to 340°. Roughly the same sensitivity toward boiling water was observed with tetra(2,4,6-trichlorophenoxy)silane and tetra(pentachlorophenoxy)silane.

On the other hand, di-*t*-butoxydiphenoxysilane survived boiling with water, but was extensively hydrolyzed by boiling 10% sulfuric acid. The extent of hydrolysis was following by testing the steam distillate with bromine water, which is reactive toward phenol but was relatively inert toward *t*-butyl alcohol and di-*t*-butoxydiphenoxysilane. When the latter was boiled with water for half an hour, the steam distillate showed no reaction with bromine water. However, upon boiling witih 10% sulfuric acid, the steam distillate gave a strong test for phenol, and a gelatinous precipitate appeared in the reaction flask.

Thermal behavior of 2-chlorophenyl orthosilicate. This compound was selected for comparison with cresyl silicate. Tests were carried out at 250° to 400° both on the presence and absence of air and metals.

The first experiments were carried out by heating the substances in open Pyrex Petri dishes in the same oven. The results were as follows:

	12 Hr. at 250°		24 Hr. at 250°	
Compound	Weight Loss, %[a]	Appearance	Weight Loss, %[a]	Appearance
Cresyl silicate[b]	48	Black, skinned, gummy	66	Black, brittle, solid
2-Chlorophenyl silicate	30	No change	52	Amber liquid

[a] These losses probably included a major proportion of simple volatilization loss. [b] Both a commercial sample of cresyl silicate and a sample prepared from it by careful fractional distillation gave the same results.

Tests were then carried out at 350° by heating under dry nitrogen, in Pyrex flasks fitted with reflux condensers. After 10 hr., both commercial cresyl silicate and 2-chlorophenyl silicate showed only a slight darkening. In neither case were solid or gummy by-products formed. The heating of 2-chlorophenyl silicate at 350° was continued. After 45 hr., there was no weight loss or viscosity increase; after 114 hr. (which accidentally included 0.5 hr. at 450°), there was a 1.5% weight loss and a 2-centistokes increase in viscosity.

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(10) E. Larsson, *Ber.*, **86**, 1382 (1953), has reported an analogous synthesis involving the preparation of dimethyldiphenoxysilane in 69% yield by heating dimethyldiethoxysilane with excess phenol and a small amount of sodium.

(11) Similar, if not more pronounced, hydrolytic instability was found in chlorinated aromatic borates. These were prepared by refluxing the appropriate chlorophenols with ethyl borate, which produced the theoretical amount of ethanol and substances presumed to be tri(2-chlorophenoxy)borane, b.p. 236–258° at 8 mm., and tri(2,4,6-trichlorophenoxy)borane, b.p. 267–271° at 10 mm. Both compounds were difficult to purify, presumably because of sensitivity to atmospheric moisture and traces of water. We were unable to obtain them pure in crystalline form in spite of efforts to exclude moisture. The synthesis of tri(2-chlorophenoxy)borane, b.p. 242° at 6 mm., m.p. 47–49°, has been reported; it was described as being very susceptible to hydrolysis by L. H. Thomas, *J. Chem. Soc.*, 820 (1946).

At the end of this treatment, the 2-chlorophenyl silicate was blackened but contained no sludge.

Thermal stability in the presence of metals was investigated by heating with metal strips under dry nitrogen in Pyrex flasks fitted with reflux condensers. Commercial cresyl silicate survived heating with black iron for 140 hr. at 350° substantially unchanged. Under the same conditions, 2-chlorophenyl silicate underwent a fivefold viscosity increase with black iron and a tenfold viscosity increase with cold-rolled steel and stainless steel. In another test at 400° for 50 hr. in the presence of cold-rolled steel, 2-chlorophenyl silicate decomposed to a black, sticky, solid mass while commercial cresyl silicate survived substantially unaffected.

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SCHENECTADY, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

Preparation of Polymeric Condensation Products Containing Functional Thiol Side Chains. Polyamides[1]

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The purpose of this work was to develop a general method of synthesis for a polyamide containing free sulfhydryl groups. Polyamides from hexamethylene diamine and the acid chlorides of α,α'-dibenzylthioadipic acid, the cyclic disulfide of α,α'-dimercaptoadipic acid, and α,α'-dicarbobenzoxythioadipic acid were prepared by the interfacial polymerization technique. Successful preparation of the polyamide with free sulfhydryl groups was achieved by quantitative removal of the carbobenzoxy group from the polyamide from hexamethylene diamine and α,α'-dicarbobenzoxythioadipic acid.

The importance of the sulfhydryl compounds in biological systems is well known.[3] In addition, their interest as reversible mercaptide-forming reagents as well as their recent applications as radioactive prophylactics has made synthesis of sulfhydryl-containing compounds of practical significance. We have reported[4] the synthesis of a polyurethan containing the sulfhydryl function in a structure of known constitution and environment and in this publication will describe the preparation of a sulfhydryl-containing polyamide.

The synthesis of polyamides requires, in general, exact molecular equivalence of reactants as well as very stringent reaction conditions, temperatures of 250° and above not being uncommon. The two synthetic approaches described, sought in the first instance to use a convenient method for obtaining the desired molecular equivalence, *e.g.*, intermediate salt formation, and in the second to employ a recently published[5] procedure for making high molecular weight polyamides under very mild reaction conditions, *i.e.*, interfacial polycondensation.

Benzylthiomethylsuccinic acid[4] would be expected to form a polymeric salt with a diamine suitable for subsequent polymerization by thermal dehydration. Only oils were obtained with hexamethylene diamine however, and with ethylene diamine a salt containing two acid molecules to one molecule of diamine was obtained. The unavailability of the second carboxyl group for salt formation is at present not understood.

We prepared *meso*-α,α'-dibenzylthioadipic acid by alkali-catalyzed displacement by benzyl mercaptan on *meso*-α,α'-dibromoadipic acid prepared by the method of Zanden[6] and found that it did not give a satisfactorily recrystallizable salt with ethylene diamine. A melting point range of 25° was observed even after five recrystallizations, as well as a small residue of the acid on addition of water.

The use of the *cis* cyclic disulfide of α,α'-dimercaptoadipic acid[7] prepared by Fredga, again did not yield a satisfactorily recrystallizable salt with hexamethylene diamine. Attempted thermal polymerization without recrystallization yielded an insoluble, infusible product. Cross-linking by a base catalyzed rupture of the disulfide bond[8] and/or

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[1] This is the 20th in a series of papers on new monomers and polymers. For the previous paper in this series, see C. G. Overberger and Herbert Aschkenasy, *J. Am. Chem. Soc.*, in press.

[2] This paper comprises part of the thesis presented by Herbert Aschkenasy in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the graduate school of the Polytechnic Institute of Brooklyn.

[3] E. S. G. Barron, *Advances in Enzymology*, Vol. XI, Interscience Publishers, Inc., N.Y., 1951, pp. 219 *et seq.*

[4] C. G. Overberger and H. Aschkenasy, *J. Am. Chem. Soc.*, in press.

[5] P. W. Morgan and S. L. Kwolek, *J. Chem. Educ.*, **36**, 182 (1959) and previous references.

[6] J. M. Zanden, *Rec. trav. chim.*, **63**, 113 (1944).

[7] A. Fredga, *Ber.*, **71B**, 289 (1938).

[8] N. A. Rosenthal and G. Oster, *J. Soc. Cosmetic Chemists*, **5**, 286 (1954).