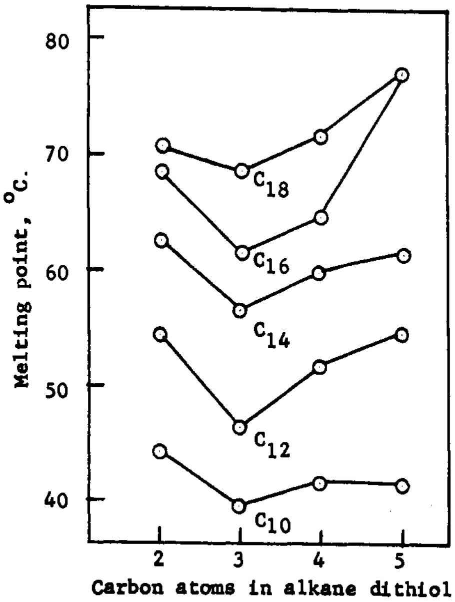

Figure 1. Melting points of α, ω-dithioalkylalkanes vs. the number of carbon atoms in the alkanedithiols

condenser, were added 50 ml. of benzene, 0.02 mole of the appropriate alkanedithiol, and 0.2 gram of benzoyl peroxide. The reaction mixture was then heated under gentle reflux on a steam bath for 5 hours. At the end of this time, the benzene was removed by distillation and the resulting solid was crystallized from acetone or acetone-alcohol. The white solid was then chromatographed with Florisil and eluted with benzene. After removal of the benzene by distillation, the compound was again crystallized from acetone or acetone-alcohol.

ALTERNATE PREPARATION. To 0.022 mole of the appropriate alkane dithiol in a 500-ml. round-bottomed flask, fitted with a reflux condenser and a calcium chloride drying tube, were added 300 ml. of dry dioxane and 0.92 gram (0.04 gram-atom) of sodium. The mixture was heated under gentle reflux for 72 hours or until all of the sodium had been consumed. To the resulting suspension was added 0.04 mole of the appropriate 1-bromoalkane dissolved in 100 ml. of dry dioxane and the mixture was heated under gently reflux for 72 hours. The mixture was then poured into 300 ml. of water and the solid which formed was separated by filtration and washed with three 50-ml. portions of water. The product was then purified as above.

OXIDATION. To 0.011 mole of the α,ω-dithioalkylalkane in a 125-ml. Erlenmeyer flask was added 25 ml. of glacial acetic acid and the flask was chilled in an ice bath. To the flask was added 0.26 mole of 30% hydrogen peroxide and the mixture was allowed to stand in the melting ice bath for 72 hours. The resulting solid was separated by filtration and crystallized from acetone until successive crystallizations showed no increase in melting point. The results are summarized in Table I.

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RECEIVED for review February 26, 1962. Accepted September 12, 1962. Supported in part by National Science Foundation grant for undergraduate research.

New Acyloxysilanes and Their Reaction with Grignard Reagents

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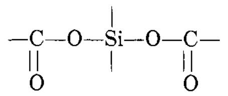
Tetra(2,4-dichlorophenoxyacetoxy)silane, tetra(α-naphthylacetoxy)silane and tetra(2,2-dichloropropionoxy)silane have been prepared by the reaction of tetrachlorosilane with the sodium salts of the acids. The infrared spectra of these acyloxysilanes have been determined between 3 and 15 microns. 2,4-Dichlorophenoxymethyl ethyl ketone and a silicone have been prepared by action of ethylmagnesium bromide on tetra(2,4-dichlorophenoxyacetoxy)silane. The infrared spectrum of the ketone was determined between 3 and 15 microns. In the same way, a ketone and a silicone were produced from tetra(α-naphthylacetoxy)silane. Acetone and chloroform have been found to be good reaction mediums for the preparation of acyloxysilanes.

THE METHOD of preparing acyloxysilanes from tetrachlorosilane and sodium salts of organic acids has been used by Schuyten, Weaver, and Reid (*11*) to prepare tetraacetoxysilane, by Lanning (*7, 8*) to prepare tetrapropionoxysilane and tetrabenzoxysilane, and by Lanning and Moore (*9*) to prepare a series of more complicated acyloxysilanes. The method has now been applied to the preparation of tetra(2,4-dichlorophenoxyacetoxy)silane, tetra(α-naphthylacetoxy)silane and tetra(2,2-dichloropropionoxy)silane in from 55.9 to 63.3% yields (Table I).

Like other acyloxysilanes (*4, 7*) these white solid compounds react with alcohol and water. They decompose when heated.

Infrared spectra of these compounds were determined between 3 and 15 microns. The spectra for tetra(2,4-dichlorophenoxyacetoxy)silane, tetra(α-naphthylacetoxy)silane and tetra(2,2-dichloropropionoxy)silane are given in Figures 1, 2, and 3.

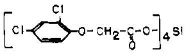
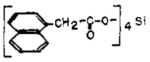
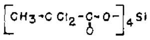
All three acyloxysilanes show significant absorption bands near 9.2, 5.8, and 10.8 microns. The 9.2 band corresponds to values reported by Richards and Thompson (*10*) to be characteristic of the Si—O bond. The 5.8 micron band is due to the C=O bond, and the ones near 10.8 microns are probably due to the



$$-\underset{\underset{O}{\|}}{C}-O-\overset{|}{\underset{|}{Si}}-O-\underset{\underset{O}{\|}}{C}-$$

structure as pointed out by Lanning and Moore (*9*).

Table I. Analysis of Acyloxysilanes

Compound	Yield, %	Silicon, %		Chlorine,%	
		Calcd.	Found	Calcd.	Found
	63.3	3.10	3.05	30.96	30.71
	55.9	3.65	3.65		
 $[CH_3-CCl_2-\underset{O}{\overset{\|}{C}}-O-]_4Si$	92.5	4.72	4.57		

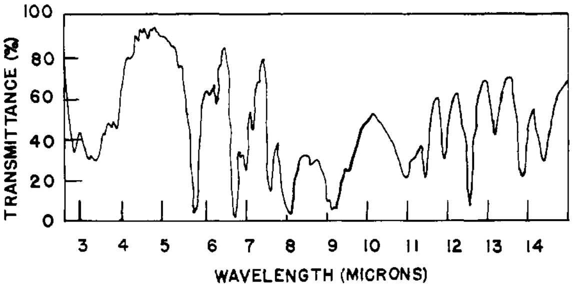


Figure 1. Infrared spectrum of tetra(2,4-dichlorophenoxyacetoxy)silane

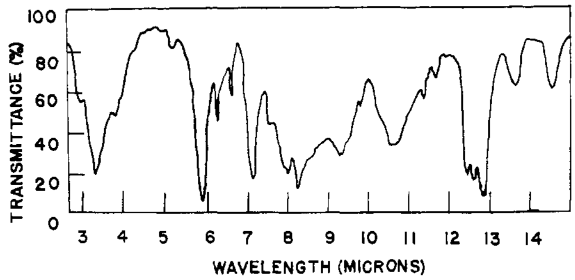


Figure 2. Infrared spectrum of tetra(α-naphthylacetoxy)silane

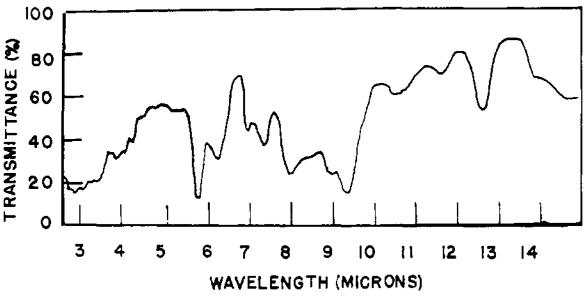


Figure 3. Infrared spectrum of tetra(2,2-dichloropropionoxy)silane

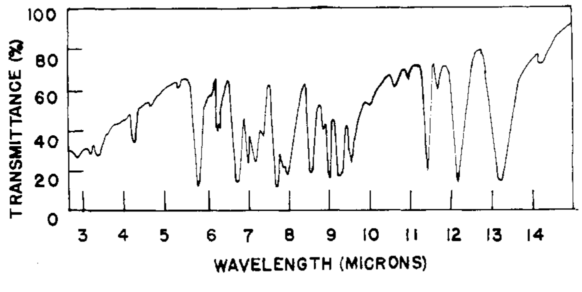


Figure 4. Infrared spectrum of 2,4-dichlorophenoxymethyl ethyl ketone

Ether solutions of tetra(2,4-dichlorophenoxyacetoxy)silane, tetra(α-naphthylacetoxy)silane and tetra(2,2-dichloropropionoxy)silane react with Grignard reagents in the same number as other acyloxysilanes (*6*, *7*, *8*). 2,4-Dichlorophenoxymethyl ethyl ketone was obtained by the reaction of tetra(2,4-dichlorophenoxyacetoxy)silane with ethylmagnesium bromide. Its melting point was 66.5° C., and it had a molecular weight of 234.4. Its infrared spectrum is shown in Figure 4. An entirely different method (*2*) was used in the first reported preparation of this compound in 1955.

The product obtained by reaction of tetra(α-naphthylacetoxy)silane with ethylmagnesium bromide gave a positive ketone test with 2,4-dinitrophenylhydrazine but the ketone was not isolated. Infrared spectra showed that ethyl silicones were produced in both of the reactions with the Grignard reagent. Tertiary alcohols were not produced in sufficient quantity to identify.

Tetra(2,2-dichloropropionoxy)silane reacts with both ethylmagnesium bromide and phenylmagnesium bromide. In both cases a mixture of compounds was produced. Infrared spectra indicate that ketones and tertiary alcohols are formed in both cases. Ethyl silicones were produced in the ethylmagnesium bromide reaction. Since chlorine atoms on aliphatic groups react with Grignard reagents, several different ketones and alcohols may have been produced. Adsorption chromatographic methods are being worked out to separate these substances.

Acetone and chloroform have been found to be good media for reactions between salts of organic acids and tetrachlorosilane. Tetrahydrofuran appears to be moderately good. The reactions also take place rapidly in triethyl phosphate but it also reacts slowly with tetrachlorosilane.

EXPERIMENTAL

The apparatus and method used in preparing the acyloxysilanes were very similar to those used by Schuyten, Weaver, and Reid (*11*), by Lanning (*7*, *8*), and by Lanning and Moore (*9*). The tetrachlorosilane used was purified by redistillation. The sodium salts were chemically pure reagents. Anhydrous diethyl ether was used as the diluent.

The preparations were carried out by adding 5.19 grams of tetrachlorosilane, dissolved in 50 ml. of ether, dropwise into a slurry of 1.5 times the calculated amount of anhydrous sodium salts dispersed in 150 ml. of ether. The temperature was lowered to −12° C. by use of a salt-ice bath. The tetrachlorosilane was added slowly over a 1½-hour period. The mixture was stirred during the addition of the tetrachlorosilane and for about 2½ hours afterwards. When the ether solution gave no test for chloride ion, the sodium chloride and excess sodium salts were removed. The ether was removed from the filtrate under reduced pressure at 0°, leaving nearly pure acyloxysilanes. The analyses and yields of these white crystalline compounds are given in Table I.

The silicon analysis was carried out by the Hyde and DeLong (*6*) method. Best results were obtained by using fuming nitric acid. Chlorine analysis was carried out by the Carius (*5*) method.

The infrared spectra of the silicon esters and for 2,4-dichlorophenoxymethyl ethyl ketone were obtained with a Perkin-Elmer, Model 137, Infrared Spectrometer. The compounds tested were made into pellets with potassium bromide. One mg. of compound was mixed with 500 mg. of potassium bromide.

To determine other solvents that might be used as reaction media for the preparation of acyloxysilanes, other solvents were substituted for diethyl ether in preparing tetrapropionoxy silane from tetrachlorosilane and sodium propionate. The yields obtained using chloroform, acetone, and triethylphosphate were about the same as those obtained by Lanning (*7*) using diethyl ether (70% or above). Chloroform and tetrahydrofuran also gave equally good yields, but the refluxing time had to be doubled to achieve a completed reaction. Triethyl phosphate reacts slowly with tetrachlorosilane to form silicon phosphates; this might be undesirable, in cases where the reaction is slow, by introducing impurities and lowering the yield.

REACTION OF ACYLOXYSILANES WITH ETHYLMAGNESIUM BROMIDE

These reactions were carried out with all three acyloxysilanes in the manner described by Lanning (*8*) and Lanning and Moore (*9*). Dilute diethyl ether solutions containing 4 grams of the acyloxysilanes were added through dropping funnels into the stoichiometric amount of ethylmagnesium bromide. In the case of tetra(2,2-dichloropropionoxy)silane, phenylmagnesium bromide was also used. Refluxing, hydrolysis, and removal of the solvents were carried out as described in the above references.

The reaction of ethylmagnesium bromide with tetra(2,4-dichlorophenoxyacetoxy)silane produced white crystals and a yellow oil. The infrared spectrum of the oil showed it to be an ethyl silicone.

The crystals were washed by Skellysolve F to remove the oil and then recrystallized from alcohol. The purified crystals melted at 66.5° and gave a positive ketone test with 2,4-dinitrophenylhydrazine. The crystals were 2,4-dichlorophenoxymethyl ethyl ketone. The molecular weight was determined by the Beckmann (*1*) method. Calcd: 233.10, found: 234.4.

The product from the reaction of tetra(αnaphthylacetoxy)silane with ethylmagnesium bromide was largely an oil with a few crystals. The infrared spectrum showed the oil to be a silicone. The crystals could not be separated in pure form but were believed to be a ketone, as a positive ketone test was obtained with 2,4-dinitrophenylhydrazine.

Tetra(2,2-dichloropropionoxy)silane reacted with both ethylmagnesium bromide and phenylmagnesium bromide to form oils. Infrared spectra indicated the presence of ketones, alcohols, and silicones. The mixtures were difficult to separate. Adsorption chromatography using silicic acid and supercel (*3*), one to one by weight, gave some separation and silicones were positively identified. Skellysolve B and Skellysolve B plus 1% of acetone were used as eluents.

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RECEIVED for review April 23, 1962. Accepted August 2, 1962. Work supported by National Institute of Health, Grant No. RG-6881. From the M.S. thesis of V.K. Emmanuel.