

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF KANSAS STATE COLLEGE]

**Acyloxysilanes and Their Reaction with Grignard Reagents<sup>1</sup>**F. C. LANNING AND M. MOORE<sup>2</sup>

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Tetrabutroxysilane, tetra(trichloroacetoxy)silane, tetracrotonoxysilane, tetra(3-phenylpropionyloxy)silane, tetra( $\beta$ -naphthoxy)silane, tetracinnamoxysilane, tetra(*o*-chlorobenzyloxy)silane, tetrastearoxysilane, and tetra(*p*-hydroxybenzyloxy)silane have been prepared by the reaction of tetrachlorosilane with the sodium salts of the organic acids. The infrared spectra of these acyloxysilanes have been determined between 3 and 15  $\mu$ .

The following alcohols and ketones have been prepared by the reaction of acyloxysilanes with ethylmagnesium bromide: 3-methyl-3-pentanol and 2-butanone from tetraacetoxysilane; 3-pentanone from tetrapropionoxysilane; 3-ethyl-3-hexanol and 3-hexanone from tetrabutroxysilane; and 3-ethyl-4-hexenol-3 and 2-hexenone-4 from tetracrotonoxysilane. 3-Ethyl-4-hexenol-3 is a new compound and its infrared spectrum has been determined between 3 and 15  $\mu$ . Ethyl siloxanes were produced along with the alcohols and ketones.

The reaction of tetrapropionoxysilane with ethylmagnesium bromide and phenylmagnesium bromide produced diphenylethylcarbinol, 3-ethyl-3-pentanol, 3-phenyl-3-pentanol, 3-pentanone, propiophenone, and a siloxane.

The method for preparing acyloxysilanes from tetrachlorosilane and sodium salts of organic acids has been used by Schuyten, Weaver, and Reid<sup>3</sup> to prepare tetraacetoxysilane and by Lanning<sup>4,5</sup> to prepare tetrapropionoxysilane and tetrabenzyloxy-silane. This method has been applied to the preparation of tetrabutroxysilane, tetra(trichloroacetoxy)silane, tetracrotonoxysilane, tetrastearoxysilane, tetra( $\beta$ -naphthoxy)silane, tetra(3-phenylpropionyloxy)silane, tetra(*o*-chlorobenzyloxy)silane, tetracinnamoxysilane, tetra(*o*-chlorobenzyloxy)silane, and tetra(*p*-hydroxybenzyloxy)silane in yields of 62.4 to 83.8% (Table I). Tetrasilyloxy-silane could not be prepared.

The infrared spectra of these compounds were determined between 3 and 15  $\mu$ . The spectra for tetrabutroxysilane, tetracrotonoxysilane, and tetra(trichloroacetoxy)silane are shown in Figs. 1, 2 and 3.

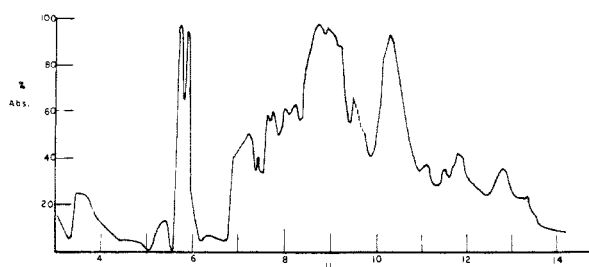


FIG. 1. INFRARED SPECTRUM OF TETRABUTYROXYSILANE.

Tetrabutroxysilane is a liquid while the others are white solids. Like other acyloxysilanes<sup>4-6</sup> these compounds react with alcohols and water. They are also unstable to heat.

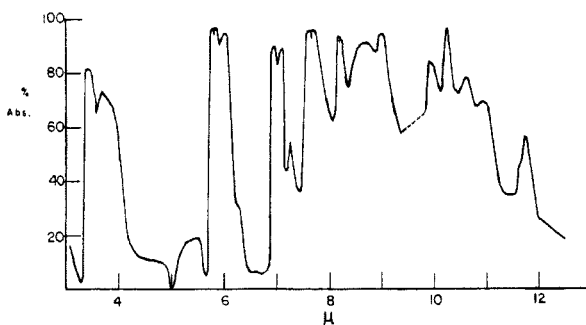


FIG. 2. INFRARED SPECTRUM OF TETRACROTONOXYSILANE.

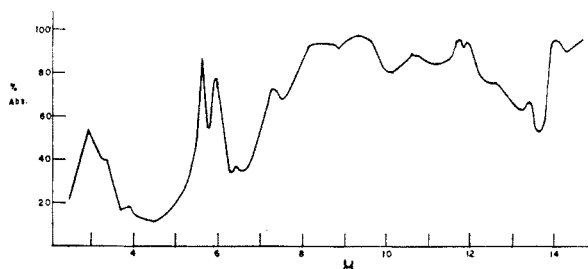


FIG. 3. INFRARED SPECTRUM OF TETRA(TRICHLOROACETOXY)-SILANE.

Petrov and Itkina<sup>7</sup> have reported the preparation of tetrabutroxysilane in a 78.6% yield by the reaction of butyric acid and tetrachlorosilane. The white solid they obtained may have been a polymer rather than the simple compound, tetrabutroxysilane, as they removed the HCl by heating the products over a water bath.

Ether solutions of tetrabutroxysilane, tetraacetoxysilane, and tetracrotonoxysilane react with Grignard reagents in the same manner that tetrapropionoxysilane<sup>4</sup> and tetrabenzyloxy-silane<sup>5</sup> do. 3-Ethyl-3-hexanol has been prepared by the reaction of ether solutions of tetrabutroxysilane with excess ethyl magnesium bromide and subsequent hydrolysis. If only 0.8 of the calculated stochio-

(1) This work was supported by a Frederick Gardner Cottrell Grant from Research Corporation.

(2) Most of this paper is from the M.S. thesis of M. Moore.

(3) H. A. Schuyten, J. W. Weaver, and J. D. Reid, *J. Am. Chem. Soc.*, **69**, 2110 (1947).

(4) F. C. Lanning, *J. Am. Chem. Soc.*, **75**, 1596 (1953).

(5) F. C. Lanning, *J. Org. Chem.*, **19**, 1171 (1954).

(6) C. Friedel and A. Ladenburg, *Ann.*, **145**, 174 (1868).

(7) K. D. Petrov and M. I. Itkina, *J. Gen. Chem. (U.S.S.R.)*, **17**, 220 (1947).

TABLE I  
 ANALYSIS OF ACYLOXYSILANES

Compound	Yield, %	RCO <sub>2</sub> <sup>-</sup> , %		Silicon, %	
		Calcd.	Found <sup>9</sup>	Calcd.	Found <sup>10</sup>
(CCl <sub>3</sub> CO <sub>2</sub> ) <sub>4</sub> Si	62.4	95.85	95.76	4.15	4.12
(C <sub>2</sub> H <sub>5</sub> CO <sub>2</sub> ) <sub>4</sub> Si	81.2	92.55	91.94	7.45	7.43
H H					
(CH <sub>3</sub> C=C—COO) <sub>4</sub> Si	74.4	92.4	92.27	7.60	7.53
(C <sub>17</sub> H <sub>35</sub> —COO) <sub>4</sub> Si	76.7	97.59	97.63	2.41	2.35
(C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> COO) <sub>4</sub> Si	83.8	95.51	95.52	4.49	4.52
(C <sub>6</sub> H <sub>5</sub> CH=CHCO <sub>2</sub> ) <sub>4</sub> Si	78.5	95.45	95.45	4.55	4.55
( <i>o</i> -ClC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> ) <sub>4</sub> Si	75.7	95.69	95.62	4.31	4.27
( <i>p</i> -HOC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> ) <sub>4</sub> Si	78.6	95.14	95.04	4.86	4.80
(2-C <sub>10</sub> H <sub>7</sub> CO <sub>2</sub> ) <sub>4</sub> Si	73.4	96.07	95.94	3.93	3.88

metric amount of the Grignard reagent was used, less 3-ethyl-3-hexanol was formed and some 3-hexanone was formed.

Up to 67% of the silicon was converted to ethylsiloxanes with infrared spectra identical with those obtained for ethyl siloxanes by Young, Servais, Currie, and Hunter.<sup>8</sup>

Tetracrotonoxysilane reacts with ethyl magnesium bromide to form 2-hexenone-4, 3-ethyl-4-hexenol-3, and ethyl siloxanes. 3-Ethyl-4-hexenol-3 is a new compound and its infrared spectra, Fig. 4, was determined between 2.5 and 15  $\mu$ .

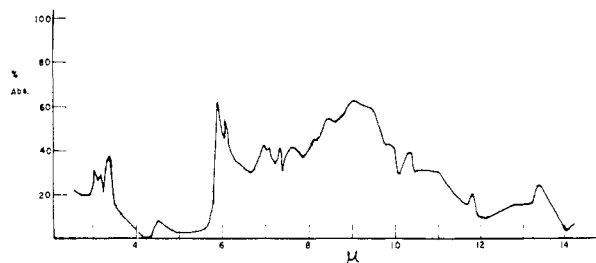


FIG. 4. INFRARED SPECTRUM OF 3-ETHYL-4-HEXENOL-3.

Tetraacetoxysilane reacts with an excess of ethyl magnesium bromide to form 3-methyl-3-pentanol and ethyl siloxanes. With 0.8 of the stoichiometric amount of ethyl magnesium bromide some methyl ethyl ketone was produced. Under these same conditions diethyl ketone was produced from tetrapropionoxysilane.

Numerous products have been prepared by treating tetrapropionoxysilane first with ethylmagnesium bromide and then with an equal amount of phenylmagnesium bromide. No excess of the Grignard reagents was used. The products identified were diphenylethylcarbinol, 3-ethyl-3-pentanol, 3-phenyl-3-pentanol, 3-pentanone, and propiophenone.

(8) C. W. Young, P. C. Servais, C. C. Currie, and M. J. Hunter, *J. Am. Chem. Soc.*, **70**, 3758 (1948).

(9) W. I. Patnode, quoted in Rochow, *An Introduction to the Chemistry of Silicones*, 2nd ed., John Wiley and Sons, New York, 1951, p. 165.

(10) J. F. Hyde and R. C. DeLong, *J. Am. Chem. Soc.*, **63**, 1194 (1941).

## EXPERIMENTAL

The apparatus used in preparing the acyloxysilanes was very similar to that used by Schuyten, Weaver, and Reid.<sup>3</sup> The tetrachlorosilane used was purified by redistillation. The sodium salts were c.p. Reagents. Anhydrous diethyl ether was used as the diluent.

The preparations were carried out by adding 10.38 grams of tetrachlorosilane, dissolved in 50 ml. of ether, dropwise into a slurry of 1.25 times the calculated amount of anhydrous sodium salts dispersed in 300 ml. of ether. Tetrachlorosilane was added at such a rate that gentle refluxing was maintained. The mixture was stirred during the addition of the tetrachlorosilane and for 1 hr. afterwards while the mixture was kept at the boiling point. 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 the nearly pure acyloxysilanes. The analyses and yields of these compounds are given in Table I.

Tetracinnamoxysilane could be prepared only by keeping the temperature at 0° throughout the reaction time. Apparently the compound was so unstable at 36° that it decomposed into cinnamic anhydride and SiO<sub>2</sub> as fast as it formed.

Tetrasilyloxysilane was apparently too unstable to be recovered even at 0°. The instability may be due to hydrogen bonding which could occur between the carbonyl group of the acid and the adjacent OH group. This could result in the formation of salicyl cations, salicylate ions, and SiO<sub>2</sub>. The salicyl cations and the salicylate ions could unite to form salicylic anhydride. A white crystalline compound, melting at 158–158.5° and having a neutral equivalent corresponding to salicylic anhydride, was recovered.

The molecular weights of tetrabutroxysilane and tetracrotonoxysilane were determined by the Beckmann<sup>11</sup> method, using benzene as a solvent. The molecular weights of the other acyloxysilanes could not be determined this way because of the high molecular weight and low solubility in benzene. Tetrabutroxysilane. Calcd.: 376.22. Found: 381.96. Tetracrotonoxysilane. Calcd.: 368.38. Found: 363.6.

*Reaction of acyloxysilanes with ethylmagnesium bromide.* These reactions were carried out with tetraacetoxysilane, tetrapropionoxysilane, tetrabutroxysilane, and tetracrotonoxysilane at several different concentrations and temperatures.

In each case a dilute diethyl ether solution of the acyloxysilane was added through a dropping-funnel drop by drop into the Grignard reagent prepared from ethyl bromide in the usual manner. The mixture was stirred for 1 hr. Then the Grignard complex was hydrolyzed in an ammonium chloride solution containing some ice. Some dilute sulfuric acid was added afterwards to dissolve the precipitate. The

(11) E. Beckmann, *Z. phys. Chem.*, **2**, 683 (1888).

TABLE II  
ALCOHOLS OBTAINED FROM THE REACTION OF ACYLOXYSILANES WITH 0.8 AND 3.5 TIMES THE  
STOICHIOMETRIC AMOUNT OF ETHYLMAGNESIUM BROMIDE

Items	Alcohols			
	3-Ethyl-3-hexanol	3-Ethyl-3-pentanol	3-Methyl-3-pentanol	3-Ethyl-4-hexenol-3
Acyloxysilane from which alcohol was prepared	Tetrabutyr-oxysilane	Tetrapropionoxy-silane	Tetraacet-oxysilane	Tetracro-tonoxy-silane
Reaction temperature	36°	36°	36°	0°
Yield, %				
1 to 0.8	45	42	43	
1 to 3.5	56	59	56	
Boiling point				
Found	160.1	142-143	101-102	
Lit.	160.5	142	102	
Melting point				68-69°
Index of refraction				
Found	$n_D^{13}$ 1.4322	$n_D^{28.5}$ 1.4246	$n_D^{20}$ 1.4182	
Lit.	$n_D^{13}$ 1.4322	$n_D^{22.3}$ 1.4266	$n_D^{21}$ 1.4180	
Allophanate derivative				
Found	153-154	172-173	151-152	126-127.5°
Lit.		172-173	152	

TABLE III  
KETONES OBTAINED FROM THE REACTION OF ACYLOXYSILANES WITH 0.8 AND 3.5 TIMES THE  
STOICHIOMETRIC AMOUNT OF ETHYLMAGNESIUM BROMIDE

Items	Ketones			
	3-Hexanone	3-Pentanone	2-Butanone	2-Hexenone-4
Acyloxysilane from which the ketone was prepared	Tetrabutyr-oxysilane	Tetrapropionoxy-silane	Tetraacet-oxysilane	Tetracro-tonoxy-silane
Reaction temperature	36°	36°	36°	0°
Yield, %				
1 to 0.8	26	27	29	Low
1 to 3.5	Much less	Much less	Much less	
B.p. of ketones				
Found	123-124°	102-103°	80-81°	
Lit.	123-123.5°	102°	80°	
Index of refraction				
Found	$n_D^{25}$ 1.3998	$n_D^{25}$ 1.3907	$n_D^{25}$ 1.3782	
Lit.	$n_D^{22}$ 1.3990	$n_D^{25}$ 1.3905	$n_D^{20}$ 1.3791	
2,4-Dinitrophenylhydrazone derivatives				
M.p. Found	129-130°	150-152°	113-114°	
Lit.	130°	156°	114°	
Semicarbazone derivative				
Found				156.5-157°
Lit.				157°

organic layer was separated and dried with  $\text{CaCl}_2$ . After evaporation of the ether, the colorless oily liquid residue was distilled.

The first set of reactions was carried out at 36° and 3.5 times the stoichiometric amount of ethylmagnesium bromide. A second set of reactions was carried out at the same temperature but with only 0.8 of the stoichiometric amount of ethyl magnesium bromide. A stoichiometric amount would be 4 molecules of the Grignard reagent to one of the acyloxysilane. Both alcohols and ketones were produced. These, along with their physical constants and derivatives, are shown in Tables 2 and 3, respectively.

The reaction of tetracrotonoxysilane with ethylmagnesium bromide was carried out at 0° to yield yellow flake-like crystals and an oil. The crystals, 3-ethyl-4-hexenol-3, were filtered out, washed with Skellysolve F, and recrystal-

ized from ethyl alcohol by precipitating it out with water. The oil was distilled. With the same concentrations of Grignard reagents as in sets 1 and 2 at a temperature of 0°, the same reactions took place more slowly and yields were somewhat lower. The siloxanes were purified by treating hot benzene solutions with activated carbon. These solutions were then filtered and the benzene evaporated. The siloxanes were shown by chemical analysis and infrared spectroscopy, to be ethyl siloxanes.

Siloxanes 1 and 2 are typical of the siloxanes obtained. Siloxane 1, 75% yield, was the residue left from the fractional distillation of the oily liquid produced by the reaction of 0.8 of the stoichiometric amount of ethylmagnesium bromide with tetrabutyr-oxysilane. Siloxane 2, 69% yield, was obtained in the same manner by use of 3.5 times the stoichiometric amount of Grignard reagent. Siloxanes 1 and

2 were, by the following analysis, indicated to be ethyl siloxanes.

*Anal.* Calcd. for  $(C_2H_5)_2SiO$ : C, 47.06; Si, 27.45; H, 9.80; O, 15.70. Found in siloxane 1: C, 40.35; Si, 31.6; H, 8.90; O, 19.15. Found in siloxane 2: C, 46.08; Si, 27.49; H, 9.82; O, 16.61.

In order to get an accurate silicon analysis by the method of Hyde and Delong,<sup>10</sup> it was necessary to use 90% pure  $HNO_3$  (fuming nitric acid).

The analysis of sample 1 corresponds to a  $C_2H_5/Si$  value of 1.55. Silicone 2 corresponds to a  $C_2H_5/Si$  value of 1.96.

*Reaction of tetrapropionoxysilane with both ethylmagnesium bromide and phenylmagnesium bromide.* A dilute diethyl ether solution containing 16.53 g. of tetrapropionoxysilane was added through a dropping funnel into an ether solution containing 0.5 of the stoichiometric amount of ethylmagnesium bromide. The mixture was stirred for 5 min. and then an ether solution containing 0.5 of the stoichiometric amount of phenylmagnesium bromide was added through the dropping funnel. Stirring was continued for 1 hr. at 36°. The mixture was hydrolyzed and the products isolated from the ether in the manner previously described.

The product consisted of nearly white crystals and an oily liquid. The crystals were filtered out and purified by recrystallization from Skellysolve F.

Distillation separated the oily liquid into diphenylethylcarbinol (m.p. found 93–94°; lit. 95°), 3-pentanone (b.p. found 100–101°; lit. 102°)  $n_D$  found 1.3935 [20°]; lit. 1.3905 [25°], 3-ethyl-3-pentanol (b.p. found 140–142°; lit. 142°) ( $n_D$  found 1.4220 [20°]; lit. 1.4266 [22°]), propiophenone ( $n_D^{20}$  found 1.5230; lit. 1.5369), and 3-phenyl-3-pentanol ( $n_D^{20}$  found 1.515; lit. 1.5165).

The following derivatives were prepared: 3-pentanone 2-4 dinitrophenylhydrazone (m.p. found 153–155°, lit. 156°), propiophenone 2-4 dinitrophenylhydrazone (m.p. found 186–187.5°; lit. 187–189°), and the nitrosochloride of 3-phenyl-3-pentanol (m.p. found 114–115°; lit. 117°).

A siloxane which was probably an ethyl phenyl siloxane, was also produced.

*Infrared absorption.* The infrared spectra of the acyloxysilanes were determined from benzene solutions or potassium bromide pellets with a Perkin-Elmer, Model 112, infrared spectrometer using a rock salt prism. The solutions or potassium bromide pellets, contained 5 to 10% by weight of the products. A background trace of pure solvent, or potassium bromide, was run so that it was superimposed, and a point by point measurement of per cent absorption was made at intervals.

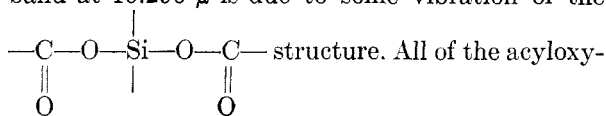
Spectra of the ethyl siloxanes were made by using very thin layers of these materials. The spectrum of 3-ethyl-4-hexenol-3 was made from a pellet containing the compound and potassium bromide.

#### DISCUSSION

The more significant infrared absorption peaks in the spectrum of tetrabutyroxyasilane, other than the Si—O band near 9.236  $\mu$  which is found in all acyloxysilanes, are at 5.74, 5.876, 8.762, and 10.296  $\mu$ . Peaks at 5.74 and 5.876  $\mu$  are due to —C=O bond. These peaks occur in organic

(12) H. Roth, *Angew Chem.*, **50**, 593 (1937).

esters<sup>13</sup> and are found in the spectra of all the acyloxysilanes studied. The peak at 8.76  $\mu$  is characteristic of esters of butyric acid.<sup>13</sup> A strong band at 10.296  $\mu$  is due to some vibration of the

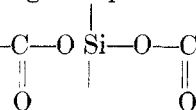


silanes show such a band between 10.296 and 10.915  $\mu$ . The position of the band shifts towards higher wavelengths as the molecular weight of the organic radical increases. The highest value was obtained for tetrabenzoxyasilane.<sup>5</sup>

Bands in the spectrum of tetracrotonoxysilane are stronger than those for tetrabutyroxyasilane due to the use of a more concentrated solution of the compound. The only major differences are the bands at 6.05 and 9.94  $\mu$  which are due to the double bonds in the molecule.

The spectrum of tetra(trichloroacetoxy)silane is somewhat different as there are no C—H bonds and the corresponding absorption bands are missing.

The band due to —C—O—Si—O—C— structure has



shifted to 10.6  $\mu$  due to the heavy C—Cl<sub>3</sub> radical. The bands at 11.74 and 11.938  $\mu$  are more pronounced in esters of trichloroacetic acid. Bands at 2.958 and 14.0  $\mu$  are due to the C—Cl bond and the C—Cl<sub>3</sub> group respectively.

The spectrum of silicone 1 is identical with the ethyl silicone spectra reported by Young, Servais, Currie, and Hunter.<sup>8</sup> Silicone 2 has an extra band at 11.7  $\mu$ . This band often occurs in straight chain polysiloxanes.<sup>14</sup>

Significant absorption bands occur in the infrared spectrum of 3-ethyl-4-hexenol-3 at 3.05, 3.20, 3.40, 4.5 to 4.6, 5.86, 6.07, 6.95 to 7.10, 7.35, 7.60 to 7.70, 8.40 to 8.50, 9.00 to 9.50, 9.90, 10.35, 11.8, and 13.4  $\mu$ . Randall, Fowler, Fuson and Dangle<sup>13</sup> report absorption bands for ethyl alcohol at 3.00, 3.40, 4.69, 6.06, 7.23, 7.39, 7.76, 7.88, and 9.18 to 9.62  $\mu$ . Strong bands at 6.07 and 8.50  $\mu$  are due to the double bond and tertiary alcohol groups, respectively.

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(13) H. M. Randall, R. G. Fowler, N. Fuson, and J. R. Dangle, *Infrared Determination of Organic Structures*, D. Van Nostrand Co., New York, 1949.

(14) N. Wright and M. J. Hunter, *J. Am. Chem. Soc.*, **69**, 803 (1947).