

PREPARATION OF SILICON ESTERS SUCH AS SILICON
TETRAPROPIONATE AND THEIR REACTION WITH
GRIGNARD REAGENTS TO FORM TERTIARY
ALCOHOLS, KETONES, AND SILICONES

by

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INTRODUCTION AND REVIEW OF LITERATURE

Silicon esters, although not a new type compound, have not been extensively studied. Silicon esters have been prepared by reactions of silicon tetrachloride with esters, anhydrides, acids, and sodium salts of organic acids. Silicon esters were first prepared by Friedel and Ladenberg (2) in 1867. They prepared silicon tetraacetate from silicon tetrachloride and acetic anhydride. In 1939 Volnov (14) prepared silicon tetraacetate from silicon tetrachloride and organic acetates. Silicon tetraacetate was prepared in 1947 by Schuyten, et al. (12) from silicon tetrachloride and sodium acetate using anhydrous benzene as a diluent. Petrov and Itkina(8) prepared silicon tetrabutryrate from silicon tetrachloride and butyric acid in the same year. Silicon tetrapropionate and silicon tetrabenzoate were prepared by Lanning (5, 6) in 1953 and 1954 respectively, from the organic salts and silicon tetrachloride. The methods of Schuyten, et al. (12), and of Volnov (14) were unsatisfactory.

Lanning (5, 6) treated silicon tetrapropionate with ethylmagnesiumbromide and silicon tetrabenzoate with phenylmagnesium bromide, which produced 3-ethyl-3-pentanol and triphenylcarbinol respectively. He noticed that a silicone-like oil formed with 3-ethyl-3-pentanol and with triphenylcarbinol. Lanning (6) believed that the tertiary alcohols were formed by the Grignard reagent reacting with silicon esters in the way it usually reacts with esters. He also believed that other tertiary alcohols, including ones having different alkyl radicals, might be prepared by this new method.

This investigation was initiated to prepare silicon tetrabutryrate from sodium butyrate and silicon tetrachloride and to study its reactions with the Grignard reagent to form tertiary alcohols and silicones. These reactions were carried out at various concentrations of reactants and several temperatures and the yields determined.

The next immediate investigation was to prepare silicon tetrasalicylate for comparison of its reaction with the Grignard reagent to that obtained with silicon tetrabutryrate. We have made several unsuccessful attempts to prepare silicon tetrasalicylate by the method of Schuyten, et al. (12). It was believed that steric hindrance was not the only factor preventing the formation of silicon tetrasalicylate, because silicon tetrabenzoate had been prepared by the same method. It seemed desirable to investigate some of the factors that might prevent the formation of silicon esters by the method of Schuyten, et al. (12). In order to carry out this investigation the following silicon esters were prepared; silicon tetraacetate, silicon tetratrifluoroacetate, silicon tetrapropionate, silicon tetrabutryrate, silicon tetracrotonate, silicon tetra-stearate, silicon tetra-*o*-chlorobenzoate, silicon tetra-*p*-hydroxybenzoate, silicon tetracinnamate, silicon tetraphenylpropionate, and silicon tetra-*B*-naphthonate.

Silicon tetraacetate, silicon tetrapropionate, and silicon tetrabutryrate, were treated with the Grignard reagent at different concentrations and temperatures for comparison.

It was noted that at low concentrations of the Grignard reagent, a large amount of ketone was formed. It was of interest to prepare a tertiary alcohol having different radicals without isolating the ketone. This was done by treating one half of the necessary amount of ethylmagnesium bromide with silicon tetrapropionate to form 3-pentanone and this was treated with phenylmagnesium bromide to form 3-phenyl-3-pentanol.

EXPERIMENTAL

Preparation of Silicon Esters

The method and apparatus used in preparing these silicon esters from silicon tetrachloride and sodium salts of organic acids were similar to that of Schuyten, et al. (12) and to Lanning (5, 6). The silicon tetrachloride was purified by distillation. The sodium salts of organic acids were prepared by the reaction of the calculated amount of sodium bicarbonate with the pure acids. The salts were dried by heating them to their melting points. Anhydrous benzene and anhydrous diethyl ether were used as solvents. The reaction proceeded in both solvents, but diethyl ether only can be satisfactorily removed from the product.

Silicon tetraacetate, silicon tetrapropionate, and silicon tetrabutylate were prepared by adding 7 ml. (10.88 g) of silicon tetrachloride dissolved in 50 ml. of ether dropwise into a slurry of 1.5 times the calculated amount of the anhydrous sodium salts dispersed in 300 ml. of ether. The silicon tetrachloride was added at such a rate that gentle refluxing was maintained. The mixture was stirred mechanically during the addition of silicon tetrachloride and for one and a half hours afterwards while the mixture was kept at the boiling point. When the ether solution gave no chlorine test, the sodium chloride and excess sodium salt were removed by filtration using diatomaceous silica as a filter aid. The residue was washed with 100 to 300 ml. of anhydrous ethyl ether. Immediately after filtering, the filtrate was stored in a cold room at 4°C. The filtrate was concentrated under reduced pressure while in an ice bath to produce nearly pure silicon esters. The esters were kept in the cold room until analyzed.

Silicon tetracrotonate, silicon tetrasterate, silicon tetra-p-hydroxybenzoate, silicon tetra-o-chlorobenzoate, silicon tetraphenylpropionate, silicon tetracinnamate, and silicon tetra-B-naphthionate were prepared by the above method, at 0°C.

The sodium salt of salicylic acid did not form silicon tetrassilylate with silicon tetrachloride, but formed salicylic anhydride instead. The preparation of the anhydride from the sodium salt of salicylic acid was carried out in an ice bath in the same manner as the preparation of silicon esters. The anhydride was identified by titration and mixed melting point.

Quantitative Analysis of Silicon Esters

The acid analysis was carried out by hydrolysis of the silicon esters and titrating with 0.1N sodium hydroxide. The complete hydrolysis of the silicon esters was slow in cold water and the method of Patnode (7) for silicon halides had to be modified by heating the solution to boiling before titrating the acid liberated.

The silicon analysis was carried out by the method of Hyde and DeLong (8). In order to get an accurate silicon analysis by this method, it was necessary to use 90 per cent HNO_3 (fuming nitric acid).

The molecular weights of the silicon esters were determined by the Beckman Method (1), using benzene as a solvent.

The infrared spectra of silicon esters were determined from benzene solutions or potassium bromide pellets with a Perkin-Elmer Model 120, Infrared Spectrometer using a rock salt prism. The solutions or potassium bromide pellets, contained 5 to 10 per cent by weight of the products. A background trace of pure solvent, or potassium bromide pellets, was run so that it was superimposed and a point by point measurement of per cent absorption was made at intervals.

Reaction of Silicon Esters With The Grignard Reagents

The reactions of silicon esters with Grignard reagents were carried out with silicon tetraacetate, silicon tetrapropionate, and silicon tetrabutyrate with ethylmagnesium bromide. These reactions of silicon esters, with the Grignard reagent to form tertiary alcohols, ketones, and silicones were carried out at various concentrations and temperatures.

The first set of reactions were carried out by adding dropwise dilute diethyl ether solution of the silicon ester through a dropping funnel into 0.8 of the stoichiometric amount of Grignard reagent prepared from ethyl bromide in the usual manner. The mixture was stirred mechanically and maintained at the boiling point for one hour after the addition was completed. The Grignard complex was hydrolyzed in an ammonium chloride solution containing some ice. Some dilute sulfuric acid was added afterwards to dissolve the magnesium precipitate. The ether layer was separated and dried with CaSO_4 . After evaporation of the ether layer, a colorless oily liquid was obtained. This liquid was separated by fractional distillation. Some ketone formed with the tertiary alcohol.

The above reactions were repeated with 3.5 times the stoichiometric amount of Grignard reagent. The tertiary alcohol was still the major product, but a very small amount of ketone was formed, along with a less viscous silicone. Yields of 67 to 71 per cent of the tertiary alcohols were obtained at 36°C .

At 0°C the relative amounts of alcohols, ketones, and silicones were in the same ratio, but in lower yields. Reactions using two and six times the stoichiometric amount of Grignard reagent were carried out with silicon tetrabutyrate at 36°C .

The products were distilled and then identified by boiling points, indices of refraction, infrared spectra, derivatives, and analysis of silicon, carbon and hydrogen. The ketones were identified by 2-4 dinitrophenylhydrazone derivatives, indices of refraction, and boiling points.

The 2-4 dinitrophenylhydrazone derivatives were prepared by adding 2 ml. of the ketones to freshly prepared 2-4 dinitrophenylhydrazone. It was purified by washing several times with water and then with skellysolve. In some cases the 2-4 dinitrophenylhydrazone was recrystallized by the method described by Shriner, et al. (15).

The alcohols were identified by indices of refractions, allophanate derivatives, and boiling points. The procedure employed in making the allophanates was to depolymerize cyanuric acid in a slow stream of carbon dioxide at 360-400°C. and to pass the cyanic acid into a 25 ml. flask containing 2 ml. of the alcohol.

The 3-ethyl 4-hexenol-3 was first dissolved in 10 ml. of anhydrous ethyl ether. Sublimation of the bulk of the cyanuric acid required about 14 minutes. The receivers were removed, stoppered and allowed to stand for 24 hours. When the reactions were complete as evidenced by disappearance of the acrid odor of cyanic acid, the allophanates were separated by filtration. After washing the allophanates in ether, they were recrystallized to constant melting points from an ethanol solution previously treated with activated carbon to aid in removal of traces of cyanuric acid.

The silicones were purified by treating hot benzene solutions with activated carbon. The solutions were then filtered and the benzene evaporated. They were identified by chemical analysis, (silicon, carbon, and hydrogen) and infrared spectra. In order to get an accurate silicon analysis by the

method of Hyde and DeLong (3) it was necessary to use 90 per cent pure HNO_3 (fuming nitric acid). Also in order to get accurate carbon hydrogen analysis on the silicones (11) V_2O_5 was used as a catalyst. The indices of refraction of the silicones were nearly the same from all silicon esters when treated with the same amount of ethylmagnesium bromide. Ethyl silicones were produced.

Reaction of Silicon Tetracpropionate with Ethylmagnesium
Bromide and Phenylmagnesium Bromide

The apparatus and method for preparation of 3-phenyl 3-pentanol was very similar to that used by Lanning (5, 6) to prepare 3-ethyl 3-pentanol and tri-phenylcarbinol. A dilute ether solution containing 16.5296 g. of silicon tetracpropionate was added through a dropping funnel, drop by drop into 0.5 of the stoichiometric amount of Grignard reagent prepared from ethyl bromide in the usual manner. The mixture was stirred mechanically for five minutes and then 0.5 of the stoichiometric amount of a Grignard reagent, prepared from bromobenzene in the usual manner, was added through a dropping funnel into the mixture. The mixture was again stirred mechanically and maintained at the boiling point for one hour after the addition was complete. The Grignard complex was hydrolyzed in ammonium chloride solution containing some ice. Some dilute sulfuric acid was added afterwards to react with the magnesium precipitate.

The ether layer was separated and dried with CaSO_4 . This anhydrous ether solution was concentrated under reduced pressure. The concentration of the anhydrous ether solution gave a colorless solid at the bottom of the flask along with a light yellow oily liquid. The oily liquid was decanted and the residue was crystallized from skellysolve. The purified white crystals of diphenylethylcarbinol had a melting point of 93-4°C. The ethyl ether derivative of diphenylethylcarbinol was prepared by making the sodium salt of diphenyl-

ethylcarbinol and refluxing the sodium salt with ethylbromide in acetone solvent. The melting point for this derivative was 158-90C. and the literature value was 160°C.

The oily liquid was fractionated by distilling from a 25 ml. distilling flask, heated in an oil bath, into test tubes on a fraction cutter. Two fractions were collected by distilling at an oil bath temperature of 155°C. Fraction I had a boiling point of 100-1°C., and an index of refraction of $n_D^{20} = 1.3935$. The literature values of 3-pentanone are respectively 102°C. and $n_D^{25} = 1.3905$. Fraction I gave a derivative of 3-pentanone 2-4 dinitrophenylhydrozone with a melting point of 153-5°C (literature value of 156°C).

Fraction II boiled at 140-2°C. and had an index of refraction of $n_D^{20} = 1.4220$. The literature values of 3-ethyl 3-pentanol are respectively 142°C. and $n_D^{22} = 1.4266$.

The higher boiling product was distilled under vacuum and another fraction collected. This fraction (III) was put in an ice bath at 0°C. and the liquid decanted.

The solid had an index of refraction of $n_D^{20} = 1.5230$ and gave propiophenone 2-4 dinitrophenylhydrazone with a melting point of 186-7.5°C. The literature values were respectively 187-89°C. and $n_D^{20} = 1.5369$. The liquid fraction IV, 3-phenyl 3-pentanol, had an index of refraction of $n_D^{20} = 1.5150$ and gave a nitrosochloride derivative with a melting point of 114-15°C. prepared by the method of Klages (4). The literature values are respectively $n_D^{20} = 1.51655$ and 117°C.

The solid silicone was purified from benzene in the same manner as before and contained 19.04 per cent silicon.

Reaction of Silicon Tetracrotonate
With Ethylmagnesium Bromide

The 3-ethyl 4-hexenol and 2-hexenone-4 were prepared by adding 16.2596 g. of silicon tetracrotonate to 1.5 of the stoichiometric amount of ethylmagnesium bromide in an ice bath prepared in the usual manner. The mixture was stirred mechanically for five hours and kept in an ice bath until hydrolyzed. The Grignard complex was hydrolyzed by a saturated solution of ammonium chloride and 400 g. of ice. 15 ml. of 6N Sulfuric acid was added and the mixture was stirred in the cold water.

The ether layer was separated and dried over CaSO_4 for two days. The ether solution was concentrated and gave mostly light yellow flake-like crystals which were washed with skellysolve and then recrystallized from ethyl alcohol by "salting out" with water. The dried crystals of 3-ethyl 4-hexenol-3 had a melting point of 68-90°C. The allophanate derivative was made from 3-ethyl 4-hexenol-3 and recrystallized until it gave a constant melting point of 126-7.50°C. The infrared spectrum of 3-ethyl 4-hexenol-3 was determined.

The skellysolve washings were evaporated and an oily liquid recovered. A semicarbazone derivative of the product was prepared by the method in The Systematic Identification of Organic Compounds by Shriner, et al. (15). The liquid was shown to be 2-hexenone-4 since the melting point of the derivative was 156.5-70°C as compared to the literature value of 157°C.

RESULTS AND DISCUSSION

Nine silicon esters, such as silicon tetraacetate, have been prepared by the Schuyten, Weaver, and Reid method (12). The yield and analysis of these esters are listed in Table 1.

Table 1. The analysis of silicon esters

Compound	Acid :		% R-COO-		% Silicon		Mol. Wt.	
	Strength :	Yield :	Calcd. :	Found :	Calcd. :	Found :	Calcd. :	Found :
$(CCl_3-C(=O)-O)_4Si$	1.50×10^{-1}	62.4	95.85	95.76	4.15	4.12	677.66	
$(CH_3(CH_2)_2C(=O)_4Si$	1.51×10^{-5}	81.2	92.55	91.94	7.45	7.43	376.44	381.96
$(CH_3C(=C-C(=O))_4Si$ Cis. Trans.	3.50×10^{-5} 2.00×10^{-5}	74.4	92.40	92.27	7.60	7.53	368.38	363.38
$(CF_3(CH_2)_6C(=O)_4Si$	$< 1.11 \times 10^{-5}$	76.7	97.59	97.63	2.41	2.35	1,161.90	1
$(\text{C}_6\text{H}_5-C(=O)-O)_4Si$	1.91×10^{-5}	83.8	95.51	95.52	4.49	4.52	624.71	
$(\text{C}_6\text{H}_5-C(=O)-O)_4Si$ Cis. Trans.	1.52×10^{-4} 3.70×10^{-5}	78.5	95.45	95.45	4.55	4.55	616.64	
$(\text{C}_6\text{H}_5-C(=O)-O)_4Si$	1.20×10^{-5}	75.7	95.69	95.62	4.31	4.27	650.31	
$(\text{C}_6\text{H}_5-C(=O)-O)_4Si$	3.50×10^{-5}	78.6	95.14	95.04	4.86	4.80	576.50	
$(\text{C}_6\text{H}_5-C(=O)-O)_4Si$	6.90×10^{-5}	73.4	96.07	95.94	5.93	5.88	712.72	

¹The mol. wt. could not be determined by the freezing point depression method in benzene solvent.

Low temperature was necessary in the preparation of some of these silicon esters. For example, at 36°C. anhydrides were formed instead of silicon tetracinnamate and silicon tetra-*B*-naphthonate.

The sodium cinnamate could not be dried at its melting point because of decomposition.

The synthesis of these nine silicon esters required rapid handling when exposed to the air because they are very unstable in the presence of a small amount of moisture and were kept below 8°C.

Anhydrous benzene, petroleum ether, and diethyl ether were used as solvents for the preparation of the silicon esters. The reaction proceeded in all three solvents but diethyl ether was the only one of the three that could be satisfactorily removed from the products. These silicon esters being very unstable to humidity, diatomaceous silica is necessary to obtain rapid filtration. They react readily with water and alcohols and are somewhat unstable to heat. The Si-O-Si-O bonding being more stable than the Si-O-C^{||}-R bonding accounts for the esters reactivity.

Silicon tetracrotonate, silicon tetraacetate, and silicon tetratrachloroacetate, silicon tetrastearate, silicon tetracinnamate, silicon tetra-*p*-hydroxybenzoate, silicon tetra-*o*-chlorobenzoate, and silicon tetra-*B*-naphthonate were white solids, while silicon tetrapropionate and silicon tetrabutyrate were dense colorless liquids.

Petrov and Itkina (8) reported silicon tetrabutyrate to be a white solid. The white solid they obtained was probably a polymer as they removed the HCl by heating the products over a water bath.

The acid strengths of the monocarboxylic acids do not appear to be an important factor in the preparation of the silicon esters. Silicon esters were prepared from sodium salts of monocarboxylic acids with acid strengths

lower and higher than that of formic acid. The sodium salt of formic acid would not form silicon tetraformate by the Schuyten, et al. (12) method, nor would it react directly with silicon tetrachloride.

The sodium salt of salicylic acid did not form silicon tetrasalicylate with silicon tetrachloride, but formed salicylic anhydride in an 82 per cent yield. The preparation of the anhydride was carried out in the same manner as the preparation of silicon esters.

The melting point of the product, salicylic anhydride, was 158-158.5°C. No reliable literature value is available. A mixed melting point with this substance and salicylic acid (157-8°) was 154.5-155.5°C. The titration of the salicylic anhydride in aqueous solution gave the correct neutral equivalent (258).

A possible mechanism in the preparation of salicylic anhydride from sodium salicylate and silicon tetrachloride is as follows and in Fig. 1. Hydrogen bonding within salicylic acid is also taking place in the intermediate product, silicon tetrasalicylate. The formation of a second ring which forms in salicylic acid through the carbonyl group, breaks the silicon ester bond then forms a salicyl carbonium ion and a salicylate ion. The salicyl carbonium ion and the salicylate ion came together to form the anhydride.

Three compounds could be formed in the reaction. These three compounds were silicon tetrasalicylate, salicylic acid, and salicylic anhydride. No silicon was found in the product, therefore this compound is not a silicon ester. A depression in mixed melting point of the product with salicylic acid ruled out the idea of its being salicylic acid. Therefore the product was salicylic anhydride.

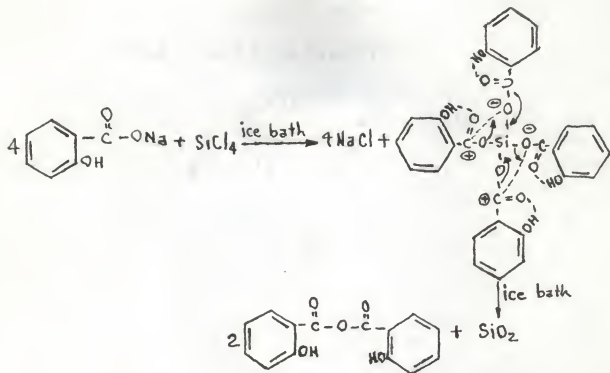


Fig. 1. Preparation of salicylic anhydride from sodium salicylate and silicon tetrachloride.

The preparation of silicon tetra-*o*-chlorobenzoate also ruled out the idea that the anhydride could have been formed from the steric hindrance effect.

Since silicon tetraesterate can be prepared, it seems probable that all silicon esters of the carboxylic acids up to 18 carbon atoms, can be prepared. After preparing silicon tetra- β -naphthanate, it seems probable that a substituted two ring silicon ester connected to the silicon in the beta position could be prepared by the Schuyten, Weaver, and Reid method (12). When the ortho position is occupied by a group that will cause hydrogen bonding, then probably the two ring silicon ester cannot be prepared.

Silicon tetraphenylpropionate and silicon tetrabenzoate are more stable compounds than silicon tetracinnamate and silicon tetra- β -naphthonate.

Silicon tetratrachloroacetate, silicon tetracrotonate, silicon tetra-stearate, silicon tetra-p-hydroxybenzoate, silicon tetra-o-chlorobenzoate, and silicon tetra-B-naphthonate are new compounds. The method for preparation of anhydrides from silicon tetrachloride and the sodium salt of monocarboxylic acids is also new.

The infrared spectra of silicon esters were determined between 3 and 15 μ . The spectra for silicon tetratrachloroacetate, silicon tetrabutyrate, and silicon tetracrotonate are shown in Plate I.

Significant strong absorption bands were found in the spectra of the silicon esters at 5.876, and between 9.040 and 9.876 μ correspond to values reported by Richard and Thompson (10) to be characteristic of the Si-O bond. No anhydride is present as no band occurs between 5.48 and 5.58 μ . Acetic anhydride has a strong wide band between 5.48 and 5.72 μ . Benzoic anhydride has a strong band at 5.584 μ . In each of the silicon esters prepared, the spectra revealed band characteristics of the corresponding carbon compounds. These spectral studies along with the analysis indicated that nine silicon esters have been prepared (Table I).

Lanning (5) reported some of the sodium salts of organic acids would not react with silicon tetrachloride according to the method of Schuyten, Weaver, and Reid (12). These salts are sodium formate and the sodium salts of dicarboxylic acids such as sodium oxalate. Sodium carbonate has been added to this group.

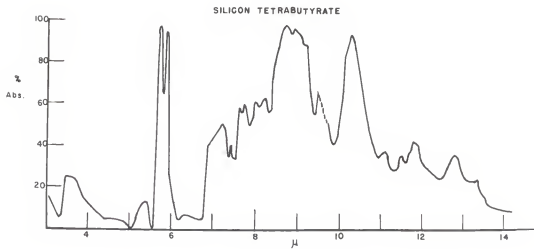
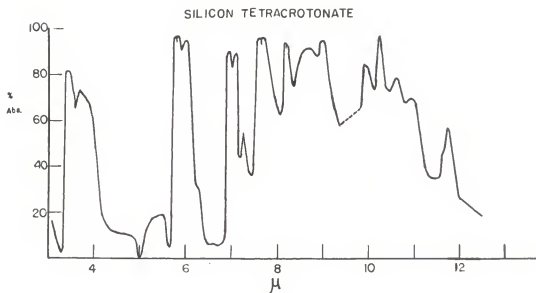
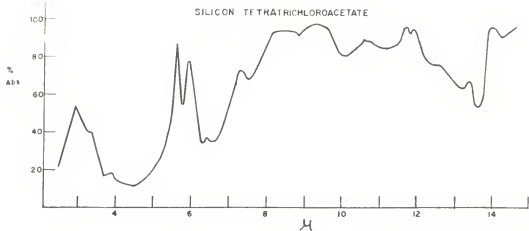
These sodium salts would not react directly with silicon tetrachloride. However, formic acid reacted with silicon tetrachloride probably to give silicon tetraformate, but the dicarboxylic acids such as oxalic acid would not react. Further study is needed before this can be explained.

EXPLANATION OF PLATE I

The infrared spectra of silicon esters.

- A. Silicon tetrachloroacetate
- B. Silicon tetrabutyrate
- C. Silicon tetracrotonate

PLATE I



The two melting points for the allophanates of 3-ethyl 3-pentanol were probably due to the reaction of one or two moles of cyanic acid to give respectively an unsubstituted urethane (II A) with the melting point of 192°C., and the allophanate (II B) with a melting point of 175-4°. As



Fig. 2. Reactions of the preparation of 3-ethyl 3-pentanol allophanate derivative.

The reason for letting the allophanates stand for 24 hours is that the rate of reaction of cyanuric acid with alcohols varies. Phenylethanol requires several days for completion while simple alcohols usually react so rapidly that the mixture becomes hot.

A V_2O_5 catalyst was necessary for accurate carbon and hydrogen analysis. Using the same ratio of ethylmagnesium bromide to silicon esters (silicon tetrapropionate, silicon tetraacetate, and silicon tetrabutyrate) the same silicones were produced. This was shown by the silicon analysis, index of refraction, and infrared spectra. Results of the carbon and hydrogen analysis for two silicones obtained from silicon tetrabutyrate with 0.8 and 3.5 times the stoichiometric amount of Grignard reagent are in Tables 2 to 7.

The analysis of silicone 1 corresponds to an $\text{C}_2\text{H}_5/\text{Si}$ value of 1.55. Silicone 2 corresponds to an $\text{C}_2\text{H}_5/\text{Si}$ value of 1.96.

The silicones formed from the reaction of the three silicon esters with

Table 2. Analysis of silicones obtained from the reaction of silicon esters with 0.8 and 3.5 times the stoichiometric amount of ethylmagnesium bromide at 36°C.

Analysis of Silicones	Compounds made from ethyl silicones			
	silicon	silicon	silicon	silicon
	tetra-butylate	tetra-propionate	tetraacetate	
% yield	1 to 0.8	75	74	75
	1 to 3.5	69	71	74
% SiO ₂	1 to 0.8	67.8	67.2	67.5
	1 to 3.5	58.53	58.2	58.56
Index of refraction	1 to 0.8	$\frac{N_{19}}{D} = 1.4460$	$\frac{N_{28}}{D} = 1.4420$	$\frac{N_{28}}{D} = 1.4425$
	1 to 3.5	$\frac{N_{19}}{D} = 1.4450$	$\frac{N_{28}}{D} = 1.4415$	$\frac{N_{28}}{D} = 1.4412$
% carbon Found	1 to 0.8	40.35		
	Calcd. 1 to 0.8	47.06		
% carbon Found	1 to 3.5	46.08		
	Calcd. 1 to 3.5	47.06		
% hydrogen Found	1 to 0.8	8.90		
	Calcd. 1 to 0.8	9.80		
% hydrogen Found	1 to 3.5	9.82		
	Calcd. 1 to 3.5	9.80		

Table 3. The analysis of alcohols obtained from the reaction of silicon esters with 0.8 and 3.5 times the stoichiometric amount of ethylmagnesium bromide carried out at 36°C.

Analysis of Alcohols	Alcohols obtained from the above reactions			
	3-ethyl	3-ethyl	3-methyl	
	3-hexanol	3-pentanol	3-pentanol	
% yield	1 to 0.8	45	45	
	1 to 3.5	56	56	
B.P. Found		160-1	142-3	
	Lit.	160.5	142	
Index of refraction	Found	$\frac{N_{15}}{D} = 1.4322$	$\frac{N_{28}^{5}}{D} = 1.4246$	$\frac{N_{20}}{D} = 1.4182$
	Lit.	$\frac{N_{15}}{D} = 1.4322$	$\frac{N_{22}^{5}}{D} = 1.4266$	$\frac{N_{21}}{D} = 1.4180$
	Found	153-4	172-3	151-2
	Lit.		172-3 and 152	152

Table 4. Analysis of ketones obtained from the reaction of silicon esters with 0.8 and 3.5 times the stoichiometric amount of ethylmagnesium bromide carried out at 36°C.

Analysis of ketones	: Ketones obtained from the above reactions		
	: 3-hexanone	: 3-pentanone	: 2-Butanone
% yield of ketones 1 to 0.8	26	27	29
1 to 3.5	10	10	14
B.P. of ketones Found	123-4	102-3	80-1
Lit.	123-3.5	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 derivative found	129-30	150-2	113-4
2-4 dinitrophenylhydrazone derivative Lit.	120	156	114

Table 5. Analysis of silicones obtained from the reaction of silicon esters with 0.8 and 3.5 times the stoichiometric amount of ethylmagnesium bromide at 90°C.

Analysis of Silicones	: Compounds made from ethyl silicones			
	: silicon	: silicon	: silicon	
	: tetra-butylate	: tetra-propionate	: tetra-acetate	
% yield	1 to 0.8	68	71	72
	1 to 3.5	66	67	66
% SiO ₂	1 to 0.8	67.32	67.54	67.61
	1 to 3.5	58.43	58.37	58.41
Index of refraction	1 to 0.8	$n_D^{20} = 1.4457$	$n_D^{20} = 1.4453$	$n_D^{20} = 1.4458$
	1 to 3.5	$n_D^{20} = 1.4455$	$n_D^{20} = 1.4458$	$n_D^{20} = 1.4456$

Table 6. Analysis of alcohols obtained from the reaction of silicon esters with 0.8 and 3.5 times the stoichiometric amount of ethylmagnesium bromide carried out at 0°C.

Analysis of Alcohols	: Alcohols obtained from the above reaction			
		3-ethyl	3-ethyl	3-methyl
		3-hexanol	3-pentanol	3-pentanol
% yield	1 to 0.8	41	39	40
	1 to 3.5	52	54	53
B.P.	Found	160-1	142-3	102-3
	Lit.	160.5	142	102
Index of refraction	Found	$n_D^{20} = 1.4293$	$n_D^{20} = 1.4275$	$n_D^{20} = 1.4183$
	Lit.	$n_D^{15} = 1.4322$	$n_D^{22} = 1.4266$	$n_D^{21} = 1.4180$
Allophanate Deriv.	Found	153-4	172-3	151-2
	Lit.		172-3 and 152	152

Table 7. Analysis of ketones obtained from the reaction of silicon esters with 0.8 and 3.5 times the stoichiometric amount of ethylmagnesium bromide at 0°C.

Analysis of Ketones	: Ketones obtained from the above reactions			
		3-hexanone	3-pentanone	2-Butanone
% yield	1 to 0.8	23	24	23
	1 to 3.5	8	7	11
B.P.	Found	123-4	122-3	80-1
	Lit.	123-5.5	102	80
Index of refraction	Found	$n_D^{20} = 1.3997$	$n_D^{20} = 1.3921$	$n_D^{20} = 1.3789$
	Lit.	$n_D^{22} = 1.3990$	$n_D^{25} = 1.3905$	$n_D^{20} = 1.3791$
2-4 dinitrophenylhydrazone Derivative found		129-30	153-4	112-3.5
2-4 dinitrophenylhydrazone Derivative Lit.		130	156	114

the Grignard reagent at the same concentration gave the same ethyl silicone as shown by the silicon analysis and infrared spectra. Equations for the reactions are shown in Plate II.

Silicone 1 was obtained by the reaction of 0.8 of the stoichiometric amount of Grignard reagent with the silicon ester. Silicone 2 was obtained by using 3 1/2 times the stoichiometric amount of Grignard reagent. The infrared spectra of silicone 1 and silicone 2, obtained from ethylmagnesium bromide with silicon tetrabutryrate, are shown in Plate III.

Significant absorption bands are found at 3.350 to 3.484, 6.782, 6.820, 6.040, 8.014, 9.040 to 9.042, 9.876, 10.232, and 13.4 μ . Young, Servais, Curie, and Hunter (16) reported significant absorption bands in the spectra of ethyl siloxanes at 3.38, 6.84, 7.08, 8.05, 9.22, 9.9, 10.4, 13.4, and 14.4 μ . Bands near 8.00 μ are due to C-Si bonds and bands between 9.040 and 9.898 are due to Si-O bonds.

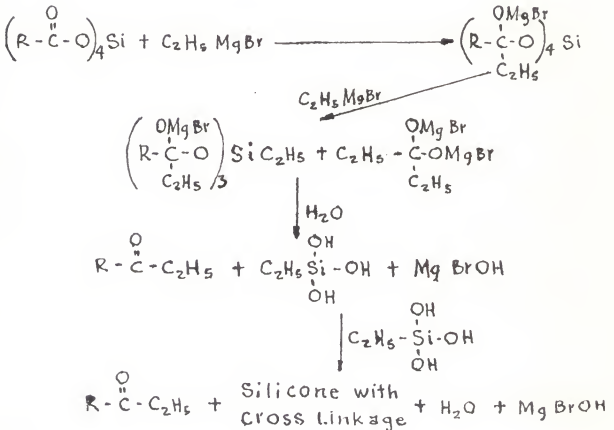
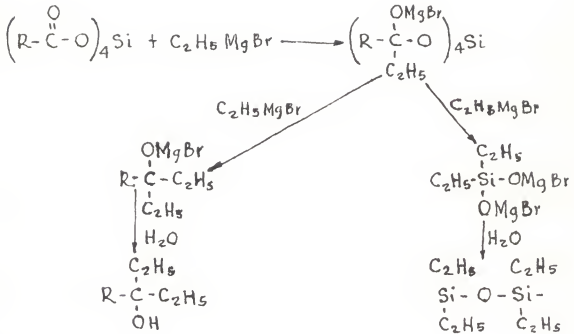
Silicon tetraacetate, silicon tetrapropionate, and silicon tetrabutryrate were treated with the same concentration of ethylmagnesium bromide at constant temperature for comparison. From the reaction of silicon tetraacetate with the Grignard reagent, 3-methyl 3-pentanol, 2-butanone, and ethyl silicone were formed. The reaction of silicon tetrapropionate with Grignard reagent formed 3-ethyl 3-pentanol, 3-pentanone, and ethyl silicone. From the reaction of silicon tetrabutryrate with the Grignard reagent, 3-ethyl 2-hexanol, 3-hexanone, and ethyl silicone were formed.

The yield and analysis of the products from the reactions of the above esters with the Grignard reagent are summarized in tables 2 to 7 and Plate III.

The reactions carried out at 0°C with 0.8 and 3.5 times the stoichiometric amount of Grignard reagent produced the same compounds as when the reactions were carried out at 36°C., but the yields were slightly higher at 36°C. When

EXPLANATION OF PLATE II

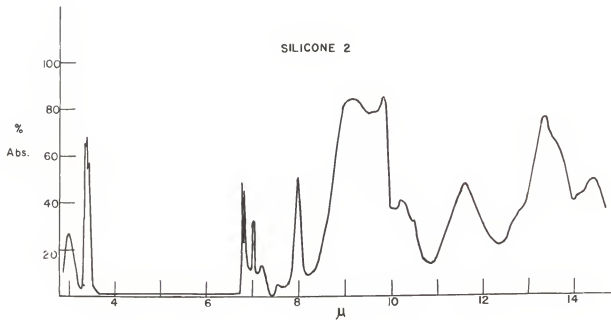
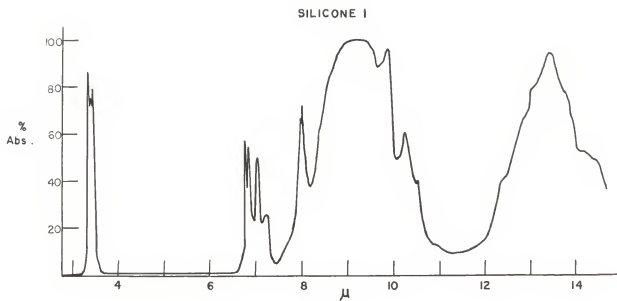
- A. Reaction of silicon esters with 3.5 times the stoichiometric amount of Grignard reagent.
- B. Reaction of silicon esters with 0.8 times the stoichiometric amount of Grignard reagent.



EXPLANATION OF PLATE III

Silicone 1 was obtained by the reaction of 0.8 the stoichiometric amount of ethylmagnesium bromide with silicon tetrabutyrate. Silicone 2 was obtained by using 1.5 times the stoichiometric amount of ethylmagnesium bromide.

- A. Silicone 1
- B. Silicone 2



six times the stoichiometric amount of Grignard reagent reacted with silicon ester only a very small amount of the ketone was formed as only a trace of the derivative was formed. The silicones were more viscous from the reactions of 0.8 the stoichiometric amount of Grignard reagent than with 8 times the amount with the silicon esters which was probably due to the cross linkage as is shown in equation form in Plate II.

Wright and Hunter (15) report absorption bands in the methyl siloxanes between 11.6 and 14 μ which they attribute to Si-C bonds. Both silicones 1 and 2 show a strong absorption band at 13.4 μ , and this is due to the C₂H₅-Si bond. In addition silicone 2 shows a band at 11.62 μ . Wright and Hunter (15) reported an absorption band near 11.7 μ in straight chain methyl polysiloxanes.

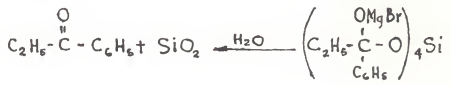
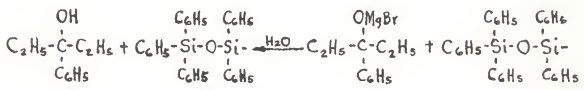
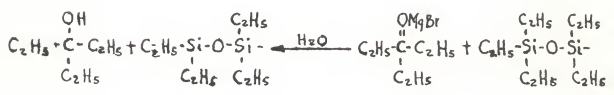
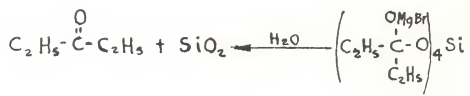
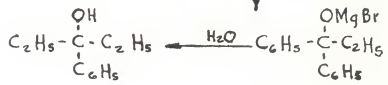
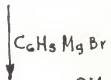
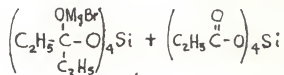
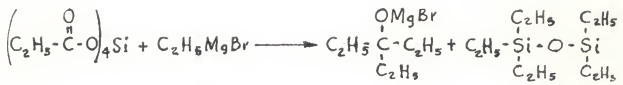
These spectral studies along with chemical analysis indicated that silicone 2 is an ethyl silicone with little cross linking and that silicone 1 may be an ethyl silicone with considerable cross linking.

The 3-phenyl 3-pentanol has been obtained from the reaction of silicon tetrapropionate with ethylmagnesium bromide without isolation of the 3-pentanone. The equations on Plate IV may represent the reactions that took place when the silicon tetrapropionate was treated with ethylmagnesium bromide and phenylmagnesium bromide.

The separation of the products was fairly good. It was possible to separate phenyl propiophenone (B.P. 218°C) from 3-phenyl 3-pentanol (B.P. 225-4°C) in an ice bath because propiophenone melts at 19-20°C whereas the other substances are liquids at that temperature. It was interesting to note that the propiophenone could not be separated from 3-phenyl 3-pentanol by crystallization of the 2-4 dinitrophenylhydrazones and extracting with an organic solvent because both products are soluble in the four organic solvents--benzene, ethyl alcohol, skelly F., and ethyl ether.

EXPLANATION OF PLATE IV

The equations for the reactions of ethylmagnesium
bromide and phenylmagnesium bromide with silicon
tetrapropionate.



The ethyl ether derivative of diphenylethylcarbinol could not be prepared by the Williamson synthesis. This was believed to be because of the low acid strength of 3-phenyl 3-pentanol. The analysis of the products from the reaction of silicon tetracarbonate with ethyl magnesium bromide gave proof that the equations on Plate IV were correct.

The 3-ethyl 4-hexenol-3 was prepared from the concentrated ether solution obtained from the reaction of silicon tetracarbonate with ethylmagnesium bromide. The liquid was decanted from the flake like crystals of 3-ethyl 4-hexenol-3 formed in the concentrated ether solution and the crystals purified from kelly F. and water ethyl alcohol mixture. On the other hand when the concentrated ether solution was distilled, some of the 3-ethyl 4-hexenol-3 was dehydrated. 3-Ethyl 4-hexenol-3 was a colorless solid with a melting point of 68-9°C. This tertiary alcohol is a new compound. The infrared spectrum is shown in Plate V.

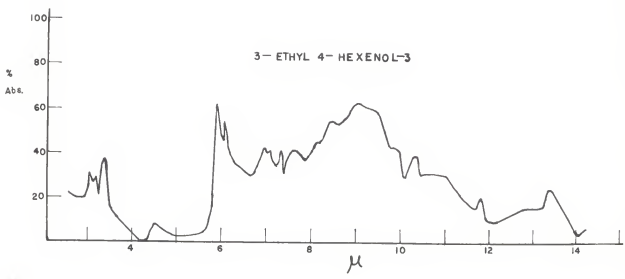
Significant absorption bands occur in the infrared spectrum of 3-ethyl 4-hexenol-3 at 3.05 (m), 3.20 (m), 3.40 (m), 4.5 to 4.6 (w) 5.86 (s), 6.07 (s), 6.95 to 7.10 (m), 7.35 (m), 7.60 to 7.70 (m), 8.40 to 8.50 (s), 9.00 to 9.50 (s), 9.90 (m), 10.35 (m), 11.8 (w), and 13.4 (w) μ . Randall, Fuson, Fowler and Dangel (9) report absorption peaks in ethyl alcohol at 3.00 (m), 3.40 (m), 4.69 (w), 6.06 (w), 7.23 (s), 7.39 (s), 7.76 (w), 7.88 (w) and 9.18 to 9.62 (s) μ .

The strong bands at 6.07 (s) and 8.50 (s) are due to double bond and tertiary alcohol respectively.

EXPLANATION OF PLATE V

The infrared spectrum of 3-ethyl 4-hexenol-3.

PLATE IV



SUMMARY

Silicon tetratrifluoroacetate, silicon tetrabutryrate, silicon tetracrotionate, silicon tetrasterate, silicon tetraphenylpropionate, silicon tetra-*p*-naphthonate, silicon tetracinnamate, silicon tetra-*o*-chlorobenzoate, and silicon tetra-*p*-hydroxybenzoate have been prepared by the method of Schuyten, et al. (12). All except possibly silicon tetrabutryrate are new compounds.

It appears that anhydrous ethyl ether may be a superior reaction medium. Diatomaceous silica is necessary for rapid filtering of these silicon esters. These silicon esters are unstable to heat and react readily with water and alcohols.

The acid strength of sodium salts of monocarboxylic acids appears to have no effect on the silicon ester formation by the Schuyten, et al. (12) method. Silicon tetratrifluoroacetate has been prepared from the sodium salt of trifluoroacetic acid, whose acid strength is 1.3×10^{-1} . Steric hindrance does not cause the anhydride to form when a group larger than hydrogen is placed in the ortho position of aromatic silicon esters.

From this investigation it was shown in one case that if the group in the ortho position causes hydrogen bonding, the anhydride forms. Salicylic anhydride was formed this way. Its melting point was 158-8.5°C.

Silicon esters can be prepared by the Schuyten, et al. (12) method from the sodium salts of monocarboxylic acids containing a chain from 2 to 18 carbons. Two ring silicon esters also can be prepared when the silicon ester is connected in the beta position.

The infrared spectra of silicones were determined between 3 and 15 μ . All of the silicon esters had significant strong absorption bands at 5.876 and 9.040-9.420 μ . No anhydride is present as there was no band between 5.48 and 5.58 μ . The band at 6.05 μ in silicon tetracrotionate is due to the

double bond. Silicon tetratrifluoroacetate had a strong band at 14.00μ which is due to the $C-Cl_3$ group in the structure.

The Grignard reagent (ethylmagnesium bromide) reacts with different silicon esters to give the same ethyl silicone when the same ratio of silicon ester with the Grignard reagent is used. The amount of cross linkage in the ethyl silicone depends on the amount of Grignard reagent used. Ethyl silicone prepared from 0.8 the stoichiometric amount of ethylmagnesium bromide with silicon ester has a C_2H_5/Si value of 1.55. When 3.5 times the stoichiometric amount of ethylmagnesium bromide is used with a silicon ester the ethyl silicone has a C_2H_5/Si value of 1.96.

Infrared spectra of the silicones were determined and agree with the literature values.

The alcohols and ketones are the products to be expected when a Grignard reagent reacts with an ester. A fair yield of ketones was obtained only when the concentration of Grignard reagent was 0.8 or less of the stoichiometric amount. The high yield of alcohols were independent of the concentration of Grignard reagent.

The alcohols and ketones produced from the reaction of silicon esters with ethylmagnesium bromide are as follows: 3-methyl 3-pentanol and 2-butanone from silicone tetraacetate; 3-pentanone from silicon tetrapropionate; 3-ethyl 3-hexanol and 3-hexanone from silicon tetrabutyrate; and 3-ethyl 4-hexenol-3 and 2-hexenone-4 from silicon tetracrotonate.

Significant absorption bands are found in the spectrum of 3-ethyl 4-hexenol-3 at 3.05, 3.40, 6.07, 8.50 and 9.65μ . The 3-ethyl 4-hexenol-3 is a new compound.

The reaction of silicon tetrapropionate with two Grignard reagents,

ethylmagnesium bromide and phenylmagnesium bromide, produced diphenyl ethyl carbinol, 3-ethyl 3-pentanol, 3-phenyl 3-pentanol, 3-pentanone and propiophenone.

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PREPARATION OF SILICON ESTERS SUCH AS SILICON
TETRAPROPIONATE AND THEIR REACTION WITH
GRIGNARD REAGENTS TO FORM TERTIARY
ALCOHOLS, KETONES, AND SILICONES

by

McDONALD MOORE

B. S., Fort Valley State College, 1954

AN ABSTRACT OF A THESIS

submitted in partial fulfillment of the

requirements for the degree

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KANSAS STATE COLLEGE
OF AGRICULTURE AND APPLIED SCIENCE

1957

Silicon esters, although not a new type compound, have not been extensively studied because only silicon tetracetate, silicon tetrapropionate, silicon tetrabutryrate, and silicon benzoate have been prepared.

This investigation was initiated to determine some of the factors that might prevent the formation of silicon esters by the method of Schuyten, Weaver and Reid. To establish these facts more silicon esters were prepared.

The next immediate investigation was to further study the reaction of silicon esters with Grignard reagents and the mechanism by which these reactions take place.

Silicon tetratrifluoroacetate, silicon tetrabutryrate, silicon tetracrotonate, silicon tetraesterate, silicon tetraphenylpropionate, silicon tetrab-naphthionate, silicon tetracinnamate, silicon tetra-*o*-chlorobenzoate, and silicon tetra-*p*-hydroxybenzoate have been prepared by the method of Schuyten, Weaver, and Reid. All except possibly silicon tetrabutryrate are new compounds.

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