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

SILICON TETRABENZOATE

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The method for preparing silicon esters from silicon tetrachloride and sodium salts of organic acids has been used by Schuyten, Weaver, and Reid (1) to prepare silicon tetraacetate and by Lanning (2) to prepare silicon tetrapropionate.

In continuing this research it seemed desirable to determine whether or not silicon esters containing aromatic groups could be prepared this way. The method has been applied to the preparation of silicon tetrabenzoate in 58.8% yields.

The infrared absorption spectra of silicon tetrabenzoate, benzoic anhydride, and benzene between 2 and 15 μ are shown in Fig. 1.

Silicon tetrabenzoate is a white crystalline solid which begins to decompose with partial melting into silicon dioxide and benzoic anhydride at 92°. Like silicon tetraacetate (4) and silicon tetrapropionate (2) it reacts with alcohols and water but at a slower rate.

Ether solutions of silicon tetrabenzoate react with Grignard reagents in the same manner that silicon tetrapropionate (2) does, and triphenylcarbinol has been prepared in 48% yield by the reaction of ether solutions of silicon tetrabenzoate with phenylmagnesium bromide and subsequent hydrolysis. Unidentified organosilicon compounds were also produced.

EXPERIMENTAL

The apparatus used in preparing silicon tetrabenzoate was very similar to that used by Schuyten, Weaver, and Reid (1). The silicon tetrachloride used was purified by redistillation. The sodium benzoate was C. P. Reagent. Anhydrous diethyl ether was used as the diluent.

The preparation was carried out by adding 0.06 mole of the silicon tetrachloride dissolved in 50 ml. of ether dropwise into a slurry of 1.15 times the calculated amount of anhydrous sodium benzoate dispersed in 150 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 the silicon tetrachloride and for one hour afterwards while the mixture was kept at the boiling point. When the ether solution gave no chlorine test the sodium chloride and excess sodium benzoate were removed. The ether was removed from the filtrate under reduced pressure at room temperature leaving a white solid which by the following analysis was indicated to be nearly pure silicon tetrabenzoate.

Anal. Calc'd for $C_{28}H_{20}O_8Si$: Si, 5.47; $C_6H_5CO_2$, 94.53.
Found: Si (5), 5.35; $C_6H_5CO_2$ (6), 94.36.

After recrystallization from petroleum ether (boiling range 35–60°) the silicon analysis was 5.46%. The molecular weight determined by the Beckman method (3), using benzene as solvent, was 512.9. The calculated value is 512.5.

The complete hydrolysis of silicon tetrabenzoate was quite slow in cold water and the method of Patnode for silicon halides (6) had to be modified to the extent of boiling the solution before titrating the benzoic acid liberated.

Reaction with phenylmagnesium bromide. A dilute diethyl ether solution containing 4.9 g. of silicon tetrabenzoate was added through a dropping-funnel drop by drop into 1½ times the calculated amount of a Grignard reagent prepared from bromobenzene in the usual

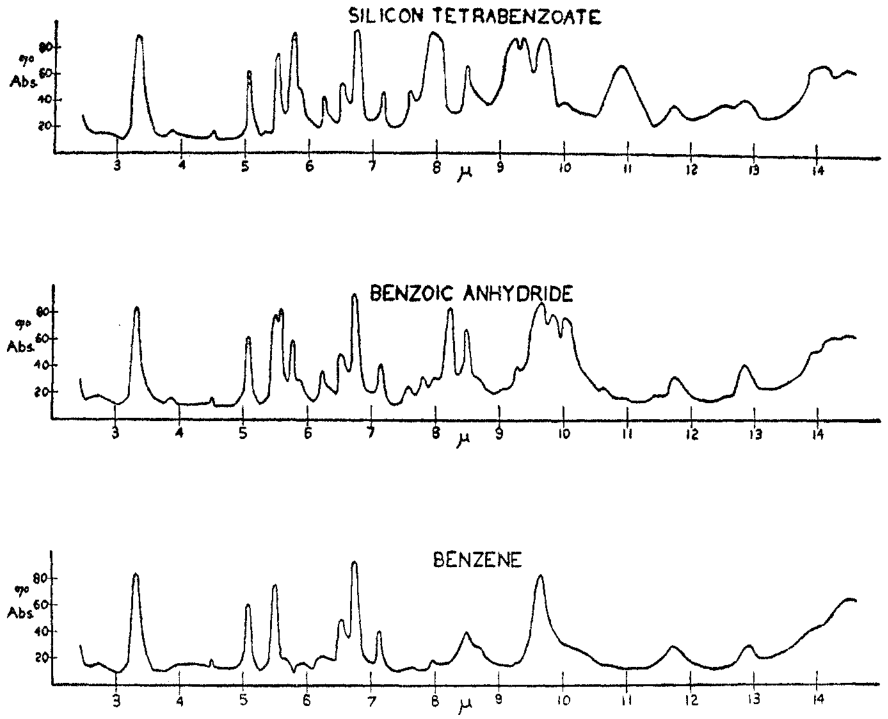


FIG. 1

manner. The mixture was stirred mechanically and maintained at the boiling point for one hour after the addition was complete. The Grignard complex was hydrolyzed in an ammonium chloride solution containing ice. Some hydrochloric acid was added afterwards to react with the magnesium precipitate. The triphenylcarbinol was extracted with three 70-ml. portions of diethyl ether.

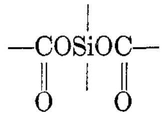
The product obtained after evaporation of the ether had a small amount of oily liquid in addition to the solid triphenylcarbinol; the oil was removed by extraction with 50 ml. of "Skellysolve F". After the extraction and drying 4.8 g. (48%) of nearly white triphenylcarbinol melting at 159–161° (mixture m.p. 160–162°) was obtained. The material extracted with "Skellysolve F" contained some silicon indicating the presence of organosilicon compounds.

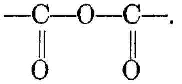
Infrared absorption. The infrared spectra of silicon tetrabenzoate and benzoic anhydride were determined from benzene solutions. This solvent adds no absorption bands to the spectra that are not given by these compounds since the benzene ring is found in both of them. The solution used for the spectra of silicon tetrabenzoate contained 8.27% by weight of the product. The solution of benzoic anhydride contained 10% by weight of pure benzoic anhydride. The spectra of the benzene was determined for control purposes and to prove that the benzene was pure.

The infrared spectra were determined with a Perkin-Elmer, Model 12C, Infrared Spectrometer using a rock salt prism.

DISCUSSION

Significant, strong absorption bands are found in the spectra of silicon tetrabenzoate at 7.92, 9.236, 9.377, and 10.915 μ. The band at 7.92 μ is found in methyl benzoate (7) and is characteristic of esters of benzoic acid. The bands at

9.236 and 9.377 μ were reported by Richards and Thompson (8) to be characteristic of the Si—O bond. The strong band at 10.915 μ is probably due to some vibration of the  $-\underset{\underset{O}{\|}}{C}O\overset{|}{\underset{|}{Si}}O\underset{\underset{O}{\|}}{C}-$ structure.

The infrared spectrum of benzoic anhydride was determined in order to find out if any of this compound was present in the product. This could be present if polysiloxanes were formed by splitting out benzoic anhydride. The strong absorption bands occurring in the spectrum of benzoic anhydride at 5.584, 8.236, 9.83, and 10.18 μ are not found in the spectrum of the silicon tetrabenzoate, indicating that benzoic anhydride could not be present in any significant amount. These absorption bands are apparently characteristic of the anhydride structure  $-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{C}-$. Acetic anhydride (7) has a strong, wide absorption band between 5.48 and 5.72 μ, a moderate band at 8.15 μ, a strong band at 9.98 μ, and a strong band at 10.06 μ. Succinic anhydride (7) shows corresponding strong bands at 5.61 and 8.2 μ.

These spectral studies along with the analysis indicate that a new compound, silicon tetrabenzoate, has been prepared.

The formation of silicon esters from sodium salts of monocarboxylic acids must be a general reaction as silicon tetraacetate (1), silicon tetrapropionate (2), and silicon tetrabenzoate have been made this way. The only exception found is sodium formate (2) which does not react with $SiCl_4$ to form silicon tetraformate.

The fact that both silicon tetrapropionate (2) and silicon tetrabenzoate react with Grignard reagents to form tertiary alcohols indicates that this is also a general reaction.

SUMMARY

Silicon tetrabenzoate was prepared from silicon tetrachloride and anhydrous sodium benzoate. The infrared spectra of silicon tetrabenzoate and benzoic anhydride were determined between 2 and 15 μ. Silicon tetrabenzoate reacted with water and alcohols; it was unstable to heat. Triphenylcarbinol was made by the reaction of silicon tetrabenzoate with phenylmagnesium bromide.

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