[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY OF KANSAS STATE COLLEGE]

Preparation and Properties of Silicon Tetrapropionate

BY F. C. LANNING

RECEIVED JUNE 27, 1952

Silicon tetrapropionate was prepared from silicon tetrachloride and anhydrous sodium propionate. It reacted readily with water and alcohols; was unstable to heat. The thermal decomposition products were characterized. A stiff silica gel containing 69% diethyl ether was prepared. A tertiary alcohol, 3-ethylpentanol-3, and a silicone-like oil were made by reaction of silicon tetrapropionate with ethylmagnesium bromide. This is a new method of preparing tertiary alcohols.

Silicon tetraacetate was prepared in 1947 by Schuyten, Weaver and Reid[1] from sodium acetate and silicon tetrachloride using anhydrous benzene as a diluent. This method has been applied to the preparation of silicon tetrapropionate in 71–74% yields whereas the methods used by Friedel and Ladenberg[2] in 1867 for the original preparation of silicon tetraacetate and of Volnov[3] are not satisfactory. The method of Schuyten, Weaver and Reid[1] does not work in any solvent tried for the preparation of silicon esters of dicarboxylic acids such as oxalic acid or for formic acid.

Silicon tetrapropionate is a colorless liquid of very low freezing point. Like silicon tetraacetate[2] it reacts readily with water and alcohols and is unstable to heat.

A stiff silica gel containing 69% diethyl ether has been made by letting a dilute ether solution of silicon tetrapropionate take up water from starch containing 10% water.

Ether solutions of silicon tetrapropionate react with ethylmagnesium bromide to yield after hydrolysis 3-ethylpentanol-3 and silicic acid.

When the reaction product of silicon tetrapropionate and excess ethylmagnesium bromide is hydrolyzed with hydrochloric acid not only is 3-ethylpentanol-3 formed, but most of the silicon is converted into a silicone-like oil. Further studies are being made to characterize this oil and explain its formation.

Experimental

The apparatus for preparing silicon tetrapropionate was very similar to that used by Schuyten, Weaver and Reid.[1] The silicon tetrachloride was purified by redistillation and the sodium propionate was anhydrous C.P. reagent. Anhydrous benzene, petroleum ether and diethyl ether were used as solvents. The reaction proceeded in all three solvents but diethyl ether is the only one of the three that can be satisfactorily removed from the product.

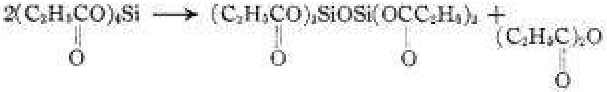
The preparation was carried out by adding 0.25 mole of the silicon tetrachloride dissolved in 50 ml. of ether dropwise into a slurry of twice the calculated amount of anhydrous sodium propionate dispersed in 200 ml. of ether. The silicon tetrachloride was added at such a rate that gentle refluxing was maintained. The mixture was stirred mechanically during the addition of silicon tetrachloride and for one 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 propionate was removed by filtration and the filtrate was concentrated under reduced pressure at room temperature. *Anal.* Calcd. for $C_{12}H_{20}O_8Si$: Si, 8.80; propionic acid, 91.26. Found: Si,[4] 8.78; propionic acid,[5] 91.22.

Decomposition of Silicon Tetrapropionate.—Silicon tetrapropionate was heated at 140° for different lengths of time and the propionic anhydride removed at low pressure. Residues which were free of SiO_2, have been obtained containing 9.33, 9.48, 9.63 and 10.92% Si.[4] The latter residue analyzed 85.72% propionic acid[5] and this analysis corresponds to that calculated for the dimer $(C_2H_5\underset{\underset{O}{\|}}{C}O)_3SiOSi(O\overset{\overset{O}{\|}}{C}C_2H_5)_3$ (10.98% Si and 85.88% propionic acid).

Reaction with Ethylmagnesium Bromide.—A dilute diethyl ether solution of silicon tetrapropionate was added through a dropping funnel drop by drop into a Grignard reagent prepared from ethyl bromide in the usual manner. The mixture was stirred mechanically and maintained at the boiling point for one-half hour after the addition was complete. The Grignard complex was hydrolyzed by a solution of ammonium chloride.

Discussion

The analysis of decomposition products indicates that the first step in the decomposition of silicon tetrapropionate by heat may be the one shown in the equation



$$2(C_2H_5\underset{\underset{O}{\|}}{C}O)_4Si \longrightarrow (C_2H_5\underset{\underset{O}{\|}}{C}O)_3SiOSi(O\underset{\underset{O}{|}}{C}C_2H_5)_3 + (C_2H_5\underset{\underset{O}{\|}}{C})_2O$$

The reaction apparently continues through similar condensations forming larger molecules.

The 3-ethylpentanol-3 probably was formed by the Grignard reagent reacting with the silicon tetrapropionate in the way it usually reacts with esters. It seems likely that other tertiary alcohols, including ones having different radicals, might be made by this new method and active investigation is being continued.

MANHATTAN, KANSAS

---

(1) H. A. Schuyten, J. W. Weaver and J. D. Reid, THIS JOURNAL, **69**, 2110 (1947).

(2) C. Friedel and A. Ladenberg, *Ann.*, **145**, 174 (1868).

(3) J. N. Volnov, *J. Gen. Chem.* (*U.S.S.R.*), **9**, 2269 (1939).

(4) J. F. Hyde and R. C. DeLong, THIS JOURNAL, **63**, 1194 (1951).

(5) W. I. Patnode in Rochow, "An Introduction to the Chemistry of Silicones," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1951.