(1:1) were placed in a one-liter flask. To this was added with rapid stirring, 320 g. (2 moles) of 1-(*n*-butoxy)-ethyl acetate over a period of fifty-five minutes. The temperature was maintained at 10–20° by means of an ice-bath. Stirring was continued for thirty minutes, the reaction mixture poured into a suspension of 106 g. (1.0 mole) of sodium carbonate in 150 ml. of water, the oil layer separated, dried over anhydrous potassium carbonate and distilled to give 295 g. (85%) of *n*-butyl acetal, b. p. 185–189°, $n^{20}\text{D}$ 1.4080.[4]

Preparation of 2-Butylmercaptoethyl Acetate.—Upon mixing 90 g. (1 mole) of *n*-butyl mercaptan, 43 g. (0.5 mole) of vinyl acetate and 0.5 ml. of boron trifluoride etherate, the temperature rose slowly to 62°. The mixture was allowed to stand overnight and 1 g. of sodium methoxide added. Distillation gave 75 g. (99% yield based on vinyl acetate) of 2-butylmercaptoethyl acetate, b. p. 72–75° (2 mm.), $n^{20}\text{D}$ 1.4616.

With mercuric sulfate as the catalyst instead of boron trifluoride etherate, the yield of the mercapto-ester was 76%; with no catalyst present the yield of this ester amounted to only 10%.

Summary

1. Acetals are produced in good yield by the reaction of vinyl acetate with primary aliphatic alcohols in the presence of an acidic mercury catalyst.
2. Ketals are produced in a similar manner from isopropenyl acetate.
3. It is suggested that the vinyl acetate and alcohol initially react to form a hemiacetal acetate, which subsequently reacts with alcohol to give an acetal and acetic acid.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Some Diethylisopropoxyhalogenosilanes and their Hydrolysis Products[1]

BY PATRICK A. MCCUSKER AND CHARLES E. GREENE

Although a number of alkoxyfluorosilanes and some alkylalkoxychlorosilanes have been prepared, no alkylalkoxyfluorosilanes have been previously reported. In the course of the preparation of a compound of this type, some previously unreported organosilicon compounds were prepared and some observations made on the hydrolysis of diethylisopropoxyhalogenosilanes.[2]

Direct reaction of excess isopropyl alcohol and diethyldichlorosilane gave yields of only 20% of diethyldiisopropoxysilane while yields of 67% have been reported for the analogous preparation of dimethyldi-*n*-butoxysilane.[3] The lower yield of the isopropoxy compound may be attributed to the greater steric requirements of the isopropoxy group or to the general lower reactivity of the secondary alcohol compared to the primary. A low yield of diethylisopropoxyfluorosilane (22%) was obtained from the reaction of zinc fluoride on diethylisopropoxychlorosilane. This is probably due to a competing reaction in which both the alkoxy and chloro substituents are replaced by fluorine.

An aqueous suspension or a homogeneous solution of 0.04 molar diethylisopropoxyfluorosilane in a methanol–water mixture, maintained a hydrogen ion concentration of less than 10^{-4} mole per liter, as indicated by the basic color given by methyl orange which is unchanged on standing several days. Using phenolphthalein as an indicator, however, the suspension in water could be rapidly titrated to a stoichiometric end-point with 0.1 N base. A calculation of the concentration of hydrogen fluoride necessary to produce a hydrogen ion concentration of 10^{-4} mole per liter indicated that the hydrolysis came to equilibrium when less than 0.3% of the fluoride has been hydrolyzed in neutral water. At a somewhat lower hydrogen ion concentration, 10^{-10} mole per liter, hydrolysis proceeded to completion very rapidly.

On the hydrolysis of diethylisopropoxychlorosilane, with an equivalent amount of base, even in the presence of excess isopropyl alcohol, the alkoxy group split off and the cyclic trimer and tetramer were formed in high yield. [Diethyldiisopropoxysilane was found, however, to be stable in excess base.] Justification for the assignment of formulas to the two cyclic compounds is based on the analytical composition, molar refraction and molecular weight determination. The absence of any hydroxyl groups was further shown by the application of the Zerewitinoff reaction.

A marked difference in the action of sodium on the cyclic trimer and the cyclic tetramer was incidentally observed. The trimer on heating with sodium in the temperature range 150 to 245° evidently underwent a polymerization resulting in a marked increase in viscosity. The tetramer, on the other hand, was completely unaffected by long heating with finely divided sodium at 295°.

Experimental

The reaction apparatus used in this work consisted of a 1-liter, 3-necked flask equipped with stirrer and reflux condenser and protected from atmospheric moisture. All products were purified by fractional distillation through a total reflux, partial take-off column, 12 mm. inside diameter and 53″ in height, packed with 1/8″ glass helices. The column was operated at a reflux ratio of ten to one. Carbon and hydrogen analyses were made by Micro-Tech Laboratories, Skokie, Illinois, and hydrolyzable halogen was determined by titration of aqueous mixtures with standard base. Molar refractions were calculated from the bond refraction values of Warrick[4] and molecular

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(1) This paper consists of a report of work done under contract with the Technical Command, Chemical Corps, U. S. Army.

(2) The authors wish to thank Dr. Charles C. Price for his helpful interest in this work.

(3) Sauer, THIS JOURNAL, **68**, 138 (1946).

(4) Warrick, *ibid.*, **68**, 2455 (1946).

weights were obtained from cryoscopic measurements in benzene.

Diethylisopropoxychlorosilane.[5]—Purified diethyldichlorosilane (1.75 moles) and 500 ml. of benzene were heated to reflux in the reaction flask. During a period of three hours, 1.75 moles of isopropyl alcohol was added dropwise to the refluxing mixture. During the first stages of the reaction a water-insoluble, combustible gas was given off in addition to the hydrogen chloride. The volume of the gas, presumably propylene, was measured and found to represent a loss of about 5 mole %. In a considerable number of preparations this same gas evolution was observed and appeared to be characteristic of the reaction under these conditions. After addition was complete the reaction mixture was fractionated in the 53″ column to give a 72% yield of diethylisopropoxychlorosilane. The properties of the purified compound are as follows: b. p. 155.5° at 750 mm., $n^{20}\mathrm{D}$ 1.4123, d^{20}_4 0.9227, MR_{D} calcd. 49.2, obs. 48.7.

Anal. Calcd. for $C_7H_{17}OSiCl$: C, 46.6; H, 9.5; Cl, 19.6; mol. wt., 180.5. Found: C, 46.7; H, 9.5; Cl, 19.2; mol. wt., 182.

Diethyldiisopropoxysilane.—In the residue from the fractionation of diethylisopropoxychlorosilane there was found in all runs about 10 mole % of the diether. For purposes of characterization further amounts of this compound were prepared by addition of diethyldichlorosilane to excess isopropyl alcohol. Only a small yield (20%) was obtained in this manner. Sufficient product, however, was obtained for characterization. The compound was purified by fractional distillation and had the following properties: b. p. 174° at 750 mm.; $n^{20}\mathrm{D}$ 1.4032; d^{20}_4 0.8423; MR_{D} calcd. 59.6, obs. 59.2.

Anal. Calcd. for $C_{10}H_{24}SiO_2$: C, 58.8; H, 11.8. Found: C, 58.8; H, 11.9.

The compound is a colorless liquid with a mild sweet odor, insoluble and non-reactive in water. Hydrolytic cleavage was found to occur very rapidly in aqueous acid but either slowly or not at all in aqueous base.

Diethylisopropoxyfluorosilane.—Diethylisopropoxychlorosilane (0.58 mole) in 250 ml. of benzene was placed in the reaction flask. Technical grade zinc fluoride (0.33 mole) dried by heating for one hour at 200°, was added slowly with stirring during one hour. The reaction was slow to start but exothermic enough to require cooling. The mixture was stirred for four hours and filtered. Fractional distillation of the filtrate gave the following fractions: Ten grams of diethyldifluorosilane, 12 g. (22% yield) of diethylisopropoxyfluorosilane, 12 g. of unreacted diethylisopropoxychlorosilane and 31 g. of unidentified residue. The purified diethylisopropoxyfluorosilane had the following properties: b. p. 127° at 750 mm., $n^{20}\mathrm{D}$ 1.3803, d^{20}_4 0.8745, MR_{D} calcd. 43.5, obs. 43.5.

Anal. Calcd. for $C_7H_{17}OSiF$: C, 51.2; H, 10.4; F, 11.5. Found: C, 51.1; H, 10.6; F, 11.5.

Cyclic Polysiloxanes.—Hydrolysis of diethylisopropoxychlorosilane was carried out under two sets of conditions. In procedure A, 50 g. (0.9 mole) of potassium hydroxide was added to 500 g. of isopropyl alcohol and the mixture heated until nearly all the solid had dissolved. Diethylisopropoxychlorosilane (0.83 mole) was added dropwise to the cold solution with agitation, while the temperature of the mixture was held below 20°. After addition was complete the potassium chloride was filtered off and the filtrate fractionated. The isopropyl alcohol which came off first gave a strongly acid reaction when dissolved in water indicating that an excess of base may not have been maintained in the reaction mixture. Distillation of the 84 g. of residue remaining after the removal of the alcohol gave 21 g. of hexaethylcyclotrisiloxane (25% yield) and 50 g. (59% yield) of octaethylcyclotetrasiloxane.

In procedure B a 20% aqueous sodium hydroxide solution containing 2.5 moles was placed in the reaction flask and 1 mole of diethylisopropoxychlorosilane added slowly under the surface of the solution with stirring. The temperature of the reaction mixture was held below 20°. The cloudy one-phase liquid was then extracted with three 50-ml. portions of ether and the combined extracts dried with anhydrous sodium sulfate. On distillation a 50-g. fraction of isopropyl alcohol was obtained. The higher boiling fraction yielded 28 g. (27% yield) of hexaethylcyclotrisiloxane, 12 g. (12% yield) of octaethylcyclotetrasiloxane and 29 g. of a high boiling residue.

The properties of the purified cyclic trimer from both procedures were as follow: b. p. 246° at 750 mm., 97° at 2 mm., $n^{20}\mathrm{D}$ 1.4305, d^{20}_4 0.9560, MR_{D} calcd. 83.7, obs. 82.9.

Anal. Calcd. for $C_4H_{10}SiO_3$: C, 47.01; H, 9.86; mol. wt., 306. Found: C, 46.91; H, 10.04; mol. wt., 319.

The purified cyclic tetramer had the following properties: b. p. 295° at 750 mm., 134° at 2 mm.; $n^{20}\mathrm{D}$ 1.4340, d^{20}_4 0.9625; MR_{D} calcd. 111.6, obs. 110.6.

Anal. Calcd. for $C_4H_{10}SiO_4$: C, 47.01; H, 9.86; mol. wt., 409. Found: C, 47.16, H. 9.83; mol. wt., 394.

Summary

1. Diethylisopropoxychlorosilane, diethylisopropoxyfluorosilane and diethyldiisopropoxysilane have been prepared and characterized.

2. The hydrolysis of the fluoro compound has been observed to proceed to only a very slight extent in neutral water but to go rapidly to completion in slightly basic solution.

3. Hydrolysis of diethylisopropoxychlorosilane in excess isopropyl alcohol, containing a nearly equivalent amount of potassium hydroxide, has been found to give high yields of cyclic trimer and tetramer. These cyclic polysiloxanes have been purified and characterized.

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[5] The authors acknowledge the assistance of Mr. O. C. Kohler in the preparation of this compound.