[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, THE UNIVERSITY OF CHICAGO]

Alkyl Fluorosilicates

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Although certain fluorosilanes of the type, R_aSiF_b, have been reported,[2] no examples of the fluorine analogs of the alkyl chlorosilicates have been described. The preparation of some members of this series was undertaken with a view toward their use as intermediates in further synthesis. They were found to exhibit such remarkable and unexpected properties, in comparison with the alkyl chlorosilicates, that they are in themselves of sufficient interest to merit a preliminary report.

The action of silicon tetrafluoride on ethyl alcohol, according to Knop,[3] results in ethyl orthosilicate and fluosilicic acid. According to Gierut, Sowa and Nieuwland,[4] who made a study of silicon tetrafluoride as a catalyst in esterification reactions, silicon tetrafluoride and ethyl alcohol form an unstable addition compound containing 4 moles of alcohol. He lists several other alcohols which behave similarly.

We examined briefly the following possible methods for preparing alkyl fluorosilicates[5]: (1) halogen exchange between an alkyl chlorosilicate and an inorganic fluoride; (2) reaction of an alkyl orthosilicate with the fluoride of an element capable of forming a stable alkoxy compound as, for example, antimony trifluoride; (3) reaction of an alkyl orthosilicate with an organic acid fluoride, such as benzoyl fluoride.

Of these methods, only the second has produced satisfactory results, and then only in the preparation of ethyl fluorosilicates. It failed in the attempted preparation of allyl fluorosilicates.

The chemical behavior of the alkyl fluorosilicates differs from that of the corresponding alkyl chlorosilicates first in the very high rate of decomposition when treated with water. In contrast with the chlorosilicates which react slowly with water at room temperature, forming eventually a clear solution, the fluorosilicates which we have prepared react instantly, forming a gel.

With alcohols, an exchange of alkyl group occurs, and there is no elimination of hydrogen fluoride analogous to the elimination of hydrogen chloride when a chlorosilicate reacts with an alcohol. It is thus possible to prepare the fluorosilicates of higher alcohols by means of alcoholysis reactions when they are not obtainable directly. This is the method by which triallyl fluorosilicate and tri-*n*-butyl fluorosilicate have been prepared.

The explanation of this apparently anomalous behavior is doubtless to be found in the catalysis of alkyloxy group elimination by hydrogen fluoride. The silicon–fluorine bond in these compounds, as well as in silicon tetrafluoride, is less reactive than the silicon–chlorine bonds of analogous compounds. But the hydrogen fluoride formed upon reaction with water must then act as a powerful catalyst for the hydrolysis, or alcoholysis, reactions involving the alkoxyl groups. The replacement of an alkoxy group by hydroxyl or by another alkoxy group is also catalyzed by hydrogen chloride, as is shown in other papers of this series, but the effect must be of a lower order of magnitude.

It is consistent with this hypothesis that in the presence of pyridine no reaction occurs between triethyl fluorosilicate and *n*-butyl alcohol, whereas triethyl chlorosilicate and *n*-butyl alcohol react readily forming triethylbutyl orthosilicate in quantitative yield. The yield is less than quantitative in the absence of pyridine, probably because of alkyl group interchange brought about by free hydrogen chloride.

Experimental

Diethyl Difluorosilicate and Triethyl Fluorosilicate.—A mixture of 833 g. (4.0 moles) of ethyl orthosilicate, 477 g. (2.7 moles) of antimony trifluoride, and 3 g. of antimony pentachloride was heated in a boiling flask connected to a 26"-packed column. After approximately fifteen minutes of heating, all of the solid had dissolved. Distillate, boiling over the range 70–140° and totalling 470 g., was collected over a three-hour period. Refractionation of the distillate at atmospheric pressure yielded 72 g. of diethyl difluorosilicate, b. p. 83–83.5°, and 63 g. of triethyl fluorosilicate, b. p. 133.0–133.5°. *Anal.*[6] Calcd. for $Si(OC_2H_5)_2F_2$: F, 24.33. Found: F, 24.17, 24.09. Calcd. for $Si(OC_2H_5)_3F$: F, 10.43; F, 10.52, 10.59.

In an attempt to prepare triethyl fluorosilicate from triethyl chlorosilicate by halogen exchange, a mixture of 2.97 g. of the latter and 16.8 g. sodium fluoride was heated for eight hours without undergoing reaction. After the addition of 0.2 g. of antimony trichloride and 0.3 g. of antimony

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[2] (a) E. A. Flood, THIS JOURNAL, **55**, 1735 (1933); (b) J. A. Gieurut, F. J. Sowa and J. A. Nieuwland, *ibid.*, **58**, 897 (1936).

[3] Knop, *J. prakt. Chem.*, **74**, 41 (1858).

[4] Gierut, Sowa and Nieuwland, THIS JOURNAL, **58**, 786 (1936).

[5] Because of possible confusion with derivatives of fluosilicic acid, H_2SiF_6, the naming of compounds of the type, $(RO)_aSiF_{(4-a)}$, as alkyl fluorosilicates is not without objection. On the other hand, the nomenclature of the closely related alkyl chlorosilicates is well established and it would obscure interrelationships if the fluorine analogs were to be named in a different system. The work described in this and other papers of this series deals almost entirely with organic silicon compounds in which silicon is fully oxidized (valence + 4) and in this restricted field it is generally more convenient to name compounds as derivatives of orthosilicic acid, following established customs, rather than as derivatives of silane.

[6] Because of interference due to fluoride ion, the following procedure, based on that described by Booth and Stilwell, THIS JOURNAL, **56**, 1531 (1934), was devised. The sample, of approximately 1 g., is transferred from a dropper-weighing bottle to a 250-cc. titration flask containing an excess of 0.5 *M* NaOH with rapid swirling of the flask contents to avoid forming large gel particles. The mixture is heated on the steam-bath for ten minutes and then an excess of neutral 20% calcium chloride solution is added. The solution, after cooling to 10°, is titrated with 0.5 *M* hydrochloric acid with methyl red as the indicator.

pentachloride, a reaction occurred yielding 16 g. of low boiling material collected in a Dry Ice trap. This distillate gave a positive test for chlorine and formed a gel with water. This indicated a disproportionation of triethyl chlorosilicate to yield silicon tetrachloride, but from a similar mixture, containing no sodium fluoride, the chlorosilicate was recovered unchanged after eight hours of heating.

No reaction was observed on heating mixtures of ethyl orthosilicate and benzoyl fluoride.

Tri-*n*-butyl Fluorosilicate.—A mixture of 36.4 g. (0.2 mole) of triethyl fluorosilicate and 53.3 g. (0.72 mole) of *n*-butyl alcohol was heated in a flask attached to a fractionating column. During a period of one hour, 27.2 g. of ethanol was removed, and the residue was then fractionally distilled at 32 mm. pressure. The yield of tri-*n*-butyl fluorosilicate, b. p. 134.0–134.5° (32 mm.), was 31.4 g. (59%). *Anal.* Calcd. for $Si(OC_4H_9)_3F$: F, 7.13. Found: F, 7.23, 7.18.

Triallyl Fluorosilicate.—An experiment similar to the preceding, taking 36.4 g. of triethyl fluorosilicate and 52.3 g. of allyl alcohol, yielded 25.7 g. ethanol over a period of two and a half hours, and from the residue was isolated 21.3 g. (49%) of triallyl fluorosilicate, b. p. 99.0–99.5° (32 mm.). *Anal.* Calcd. for $Si(OC_3H_5)_3F$: F, 8.70. Found: F, 8.76, 8.64. As in the previous case mechanical losses due to column holdup were proportionately large.

An attempted preparation of diallyl difluorosilicate from diethyl difluorosilicate and allyl alcohol did not yield the desired compound but instead the products were triallyl fluorosilicate and low boiling materials.

Allyl orthosilicate did not react with antimony trifluoride alone or in the presence of any of the following: antimony pentachloride, aluminum chloride, zinc chloride and triallylchlorosilicate. Nor was any reaction observed when allyl orthosilicate was heated with benzoyl fluoride, with or without antimony pentachloride.

Hydrolysis Reactions.—All of the above-mentioned alkyl fluorosilicates were observed to react instantly with cold water to form gels. With dry pyridine, solid (non-gelatinous) products were obtained which were immediately hydrolyzed by water to form gels.

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Summary

1. Triethyl fluorosilicate and diethyl difluorosilicate have been prepared by the action of antimony trifluoride on ethyl orthosilicate in the presence of antimony pentachloride. Allyl orthosilicate failed to react similarly with antimony trichloride.

2. Triallyl fluorosilicate and tri-*n*-butyl fluorosilicate have been prepared from the ethyl compound by alcoholysis reactions.

3. These alkyl fluorosilicates are instantly hydrolyzed by cold water with the formation of gels.

4. Contrasts with the behavior of analogous alkyl chlorosilicates are pointed out.

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Transesterification Reactions of Alkyl Silicates

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The interchange of alkoxy groups between one alkyl orthosilicate and another, with the formation of mixed esters, has been effected by Friedel and Crafts,[2] and by Post and Hofrichter.[3] The latter authors refluxed a mixture of *n*-butyl orthosilicate and ethyl orthosilicate under atmospheric pressure for fifteen hours and then isolated the mixed esters by fractional distillation at reduced pressure. Transesterification reactions involving an orthosilicate and esters of other types have not been reported. The work described herein was undertaken to evaluate this method for the introduction of radicals, *e. g.*, vinyloxy, which cannot be introduced by conventional methods.

The present study, covering various combinations of alkyl silicates, borates and carboxylic esters, indicates that the redistribution of alkoxy groups takes place slowly in the absence of catalysts. However, the reactions are catalyzed by the more reactive metal alkoxides, *e. g.*, by alkoxides of aluminum, magnesium and antimony, and also by aluminum chloride.

The catalyzed reactions may be utilized to prepare mixed esters, and it is shown that the yield of mixed esters approaches that corresponding to a statistical redistribution of alkoxy groups. Alternatively, the displacement of alkoxy groups may be driven to completion in cases where one of the products is the most volatile component of the system. This constitutes one of the most satisfactory methods available for the preparation of higher alkyl silicates.

Experimental

Reactions Between Two Orthosilicates.—On refluxing a mixture of ethyl orthosilicate and *n*-butyl orthosilicate for a long period of time, as Post and Hofrichter[3] had done, the mixed esters were obtained in relatively small yields, indicating that the reaction had not reached equilibrium. When the period of reflux was reduced to four and a half hours, no evidence for any reaction was noted. Mixtures of ethyl orthosilicate and allyl orthosilicate behaved similarly. In the presence of a relatively small proportion of magnesium aluminum ethoxide,[4] an essentially statistical redistribution of alkoxy groups occurred within a refluxing period of four and a half hours as is indicated by the relative yields shown in Tables I and II. In these experiments the catalyst was destroyed prior to separation of the components to avoid further reaction during the distillation.

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(2) Friedel and Crafts, *Ann.*, **136**, 203 (1865).

(3) Post and Hofrichter, *J. Org. Chem.*, **5**, 572 (1940).

(4) Prepared according to Meerwein and Bersin, *Ann.*, **476**, 113 (1929).