[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF BUFFALO]

STUDIES IN SILICO-ORGANIC COMPOUNDS. VI. THE PREPARATION AND PROPERTIES OF POLYETHERS FROM TRICHLOROSILANE[1]

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INTRODUCTION

In the beginning of this work, silicon polyethers such as $HSi(OR)_3$ were desired, but certain properties of hydrogen connected to silicon made it advisable to spend considerable time on the preparation of compounds with hydrogen thus linked, and to study their reaction with caustic alkali. The problem opened with a preliminary study of the action of certain low-molecular-weight alcohols on trichlorosilane.

In 1867, Friedel and Ladenburg (1) prepared triethoxysilane by the treatment of trichlorosilane with anhydrous ethyl alcohol. Ruff and Albert (2) attempted the same preparation starting with trifluorosilane but obtained tetraethoxysilane instead of the expected tri ether:

I. $$2HSiF_3 + 4C_2H_5OH \rightarrow Si(OC_2H_5)_4 + H_2SiF_6 + 2H_2$$

Taurke (3) extended this synthesis to include higher alcohols and other investigators followed (4).

The work herein described on the preparation or attempted preparation of several trialkoxysilanes very early led to the realization that at room temperatures, in the presence of hydrochloric acid, hydrogen is lost, in fact quantitatively when the radical weights are low. Higher homologs lose this tendency somewhat. The trialkoxysilanes pass over to tetraalkoxysilanes and hexaalkoxydisiloxanes. In most cases these compounds were successfully prepared and kept without reaction at zero degrees but hydrogen evolution began with slow spontaneous warming up to room temperatures.

Thus anhydrous ethyl alcohol and trichlorosilane reacted to form tetraethoxysilane and hexaethoxydisiloxane. The result was analogous when propyl alcohol was used. Butyl alcohol formed tributoxysilane in small amounts. Most of the product even here was tetrabutoxysilane. In all of these reactions the temperature was kept below that of the room, and all access to the atmosphere was closed. The system in each case was kept closed until long after room temperatures had been reached, to capture all hydrogen which escaped. Runs were made with varying proportions of alcohol. The amount of hydrogen collected was proportional to the amount of silicon ether present. The formation of tetraalkoxysilanes might be tentatively illustrated by the following equations:

II. $$HSiCl_3 + 3\ C_3H_7OH \rightarrow HSi(OC_3H_7)_3 + 3\ HCl$$

III. $$HSi(OC_3H_7)_3 + HCl \rightarrow H_2 + ClSi(OC_3H_7)_3$$

IV. $$C_3H_7OH + ClSi(OC_3H_7)_3 \rightarrow Si(OC_3H_7)_4 + HCl$$

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[1] The work on which this paper is based comprises a part of a program of research being carried out under contract with the Office of Naval Research.

Disiloxanes might have formed through hydrolysis. These assumptions are quite tentative; a more complete mechanism is under consideration and the laboratory investigation is being continued.

Attempts were made to remove hydrogen chloride by sweeping it out with nitrogen, but there was no increased yield of the desired trialkoxysilane when this was done. Interaction of trichlorosilane and a sodium alkoxide had no effect in this direction. The best yields of trialkoxysilanes were obtained when benzene was added to the system, as a solvent. These results are illustrated in Table I.

Thus benzene definitely exerts a stabilizing effect on the trialkoxysilanes, inhibiting the transformation to tetraalkoxysilane and hexaalkoxydisiloxanes.

TABLE I

Effect of Reaction Conditions on Yields

1. C_2H_5OH	$Si(OC_2H_5)_4 + (C_2H_5O)_3SiOSi(OC_2H_5)_3$
2. C_2H_5OH in C_6H_6	$HSi(OC_2H_5)_3$ 45%
3. C_2H_5OH in C_6H_6 with standing	$HSi(OC_2H_5)_3$ 28.8%
4. C_3H_7OH	$Si(OC_3H_7)_4$
5. C_3H_7OH in C_6H_6	$HSi(OC_3H_7)_3$ 53%
6. C_4H_9OH	$HSi(OC_4H_9)_3$ 16%
7. C_4H_9OH in C_6H_6	$HSi(OC_4H_9)_3$ 71%
8. i-C_4H_9OH in C_6H_6	$HSi(OC_4H_9i)_3$ 48.5%

EXPERIMENTAL PART

Trichlorosilane and ethyl alcohol. Absolute ethyl alcohol (72 cc., 1.25 moles) was added dropwise to 25 cc. (0.25 moles) of trichlorosilane, at temperatures around 0°. After addition, the reaction mixture was slowly allowed to warm up to room temperatures, then refluxed and distilled. Approximately 15 cc. of the product boiled between 164° and 172°, probably tetraethoxysilane, while 15.7 cc. boiled between 232° and 240°. No triethoxysilane was detected. During the second later runs, apparatus was set up to catch any gas evolved, by water displacement. No evolution of gas was noticed as long as the temperature of the system was kept at 0° or thereabouts. Enough liquid product was collected from four runs to fractionate. There were isolated tetraethoxysilane, b.p. 135° (18 mm.) and hexaethoxydisiloxane, b.p. 160° (18 mm.), literature 95.5-96.5° (3-5 mm.) (6) and 235° (760 mm.) (7). The boiling point of hexaethoxydisiloxane was further checked against a sample prepared in this laboratory as described below.

Trichlorosilane and ethyl alcohol in benzene. Dry ethyl alcohol (35 cc., 0.6 mole) was added dropwise at 0° to a mixture of 0.15 mole (15 cc.) of trichlorosilane and 50 cc. of benzene. After two hours standing, and distillation of excess alcohol, there were obtained, at 760 mm., 12 g. of triethoxysilane, (45% yield) b.p. 132-135°, d^{25}_{4} 0.8745 and 3 g. of tetraethoxysilane, b.p. 165-170°, literature 134° (1) and 165-166° (2) respectively. Triethoxysilane hydrolyzes in water but more easily in caustic. To determine the effect of standing, the reaction was repeated with a twelve-hour interval at room temperatures between complete addition of the alcohol and distillation. Using the same amounts as above, 7 g. of triethoxysilane (28.8% yield) was obtained and 9 g. of tetraethoxysilane.

Trichlorosilane and propyl alcohol. Anhydrous propyl alcohol (50 cc., 0.66 mole) was added dropwise over a period of one hour to 17 cc. (0.17 mole) of trichlorosilane. The addition was carried out in an ice-bath and the reaction mixture was allowed to warm up to room temperature and stand overnight. Only propyl alcohol and 26 cc. of tetraethoxysilane were obtained, b.p. 224–225° (750 mm.), literature 225–227° (760 mm.) (5), d^{25}_4 0.9150; literature d^{20}_4 0.9158 (5). Evolution of hydrogen did not begin until the system had warmed to room temperature. Three more runs were made and the evolved hydrogen collected for quantitative determination. Description of hydrogen determinations will be found elsewhere in this paper. Use of sodium propoxide instead of propyl alcohol proved unsatisfactory. Sweeping out the apparatus with dry nitrogen did not produce better results.

Trichlorosilane and propyl alcohol in benzene. Anhydrous propyl alcohol (40 cc., 0.6 mole) was added dropwise to a solution of 15 cc. (0.15 mole) of trichlorosilane and 50 cc. of benzene. After standing for 24 hours, there were isolated 4 g. of tetrapropoxysilane and 16 g. (53% yield) of tripropoxysilane, b.p. 190–194° (750 mm.), d^{25}_4 0.882; literature d^{20}_4 0.895 (3).

Trichlorosilane and butyl alcohol. Anhydrous butyl alcohol (45 cc., 0.5 mole) was added dropwise to 15 cc. (0.15 mole) of trichlorosilane at 0°. The reaction mixture was allowed to warm up to room temperature by standing overnight, and on distillation there was obtained 6 g. of tributoxysilane (16% yield), b.p. 115–120° (13 mm.), 228–237° (760 mm.); Si: 11.10, 11.15, theoretical: 11.30, mol. wt.: 244 (cryoscopic in benzene), theoretical: 248; d^{25}_4 0.889. Tetrabutoxysilane was also obtained, 12 g., b.p. 135–146° (13 mm.).

Trichlorosilane and butyl alcohol in benzene. Anhydrous butyl alcohol (50 cc. 0.54 mole) was added dropwise to a solution of 15 cc. (0.15 mole) of trichlorosilane in 50 cc. of benzene at 0°. After 3 hours of standing, there were obtained 26.1 g. of tributoxysilane (71% yield), b.p. 237–238° (760 mm.), and 2.5 g. of tetrabutoxysilane, b.p. 273–277° (760 mm). A duplicate run, after standing two days gave only 7 g. of tributoxysilane, 20% yield.

TABLE II

HYDROGEN DETERMINATIONS, LATER RUNS, NaOH TREATMENT

COMPOUND USED	GRAMS	H_2 FOUND	H_2 (CORR.)	H_2 (THEORETICAL)	DEVIATION FROM THEORETICAL
$HSi(OC_2H_5)_3$	0.890	126 cc.	114 cc.	121.5 cc.	6%
$HSi(OC_3H_7)_3$	1.102	131 cc.	119 cc.	120.5 cc.	1%
$HSi(OC_4H_9)_3$	1.353	128 cc.	116 cc.	122 cc.	5%
$HSi(OC_4H_9i)_3$	1.251	123 cc.	111 cc.	114.2 cc.	3%

Trichlorosilane and i-butyl alcohol in benzene. *i*-Butyl alcohol (50 cc., 0.54 mole) and 10 cc. (0.10 mole) of trichlorosilane in 50 cc. of benzene, treated as above, reacted to form 11.5 g. (48.5% yield) of tri-*i*-butoxysilane, b.p. 224–228° (751 mm.), literature 240–242° (760 mm.) (3). Tetra-*i*-butoxysilane, 32 g., b.p. 255–258° (760 mm.) was also obtained; d^{25}_4 0.891; Si: 11.22, 11.45, theoretical: 11.30, mol. wt. (cryoscopic in benzene): 251, theoretical: 248.

Gas analyses. A Fisher Orsat apparatus was used. Pyrogallic acid first took out oxygen, if any, thus giving an approximation of the amount of air present. The gas was then passed through a copper oxide tube, heated to 300–325° to take out hydrogen. This was repeated several times until constant volume had been attained. The gas was then run through sodium hydroxide to ascertain the presence or absence of carbon dioxide which might have resulted from the burning of hydrocarbons. None was found.

Results in Table II were obtained by treating each sample with 10 cc. of 30% NaOH and collecting the evolved gas by water displacement. An aliquot portion of this gas was analyzed as described above. Theoretical values for hydrogen were determined from the equation: V. $2HSi(OC_2H_5)_3 + HOH\ (NaOH) \rightarrow 2\ H_2 + (C_2H_5O)_3SiOSi(OC_2H_5)_3$.

Silicon analyses were carried out according to a method already in the literature, (8).

SUMMARY

1. Under the conditions of these experiments, trichlorosilane and ethyl alcohol react at 0° in normal manner but when the reaction mixture is warmed to room

temperatures, secondary reactions take place by which tetraethoxysilane, hexaethoxydisiloxane, and hydrogen are formed. Propyl alcohol reacts similarly but butyl alcohol gives a 16% yield of tributoxysilane.

2. The yield of trialkoxysilane is considerably increased by the use of benzene as a solvent. The yields vary in the order $C_2H_5 < C_3H_7 < C_4H_9$. Tri-*i*-butoxysilane has also been prepared.

3. Evolution of hydrogen when a silane is treated with aqueous caustic at room temperatures has been studied and has been found to be nearly quantitative.

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