[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Hydrogen–Halogen Exchange Reactions of Triethylsilane. A New Rearrangement of Neopentyl Chloride[1]

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In continuation of previous work on the chemistry of trialkylsilyl compounds, the present paper reports two types of hydrogen–halogen exchange reactions of triethylsilane in the presence of aluminum chloride.

Type I, exchange of Si–H with C–Cl, is represented by the following general equation in which R and R′ are the same or isomeric.

$$(C_2H_5)_3SiH + RCl \xrightarrow{AlCl_3} (C_2H_5)_3SiCl + R'H$$

n-Hexyl chloride gave *n*-hexane; neopentyl chloride and neopentylcarbinyl chloride (1-chloro-3,3-dimethylbutane) gave rearrangement products, isopentane and 2,3-dimethylbutane, respectively. The conversion of neopentyl chloride to isopentane is the first clean cut *formation of a rearranged saturated hydrocarbon from an alkyl halide.*

Type II, exchange of Si–H with Si–Cl, was realized with diethyldichlorosilane.

$$(C_2H_5)_3SiH + (C_2H_5)_2SiCl_2 \xrightarrow{AlCl_3} (C_2H_5)_3SiCl + (C_2H_5)_2SiHCl + (C_2H_5)_2SiH_2$$

This reaction provides a convenient synthesis of dialkylchlorosilanes and dialkylsilanes.

Analogous hydrogen–halogen exchange reactions of inorganic silicon hydrides in the presence of aluminum chloride have been reported: trisilane, Si_3H_8, gave Type I exchange with chloroform; silane, SiH_4, gave Type II exchange with dichlorosilane, SiH_2Cl_2.[3]

Apparently alkyl–hydrogen exchange does not take place under the conditions used. No indication of tetraethylsilane was found.

Experimental

Trichlorosilane.—Since experience showed the importance of carefully controlled conditions for obtaining good yields of this compound, and since published procedures[4] differ somewhat from ours, a detailed description of our method is given.

Preparations were made in a horizontal, electrically heated, Pyrex tube, 3 cm. in diameter and 45 cm. in length, with its entrance connected to a sulfuric acid drying tower and calibrated flow meter. The exit was attached to a water-cooled condenser, which led to a flask cooled in salt-ice. As a precaution against moisture and loss of material, the flask was connected to a trap, immersed in Dry Ice and acetone, which led to a sulfuric acid drying tower. The tube was charged with 375 g. of granular ferrosilicon (*ca.* 90% Si), and the system was dried by passing nitrogen through it for twenty-four hours at a furnace temperature of 300°. Dry hydrogen chloride was then passed in at 350° until liquid condensed in the receiver. The temperature was then lowered and kept at 290–310°, while maintaining the flow of hydrogen chloride at 0.6–0.85 mole per hour. Nitrogen was passed through for ten minutes at approximately ten-hour intervals. In sixty hours, this gave 1370 g. of liquid product. In the tube there remained 103 g. of residue, of which approximately 50 g. was unreacted ferrosilicon. Fractionation of the liquid product through a column[5] of about 15 theoretical plates gave 1045 g. of trichlorosilane, b. p. 31.5–32° at 729 mm., 77% of the crude liquid, the remainder being mainly silicon tetrachloride. Repeated preparations gave values of 70–77%. A more rapid flow of hydrogen chloride over ferrosilicon at 360–370° gave yields as low as 32%.

Triethylsilane.—Preparation of this compound in 56.5% yield by the simultaneous addition of equivalent amounts of trichlorosilane and ethylmagnesium bromide has been reported.[6] The following procedure is more convenient and gives yields of 70–78%.

Ethylmagnesium bromide, 12.6 moles, was prepared in a 5-liter, three-necked flask, fitted with an efficient stirrer, dropping funnel and large bulb condenser, each connected to a trap, cooled in Dry Ice and acetone. A cold solution of trichlorosilane, 406.5 g., 3.0 moles, in 1200 cc. of anhydrous ethyl ether was added in six hours with cooling and vigorous stirring. The mixture was stirred for eight hours at room temperature and then heated to reflux for five hours. Ether was removed from the reaction mixture through a 20-plate column[5] and the residue was heated on the steam-bath for ten hours. With cooling, the solid residue was hydrolyzed with 180 cc. of water, followed by 372 cc. of concentrated hydrochloric acid. The aqueous layer was separated and extracted twice with 500-cc. portions of ether. The ether extracts and product were combined, washed with water, and then dried over 150 g. of anhydrous potassium carbonate for two hours. Fractional distillation through the 20-plate column[5] gave 270.3 g. of triethylsilane, b. p. 107° at 733 mm., n^{20}_D 1.4117, d^{20} 0.7302, 77.5% yield.

***n*-Hexyl Chloride, Triethylsilane and Aluminum Chloride.**—Triethylsilane, 18.5 g., 0.16 mole and *n*-hexyl chloride, 21.7 g., 0.18 mole, were placed in a 500-cc., 3-necked flask, equipped with a mercury-sealed stirrer and a large bulb condenser, which was connected to a trap, cooled in Dry Ice and acetone, which led to a sulfuric acid tower. In three hours, 0.2 g. of anhydrous aluminum chloride was added in *small* portions with cooling and stirring. Some reaction occurred as evidenced by bubbling at the surface of the aluminum chloride particles. The reaction mixture was then allowed to come to room temperature and 0.5 g. of aluminum chloride was added during eight hours with intermittent cooling and stirring. The mixture then stood at room temperature for ten hours. After adding an additional 0.7 g. of aluminum chloride during five hours with intermittent stirring *a vigorous exothermic reaction occurred.* Further addition of small amounts of catalyst caused little apparent reaction and the mixture was therefore warmed slightly to insure complete reaction. The light-yellow, fuming liquid was filtered through glass wool and fractionally distilled through a 15-plate column[5] to give 9.25 g. of low-boiling hydro-

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[1] Paper 10 in a series on organosilicon compounds. Also Paper 10 in a series on molecular rearrangements. For Paper 9 in both series see Whitmore, Sommer and Gold, THIS JOURNAL, **69**, 1976 (1947).

[2] Allied Chemical and Dye Corporation Fellow 1945–1947.

[3] Stock and Stiebeler, *Ber.*, **56**, 1087 (1923); Stock and Somieski, *ibid.*, **52**, 695 (1919).

[4] Booth and Stillwell, THIS JOURNAL, **56**, 1529 (1934); Kraus and Nelson, *ibid.*, **56**, 195 (1934); Taylor and Walden, *ibid.*, **66**, 842 (1944).

[5] The columns used were packed with single turn $^3/_{32}$ inch glass helices.

[6] Kraus and Nelson, THIS JOURNAL, **56**, 195 (1934).

carbon, of which 7.88 g. was *n*-hexane, b. p. 68° at 729 mm., $n^{20}\text{D}$ 1.3750, d^{20} 0.6598, 57% yield, and 21.3 g. of triethylchlorosilane, b. p. 144° at 729 mm., 88% yield.

Anal. Calcd. for $C_6H_{15}SiCl$: Cl, 23.6. Found: Cl, 23.5.

Earlier runs, in which aluminum chloride was added more rapidly, could not be controlled and resulted in extensive loss of product.

Neopentyl Chloride, Triethylsilane and Aluminum Chloride.—Triethylsilane, 116 g., 1.0 mole, and neopentyl chloride, 117.2 g., 1.1 moles, b. p. 84°, $n^{20}\text{D}$ 1.4042, were placed in a 3-liter four-necked flask, equipped with a mercury-sealed stirrer, and two large bulb condensers, each of which were connected to three traps and a sulfuric acid tower. Four of the traps were cooled in Dry Ice and acetone and the other two in liquid air. The 6-mm. neck was connected by rubber tubing to a glass vial, containing 3.0 g. of anhydrous aluminum chloride. *In five hours, 0.1 g.* of the aluminum chloride was added in *small* portions with cooling and stirring. Reaction was evidenced by bubbling on the aluminum chloride particles. The mixture was allowed to come to room temperature and an additional 0.2 g. of aluminum chloride was added during four hours with intermittent stirring and cooling. Since the reaction might be autocatalytic, 2 cc. of yellow-colored end-product (mainly triethylchlorosilane), obtained from the reaction of a small amount of neopentyl chloride with triethylsilane, was then added to the reaction mixture. Since little action resulted, an additional 0.2 g. of aluminum chloride was added at room temperature with intermittent stirring. This brought about greater reaction as evidenced by occasional puffs of white vapor, which arise from the surface of the liquid. Warming with a water-bath for one hour gave no effect. The reaction mixture was therefore cooled to room temperature and 0.14 g. of aluminum chloride was added in small portions during two hours with stirring. Addition of the last small portion of catalyst initited *a violent exothermic reaction.* Both condensers were filled with liquid, and the rubber stopper holding the clamped mercury-sealed stirrer gave way resulting in a 34% loss of material. The liquid remaining in the flask amounted to 100.7 g., and 53.5 g. of liquid was found in the traps. The latter was fractionated in a special vacuum-jacketed 30-plate column[5] to give 35.0 g. of isopentane, b. p. 28° at 734 mm., $n^{20}\text{D}$ 1.3540, 48.6% yield, based on the triethylsilane used. No lower boiling material was obtained. Thus neopentane was not formed. Fractionation of the material in the flask and the liquid residue from the above distillation gave 79.9 g. of triethylchlorosilane, b. p. 144° at 737 mm., 53% yield, 8.9 g. of recovered triethylsilane, 7.69%, and 14.20 g. of recovered neopentyl chloride, 12.10%. The loss due to the violent reaction was 79.2 g., 34% of the total weight of reaction mixture.

Anal. Calcd. for $C_6H_{15}SiCl$: Cl, 23.6. Found: Cl, 23.5.

A 0.2-mole run, made under the same conditions used in the *n*-hexyl chloride study, in which 1.4 g. of aluminum chloride was added in twenty-eight hours, gave no loss of material. There were obtained 8.9 g. of low-boiling hydrocarbon, of which 5.27 g. was isopentane, 36.6% yield, and 22.0 g. of triethylchlorosilane, 73% yield. It is noteworthy that the long reaction time used in this run and in that with *n*-hexyl chloride gave hydrocarbon mixtures, whereas the more rapid experiment with neopentyl chloride gave only isopentane. The hydrocarbon by-products are probably formed by isomerization and fission of the primary product by long contact with aluminum chloride. This is also the case in the following run with neopentylcarbinyl chloride.

Neopentylcarbinyl Chloride, Triethylsilane and Aluminum Chloride.—A 0.2-mole run was made under the same conditions employed in the *n*-hexyl chloride run, in which 1.4 g. of aluminum chloride was added during twenty-eight hours. There were obtained 10.6 g. of low-boiling hydrocarbon, of which 8.6 g. was 2,3-dimethylbutane, b. p. 58° at 739 mm., $n^{20}\text{D}$ 1.3752, d^{20} 0.6613, 50% yield, and 25.2 g. of triethylchlorosilane, b. p. 144° at 738 mm., 84% yield.

Anal. Calcd. for $C_6H_{15}SiCl$: Cl, 23.6. Found: Cl, 23.4.

Diethyldichlorosilane, Triethylsilane and Aluminum Chloride.—In a 500 cc., three-necked flask, equipped with a mercury-sealed stirrer and large bulb condenser, which was connected to a trap cooled in Dry Ice and acetone, leading to a sulfuric acid tower, 38.3 g., 0.33 mole, of triethylsilane and 47.1 g., 0.30 mole, of diethyldichlorosilane were placed. In one hour, 0.7 g. of anhydrous aluminum chloride was added in small portions. The mixture was then stirred for two hours at room temperature. No heat was evolved but a reaction seemed to occur as evidenced by bubbling around the particles of aluminum chloride. The stirrer was removed and the mixture was heated to reflux for ten hours. The mixture was then filtered through glass wool and the light yellow solution was fractionally distilled through a 15-plate column.[5] There were obtained: 5.7 g. of diethylsilane, b. p. 56° at 741 mm., $n^{20}\text{D}$ 1.3921, d^{20} 0.6843-4, 43% yield; 16.1 g. of diethylchlorosilane, b. p. 99° at 741 mm., 44% yield; 5.5 g. of diethyldichlorosilane, b. p. 129° at 741 mm., and 40.5 g. of triethylchlorosilane, b. p. 144° at 741 mm., 90% yield. Diethylsilane is a colorless liquid, which reduces a dilute silver nitrate solution with evolution of a gas and deposition of black silver particles.

Cryoscopic molecular weight determinations of diethylsilane in benzene gave mol. wt., 89, 90 (calcd. 88.0). Analysis for percentage hydrogen attached to silicon % H(–Si) was performed by a known method,[7] based on the reaction of the –Si–H bond with aqueous or alcoholic base to give a mole of hydrogen. Weighed samples were treated with ethanolic potassium hydroxide in a Zerewitinoff apparatus.

Anal. Calcd. for $C_4H_{12}Si$: H(–Si), 2.26. Found: H(–Si), 2.23, 2.25.

The chlorosilanes obtained were analyzed.

Anal. Calcd. for C_4HSiCl: Cl, 29.0. Found: Cl, 28.7. Calcd. for $C_4H_{10}SiCl_2$: Cl, 45.2. Found: Cl, 44.0. Calcd. for $C_6H_{15}SiCl$: Cl, 23.6. Found: Cl, 23.4.

The low value for the known diethyldichlorosilane indicates some contamination with one or both of the other chlorosilanes.

Discussion

The most striking common characteristic of hydrogen–halogen exchange reactions between triethylsilane and alkyl halides is their highly exothermic nature. This corresponds to bond energies, which indicate a release of 31.5 kcal./mole,[8] and the fact that silicon is more electropositive than carbon. In sharp contrast to the above reactions is that of triethylsilane with chlorosilanes, which requires heat. Here, little energy change is expected since the bonds broken and formed are similar in energy content.

Previous studies have emphasized carbonium ion formation as a prerequisite for the rearrangement of organic halides.[9] Formation of isopentane and 2,3-dimethylbutane from neopentyl chloride and neopentylcarbinyl chloride, respectively, indicates that Type I exchange proceeds by a carbonium ion mechanism. Furthermore, the hydrogen-forming reactions of silicon hydrides with hydrogen chloride in the presence of alumi-

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[7] Sauer, Scheiber and Brewer, THIS JOURNAL, **68**, 962 (1946).

[8] *Cf.* Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1942, p. 53.

[9] See (1) and references there cited.

num chloride,[8] with aqueous and alcoholic bases,[7] and with lithium amide in ammonia,[6] offer evidence that the silicon–hydrogen bond readily undergoes fission to give a hydride ion $(H:)^-$[10]. These data indicate that hydrogen–halogen exchange of Type I proceeds by the following mechanism

$$C—Cl + AlCl_3 \rightleftarrows C^+ + AlCl_4^- \qquad (a)$$

$$C^+ + Si—H \longrightarrow C—H + Si^+ \qquad (b)$$

$$Si^+ + AlCl_4^- \rightleftarrows Si—Cl + AlCl_3 \qquad (c)$$

In (a) the electrophilic aluminum chloride, which is known to ionize the carbon–halogen bond catalytically,[9] gives a carbonium ion. This electronically deficient fragment must stabilize itself by attracting an electron pair. While this ordinarily occurs intramolecularly,[11] or by union with an anion such as Cl^-, in this case the carbonium ion first formed or a rearranged carbonium ion stabilizes itself by attack on the Si-H bond, taking the electron pair with the attached H as in (b). Probably simultaneously, step (c) occurs with formation of the silicon–chlorine bond and regeneration of the catalyst. In the present study, the *n*-hexane obtained from *n*-hexyl chloride may have been formed by step (b) from a *n*-hexyl or *s*-hexyl carbonium ion. The isopentane and 2,3-dimethylbutane obtained from neopentyl chloride and 1-chloro-3,3-dimethylbutane, respectively, resulted from rearranged carbonium ions formed in the usual way.[11]

A similar mechanism is involved in the hydrogen–halogen exchange of alkyl halides and isoparaffins in the presence of aluminum halides.[12] The same type of transfer of an electron pair with the attached H occurs in ordinary alkylation reactions,[13] involving such a step as

$$R^+ + (CH_3)_3CH \longrightarrow RH + (CH_3)_3C^+$$

Other cases of the formation of a saturated hydrocarbon by rearrangement reported in the literature are the occurrence of small amounts of neopentane in the hydrogenation of trimethylethylene in a silent electric discharge[14] and of 2,3-dimethylbutane in the action of neopentylcarbinyl chloride with a large excess of isobutane and aluminum chloride under thirty atmospheres pressure.[12b]

Acknowledgment.—We thank Dr. T. J. Brice for the fractional distillation of the isopentane.

Summary

1. Hydrogen–halogen exchange reactions of triethylsilane with three aliphatic chlorides in the presence of aluminum chloride are reported.

2. *n*-Hexyl chloride gave *n*-hexane; neopentyl chloride and neopentylcarbinyl chloride gave the rearrangement products, isopentane and 2,3-dimethylbutane, respectively.

3. A mechanism for exchange of silicon–hydrogen with carbon–chlorine in the presence of aluminum chloride is proposed.

4. Reaction of triethylsilane with diethyldichlorosilane in the presence of aluminum chloride gave two new compounds, diethylsilane and diethylchlorosilane. This apparently provides a good preparation for compounds of the type R_2SiH_2 and R_2SiHCl, in which R is an organic group.

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(10) *Cf.* Meals, THIS JOURNAL, **68**, 1880 (1946).

(11) *Cf.* Whitmore, (a) *ibid.*, **54**, 3274 (1932); (b) *Ind. Eng. Chem.*, **26**, 94 (1934).

(12) (a) Barlett, Condon and Schneider, THIS JOURNAL, **66**, 1531 (1944); (b) Schmerling, *ibid.*, **67**, 1778 (1945).

(13) Ciapetta, *Ind. Eng. Chem.*, **37**, 1210 (1945).

(14) Meneghini and Sargato, *Gazz. chim. ital.*, **62**, 621 (1932).

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[CONTRIBUTION FROM SOUTHERN REGIONAL RESEARCH LABORATORY[1]]

Preparation of Substituted Acetoxy Silanes

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Introduction

The use of alkyl chlorosilanes, such as dimethyldichlorosilane, to impart water repellency to cotton textiles has been patented.[1a] Unfortunately, the hydrogen chloride produced during the reaction of the silane with adsorbed moisture or cellulosic hydroxyls may seriously weaken the cloth unless elaborate and efficient equipment is employed to avoid this difficulty.

With the object of preventing acid degradation, the writers prepared a number of short chain substituted acetoxy silanes for application to cloth in place of the chlorosilanes. The present paper describes the preparation and properties of a number of these acetoxy silanes.

During the preparation of this paper, a patent was issued to Barry,[2] describing the use of alkyl and alkoxy acetoxy silanes with aliphatic chains containing at least eight carbon atoms as good water-repellent agents.

Silicon tetraacetate was first prepared in 1867 by Friedel and Ladenburg[3] by the reaction of silicon tetrachloride with acetic anhydride. More recently the same compound was obtained in low yields by Volnov[4] through the action of organic

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(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

(1a) W. I. Patnode, U. S. Patent 2,306,222, December 22, 1942.

(2) A. J. Barry, U. S. Patent 2,405,988, August 20, 1946.

(3) C. Friedel and A. Ladenburg, *Ann.*, **145**, 174 (1867).

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