

Summary

Evidence based upon cryoscopic and spectroscopic data is presented showing that ethyl nitrate yields NO_2^+ ions in sulfuric acid. It is suggested that this ester exhibits the same complex ioniza-

tion which, as Hammett found, is shown by certain sterically hindered benzoic acids. Hydrolysis and esterification experiments confirm this belief.

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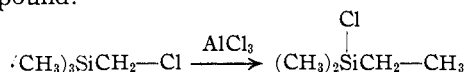
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Intramolecular Rearrangement of Chloromethyltrimethylsilane¹

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Reactions of neopentyl compounds which deprive the neopentyl group of its electron pair result in rearranged products containing the *t*-amyl group.²

The present paper reports an analogous reaction of silico-neopentyl chloride (chloromethyltrimethylsilane) with aluminum chloride to give ethyldimethylchlorosilane. This is the first intramolecular rearrangement in an organosilicon compound.



Experimental

Chloromethyltrimethylsilane.—This chloride³ was prepared in 90% yield from chloromethyltrimethylchlorosilane⁴ and methylmagnesium bromide.⁵

Rearrangement of the Chloride.—In a 500-cc. round-bottomed flask fitted with a reflux condenser, thermometer in liquid, and a sulfuric acid trap, there were placed 184 g. (1.5 moles) of the chloride and 2 g. of powdered anhydrous aluminum chloride. Heating of the reaction mixture to 85° with a small flame initiated a *vigorous exothermic reaction*, which continued spontaneously for one-half hour after removal of the flame. It was necessary to cool the reaction flask intermittently in order to prevent loss of material through the condenser. At the end of this reaction the liquid temperature was 90° with little reflux. No loss in weight occurred during the reaction.

After cooling, a sample of the clear supernatant liquid was withdrawn, dissolved in isopropyl alcohol and titrated with 0.5 *N* sodium hydroxide. The calculated neutral equivalent for complete rearrangement of chlorine from carbon to silicon is 122.6. The value obtained, 155, indicated about 79% rearrangement. Silico-neopentyl chloride does not react with dilute alkali under these conditions.³

The reaction product was then flash distilled under reduced pressure. The distillate was fractionated at 734 mm. through a column of 12 theoretical plates to give fractions of the indicated boiling ranges and weights (g.): I, 57–89°, 13.2; II, 89–92.2°, 98; III, 92.2–98.5°, 18.2; IV, 98.5–113°, 5; res. 7.0.

Fraction II represents a 53% yield of slightly impure ethyldimethylchlorosilane containing a small amount of

unchanged chloromethyltrimethylsilane. Since a total chlorine analysis or a silicon analysis would not distinguish these isomers, the product was analyzed in the usual way for chlorine attached to silicon.

Anal. Calcd. for $\text{C}_4\text{H}_{11}\text{SiCl}$: Cl, 29.0. Found: 27.5.

The identity of the product was confirmed by its action with methylmagnesium bromide to give the known ethyltrimethylsilane,⁶ in 73% yield, b. p. 62.7–63.2° at 736 mm., n_D^{20} 1.3820, d_4^{20} 0.6842. Since the submission of this paper, the rearranged chloride has been prepared from dimethyldichlorosilane and ethylmagnesium bromide.⁷

The components of the reaction product boiling outside the range of ethyldimethylchlorosilane and silico-neopentyl chloride, 89–97°, are due to a partial redistribution of the ethyldimethylchlorosilane by aluminum chloride to give trimethylchlorosilane (b. p. 57°) and diethylmethylchlorosilane (b. p. 119°). The analogous ethyldimethyllead chloride gives the four R_3PbCl compounds in a random equilibrium mixture, as does also a mixture of trimethyl- and triethyllead chlorides.⁸ In order to check the redistribution of trialkylchlorosilanes, a mixture of trimethylchlorosilane, 43.5 g. (0.4 mole), triethylchlorosilane, 60 g. (0.4 mole), and 2.0 g. of powdered aluminum chloride was refluxed for four hours. After flash distillation under vacuum, fractionation at 734 mm. of the 99 g. distillate gave 4 g. of impure trimethylchlorosilane, b. p. 57–60°; 25.7 g. (0.21 mole) of ethyldimethylchlorosilane, b. p. 89–90.5°, neut. equiv. 121.5; 35.8 g. (0.26 mole) of diethylmethylchlorosilane, b. p. 119–120°, neut. equiv. 137.2 (calcd., 136.5); and 5.5 g. (0.03 mole) of triethylchlorosilane, b. p. 144°.

In comparison experiments, neopentyl chloride⁹ behaved very differently from chloromethyltrimethylsilane. The former was practically unchanged by a small proportion of anhydrous aluminum chloride. A proportion of 15 g. of chloride to 2 g. of aluminum chloride gave more complete reaction. Hydrogen chloride was evolved at room temperature. No appreciable heat was noted. Less than 0.5 cc. of liquid condensed in a Dry Ice trap. This did not decolorize bromine in carbon tetrachloride. When action had ceased, the mixture was treated with sodium carbonate solution. The organic layer was separated and distilled to give 4 g. of material boiling 65–220° and 3 g. of residue. The products were unchanged chloride and polyisoamylenes.

Discussion

Chloromethyltrimethylsilane, like neopentyl chloride,⁹ can be distilled at atmospheric pressure and undergoes no change on long standing. In the preparation of the former by the photochemical chlorination of tetramethylsilane, no ethyldi-

(1) Paper 9 in a series on molecular rearrangements. For Paper 8 see Whitmore and Carney, *THIS JOURNAL*, **63**, 2633 (1941). Also Paper 9 in a series on organosilicon compounds. For paper 8 see Sommer, Pietrusza and Whitmore, *ibid.*, **68**, 2282 (1946).

(2) (a) Whitmore and Rothrock, *ibid.*, **54**, 3431 (1934); (b) Whitmore and Fleming, *J. Chem. Soc.*, 1269 (1934); (c) Whitmore, Wittle and Popkin, *THIS JOURNAL*, **61**, 1586 (1939).

(3) Whitmore and Sommer, *ibid.*, **68**, 481 (1946).

(4) Krieble and Elliott, *ibid.*, **67**, 1810 (1945).

(5) For a similar synthesis of α -chloroethyltrimethylsilane see Sommer and Whitmore, *ibid.*, **68**, 485 (1946).

(6) Whitmore, Sommer, DiGiorgio, Strong, Van Strien, Bailey, Hall, Pietrusza and Kerr, *ibid.*, **68**, 475 (1946).

(7) Lewis, *ibid.*, **69**, 717 (1947).

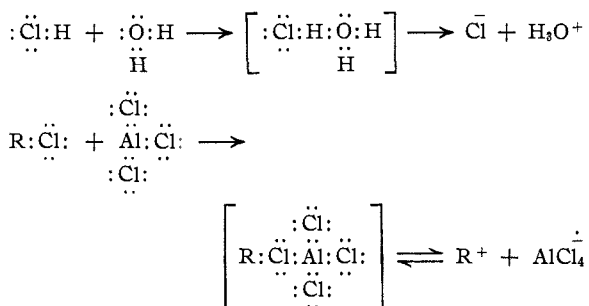
(8) Calingaert, *et al.*, *ibid.*, **62**, 1104 (1940).

(9) Fleming and Whitmore, *ibid.*, **54**, 2460 (1932).

methylchlorosilane is formed.³ This parallels the non-formation of *t*-amyl chloride in the chlorination of neopentane.⁹

Sodium iodide in dry acetone, a reagent which attacks organic halides by a non-ionization, rearward attack S_N^2 mechanism,¹⁰ reacts with chloromethyltrimethylsilane to give the unrearranged product, iodomethyltrimethylsilane.³ Although this reagent does not act with neopentyl chloride it attacks the bromide by an S_N^2 mechanism.¹¹ Other reagents, such as potassium acetate in ethanol and sodium ethylate in ethanol, which also react generally by an S_N^2 mechanism, likewise give some unrearranged products with neopentyl halides.^{2c,12}

On the other hand, reagents such as silver nitrate and aqueous ethanol which act with organic halides by attacking the halogen with its shared electron pair (electrophilic attack on halogen, S_N^1) give only the rearranged *t*-amyl products.^{2c,13} Thus, "ionization" of the carbon-halogen bond of a neopentyl halide by an electrophilic reagent is a necessary condition for rearrangement. Such S_N^1 reagents do not attack chloromethyltrimethylsilane in any reasonable time.³ To achieve such a reaction requires a more powerfully electrophilic reagent than silver ion. Such a reagent is anhydrous aluminum chloride which causes ionization of the carbon-halogen bond.¹⁴ It may be worth while to compare the mechanism of such an ionization with that of the ionization of hydrogen chloride by water.



Regardless of the mechanism by which the carbonium ion is formed, it may undergo rearrangement to a greater or lesser extent depending on its structure.¹⁵ Neopentyl chloride gives a carbonium ion of such steric relations that its rearrangement to a *t*-amyl ion is practically complete. This gives isoamylenes which are polymerized completely in the presence of the catalyst.¹⁶

(10) Cf. Bartlett and Rosen, THIS JOURNAL, 64, 543 (1942).

(11) Dostrovsky and Hughes, J. Chem. Soc., 161 (1946).

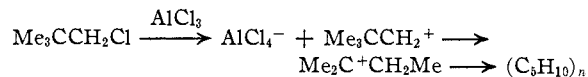
(12) Dostrovsky and Hughes, *ibid.*, 157 (1946).

(13) Dostrovsky and Hughes, *ibid.*, 166 (1946).

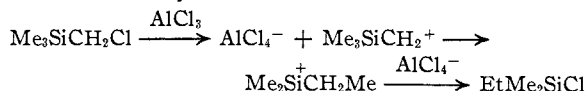
(14) For example, aluminum chloride is known to favor ionization of triphenylmethyl chloride. See Norris and Sanders, *Am. Chem. J.*, 26, 54 (1901); Gomberg, *Ber.*, 34, 2726 (1901); Kehrmann and Wentzel, *ibid.*, 34, 3815 (1901). See also C. A. Thomas, "Anhydrous Aluminum Chloride in Organic Chemistry," Reinhold Publishing Co., New York, N. Y., 1941, p. 59-62.

(15) Whitmore, THIS JOURNAL, 54, 3274 (1932).

(16) Cf. Whitmore, *Ind. Eng. Chem.*, 26, 94 (1934).



Similarly, chloromethyltrimethylsilane is "ionized" by aluminum chloride but the resulting "siliconium" ion differs from the analogous carbonium ion in at least two ways. It cannot release a proton to give a silicon-carbon double bond. It unites with chloride ion more readily than does *t*-amyl.



It is important to note the large amount of heat evolved in this reaction. So great is this that the reaction must be carefully controlled by cooling to prevent extensive loss. In other studies of rearrangements of organosilicon compounds in this Laboratory even this precaution has failed to prevent loss of the entire reaction mixture. Of interest are the data on the bond energies of the linkages C-Si, C-Cl, C-C and Si-Cl.¹⁷ The sum of the bond energies of C-Cl and C-Si is 124.1 kcal./mole. The corresponding value for C-C and Si-Cl is 144.4 kcal./mole. Thus, the thermodynamic stability of ethyldimethylchlorosilane exceeds that of chloromethyltrimethylsilane by 20.3 kcal./mole. This is a graphic example of the fact that silicon shows greater affinity for electronegative elements such as halogen, than for neutral elements such as carbon.¹⁸

Summary

The significance of the present work for the general knowledge of molecular rearrangements is as follows:

1. It extends the already wide applicability of the conception of the carbonium ion (electronically deficient fragment).¹⁵

2. By the contrast in the behavior of chloromethyltrimethylsilane with sodium iodide (no rearrangement), with alcoholic silver nitrate (no appreciable reaction), and with anhydrous aluminum chloride (rearrangement), it emphasizes the dependence of rearrangement on conditions which favor ionization.

3. It indicates that energy relations are secondary to mechanism of reaction in determining whether or not rearrangement takes place. Thus the S_N^2 reaction of sodium iodide with chloromethyltrimethylsilane gives no rearrangement in spite of the fact that the product of a rearrangement, ethyldimethyliodosilane, exceeds the observed product, iodomethyltrimethylsilane, by 6.6 kcal. in thermodynamic stability.¹⁷

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(17) Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1942, p. 53.

(18) A similar generalization has been put forth by Stock "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y. 1933, p. 36, to account for the chemical behavior of inorganic silicon compounds compared to that of organic compounds.

(19) Original manuscript received September 9, 1946.