

The Base-Catalyzed Conversion of Triphenylfluorosilane and Triphenylsilanol to Hexaphenyldisiloxane

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An observation that triphenylfluorosilane on heating with a sodium hydroxide solution yielded hexaphenyldisiloxane rather than the expected triphenylsilanol led us to perform a number of systematic experiments in order to elucidate the mechanism of this reaction. This information seemed to be of particular interest in view of the recent kinetic study of Swain¹ in which the hydrolytic behavior of trityl fluoride was critically compared to that of triphenylfluorosilane. Since in the last mentioned paper the products of hydrolysis were assumed to be the corresponding hydroxy derivatives, our initial observation suggested a possible necessity of reinterpretation of the data of Swain.

Experimental

The amounts of starting materials, reagents and products, as well as the conditions of the experiments are summarized in Table I. The products were isolated by concentration of

Reaction (1) does not require any comments.¹ The formation of the disiloxane by (3) or (4) requires the presence of the silanolate ion, and the latter is produced in sufficient concentration only when strong alkali is present. Since sodium salts of silanols are known to hydrolyze in the presence of water, it is clear that in (2) we are dealing with an equilibrium rather than with an unidirectional process. The formation of the disiloxane was observed only under elevated temperature conditions. Thus, the temperature factor may be involved in the following fashion: (a) it may affect the equilibrium (2) favorably with respect to the formation of the silanolate ion; and/or, (b) it may be required to provide the energy of activation in the nucleophilic attack of the bulky triphenylsilanolate ion on the silicon atom in reaction (3) or (4). While reaction (4) is rather well substantiated, the formation of the disiloxane from triphenylfluorosilane may proceed by a sequence of reactions (1), (2) and (3), rather than through (4). The success of the last mentioned experiment in Table I provides, in our opinion, an excellent argument in favor of reaction mechanisms in which a penta-

TABLE I
THE HYDROLYSIS OF TRIPHENYLFLUOROSILANE

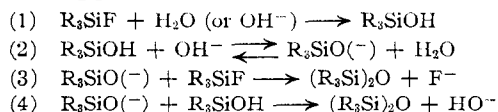
Ph ₃ SiF, mole	NaOH, mole	Medium	Reacn. conditions		Products		Yields of prod., %
			Time, hr.	Temp., °C.	Wt., g.	M. p., °C. ^a	
0.0035	50 cc. of H ₂ O-Me ₂ CO (30-70)	120	25	0.9	52-54 ^b	ca. 90 Ph ₃ SiF
					.12	140-150 ^c	ca. 10 Ph ₃ SiOH
.0035	50 cc. of H ₂ O-dioxane (30-70)	56	100	.01	135 ^c	ca. 1 Ph ₃ SiOH
.0035	0.0035	500 cc. of H ₂ O-Me ₂ CO (30-70)	24	25	.5	58-60 ^b	ca. 50 Ph ₃ SiF
					.08	151	8 Ph ₃ SiOH
.0035	.03	150 cc. of H ₂ O-dioxane (10-90)	96	25	.7	151	70 Ph ₃ SiOH
.0035	.05	50 cc. of H ₂ O-dioxane (30-70)	12	100	.75	220 ^d	81 (Ph ₃ Si) ₂ O
.0025 ^e	.05	50 cc. of H ₂ O-dioxane (30-70)	6	100	.5	219	76 (Ph ₃ Si) ₂ O

^a All melting points are uncorrected. ^b Impure triphenylfluorosilane (m. p. 64°). ^c Impure triphenylsilanol (m. p. 150-151°). ^d Crude product fused partially at 143° and melted completely at 220°. Crystallization gave 0.2 g. of product melting sharply at 219°. Hexaphenyldisiloxane, m. p. 220-221°. ^e Triphenylsilanol was used in this experiment.

the reaction solvents and by crystallization of the crude solids. Since the disiloxane is quite insoluble in cold benzene, the crude products were crystallized from hot benzene; the unreacted starting material or the silanol were obtained only on concentration of the benzene solution while any disiloxane could be isolated on cooling of the hot solution. The products were identified by means of mixed melting point determinations.

The results of the experiments can be summarized as follows. The hydrolysis of triphenylfluorosilane in a neutral or weakly alkaline medium produces only the expected triphenylsilanol. The conversion of the fluoride to hexaphenyldisiloxane occurs under strongly alkaline conditions and at an elevated temperature. Under these conditions triphenylsilanol is converted also to the disiloxane.

The last mentioned observation suggests the following paths of the reactions



(1) Swain, Esteve and Jones, *THIS JOURNAL*, **71**, 965 (1949).

covalent silicon atom exists in the transition state.^{1,2,3}

(2) Price, *ibid.*, **69**, 2600 (1947).

(3) Gilman and Dunn, *ibid.*, **72**, 2178 (1950).

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Pyrithiamine and Neopyrithiamine

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The pyridine analog of thiamine (2-methyl-4-amino-5-pyrimidylmethyl-[2-methyl-3-(β-hydroxyethyl)]-pyridinium bromide hydrobromide) was first prepared by Tracy and Elderfield² by condensing 2-methyl-4-amino-5-bromomethylpyrimidine hydrobromide with 2-methyl-3-(β-hydroxyethyl)-pyridine. The product gave acceptable analysis for C and H provided that a molecule of water of crystallization was assumed. A substance

(1) With the technical assistance of N. Smith and E. A. Singer.

(2) A. H. Tracy and R. C. Elderfield, *J. Org. Chem.*, **6**, 54 (1941).