The Base-Catalyzed Conversion of Triphenylfluorosilane and Triphenylsilanol to Hexaphenyldisiloxane

BY H. HARRY SZMANT AND GENE A. BROST

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 Swain[1] 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 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.

TABLE I

THE HYDROLYSIS OF TRIPHENYLFLUOROSILANE

Ph_3SiF, mole	NaOH mole	Medium	Reacn. conditions Time, hr.	Reacn. conditions Temp., °C.	Products Wt., g.	Products M. p., °C.[a]	Yields of prod., %
0.0035	....	50 cc. of H_2O–Me_2CO (30–70)	120	25	0.9	52–54[b]	*ca.* 90 Ph_3SiF
					.12	140–150[c]	*ca.* 10 Ph_3SiOH
.0035	....	50 cc. of H_2O–dioxane (30–70)	56	100	.01	135[c]	*ca.* 1 Ph_3SiOH
.0035	0.0035	500 cc. of H_2O–Me_2CO (30–70)	24	25	.5	58–60[b]	*ca.* 50 Ph_3SiF
					.08	151	8 Ph_3SiOH
.0035	.03	150 cc. of H_2O–dioxane (10–90)	96	25	.7	151	70 Ph_3SiOH
.0035	.05	50 cc. of H_2O–dioxane (30–70)	12	100	.75	220[d]	81 $(Ph_3Si)_2O$
.0025[e]	.05	50 cc. of H_2O–dioxane (30–70)	6	100	.5	219	76 $(Ph_3Si)_2O$

[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 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) $R_3SiF + H_2O$ (or OH^-) $\longrightarrow R_3SiOH$

(2) $R_3SiOH + OH^- \rightleftarrows R_3SiO(^-) + H_2O$

(3) $R_3SiO(^-) + R_3SiF \longrightarrow (R_3Si)_2O + F^-$

(4) $R_3SiO(^-) + R_3SiOH \longrightarrow (R_3Si)_2O + HO^-$

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 diloxane 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 pentacovalent silicon atom exists in the transition state.[1,2,3]

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

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

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

DEPARTMENT OF CHEMISTRY
DUQUESNE UNIVERSITY
PITTSBURGH, PA.

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Pyrithiamine and Neopyrithiamine

BY D. W. WOOLLEY[1]

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 Elderfield[2] 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

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(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).