The new arylidene derivatives (IIc–f, h, j, l) listed in Table I, are difficultly soluble in cold ethyl alcohol, ether and acetic acid, but soluble in acetone and boiling benzene.

Method (B). By the Oxidation of 2-Arylidene-3(2H)-thianaphthenone Derivatives(III).—A solution of 1.0 g. of each of IIIa,[13] IIIb,[14] IIIc,[15] IIId[16] and IIIe[17] in 20 ml. of glacial acetic acid was treated with 3 ml. of hydrogen peroxide (30%) and the reaction mixture was heated on a boiling water-bath for half an hour. The cooled reaction mixture was then poured into ice-cold water. The solid that separated was filtered off, washed with cold water and crystallized from benzene in almost colorless crystals.

Oxidation products IIa, b, g, i, and k are obtained in 82, 90, 87, 81 and 85% yield, respectively (identified by m.p. and mixed m.p.).

Action of *p*-Thiocresol on 2-Arylidene-3(2H)-thianaphthenone-1,1-dioxides. General Procedure.—A mixture of 0.5 g. of the appropriate arylidene derivative (II) and 0.5 g. of *p*-thiocresol was heated on an oil-bath at the given temperature (*cf*. Table [illegible]) for 3 hours. The cooled reaction mixture was washed with light petroleum (b.p. 40–60°) and the resulting solid was crystallized from benzene–petr. ether (b.p. 60–80°).

The thiol-adducts V listed in Table II are colorless crystalline compounds which dissolve readily in benzene and chloroform, but are difficultly soluble in cold ethyl alcohol, ether and acetic acid. They dissolve in aqueous sodium hydroxide (10%) with a yellow color.

Action of Grignard Reagents on 2-Arylidene-3(2H)-thianaphthenone-1,1-dioxides (IIa–b, g–l).—The following illustrates the general procedure: To a Grignard solution (prepared from 0.9 g. of magnesium and 9.0 g. of bromobenzene in 50 ml. of dry ether) was added a solution of 1.0 g. of each of (IIa–b, g–l) in dry benzene (50 ml.). After evaporation of the ether, the mixture was heated for three hours on a steam-bath. After standing overnight at 25°, it was poured slowly into 100 ml. of saturated aqueous ammonium chloride solution to which 3 ml. of concentrated hydrochloric acid was added, and then extracted with ether. The ethereal layer was dried over anhydrous sodium sulfate, filtered and evaporated. The residue left behind was washed several times with light petroleum and a little ethyl alcohol until it solidified. It was crystallized from benzene.

The Grignard products VII, listed in Table III, are difficultly soluble in ethyl alcohol and ether, give no color with ferric chloride solution and are insoluble in aqueous sodium hydroxide (10%).

Action of Phenylmagnesium Bromide on 3(2H)-Thianaphthenone-1,1-dioxide (Ia).—To a Grignard solution (prepared from 0.9 g. of magnesium and 9.0 g. of bromobenzene in 50 ml. of dry ether) was added a solution of 1.0 g. of Ia in dry benzene (50 ml.). The reaction was processed as mentioned previously. The product obtained was identified as 3(2H)-thianaphthenone-1,1-dioxide (m.p. and mixed m.p.).

Action of Acetic Anhydride on VIIc.—A suspension of 0.5 g. of VIIe in acetic anhydride (10 ml.) was refluxed for one hour. The resulting solution was poured into ice-cold water. The solid product that separated was filtered off and crystallized from acetic acid as colorless crystals, m.p. 164°.

Anal. Calcd. for $C_{24}H_{20}O_4S$: C, 71.29; H, 4.95; S, 7.92. Found: C, 71.13; H, 5.13; S, 8.20.

The monoacetyl derivative VIII was soluble in aqueous sodium hydroxide and gave a yellow color with concentrated sulfuric acid.

Acknowledgment.—The authors are indebted to Professor C. L. Stevens of Wayne State University for the determination of the infrared and ultraviolet absorption spectra.

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[CONTRIBUTION FROM THE DOW CORNING CORPORATION]

The Effect of Substituent Fluoroalkyl Groups on the Alkali-catalyzed Hydrolysis of Silanes[1]

BY OMAR W. STEWARD AND OGDEN R. PIERCE

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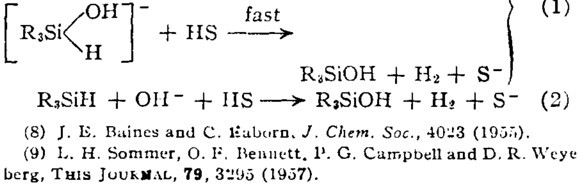
The second-order rate constants for the alkali-catalyzed hydrolysis of the silicon-hydrogen bond in four fluoroalkylsilanes have been determined. It was found that a trifluoromethyl group, even though separated from the silicon atom, *i.e.*, the reaction center, by two or three methylene groups, increases the rate of hydrolysis by an appreciable amount. The ease of polarization of the silicon atom has been suggested for this quite large increase in rate.

Introduction

During the course of work in this Laboratory, it became apparent that information was needed on the effect of various fluoroalkyl groups on the reactivity of the silicon atom in fluoroalkylsilicon compounds. Therefore, a program was initiated to study the influences of various fluoroalkyl groups on the rate of alkali-catalyzed hydrolysis of the silicon–hydrogen bond. This reaction was selected since the kinetics were quite well defined by several previous studies.[2–9]

Price[2] made the first kinetic study of the alkali-catalyzed hydrolysis and found the reaction was first order in silane, first order in hydroxide ion and probably first order in solvent. Using an alcohol–water medium, pseudo first-order kinetics were observed, since the base is regenerated from the water present in the reaction solvent.

Two mechanisms consistent with the observed data have been formulated[6]



$$\left.\begin{array}{l} R_3SiH + OH^- \xrightarrow{\text{slow}} \left[R_3Si\begin{smallmatrix}OH\\H\end{smallmatrix}\right]^- \\ \left[R_3Si\begin{smallmatrix}OH\\H\end{smallmatrix}\right]^- + HS \xrightarrow{\text{fast}} \\ \qquad\qquad R_3SiOH + H_2 + S^- \end{array}\right\} \quad (1)$$

$$R_3SiH + OH^- + HS \longrightarrow R_3SiOH + H_2 + S^- \quad (2)$$

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[1] Presented at the 134th Meeting of the American Chemical Society in Chicago, Ill., September 7–12, 1958.

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Mechanism 1 involves the rate-determining attack of hydroxide ion on the silane to form a pentacovalent intermediate which reacts rapidly with the solvent to yield the products. Mechanism 2 involves a nucleophilic attack of hydroxide ion on the silicon atom in a concerted reaction involving a solvent molecule. At the present time information is not available to determine which mechanism is correct. However, the mechanisms can be considered equivalent for discussion of polar effects.

Results and Discussion

The first attempts to measure the kinetics of 3,3,3-trifluoropropyldimethylsilane led to anomalous results. Using a silane-to-base ratio of 1:1 to 1:3, the same ratio Price[2] used, first-order kinetics were not observed throughout the reaction. Second-order kinetics were observed for the first portion of the reaction. As the reaction proceeded the kinetics passed through a mixed-order period until the last portion of the reaction followed first-order kinetics. However, when the silane-to-base ratio was increased to 1:9 or greater, first-order kinetics were observed throughout the reaction. The rate constants calculated from the first-order plots using a 1:9 ratio of silane to base were slightly larger than those calculated from the first-order portion of the previous plots.

It would seem logical to assume that the reason for the deviation from first-order kinetics when there was only a small excess of base is due to the acidity of 3,3,3-trifluoropropyldimethylsilanol. Previous experience in this Laboratory has indicated that 3,3,3-trifluoropropylsilanols are more stable toward basic condensation to siloxanes and are more acidic than the corresponding alkylsilanols. A similar situation was encountered by Baines and Eaborn[8] using aryldimethylsilanes.

TABLE I

RATE DATA FOR THE ALKALI-CATALYZED HYDROLYSIS OF THE FLUOROALKYLSILANES AT 0° IN 93.7% ETHANOL

RR'(CH$_3$)SiH R	R'	C_{silane}, mole l.$^{-1}$	C_{KOH}, mole l.$^{-1}$	k_1, min.$^{-1}$	k_2, l. mole^{-1} min.$^{-1}$
$CF_3CH_2CH_2$	CH_3	0.00356	0.0389	0.0385	0.990
		.00449	.0486	.0454	.934
		.0202	.1945	.166	.853
		.0260	.3615	.280	.774
		.0210	.3615	.281	.777
		.0222	.4784	.344	.719
		.0217	.4784	.339	.709
		.0547	.4784	.335	.703
$CF_3CH_2CH_2CH_2$	CH_3	.0245	.3615	.0391	.108
		.0233	.4781	.0479	.100
		.0333	.4784	.0478	.100
$CF_3CF_2CH_2CH_2$	CH_3	.0273	.1945	.240	1.23
		.0251	.1945	.242	1.24
		.0285	.3615	.382	1.06
$CF_3CH_2CH_2$	$CF_3CH_2CH_2$	.00339	.0389	1.40	35.9
		.00377	.0389	1.40	35.9
		.00497	.0486	1.60	32.9
$CH_3CH_2CH_2$	CH_3	.0259	.4784	0.00564	0.0118
		.0506	.4784	.00580	.0121

From the data in Table I it can be seen that the second-order rate constants, obtained by dividing the first-order rate constants by the base concentration, increased as the base concentration decreased. This drift of the rate constants is attributed to the salt effect. Baines and Eaborn[8] also reported observing a drift in the same direction with triethylsilane and observed that adding salts containing the same cation as the hydroxide lowered the second-order rate constant. Varying the silane concentration had little effect on the second-order rate constants. This was as expected since the silanes are neutral molecules.

Taking into consideration the drift of the second-order rate constants, the relative rates of hydrolysis of the fluoroalkylsilanes compared to that of *n*-propyldimethylsilane were calculated. They are given in Table II.

TABLE II

RELATIVE RATES FOR THE ALKALI-CATALYZED HYDROLYSIS OF THE FLUOROALKYLSILANES AT 0° IN 93.7% ETHANOL

RR'(CH$_3$)SiH R	R'	Relative rate
$CH_3CH_2CH_2$	CH_3	1.0
$CF_3CH_2CH_2$	CH_3	59
$CF_3CH_2CH_2CH_2$	CH_3	8.3
$CF_3CF_2CH_2CH_2$	CH_3	83
$CF_3CH_2CH_2$	$CF_3CH_2CH_2$	2100

It is interesting to note that substitution of a 3,3,3-trifluoropropyl group for a *n*-propyl group in the alkyldimethylsilane increases the rate 59-fold, even though the highly polar trifluoromethyl group is separated from the silicon atom, *i.e.*, the reaction center, by two methylene spacers. This is quite a surprising effect, since the fluorine atoms are quite far removed from the silicon atom. Steric effects should not be too important since the 3,3,3-trifluoropropyl group would be expected to be only slightly larger than the *n*-propyl group. The introduction of a second 3,3,3-trifluoropropyl group increases the rate by an additional factor of 36, even though the steric forces are considerably greater. At 35° Price[2] showed that the rate of hydrolysis of *n*-propyldimethylsilane is 3.4 times faster than di-*n*-propylmethylsilane.

Replacing a 3,3,3-trifluoropropyl group with a 3,3,4,4,4-pentafluorobutyl group in the fluoroalkyldimethylsilane increases the rate slightly. Longer 1,1,2,2-tetrahydroperfluoroalkyl groups would be expected to have similar rates or even slightly slower rates due to increased steric hindrance of the longer groups.

When the 3,3,3-trifluoropropyl group is replaced by a 4,4,4-trifluorobutyl group in the fluoroalkyldimethylsilane, the rate of alkali-catalyzed hydrolysis is reduced 7.1-fold. However, the rate is still 8.3 times that of *n*-propyldimethylsilane.

In general, it can be concluded that the inductive effect of the trifluoromethyl group removed from the silicon atom by two or three methylene groups is quite large. A reasonable explanation of these results is that the silicon atom is quite readily polarized by highly polar substituents.

Starting Materials.—Dimethylchlorosilane, methyldichlorosilane, triethylchlorosilane, 3,3,3-trifluoropropene[10] and 3-bromo-1,1,1-trifluoropropane[10] were available in research quantities in this Laboratory. They were fractionally distilled before being used.

Preparation of 3,3,4,4,4-Pentafluorobutene.—This compound was prepared by D. D. Smith of this Laboratory by

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(10) P. Tarrant, A. M. Lovelace and M. R. Lilyquist, THIS JOURNAL, **77**, 2783 (1955).

the method of McBee, *et al.*[11] The boiling point has not been previously reported, b.p. 5–6°.

Addition of Fluoroölefins to Dimethylchlorosilane and Methyldichlorosilane.—The procedure used is described by Tarrant, *et al.*[12]

(a) Addition of 3,3,3-trifluoropropene to dimethylchlorosilane gave 3,3,3-trifluoropropyldimethylchlorosilane, b.p. 118°, $n^{25}_{\rm D}$ 1.3727, d^{25}_{4} 1.113.

Anal. Calcd. for $C_5H_{10}ClF_3Si$: Cl, 18.6; C, 31.5; F, 29.9; *MR*D, 39.3. Found: Cl, 18.3; C, 31.0; F, 30.4; *MR*D, 39.0.

(b) Addition of 3,3,3-trifluoropropene to methyldichlorosilane gave 3,3,3-trifluoropropylmethyldichlorosilane,[12] b.p. 122°, $n^{25}_{\rm D}$ 1.3817.

(c) Addition of 3,3,4,4,4-pentafluorobutene to dimethylchlorosilane gave 3,3,4,4,4-pentafluorobutyldimethylchlorosilane, b.p. 129° (750 mm.), $n^{25}_{\rm D}$ 1.3608, d^{25}_{4} 1.199, a 39% yield.

Anal. Calcd. for $C_6H_{10}ClF_5Si$: Cl, 14.7; C, 29.9; F, 39.5; *MR*D, 43.95. Found: Cl, 14.5; C, 29.8; F, 39.6; *MR*D, 44.4.

Preparation of Bis-(3,3,3-trifluoropropyl)-methylchlorosilane.—3,3,3-Trifluoropropylmagnesium bromide dissolved in 900 ml. of ether, prepared from 3-bromo-1,1,1-trifluoropropane (265 g., 1.5 moles) and magnesium (36.6 g., 1.5 moles), was added to 3,3,3-trifluoropropylmethyldichlorosilane (422 g., 2.0 moles) dissolved in 300 ml. of ether. The reaction flask was cooled in an ice-bath throughout the addition. The resulting mixture was allowed to stir overnight. Since the magnesium salts did not precipitate, approximately 600 ml. of ether was removed by distillation. The remaining material was filtered through a Büchner funnel, and the filtrate was fractionally distilled under reduced pressure. Bis-(3,3,3-trifluoropropyl)-methylchlorosilane (83.1 g., 0.30 mole), b.p. 88° (40 mm.), $n^{25}_{\rm D}$ 1.3666, d^{25}_{4} 1.289, was obtained in a 20% yield.

Anal. Calcd. for $C_7H_{11}ClF_6Si$: Cl, 13.0; C, 30.8; F, 41.8; *MR*D, 48.6. Found: Cl, 13.0; C, 31.0; F, 41.6; *MR*D, 47.5.

Lithium Aluminum Hydride Reduction of Chlorosilanes.—The procedure used is described by R. West.[7]

(a) Reduction of triethylchlorosilane gave triethylsilane,[2] b.p. 109° (750 mm.), $n^{25}_{\rm D}$ 1.4092, a 76% yield.

(b) Reduction of 3,3,3-trifluoropropyldimethylchlorosilane gave 3,3,3-trifluoropropyldimethylsilane, b.p. 80° (748 mm.), $n^{25}_{\rm D}$ 1.3485, d^{25}_{4} 0.954, a 72% yield.

Anal. Calcd. for $C_5H_{11}F_3Si$: H(sih), 0.64; C, 38.4; F, 36.5; *MR*D, 35.3; mol. wt., 156. Found: H(sih), 0.66; C, 38.1; F, 36.1; *MR*D, 35.1; mol. wt., 151.

(c) Reduction of 3,3,4,4,4-pentafluorobutyldimethylchlorosilane gave 3,3,4,4,4-pentafluorobutyldimethylsilane, b.p. 94° (743 mm.), $n^{25}_{\rm D}$ 1.3387, d^{25}_{4} 1.078, a 73% yield.

Anal. Calcd. for $C_6H_{11}F_5Si$: H(sih), 0.49; C, 34.9; F, 46.1; *MR*D, 39.95. Found: H(sih), 0.49; C, 34.7; F, 46.5; *MR*D, 39.95.

(d) Reduction of bis-(3,3,3-trifluoropropyl)-methylchlorosilane gave bis-(3,3,3-trifluoropropyl)-methylsilane, b.p. 64° (40 mm.), $n^{25}_{\rm D}$ 1.3500, d^{25}_{4} 1.163, a 49% yield.

Anal. Calcd. for $C_7H_{12}F_6Si$: H(sih), 0.42; C, 35.3; F, 47.9; *MR*D, 44.6. Found: H(sih), 0.43; C, 35.5; F, 47.4; *MR*D, 44.1.

Preparation of 4,4,4-Trifluorobutan-1-ol.—γ,γ,γ-Trifluorobutyric acid was prepared by adding the Grignard reagent of 3-bromo-1,1,1-trifluoropropane to solid carbon dioxide.[13] The acid was not isolated, but was esterified with ethanol using a sulfuric acid catalyst. Ethyl γ,γ,γ-trifluorobutyrate,[14] b.p. 128° (750 mm.), $n^{25}_{\rm D}$ 1.3500, d^{25}_{4} 1.160, was obtained in a 57% yield. Reduction with lithium aluminum hydride in ether gave 4,4,4-trifluorobutan-1-ol,[15] b.p. 126° (745 mm.), $n^{25}_{\rm D}$ 1.3410, d^{25}_{4} 1.217, a 78% yield.

Preparation of 4-bromo-1,1,1-trifluorobutane.—This compound was prepared by the method of Gavlin and Maguire.[16] Addition of 4,4,4-trifluorobutan-1-ol to phosphorus tribromide gave 4-bromo-1,1,1-trifluorobutane, b.p. 105° (751 mm.), $n^{25}_{\rm D}$ 1.3800, d^{25}_{4} 1.577, a 79% yield.

Anal. Calcd. for $C_4H_6BrF_3$: C, 25.15; F, 29.8; *MR*D, 28.4. Found: C, 25.4; F, 30.0; *MR*D, 28.4.

Addition of Grignard Reagents to Dimethylchlorosilane.—(a) 4,4,4-Trifluorobutylmagnesium bromide, dissolved in 250 ml. of ether, prepared from 4-bromo-1,1,1-trifluorobutane (112.5 g., 0.59 mole) and magnesium (14.6 g., 0.60 mole), was added over a period of 1 hour to dimethylchlorosilane (55.8 g., 0.59 mole) dissolved in 200 ml. of ether. The reaction mixture was allowed to stir overnight. This mixture was poured into cracked ice, and the water layer was extracted twice with ether. The combined ether layer was dried over anhydrous calcium sulfate. After the ether was removed, fractional distillation gave 4,4,4-trifluorobutyldimethylsilane (51.9 g., 0.30 mole), b.p. 105° (756mm.), $n^{25}_{\rm D}$ 1.3612, d^{25}_{4} 0.950, a 52% yield.

Anal. Calcd. for $C_6H_{13}F_3Si$: H(sih), 0.59; C, 42.3; F, 33.5; *MR*D, 39.9. Found: H(sih), 0.60; C, 42.3; F, 33.9; *MR*D, 39.7.

(b) *n*-Propyldimethylsilane,[2] b.p. 74° (750 mm.), $n^{25}_{\rm D}$ 1.3884, d^{25}_{4} 0.692, was synthesized in a 46% yield by the above procedure.

Anal. Calcd. for $C_5H_{14}Si$: H(sih), 0.99. Found: H(sih), 0.96.

Methods and Apparatus. Kinetic Procedure.—For the rate determinations the following procedure was used. A 250-ml., round-bottom, three-necked flask was equipped with a mercury-sealed stirrer, a self-sealing rubber stopper, and an outlet tube leading to a mercury-filled 100-cc. gas buret and manometer. Standardized alcoholic potassium hydroxide (50.2 ml.) was placed in the flask which was maintained at a constant temperature (0.00 ± 0.05°) by a water-ice-bath. In the studies with bis-(3,3,3-trifluoropropyl)-methylsilane a 500-ml. flask was used, and alcoholic potassium hydroxide aliquots of 200.8 ml. and 251.0 ml. were used. When the apparatus reached thermal equilibrium it was adjusted to atmospheric pressure by leveling the manometer. The silane sample, calculated to give a reasonable volume of gas, was injected into the stirred reaction mixture from a weighed hypodermic syringe. Readings were taken at various time intervals by adjusting the system to atmospheric pressure. The error in the buret reading was about 0.1 cc., and the error in timing was about two seconds.

The volume of hydrogen was taken as a measure of the amount of reacted silane. The rate constants were determined from the slope of the line obtained by plotting log $[(V_\infty - V_t)/(V_\infty) \times 10^2]$ *vs.* time, where V_∞ = volume of gas evolved at infinite time and V_t = volume of gas evolved at time t. Straight lines were usually obtained to better than 80% reaction.

Triethylsilane was taken as a standard to compare the observed second-order rate constant with the value reported by Price.[2] Using 0.1904 *N* alcoholic potassium hydroxide containing 6.3% water and silane concentration varying between 0.028–0.052 mole per liter, the average of four determinations was 0.0834 liter mole^{-1} min.$^{-1}$ at 34.7°. Price reported the average value of 0.093 liter mole^{-1} min.$^{-1}$ at 34.45° using 0.119–0.297 *N* alcoholic potassium hydroxide containing 5% water and a silane concentration of 0.1 mole per liter.

Gas Analyses.—Using conditions similar to those described under kinetic procedure, a sample of the gas evolved from 3,3,3-trifluoropropyldimethylsilane was collected and analyzed using a mass spectrometer. The analysis indicated the gas was 99.7% hydrogen, 0.27% ethanol and <0.1% other constituents.

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