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CLEAVAGE OF ALKYLSILANES BY STRONG ACIDS

III. THE REACTIONS OF (HALOMETHYL)TRIMETHYLSILANES WITH FLUOROSULFONIC ACID

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Summary

The stepwise cleavage of alkyl groups from (bromomethyl)trimethylsilane and (iodomethyl)trimethylsilane by fluorosulfonic acid has been studied with proton magnetic resonance. Exclusive methyl cleavage is observed in the first reaction of both compounds. The reaction of (bromomethyl)dimethylsilyl fluorosulfonate occurs with cleavage of both methyl and bromomethyl from silicon. The reaction of (iodomethyl)dimethylfluorosilane occurs with exclusive cleavage of the iodomethyl group.

Introduction

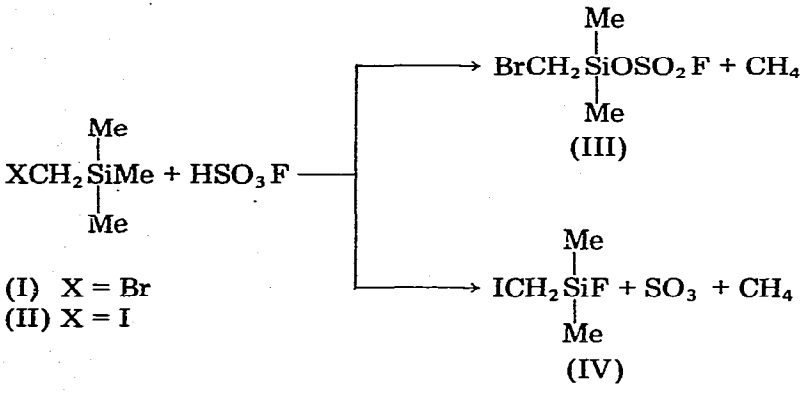
Alkyl groups are easily cleaved from silicon by strong proton acids [1]. Tetraalkylsilanes react with sulfuric acid at moderate temperatures (30 to 80°C) to give alkanes and trialkylsilyl sulfonates [2—6]. Cleavage of a second alkyl group from these sulfonates requires more vigorous conditions because of back donation of electron density from oxygen to silicon. We have recently reported the stepwise cleavage of two methyl groups from tetramethylsilane and (chloromethyl)trimethylsilane by fluorosulfonic aicd [7,8]. Relative rate studies of the low temperature cleavage of the first methyl showed that the important step is electrophilic attack by the acid at a methyl carbon [7]. Cleavage of a second methyl from the trialkylsilyl fluorosulfonate occurred at a much slower rate and was studied at higher temperatures. In this second cleavage reaction, two cleavage products were formed, methane and methanesulfonyl fluoride. The methanesulfonyl fluoride was formed through the intramolecular migration of a methyl from silicon to sulfur in a pentacoordinate intermediate [8].

Results and discussion

The reactions of (bromomethyl)trimethylsilane (I) and (iodomethyl)trimethylsilane (II) with fluorosulfonic acid have now been investigated. Unlike the reaction of tetramethylsilane and (chloromethyl)trimethylsilane, the reactions of I and II were considerably more complex. Reactions took place at the methyl and the halomethyl carbons. Kinetics could not be obtained using nuclear magnetic resonance (NMR) because of the variety of products which resulted in much overlap in the silicon-methyl region of the spectra. However, qualitative reactivity trends were obtained.

(Halomethyl)trimethylsilanes

When I and II are allowed to react with neat fluorosulfonic acid at low temperatures (−78°C), exclusive electrophilic attack at the methyl carbons takes place, forming (bromomethyl)dimethylsilyl fluorosulfonate (III) from I and (iodomethyl)dimethylfluorosilane (IV) from II (eq. 1). The NMR spectrum of



the reaction of I showed the appearance of two singlets for the silicon methyls and for the bromomethylene hydrogens (relative intensity, 6 : 2). For the reaction of II, two doublets appeared, showing that the fluorosilane rather than the fluorosulfonate was the first cleavage product. Except for the singlet characteristic of methane dissolved in fluorosulfonic acid, no other resonances were observed in the low temperature cleavage of the first methyls from I and II.

(Halomethyl)dimethylsilanes

The more difficult cleavage of a second alkyl group from III and IV was studied qualitatively at 30° C. As the reaction of III with fluorosulfonic acid proceeded, a number of new resonances appeared (Fig. 1). These resonances included two triplets (relative intensity, 3 : 2), one in the silicon methyl region and one slightly upfield of the bromomethylene singlet. This indicates the formation of (bromomethyl)methyldifluorosilane (V). Similar to the reactions of tetramethylsilane and (chloromethyl)trimethylsilane [8], methanesulfonyl fluoride is formed during this second cleavage reaction of III as indicated by the doublet at δ 3.51 ppm (J(H—F) 5.9 Hz.). The chemical shifts and coupling constants for the products of the reactions of I and II with fluorosulfonic acid are summarized in Table 1.

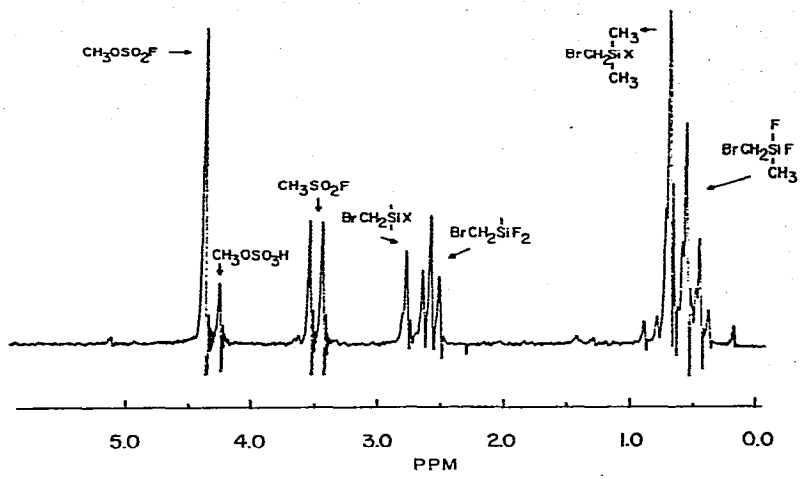


Fig. 1. The proton NMR of the reaction of (bromomethyl)dimethylsilyl fluorosulfonate with fluorosulfonic acid (X = OSO_2F).

The cleavage of alkyl groups from III is complicated by competing reactions. During the reaction two new resonances appear in the methyl oxygen region. Close inspection of the resonance at δ 4.38 ppm shows it to be a doublet. A quartet with the same small long range coupling was found in the fluorine-19 spectrum. These resonances were assigned to methyl fluorosulfonate (IX, CH_3OSO_2F). This assignment was confirmed by the observation of the same coupling constant and similar chemical shifts for a sample of IX dissolved in fluorosulfonic acid. The proton chemical shift was found to be concentration sensitive (δ 4.1 to 4.4 ppm). This sensitivity probably reflects slight changes in the degree of protonation of methyl fluorosulfonate by fluorosulfonic acid. The smaller upfield singlet at δ 4.26 ppm was identified as methyl hydrogen sulfate by comparison to a sample dissolved in fluorosulfonic acid. The size of this singlet increased at the expense of the methyl fluorosulfonate doublet even after the cleavage reaction was complete. This shows that methyl hydrogen sulfate was formed through hydrolysis of the initially formed methyl fluorosulfonate, probably due to trace amounts of moisture.

Underlying the silicon methyl resonances of III and V were resonances due to dimethylsilyl bis(fluorosulfonate)($Me_2Si(OSO_2F)_2$), dimethylfluorosilyl fluorosulfonate ($Me_2FSiOSO_2F$) and dimethyldifluorosilane [8]. These products could not be clearly observed in the NMR spectra until the completion of the reaction because of overlap with the silicon-methyl resonances of III and V. These minor products arise from the cleavage of the bromomethylene group and their presence was suggested by the observation of methylfluorosulfonate in the NMR during the reaction. Further, the integrated intensity of the silicon methyl region during the reaction was consistently too large to be accounted for by the intenisty calculated on the basis of the bromomethylene singlet of III and the bromomethylene triplet of V. The inability to separate the silicon-methyl region of the spectrum was the principle reason which precluded following the reaction of III kinetically with NMR.

A reasonable scheme for the complex reactions of III and IV with fluoro-

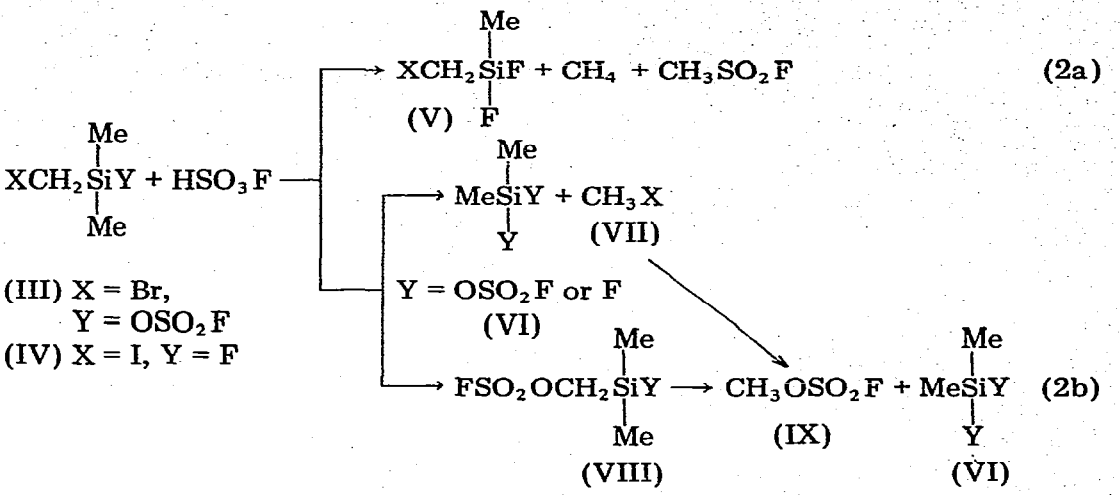
TABLE 1

CHEMICAL SHIFTS AND COUPLING CONSTANTS FOR THE PRODUCTS OF THE REACTIONS OF I AND II WITH FLUOROSULFONIC ACID [a]

Compound	—CH_3		—CH_2—		Compound	—CH_3		—CH_2—	
	δ (^{1}H)	J(H—F)	δ (^{1}H)	J(H—F)		δ (^{1}H)	J(H—F)	δ (^{1}H)	J(H—F)
$BrCH_2SiMe_2OSO_2F$ (III)	0.76(1)		2.80(1)		Me_2SiF_2	0.39(3)	6.7		
					$BrCH_2SiMeF_2$ (V)	0.57(3)	6.2	2.62(3)	3.7
					$Me_2FSiOSO_2F$	0.68(2)	6.6		
					$Me_2Si(OSO_2F)_2$	0.89(1)			
					CH_3OSO_2F (IX)	4.38(2)	0.4		
					CH_3SO_2F	3.51(2)	5.9		
ICH_2SiMe_2F (IV)	0.58(2)	7.5	3.58(2)	6.8	$FSO_3CH_2SiMe_2F$ (VIII)	0.47(2)	7.9	4.51(2)	6.2
					Me_2SiF_2 (VI)	0.39(3)	6.7		
					CH_3OSO_2F (IX)	4.31(2)	0.4		
					CH_3OSO_2OH	4.19(1)			
					CH_3I (VII)	3.03(1)			

[a] ^{1}H shifts in ppm downfield from TMS (internal); figures in parentheses represent multiplicity of peaks; coupling constants in Hz.

sulfonic acid is presented in eq. 2. Two pathways may be noted in this scheme:



cleavage of methyl (eq. 2a) and cleavage of halomethyl (eq. 2b). In the reaction of III formation of V may occur only through electrophilic attack at a methyl carbon. On the other hand, IX and VI may be formed in two ways: initial cleavage followed by substitution (eq. 2b: III → VI + VII; VII → IX) or initial substitution followed by cleavage (eq. 2b: III → VIII → IX + VI). However, neither methyl bromide (VII) nor VIII were observed in NMR detectable amounts for the reaction of III with fluorosulfonic acid. Therefore, it can not be definitely established whether reaction at the bromomethyl of III requires

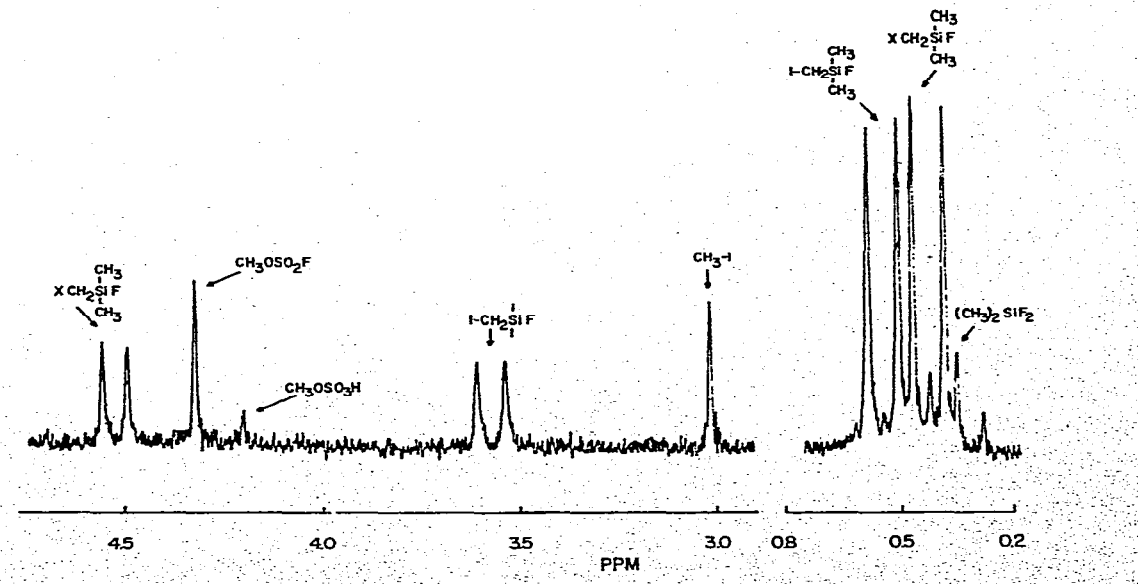


Fig. 2. The proton NMR of the reaction of (iodomethyl)dimethylfluorosilane with fluorosulfonic acid (X = OSO_2F).

the intermediacy of VIII. Despite this ambiguity, it should be emphasized that two cleavage pathways are observed for the raection of III.

The reaction of (iodomethyl)dimethylfluorosilane (IV) at 30°C was also complex (Fig. 2). During the reaction, the two doublets for IV slowly disappeared and were replaced by two new doublets due to dimethylfluorosilyl methyl fluorosulfonate (VIII, Y = F). The formation of methyl iodide was indicated by the appearance of a singlet at δ 3.03 ppm. The spectrum also showed two singlets due to methyl fluorosulfonate and methyl hydrogen sulfate. No (iodomethyl)methyldifluorosilane or methanesulfonyl fluoride were observed in the NMR. In sharp contrast to the reaction of III, IV reacts only at the halomethyl carbon.

If the reactions of III and IV are compared to the previously reported reactions of (chloromethyl)dimethylsilyl fluorosulfonate [8], it is seen that there is a change in the cleavage pathway from exclusive methyl cleavage with chloromethyl to exclusive halomethyl cleavage with iodomethyl (Table 2). It is unlikely that this change in cleavage pathway can be rationalized only on the basis of a change in the inductive influence of the α-halogen. If only a change in inductive influence is operating, one would expect that electrophilic cleavage of the halomethyl would become more competitive with methyl cleavage as the electron-withdrawing power of the halogen decreases. However, one would not expect the complete loss of methyl cleavage as is observed in the reaction of IV.

The chemical shifts of halomethanes and halomethylsilanes presented in Table 3 offer an explanation. In non-polar, aprotic solvents such as carbon tetrachloride, the proton shifts of the halomethanes show the expected upfield trend in going from chlorine to bromine to iodine. A similar trend is seen for the shifts of (halomethyl)trimethylsilanes in carbon tetrachloride. When halomethanes are dissolved in fluorosulfonic acid, a reversal of this trend occurs. Iodomethane in fluorosulfonic acid is further downfield than bromomethane. It was also found that the chemical shift of iodomethane in fluorosulfonic acid is concentration dependent. The downfield chemical shift of iodomethane is most likely due to protonation of the iodine (eq. 3). This explanation is supported by the chemical shifts found for dialkylhalonium ions. For example, the chemical shift of dimethyliodonium ion, ($CH_3—\overset{+}{I}—CH_3$), in liquid sulfur dioxide is δ 3.48 ppm [9].

$$CH_3I + HSO_3F \rightleftharpoons CH_3—\overset{+}{I}—H + {}^{-}SO_3F \qquad (3)$$

Based on the chemical shift values presented in Table 3, the degree of proton-

TABLE 2

PRODUCT DISTRIBUTIONS FOR THE REACTIONS OF (HALOMETHYL)DIMETHYLSILANES WITH FLUOROSULFONIC ACID [a]

Compound	Methyl cleavage		Halomethyl cleavage (%)	$t_{1/2}$ (h)	Notes
	CH_4 (%)	CH_3SO_2F (%)			
$(ClCH_2)Me_2SiOSO_2F$	32	68	0	28	Ref. 8
$(BrCH_2)Me_2SiOSO_2F$	48	7	45	19	This work
$(ICH_2)Me_2SiF$	0	0	100	5	This work

[a] Reactions run at 30°C in neat fluorosulfonic acid; yields based on integration of the appropriate peaks in the NMR during the reaction.

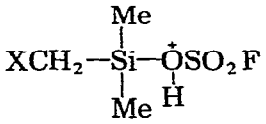
TABLE 3

CHEMICAL SHIFTS OF HALOMETHANES AND HALOMETHYLSILANES IN CARBON TETRACHLORIDE AND FLUOROSULFONIC ACID

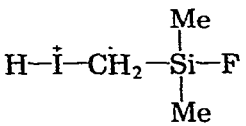
Compound	δ (^{1}H)	
	CCl_4	HSO_3F
CH_3Cl	3.05	—
CH_3Br	2.37	2.33
CH_3I	2.16	2.80 to 3.15 [a]
Me_3SiCH_2Cl	2.76	—
Me_3SiCH_2Br	2.46	—
Me_3SiCH_2I	2.00	—
Me_2FSiCH_2Cl	—	3.02
Me_2FSiCH_2I	—	3.58

[a] Concentration dependent.

ation is much greater for iodomethane than for bromomethane. The downfield chemical shift observed for the methylene hydrogens of (iodomethyl)dimethylfluorosilane (IV, δ 3.58 ppm) indicates a substantial degree of iodine protonation. Previous kinetic data strongly implicated a protonated species like X in the cleavage reactions of trimethylsilyl fluorosulfonate and (chloromethyl)dimethyl-



(X)
X = H or Cl



(XI)

silyl fluorosulfonate [8]. A similar but iodine protonated species (XI) may be responsible for exclusive reaction at the iodomethyl of IV. Iodine protonation would enhance nucleophilic attack by fluorosulfonic acid at the iodomethyl carbon to give VIII while attack at silicon would yield VI and iodomethane.

Experimental

General

(Bromomethyl)trimethylsilane, methyl hydrogen sulfate, methanesulfonyl fluoride, dimethyldifluorosilane, methyl iodide and methyl bromide were commercially available materials and were used without further purification. Fluorosulfonic acid was purified by passing a stream of dry nitrogen through it at reflux to remove entrapped hydrogen fluoride. It was then distilled and stored in teflon bottles.

Varian Associates Models A-60 and HA-100 spectrometers equipped with variable temperature probes were used for all proton spectra. Proton chemical shifts are reported in parts per million downfield from tetramethylsilane (internal). Fluorine spectra were obtained using a Varian Associates Model HA-100 spectrometer equipped with a V-4311 radio frequency unit operating at 94.1

MHz. Fluorine chemical shifts were measured using sidebands from a Hewlett—Packard Model 200 CD audio oscillator.

Synthesis

(Iodomethyl)trimethylsilane (II). Preparation of II was carried out in a manner similar to that described by Whitmore and Sommer [10]. To a 500 ml flask was added 200 ml of dry acetone and dry sodium iodide (25 g, 0.17 mol). (Chloromethyl)trimethylsilane (36 g, 0.30 mol) was added and the reaction mixture refluxed for 24 h. The mixture was filtered to remove sodium chloride and approximately 150 ml of acetone was distilled. The mixture was extracted with ether, dried and the ether distilled. Fractionation of the residue gave (iodomethyl)-trimethylsilane (47 g, 0.22 mol, 73% yield, b.p. 138—140°C/755 mmHg, lit. [10]: b.p. 139.5°C/744 mmHg).

Sample preparation

Samples were prepared by adding the cooled (—78°C) silane, either I or II, to cooled fluorosulfonic acid (—78°C). The concentration of the silane was approximately 0.2 *M*. After mixing the sample, it was transferred to a cooled NMR tube and the first cleavage reaction was observed at —78°C. After the completion of this reaction, the NMR probe was allowed to warm to 30°C and the second cleavage reaction was followed.

Since the reactions were carried out in an excess of fluorosulfonic acid, it was not practicable to identify the products of the reaction by isolation. Several attempts in this direction resulted in further reaction and destruction of the product. For this reason, proton NMR was ideally suitable for product identification. Where practical, NMR resonances were assigned by comparison of the chemical shift(s) in the reaction mixture to the chemical shift(s) of the suspected product dissolved in fluorosulfonic acid.

Acknowledgement

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