Preliminary communication
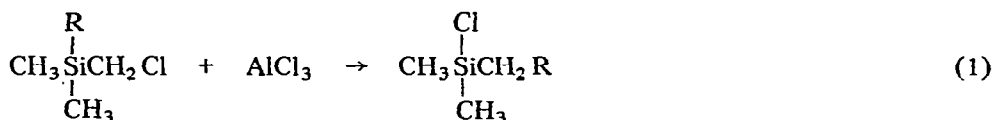

The reaction of α-halosilanes with antimony pentafluoride

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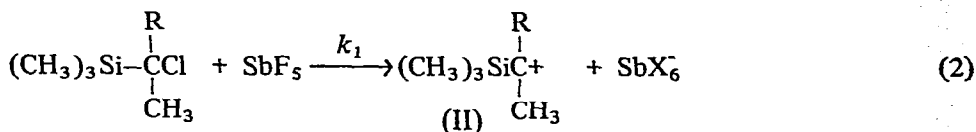
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Intramolecular rearrangements of α-halosilanes with Lewis acids were first reported by Sommer and subsequently have been extensively investigated[1,2]. Such reactions lead to the facile rearrangement of aryl and alkyl groups from silicon to carbon with primary halides and to a combination of rearrangement and hydride shift followed by β-elimination with secondary and tertiary halides[3,4]. Kinetic studies have been carried out using aluminum chloride with primary halides (eqn. 1; R = CH_3, p-$CH_3C_6H_4$, p-ClC_6H_4, C_6H_5)[5]. The order with respect to the Lewis acid could not be determined because it was

$$
\underset{\underset{CH_3}{|}}{\overset{\overset{R}{|}}{CH_3SiCH_2Cl}} \;+\; AlCl_3 \;\rightarrow\; \underset{\underset{CH_3}{|}}{\overset{\overset{Cl}{|}}{CH_3SiCH_2R}} \tag{1}
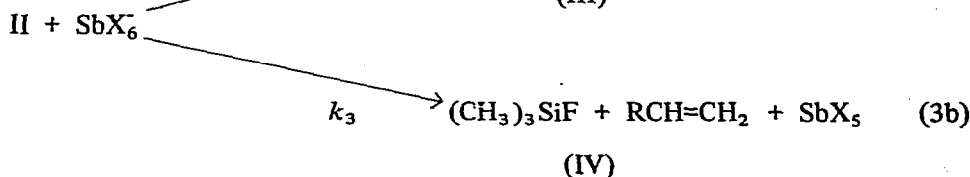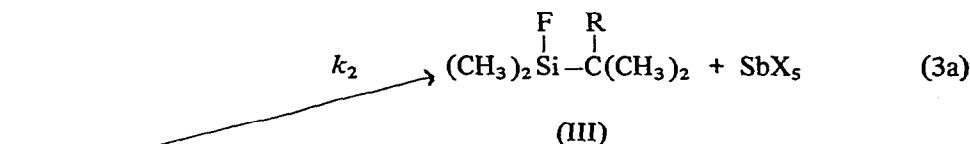$$

used only in catalytic amounts. It was stated that satisfactory kinetic data could not be obtained and that the first-order plots were not linear after about 60% reaction. A four-centered intramolecular transition state was proposed on the basis of these data[5].

We wish to report the NMR observation of the stepwise nature of this reaction using antimony pentafluoride dissolved in nitromethane. Antimony pentafluoride is advantageous in that it is easily purified and dissolves readily in nitromethane to give homogeneous solutions. For both compounds studied (Ia, Ib; eqn. 2), it was possible to determine the kinetic order with respect to the Lewis acid and the silane. In addition, with the tertiary halide (Ia) it was possible to determine the order with respect to the negative ion of the Lewis acid (hexahaloantimonate ion).

The initial ionization and subsequent rearrangement or β-elimination both can be followed with NMR if the starting halide is tertiary. The reaction of 2-trimethylsilyl-2-chloropropane (Ia, eqn. 2) with antimony pentafluoride, both diluted to approximately 0.1 molar with nitromethane and allowed to warm to 40°, results in the slow appearance of new methyl resonances at 0.32δ and 1.69δ (integrated intensity 3.0 : 2.0; Fig.1). Good kinetic data could be obtained over several half-lives by careful integration of the

$$(CH_3)_3Si-\overset{\overset{\textstyle R}{|}}{\underset{\underset{\textstyle CH_3}{|}}{C}}Cl \; + \; SbF_5 \; \xrightarrow{\;k_1\;} \; (CH_3)_3Si\overset{\overset{\textstyle R}{|}}{\underset{\underset{\textstyle CH_3}{|}}{C}}+ \; + \; SbX_6^- \tag{2}$$

$$(II)$$

$$(Ia, \; R = CH_3; \; Ib, \; R = H)$$

$$II \; + \; SbX_6^- \begin{cases} \xrightarrow{\;k_2\;} (CH_3)_2\overset{\overset{\textstyle F}{|}}{Si}-\overset{\overset{\textstyle R}{|}}{C}(CH_3)_2 \; + \; SbX_5 \quad (3a) \\ \qquad\qquad\qquad (III) \\ \\ \xrightarrow{\;k_3\;} (CH_3)_3SiF \; + \; RCH{=}CH_2 \; + \; SbX_5 \quad (3b) \\ \qquad\qquad\qquad (IV) \end{cases}$$

appropriate resonances as a function of time. This ion then reacts further to form the rearranged product (III) and the β-elimination product (IV) (eqn. 3; Fig.1). The first reaction was first-order in both Ia and antimony pentafluoride. The second reaction occurred in a competitive second-order manner, first-order in both ion (II) and hexahalo-antimonate ion. The first-order dependence on hexahaloantimonate ion was verified by the addition of potassium hexafluoroantimonate to the reaction (Table 1).

When the halide is secondary, the initial ionization becomes rate-determining and kinetic measurements lead to no useful mechanistic information concerning β-elimination or rapid rearrangement following the slow initial ionization. The reaction of 1-trimethyl-silyl-1-chloroethane (Ib, eqn. 2) with antimony pentafluoride in nitromethane showed

TABLE 1

KINETIC DATA FOR THE REACTION OF I WITH ANTIMONY PENTAFLUORIDE, 40.0°

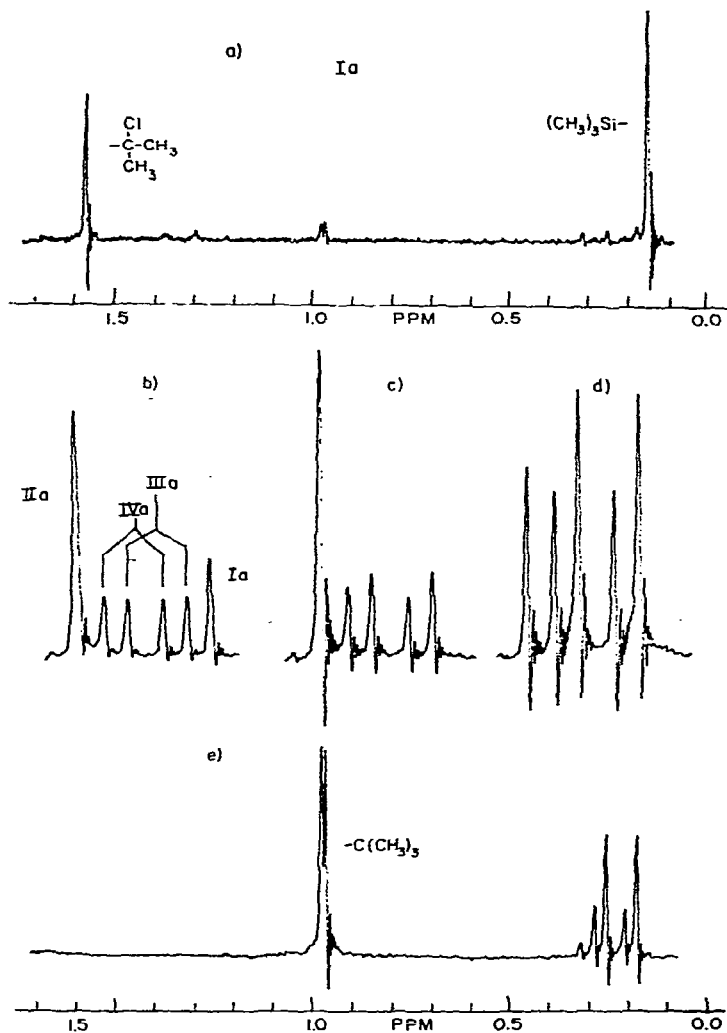| Run	I (mole/l)	SbF$_5$ (mole/l)	$k_1 \cdot 10^5$ (l·mole^{-1}·sec^{-1})	$(k_2 + k_3) \cdot 10^5$ (l·mole^{-1}·sec^{-1})	Comments
Ia–1 to Ia–5	0.111 to 0.188	0.108 to 0.203	256. ± 1	243. ± 1	%III = 89.9 ± 0.3
Ia–6	0.124	0.123	254.	241.	0.101 KSbF$_6$; %III = 89.4
Ia–7	0.144	0.108	254.	243.	0.086 KSbF$_6$; %III = 90.0
			$k \cdot 10^5$ (sec^{-1})	$k_1 \cdot 10^5$ (l·mole^{-1}·sec^{-1})	
Ib–1	0.162	0.104	0.910	8.74	%IV = ~98
Ib–2	0.163	0.165	1.44	8.72	%IV = ~98
Ib–3	0.162	0.193	1.69	8.73	%IV = ~98; 0.074 KSbF$_6$

Fig. 1. The Reaction of 2-trimethylsilyl-2-chloropropane (Ia) with antimony pentafluoride: (a) proton spectrum at beginning of reaction; (b), (c), (d): expanded silicon—methyl resonances during the course of the reaction; (b) ionization (Ia→IIa) ~70% complete; (c) ionization complete; rearrangement-elimination (IIa→IIIa + IVa) ~50% complete; (d) rearrangement-elimination ~85% complete; (e) proton spectrum at end of reaction.

only the disappearance of resonances due to β-elimination (~98%). The initial ionization of Ia was faster by a factor of about thirty when compared to Ib. For the reaction of Ib, pseudo first-order plots were obtained with the value of the rate constant dependent upon the antimony pentafluoride concentration. This verifies that the Lewis acid is acting as a catalyst in the reaction of this secondary halide (Table 1; eqn. 2, 3).

These kinetic data allow a more detailed mechanistic picture for this important reaction. The initially formed species (II) is perhaps best described as a donor—acceptor complex rather than a free carbonium ion because of the relatively small downfield chemical shifts from the starting silane resonances. The first-order kinetic dependence for the disappearance of IIa upon the hexahaloantimonate ion shows that the reaction is better described by the attack of this ion at silicon before or during the rate-determining step rather than the four-centered process previously described[5]. Rate-determining nucleophilic attack at silicon by the hexahaloantimonate ion would make it extremely unlikely that substantial positive charge ever develops on the silicon atom. Therefore, either direct observation of a siliconium ion or the trapping of such a species by nucleophilic agents in a Friedel—Crafts type reaction in these systems is quite remote.

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