

SOLVENT-INDUCED ISOMERIZATION OF HALOSILACYCLOBUTANES. A MECHANISM WITH IONIC INTERMEDIATES WITH EXPANDED COORDINATION

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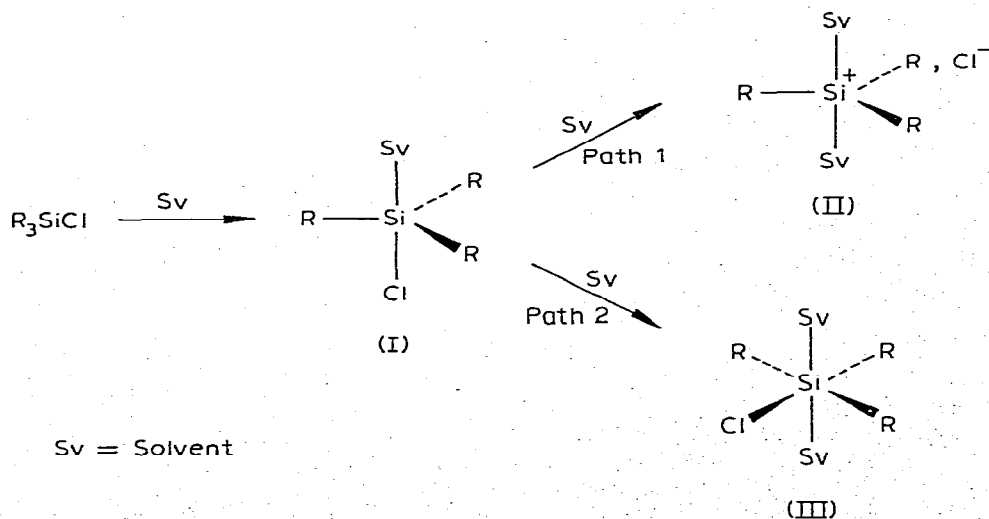
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Summary

A study of the isomerization of halosilacyclobutane geometric isomers in the presence of HMPT has been carried out. Kinetics and the observation of HMPT-catalyzed exchange are interpreted in terms of an intermediate penta-coordinate siliconium ion with two moles of HMPT.

Haloorganosilanes are the most common synthetic intermediates for preparation of all organosilanes. A thorough understanding of reaction mechanisms of halosilanes is therefore desirable. A necessary starting point for this understanding is an appreciation of the nature of interactions with common organic solvents. The racemization of triorganochlorosilanes with solvents of



SCHEME 1

high dielectric constant, first reported by Sommer [1], has been studied extensively by Corriu and coworkers [2]. Primarily on the bases of observed steric effects and kinetics (first-order in silane and second-order in solvent) Corriu has suggested two possible mechanisms. Both involve an initial coordination of a solvent molecule to form a pentacoordinate species I (Scheme 1), followed by either displacement of chloride ion by a second solvent molecule (Path 1), or coordination of the second solvent molecule to form a hexacoordinate intermediate (Path 2). A study of substituent effects failed to clearly distinguish between the two mechanisms.

A method potentially capable of distinguishing between the two is the study of 1-chloro-1,2-dimethyl-1-silacyclobutane (IV). If Path 1 were operating IV would be expected to isomerize slowly, if at all, since the C—Si—C angle in the intermediate is 120° but in IV is only approximately 80° [3]. Conversely if Path 2 were operating IV would probably react faster than comparable acyclic systems since the C—Si—C angle in the hexacoordinate intermediate is ca. 90° .

The isomerization of an 85 : 15 mixture of IVa and IVb, the *E* and *Z* isomers respectively, with hexamethylphosphoric triamide (HMPT) in CCl_4 to a 48 : 52 mixture of IVa and IVb was followed by NMR utilizing HMPT concentrations of 2.0×10^{-3} to 2.5×10^{-5} M and chlorosilane concentration of 0.75 M. The pseudo-first order rate constants k obtained at various HMPT concentrations are shown in Table 1. A plot of $k/[\text{HMPT}]$ vs. $[\text{HMPT}]$ (Fig. 1) shows that at high HMPT concentration ($> 5 \times 10^{-4}$ M) the reaction is first order in HMPT (slope 0) but at lower concentrations the reaction is becoming second order in HMPT. These kinetic observations are consistent with two step formation of an intermediate, in which the rate-determining step changes with changing HMPT concentration. Application of the steady state assumption to the adduct containing one Sv yields the kinetic law of eq. 1. The line shown in Fig. 1 is a plot of

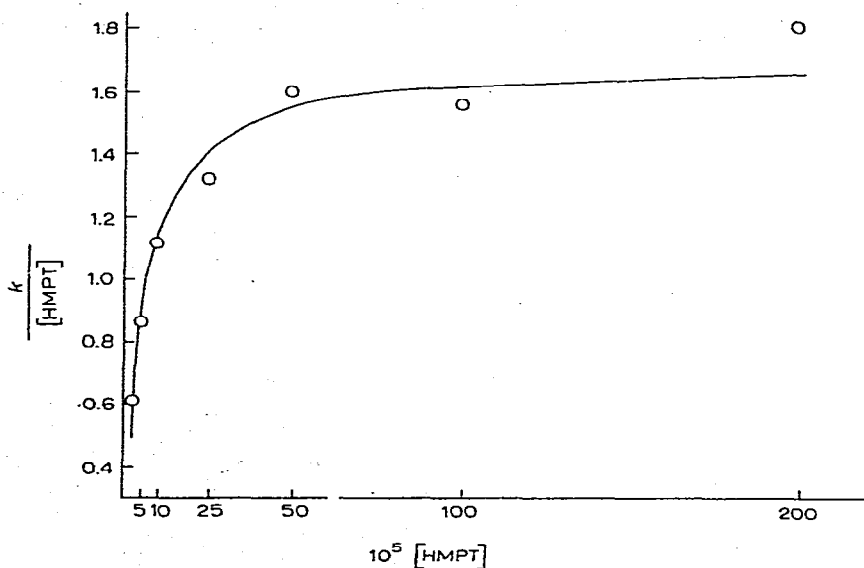
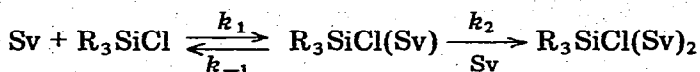


Fig. 1. Plot of $k/[\text{HMPT}]$ vs. $[\text{HMPT}]$ for isomerization of 1-chloro-1,2-dimethylsilacyclobutane.



eq. 1 with $k_1 = 1.7 M^{-1} \text{sec}^{-1}$ and $k_2/k_{-1} = 2.0 \times 10^4 M^{-1}$. Similar kinetics were observed recently in the hydrolysis of an aryloxytriphenylsilane [4].

$$k = \frac{k_1 k_2 [\text{Sv}]^2}{k_{-1} + k_2 [\text{Sv}]} \quad (1)$$

The observations of the latter study have been challenged [5] and the suggestion has been made that the solvent acetonitrile used in that study contained an acidic impurity which was altering the effective $[\text{OH}^-]$ at low nominal $[\text{OH}^-]$. We are using rigorously purified solvents, including HMPT distilled from CaH_2 . One can never eliminate all possibility of an impurity influencing the observed rates, particularly at low concentrations. We are convinced, however, that the kinetics being observed are real because we have done similar studies with 1-chloro-1,2-dimethylsilacyclopentane isomers using the same solutions [6], and in that case we do not observe a curved plot of $k_1/[\text{HMPT}]$ vs. $[\text{HMPT}]$.

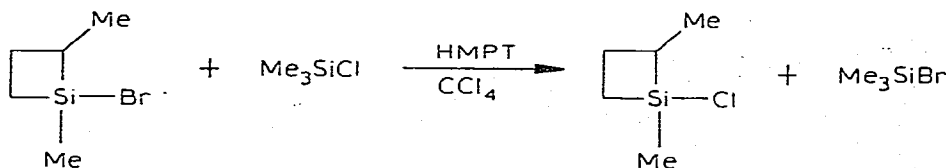
At low HMPT concentration the $k_2 [\text{HMPT}]$ term is negligible compared to k_{-1} , allowing a third-order rate constant k_3 to be derived (eq. 2). This value cal-

$$k_3 = \frac{k}{[\text{Sv}]^2} = \frac{k_1 k_2}{k_{-1}} = 3.4 \times 10^4 M^{-2} \text{sec}^{-1} \quad (2)$$

culated from the previously derived k_1 and k_2/k_{-1} values is in good agreement with an observed $k/[\text{HMPT}]^2 = 2.4 \times 10^4 M^{-2} \text{sec}^{-1}$ for the isomerization with $2.5 \times 10^{-5} M$ HMPT. Comparison of k_3 with the third-order rate constant previously reported for racemization of *i*-PrPhNpSiCl (V), with HMPT [7] ($k_3 = 4 \times 10^{-2} M^{-2} \text{sec}^{-1}$) revealed that IV reacted ca. 5×10^5 times faster.

Observations of a different nature lead to the conclusion that ionic intermediates are probably involved in the isomerization. When 1-bromo-1,2-dimethyl-1-silacyclobutane (VI) and trimethylchlorosilane are combined in the presence of HMPT, halide-halide exchange occurs at a rate comparable to that of isomerization of the halosilane. No exchange occurs in the absence of HMPT. Presumably the exchange occurs between an ionic intermediate and another halosilane molecule (eq. 3 and/or 4).

The exchange probably occurs with predominant retention of configuration in view of the solvent [8] (CCl_4) and the known stereochemistry of reactions at silicon when incorporated in small rings [9]. Furthermore, if exchange with inversion occurred isomerization would result, yet the kinetics observed for isomerization of IV are not interpretable in terms of such a mechanism. Exchange



(VI)

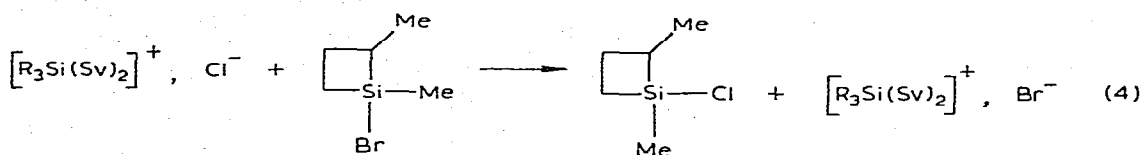
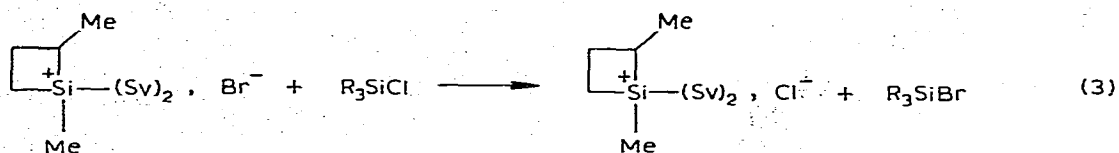
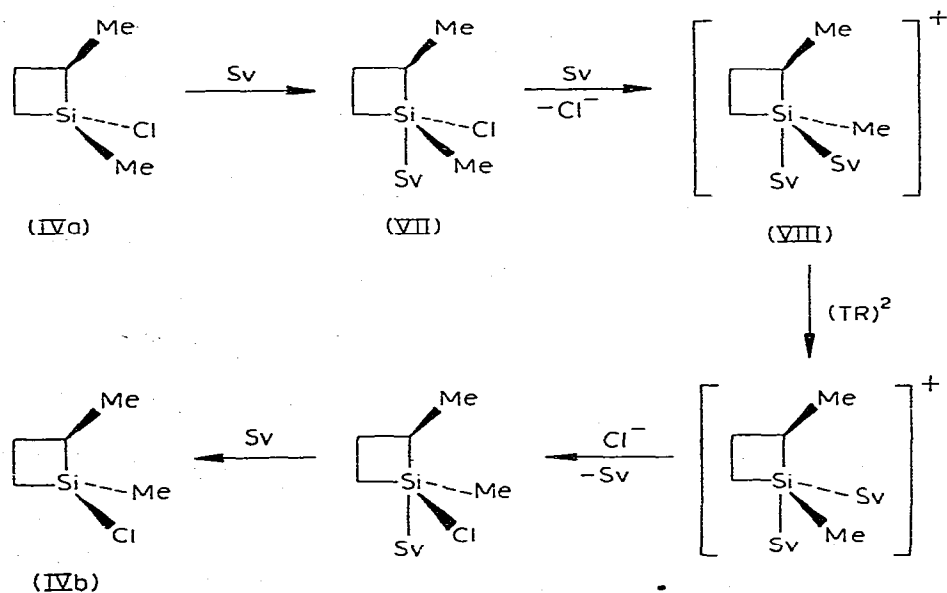


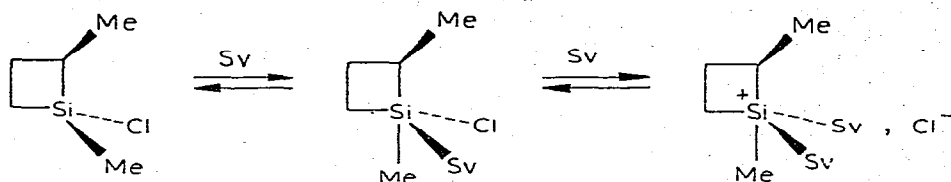
TABLE 1

FIRST ORDER RATE CONSTANTS FOR ISOMERIZATION OF *E*-1-CHLORO-1,2-DIMETHYLSILACYCLOBUTANE IN CCl_4 AT $45^\circ \pm 1^\circ\text{C}$

10^5 [HMPT] (M)	$10^5 k$ (sec ⁻¹)
200	360 ± 30
100	160 ± 10
50	80 ± 3
25	31 ± 2
10	11 ± 1
5.0	4.3 ± 0.2
2.5	1.5 ± 0.1



SCHEME 2



SCHEME 3

with exclusive retention of configuration at Si in a silacyclobutane probably does not occur either, since IV is isomerized slowly by alkylammonium halides.

From the evidence presented here, it is probable that a two step coordination of two HMPT molecules to displace halide ions, such as by Path 1 (Scheme 1) does occur. However, the structures for the intermediates proposed by Corriu, I and II, are inconsistent with the reactivity of IV, since both require C—Si—C angles of 120° . Although they may well be the structures for intermediates in the reactions of large ring and acyclic halosilanes, the small angle in IV requires apical—equatorial placement of the ring [10, 11]. In view of this requirement and the postulate in phosphorus chemistry of apical entry and departure of nucleophiles [10, 11], a more reasonable possibility is apical entry of Sv to give VI (Scheme 2) followed by displacement of chloride ion to give VIII. A double turnstile rotation [11, 12] (TR)² followed by stepwise loss of the two solvent molecules would result in formation of the *Z* isomer IVb. Alternatively, a mechanism involving equatorial entry and departure of solvent and chloride can be envisioned, and this latter possibility does not require an intermediate pseudo-rotation (Scheme 3).

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