Thermal Rearrangement of (Chloromethyl)silanes

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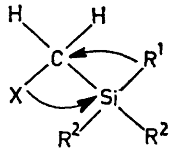
Summary Thermal rearrangements of hydridic (chloromethyl)silane and (chloromethyl)chlorosilane occur through an intermolecular process and not *via* the intramolecular reaction of the type invoked for analogous reactions in other (halogenoalkyl)silanes.

Rearrangement reactions in carbon-functional organosilanes have been observed in many systems, both in the presence[1] and absence[2] of added Lewis acids. During the course of the rearrangement in equation (**1**), an electronegative atom or group (X) migrates from carbon to silicon while concurrently a less electronegative substituent (R) is transferred from silicon to carbon. This reaction has been

$$XCH_2SiR^1R^2_2 \longrightarrow R^1CH_2SiXR^2_2 \qquad (1)$$

universally interpreted in terms of an intramolecular pathway [structure (A)], although in the Al_2Cl_6-catalysed rearrangement, the extent of charge separation in the transition state is a matter of debate.[3] ^{1}H N.m.r. evidence from the thermal rearrangement at 90 °C of $ClCH_2SiH_3$ and $ClCH_2SiH_2Cl$, however, indicates that in these hydridic compounds the reaction occurs through a bimolecular process.

Carefully purified samples of $ClCH_2SiH_3$ and $ClCH_2SiH_2Cl$ were each heated to 90 °C in sealed n.m.r. tubes which had been previously conditioned with the silanes. The contents of the tubes were monitored periodically by ^{1}H n.m.r. spectroscopy at 60 or 220 MHz.



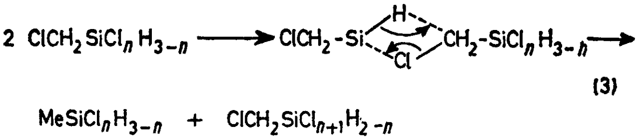
(A)

In the rearrangement of $ClCH_2SiH_3$, the first changes in the n.m.r. spectrum appeared after 40 h. Two quartets [$MeSiH_3$, δ (Me) 0·14, δ (SiH_3) 3·52, ^1J (H–H) 4·6 Hz] and two triplets [$ClCH_2SiH_2Cl$, δ (Me) 3·06, δ (SiH_3) 4·74 ^1J (H–H) 3·3 Hz] increased slowly in intensity with time. These resonances were assigned to $MeSiH_3$ and $ClCH_2SiH_2Cl$, respectively, indicating that the first step of the rearrangement is not intramolecular, but rather involves the reaction of two molecules of the substrate [equation (2)]. During

$$2\ ClCH_2SiH_3 \xrightarrow{90^\circ} MeSiH_3 + ClCH_2SiH_2Cl \qquad (2)$$

the 8 month reaction period absorptions due to each of the (chloromethyl)chlorosilanes ($ClCH_2SiH_2Cl$, $ClCH_2SiHCl_2$ and

$ClCH_2SiCl_3$) grew in intensity and then diminished in relative size as peaks ascribed to the methylchlorosilanes, $MeSiH_nCl_{3-n}$, grew steadily larger until the latter species accounted for 98% of the integrated intensity of the entire spectrum. After 8 months the methylchlorosilanes were present in the molar ratio: $MeSiH_3$, 0·76; $MeSiH_2Cl$, 1·00; $MeSiHCl_2$, 0·56; and $MeSiCl_3$, 0·10. At the end of the experiment, the n.m.r. tubes were opened and the products were separated and identified. The identities were also confirmed by i.r. spectroscopy. Noncondensible material (−196 °C) or HCl were not detected.



(3)

In the rearrangement of $ClCH_2SiH_2Cl$, the first changes in the spectra, observed after 100 h, indicated that the initial products formed in the reaction were equal amounts of $MeSiH_2Cl$ [δ (SiH_2) 4·70, δ (Me) 0·50; ^1J (H–H) 3·5 Hz] and $ClCH_2SiHCl_2$ [δ (SiH) 5·60, δ (CH_2) 3·17; ^1J (H–H) 2·5 Hz], rather than $MeSiHCl_2$ which would be expected on the basis of equation (**1**). At the end of the experiment the signals due to the intermediates $ClCH_2SiHCl_2$ and $ClCH_2SiCl_3$ had disappeared from the spectra, and the final products consisted of $MeSiH_2Cl$, $MeSiHCl_2$, and $MeSiCl_3$ in the molar ratio 0·53 : 1·00 : 0·46. $MeSiH_3$ or noncondensible material were not detected.

Thus, the identities and relative amounts of the final products in the reaction of $ClCH_2SiH_3$ can be accounted for by the type of reaction sequence previously suggested:[1,2] an intramolecular rearrangement (similar to the Wagner–Meerwein reaction), followed by redistribution[4] reactions (ligand scrambling among silicon centres). Clearly, however, the first products to be observed experimentally are not consistent with an intramolecular reaction. A more reasonable mechanism for these hydridic compounds is shown in equation (3). The absence of $MeSiH_3$ from the reaction products of $ClCH_2SiH_2Cl$ indicates that the redistribution[4] reaction has a higher activation energy than the exchange of ligands between carbon and silicon. Therefore, redistribution occurs at a much slower rate under these conditions.

We thank Dr. E. D. Becker of the National Institutes of Health for assistance with the 220 MHz spectra, and the Center of Materials Research of the University of Maryland for support.

(*Received, 2nd October* 1975; *Com.* 1125.)

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