Cleavage of 1-Halogenomethyl-1-phenyldisilanes by Sodium Ethoxide in Ethanol

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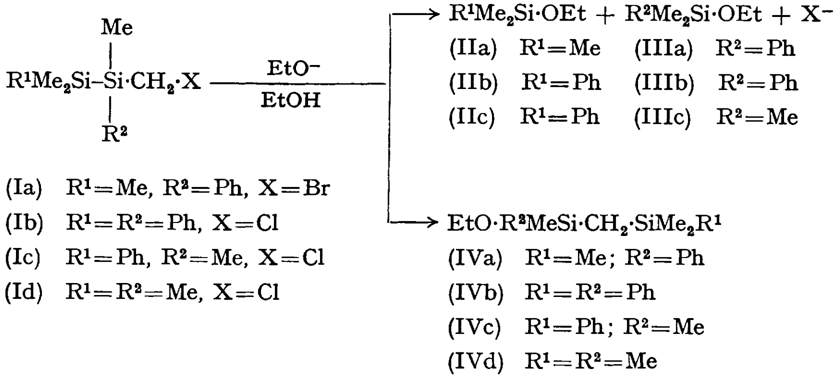
THE recent publication by Gusel'nikov and Flowers[1] concerning the possible formation of methylenedimethylsilane, $Me_2Si{=}CH_2$, as an intermediate during the thermal decomposition of 1,1-dimethyl-1-silacyclobutane to ethylene and 1,1,3,3-tetramethyl-1,3-disilacyclobutane prompts us to report the action of sodium ethoxide in ethanol on some disilanes, substituted by halogenomethyl and phenyl groups.

1-Bromomethyltetramethyl-1-phenyldisilane Ia) reacted vigorously with sodium ethoxide in ethanol, at room temperature, with cleavage of the silicon–silicon bond up to 83%, to give trimethylethoxysilane (IIa) and ethoxydimethylphenylsilane (IIIa). The remaining 17% of the reaction by an intramolecular rearrangement yielded (ethoxymethylphenylsilyl)(trimethylsilyl)methane (IVa). A similar ratio of cleavage to re-arrangement was obtained from 1-chloromethyltrimethyl-1,2-diphenyldisilane (Ib), under the same conditions, while, the analogous reaction with 1-chloromethyltetramethyl-2-phenyldisilane (Ic) led to only about 22% cleavage, with 78% intramolecular rearrangement. With chloromethylpentamethyldisilane (Id), an essentially exclusive intramolecular rearrangement has been reported.[2] In no case was evolution of hydrogen observed during the reaction; and no evidence for migration of the phenyl group from silicon to carbon was obtained.

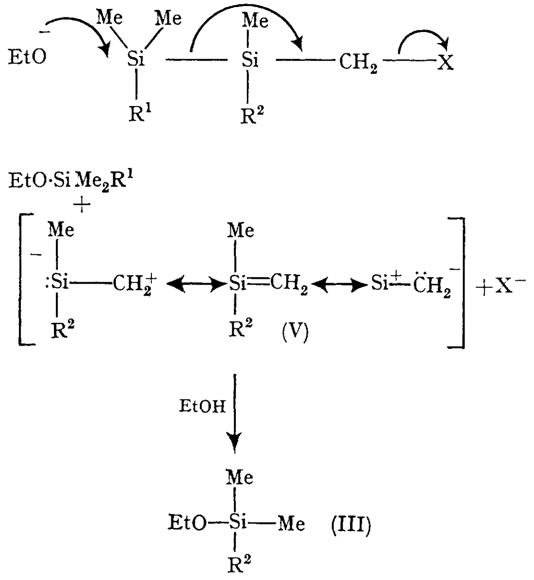


(Ia) R^1=Me, R^2=Ph, X=Br
(Ib) R^1=R^2=Ph, X=Cl
(Ic) R^1=Ph, R^2=Me, X=Cl
(Id) R^1=R^2=Me, X=Cl

(IIa) R^1=Me (IIIa) R^2=Ph
(IIb) R^1=Ph (IIIb) R^2=Ph
(IIc) R^1=Ph (IIIc) R^2=Me

(IVa) R^1=Me; R^2=Ph
(IVb) R^1=R^2=Ph
(IVc) R^1=Ph; R^2=Me
(IVd) R^1=R^2=Me

The formation of the ethoxysilane (III) from the cleavage of (I) can best be explained as a β-elimination involving two silicon atoms, to give an intermediate, (V), as the first step. Solvent ethanol then adds to this unstable species. The experimental results clearly indicate that the presence of a phenyl group on the silicon atom bearing the halogenomethyl group greatly favours the silicon–silicon cleavage over the intramolecular rearrangement, probably by stabilization of the intermediate.



An alternative pathway involves initial formation of hydride $HSiR^2Me(CH_2X)$ as a cleavage fragment, which subsequently undergoes nucleophilic intramolecular rearrangement involving the migration of hydrogen from silicon to carbon. This can be ruled out, since evolution of hydrogen would result from the simultaneous ethanolysis of the silicon–hydrogen bond. Indeed, the action of potassium hydroxide in 95% ethanol on chloromethyldimethylsilane, $Me_2SiH·CH_2Cl$, gave 31% of the silicon–hydrogen solvolysis product, $Me_2Si(OH)CH_2Cl$, with evolution of hydrogen, as well as 69% of the re-arrangement product, Me_3SiOH.[3] Further, chloromethylmethylphenylsilane, $PhMeSiH·CH_2Cl$, underwent 24% solvolysis, with hydrogen gas evolution, in addition to 76% intramolecular rearrangement, involving migration of hydrogen from silicon to carbon, on treatment with 2·2M-sodium ethoxide in ethanol at room temperature.

(*Received, March 18th, 1968; Com.* 335.)

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[3] L. H. Sommer, W. P. Barie, jun., and D. R. Weyenberg, *J. Amer. Chem. Soc.*, **1959**, **81**, 251.