Unimolecular Alcoholysis of Organosilicon Halides of the Type $(Me_3Si)_2C(SiMe_2OMe)(SiR'_2X)$. Anchimeric Assistance by and Migration of the OMe Group

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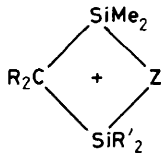
The compound $R_2C(SiMe_2OMe)(SiMe_2Cl)$ (R = $SiMe_3$ throughout) reacts more rapidly with CF_3CH_2OH than with MeOH, and $R_2C(SiMe_2OMe)(SiPh_2Br)$ reacts with EtOH to give exclusively the rearranged product $R_2C(SiMe_2OEt)(SiPh_2OMe)$, indicating that the rate-determining step of the solvolyses involves formation of a methoxy-bridged cation; migration of the OMe group also occurs in the reaction of the bromide with $AgBF_4$.

Organosilicon iodides of the type $R_3CSiR'_2I$ ($R = SiMe_3$ throughout), in which steric hindrance greatly inhibits direct nucleophilic attack at the functional silicon centre, react with silver salts AgY to give wholly ($R' = Ph$) or in part ($R' = Et$) rearranged products of the type $R_2C(SiR'_2Me)(SiMe_2Y)$, and it is thought that the reactions proceed *via* the bridged cations (**1**, Z = Me). Analogous rearrangement occurs in the trifluoroacetolysis of R_3CSiEt_2I, which thus appears to involve rate-determining ionization to a bridged cation of type (**1**, Z = Me; R′ = Et).[1] In these reactions the migrating Me group is assumed to provide anchimeric assistance to the leaving of I^-.

The methanolysis of R_3CSiMe_2X compounds with X = I, $OClO_3$, or OSO_2CF_3, is known not to be significantly accelerated by the presence of NaOMe,[2,3] and so at first it seemed likely that this reaction also involved anchimerically-assisted formation of the bridge cation (**1**; R′ = Me), but (a) solvolysis was much slower in the more electrophilic solvent CF_3CH_2OH, in which ionization would be expected to occur more readily, and (b) the hydrolysis and methanolysis of R_3CSiEt_2I were found to proceed without rearrangement.[4] It thus appears that the reaction does not proceed through a cation, and that the solvent is nucleophilically involved in the rate-determining step,[4] possibly in nucleophilic solvation in an S_N2 (intermediate) type of process.[5]

In the hope of observing rate-determining unimolecular cleavage of a silicon–halogen bond in alcoholysis without nucleophilic participation by the solvent we turned to compounds of the type $R_2C(SiMe_2OMe)(SiR_2X)$, in which the γ-OMe group could be expected to lead to much more stable bridged ions of the type (**1**, Z = OMe). (Compare the



(1) R = SiMe$_3$

calculations by Kos and Schleyer quoted in ref. 6.) The methoxychloride $R_2C(SiMe_2OMe)(SiMe_2Cl)$ was previously shown to undergo methanolysis $> 10^6$ times as rapidly as R_3CSiMe_2Cl,[6] and we have now found that (a) its rate of reaction with 9:1 v/v MeOH–dioxane is not very sensitive to the presence of NaOMe (the half-lives, measured by n.m.r. spectroscopy, at 35 °C with 0.00, 0.08, 0.16, 0.32, and 0.64 M NaOMe were 7.5, 5.1, 4.4, 6.1, and 6.4 min, respectively), and (b) its reaction with 8:1 v/v CF_3CH_2OH–dioxane [in which the alcohol:dioxane molar ratio is similar to that in the mixture in (a)], to give $R_2C(SiMe_2OMe)(SiMe_2OCH_2CF_3)$, is markedly faster, being complete before the first measurement can be made, *i.e.* in < 45 s; there is a subsequent slower reaction, to give $R_2C(SiMe_2OCH_2CF_3)_2$, which does not occur in the presence of Et_3N.

We have furthermore found that the reaction of $R_2C(SiMe_2OMe)(SiPh_2Br)$ with EtOH for 5 min at room temperature gives a single product [m.p. 168 °C; δ_H (CCl_4) 0.10 (s, $SiMe_2$), 0.18 (s, $SiMe_3$), 1.32 (t, CH_2Me), 3.55 (s, OMe), 3.65 (q, CH_2), and 7.2—8.0 (m, Ph)], which has been shown by *X*-ray diffraction[7] to be the rearranged species $R_2C(SiMe_2OEt)(SiPh_2OMe)$. (The same product is formed in the reaction with $AgClO_4$ in EtOH.) It can thus be assumed that the reactions proceed *via* cations of type (**1**, Z = OMe; R′ = Me, or Ph), which are rapidly attacked by the solvent nucleophile at the less hindered end of the bridge. It seems that there can be rate-determining ionization in these crowded systems of the type $R_2C(SiMe_2Z)(SiR'_2X)$ if there is either a weak bridging group (Z) such as Me in association with a strongly electrophilic solvent such as CF_3CO_2H, or a powerful bridging group such as OMe in association with a more weakly electrophilic solvent such as MeOH, and presumably some intermediate combinations would also be effective.

Predominant, but not complete, rearrangement occurred when $R_2C(SiMe_2OMe)(SiPh_2Br)$ was treated with $AgBF_4$ in Et_2O, the product being a 4:1 mixture of $R_2C(SiMe_2F)(SiPh_2OMe)$ [for $SiMe_2F$, δ_H 0.22 (d), δ_F −138.1 p.p.m.] and $R_2C(SiMe_2OMe)(SiPh_2F)$ [for $SiMe_2OMe$, δ_H 0.11 (s); for $SiPh_2F$, δ_F −161.3 p.p.m.].

The observation that with sufficient anchimeric assistance alcoholysis of organosilicon halides can take place without nucleophilic involvement of the solvent in the rate-determining step extends the analogy between mechanisms of substitution at a saturated carbon atom and those at a sterically hindered silicon atom.[4] It will be of interest to see whether variations in the nature of the solvent affect such reactions of organosilicon halides in the way they do S_N1 reactions of organic halides.[8]

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