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Preliminary communication

The nature of the anchimeric assistance by the acetoxy group in solvolysis of $(Me_3Si)_2C(SiMe_2OCOMe)(SiMe_2Cl)$

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Abstract

Solvolysis of $(Me_3Si)_2C(SiMe_2OCOMe)(SiMe_2Cl)$ in 3/2 v/v MeOH/dioxane at 35 °C is ca. 11–14 times as fast as that of $(Me_3Si)_2C(SiMe_2OMe)(SiMe_2Cl)$, which suggests that the anchimeric assistance by the acetoxy group is provided through the carbonyl oxygen.

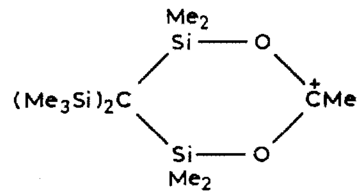
The remarkable anchimeric assistance that can be provided by the γ-substituent Z to departure of X in reactions of compounds of the type $(Me_3Si)_2C(SiMe_2Z)(SiMe_2X)$ (see refs. 1 and 2) was first observed for Z = OCOMe, in the reaction of $(Me_3Si)_3CSiMeICl$ with $Hg(OCOMe)_2$ in $MeCO_2H$ [3]. The rapid formation of $(Me_3Si)_2C(SiMe_2OCOMe)_2$ was interpreted in terms of initial generation of $(Me_3Si)_2C(SiMe_2OCOMe)(SiMe_2Cl)$ (**1**) (the migration of the Me group involved in the process being of a well-established type [4]), which then underwent rapid solvolysis

$(Me_3Si)_2C(SiMe_2OCOMe)(SiMe_2Cl)$

(**1**)

$(Me_3Si)_2C(SiMe_2OMe)(SiMe_2Cl)$

(**2**)



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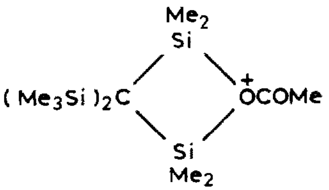

(II)

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to give the diacetate. This rapid solvolysis of **1** under conditions in which $(Me_3Si)_3CSiMe_2Cl$ is inert, was attributed to assistance by the acetoxy group to the leaving of the chloride ion, resulting in formation of the cationic species I, which is then rapidly attacked by the solvent at either of the bridged silicon atoms to give the diacetate [3].

Later it was observed that a γ-OMe group provides powerful assistance in methanolysis of $(Me_3Si)_2C(SiMe_2OMe)(SiMe_2Cl)$ (**2**) (which reacts with MeOH at 35 °C at least 10^6 times as rapidly as $(Me_3Si)_3CSiMe_2Cl$), and this suggested that the bridging by the acetoxy group might be through the ether oxygen, as in II, rather than the carbonyl oxygen [2]. If this were the case, then the assistance by the OCOMe would, because of the electron-withdrawal from the ether oxygen by the carbonyl group, be expected to be markedly smaller than that by the OMe group. To provide information about the nature of the assistance by the acetoxy group we have compared the rates of solvolysis of compounds **1** and **2**.

The reaction of **1** (made from $(Me_3Si)_2C(SiMe_2OH)_2$ [5] and CH_3COCl) with 3/2 v/v MeOH/dioxane at 35 °C gave, upon work-up after 30 min an 8/1 mixture of the expected $(Me_3Si)_2C(SiMe_2OCOMe)(SiMe_2OMe)$ and the dimethoxide $(Me_3Si)_2C(SiMe_2OMe)_2$, with the latter apparently formed by solvolysis of some of the $(Me_3Si)_2C(SiMe_2OCOMe)(SiMe_2OMe)$, the departure of the OCOMe group being electrophilically assisted by the HCl generated in the initial reaction (and nucleophilically by the OMe group). The rate of reaction was determined by monitoring the relative heights at various times of the ^1H NMR signals from the $SiMe_2$ protons of the substrate $SiMe_2OCOMe$ and product $SiMe_2OMe$ groups, and a good first order plot, with $t_{1/2}$ 124 s, was obtained. There was probably little interference from the secondary formation of the diacetate in the relevant part of the run, but after 30 min about 10% of the diacetate was present. (When the reaction was repeated in the presence of a one molar proportion of Et_3N, $(Me_3Si)_2C(SiMe_2OCOMe)(SiMe_2OMe)$ was the sole product after 5 h, and again a good first order plot was obtained, with a slightly lower value of $t_{1/2}$ (107 s).) A run carried out with **2** in the same medium (without Et_3N) gave a value of $t_{1/2}$ of 24 min, and so **1** is ca. 11 times as reactive as **2**. The higher reactivity of **1** than of **2** implies that the acetoxy group bridges via the carbonyl atom, as in I and as in 1,2-bridging in carbocations [7].

The superiority of the acetoxy over the methoxy group in providing anchimeric assistance in methanolysis was even more evident in the reactions of $(Me_3Si)_2C(SiMe_2OCOMe)(SiMe_2N_3)$ and $(Me_3Si)_2C(SiMe_2OMe)(SiMe_2N_3)$. The latter is known to undergo no detectable reaction with MeOH during 20 days at 50 °C (although reaction takes place in the presence of HBr) [6]. In contrast, the corresponding acetoxy compound reacts at 50 °C with MeOH containing one equivalent of Et_3N to give exclusively $(Me_3Si)_2C(SiMe_2OCOMe)(SiMe_2OMe)$, in a first order process with $t_{1/2}$ 55.5 h. Thus the acetoxy-containing azide is at least 90 times as reactive as the methoxy-containing analogue. The much larger difference between the reactivities of the two azides compared with those between the two chlorides can be understood in terms of the greater need for assistance by the very poor leaving group, azide.

The effectiveness of the anchimeric assistance by the acetoxy group suggests that the corresponding assistance by groups such as $OClO_3$ and OSO_3CF_3 (cf. ref. 2) may also involve bridging through 6- rather than 4-membered rings.

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