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Preliminary communication

The effect of α-chloro substitution on the reactivity of β-functional silanes

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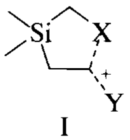
Abstract

Some compounds with the general formula $ClCH_2Me_2SiCH_2CH_2Y$ have been prepared and their solvolysis rates determined. The compounds with Y=OH or OCH_3 underwent the normal solvolysis reaction involving elimination of ethene. The compound with Y=Cl reacted but did not produce alkene.

Keywords: Silicon; Mechanism

It was suggested to us [1] that compounds of the type $XCH_2R_2SiCH_2CH_2Y$ might show interesting chemical and/or biological properties due to the through-silicon effect of X on Y and vice versa. In addition there was the possibility of neighbouring group participation in the solvolysis reaction. Interaction of the X group at the developing positive charge on the β-carbon would give the most favoured neighbouring group system, a five atom cyclic transition state (I), and this could have a profound effect on the rate of the solvolysis reaction.



I

A series of compounds $ClCH_2Me_2SiCH_2CH_2Y$ was prepared with Y=Cl, OH or OMe and their solvolysis rates determined.

The compounds $ClCH_2Me_2SiCH_2CH_2OH$ and $ClCH_2Me_2SiCH_2CH_2OMe$ underwent solvolysis (5 M H_2SO_4/50% aqueous methanol at 30°C) by the normal pathway with generation of ethene, but generally more slowly (first order rate constants 3.15×10^{-4} and 3.97×10^{-5} s^{-1}, respectively) than the analogous trimethylsilyl derivatives (1.84×10^{-3} and 7.23×10^{-4} s^{-1}, respectively).

The β-chloro-compound $ClCH_2Me_2SiCH_2CH_2Cl$ (II) did not appear to react under typical solvolysis conditions (80% aqueous ethanol, 30°C). There was no evidence of ethene production even after 14 days. The reaction was repeated in more polar media (60 and 70% aqueous ethanol and 70 and 90% aqueous trifluoroethanol), a higher temperature (50°C), and with the addition of a base, but there was no evidence of ethene production under any of these conditions.

Although the absence of gas production suggested that the $ClCH_2Me_2SiCH_2CH_2Cl$ (II) did not react under solvolytic conditions, examination of the products from scaled up (2 g, II) systems by ^1H NMR spectroscopy established that reaction had indeed occurred. After 24 h in 70% aqueous ethanol the mixture appeared to be made up of the starting material (II) and equal quantities of the siloxane, $ClCH_2Me_2SiOSiMe_2CH_2Cl$ and the β-hydroxy compound, $ClCH_2Me_2SiCH_2CH_2OH$ in an ca. 7:1:1 ratio. After 5 days the ratio was 1:1:1.

$$\begin{aligned} &ClCH_2Me_2SiCH_2CH_2Cl + H_2O \\ &\quad \longrightarrow ClCH_2Me_2SiCH_2CH_2OH \\ &\qquad + ClCH_2Me_2SiOSiMe_2CH_2Cl \end{aligned} \tag{1}$$

The formation of the siloxane established that cleavage of the silicon–carbon bond did occur. Since ethene was not formed the most obvious route to the siloxane seemed to be nucleophilic attack at the silicon. The expected products from that reaction would be the

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siloxane and ethyl chloride and the latter, being soluble in the reaction medium, would not be detected.

The ^{1}H NMR chemical shifts of the methyl and methylene groups of ethanol and ethyl chloride are relatively close. It was though that it would be easier to find ethyl chloride in the absence of ethanol and for that reason the scaled up (2 g, II) reaction was repeated using 70% trifluoroethanol rather than ethanol as the solvolytic medium. After 14 days the reaction vessel was connected to a trap containing acetone and immersed in liquid nitrogen. Dinitrogen was passed through the reaction mixture for several hours. It was hoped by this process to flush out the ethyl chloride. There was no evidence of ethyl chloride production on subsequent examination by NMR spectroscopy. The reaction mixture was worked up and analysed by NMR spectroscopy; the products were the siloxane and the hydroxyethylsilane in a 1 : 1 ratio.

Differences in the effect of substituents on the behaviour of β-hydroxy- and β-haloethylsilyl systems have been observed previously. Corriu et al. [2] reported that β-chloroethyltriphenylsilane was stable below 200°C in solvolytic media. Other workers found that the β-bromoethyltriphenylsilane showed similar stability [3] and could be recovered unchanged after 5 days reflux in THF/water (50/50). The β-bromopropyltriphenylsilane reacted solvolytically but not by the usual route; it did not lose propene but instead gave the substitution product β-hydroxypropyltriphenylsilane in almost quantitative yield [3]. The β-hydroxyethyltriphenyl systems behave like the β-hydroxy- and β-methoxyethylchloromethyldimethylsilanes in that they are generally less reactive than their trimethyl analogues but when they do react [4], they follow the normal pathway and eliminate alkene.

Further studies are required to elucidate the mechanism of solvolysis of $ClCH_2Me_2SiCH_2CH_2Cl$(II) and it would also be of interest to look at the effect of a range of α-electronegative substituents other than chlorine on the β-elimination process.

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