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THE MECHANISM OF SOLVOLYSIS OF (2-BROMOETHYL)TRIMETHYLSILANE. EVIDENCE FOR THE MIGRATION OF THE TRIMETHYLSILYL GROUP

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SUMMARY

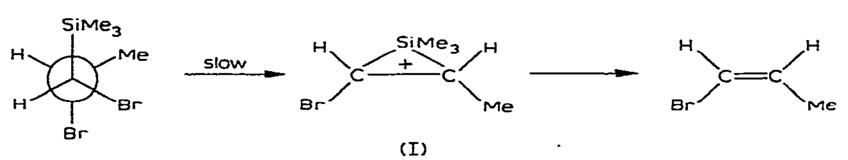
When solvolysis of the bromide $Me_3SiCH_2CD_2Br$ by aqueous methanol is allowed to proceed to about 50% completion, the recovered bromide contains $Me_3SiCD_2CH_2Br$ and $Me_3SiCH_2CD_2Br$, in 1/2 ratio. This migration of the Me_3Si group is consistent with a mechanism involving anchimerically assisted ionization of the C–Br bond to give a silacyclopropenium ion.

INTRODUCTION

Sommer and Baughman[1] some years ago observed that the very ready solvolysis of 2-(triorganosilyl)alkyl halides, represented by eqn. (1):

$$Me_3SiCH_2CH_2Cl + ROH \rightarrow Me_3SiOR + CH_2{=}CH_2 + HCl \qquad (1)$$

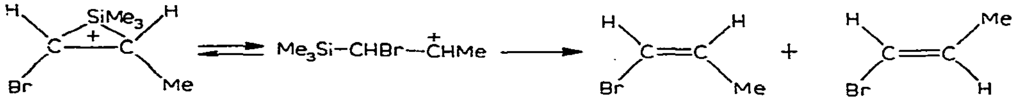
involved a large change separation in the transition state, and concluded that it proceeded by a "limiting siliconium ion" mechanism, a finding which was later criticized[2]. Baughman also suggested, however, that the rate-determining step might be the ionization of the carbon–chlorine bond, possibly with assistance from the β-silicon atom[3]. More recently Jarvie, Holt, and Thompson showed that the elimination involved in the solvolysis of (*erythro*-1,2-dibromopropyl)trimethylsilane in aqueous ethanol is a highly stereospecific *trans*-process, and suggested that the Me_3Si group gives anchimeric assistance to the ionization of the C–Br bond, a non-classical silicon-bridged ion, (I), being formed in the rate-determining step, as in eqn. 2[4]. However,



(I)

(2)

to explain the fact that the proportion of *cis*-elimination increased with the ionizing power of the medium, reaching 15% in moist formic acid, it was necessary to postulate that the silicon-bridged ion is in equilibrium with a classical carbonium ion, (II), the proportion of which increases with increasing ionizing power of the medium. Jarvie



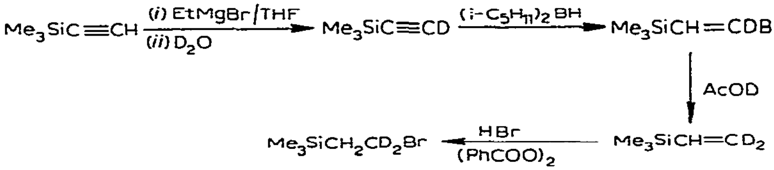
(3)

(I) (II)

and her colleagues pointed out that reaction by eqn. (2) might be accompanied by rearrangement involving migration of the Me_3Si group, and while they did not observe this, they found that the alcohol $Me_3SiCH_2CD_2OH$ gave mixtures of $Me_3SiCH_2CD_2X$ and $Me_3SiCD_2CH_2X$ (X = Cl or Br) on treatment with thionyl chloride or phosphorus tribromide, a result which would be consistent with rearrangement within an intermediate carbonium ion such as (III)[4]. We have now found that solvolysis of the bromide $Me_3SiCH_2CD_2Br$ in aqueous methanol is, indeed, accompanied by rearrangement to the compound $Me_3SiCD_2CH_2Br$.

RESULTS AND DISCUSSION

The compound $Me_3SiCH_2CD_2Br$ was synthesized by the following sequence:

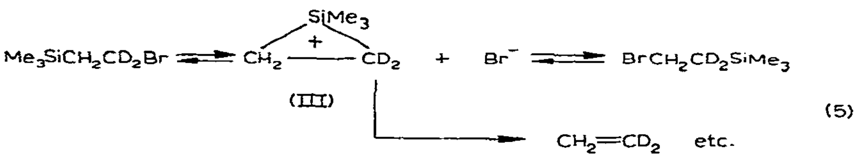


(4)

No isotopic impurities could be detected in the product by NMR spectroscopy, which means that it was >98% isotopically pure. This not only justifies the synthetic sequence used but also reveals that migration of the trimethylsilyl group does not occur in the vapour or the neat liquid, even during reduced pressure distillation at 65°.

Exploratory experiments with undeuterated $Me_3SiCH_2CH_2Br$, involving monitoring of the reaction by measurement of the volume of the ethylene evolved[1], revealed that 300 seconds were required for the solvolysis to go to $50 \pm 5\%$ completion in a mixture of the bromide with an equal volume of 30% aqueous methanol at 20°. The solvolysis of the β-deuterated compound $Me_3SiCH_2CD_2Br$ was then permitted to proceed for the same time under exactly similar conditions, and the organic bromide was then recovered. The recovered material was shown by NMR analysis to contain $33 \pm 2\%$ of α-deuterated compound, $Me_3SiCD_2CH_2Br$. Since only 50% of this isomer would be produced at equilibrium, the rate of the rearrangement must be somewhat greater than that of the solvolysis under the conditions used. The absence from the product of any detectable material of formula $Me_3SiCHDCHDBr$ shows that migration of hydrogen does not contribute significantly to the observed rearrangement.

The occurrence of this rearrangement indicates that reversible ionization of the C–Br bond occurs, and rules out the possibility[2] that some driving force is provided by fragmentation to olefin and other products synchronously with separation of halide ion. It is consistent either with anchimerically assisted reversible ionisation of the halide $Me_3SiCH_2CD_2Br$ to a non-classical cyclopropenium-type ion, (III), as



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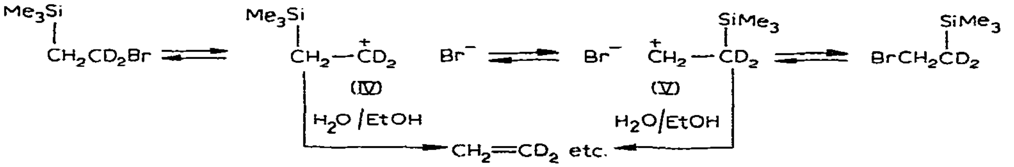
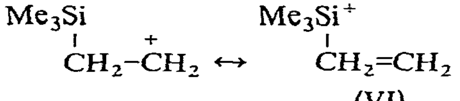


(6)

in eqn. (5), or with initial formation of a classical carbonium ion, (IV), which can then rearrange to its isomer, (V) (eqn. 6)*.

A demonstration that the rates of solvolysis of the halides $Me_3SiCH_2CH_2X$ are substantially greater than would be expected in the absence of assistance would be evidence in favour of anchimeric assistance. Without any participation, the Me_3SiCH_2 group can be expected to provide strong electronic stabilization of a carbonium ion centre to which is attached, the electron release mainly involving hyperconjugation from the Me_3Si–CH_2 bond (σ–π conjugation), associated with contributions from structures such as (VI)[5-7].



$$\overset{Me_3Si}{CH_2}{-}\overset{+}{C}H_2 \leftrightarrow \overset{Me_3Si^+}{CH_2}{=}CH_2$$

(VI)

In the absence of direct participation by the group Z, the stabilization of the ion ZCH_2^+ can be expected to follow roughly the σ^+ constant of p-Z**. The MeO group, for which $\sigma_p^+ = -0.778$, raises the rate of S_N1 solvolysis of the halide $MeOCH_2Cl$ by a factor of about 10^{14} over that of methyl chloride[9]; assuming a linear free-energy relationship, electron release by the Me_3SiCH_2 group, for which $\sigma_p^+ = -0.54$, should make the halide $Me_3SiCH_2CH_2Cl$ some $10^{9.5}$ times more reactive than methyl chloride. This represents a very large activating effect***. However, by the same reasoning, one Me_3SiCH_2 group should have a rather smaller stabilizing effect on the carbonium ion than two Me groups (σ_p^+ for Me $= -0.31$), so that the chloride Me_3Si-CH_2CH_2Cl should undergo solvolysis somewhat less readily than isopropyl chloride whereas it reacts somewhat faster than tert-butyl chloride, and thus some 10^5 times

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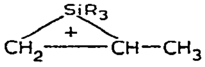
* For simplicity we neglect the possibility that formation of the ion (IV) could involve some anchimeric assistance from interaction between the silicon and the forming carbonium ion even if this interaction were not large enough to result in formation of symmetrical silacyclopropenium ion.

** The σ^+ constants are by definition associated with the effects of the Z groups on the stability of the related ions p-$ZC_6H_4\overset{+}{C}H_2$. Stabilization energies of XCH_2^+ ions in the gas phase correlate[8] roughly with σ^+.

*** This finding, which was made possible by our recent studies of the electronic effects of $(Me_3Si)_xCH_{(3-x)}$ groups[6,7], must now replace the earlier view[2,10] that there was no good ground for expecting ionisation of the C–Cl bond to be so much easier for $\equiv SiCH_2CH_2Cl$ compounds than for ordinary primary alkyl chlorides. Stabilization of the ions $Me_3MCH_2CH_2^+$ should increase in the order Si < Ge ≪ Sn.

as fast as isopropyl chloride. Taken along with the stereochemical results obtained by Jarvie *et al.* for the (*erythro*-1,2-dibromopropyl)trimethylsilane solvolysis, this analysis, while admittedly very rough, provides some justification for favouring process (5), involving substantial anchimeric assistance and formation of a non-classical ion, over process (6), involving equilibration of classical carbonium ions. That Jarvie and her colleagues found it necessary to postulate that the ion (I) is in equilibrium with significant amounts of the ion (II)[4] somewhat weakens the case for *substantial* (though not for *some*) anchimeric assistance since there is unlikely to be large assistance unless the nonclassical ion is substantially stabilized relative to the classical ion. The observed result would be consistent with anchimeric assistance, however, if the silacyclopropenium ion (I) had a fairly long life, while the classical ion (II) underwent rapid fragmentation to solvolysis products; in these circumstances a significant proportion of the olefin formation could proceed through (II) even though at equilibrium very little of this ion would co-exist with (I). An alternative possibility is that the *cis*-elimination observed by Jarvie and her colleagues resulted from formation of the compound $Me_3SiCHMeCHBr_2$, in a rearrangement such as we observed, followed by solvolysis of this new halide*. It is noteworthy that in general the increase in the ionizing power of the solvents used by Jarvie *et al.* is accompanied by decrease in the nucleophilicity towards silicon, and certainly the nucleophilicity is lowest in the most ionizing media used, namely formic acid/acetic acid and moist formic acid. Since the loss of the Me_3Si group from the intermediate ions probably involves nucleophilic attack at silicon, decrease in the nucleophilicity would lead to a greater amount of reversion of the carbonium ion(s) to covalent bromide, and thus to more rearrangement. It should be noted, however, that Jarvie *et al.* sought, but failed to find, evidence for a rearrangement of this type during bromination of $Me_3SiCH{=}CHMe$[4].

The very large stabilizing effect of a β-R_3Si group on a carbonium ion centre, with or without anchimeric assistance, has implications for other reactions (see also ref. 6). For example, the very rapid acid-catalysed cleavage of the allyl–Si bonds in $R_3SiCH_2CH{=}CH_2$ compounds can be associated with stabilization of the ion $R_3SiCH_2\overset{+}{C}HCH_3$, possibly involving anchimeric assistance associated with formation of the non-classical ion (VII).



(VII)

EXPERIMENTAL

NMR spectra

These were recorded with the neat liquids, containing benzene as internal standard, on a Varian A60 Spectrometer.

(2-Bromoethyl)trimethylsilane

Hydrogen bromide gas, generated from bromine and tetralin, was bubbled

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* With classical ions the rearrangement would be from $Me_3SiCHBr\overset{+}{C}HMe$ to $Me_3SiCHMe\overset{+}{C}HBr$, and it is noteworthy that the ion $BrCH_2^+$ is more stable[8] than $MeCH_2^+$.

for 12 h at room temperature through trimethylvinylsilane (10 g, 0.10 mole) containing benzoyl peroxide (0.1 g) which had been recrystallized from carbon tetrachloride and dried under vacuum. Careful distillation gave (2-bromoethyltrimethyl)silane (9.0 g, 40 %), b.p. 65°/40 mm (lit.[11] b.p. 64–65°/39 mm). A ^{1}H NMR spectrum showed triplets centred at τ 8.7 ($SiCH_2$) and τ 6.7 ($BrCH_2$), and a singlet at τ 10.0 (Me_3Si).

Ethynyltrimethylsilane

Chlorotrimethylsilane (76 g, 0.70 mole) was added during 1 h at room temperature to a solution of ethynylmagnesium bromide (0.80 mole) in tetrahydrofuran (400 ml). The mixture was subsequently stirred for 12 h, then treated with water, and organic products were extracted with light petroleum (b.p. 100–120°). The combined organic extracts were then fractionally distilled through a 1 m column packed with glass helices, and a mixture of water and a crude product of b.p. 45–60° was collected in the ice-cooled receiver. The organic layer was separated, dried with a large quantity of anhydrous magnesium sulphate, and then carefully redistilled to give ethynyltrimethylsilane (43 g, 51 %), b.p. 52° (lit.[12] b.p. 52°). The NMR spectrum showed singlets at τ 7.72 ($C{\equiv}CH$) and τ 9.85 (Me_3Si).

(Deuteroethynyl)trimethylsilane

Ethynyltrimethylsilane (50 g, 0.50 mole) was added to ethylmagnesium bromide (0.65 mole) in tetrahydrofuran (500 ml). The mixture was boiled under reflux for 30 min then treated with deuterium oxide (200 ml) followed by solid ammonium chloride. The organic layer was separated and combined with the light petroleum (b.p. 100–120°) extracts of the aqueous layer. Work-up as for ethynyltrimethylsilane gave (deuteroethynyl)trimethylsilane (42 g, 83 %), b.p. 53°. The NMR spectrum showed a singlet at τ 9.85 (Me_3Si) and no resonance at τ 7.72 ($C{\equiv}CH$).

(2,2-Dideuterovinyl)trimethylsilane

(Deuteroethynyl)trimethylsilane (20 g, 0.20 mole) was added rapidly to a vigorously stirred solution of diisoamylborane prepared from boron trifluoride etherate (26 g, 0.18 mole), 2-methyl-2-butene (25 g, 0.36 mole) and sodium borofluoride (6.0 g, 0.15 mole) in diglyme (50 ml). The mixture was maintained at 0° for 6 h, then treated with O-deuteroacetic acid (100 ml), and subsequently stirred for a further 12 h at room temperature. Partitioning between light petroleum and a saturated aqueous chloride was followed by separation, drying (Na_2SO_4), and fractionation of the organic layer to give (2,2-dideuterovinyl)trimethylsilane (12 g, 60 %), b.p. 53°. The NMR spectrum showed singlets at τ 9.95 (Me_3Si) and τ 3.93 ($CH{=}CD_2$), the latter being slightly broadened as expected for a deutero compound.

(2-Bromo-2,2-dideuteroethyl)trimethylsilane

This compound, b.p. 65°/40 mm, was prepared from hydrogen bromide and (2,2-dideuterovinyl)trimethylsilane in the presence of benzoyl peroxide, as described for the undeuterated compound. The NMR spectrum of the product showed singlet resonances at τ 10.0 (Me_3Si) and τ 8.7 (CH_2CD_2Br, slightly broadened). There was no resonance at τ 6.7.

Partial solvolysis of (2-bromo-2,2-dideuteroethyl)trimethylsilane

(2-Bromo-2,2-dideuteroethyl)trimethylsilane (5 ml) was added rapidly to an equal volume of a mixture of methanol (70 vol.-%) and water. The resulting homogeneous mixture was shaken for 300 sec at 20 ± 1°, and then quickly extracted with 10 ml of light petroleum of b.p. < 40°. (Measurement of the evolution of ethylene[1] from the undeuterated compound had revealed that the solvolysis was 50 ± 5% complete in this time under the conditions used.) The organic extract was rapidly dried (Na_2SO_4), and distilled under reduced pressure to give (2-bromoethyl)trimethylsilane, the NMR spectrum of which showed resonances at τ 8.7 (CH_2CD_2Br) and at τ 6.7 (CD_2CH_2Br) in the ratio 2.0/1.0.

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