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# THE $S_N1$ METHANOLYSIS OF A TERTIARY ORGANOSILICON IODIDE, $(Me_3Si)_3CSiMe_2I$

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## Summary

The highly sterically-hindered organosilicon iodide $(Me_3Si)_3CSiMe_2I$ undergoes solvolysis in MeOH by an $S_N1$ process; the half-life is approximately 13 days at 50°C, and the reaction is little accelerated by the presence of NaOMe, which does, however, induce a competing fragmentation.

## Introduction

The tertiary organosilicon perchlorate $TsiSiMe_2OClO_3$ (Tsi = $(Me_3Si)_3C$) and the secondary iodides TsiSiRHI (R = Me or Ph) were recently shown to undergo solvolysis in MeOH by an $S_N1$ mechanism [1]. We have now found that the tertiary iodide $TsiSiMe_2I$ also undergoes $S_N1$ methanolysis, but at a much lower rate.

## Results and discussion

The rate of the reaction of $TsiSiMe_2I$ with MeOH can be determined by observing the change in the relative heights (or integrations) of the $^1H$ NMR signals from $(Me_3Si)_3C$ protons in the $TsiSiMe_2I$ (**A**) and the product $TsiSiMe_2OMe$ (**B**). Thus a solution of the iodide **A** in anhydrous MeOH was kept at 50°C, samples were withdrawn at appropriate intervals and evaporated, the residue was taken up in $CCl_4$ and its $^1H$ NMR spectrum recorded, to give the **A**/**B** ratio. The first order rate constant, $k_1^S$, for the solvolysis was derived from the **A**/**B** ratio, with the result shown in Table 1. The same procedure worked satisfactorily for runs in the presence of LiCl or 0.05 *M* NaOMe, but at higher base concentrations allowance had to be made for the competing fragmentation reaction which gives $(Me_3Si)_2CHSiMe_2OMe$ (**C**) by bimolecular attack of $MeO^-$ on a $Me_3Si$ group [2]. When a reaction in MeOH containing 0.40 *M* NaOMe

 

TABLE 1

APPROXIMATE FIRST-ORDER RATE CONSTANTS FOR THE REACTION OF $TsiSiMe_2I$ IN MeOH AT 50°C

| Added salt | $10^7\ k_1^T/s^{-1}$ [a] | $10^7\ k_1^S/s^{-1}$ [b] |
|---|---|---|
| None | 6.4 | 6.4 (± 0.4) |
| LiCl | 7.1 | 7.1 (± 0.4) |
| NaOMe, 0.05 *M* | 7.6 | 7.6 (± 0.4) |
| NaOMe, 0.10 *M* | 9.5 | 8.1 (± 0.5) |
| NaOMe, 0.20 *M* | 10.6 | 8.0 (± 0.6) |
| NaOMe, 0.40 *M* | 14.3 | 8.6 (± 0.8) |

[a] Apparent first-order rate constant for disappearance of $TsiSiMe_2I$. [b] First-order rate constant for appearance of $TsiSiMe_2OMe$ (with estimated uncertainties).

was stopped after 8 days at 50°C (i.e. after ca. 64% of **A** had reacted), the $^1H$ NMR spectrum of the product mixture showed that it contained **A**, **B**, and **C** in ca. 36/38/26 ratio. Allowance for the formation of **C**, on the assumption that the ratio of **B**/**C** was ca. 3/2 in 0.40 *M*, 3/1 in 0.02 *M*, and 6/1 in 0.10 *M* NaOMe. then gave the approximate first-order rate constants $k_1^T$, for the overall disappearance of $TsiSiMe_2I$, and $k_1^S$ for the appearance of the solvolysis product **B**. (The corresponding correction of the observed rate constant for 0.05 *M* NaOMe is too small to be significant.)

While the rate constants listed in Table 1 are subject to substantial uncertainty (the value of $k_1^S$ for reaction in MeOH alone is estimated to be accurate within ca. ±5%, while that in the presence of 0.4 *M* NaOMe could easily be in error by ±10%), some clear features are apparent:

(a) The solvolysis of $TsiSiMe_2I$ is much slower than that of the perchlorate $TsiSiMe_2OClO_3$ or the iodides TsiSiRHI (R = Me or Ph); the half-life is ca. 13.2 days at 50°C.

(b) The presence of 0.05 *M* NaOMe increases the rate of the solvolysis by ca. 20%. Subsequent increases in the NaOMe concentration cause smaller increases in the rate of solvolysis.

(c) The presence of 0.40 *M* LiCl increases the rate by ca. 10%, consistent with a salt effect.

As in the methanolysis of $TsiSiOClO_3$ and TsiSiRHI [1], the effects of NaOMe are too small to be attributed to a bimolecular reaction involving attack of $MeO^-$ on the $TsiSiMe_2I$, and this is strong evidence that the methanolysis is of the $S_N1$ type, involving rate-determining ionization of the iodide. (The possible nature of the special rate-increasing salt effect of a small amount of NaOMe has been considered previously [1].)

The diphenyl iodide $TsiSiPh_2I$ was found to react much more slowly, if at all, with MeOH under similar conditions; after 5 days under reflux there was no detectable reaction.

The results obtained with 0.4 *M* NaOMe in MeOH lead to a rough value of $6 \times 10^{-7}\ s^{-1}$ at 50°C for the apparent pseudo first-order rate constant for the fragmentation of $TsiSiMe_2I$ to give $(Me_3Si)_2CHSiMe_2OMe$ (**C**), corresponding to a specific second order rate constant of ca. $1.5 \times 10^{-6}\ l\ mol^{-1}\ s^{-1}$. If the rate of the fragmentation were proportional to the concentration of NaOMe, then with

2 *M* NaOMe in MeOH at 50°C the fragmentation would account for about 80% of the reaction. However, studies of other Si—C bond cleavages by NaOMe in MeOH indicate that the specific second-order rate constant in 2 *M* base would be at least twice as large as that in 0.4 *M* NaOMe [3], and so the fragmentation would constitute some 90% of the reaction, and this is consistent with the earlier observation that $(Me_3Si)_2CHSiMe_2OMe$ (**C**) is the greatly predominant product in 2 *M* NaOMe in MeOH under reflux [2].

## Experimental

### *Materials*

The iodides $TsiSiMe_2I$ and $TsiSiSiPh_2I$ [1] and samples of the products $TsiSiMe_2OMe$ [1] and $(Me_3Si)_2CHSiMe_2OMe$ [2] used for reference purposes were prepared as previously described.

Methanol was dried by refluxing with $Mg(OMe)_2$ followed by distillation from the latter.

*NMR spectra.* The $^1H$ NMR spectra were recorded at 90 MHz with solutions in $CCl_4$ containing $CH_2Cl_2$ as lock and reference.

### *Reaction products*

(a) A solution of $TsiSiMe_2I$ (0.1 g) in MeOH (15 $cm^3$) was kept at 50°C for 22 days. (During the first hour, the mixture was shaken from time to time to ensure complete dissolution of the iodide.) The solution was then evaporated off under reduced pressure and the residue was taken up in $CCl_4$. The $^1H$ NMR spectrum of the solution showed it to contain only $TsiSiMe_2OMe$ and $TsiSiMe_2I$, in ca. 75/25 ratio.

(b) A similar result was obtained when the same procedure was carried out with MeOH containing 0.40 *M* LiCl.

(c) A similar procedure was used starting with a solution of $TsiSiMe_2I$ (ca. 0.2 g) in MeOH (20 $cm^3$) containing 0.40 *M* MeONa. When the reaction was stopped after 8 days the NMR spectrum of the product mixture in $CCl_4$ showed that it contained $TsiSiMe_2I$ ($\delta$ 0.36 and 1.06 ppm), $TsiSiMe_2OMe$ ($\delta$ 0.21, 0.28 ppm) and $(Me_3Si)_2CHSiMe_2OMe$ ($\delta$ −0.54, 0.10 and 0.17 ppm) in ca. 36/38/26 ratio. The presence of two types of OMe group showed up as an unresolved doublet centred at $\delta$ 3.36 ppm.

(d) A solution of $TsiSiMe_2OMe$ (0.1 g) in MeOH (15 $cm^3$) containing 0.4 *M* NaOMe was kept at 50°C for 8 days. The solvent was removed, and the residue extracted with $CCl_4$. The $^1H$ NMR spectrum of the extract showed it to contain only unchanged $TsiSiMe_2OMe$.

(e) A solution of $TsiSiPh_2I$ (0.2 g) in MeOH (20 $cm^3$) was refluxed for 5 days. The usual work-up gave only unchanged $TsiSiPh_2I$.

### *Rate measurements*

(a) In a typical run in MeOH alone, a solution of $TsiSiMe_2I$ (0.1 g) in MeOH (20 $cm^3$) in a stoppered vessel was placed in a thermostatted bath kept at 50 ± 0.02°C. At appropriate intervals samples (ca. 2 $cm^3$) were removed and quickly evaporated to dryness under reduced pressure. The residue was taken up in $CCl_4$ (ca. 2 $cm^3$), the $^1H$ NMR spectrum of the solution was recorded and the relative heights of the $(Me_3Si)_3$ peaks at δ 0.36 ppm (**A**; $TsiSiMe_2I$) and δ 0.21 ppm (**B**; $TsiSiMe_2OMe$) were noted. The **A**/**B** ratios at various times were as follows:

| Time (h) | 72 | 168 | 264 | 366 | 504 | 648 |
|---|---|---|---|---|---|---|
| A/B | 87/13 | 71/29 | 63/37 | 47/53 | 32/68 | 23/77 |

These data gave a satisfactory first-order plot, and a first-order rate constant for the conversion of **A** into **B** of $6.4 \times 10^{-7}$ s$^{-1}$.

Use of integrated signals from the Tsi peaks gave identical results within the experimental uncertainty.

(b) The same experimental procedure was used for solutions of $TsiSiMe_2I$ (0.1 g) in MeOH (25 cm$^3$) containing NaOMe. In a typical run in 0.40 *M* NaOMe. ratios of $TsiSiMe_2I$ (**A**) to $TsiSiMe_2OMe$ (**B**) at various intervals were as shown below. It was assumed that $(Me_3Si)_2CHSiMe_2OMe$ (**C**) was present throughout in a **C**/**B** ratio of 2/3, and the percentage of **A** remaining was calculated.

| Time (h) | 0 | 72 | 168 | 264 | 366 | 480 |
|---|---|---|---|---|---|---|
| % A/(A + B) | 100 | 79 | 49 | 265 | 24 | 14 |
| % A/(A + B + C) | 100 | 69 | 37 | 18 | 16 | 9 |

The data lead to a first-order rate constant ($k_1^T$) of $14.3 \times 10^{-7}$ s$^{-1}$ for overall conversion of **A** into **B** and **C**, and corresponding constants of $8.6 \times 10^{-7}$ and $5.7 \times 10^{-7}$ s$^{-1}$ for formation of **B** and **C**, respectively, assuming the **B**/**C** ratio of 3/2.

Similar procedures were used for reactions with 0.20, and 0.10 *M* NaOMe in MeOH, the ratios of **B**/**C** being assumed to be 3/1 and 6/1, respectively. The results are shown in Table 1.

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