

# 1,3-Si-to-Si migration of a methyl group. Ratio of rearranged and unrearranged products in the reactions of the iodide $(\text{Me}_3\text{Si})_3\text{CSi}(\text{CD}_3)_2\text{I}$ with ICl

Abdulrahman I. Almansour <sup>a,\*</sup>, Haya A. Abubishait <sup>a</sup>, Colin Eaborn <sup>b</sup>

<sup>a</sup> Department of Chemistry, College of Science, King Saud University, PO Box 2455, Riyadh, 11451, Saudi Arabia

<sup>b</sup> School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, UK

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## Abstract

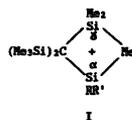
In the reactions of  $(\text{Me}_3\text{Si})_3\text{CSi}(\text{CD}_3)_2\text{I}$  with ICl in inert solvents the unrearranged product  $(\text{Me}_3\text{Si})_2\text{CSi}(\text{CD}_3)_2\text{Cl}$  predominates over the rearranged isomer  $(\text{Me}_3\text{Si})_2\text{C}[\text{Si}(\text{CD}_3)_2\text{Me}](\text{SiMe}_2\text{Cl})$ . The proportion of rearranged isomer falls from ca. 42% in  $\text{CH}_2\text{Cl}_2$  to ca. 25% in benzene, 20% in  $\text{CCl}_4$ , and 15% in  $\text{CHCl}_3$ . In MeOH the reaction gives 84% of the methoxides  $(\text{Me}_3\text{Si})_2\text{CSi}(\text{CD}_3)_2\text{OMe}$  and  $(\text{Me}_3\text{Si})_2\text{C}[\text{Si}(\text{CD}_3)_2\text{Me}](\text{SiMe}_2\text{OMe})$  in 62/22 ratio, along with 16% of the unrearranged chloride  $(\text{Me}_3\text{Si})_2\text{CSi}(\text{CD}_3)_2\text{Cl}$ . The results indicate that the intermediate cations generated by abstraction of  $\text{I}^-$  by ICl are mainly not fully free before undergoing nucleophilic attack.

**Keywords:** Silicon; Mechanism; Iodine monochloride; Rearrangement

## 1. Introduction

Reactions of organosilicon iodides  $(\text{Me}_3\text{Si})_3\text{CSiRR}'\text{I}$  with electrophiles such as silver salts, iodine monochloride or trifluoroacetic acid have been shown to give rearranged products of the type  $(\text{Me}_3\text{Si})_2\text{C}(\text{SiRR}'\text{Me})(\text{SiMe}_2\text{Y})$ , sometimes virtually exclusively and sometimes along with the unrearranged isomer  $(\text{Me}_3\text{Si})_3\text{CSiRR}'\text{Y}$  [1,2]. For example, with ICl in  $\text{CCl}_4$   $(\text{Me}_3\text{Si})_3\text{CSiPh}_2\text{I}$  gave exclusively the rearranged chloride  $(\text{Me}_3\text{Si})_2\text{C}[\text{SiPh}_2\text{Me}](\text{SiMe}_2\text{Cl})$ , whereas  $(\text{Me}_3\text{Si})_3\text{CSiEt}_2\text{I}$  gave the rearranged  $(\text{Me}_3\text{Si})_2\text{C}[\text{SiEt}_2\text{Me}](\text{SiMe}_2\text{Cl})$  and unrearranged  $(\text{Me}_3\text{Si})_3\text{CSiEt}_2\text{Cl}$  in 65/35 ratio [3]. The rearrangements were attributed to the formation of a methyl-bridged cation of type I, which could be attacked by a nucleophile either at the  $\alpha$ -Si to give the unrearranged product or at the  $\gamma$ -Si to give the rearranged isomer [1–4]. Since within a range of related iodides  $(\text{Me}_3\text{Si})_3\text{CSiRR}'\text{I}$  the proportion of rearranged product increased in line with the increasing size of R and R', it was suggested that within such a series the extent of

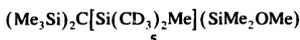
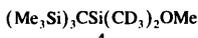
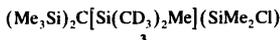
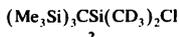
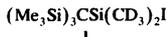
rearrangement is determined largely by the relative degrees of steric hindrance at the  $\alpha$ - and  $\gamma$ -Si centres in I, but it became clear later that this was not the only relevant factor [5].



In order to gain clear information about the effects of other factors on the proportion of rearranged products from various reactions, it is necessary to study a system in which the steric hindrance is essentially the same at the  $\alpha$ - and  $\gamma$ -centres. To this end we synthesized the labelled iodide  $(\text{Me}_3\text{Si})_3\text{CSi}(\text{CD}_3)_2\text{I}$ , 1, and initially examined its reactions with silver salts in a range of non-hydroxylic solvents [6]. Surprisingly, in most of the solvents used the proportion  $P_R$  of the rearranged product in the isomer mixture was well below the 50%

\* Corresponding author.

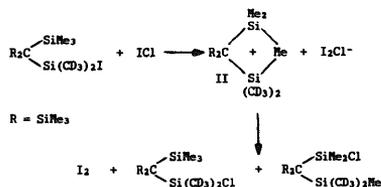
expected for attack on the free cation **I** with  $R = R' = CD_3$ , although in  $CH_2Cl_2$  it sometimes exceeded 50%, apparently because of some isomerization of **1** before substitution. It thus seemed of interest to examine the reactions of **1** with ICl in some of the solvents, and also in MeOH, in which the reaction of  $(Me_3Si)_3CSiMe_2I$  has been shown to give a mixture of  $(Me_3Si)_3CSiMe_2Cl$  and  $(Me_3Si)_2CSiMe_2OMe$  [7]. (Unfortunately  $Et_2O$ , in which the reactions with  $AgX$  give especially low values of  $P_R$ , could not be used because it reacts with ICl.)



## 2. Results and discussion

For reactions in the inert media a mixture of **1** (0.12 mmol) and ICl (usually 0.12 mmol) in the relevant solvent (1.0 cm<sup>3</sup>) was stirred overnight at room temperature. The solvent was then evaporated off under reduced pressure and the residue taken up in light petroleum. The solution was shaken with aqueous  $NaHSO_3$ , then separated, dried, and evaporated, and the solid was dissolved in  $CDCl_3$  for recording of the <sup>1</sup>H NMR spectrum. The ratio of unrearranged chloride, **2**, to rearranged chloride, **3**, was determined from the ratio of the carefully measured integrals of the signals from the  $SiMe_2$  and  $[Me_3Si + Me(CD_3)_2Si]$  protons. The results are shown in Table 1, and the main features, with comments, are as follows.

(a) As observed for the reactions with silver salts [6],



Scheme 1. Initially assumed course of the reaction of  $(Me_3Si)_3Si(CD_3)_2I$ , **1**, with ICl.

the value of  $P_R$  was usually well below the 50% expected on the simple picture (Scheme 1) in which a free bridged ion **II** takes up  $Cl^-$  from  $I_2Cl^-$ , approaching that value only for the reaction in  $CH_2Cl_2$ .

(b) The sequence of values of  $P_R$  in the four solvents is  $CH_2Cl_2 > C_6H_6 > CCl_4 > CHCl_3$ ; in the silver salt reactions the sequence of values of  $P_R$  varied with the silver salt used, but the value was always highest in  $CH_2Cl_2$ , as in the present case.

(c) In contrast to the outcome of some of the reactions with silver salts, no rearranged iodide was observed in the three cases in which the reaction was not taken to completion.

A further observation was that  $I_2$  was ineffective in promoting ionization of **1**. Treatment of **1** with a four-fold excess of  $I_2$  in refluxing  $CH_2Cl_2$  for 5 h appeared possibly to give a very small amount of rearranged iodide (up to ca. 2%), but there was no detectable formation of the latter under similar conditions in benzene.

If the reaction with ICl is assumed to have the mechanism indicated in Scheme 1, as previously suggested, involving the intermediate bridged cation **II**, then the predominance of unrearranged chloride can be rationalized in terms of preferential take up of  $Cl^-$  at the  $\alpha$ -Si centre from the  $I_2Cl^-$  before the latter has diffused away and become available for attack at the

Table 1  
Products from the reactions of  $(Me_3Si)_3Si(CD_3)_2I$ , **1** (0.12 mmol) with ICl in various solvents (1.0 cm<sup>3</sup>)

Solvent	ICl (mmol)	Product composition (%)			$P_R^a$
		Chloride <b>2</b>	Chloride <b>3</b>	Iodide <b>1</b>	
$CCl_4$	0.06	36	9	54	20
	0.12	82	18	0	18
	0.48	80	20	0	20
$CHCl_3$	0.12	85	15	0	15
	0.06	31	11	58	26
$C_6H_6$	0.12	78	22	0	22
	0.06	28	22	50	44
$CH_2Cl_2$	0.12	56	42	0	42

<sup>a</sup> Estimated uncertainty  $\pm 3$ .

$\gamma$ -Si centre. More efficient stabilization of the cation by  $\text{CH}_2\text{Cl}_2$  [6] would give it a longer life and so more opportunity to react at the  $\gamma$ -Si centre. This type of explanation was suggested for the reactions with silver salts  $\text{AgX}$ , the cation in that case preferentially taking up the  $\text{X}^-$  liberated at the  $\alpha$ -Si centre [6]. For those reactions the formation of rearranged iodide was tentatively attributed to return of  $\text{I}^-$  before the formed  $\text{AgI}$  had fully separated. Any such internal return from separating  $\text{I}_2\text{Cl}^-$  would be much more likely to form an Si–Cl rather than a much weaker Si–I bond, so no isomerization of the iodide would be expected.

The results are in themselves, however, consistent with the possibility [6] that an unbridged cation is initially formed and can sometimes be captured before it goes on to give the bridged species **II**, and the outcome of the reaction in MeOH is very relevant in this connection. In this solvent the reaction is much slower and the iodide less soluble, and so an excess of  $\text{ICl}$  (1.92 mmol) was used along with 0.24 mmol of **1** in  $12\text{ cm}^3$  of the solvent (cf. Ref. [7]). After 60 h the solvent was taken off and the  $^1\text{H}$  NMR spectrum of the residual solid revealed that all of the iodide had been consumed, to give a mixture of the unrearranged methoxide **4** (62%), rearranged methoxide **5** (22%) and unrearranged chloride **2** (16%).

The absence of a detectable amount of rearranged chloride in the reaction in MeOH could again be readily accounted for in terms of internal return of  $\text{Cl}^-$  from the formed  $\text{I}_2\text{Cl}^-$  before complete departure of the latter, along with its preferential attack at the  $\alpha$ -site after separation but before diffusion away. The MeOH, however, would be expected to be equally available at the  $\alpha$ - and  $\gamma$ -sites and so give rise to approximately equal amounts of rearranged and unrearranged methoxide. It is conceivable that MeOH molecules in the neighbourhood of the  $\alpha$ -site are activated by association with the formed  $\text{I}_2\text{Cl}^-$  ions, but some capture of an initially formed unbridged ion before the generation of the bridged ion **II** provides a conceptually much simpler explanation. In contrast to the situation for better bridging groups such as Ph, there is no compelling evidence that Me groups do provide anchimeric assistance to the departure of the leaving group, and thus give rise to direct formation of the bridged ion. Detailed discussion of this issue must await completion of a systematic study of the reactions of **1** with silver salts in a variety of alcohols, in which unrearranged products again dominate [8].

We should also note the possibility that in such highly crowded systems the slightly smaller size of  $\text{CD}_3$  than of  $\text{CH}_3$  groups [9] could significantly favour attack at the  $\alpha$ -site in **II**, but we think this effect unlikely to be large enough to give rise to the very low values of  $P_R$  in some of the reactions with  $\text{AgX}$  or  $\text{ICl}$ , or to account for the large variations in  $P_R$  with change of solvent.

### 3. Experimental

#### 3.1. Reactions in inert solvents

(i) A solution of **1** (0.12 mmol) and the appropriate amount (see Table 1) of  $\text{ICl}$  in the chosen solvent ( $1.0\text{ cm}^3$ ) was stirred overnight at room temperature (ca.  $24^\circ\text{C}$ ). The solvent was then evaporated under reduced pressure and the residue was dissolved in light petroleum (b.p.  $30$ – $40^\circ\text{C}$ ). The solution was shaken with aqueous  $\text{NaHSO}_3$ , separated, dried ( $\text{MgSO}_4$ ), and evaporated. The residual solid was taken up in  $\text{CDCl}_3$  for the recording of the  $^1\text{H}$  NMR spectrum at 400 MHz. The relevant chemical shifts ( $\delta$ ) are: for **1**, 0.35; for **2**, 0.27; for **3**, 0.27 and 0.62 ( $\text{SiMe}_2\text{Cl}$ ); for  $(\text{Me}_3\text{Si})_2\text{C}[\text{Si}(\text{CD}_3)_2\text{Me}][\text{Si}(\text{Me}_2)_2]$ , 0.25 and 1.08 ( $\text{SiMe}_2$ ). The relative integrations of the signals from the  $(\text{Me}_3\text{Si} + \text{Me}(\text{CD}_3)_2\text{Si})$  and  $\text{SiMe}_2\text{Cl}$  groups gave the ratio of compound **2** to compound **3**.

(ii) A solution of **1**<sub>2</sub> (0.96 mmol) and **1** (0.24 mmol) in  $\text{CH}_2\text{Cl}_2$  ( $2\text{ cm}^3$ ) was refluxed for 5 h, separated and shaken with aqueous  $\text{NaHSO}_3$ . The organic layer was separated, dried ( $\text{MgSO}_4$ ) and evaporated, and the residue dissolved in  $\text{CDCl}_3$  for recording of the  $^1\text{H}$  NMR spectrum, which showed that perhaps a very small amount, up to ca. 2%, of the rearranged iodide had been formed. When the reaction was repeated in  $\text{C}_6\text{H}_6$  no rearranged iodide could be detected.

#### 3.2. Reaction in MeOH

The iodide **1** (0.24 mmol) was dissolved in a small drop of  $\text{CCl}_4$  and a solution of  $\text{ICl}$  (1.92 mmol) in MeOH ( $12\text{ cm}^3$ ) was added. The mixture was stirred at room temperature for 60 h, the solvent was then removed under reduced pressure and the residue taken up in  $\text{CDCl}_3$ . The  $^1\text{H}$  NMR spectrum showed that no **1** remained and that methoxide **4**, methoxide **5**, and chloride **2** were present in 62/22/16 ratio. The relevant chemical shifts for  $(\text{Me}_3\text{Si})_2\text{CSiMe}_2\text{OMe}$  are 0.21 ( $\text{Me}_3\text{Si}$ ) and 0.26 ( $\text{SiMe}_2\text{O}$ ).

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