Journal of Organometallic Chemistry, 170 (1979) C9—C12

Preliminary communication

NOVEL REARRANGEMENTS IN REACTIONS OF TRIS(TRIMETHYLSILYL)-METHYLSILICON IODIDES AND HYDRIDES WITH ELECTROPHILIC REAGENTS, AND THE POSSIBILITY OF CATIONIC INTERMEDIATES*

COLIN EABORN*, DUNCAN A.R. HAPPER, STEVEN P. HOPPER and KAZEM D. SAFA
School of Molecular Sciences, University of Sussex, Brighton, BN1 9QJ (Great Britain)
(Received February 12th, 1979)

Summary

Unprecedented 1,3-migrations of methyl groups occur when compounds of the type $(Me_3Si)_3CSiRR'X$ (X = I, or in some cases, H) react with electrophilic reagents, such as silver(I) or mercury(II) salts in CH_3CO_2H, CF_3CO_2H, or alcohols, to give products of the type $(Me_3Si)_2C(SiMe_2Y)(SiRR'Me)$; it is suggested that as X^- leaves a cation is formed in which a Me group bridges the 1- and 3-silicon atoms.

We recently reported that the chemistry of tris(trimethylsilyl)methylsilicon compounds, $(Me_3Si)_3CSiR_2X$, shows some highly unusual features [1]. These are mainly associated with the powerful steric hindrance to the normal attack of nucleophiles on the silicon of the Si—X bond, which provides the opportunity for other mechanisms to be observed. We now present a brief, preliminary account of a study of the novel 1,3-rearrangements which take place when certain $(Me_3Si)_3CSiR_2X$ compounds are exposed to conditions expected to favour generation of a silico-cation. For convenience the $(Me_3Si)_3C$ group is referred to as the trisyl group, and denoted by the symbol Tsi [1].

Some typical results are outlined in Table 1. We first treated the compounds $TsiSiPh_2X$ with $AgNO_3$ in AcOH (Ac = CH_3CO). No reaction took place for X = Cl or Br, but for X = I rapid precipitation of AgI occurred. However, the major product was not the expected $TsiSiPh_2OAc$, but the rearranged isomer, $(Me_3Si)_2C(SiMe_2OAc)(SiPh_2Me)$, as was clearly revealed by its ^1H NMR spectrum (see Table 2), and this was accompanied by rearranged nitrate, $(Me_3Si)_2C(SiMe_2ONO_2)SiPh_2Me$. Again, when $TsiSiPh_2I$ was treated with $Hg(OAc)_2$ or AgOAc in AcOH the sole product was the rearranged acetate, $(Me_3Si)_2C(SiMe_2OAc)(SiPh_2Me)$. Reaction with $AgNO_3$ in MeOH gave a 13/87

---

*No reprints available.

TABLE 1

REACTIONS OF $(Me_3Si)_3CSiRR'X$ COMPOUNDS WITH ELECTROPHILIC REAGENTS[a]

Substrate RR'X	Solvent	Salt	Products and yields (%)	
			Y in $(Me_3Si)_2C(SiMe_2Y)$-$(SiRR'Me)$	Y in $(Me_3Si)_3SiRR'Y$
Ph_2I	AcOH	$AgNO_3$	OAc, 90; ONO_2, 10	
Ph_2I	AcOH	$Hg(OAc)_2$	OAc, 100	
Ph_2I	MeOH	$AgNO_3$	OMe, 87; ONO_2, 13	
Ph_2I	i-PrOH	$AgNO_3$	OPr-i, 28; ONO_2, 62	OPr-i, 10
PhMeI	AcOH	$Hg(OAc)_2$	OAc, 78	OAc, 22
Me_2I	AcOH	$Hg(OAc)_2$	OAc, 100	
Me_2I	MeOH	$AgNO_3$	OMe, 84; ONO_2, 16	
Me_2I	AcOH/MeOH[b]	$Hg(OAc)_2$	OAc, 68; OMe, 32	
Me_2H	AcOH/MeOH[b]	$Hg(OAc)_2$	OAc, 66; OMe, 34	
Et_2I	CF_3CO_2H[c]	none	O_2CCF_3, 55	O_2CCF_3, 45
Et_2I	CF_3CO_2H	AgO_2CCF_3	O_2CCF_3, 75	O_2CCF_3, 25
Et_2H	CF_3CO_2H	AgO_2CCF_3	O_2CCF_3, 40	O_2CCF_3, 60
EtMeI	CF_3CO_2H[d]	none	O_2CCF_3, 44	O_2CCF_3, 56
EtMeI	CF_3CO_2H	AgO_2CCF_3	O_2CCF_3, 72	O_2CCF_3, 28

[a] In a typical reaction, 0.1 mmol of organosilane was heated at 90°C for 30 min with 10 cm^3 of solvent containing 0.2 mmol of salt. [b] Equimolar. [c] Refluxed for 7 days. [d] Refluxed for 4 days.

TABLE 2

^1H NMR SPECTRA OF SOME REPRESENTATIVE PRODUCTS[a]

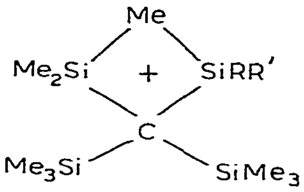
Product	δ (ppm)
$(Me_3Si)_3CSiMe_2OAc$	2.00(s, 3H, $COCH_3$); 0.52(s, 6H, $SiMe_2$); 0.27(s, 27H, Me_3Si)
$(Me_3Si)_2C(SiPh_2Me)(SiMe_2OAc)$	8—7(m, 10H, Ph); 2.2(s, 3H, $COCH_3$); 0.95(s, 3H, MeSi); 0.38(s, 6H, Me_2Si); 0.25(s, 18H, Me_3Si)
$(Me_3Si)_2C(SiPh_2Me)(SiMe_2OMe)$	8.1—7.1(m, 10H, Ph); 3.55(s, 3H, OMe); 0.96(s, 3H, MeSi); 0.20(s, 18H, Me_3Si); 0.02(s, 6H, Me_2Si)
$(Me_3Si)_2C(SiPh_2Me)(SiMe_2ONO_2)$	8.2—7.2(m, 10H, Ph); 1.1(s, 3H, MeSi); 0.47(s, 6H, Me_2Si); 0.40(s, 18H, Me_3Si)
$(Me_3Si)_3C(SiPh_2OPr$-i)	8—7(m, 10H, Ph); 4.14(m, 1H, OCH); 1.06(d, 6H, CMe_2); 0.30(s, 27H, Me_3Si)
$(Me_3Si)_2C(SiPh_2Me)(SiMe_2OPr$-i)	8.3—7.2(m, 10H, Ph); 4.32(m, H, OCH); 1.5(d, 6H, CMe_2); 1.07(s, 3H, MeSi); 0.43(s, 6H, Me_2Si); 0.37(s, 18H, Me_3Si)

[a] In CCl_4 with CH_2Cl_2 as internal standard.

mixture of the rearranged nitrate and methoxide, while $AgNO_3$ in i-PrOH gave a 62/28 ratio of rearranged nitrate to rearranged i-propoxide, but in this case about 10% of the unrearranged $TsiSiPh_2OPr$-i was also obtained. In the one experiment carried out with TsiSiPhMeI there was predominant but not exclusive rearrangement. Rearrangement would escape detection in reactions of $TsiSiMe_2I$, but in view of the results, described below, obtained with $TsiSiEt_2I$ and TsiSiMeEtI, it seems very likely that it does occur; the fractionation of products between the various nucleophiles Y present is rather similar to that for $TsiSiPh_2X$. The hydride $TsiSiMe_2H$ reacts with mercury(II) salts in AcOH/ROH mixtures, and the product ratios $TsiSiMe_2(OAc)/TsiSiMe_2(OR)$ are very similar to those from the iodide.

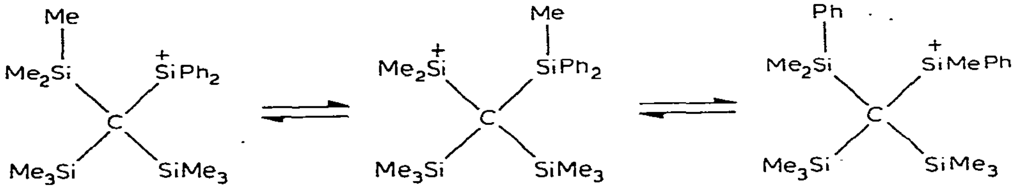
The iodides $TsiSiMe_2I$, TsiSiMeEtI, and $TsiSiEt_2I$ react, though relatively slowly, with boiling CF_3CO_2H to give trifluoroacetates, and the rate of reaction is not significantly affected by the presence of NaO_2CCF_3. The reaction is much faster in the presence of AgO_2CCF_3. In CF_3CO_2H alone, $TsiSiEt_2I$ and TsiSiMeEtI give 55 and 44%, respectively, of rearranged product, and in the presence of silver salt these proportions are increased to 75 and 72%. The hydride $TsiSiEt_2H$ reacts in the presence of silver salt to give 40% of rearranged product.

The results can be most satisfactorily accounted for in terms of formation of bridged cations of type I as halide or hydride ion is abstracted. (The structure could be represented in other ways, and the simple form we have written is not meant to imply any decision on the nature of the bonding.) The nucleophiles present then compete for cation I; in principle they can attack at either of the bridged Si atoms, but attack at the least sterically hindered centre will be favoured, so that the cations I with R = R′ = Ph or with R = Ph, R′ = Me will give very predominantly or exclusively rearranged products of the form $(Me_3Si)_2C(SiMe_2Y)(SiRR'Me)$. With R = R′ = Et and with R = Me, R′ = Et, there should be less steric discrimination, and thus less rearrangement, as observed.



(I)

To our knowledge, these 1,3-migrations of Me groups have no precedent in organosilicon or organic chemistry. Accurate scale models show that in the reactants $(Me_3Si)_3CSiRR'X$ the Me groups are almost in contact with the silicon atom of the SiRR′X entity, so that as X^- leaves very little movement of a Me group would be needed to form a cation of type I. We prefer the bridged ion to a rapidly interconverting mixture of classical silico cations, because (a) the system seems to have nothing to gain by going to a mixture of classical ions, whereas the formation of the bridged ion in an anchimerically assisted process as X^- leaves means that generation of the silico cation, which appears to be highly disfavoured species, is avoided, and (b) with $TsiSiPh_2X$, if a mixture of classical ions were formed, as shown in eq. 1 below, then migration of a Ph group, which would reduce steric strain, would be expected, giving at least some rearranged product of the type $(Me_3Si)_2C(SiMe_2Ph)(SiMePhY)$, which we have never observed.



(1)

A fuller discussion will take account of secondary features and also consider more complex mechanisms.

We thank the S.R.C. (grant to C.E.) and the Petroleum Research Fund, administered by the American Chemical Society (grant to S.P.H.) for support of this work; K.D.S. thanks the Ministry of Higher Education and Science of Iran for financial assistance.

Reference

1 C. Eaborn, D.A.R. Happer, K.D. Safa and D.R.M. Walton, J. Organometal. Chem., 157 (1978) C50.