Journal of Organometallic Chemistry, 157 (1978) C50—C52

Preliminary communication

THE UNUSUAL BEHAVIOUR OF TRIS[(TRIMETHYLSILYL)METHYL]-SILICON COMPOUNDS*

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(Received July 13th, 1978)

Summary

The $(Me_3Si)_3C$ group causes very large steric hindrance to nucleophilic displacement at a silicon atom to which it is attached, and $(Me_3Si)_3CSiMe_2Cl$ is even less reactive than $t\text{-}Bu_3SiCl$ towards base. The compounds $(Me_3Si)_3CSiMe_2X$ (X = Cl, Br, or I) are cleaved by MeOH/MeONa to give $(Me_3Si)_2CHSiMe_2OMe$, possibly via the silaolefin $(Me_3Si)_2C{=}SiMe_2$, and the corresponding $(Me_3Si)_3CSiPh_2X$ compounds undergo the analogous reaction even more readily. The halides $(Me_3Si)_3CSiR_2X$ (X = Cl or Br) and $(Me_3Si)_3CSiCl_3$ do not react with boiling alcoholic silver nitrate, but the iodides $(Me_3Si)_3CSiR_2I$ are rapidly attacked.

We report below some preliminary results on the reactions of $(Me_3Si)_3CSiR_2X$ compounds (R = Me, Ph, or Cl) which reveal that the $(Me_3Si)_3C$ group which we refer to as the 'Trisyl' group, and denote by Tsi, causes very large steric hindrance towards attack by nucleophiles at the adjacent silicon atom, and that this allows novel types of reaction to be observed.

The metallation of TsiH to give TsiLi, and the coupling of the latter with Me_3SiCl to give $TsiSiMe_3$ have been described previously [1]. The TsiLi reacts analogously with other silicon halides, e.g., with $SiCl_4$ [2], $MeSiCl_3$ [2], Me_2SiCl_2, $PhSiCl_3$ [2], or Ph_2SiF_2 to give, respectively, $TsiSiCl_3$, $TsiSiMeCl_2$, $TsiSiMe_2Cl$, $TsiSiPhCl_2$, and $TsiSiPh_2F$. The trichloro derivative $TsiSiCl_3$ possibly provides the most striking evidence of the remarkable steric effect of the Tsi group, since the compound is stable to boiling neutral methanol or aqueous ethanol, alone or in the presence of silver nitrate though it does react with boiling methanolic sodium methoxide**. While $TsiSi(OMe)_2Cl$ is formed in about 35% yield, the

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*No reprints available.

**On pyrolysis it loses Me_3SiCl, possibly to give initially $(Me_3Si)_2C{=}SiCl_2$ [3]. The base peak in the mass spectrum of $TsiSiPh_2F$ is at a mass number of 340, which is consistent with ready loss of Me_3SiF to give $(Me_3Si)_2C{=}SiPh_2$. $TsiSiPh_2F$ loses Me_3SiF on refluxing, to give solid products which have analyses and mass spectra consistent with the stoicheiometry $(Me_3Si)_2CSiPh_2$, but which are thought not to contain a C=Si bond; these are being studied [3].

main product is probably $(Me_3Si)_2CHSi(OMe)_3$, formed via an elimination, as discussed below.

The compound $TsiSiMe_2Cl$ is even less reactive towards aqueous ethanolic sodium hydroxide than is $t\text{-}Bu_3SiCl$; under conditions which cause virtually complete conversion of $t\text{-}Bu_3SiCl$ into $t\text{-}Bu_3SiOH$ [4], $TsiSiMe_2Cl$ undergoes only 70% reaction, as indicated by liberated Cl^- ($>$ 15% of the $TsiSiMe_2Cl$ was recovered unchanged). Even then the main reaction is not direct replacement of the chlorine atom, but probably a fragmentation analogous to that observed in the reaction with 2 *M* MeONa in MeOH, which gives very predominantly $(Me_3Si)_2CHSiMe_2OMe$. The diphenyl compound $TsiSiPh_2Cl$ reacts even more readily with MeONa/MeOH, and gives a high yield of $(Me_3Si)_2CHSiPh_2OMe$. The products $(Me_3Si)_2CHSiR_2OMe$ are thought to be formed from a novel type of β-elimination to give $(Me_3Si)_2C{=}SiR_2$ species (eq. 1a) followed by addition of methanol to the latter (eq. 1b). We favour this mechanism rather than Me_3Si—C cleavage to give

$$MeO^{-}\curvearrowright Me_3Si\text{—}\curvearrowright C(SiMe_3)_2\text{—}SiR_2\text{—}\curvearrowright X \rightarrow MeOSiMe_3 + (Me_3Si)_2C{=}SiR_2 + X^- \quad (1a)$$

$$(Me_3Si)_2C{=}SiR_2 + MeOH \rightarrow (Me_3Si)_2CHSiR_2OMe \quad (1b)$$

the carbanion $(Me_3Si)_2(Me_2XSi)C^-$ (which could then either (i) lose X^- to give the silaolefin, or (ii) acquire a proton to give $(Me_3Si)_2CHSiMe_2X$, which would rapidly undergo solvolysis to $(Me_3Si)_2CHSiMe_2OMe$) because (a) no detectable reaction occurs under comparable conditions in the case of $(Me_3Si)_4C$, and it is unlikely that the carbanions $(Me_3Si)_2(Me_2XSi)C^-$ would be significantly more readily formed than $(Me_3Si)_3C^-$, (b) the ease of the reaction of the $TsiSiR_2X$ species with both R = Me and Ph increases significantly in the sequence $X = F < Cl < Br < I$, and while the stabilities of the carbanions $(Me_3Si)_2(Me_2SiX)C^-$ are unlikely to vary significantly, such a sequence would be expected in terms of the leaving group abilities of X in a reaction of type 1a, and (c) the reactions are markedly faster for R = Ph than for R = Me, which again would be difficult to reconcile with rate-determining formation of the carbanion but is consistent with stabilisation of the forming silaolefin by conjugation with the phenyl groups.

The only direct displacement reactions we have been able to observe for the $TsiSiR_2X$ species involve either introduction of the small hydrogen atom in place of X (viz. reduction by $LiAlH_4$ to $TsiSiR_2H$) and reactions which probably involve predominant electrophilic attack at X, e.g. $TsiSiR_2H + ZY \rightarrow TsiSiR_2Z$ (ZY = Cl_2, Br_2 or ICl). None of the compounds $TsiSiCl_3$, $TsiSiMe_2X$ or $TsiSiPh_2X$ (X = Cl or Br) react with methanol or aqueous ethanol, either alone or in the presence of silver nitrate. This behaviour is an impressive illustration of the reluctance of silicon compounds to form siliconium ions (silicenium [5] or silylenium [6] ions) in solution; it has been suggested that if the usual nucleophilic attack at silicon could be prevented, silicon halides might react by a siliconium ion mechanism [7], but clearly such a mechanism is not readily available even in the case of $TsiSiPh_2X$, where the siliconium ion $TsiSiPh_2^+$ might be expected to be markedly stabilised not only by the Ph groups but also by the $(Me_3Si)_3C$ group (compare the stabilisation of the ion $Me_3SiCH_2CH_2^+$ [8]), and where considerable release of steric strain would accompany the ionisation. The failure to form siliconium ions from halides has also been attributed to the strength of Si—halogen bonds*,

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*For a review of attempts to detect siliconium ions in solution see ref. 9 and for later leading references see ref. 5.

TABLE 1

Compound	M.p. (°C)	δ (ppm)
$(Me_3Si)_3CSiMe_2Cl$	[a]	0.30 (s, 27H); 0.62 (s, 6H)
$(Me_3Si)_3CSiMe_2I$	[a]	0.33 (s, 27H); 1.03 (s, 6H)
$(Me_3Si)_3CSiPh_2F$	140	0.20 (s, 27H); 7—8 (m, 10H)
$(Me_3Si)_3CSiPh_2H$	132	0.17 (s, 27H); 5.05 (s, 1H); 7—8 (m, 10H)
$(Me_3Si)_3SiPh_2I$	227	0.33 (s, 27H); 7—8 (m, 10H)
$(Me_3Si)_3CSiMe_2OCOMe$	[a]	0.17 (s, 27H); 0.43 (s, 6H); 1.9 (s, 3H)
$(Me_3Si)_3CSiH_2OCOMe$	[a]	0.22 (s, 27H); 4.77 (s, 2H); 2.03 (s, 3H)
$(Me_3Si)_2(Ph_2Me)SiMe_2OCOMe$	118	0.08 (s, 18H); 0.23 (s, 6H); 0.80 (s, 3H); 2.03 (s, 3H); 7—8 (m, 10H)
$(Me_3Si)_2CHSiMe_2OMe$	[b]	0.08 (s, 18H); 0.15 (s, 6H); −0.58 (s, 1H); 3.33 (s, 3H)
$(Me_3Si)_2CHSiPh_2OMe$	[b]	−0.10 (s, 18H); 0.13 (s, 1H); 3.33 (s, 3H); 7—8 (m, 10H)

[a] Sublimes. [b] Liquid.

but even $TsiSiMe_2I$ and $TsiSiPh_2I$, containing the relatively weak Si—I bond, fail to react with neutral methanol. However, both these iodides react readily with silver nitrate in methanol or silver acetate in acetic acid; with the latter reagent $TsiSiMe_2I$ and $TsiSiH_2I$ give the expected $TsiSiMe_2OCOMe$ and $TsiSiH_2OCOMe$, but while the product from $TsiSiPh_2I$ gives the correct analyses for $TsiSiPh_2OCOMe$ the ^1H NMR spectrum is inconsistent with this formulation, and points strongly to the isomeric $(Me_3Si)_2(SiPh_2Me)SiMe_2OCOMe$; this novel rearrangement, if confirmed, could be most attractively accounted for in terms of a siliconium ion intermediate, but a concerted multi-centre process avoiding such an ion cannot be ruled out.

Melting points and NMR data for some of the compounds mentioned above are listed in the Table, but it should be appreciated that some identifications are still tentative.

Acknowledgements

We thank Dr. S.S. Washburne (Temple University, Philadelphia, U.S.A.) for valuable advice and suggestions, Dr. Nazmi Ramadan (University of Tripoli) for important preliminary studies, the Ministry of Science and Higher Education of Iran for financial aid to K.D.S., and Dow Corning Ltd. for gifts of organosilicon chemicals.

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