

Preliminary communication

BIMOLECULAR DISPLACEMENTS OF IODINE IN REACTIONS OF DIMETHYL[TRIS(TRIMETHYLSILYL)METHYL] SILYL IODIDE WITH SALTS

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Summary

Direct nucleophilic displacement of iodine to give $(\text{Me}_3\text{Si})_3\text{CSiMe}_2\text{Y}$, where $\text{Y} = \text{F}, \text{NCO}, \text{NCS}, \text{CN}$ or N_3 , takes place when $(\text{Me}_3\text{Si})_3\text{CSiMe}_2\text{I}$ is treated with solutions of CsF , KOCN , KSCN , KCN , or NaN_3 in MeOH or CH_3CN . The order of effectiveness of the nucleophiles appears to be $\text{N}_3 > \text{F} > \text{CN} > \text{NCS} > \text{NCO}$ in MeOH and $\text{NCS} > \text{NCO} > \text{CN}, \text{F}$ in CH_3CN .

Direct bimolecular displacement of the X groups in TsiSiR_2X species ($\text{Tsi} = (\text{Me}_3\text{Si})_3\text{C} = \text{trisyl}$) by nucleophiles is known to be very seriously inhibited by steric hindrance [1–5]. In particular, the rates of methanolysis of the $\text{TsiSiMe}_2\text{X}$ compounds with $\text{X} = \text{OCIO}_3, \text{OSO}_2\text{CF}_3$, or I have been shown to be relatively little affected by the presence of NaOMe up to about 0.5 M , so that the reactions were thought to involve rate-determining ionization of the $\text{Si}-\text{X}$ bonds [1,4,5]. We have now found, however, that with some nucleophiles, namely pseudohalide and fluoride ions, direct displacements can occur quite readily under some circumstances*.

We initially examined the reactions of $\text{TsiSiMe}_2\text{I}$ ($7 \times 10^{-4} \text{ M}$) with a large excess of NaN_3 ($0.025\text{--}0.40 \text{ M}$) in MeOH , monitoring the reaction by observing the changes in the relative heights (or integrals) of the ^1H NMR peaks from the $(\text{Me}_3\text{Si})_3\text{C}$ protons in $\text{TsiSiMe}_2\text{I}$, $\text{TsiSiMe}_2\text{N}_3$, and $\text{TsiSiMe}_2\text{OMe}$. Above about 0.1 M NaN_3 , the amount of $\text{TsiSiMe}_2\text{OMe}$ formed was insignificant, and the observed pseudo first-order rate constant, k , for the disappearance of the iodide was proportional to the NaN_3 concentration; the approximate values of $10^5 k$ at 60°C at $0.10, 0.20$, and 0.40 M salt concentration were $1.7, 3.5$, and 7.0 s^{-1} ,

*It is likely that direct nucleophilic displacements are involved in reactions of $\text{TsiSiMe}_2\text{X}$ ($\text{X} = \text{Cl}$ or Br) with Bu_4PbCl in tetradecane [6].

respectively. (The proportionality applies approximately at lower NaN_3 concentrations when allowance is made for concomitant formation of $\text{TsiSiMe}_2\text{OMe}$; with 0.025 M NaN_3 the latter constitutes about 20% of the products). There seems no reason to doubt that these reactions involve direct bimolecular attack of N_3^- on $\text{TsiSiMe}_2\text{I}$.

The reactions of other salts MY (0.1 M), namely CsF , KOCN , KSCN , and KCN , with $\text{TsiSiMe}_2\text{I}$ ($7 \times 10^{-4}\text{ M}$) in refluxing MeOH gave mixtures of $\text{TsiSiMe}_2\text{Y}$ and $\text{TsiSiMe}_2\text{OMe}$. Approximate percentages of $\text{TsiSiMe}_2\text{I}$ which had reacted after 24 h, with the approximate $\text{TsiSiMe}_2\text{Y}/\text{TsiSiMe}_2\text{OMe}$ ratios in parentheses, were ($\text{Y} =$) NCO , 33 (0.6); NCS , 62 (4); CN , 70 (6); F , 92 (8). (In the absence of salt, ca. 15% of the $\text{TsiSiMe}_2\text{I}$ reacted in 24 h). The order of effectiveness of the salts is thus: NaN_3 , $\text{CsF} > \text{KCN} > \text{KSCN} > \text{KOCN}$.

The reactions of $\text{TsiSiMe}_2\text{I}$ with the same salts were then examined in CH_3CN at the reflux temperature. (The CH_3CN was dried by refluxing over CaH_2 , but since $\text{TsiSiMe}_2\text{I}$ was converted into $\text{TsiSiMe}_2\text{OH}$ in the refluxing solvent ($k = \text{ca. } 7.7 \times 10^{-6}\text{ s}^{-1}$) it evidently contained a significant amount of water, perhaps as much as 0.4 M .) Sodium azide was not sufficiently soluble in this medium to permit kinetic studies, but $\text{TsiSiMe}_2\text{N}_3$ (contaminated with a little of the hydroxide) was formed when the iodide was refluxed with a suspension of the salt. Values of $10^6 k$, where k is the observed pseudo first-order constant for reactions of iodide ($7 \times 10^{-4}\text{ M}$) with 0.025 , 0.05 , 0.075 , or 0.10 M KSCN at 35.0°C were ca. 4.0 , 7.7 , 11.5 and 15.5 s^{-1} , indicating that the reaction is of first-order in the salt, and thus can be assumed to involve direct bimolecular interaction. In a solution of the iodide ($7 \times 10^{-4}\text{ M}$) in CH_3CN containing no salt or 0.1 M KOCN , KSCN , KCN or CsF , after 6 h under reflux 16, 60, 100, 55 and 55%, respectively, of the iodide had reacted, the product being the $\text{TsiSiMe}_2\text{OH}$ in the absence of salt and exclusively the $\text{TsiSiMe}_2\text{Y}$ species ($\text{Y} = \text{NCO}$, NCS , CN and F) in the other cases. The order of effectiveness of the anions as nucleophiles in this medium ($\text{NCS} > \text{NCO} > \text{CN}$, F) is thus different from that in MeOH . The absence of hydroxide product in the presence of salts is of interest, since on the basis of the rate of its formation in the absence of the salts significant amounts of it could be expected; it is possible that the water is deactivated by being taken up in solvation of the salts.

Fluoride ion has long been known to be a very effective nucleophile towards silicon, and in view of its small size it is not surprising that it can directly displace iodine in these highly hindered systems. Since silicon has such a high affinity for oxygen, it was, however, rather surprising that pseudohalide ions should be so much more effective than methoxide ion. It is noteworthy that with these pseudohalides the attacking centre in the nucleophile in all cases is a small nitrogen or carbon atom, and this and the linear nature of the ions (and probably a very different spread of solvent molecules around the ions than that with, say, OMe^- or Cl^-) may account for their relatively high activities in these crowded systems.

The reactions of the salts in CH_3CN provide satisfactory routes to the $\text{TsiSiMe}_2\text{Y}$ compounds with $\text{Y} = \text{CN}$, NCO , NCS , or F . For $\text{Y} = \text{N}_3$ the low solubility of the NaN_3 in CH_3CN results in contamination by the hydroxide, and the azide is better prepared by using MeOH containing a high concentra-

tion of the salt. It is noteworthy that the reaction of $\text{TsiSiMe}_2\text{I}$ with KOCN gives exclusively the isocyanate, $\text{TsiSiMe}_2\text{NCO}$, whereas the reaction with AgOCN in CH_2Cl_2 gives exclusively the normal cyanate, $\text{TsiSiMe}_2\text{OCN}$ [7].

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