A Novel Mode of Reaction of a Substituted Alkyl Halide. Reduction of Tris(trimethylsilyl)methyl Iodide by Methanol

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Tris(trimethylsilyl)methyl iodide undergoes rapid reduction to tris(trimethyl)silylmethane in methanol containing sodium methoxide or silver trifluoromethanesulfonate.

After more than a century of study of reactions of alkyl and substituted-alkyl halides with alcohols, including some sixty years of detailed mechanistic investigations, it might reasonably have been assumed that all possible modes of reaction had been observed, but we describe below one we believe not to have been previously recognised.

We thought it likely that unusual behaviour towards nucleophiles might be encountered with compounds of the type $(Me_3Si)_3CX$, where X is a potential nucleofuge such as halogen, since: (*a*) there should be severe steric hindrance to S_N2-type attack by a nucleophile at carbon; (*b*) β-elimination of HX is impossible; and (*c*) formation of the cation $(Me_3Si)_3C^+$ is very unlikely. (An α-Me_3Si group is known to be much less effective at stabilizing a carbocation than an α-Me or α-Me_3C group,[1,2] and the limited experimental evidence from solution reactions[1,3] provides no support for predictions based on calculations[2] that it is more effective than α-H.) We thus decided to examine the reaction of the iodide $(Me_3Si)_3CI$ **1** with methanolic sodium methoxide.

$$(Me_3Si)_3CX$$
$$\mathbf{1}, X = I;\ \mathbf{2}, X = H;\ \mathbf{3}, X = Cl$$

To our surprise a fast reaction occurred in refluxing $0.1\ mol\ dm^{-3}$ NaOMe–MeOH and tris(trimethylsilyl)methane **2** was formed in virtually quantitative yield. In methanol alone **2** was formed very slowly (<1% per hour), but when one equivalent of AgO_3SCF_3 was added it was produced rapidly and AgI separated. The reduction also took place in EtOH or Pr^iOH in the presence of either the corresponding alkoxide or AgO_3SCF_3. When $1\ mol\ dm^{-3}$ solutions of alcohols in benzene containing AgO_3SCF_3 were used, the reduction of **1** on heating took place at comparable rates with EtOH and MeOH, but it was about five times slower with Pr^iOH, and under conditions in which *ca.* 30% conversion into **2** occurred with MeOH and EtOH there was no significant reaction with *tert*-butyl or neopentyl alcohol. There was also no reaction when **1** was refluxed with AgO_3SCF_3 in benzene alone.

The formation of **2** rules out the intermediacy of the cation $(Me_3Si)_3C^+$, since in MeOH this would surely give $(Me_3Si)_3COMe$ or an isomer of it. In view of its known stability (reflected in the acidity of **2**[4]) the anion $(Me_3Si)_3C^-$ would not have been a surprising intermediate, but this was ruled out by the observation that only undeuteriated **2** was formed in CH_3OD in the presence of either MeONa or AgO_3SCF_3. Very significantly, the Ag^+-catalysed reaction was much slower in CD_3OD than in CH_3OH, indicating that C–H bond formation must take place in a rate-limiting step. In 1:1 CH_3OD–CD_3OD in both the methoxide and Ag^+-catalysed processes there was about 4–6% incorporation of deuterium, corresponding to a kinetic isotope effect k_H/k_D in the range 15–25. (Values in this range have been observed for both proton and hydrogen atom transfers to sterically hindered centres, and are commonly attributed to quantum mechanical tunnelling.[5])

It seemed very likely from the above observations that the radical $(Me_3Si)_3C\cdot$ was the effective intermediate in both reactions, especially since it is known that it can be readily formed and under appropriate conditions can be highly persistent.[6,7] However there was also a possibility that C–I bond breaking was concerted with C–H bond formation; but this was excluded by the observation that when the methoxide- and Ag^+-catalysed reactions catalysed by an equivalent of

AgO_3SCF_3 or 0.1 mol dm^{-3} NaOMe were carried out in MeOH containing 1 mol dm^{-3} CCl_4 they were much slower, and that both **2** and the chloride $(Me_3Si)_3CCl$ **3** were formed. Thus whereas the reaction in refluxing 0.1 mol dm^{-3} NaOMe–MeOH had a half-life of <10 min, there was only *ca.* 5% conversion of **1** after 3 h in the presence of 0.1 mol dm^{-3} CCl_4, and in the Ag^+-catalysed reaction under conditions in which **1** normally had a half-life of a few minutes there was only 20% conversion after 3 h. In both cases the amounts of **2** and **3** increased with time. Addition of toluene also strongly retarded the reactions.

It seems clear that the reactions are free-radical chain processes involving $(Me_3Si)_3C\cdot$ and, in keeping with this view, when photolysis of the mercurial $[(Me_3Si)_3C]_2Hg$, which is known to give such radicals very readily,[6] was carried out in MeOH containing 1 mol dm^{-3} CCl_4 roughly equal amounts of **2** and **3** were produced. Furthermore, when the photolysis was repeated but in 1 : 1 CH_3OD–CD_3OD containing 1 mol dm^{-3} CCl_4 (necessary because the mercurial is practically insoluble in MeOH alone) deuterium was incorporated into **2** to the extent of *ca.* 4%, corresponding to a value of k_H/k_D of *ca.* 25, within the range of approximate values for the catalysed reactions of **1** in MeOH.

In the Ag^+-catalysed process the radical $(Me_3Si)_3C\cdot$ presumably reacts with CH_3OH to give **2** and the radical $HOCH_2\cdot$, which then abstracts $I\cdot$ from **1** to regenerate $(Me_3Si)_3C\cdot$. (The $Me\cdot$ radical is known to abstract a hydrogen atom 45 times as readily from carbon as from oxygen in MeOH.[8]) The other product, ICH_2OH, would break down to HCHO and HI and hence AgI. In the methoxide-catalysed reaction the hydrogen atom abstraction step might involve $^-OCH_2\cdot$ rather than $HOCH_2\cdot$, since the latter has a pK_a of 10.7.[9] In the presence of CCl_4 the radical $(Me_3Si)_3C\cdot$ is frequently trapped to give **3**. An implication of the proposed mechanism is that in the Ag^+-catalysed reaction Ag^+ is not involved in the propagation steps, so that complete reduction should be possible even if less than one equivalent of AgO_3SCF_3 is used, and we confirmed that under such conditions more **2** was formed than Ag^+ was consumed, but the reaction was much slower.

The chain-initiating processes have still to be identified, but we note that the progressive (though slow) formation of **1** and **3** in the catalysed reactions in the presence of CCl_4 implies that initiation is a continuing process, and so is not dependent on the initial presence of traces of radical impurities. In the methoxide-catalysed reaction there may be single electron transfer from MeO^- to give the radical anion $(Me_3Si)_3CI^{\cdot -}$ and hence $(Me_3Si)_3C\cdot$ and I^-, but the corresponding process, involving single electron transfer to Ag^+ to give the radical cation $(Me_3Si)_3CI^{\cdot +}$, and hence $(Me_3Si)_3C\cdot$ and I^+, seems less likely.

It is noteworthy that prolonged refluxing of neopentyl iodide with concentrated ethanolic potassium hydroxide was shown many years ago to give some neopentane, among other products,[10] and it is likely that the mechanism of the reduction is similar to that for **1**. The reaction is many orders of magnitude slower, however, perhaps because the radical $Bu^tCH_2\cdot$ is much less readily formed than $(Me_3Si)_3C\cdot$.

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