

Preliminary communication

UNUSUAL REACTIONS OF [TRIS(TRIMETHYLSILYL)METHYL]- DIMETHYL-CHLORO- AND -BROMO-SILANE WITH TETRA-*n*-BUTYL- PHOSPHONIUM CHLORIDE

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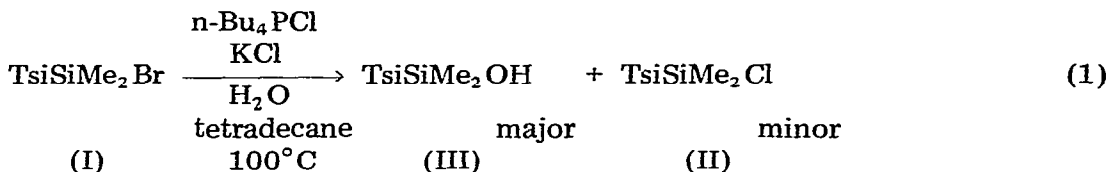
Summary

[Tris(trimethylsilyl)methyl] dimethylbromosilane undergoes facile halide exchange reaction with tetra-*n*-butylphosphonium chloride. In addition, under phase-transfer conditions with tetra-*n*-butylphosphonium chloride, both [tris(trimethylsilyl)methyl] dimethylbromosilane and the analogous chlorosilane undergo halide substitution. Other phase-transfer reagents do not affect these reactions.

A number of recent studies by Eaborn and coworkers on [tris(trimethylsilyl)methyl] *s*-substituted silicon compounds have uncovered not only the remarkable steric effects of the trisyl group, but also a host of unusual reactions mediated or controlled by the trisyl group [1—9]. In particular, although TsiSiMe₂ Br (I) and TsiSiMe₂ Cl (II) react with LiAlH₄, they have been shown to be unreactive to boiling methanol [1,4,5]. Under strongly electrophilic conditions (silver nitrate in boiling methanol), the chlorosilane is inert, but the bromosilane reacts slowly [4]; the only trisyl halides which react readily under electrophilic conditions are the iodides [2,5,7].

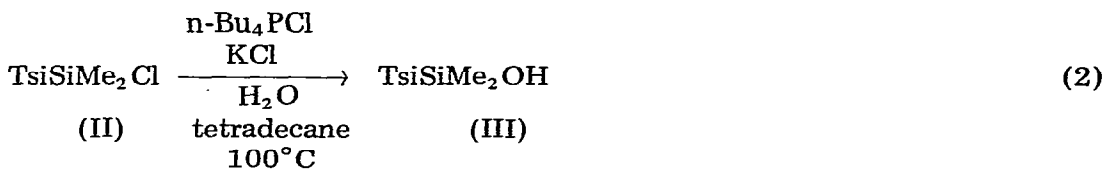
We have discovered conditions under which both the bromo- and chlorosilane (I and II) react, albeit slowly. In addition, we report a facile direct reaction between I and *n*-Bu₄PCl. The bromosilane I (2.0 g; 5.4 mmol) when magnetically stirred at 100°C in a three-phase mixture also containing *n*-Bu₄PCl (1.6 g; 5.4 mmol), *n*-heptane (13 ml), potassium chloride (8.0 g; 107 mmol), and water (20 ml) gives a high yield of TsiSiMe₂OH (~97%) and small amounts of the chlorosilane II (~3%) (eq. 1). The three-phase

* (Me₃Si)₃C = trisyl group; also abbreviated Tsi.



mixture consists of an upper heptane layer in which I is dissolved, an intermediate layer of n-Bu₄PbCl, and a lower aqueous KCl layer. After reaction times of 2 to 4 days (monitored by gas chromatography), the silanol III is isolated by separating the heptane layer and removing solvent. The silanol is exceedingly difficult to purify since it is slightly contaminated by the chlorosilane II. These have remarkably similar solubility properties and both readily sublime. Nevertheless, we have obtained analytically pure silanol by subliming (90°C; 3 mmHg) the crude reaction product twice. Even so GC analysis shows a small amount (~1–2%) of the chlorosilane. Because of discrepancies between our properties for III and those previously reported [9], we report the following for III: (a) IR in CCl₄: 3655 cm⁻¹, (b) NMR (60 and 360 MHz) in CDCl₃: δ 0.23 (s, 27H), 0.32 (s, 6H), and 1.4 ppm (s, 1H), (c) the mass spectrum (chemical ionization) shows only one large peak at *m/e* 291 (*M* – 15), and (d) elemental analysis (Found: C, 47.21; H, 10.89. Calcd. for C₁₂H₃₄Si₄O: C, 46.99; H, 11.17%). Contrary to the previous report [9], we were unable to exchange the OH of the silanol either by shaking a CCl₄ solution with D₂O [9] or by using more drastic conditions including reaction with n-BuLi followed by a D₂O quench. The chlorosilane II was not isolated, but by retention time measurements and GC-MS was shown to be identical to an authentic sample [4]. In addition, a 360 MHz NMR spectrum of the solid (sublimed once) isolated from the reaction clearly showed it to be the silanol with a small impurity of the chlorosilane.

We believe that the chlorosilane and the silanol are formed independently in reaction 1. Although it might seem possible that under the conditions of reaction 1 the bromosilane would react to give the chlorosilane which in turn would give the silanol, we have independently observed that the conversion of II to III is extremely slow (eq. 2). Reaction 2 (followed to about 90% completion) takes about a month and gives only the silanol III, so it is clear

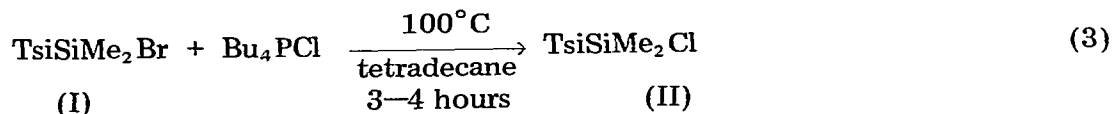


that this reaction is not the primary path to III in reaction 1. Reaction 2 is the second one reported for the chlorosilane II and, indeed, the first reported under non-hydride reducing conditions [4].

Although we originally added potassium chloride in order to explore the possibility of a direct nucleophilic displacement by chloride ion,* we believe

*We have subsequently found that KCl is indispensable in that it promotes clean separation of the aqueous, tributylphosphonium chloride, and organic layers; this aids our sampling for gas chromatographic analysis greatly.

that the chlorosilane II is formed by a direct reaction of I with $n\text{-Bu}_4\text{PCl}$. Indeed, if stoichiometric quantities of I and $n\text{-Bu}_4\text{PCl}$ are allowed to react (eq. 3), a relatively fast reaction occurs and chlorosilane II is formed in quantitative yield.



While each of the reactions reported has some unusual feature with respect to the behavior of trisyl compounds [1-9], a unifying aspect in each is the presence of $n\text{-Bu}_4\text{PCl}$. Indeed, a limited number of attempts to carry out reactions analogous to reaction 1 using tetraalkylammonium phase-transfer agents failed. Although we have been unable to find examples of phosphonium salts behaving as in reactions 1-3 [10], reports of alcohol to halide conversions carried out by triphenylphosphine dihalides are relevant [11-15]. In particular, neopentyl alcohol and phenol have been converted to neopentyl bromide and bromobenzene by triphenylphosphine dibromide [11]. An intermediate of the type $\text{Ph}_3\text{P}^+\text{OR}^-\text{XHX}$ has been proposed [12]. Depending on the nature of R, such an intermediate could collapse to products, although the exact details in the case of neopentyl and phenyl are unknown and problematic. One can only speculate that the highly ionic nature of such intermediates encourages substitution by the halide in the neopentyl and phenyl cases. Similarly, we suggest that $n\text{-Bu}_4\text{PCl}$ facilitates reactions 1-3 largely by providing a highly ionic environment for such reactions. In addition, the rather severe reaction temperatures may be important.

We are continuing our work in this area with particular interest in whether these reactions occur with rearrangement [2-9] and what reactivity other phosphonium salts might have.

Acknowledgments

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