

Miscellaneous reactions of some tris(trimethylsilyl)methylsilicon compounds

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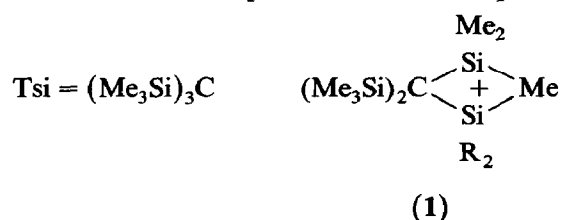
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Abstract

TsSiMe₂I (Tsi = (Me₃Si)₃C) gives TsSiMe₂OMe on treatment with AgBF₄ in MeOH but some TsSiMe₂F if an excess of CsF is also present. The triflates TsSiMe₂OSO₂CF₃ and (Me₃Si)₂C(SiMePh₂)(SiMe₂OSO₂CF₃) react with alkali metal salts MX to give the corresponding derivatives TsSiMe₂X and (Me₃Si)₂C(SiMePh₂)(SiMe₂X). TsSiMe₂OSO₂CF₃ does not react with CF₃CH₂OH. The relative rates of reaction of the halides TsSiMe₂X with X = Cl, Br or I with KSCN in boiling MeCN are roughly 1/2.5/6, revealing a suprisingly little variation in reactivity among the halides. TsSiPh₂I and TsSiMePhI undergo hydrolysis in MeCN or Me₂SO to give TsSiPh₂OH and TsSiMePhOH, the absence of rearrangement showing that cationic intermediates are not involved. TsSiPh₂I reacts slowly with KSCN in MeCN to give TsSiPh₂NCS. TsSiPh₂H reacts with IBr to give the rearranged bromide (Me₃Si)₂C(SiMePh₂)(SiMe₂Br). Under UV irradiation: (i) TsSiPh₂I in 1-bromohexane gives the rearranged bromide (Me₃Si)₂C(SiMePh₂)(SiMe₂Br); (ii) TsSiMe₂N₃ in MeOH undergoes solvolysis; (iii) ^tBu₃SiI in CCl₄ gives ^tBu₃SiCl and Cl₃CCl₃, and in MeOH undergoes photocatalysed methanolysis.

Introduction

Several novel aspects of organosilicon chemistry have been revealed by studies of highly sterically hindered compounds of the type TsSiR₂X (Tsi = (Me₃Si)₃C) [1,2] and, to lesser extent, ^tBu₃SiX [3,4]. We present here some miscellaneous observations that serve to provide a more complete picture of the relevant chemistry.



Results and discussion

Reaction of TsiSiMe₂I with AgBF₄

Reactions of the iodides TsiSiR₂I with Ag^I or Hg^{II} salts, AgY or HgY₂, in inert media such as CCl₄, CH₂Cl₂, or Et₂O are known to give the rearranged products (Me₃Si)₂C(SiR₂Me)(SiMe₂Y), either exclusively (R = Ph) or (R = Et) along with unarranged products TsiSiR₂Y, apparently via intermediate cations of type **1** [5]. In reaction of TsiSiPh₂I with AgNO₃ in MeOH, however, the rearranged methoxide (Me₃Si)₂C(SiPh₂Me)(SiMe₂OMe) and the corresponding nitrate are formed in ca. 87/13 ratio, and it seems that the solvent MeOH competes effectively with NO₃⁻ as a nucleophile in the capture of the intermediate cation. The reaction of the iodide TsiSiMe₂I with silver salts can be assumed also to proceed through a cation (**1**, R = Me), and reaction with either AgNO₃ or Hg(NO₃)₂ in MeOH likewise gives a mixture of TsiSiMeOMe and TsiSiMe₂ONO, in ca. 75/25 ratio, through somewhat surprisingly, this ratio is not affected by the presence of an excess of NaNO₃ or LiNO₃. With silver salts containing more weakly nucleophilic anions, such as AgClO₄, Ag₂SO₄, and AgOCN [6], only the methoxide is produced, though it is possible that some of the relevant TsiSiMe₂Y species are initially formed, since they would, in these cases, undergo rapid solvolysis. The tetrafluoroborate AgBF₄ is a very effective reagent for converting TsiSiMe₂I into TsiSiMe₂F in non-hydroxylic media, and it seemed of interest to determine the outcome of the reaction in MeOH, since any TsiSiMe₂F formed would remain intact. In the present work we found that reaction of the iodide with AgBF₄ in 1/6 molar ratio gave only the methoxide, but when it was carried out with a 1/1 molar ratio in the presence of an excess of CsF the fluoride TsiSiMe₂F and the methoxide were obtained in ca. 1/1 ratio. It thus seems that F⁻ can compete with MeOH for the intermediate cation, and can do so much more effectively than BF₄⁻. Reaction of CsF alone with TsiSiMe₂I in MeOH was, of course, much slower, and use of a 100-fold excess of the salt in refluxing MeOH for 24 h gave an ca. 92/8 mixture of TsiMe₂F and TsiSiMe₂OMe.

Hydrolysis of TsiSiPh₂I and TsiMePhMeI

We found that both TsiSiPh₂I and TsiSiPhMeI could be hydrolysed, though slowly. The former required 60 days refluxing with 5% (by volume) H₂O in MeCN or 24 h with 20% H₂O in Me₂SO. TsiSiPhMeI correspondingly gave TsiSiPhMeOH during 24 h refluxing in 7/2/1 (vol/vol) Me₂SO/MeCN/H₂O (the MeCN being added to increase the solubility of the iodide). These observations were of considerable significance, not only because they made the hydroxides available for the first time but also, more importantly, because the formation of only unrearranged products showed [7] that the solvolysis did not proceed through a cationic intermediate of type **1** as had been previously suspected [8]. (In contrast, TsiSiPh₂I gives exclusively the rearranged hydroxide (Me₃Si)₂C(SiPh₂Me)(SiMe₂OH) on treatment with H₂O–MeCN containing AgClO₄ [9].)

The silanol TsiSiPh₂OH, in contrast to the less hindered TsiSiMe₂OH [10], does not react with MeCOCl, no reaction being observed during 3 days' refluxing with an excess of the neat halide.

Relative reactivities of the halides TsiSiMe₂X (X = Cl, Br, I) towards KSCN in MeCN

We thought it of interest to compare the reactivities of the halides TsiSiMe₂X, with X = Cl, Br, or I, in a typical S_N2 substitution reaction. Thus pairs of the

halides in equimolar amounts were refluxed with a saturated solution of KSCN in MeCN (to give the isothiocyanates $\text{TsiSiMe}_2\text{NCS}$): samples were removed after 30 min and quickly evaporated under reduced pressure, and the ^1H NMR spectra of the residues were recorded. From the heights of the signals from the SiMe_2X and SiMe_2NCS protons the percentage of each halide which had reacted was calculated. For the pair with $\text{X} = \text{I}$ and Br , ca. 80 and 60% respectively had reacted; for the pair with $\text{X} = \text{I}$ and Cl the corresponding percentage were 80 and 40, and for $\text{X} = \text{Br}$ and Cl the percentages were 60 and 40. For pseudo first order reactions the data correspond to relative reactivities of the chloride, bromide, and iodide of 1/2.5/6. These ratios are, of course, very rough, but leave no doubt that there is surprisingly little variation in reactivity among these halides. It has been noted previously [4] that this is consistent with the small spread of reactivity for the even more hindered halides $^t\text{Bu}_3\text{SiX}$ with $\text{X} = \text{Cl}$, Br , or I , though in the latter case the chloride is actually more reactive than the iodide.

Reaction of $\text{TsiSiPh}_2\text{I}$ with KSCN

An indication of the effect of the greater steric hindrance to nucleophilic attack on $\text{TsiSiPh}_2\text{I}$ than on $\text{TsiSiMe}_2\text{I}$ was provided by the observation that the reaction of the latter iodide with a saturated solution of KSCN in refluxing MeCN was ca. 80% complete in 0.5 h and close to 100% complete in 1 h, whereas that of the former required ca. 30 days for completion. It can be estimated that $\text{TsiSiPh}_2\text{I}$ is at least 300 times less reactive than $\text{TsiSiMe}_2\text{I}$ under these conditions, and so (on the basis of data from ref. 4), probably at least 150 times less reactive than $^t\text{Bu}_3\text{SiI}$.

Treatment of $\text{TsiSiMe}_2\text{OSO}_2\text{CF}_3$ with (a) alkali metal salts in MeOH and in MeCN, and (b) $\text{CF}_3\text{CH}_2\text{OH}$

The triflate $\text{TsiSiMe}_2\text{OSO}_2\text{CF}_3$ is much more reactive than the corresponding iodide towards MeOH: thus the conversion of the triflate into the methoxide in refluxing MeOH was found to be complete within 10 min, whereas the reaction of the iodide is only 15% complete after 24 h under similar conditions [11]. We thought it of interest to see whether alkali metal salts could compete effectively with the MeOH in reaction with the triflate, and found that use of a saturated solution of NaN_3 gave, within 5 min at room temperature, exclusively the azide $\text{TsiSiMe}_2\text{N}_3$. Saturated solutions of the salts KOCN, KSCN, and KCN gave the expected derivatives $\text{TsiSiMe}_2\text{NCO}$, $\text{TsiSiMe}_2\text{NCS}$, and $\text{TsiSiMe}_2\text{CN}$, along with ca. 20% of the methoxide $\text{TsiSiMe}_2\text{OMe}$ in each case.

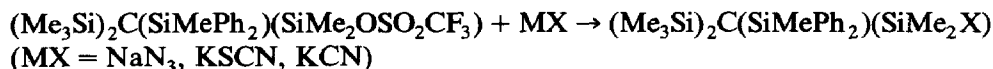
The triflate was also found to react readily with a large excess of LiCl , LiBr , or NaI in MeCN to give the corresponding $\text{TsiSiMe}_2\text{Y}$ species, but substantial amounts of the hydroxide were also obtained. This probably came from traces of water in the MeCN (though it had been dried by a standard method), but could have been formed during work-up after incomplete reaction of the triflate. It seems likely that reactions taken to completion with the salts in fully anhydrous MeCN would give the pure organosilicon halides.

No reaction was detected when a solution of $\text{TsiSiMe}_2\text{OSO}_2\text{CF}_3$ in $\text{CF}_3\text{CH}_2\text{OH}$ was refluxed for 24 h.

Reactions of $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMePh}_2)(\text{SiMe}_2\text{OSO}_2\text{CF}_3)$ with alkali metal salts in MeCN

The triflate $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMePh}_2)(\text{SiMe}_2\text{OSO}_2\text{CF}_3)$, which is somewhat less readily hydrolysed than $\text{TsiSiMe}_2\text{OSO}_2\text{CF}_3$, was found to react fairly readily in MeCN

with an excess of NaN_3 , KSCN , or KCN to give the corresponding silicon pseudohalides:



These reactions could be of use, since the products cannot in these cases be obtained directly from $\text{TsiSiPh}_2\text{I}$ by reaction with the silver salts AgX .

Reaction of TsiSiPh₂I with IBr

In reaction analogous to that with ICl [12], $\text{TsiSiPh}_2\text{I}$ was found to react with IBr in CCl_4 to give the rearranged bromide:



Photoinduced reactions

Ultra-violet irradiation of $\text{TsiSiPh}_2\text{I}$ in CCl_4 was shown previously to give the unrearranged chloride $\text{TsiSiPh}_2\text{Cl}$, apparently via the free radical $\text{TsiSiPh}_2^\cdot$, whereas irradiation in *n*-hexane or Et_2O gave the rearranged iodide $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMePh}_2)(\text{SiMe}_2\text{I})$ [13]. We were thus somewhat surprised to find that irradiation of $\text{TsiSiPh}_2\text{I}$ in 1-bromohexane for 160 h gave, as indicated by ^1H NMR spectroscopy, a 40/60 mixture of the original iodide and the rearranged bromide $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMePh}_2)(\text{SiMe}_2\text{Br})$ (possibly along with a small amount of $\text{TsiSiPh}_2\text{Br}$ which could have escaped detection). As in the case of the formation of the rearranged iodide in the reactions in hexane [13], we cannot decide between a cationic or free radical intermediate for this transformation. No rearrangement of the radical $\text{TsiSiPh}_2^\cdot$ was observed under the conditions used for an ESR study [14], but thermolysis of $\text{TsiSiPh}_2\text{I}$ is thought to involve such rearrangement [15].

The azide $\text{TsiSiMe}_2\text{N}_3$ reacted completely when its solution in MeOH was exposed to UV light for 2 h. (No reaction takes place on prolonged reflux of a methanol solution in the absence of irradiation.) Surprisingly, formation of the methoxide $\text{TsiSiMe}_2\text{OMe}$ was accompanied by that of the hydroxide $\text{TsiSiMe}_2\text{OH}$, with these products in 45/55 ratio. Formation of such a high proportion of hydroxide from traces of water would not be expected if the reaction involved the same cationic intermediate as that apparently involved in photocatalysed methanolysis of $\text{TsiSiMe}_2\text{I}$, and further study of the azide reaction is called for.

Ultra-violet irradiation of a solution of $^t\text{Bu}_3\text{SiI}$ in CCl_4 for 35 h gave a mixture of three compounds. Linked GLC-mass spectrometry showed these to be $^t\text{Bu}_3\text{SiCl}$, $^t\text{Bu}_3\text{SiI}$, and Cl_3CCCl_3 in 25/55/20 ratio. The reaction presumably involves the radical $^t\text{Bu}_3\text{Si}^\cdot$, which abstracts a Cl atom from CCl_4 to give $\text{Cl}_3\text{C}^\cdot$, and dimerization of the latter gives Cl_3CCCl_3 .

Irradiation of a solution of $^t\text{Bu}_3\text{SiI}$ in MeOH for 10 h gave a mixture of $^t\text{Bu}_3\text{SiOMe}$ and $^t\text{Bu}_3\text{SiI}$ in 75/25 ratio. There is evidently substantial photocatalysis (possibly involving an intermediate silicenium ion), since methanolysis of iodide without irradiation was previously shown to be only ca. 4% complete after 30 days at 60°C [4].

Experimental

Solvents

n-Pentane, n-hexane, diethyl ether, and tetrahydrofuran (THF) were stored over Na wire. CH_2Cl_2 , CCl_4 , $\text{CF}_3\text{CH}_2\text{OH}$, and MeCN were refluxed over and distilled from CaCl_2 and stored over a 4 Å molecular sieve. MeOH was refluxed with and distilled from $\text{Mg}(\text{OMe})_2$ and stored over a 3 Å molecular sieve under dry N_2 . CHCl_3 was shaken four times with water, dried over MgSO_4 , distilled, and stored over a 4 Å molecular sieve.

Spectra

Proton NMR spectra recorded at 60 MHz on a Perkin Elmer R12 or at 90 MHz on Perkin Elmer R32 spectrometer; unless otherwise indicated solutions were in CCl_4 containing either CHCl_3 or CH_2Cl_2 as lock and reference. The ^{19}F spectra were recorded at either 84.6 MHz on a Perkin Elmer R32 or at 75.4 MHz on a Bruker WP80 spectrometer. The IR spectra were recorded as liquid films between NaCl plates or as solutions in CCl_4 on a Perkin Elmer 157G spectrophotometer. Mass spectra were recorded at 70 eV under electron impact. Halogen-containing ions showed the expected isotope patterns.

Reaction of $\text{TsiSiMe}_2\text{I}$ with AgBF_4 in MeOH

(a) A mixture of $\text{TsiSiMe}_2\text{I}$ (0.15 g, 0.36 mmol), AgBF_4 (0.27 g, 2.03 mmol), and MeOH (50 cm^3) was stirred at room temperature for 1 h (though reaction was probably complete in a few minutes). The solution was decanted from the AgI then hexane was added, followed by an excess of water. The hexane layer was washed several times with water then evaporated under vacuum, to leave a residue that was shown by ^1H NMR spectroscopy to be exclusively $\text{TsiSiMe}_2\text{OMe}$ (δ 0.23 (s, SiMe_3), 0.27 (s, SiMe_2), and 3.33 (s, OMe).

(b) A mixture of CsF (0.15 g, 1.83 mmol) and MeOH (50 cm^3) was heated under reflux for 30 min then cooled to room temperature to give a saturated solution and $\text{TsiSiMe}_2\text{I}$ (0.10 g, 0.24 mmol) was added, followed by AgBF_4 (0.046 g, 0.24 mmol). The mixture was stirred for 1 h then worked up as in (a), to give a solid, which was shown by ^1H NMR spectroscopy to be an ca. 55/45 mixture of $\text{TsiSiMe}_2\text{F}$ (δ 0.23 (s, SiMe_3) and 0.39 (d, SiMe_2) and TsiSiMeOMe .

Hydrolysis of $\text{TsiSiPh}_2\text{I}$ and TsiPhMeSiI

(a) A solution of $\text{TsiSiPh}_2\text{I}$ (0.10 g) in a mixture of MeCN (50 cm^3) and H_2O (2.5 cm^3) was refluxed for 60 days; samples were withdrawn at intervals for recording of their ^1H NMR spectra then returned to the solution. Reaction appeared to be complete after 60 days and the solvent was removed under vacuum and the residue sublimed (120°/0.2 mmHg) to give $\text{TsiSiPh}_2\text{OH}$ (0.088 g, 90%), m.p. 132° C (Found: C, 61.4; H, 8.8. $\text{C}_{22}\text{H}_{38}\text{OSi}_4$ calcd.: C, 61.4; H, 8.8%); δ_{H} 0.22 (s, 27H, SiMe_3), 2.02 (s, 1H, OH), 7.2–8.0 (s, 10H, SiPh_2); m/z 415 (40%, $[\text{M} - \text{Me}]^+$), 399 (25), 398 (10), 337 (100; $[\text{M} - \text{PhH} - \text{Me}]^+$), 325 (15), 274 (15), 249 (30), 199 (20), 175 (20), 135 (55), 73 (50).

(b) When a similar procedure was used but with a 4/1 v/v $\text{Me}_2\text{SO}/\text{H}_2\text{O}$ mixture as solvent, reaction was complete in 24 h and the hydroxide was isolated in 88% yield.

(c) A mixture of TsiSiMePhI (0.10 g), H_2O (1 cm^3), MeCN (2 cm^3), and Me_2SO (7 cm^3) was refluxed for 24 h then cooled. An excess of ether was added, followed

by water, and the ether layer was washed several times with water then dried (MgSO_4) and evaporated to dryness. The residue was sublimed ($80^\circ\text{C}/0.2\text{ mmHg}$) to give TsiSiMePhOH (0.085 g, 85%), m.p. 101°C ; δ_{H} 0.20 (s, 27H, SiMe_3), 0.53 (s, 3H, SiMe), 1.55 (s, 1H, OH), 6.9–7.6 (m, 5H, Ph); m/z 353 ($[\text{M} - \text{Me}]^+$), 337 ($[\text{M} - \text{Me} - \text{MeH}]^+$), 275 ($[\text{M} - \text{Me} - \text{Ph}]^+$), 187, 135, 75. (The record of the relative abundances of the ions was unfortunately lost).

Treatment of $\text{TsiSiPh}_2\text{OH}$ with MeCOCl

A mixture of $\text{TsiSiPh}_2\text{OH}$ (0.10 g) and MeCOCl (10 cm^3) was refluxed for 48 h. Evaporation of the MeCOCl left unchanged $\text{TsiSiPh}_2\text{OH}$, as shown by its ^1H NMR spectrum.

Relative reactivities of $\text{TsiSiMe}_2\text{X}$, $\text{X} = \text{Cl, Br, or I}$, towards KSCN in MeCN

A mixture of KSCN (0.20 g) and MeCN (10 cm^3) was refluxed for 1 h and $\text{TsiSiMe}_2\text{I}$ (0.05 g, 0.12 mmol) and $\text{TsiSiMe}_2\text{Br}$ (0.05 g, 0.14 mmol) were then added. Refluxing was continued for 30 min and a sample (1 cm^3) then removed and evaporated quickly to dryness under vacuum. The ^1H spectrum of the residue showed that ca. 80% of the iodide and 60% of the bromide had been converted into $\text{TsiSiMe}_2\text{NCS}$.

In a similar procedure with $\text{X} = \text{I}$ and Cl the corresponding ratio was ca. 80/40, and for $\text{X} = \text{Br}$ and Cl it was ca. 60/40.

Preparation of $\text{TsiSiPh}_2\text{NCS}$

A mixture of $\text{TsiSiPh}_2\text{I}$ (0.50 g, 0.93 mmol), anhydrous KSCN (0.45 g, 4.63 mmol), and MeCN (25 cm^3) was refluxed and small samples were removed at intervals for recording of the ^1H NMR spectrum then returned to the the solution. After 30 days reaction appeared to be complete, and the mixture was cooled and an excess of hexane was added, followed by water. The organic layer was washed several times with water then dried (MgSO_4) and evaporated. The solid residue was sublimed ($135^\circ\text{C}/0.2\text{ mmHg}$) to give $\text{TsiSiPh}_2\text{NCS}$ (0.39 g, 90%), m.p. $138\text{--}141^\circ\text{C}$ (Found: C, 58.5; H, 8.2; N 3.3. $\text{C}_{23}\text{H}_{37}\text{NSSi}_4$ calcd.: C, 58.6; H, 7.9; N, 3.0%); δ_{H} 0.30 (s, 27H, SiMe_3) and 7.2–8.1 (m, 10H, SiPh_2); $\nu(\text{NCS})$ 2080 cm^{-1} ; m/z 456 (70%, $[\text{M} - \text{Me}]^+$), 397 (80), 335 (75), 309 (60), 265 (50), 247 (70), 197 (60), 175 (70), 135 (80), 73 (100).

Reaction of $\text{TsiSiMe}_2\text{OSO}_2\text{CF}_3$ with alkali metal salts

(i) *In MeOH.* A mixture of KCN (0.50 g) and MeOH was refluxed for 1 h then cooled to room temperature and added to $\text{TsiSiMe}_2\text{OSO}_2\text{CF}_3$ (0.10 g). The mixture was stirred at room temperature for 5 min then an excess of hexane was added, followed by water. The organic layer was washed several times with water then dried (MgSO_4) and evaporated, to leave solid, which was shown by ^1H NMR spectroscopy to be an ca. 80/20 mixture of $\text{TsiSiMe}_2\text{CN}$ and $\text{TsiSiMe}_2\text{OMe}$.

Similar procedures with the salts KOCN and KSCN also gave the corresponding $\text{TsiSiMe}_2\text{X}$ ($\text{X} = \text{NCO}$ or NCS) and $\text{TsiSiMe}_2\text{OMe}$ in ca. 80/20 ratio. When NaN_3 was used, however, the product appeared to be exclusively $\text{TsiSiMe}_2\text{N}_3$ though the presence of < 5% of $\text{TsiSiMe}_2\text{OMe}$ could have escaped detection.

(ii) *In MeCN.* A mixture of $\text{TsiSiMe}_2\text{OSO}_2\text{CF}_3$ (0.10 g), LiCl (0.10 g), and MeCN (10 cm^3) was refluxed for 30 min. The solvent was evaporated under vacuum and the residue was extracted with hexane. The extract was shaken several times

with water then dried (MgSO_4) and evaporated, and shown by ^1H NMR spectroscopy to be an ca. 80/20 mixture of $\text{TsiSiMe}_2\text{Cl}$ and $\text{TsiSiMe}_2\text{OH}$.

A similar procedure but with LiBr gave an ca. 65/35 mixture of $\text{TsiSiMe}_2\text{Br}$ and $\text{TsiSiMe}_2\text{OH}$, and that with NaI gave a 50/50 mixture of $\text{TsiSiMe}_2\text{I}$ and $\text{TsiSiMe}_2\text{OH}$.

Preparation of pseudohalide derivatives $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMePh}_2)(\text{SiMe}_2\text{X})$ ($\text{X} = \text{N}_3$, NCS , CN)

The triflate $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMePh}_2)(\text{SiMe}_2\text{OSO}_2\text{CF}_3)$ was made from $\text{TsiSiPh}_2\text{I}$ and $\text{AgOSO}_2\text{CF}_3$ in CH_2Cl_2 [16].

(a) A mixture of the triflate (0.10 g), NaN_3 (0.06 g), and MeOH (25 cm^3) was refluxed for 4 h then cooled. An excess of hexane was added followed by water, and the organic layer was washed several times with water then dried (MgSO_4) and evaporated. The residue was recrystallized from pentane to give $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMePh}_2)(\text{SiMe}_2\text{N}_3)$ (0.081 g, 80%), m.p. $89\text{--}91^\circ\text{C}$ (Found: C, 58.2; H, 8.3; N, 8.9. $\text{C}_{22}\text{H}_{37}\text{N}_3\text{Si}_4$ calcd.: C, 58.0; H, 8.1; N, 9.5%); δ_{H} 0.28 (s, 18H, SiMe_3), 0.36 (s, 6H, SiMe_2), 0.99 (s, 3H, SiMe), and 7.2–8.1 (m, 10H, Ph); $\nu(\text{N}_3)$ 2130 cm^{-1} ; m/z 440 (25%, $[\text{M} - \text{Me}]^+$), 412 (90, $[\text{M} - \text{N}_2 - \text{Me}]^+$), 397 (60), 335 (100), 320 (20), 262 (80), 247 (50), 216 (85), 135 (95), 73 (100).

(b) A solution of the triflate (0.10 g) and KSCN (0.86 g) in MeCN (25 cm^3) was refluxed for 3 h then evaporated under vacuum. The residue was extracted with hexane, and the extract was washed with water, dried (MgSO_4), and evaporated, and the residue was recrystallized from pentane to give $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMePh}_2)(\text{SiMe}_2\text{NCS})$ (0.975 g, 75%), m.p. $131\text{--}132^\circ\text{C}$ (Found: C, 58.2; H, 8.1; N, 2.9. $\text{C}_{22}\text{H}_{37}\text{NSSi}_4$ calcd.: C, 58.6; H, 7.85; N, 3.1%); δ_{H} 0.30 (s, 18H, SiMe_3), 0.40 (s, 6H, SiMe_2), 1.00 (s, 3H, SiMe), and 7.2–8.0 (m, 10H, Ph); $\nu(\text{NCS})$ 2070 cm^{-1} ; m/z 456 (40%, $[\text{M} - \text{Me}]^+$), 397 (80, $[\text{M} - \text{HNCS}]^+$), 378 (85), 335 (65), 309 (35), 259 (75), 247 (70), 216 (35), 197 (100), 175 (80), 105 (40), 135 (95), 75 (100).

(c) A similar procedure and work-up to that described under (b) above, but starting with KCN (0.11 g) and with reflux for 5 h, gave $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMePh}_2)(\text{SiMe}_2\text{CN})$ (0.066 g, 66%) (Found: C, 62.8; H, 8.7; N, 3.6. $\text{C}_{22}\text{H}_{37}\text{NSi}_4$ calcd.: C, 62.9; H, 8.3; N, 3.2%); δ_{H} 0.32 (s, 18H, SiMe_3), 0.40 (s, 6H, SiMe_2), 0.98 (m, 3H, SiMe), and 7.0–8.0 (m, 10H, Ph); $\nu(\text{CN})$ 2090 cm^{-1} .

Preparation of $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMePh}_2)(\text{SiMe}_2\text{Br})$

A solution of IBr (0.080 g, 0.36 mmol) in CCl_4 (5 cm^3) was added to one of $\text{TsiSiPh}_2\text{I}$ (0.10 g, 0.18 mmol) in CCl_4 (10 cm^3) and the mixture was stirred at room temperature for 3 h. Volatile materials were removed under reduced pressure and the residue sublimed ($80^\circ\text{C}/0.2\text{ mmHg}$) to give $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMePh}_2)(\text{SiMe}_2\text{Br})$ (0.085 g, 82%), m.p. 159°C (Found: C, 53.8; H, 7.7. $\text{C}_{22}\text{H}_{37}\text{BrSi}_4$ calcd.: C, 53.7; H, 7.5%); δ_{H} 0.35 (s, 18H, SiMe_3), 0.77 (s, 6H, SiMe_2), 1.04 (s, 3H, SiMe), and 7.2–8.1 (m, 10H, Ph); m/z 477 (15%, $[\text{M} - \text{Me}]^+$), 399 (50, $[\text{M} - \text{Me} - \text{PhH}]^+$), 325 (25), 282 (20), 267 (20), 135 (80), 105 (30), 73 (100).

Photoinduced reactions

Reactions carried out with stirring under N_2 in a quartz vessel irradiated with the light from a Hanovia medium pressure Hg lamp UVS 500 at a distance of 10 cm. The irradiation substantially raised the temperature of the solution.

(a) A solution of $\text{TsiSiPh}_2\text{I}$ (0.50 g) in 1-bromohexane (20 ml) was irradiated for 160 h. Ether was added followed by water, and the organic layer was dried (MgSO_4) filtered, and evaporated, to leave a solid which from its ^1H NMR spectrum was judged to be a 40/60 mixture of unchanged $\text{TsiSiPh}_2\text{I}$ and $(\text{Me}_3\text{Si})_2\text{C}(\text{SiMePh}_2)(\text{SiMe}_2\text{Br})$.

(b) A solution of $\text{TsiSiMe}_2\text{N}_3$ (0.20 g) in MeOH (10 cm^3) was irradiated for 2 h. Evaporation of the solvent under vacuum left a solid, which from its ^1H NMR spectrum was judged to be a 55/45 mixture of $\text{TsiSiMe}_2\text{OH}$ and $\text{TsiSiMe}_2\text{OMe}$.

(c) A solution of $^t\text{Bu}_3\text{SiI}$ (0.10 g) in CCl_4 (10 cm^3) was irradiated for 35 h then shaken with aqueous NaHSO_3 to remove some free I_2 and finally shaken with water and evaporated under vacuum. The ^1H NMR spectrum of the residue was complex. Mass spectroscopy linked to GLC (5% OV101 at 230°C) revealed the presence of 3 components, A, B, and C, with peaks in an approximate area ratio of 25/20/55, which were judged to be respectively: (i) $^t\text{Bu}_3\text{SiCl}$, m/z 177 (10%, $[\text{M} - \text{Bu}]^+$), 93 (100, $[\text{Me}_2\text{SiCl}]^+$), with the expected isotope patterns; (ii) Cl_3CCCl_3 , m/z 199 ($[\text{M} - \text{Cl}]^+$), 165, 149, 117 ($[\text{CCl}_3]^+$); and (iii) $^t\text{Bu}_3\text{SiI}$, m/z 269 (25%, $[\text{M} - \text{Bu}]^+$), 185 (100, $[\text{Me}_2\text{SiI}]^+$).

(d) A solution of $^t\text{Bu}_3\text{SiI}$ (0.10 g) in MeOH (10 cm^3) was irradiated for 10 h. The solvent was evaporated off under vacuum to leave a residue, which from its ^1H NMR spectrum and data from linked GLC-mass spectrometry was judged to be a roughly 75/25 mixture of $^t\text{Bu}_3\text{SiI}$ (δ_{H} 1.24 (s)) and $^t\text{Bu}_3\text{SiOMe}$ (δ_{H} 1.14(s) and 3.40(s); m/z 173 (15%, $[\text{M} - \text{Bu}]^+$), 89 (100, $[\text{Me}_2\text{SiOMe}]^+$)).

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