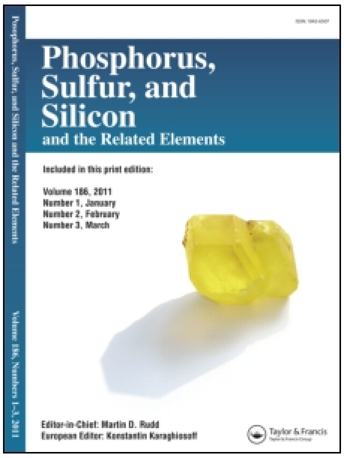

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# The Reactions of the Highly Sterically Hindered Organosilicon Compound Tsisi($C_6H_4$Me-*P*)Mei with Electrophilic Reagents and Synthesis Of Tsisii$_3$

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# THE REACTIONS OF THE HIGHLY STERICALLY HINDERED ORGANOSILICON COMPOUND TsiSi($C_6H_4$Me-*p*)MeI WITH ELECTROPHILIC REAGENTS AND SYNTHESIS OF $TsiSiI_3$

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*The iodide TsiSi($C_6H_4$Me-*p*)MeI reacts with a range of silver (I) salts, AgY (Y = $OCN^-$, $BF_4^-$, $OOCCF_3^-$, $SO_4^{2-}$) and mercury (II) salts, $Hg_2Y$ (Y = $OCCH_3^-$, $SO_4^{2-}$) to give the corresponding species $(Me_3Si)_3$CSi($C_6H_4$Me-*p*)MeY and $(Me_3Si)_2$C($SiMe_2$Y)$SiMe_2$($C_6H_4$Me-*p*). The reactions with AgOCN give either the isocyanate alone or a mixture of this with the normal cyanate, depending on the reaction conditions. The reaction with $AgBF_4$ in $Et_2O$ gives only TsiSi($C_6H_4$Me-*p*)MeF while in MeOH, EtOH or i-PrOH gives the corresponding rearranged product $(Me_3Si)_2$C($SiMe_2$Y)$SiMe_2$($C_6H_4$Me-*p*) (Y = $OMe^-$, $OEt^-$, i-$OPr^-$). The iodide also reacts with IBr to give the rearranged bromide $(Me_3Si)_2$C($SiMe_2$Br)$SiMe_2$($C_6H_4$Me-*p*). The highly sterically hindered triiodide, $TsiSiI_3$ was also synthesized.*

*Keywords:* Silicon; steric hindrance; trisyl

## INTRODUCTION

It has been shown that the presence of the tris(trimethylsilyl)methyl ("trisyl"), $(Me_3Si)_3$C-(denoted Tsi), in compounds of the type TsiSiRR' X cause a very large steric hindrance toward electrophilic displacement of X.[1–4] In reactions of TsiSiRR'I (R = Me, $R^1$ = $C_6H_4$Me-*p*) species with electrophilic Ag(I)Y salts give rearranged products $(Me_3Si)_2$C ($SiMe_2$Y) (SiRR'Me), either exclusively or with the unrearranged products TsiSiRR'Y.[5] There is strong evidence that these reactions involve formation of a bridged cation of type I (the migrating Me group), which is then attacked by a nucleophilic $Y^-$, with opening of the four-membered

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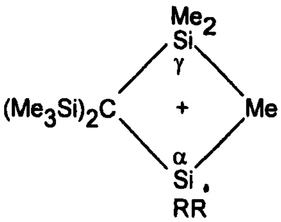

FIGURE 1

ring, at either the Si atom, attack at the least hindered center normally being favored. In this work, some other electrophilic reactions on TsiSi($C_6H_4$Me-*p*)MeI with different electrophiles such as AgOCN, $AgBF_4$, $AgO_2CCF_3$, $Ag_2SO_4$, and $AgO_2CCH_3$ have been examined. The results are described below.

## RESULTS AND DISCUSSION

The study began with the iodide TsiSi($C_6H_4$Me-*p*)MeI, which was made as described previously by treatment of TsiSi($C_6H_4$Me-*p*)MeH with one molar proportion of ICl in carbon tetrachloride.[6] We thought it of interest to examine its reactions with some other silver and mercury salts. The obtained results show that steric hindrance and the reactivity of the starting reagents in the reactions of iodide are the major points.

### Reactions of TsiSi($C_6H_4$Me-*p*)MeI with Silver(I) Salts

a) Treatment of iodide with AgOCN in refluxing $Et_2O$ gave exclusively the isocyanate TsiSi($C_6H_4$Me-*p*)Me(NCO) as judged from the presence of an IR band at 2300 $cm^{-1}$.[6] However, when the reactions was carried out in $CH_2Cl_2$ at room temperature for 20 h, its IR spectrum showed also the band at 2300 $cm^{-1}$, and a band approximately at 2240 $cm^{-1}$ characteristic of a normal cyanate TsiSi ($C_6H_4$Me-*p*) Me(OCN).[6,7] The ratio were 2:1, respectively.

b) In keeping with the results described above, when the iodide TsiSi ($C_6H_4$Me-*p*)MeI was treated with $AgBF_4$ in refluxing $Et_2O$, the product was exclusively TsiSi($C_6H_4$Me-*p*)MeF (as judged) from the $^1$HNMR spectrum.[8]

c) The iodide was found to react with $AgBF_4$ in MeOH, conversion into the rearranged methoxide $(Me_3Si)_2C(SiMe_2OMe)SiMe_2(C_6H_4Me$-*p*) complete within 3 h (may be completed at less than 3 h) at room temperature. When the same iodide was stirred with $AgBF_4$ in EtOH at room temperature for 3 h (3 h period used may not be necessary) gave the rearranged ethoxide $(Me_3Si)_2C(SiMe_2OEt)SiMe_2(C_6H_4Me\text{-}p)$. The iodide was also found to react with $AgBF_4$ in *i*-PrOH to give the rearranged isopropoxide $(Me_3Si)_2C(SiMe_2O\text{-}i\text{-}Pr)SiMe_2(C_6H_4Me\text{-}p)$ when the mixture was stirred for 4.5 h at room temperature.

d) Reaction of $TsiSi(C_6H_4Me\text{-}p)MeI$ with $AgOCOCF_3$ in refluxing $Et_2O$ gave a mixture of rearranged product $(Me_3Si)_2C(SiMe_2OCOCF_3)SiMe_2(C_6H_4Me\text{-}p)$ and unrearranged product $TsiSi(C_6H_4Me\text{-}p)Me(OCOCF_3)$ in 3:1 ratio, respectively.

e) Reaction of $TsiSi(C_6H_4Me\text{-}p)MeI$ with $Ag_2SO_4$ in glacial $CH_3COOH$ gave mainly the rearranged acetate $(Me_3Si)_2C(SiMe_2OAc)SiMe_2(C_6H_4Me\text{-}p)$.

f) The reaction of starting iodide $TsiSi(C_6H_4Me\text{-}p)MeI$ with $HgSO_4$ or $Hg(O_2CH_3)_2$ in glacial $CH_3COOH$ also gave mainly rearranged acetate $(Me_3Si)_2C(SiMe_2O_2CCH_3)SiMe_2(C_6H_4Me\text{-}p)$.

An attempt to make $TsiSiAn_2I$ by the reaction of the $TsiSiAn_2H$ with ICI by analogy with corresponding reaction of $TsiSiPh_2H$[9] was unsuccessful.[10] We were aware that the HCl or HI generated would very readily cleave the Si-An bonds[11] and so we carried out the reaction in the presence of a large excess of $AnSiMe_3$ to take up the HX preferentially. This did ensure survival of the Si-An bonds of the $TsiSiAn_2H$, but unfortunately, the product was the chloride, not the iodide. So we carried out the reaction of $TsiSiAn_2H$ with $I_2$ and Al powder since $I_2\text{-}AlI_3$ is a very reactive reagent, but the result showed that the An groups were cleaved off and highly sterically hindered triiodide $TsiSiI_3$ was obtained. When $TsiSiPh_2H$ was also treated with $I_2$ and Al powder in benzene, the Ph groups were also cleaved off and $TsiSiI_3$ was produced. Finally we found that the simplest way to get $TsiSiI_3$ is to treat $TsiSiH_3$ with $I_2$ and Al powder under the conditions used for $TsiSiAn_2H$ and $TsiSiPh_2H$. The iodide $TsiSi(C_6H_4Me\text{-}p)MeI$ was found to react with IBr in $CCl_4$ to give the rearranged bromide $(Me_3Si)_2C(SiMe_2Br)SiMe_2(C_6H_4Me\text{-}p)$.[12,13]

## EXPERIMENTAL

### Solvents and Reagents

Cyclohexane, n-pentane, n-hexane, diethylether, dichloromethane, tetrachloromethane, methanol were dried by standard methods, silver salts Ag(I)Y (Y = $OCOCF_3$, OCN) freshly made.

## Spectra

The $^1$HNMR spectra were recorded on Perkin Elmer (80 MHz) with $CDCl_3$ as a solvent and $CH_2Cl_2$ or $SiMe_4$ as internal standard. The FT-IR spectra were recorded with KBr disk on DR 408-Shimadzu. Melting points were determined with a 9100 Electrothermal apparatus. Mass spectra were obtained with a Shimadzu-QP-100X, 70ev.

## Reaction of TsiSi($C_6H_4Me$-*p*)MeI with $AgBF_4$ in $Et_2O$

A mixture of TsiSi($C_6H_4Me$-*p*)MeI (0.2 g, 0.4 mmol), $AgBF_4$ (0.155 g, 0.8 mmol) in dried $Et_2O$ (50 ml) was stirred under reflux for 1h. The solvent was evaporated off and the residue extracted with pentane. The extract was filtered and evaporated and then the residue was recrystallized from MeOH to give TsiSi($C_6H_4Me$-*p*)MeF (92%), m.p. 117°C. $^1$HNMR ($CDCl_3$) 0.1 (s, 27 H, $SiMe_3$), 0.35 (s, 3 H, MeSi), 2.2 (s, 3 H, $\underline{Me}$-aryl), and 6.7–7.8 ppm (m, 4 H, aryl); *m/z* (EI) 385 (6.8%, $[M]^+$), 370 (100%, [M-Me]), 349 (4%), 277 (22.4%), 261 (21.3%), 201 (53.8%), 149 (31%), 73 (38.6%).(Found: C, 55.76; H, 9.28. $C_{18}H_{37}FSi_4$ calculated: C, 56.18; H, 9.69).

## Reaction of TsiSi($C_6H_4Me$-*p*)MeI with $AgBF_4$ in MeOH

A mixture of TsiSi($C_6H_4Me$-*p*)MeI (0.24 g, 0.5 mmol) and $AgBF_4$ (0.38 g, 2.7 mmol) in dried MeOH (50 ml) was stirred at room temperature for 3 h. The solution was decanted from AgI and water and cyclohexane was added. The cyclohexane layer was shaken several times with water. The residue was recrystallized from MeOH and then purified further with sublimation at 100°C at 5 mmHg to give pure rearranged methoxide $(Me_3Si)_2C(SiMe_2OMe)SiMe_2(C_6H_4Me$-*p*) with properties identical to those described before,[5] m.p. 118°C.

## Reaction of TsiSi($C_6H_4Me$-*p*)MeI with $AgBF_4$ in EtOH

A mixture of TsiSi($C_6H_4Me$-*p*)MeI (0.24 g, 0.5 mmol) with $AgBF_4$ (0.38 g, 2.7 mmol) in dried EtOH (50 ml) was stirred at room temperature for 3h. The solution was decanted from AgI and water and cyclohexane was added. The cyclohexane layer was shaken several times with water. The viscous residue was recrystallized from EtOH to give the rearranged ethoxide $(Me_3Si)_2C(SiMe_2OEt)SiMe_2(C_6H_4Me$-*p*) (85%); m.p. 77–78°C. $^1$HNMR ($CDCl_3$) 0.1 (s, 6 H, $\underline{SiMe_2}$-aryl), 0.15 (s, 18 H, $(SiMe_3)_2$), 0.5 (s, 6 H, $\underline{SiMe_2}OEt$), 1–1.3 (t, 3 H, $\underline{CH_3}CH_2$-), 2.2 (s, 3 H, $\underline{Me}$-aryl), 3.4–3.7 (q, 2 H, $CH_3\underline{CH_2}$-) and 6.7–7.8 ppm (m, 4 H, aryl).

## Reaction of TsiSi($C_6H_4$Me-*p*)MeI with $AgBF_4$ in *i*-PrOH

A mixture of TsiSi($C_6H_4$Me-*p*)MeI (0.24 g, 0.5 mmol) and $AgBF_4$ (0.38 g, 2.7 mmol) in dried *i*-PrOH (50 ml) was stirred at room temperature for 4.5 h. The solution was decanted from AgI and water and cyclohexane was added. The cyclohexane layer was shaken several times with water and evaporated. The viscous residue was purified by preparative TLC (silicagel 2:1 dichloromethane-cyclohexane) to give the rearranged isopropoxide $(Me_3Si)_2C(SiMe_2O\text{-}i\text{-}Pr)SiMe_2(C_6H_4Me\text{-}p)$ (78%). $^1$HNMR ($CDCl_3$) 0.3 (s, 18 H, $(SiMe_3)_2$), 0.5 (s, 6 H, $\underline{SiMe_2}O$-*i*-Pr), 0.65 (s, 6 H, $\underline{SiMe_2}$-aryl), 1.1–1.4 (d, 6 H, $\underline{(CH_3)_2}CH$-), 2.4 (s, 3 H, $\underline{Me}$-aryl), 3.9–4.1 (m, 1 H, $(CH_3)_2\underline{CH}$-) and 6.7–7.8 ppm (m, 4 H, aryl).

## Reaction of TsiSi($C_6H_4$Me-*p*)MeI with $Ag_2SO_4$

A mixture of TsiSi($C_6H_4$Me-*p*)MeI (0.24 g, 0.5 mmol) with $Ag_2SO_4$ (0.5 g, 1.6 mmol) in glacial $CH_3COOH$ (15 ml) was refluxed for 2 h. The solution was decanted from AgI and water and cyclohexane was added. The cyclohexane layer was shaken several times with water and then evaporated. The residue was then purified by preparative TLC (silicagel 3:1 dichloromethane-cyclohexane as eluent) to give rearranged acetate $(Me_3Si)_2C(SiMe_2OAc)SiMe_2(C_6H_4Me\text{-}p)$ (80%) with properties identical to those described before.[5]

## Reaction of TsiSi($C_6H_4$Me-*p*)MeI with $HgSO_4$

A mixture of TsiSi($C_6H_4$Me-*p*)MeI (0.24 g, 0.5 mmol) and $HgSO_4$ (0.5 g, 1.6 mmol) in glacial $CH_3COOH$ (15 ml) was refluxed for 2.5h. The solution was decanted and water and cyclohexane was added. The cyclohexane layer was shaken several times with water and then evaporated. The residue was purified by preparative TLC (silicagel 3:1 dichloromethane-cyclohexane as eluent) to give rearranged acetate $(Me_3Si)_2C(SiMe_2OAc)SiMe_2(C_6H_4Me\text{-}p)$ (75%) with properties identical to those described before.[5]

## Reaction of TsiSi($C_6H_4$Me-*p*)MeI with $Ag(O_2CCH_3)_2$

A mixture of TsiSi($C_6H_4$Me-*p*)MeI (0.24 g, 0.5 mmol) with $Ag(O_2CCH_3)_2$ (0.32 g, 1.0 mmol) in glacial $CH_3COOH$ (15 ml) was refluxed for 2 h. The solution was decanted and water and cyclohexane was added. The cyclohexane layer was shaken several times with water and then evaporated. The residue was purified by preparative TLC (silicagel 3:1 dichloromethane-cyclohexane as eluent) to give rearranged acetate

$(Me_3Si)_2C(SiMe_2OAc)\ SiMe_2(C_6H_4Me\text{-}p)$ (70%) with properties identical to those described before.[5]

## Reaction of $TsiSi(C_6H_4Me\text{-}p)MeI$ with IBr

A solution of IBr (0.084 g, 0.4 mmol) in $CCl_4$ (10 ml) was added to $TsiSi(C_6H_4Me\text{-}p)MeI$ (0.1 g, 0.2 mmol) in $CCl_4$ (30 ml) and the mixture was stirred at room temperature for 4 h and then evaporated under vaccum. The residue was purified by preparative TLC (silicagel 1:1 dichloromethane-cyclohexane as eluent) to give $(Me_3Si)_2C(SiMe_2Br)\ SiMe_2(C_6H_4Me\text{-}p)$ (42%);. $^1$HNMR ($CDCl_3$) 0.2 (s, 18 H, $SiMe_3$), 0.55 (s, 6 H, $SiMe_2Br$), 1.1 (s, 6 H, $\underline{SiMe_2}$-aryl), 2.3 (s, 3 H, $\underline{Me}$-aryl), and 6.7–7.8 ppm (m, 4 H, aryl); *m/z* (EI) 445 (3.6%, $[M]^+$), 430 (12.6%, [M-Me]), 367 (56.6%), 351 (26.5%), 291 (4.8%), 275 (93.9%), 73 (100%). (Found: C, 49.18; H, 9.05. $C_{18}H_{37}BrSi_4$ calculated: C, 48.5; H, 8.37).

## Preparation of Tris(trimethylsilyl)triiodidosilane, $TsiSiI_3$

A solution of $I_2$ (0.96 g, 3.81 mmol) in benzene (10 ml) was added dropwise to a mixture of $TsiSiH_3$[2] (0.0.5 g, 1.91 mmol) and Al powder (0.3 g, 11.11 mmol) in benzene (40 ml) at room temperature. The reaction was followed by analytical TLC. After the completion of the reaction (60h) the excess $I_2$ was neutralized with sodium thiosulfate. Petroleum ether (40–60) was added, then the organic layer was shaken several times with water and evaporated. The solid residue was recrystallized from cold EtOH to give pure $TsiSiI_3$ (72%); m.p. > 360°C. $^1$HNMR ($CDCl_3$), 0.5 (s, 9 H, $SiMe_3$) and 1.3 ppm (s, 18 H, $SiMe_3$); *m/z* (EI) 625 (M-Me), 513 (M-I), 425, 313, 186, 128, 73. (Found: C, 18.9; H, 4.2. $C_{10}H_{27}Si_4I_3$ calculated: C, 19.7; H, 4.3).

## Reaction of $TsiSi(C_6H_4OMe\text{-}p)_2H$ with $I_2$/Al

a) In a attempt to make $TsiSi(C_6H_4OMe\text{-}p)_2I$, a mixture of $TsiSi(C_6H_4\ OMe\text{-}p)_2H$ (0.5 g, 1.05 mmol), $I_2$ (0.81 g, 3.18 mmol) and Al powder (0.3 g, 11.11 mmol) in benzene (50 ml) was stirred at room temperature. The reaction was followed by analytical TLC. After the completion of the reaction (12 h) the excess $I_2$ was neuterized with sodium thiosulfate. Water was added followed by petroleum ether (40–60) and the organic layer was shaken several times with water and evaporated. The solid residue was recrystallized with EtOH to give pure $TsiSiI_3$, (not the expected $TsiSi(C_6H_4OMe\text{-}p)_2I$) (72%) with properties identical to those described above; m.p. > 360°C.

b) When the procedure was repeated but starting from $TsiSiPh_2H$, pure $TsiSiI_3$ was also obtained in good yield.

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