The Effects of the Vinyl Groups in Reactions of the Highly Sterically Hindered Compound [Tris(trimethylsilyl)methyl]divinylsilyl Chloride

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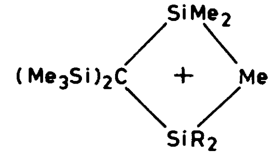
The compound $TsiSi(CH=CH_2)_2Cl$, (**1**) [Tsi = $(Me_3Si)_3C$] has been found to react with CsF, NaN_3, KSCN, and KOCN in MeOH or MeCN to give $TsiSi(CH=CH_2)_2X$ compounds with X = F, N_3, NCS, and NCO, respectively; in the reaction with KSCN in MeCN and CsF in MeOH, (**1**) is a little more reactive than $TsiSiMe_2Cl$, (**2**). Reaction of (**1**) with AgO_3CCF_3 in CF_3CO_2H gave a *ca.* 1:1 mixture of $TsiSi(CH=CH_2)_2O_2CCF_3$ and its isomer $(Me_3Si)_2C[Si(CH=CH_2)_2Me](SiMe_2O_2CCF_3)$, in a process thought to involve an intermediate methyl-bridged silico-cation; in this reaction, (**1**) is *ca.* 5 times less reactive than (**2**), and the significance of this is discussed. Reaction of (**1**) with 2M NaOMe–MeOH gives the fragmentation product $(Me_3Si)_2CHSi(CH=CH_2)_2OMe$, probably *via* a sila-olefin intermediate. In the reaction of (**1**) with $LiAlH_4$ in Et_2O there is unexpected reduction of vinyl groups, to give a mixture of $TsiSi(CH=CH)_2H$, $TsiSiEt(CH=CH_2)H$, and $TsiSiEt_2H$.

Much novel chemistry has emerged from studies of reactions of compounds of the type $TsiSiR_2X$ [Tsi = $(Me_3Si)_3C$], with R = Me, Et, or Ph, for example.[1–4] We have now extended the investigation to compounds of this type having R = $CH=CH_2$, in order to determine the effects of the vinyl groups in various types of reaction. We were especially interested in observing the effects in reactions with silver salts, which are believed to involve rate-determining formation of bridged ions of type (**I**).[2]


(**I**)

$TsiSi(CH=CH_2)_2Cl$
(**1**)

$TsiSiMe_2Cl$
(**2**)

Results and Discussion

We had hoped to make the iodide $TsiSi(CH=CH_2)_2I$ in order to compare its reaction with those of the corresponding iodides $TsiSiR_2I$ having R = Me, Et, or Ph, which have been examined in detail.[1,2] To this end we made $TsiSi(CH=CH_2)_2Cl$, (**1**), by treatment of TsiLi with $(CH_2=CH)_2SiCl_2$, intending to reduce it to the hydride $TsiSi(CH=CH_2)_2H$, which should be convertible into the iodide. To our surprise, attempted reduction of (**1**) with $LiAlH_4$ in Et_2O gave a mixture of $TsiSi(CH=CH_2)_2H$, $TsiSi(CH=CH_2)EtH$, and $TsiSiEt_2H$ (in a 1:2:1 ratio); *i.e.* there had been reduction of the vinyl groups. Such reduction does not normally occur in reactions of vinylchlorosilanes with $LiAlH_4$; *e.g.* treatment of $R_2(CH_2=CH)SiCl$ compounds with R = Me, Et, or Ph with the hydride in Et_2O gave the compounds $R_2(CH=CH_2)SiH$ in good yield.[5] However, reduction of olefinic bonds by $LiAlH_4$ in Et_2O in the presence of $AlCl_3$ is known,[6] and we suggest that in the reaction of (**1**) steric hindrance reduces the ease of reaction at the Si–Cl bond to such an extent that, after release of some $AlCl_3$ in that reaction, the reduction of the double bonds becomes competitive.

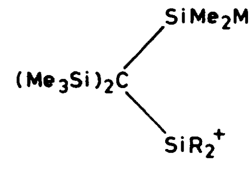
Since the iodide $TsiSi(CH=CH_2)_2I$ was not available we had to use the chloride (**1**) in the subsequent studies.

Reactions of (**1**) *with Silver Salts.*—As expected from the observations on (**2**),[2] chloride (**1**) was found not to react upon prolonged reflux with: (i) $AgNO_3$ in MeOH; (ii) $AgNO_3$ in a mixture of MeOH and tetrahydrofuran (THF) containing pyridine (which is reported to catalyse the reaction of Bu^tMe_2SiCl with $AgNO_3$ in MeOH–THF);[7] and (iii) AgOCN or $AgNO_3$ in CH_2Cl_2. However, like (**2**)[2] the chloride (**1**) does react with AgO_2CCF_3 in CF_3CO_2H under reflux; analysis by g.l.c. revealed that the reaction was *ca.* 17% complete in 9 h, 40% in 24 h, and 85% in 95 h, indicating a half-life of *ca.* 33 h. After 200 h, work-up yielded a solid, which gave two singlets of equal height in the ^{19}F n.m.r. spectrum, at −76.1 and −75.8 p.p.m., and which was judged to be a *ca.* 1:1 mixture of the unrearranged $TsiSi(CH=CH_2)_2O_2CCF_3$ and the rearranged $(Me_3Si)_2C[Si(CH=CH_2)_2Me](SiMe_2O_2CCF_3)$. The ^1H n.m.r. spectrum was consistent with this [*e.g.*, signals were observed from the $Si(CH=CH_2)_2$*Me* and $SiMe_2O_2CCF_3$ protons]. Examination by linked g.l.c.-mass spectrometry gave only one peak, with a mass spectrum consistent with either isomer.

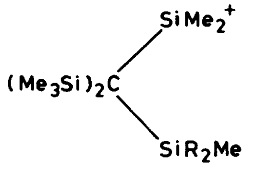
The observation of the migration of an Me group confirms that the reaction involves an intermediate cation (**I**; R = $CH=CH_2$), and the fact that there are approximately equal amounts of rearranged and unrearranged products (as in the reaction of $TsiSiEt_2I$) can be taken to indicate that in the attack of the nucleophile on (**I**), the steric effect of the vinyl groups is not much different from that of Me or Et groups. The absence of any observable migration of the vinyl group has an important bearing on the possibility that the intermediate might be an equilibrium mixture of open ions such as (**IIa**) and (**IIb**), rather than the cyclic species (**I**), since if these open ions were present one of the vinyl groups in (**IIb**) would be expected to migrate much more readily than a Me group. [The vinyl group should be a more effective bridging group than Me, as it is in bridging between Al centres, and has been shown to provide much more powerful anchimeric assistance than Me in reactions of $(Me_3Si)_2C(SiMe_2CH=CH_2)(SiMe_2I)$ with silver salts.[8]]

When (**2**) was treated with AgO_2CCF_3–CF_3CO_2H under identical conditions, the conversion into $TsiSiMe_2O_2CCF_3$ was *ca.* 10% complete in 1 h, 20% in 2 h, and 75% in 13 h, indicating a half-life of *ca.* 6.5 h, and showing that (**2**) is *ca.* 5 times as reactive as (**1**) under these conditions.

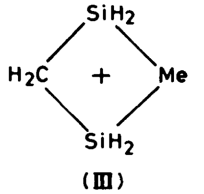
In order to discuss the influence of the vinyl groups in this



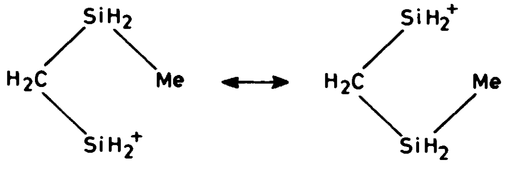
(IIa)



(IIb)



(III)



(IIIa) (IIIb)

reaction we first consider the nature of the cation (**I**). Calculations on the model bridged ion (**III**) indicate that the positive charge is shared between the two silicon atoms in the four-membered ring,[9] and so it is reasonable to regard the ion as a hybrid of the two canonical forms (**IIIa**) and (**IIIb**). If the ion (**I**) is regarded in the same light, then if R stabilizes a silicenium ion centre more than does Me, it should also stabilize (**I**), and a transition state on the way to it, more than does Me. The steric effect of the vinyl group seems not to differ much from that of an Me group in these systems, as indicated by the formation of equal amounts of rearranged and unrearranged products from (**1**; R = $CH=CH_2$) (see above), and also by the fact that in reactions with alkali metal salts MX, which involve attack of the nucleophiles X^- at silicon, (**1**) and (**2**) have very similar reactivities. Thus it seems that relative to methyl groups, vinyl groups may destabilize (**I**) by inductive electron withdrawal, which cannot be effectively opposed by conjugative electron release. The simplest explanation of this would be that such electron release requires $(p \rightarrow p)_\pi$ bonding, which is normally regarded as greatly disfavoured for silicon, although very effective for carbon centres, attachment of a vinyl group to a carbenium ion centre producing a considerably stabilized allyl cation. This interpretation would, however, be in conflict with recent calculations which indicate that replacement of two hydrogen atoms of the planar ion MH_3^+ by two vinyl groups leads to about 60% as much stabilization for M = Si as for M = C, and that the stabilization is largely conjugative.[10] The conclusions from the calculations and from our observations can be reconciled if it is assumed that the geometry of the ion (**1**) is unfavourable for conjugation between the vinyl groups and the electron-deficient silicon centre, the disposition of bonds around the silicon being well removed from that of a planar silicenium ion, and steric hindrance by the Me_3Si groups also possibly preventing the vinyl groups from taking up positions appropriate to effective conjugation.

Reactions of (**1**) *with Alkali Metal Salts.*—Chloride (**1**) was found to react with an excess of salts MX, *viz.* CsF, NaN_3, KSCN, and KOCN, in MeCN or MeOH to give the corresponding $TsiSi(CH=CH_2)_2X$ species (the isothiocyanate and isocyanate from KSCN and KOCN, respectively). The absence of detectable amounts of $TsiSi(CH=CH_2)_2OMe$ in the products from the reactions in MeOH is noteworthy, since under similar conditions reaction of the iodide $TsiSiMe_2I$ gave $TsiSiMe_2OMe$ along with the $TsiSiMe_2X$ species.[11] This difference between the outcome of the reactions of the chloride (**1**) and the iodide $TsiSiMe_2I$ is attributable to the fact that, in these sterically hindered systems at least, chlorides are much less reactive than the corresponding iodides in methanolysis (which seems to involve a transition state with substantial silicocationic character[12]), but not much less reactive than the iodides in direct bimolecular substitutions by the nucleophiles X^-.[13]

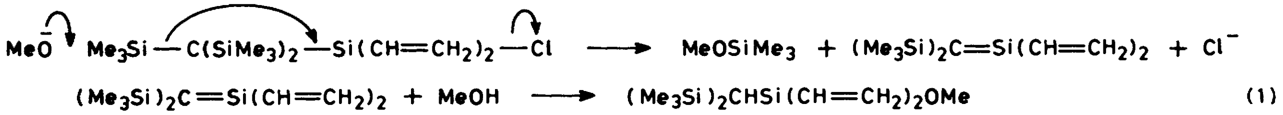
The reactivities of the chlorides (**1**) and (**2**) towards KSCN in MeCN were compared by keeping under reflux in the same bath separate solutions of the chlorides (0.15 mmol) in MeCN (20 cm^3) containing an excess of KSCN (2.06 mmol) and monitoring the progress of the reactions by g.l.c. After 2 h, 73% of (**1**) and 52% of (**2**) had been converted into the corresponding isothiocyanates, and after 5 h 100% of (**1**) and 85% of (**2**) had reacted. The results indicate that (**1**) is *ca.* twice as reactive as (**2**) in this type of reaction.

When a solution of (**1**) (0.40 mmol) in MeCN (20 cm^3) containing KOCN (6.2 mmol) was boiled under reflux, the conversion into isocyanate was *ca.* 20% complete after 2 h and effectively complete in 30 h. With CsF under similar conditions, reaction of (**1**) was 40% complete in 8 h, and effectively complete in 60 h. With NaN_3 reaction was complete in 48 h. The order of effectiveness of the salts appears to be KSCN > KOCN > NaN_3 > CsF, as observed for the corresponding reactions of $TsiSiMe_2I$;[11] this cannot, however, be taken as the order of effectiveness of the nucleophiles X^- since the salts did not all dissolve fully, NaN_3 having an especially low solubility. (Because of this the reaction with NaN_3 is faster in MeOH, in which the salt dissolves readily, than in MeCN, whereas the opposite is true for the other salts.)

Reaction of (**1**) (0.40 mmol) with NaN_3 (6.2 mmol) in refluxing MeOH (20 cm^3) was 50% complete after *ca.* 6 h (and complete in 30 h). Under similar conditions, reaction with KOCN was 50% complete in *ca.* 2 days (and complete within 12 days), and that with KSCN was complete within 10 days. When a solution of (**1**) (0.029 mmol) and CsF (0.25 mmol) in MeOH (1 cm^3) was kept in an n.m.r. tube at 60 °C, monitoring by ^1H n.m.r. spectroscopy gave a good first-order plot with a half-life of *ca.* 28 h; under similar conditions the half-life for reaction of (**2**) was *ca.* 38 h, so that under these conditions (**1**) is 1.4 times as reactive as (**2**). After allowance for temperature and concentration differences the order of effectiveness of the nucleophiles appears to be $N_3^- > F^- > SCN^-, OCN^-$, consistent with that observed for reaction of $TsiSiMe_2I$.[11] (It is likely that SCN^- is more effective than OCN^-, as in the reaction with $TsiSiMe_2I$, but our results did not permit a distinction.)

No reaction took place when solutions of the $TsiSi(CH=CH_2)_2X$ compounds with X = N_3, NCO, NCS, or F in MeOH were kept at 60 °C for 7 days.

Reaction of (**1**) *with* NaOMe–MeOH.—When a solution of (**1**) in 2.0M NaOMe–MeOH was boiled under reflux for 18 h, the sole product was $(Me_3Si)_2CHSi(CH=CH_2)_2OMe$. (We should note, however, that this was isolated in only 20% yield; this was probably because of mechanical losses in isolating an oil from a small-scale experiment, but it is conceivable that other fragmentation products were produced which were more volatile and so could have been lost on work-up; the most likely alternative product, however, would be TsiH, and this would



$$MeO^- \; Me_3Si—C(SiMe_3)_2—Si(CH{=}CH_2)_2—Cl \longrightarrow MeOSiMe_3 + (Me_3Si)_2C{=}Si(CH{=}CH_2)_2 + Cl^-$$

$$(Me_3Si)_2C{=}Si(CH{=}CH_2)_2 + MeOH \longrightarrow (Me_3Si)_2CHSi(CH{=}CH_2)_2OMe \qquad (1)$$

have remained in the oil and have been detected.) The product is analogous to that obtained from (**2**) under similar conditions,[3] and its formation can be attributed to a β-elimination process followed by addition of MeOH to the sila-alkene initially produced, as in equation (1).

Experimental

Materials.—Diethyl ether, hexane, and pentane were stored over Na wire; THF was boiled under reflux with Na wire and benzophenone until a deep purple colour developed, and distilled from the mixture immediately before use; CCl_4 and CH_2Cl_2 were boiled with $CaCl_2$ for 1 h then distilled off and stored over Molecular Sieve 4A; MeOH was dried with $Mg(OMe)_2$ and stored over Molecular Sieve 3A; CF_3CO_2H was distilled from Ag_2O then from concentrated H_2SO_4. Salts were dried at 120 °C *in vacuo*.

Physical Constants.—M.p.s were determined in sealed capillaries. The ^1H n.m.r. and i.r. spectra refer to solutions in CCl_4 unless otherwise indicated, and the ^{19}F n.m.r. spectra to solutions in $CDCl_3$ (with shifts relative to $CFCl_3$). Mass spectra were by electron impact at 70 eV.

Preparation of $TsiSi(CH{=}CH_2)_2Cl$ (**1**).—A solution of TsiH (7.50 g, 0.032 mol) in THF (80 cm^3) was added with stirring under N_2 to a solution of MeLi (0.035 mol) (prepared from MeCl and Li) in ether (20 cm^3). The ether was distilled off and the residual mixture boiled under reflux for 2 h. A solution of $(CH_2{=}CH)_2SiCl_2$[14] (5.30 g, 0.035 mol) in THF (20 cm^3) was added dropwise with stirring during 30 min, and the mixture was boiled under reflux for 15 min, then cooled to room temperature, and treated cautiously with an excess of aqueous NH_4Cl. Ether extraction, followed by washing, drying ($MgSO_4$), and evaporation of the extract left a solid, which was recrystallized twice from ethanol then sublimed (100 °C at 0.1 Torr) to give *(chlorodivinylsilyl)[tris(trimethylsilyl)]methane* (8.4 g, 51%), m.p. 280 °C; δ_H 0.35 (27 H, s, $SiMe_3$) and 5.9—6.7 (6 H, m, $CH{=}CH_2$); $\nu_{max.}$(KBr) 1 625 cm^{-1} (C=C); *m/z* 333 (50%, $[M - Me]^+$), 225 (25, $[M - Me_3SiCl - Me]^+$), 213 (10), 201 (10), 155 (10), 141 (10), 129 (10), 113 (10), 85 (20, $[SiMe_2CH{=}CH_2]^+$), 73 (100, $[Me_3Si]^+$), and 59 (35, $[SiMe_2H]^+$) (the expected isotope pattern was observed for chlorine-containing ions) (Found: C, 48.3; H, 9.8. $C_{14}H_{33}ClSi_4$ requires C, 48.2; H, 9.5%).

Reaction of (**1**) *with* $LiAlH_4$.—A mixture of (**1**) (0.60 g, 1.7 mmol) and $LiAlH_4$ (0.26 g, 6.8 mmol) in THF (60 cm^3) was boiled under reflux for 24 h and then cooled. The residual $LiAlH_4$ was cautiously destroyed with moist ether, then an excess of saturated aqueous NH_4Cl was added, followed by a little dilute hydrochloric acid. The usual work-up of the ether layer (see above) left a solid, which was recrystallized from pentane. Its ^1H n.m.r. spectrum showed singlets at δ 0.17, 0.18, and 0.19, in a height ratio of *ca.* 1:2:1, and multiplets at δ 0.89—1.05, 3.96—3.99, and 5.75—6.32. The i.r. spectrum showed a strong SiH band at 2 100 cm^{-1}. Analysis by linked g.l.c.–mass spectrometry (5% OV101 on Chromasorb G at 180 °C) showed the presence of three components in 1:2:1 ratio, which were judged to be, respectively: (*a*) $TsiSi(CH{=}CH_2)_2H$, *m/z* 299 (100%, $[M - Me]^+$), 225 (20, $[M - Me_3SiH - Me]^+$), 211 (20, $[M - Me_4Si - Me]^+$), 199 (20, $[M - Me_3SiCH{=}CH_2 - Me]^+$), 185 (10), 141 (10), 85 (10), 73 (65), and 59 (15); (*b*) $TsiSiEt(CH{=}CH_2)H$, *m/z* 301 (100, $[M - Me]^+$), 287 (95, $[M - Et]^+$), 274 (45, $[M - Me - CH{=}CH_2]^+$), 214 (35, $[M - Me_3SiEt]^+$), 199 (60, $[M - Me_3SiEt - Me]^+$), 185 (10), 73 (90), and 59 (20); and (*c*) $TsiSiEt_2H$, *m/z* 303 (45, $[M - Me]^+$), 289 (100, $[M - Et]^+$) 215 (20), 201 (36), 185 (30), 129 (15), 73 (50), and 59 (20). The retention time and mass spectrum of the last component were identical with those of an authentic sample of $TsiSiEt_2H$.[2]

Treatment of (**1**) *with* LiH.—A mixture of (**1**) (2.87 mmol), LiH (11.5 mmol), and Bu_2O (30 cm^3) was boiled under reflux for 72 h. Work-up as in the preceding experiment gave unchanged (**1**).

Treatment of (**1**) *with* MeOH *and with* $AgNO_3$–MeOH.—(*a*) A solution of (**1**) (0.06 g) in MeOH (20 cm^3) was boiled under reflux for 48 h. Evaporation of the solvent left unchanged (**1**) (m.p.; i.r. and ^1H n.m.r. spectra).

(*b*) A solution of (**1**) (0.07 g) in MeOH (25 cm^3) containing $AgNO_3$ (0.17 g, 1.0 mmol) was refluxed for 20 h. The solvent was evaporated, and the residue extracted with hexane. The extract was evaporated to give unchanged (**1**) (0.06 g, 86%).

(*c*) A solution of (**1**) (0.07 g, 0.17 mmol), $AgNO_3$ (0.86 g, 4.6 mmol), and C_5H_5N (0.40 g, 48.5 mmol) in a mixture of MeOH (5 cm^3) and THF (15 cm^3) was boiled under reflux for 48 h. Work-up as in (*b*) gave unchanged (**1**) (0.05 g, 71%).

Reaction of (**1**) *with* NaOMe–MeOH.—A solution of (**1**) (0.20 g, 0.57 mmol) in 2.0M NaOMe–MeOH (20 cm^3) was boiled under reflux for 18 h then added to pentane (20 cm^3). Sufficient 2M aqueous HNO_3 was added to neutralize the base present, then the organic layer was separated, washed, dried ($MgSO_4$), and evaporated under reduced pressure. The residue (0.03 g, 20%) was judged to be $(Me_3Si)_2CHSi(CH{=}CH_2)_2OMe$; δ_H −0.55 (1 H, s, CH), 0.16 (18 H, s, $SiMe_3$), 3.40 (3 H, s, OMe), and 5.1—5.9 (6 H, m, $CH{=}CH_2$); *m/z* 257 (100%, $[M - Me]^+$), 245 (10, $[M - CH{=}CH_2]^+$), 141 (10, $[M - Me_3SiOMe - CH{=}CH_2]^+$), 127, (10), 89 (20, $[Me_2SiOMe]^+$), 73 (40), and 59 (50).

Treatment of (**1**) *with Silver Salts.*—(*a*) A solution of (**1**) (0.1 g) in CH_2Cl_2 (20 cm^3) was stirred under reflux with an excess (0.30 mmol) of AgOCN for 48 h or of $AgNO_3$ for 24 h. In each case work-up gave unchanged (**1**).

(*b*) A mixture of (**1**) (0.07 g, 0.20 mmol), AgO_2CCF_3 (0.51 g, 0.23 mmol), and CF_3CO_2H (20 cm^3) was boiled under reflux, and samples were taken at appropriate intervals for analysis by g.l.c. (3% OV-17 on Chromasorb G at 220 °C). The extents of reaction at various times were: 17%, 9 h; 40%, 24 h; and 85%, 85 h. After 120 h an excess of hexane was added followed by an excess of water, and the organic layer was separated, washed several times with water until neutral, then dried ($MgSO_4$) and evaporated, to give a solid (0.05 g, 60%), whose n.m.r. spectra were consistent with its being a 1:1 mixture of $TsiSi(CH{=}CH_2)_2O_2CCF_3$ and $(Me_3Si)_2C[Si(CH{=}CH_2)_2Me](SiMe_2O_2CCF_3)$ [Found (for mixture): C, 45.1, H, 7.8. $C_{16}H_{33}F_3O_2Si_4$ requires C, 45.1; H, 7.75%]; the former was judged to give ^1H n.m.r. peaks at δ 0.31 (s, $SiMe_3$) and 5.6—6.5 (m, $CH{=}CH_2$), and the latter at δ 0.31 (Me_3Si), 0.47 (s, $SiMe_2$), 0.66 (s, $SiMe_2$) (the last two singlets were of equal height), and 5.6—6.5 (m,

$CH=CH_2$). The ^{19}F spectrum of the mixture showed two peaks of equal height, at −76.1 and −75.8 p.p.m. Examination by linked g.l.c.–mass spectrometry (3% OV17 on Chromasorb G at 220 °C) gave only one peak, presumably arising from both isomers; m/z 411 (30%, $[M - Me]^+$), 361 (45), 225 (5, $[M - Me_3SiO_2CCF_3 - Me]^{+\cdot}$, 217 (20), 73 (100), and 59 (30).

Reaction of $TsiSiMe_2Cl$ *with* AgO_2CCF_3 *in* CF_3CO_2H.—The procedure described above was repeated but with $TsiSiMe_2Cl$ in place of (**1**). The extents of reaction at various times were: 10%, 1 h; 20%, 2 h; 75%, 13 h. After 30 h, work-up gave a solid, which was shown to be $TsiSiMe_2O_2CCF_3$ by comparison with an authentic sample.

Reactions of (**1**) *with Alkali Metal Salts*.—(*a*) A solution of (**1**) (0.14 g, 0.40 mmol) in MeCN (25 cm^3) was boiled under reflux for 2 h with an excess of KSCN (0.50 g, 5.15 mmol) then cooled. Hexane was added, followed by an excess of water, and the organic layer was separated, washed several times, dried ($MgSO_4$), filtered, and evaporated, to leave a solid which was sublimed (100 °C at 0.1 Torr) to give *(isothiocyanatodivinylsilyl)tris(trimethylsilyl)methane* (0.12 g, 80%), m.p. 256 °C; δ_H 0.34 (27 H, s, $SiMe_3$) and 5.8—6.4 (6 H, m, $CH=CH_2$); $\nu_{max.}(CCl_4)$ 1 590 (C=C) and 2 065 cm^{-1} (SiNCS); m/z 356 (75%, $[M - Me]^+$), 344 (5, $[M - CH=CH_2]^+$), 297 (10, $[M - HNCS - Me]^+$), 129 (10), 85 (25), 73 (100), and 59 (35) (Found: C, 48.2; H, 9.1; N, 3.5. $C_{15}H_{33}NSi_4S$ requires C, 48.5; H, 8.9; N, 3.8%).

(*b*) A mixture of (**1**) (0.15 mmol), KSCN (2.06 mmol), and MeCN (20 cm^3) was placed in one flask and a similar mixture containing $TsiSiMe_2Cl$ instead of (**1**) was placed in another. The flasks were placed alongside one another in a bath, and the solutions were boiled gently under reflux. Samples (1 cm^3) were withdrawn at intervals from each flask and evaporated, and the residual solids were taken up in CCl_4 for analysis by g.l.c. (3% OV17 on Chromasorb G at 200 °C). This showed that after 2 h 73% of (**1**) and 52% of $TsiSiMe_2Cl$ had been converted into the corresponding isothiocyanates, and after 5 h the conversions were respectively 100 and 86% complete. After 9.5 h all the $TsiSiMe_2Cl$ had reacted.

(*c*) A solution of (**1**) (0.17 g, 0.49 mmol) and KSCN (7.0 mmol) in MeOH (10 cm^3) was refluxed for 10 days. Work-up as in (*a*) gave exclusively $TsiSi(CH=CH_2)_2NCS$ (0.10 g, 55%), with properties identical to those described above.

(*d*) A solution of (**1**) (0.14 g, 0.40 mmol) in MeCN (20 cm^3) was boiled under reflux with KOCN (0.50 g, 6.2 mmol). After 2 h a sample (2 cm^3) of the solution was withdrawn and the solvent was quickly evaporated under reduced pressure. The solid residue was extracted with CCl_4, and analysis of the extract by linked g.l.c.–mass spectrometry (5% OV101 on Chromasorb G) showed it to be a mixture of (**1**) and $TsiSi(CH=CH_2)_2NCO$ in 5:1 ratio. After 30 h, work-up as in (*a*), culminating in sublimation (100 °C at 0.1 Torr), gave (isocyanatodivinylsilyl)-tris(trimethylsilyl)methane (0.11 g, 78%), m.p. 275 °C; δ_H 0.34 (27 H, s, $SiMe_3$) and 5.7—6.4 (6 H, m, $CH=CH_2$); $\nu_{max.}(CCl_4)$ 2 275 cm^{-1} (SiNCO); m/z 340 (55%, $[M - Me]^+$), 297 (15, $[M - HOCN - Me]^+$), 85 (20), 73 (100), and 59 (35) (Found: C, 50.9; H, 9.4; N, 3.8. $C_{15}H_{33}NOSi_4$ requires C, 50.7; H, 9.3; N, 3.7%).

(*e*) The procedure described under (*d*) was repeated but with MeOH in place of MeCN. After 14 h the mixture contained (**1**) and $TsiSi(CH=CH_2)_2NCO$ in *ca.* 1:1 ratio. After 72 h, work-up as in (*a*) gave $TsiSi(CH=CH_2)_2NCO$ (0.10 g, 72%), with properties identical with those described above.

(*f*) A mixture of (**1**) (0.14 g, 0.40 mmol), CsF (0.94 g, 6.2 mmol), and MeCN (20 cm^3) was boiled under reflux. After 8 h a sample (2 cm^3) was removed and worked up and analysed as in (*c*), to reveal that (**1**) and $TsiSi(CH=CH_2)_2F$ were present in *ca.* 3:2 ratio. After 60 h, work-up as in (*a*), but culminating in recrystallization from EtOH instead of sublimination, gave (fluorodivinylsilyl)tris(trimethylsilyl)methane (0.08 g, 60%), m.p. 248 °C; δ_H 0.28 (27 H, s, $SiMe_3$) and 5.6—6.6 (6 H, m, $CH=CH_2$); m/z 317 (100%, $[M - Me]^+$), 257 (10), 243 (10), 225 (25, $[M - Me_3SiF - Me]^+$), 213 (10, $[M - Me_3SiF - CH=CH_2]^+$), 129 (10), 97 (10), 85 (20), 73 (95), and 59 (40) (Found: C, 51.0; H, 9.7. $C_{14}H_{33}FSi_4$ requires C, 50.6; H, 9.9%).

(*g*) A solution of (**1**) (0.10 g, 0.29 mmol) and CsF (0.70 g, 4.6 mmol) in MeOH (20 cm^3) was boiled under reflux for 40 h. Work-up as in (*e*) gave $TsiSi(CH=CH_2)_2F$ (0.63 g, 63%) with properties identical with those described above.

(*h*) A mixture of (**1**) (0.14 g, 0.40 mmol) and NaN_3 (0.40 g, 6.2 mmol) in MeCN (20 cm^3) was boiled under reflux for 48 h. Work-up as in (*a*) (but with pentane in place of hexane), culminating in sublimation (100 °C at 0.1 Torr), gave (azidodivinylsilyl)tris(trimethylsilyl)methane (0.11 g, 76%), m.p. 288 °C; $\nu_{max.}$ 2 135 cm^{-1} (SiN_3); m/z 340 (20%, $[M - Me]^+$), 325 (10), 313 (5, $[M - N_3]^+$), 284 (10), 270 (10), 224 (20), 214 (30), 202 (30), 188 (70), 172 (20), 155 (10), 141 (15), 130 (30), 116 (20), 113 (20), 100 (45, $[Me_2SiN_3]^+$), 85 (20), 73 (100), and 59 (30) (Found: C, 47.0; H, 9.6. $C_{14}H_{33}N_3Si_4$ requires C, 47.3; H, 9.3%).

(*i*) The procedure described under (*h*) was repeated but with MeOH in place of MeCN. After 6 h (**1**) and the corresponding azide were present in a 1:1 ratio. After 24 h, work-up as in (*g*) but without the sublimation gave $TsiSi(CH_2=CH_2)_2N_3$ (0.10 g, 72%), with properties identical with those described above.

(*j*) A solution of (**1**) (0.010 g, 0.029 mmol) in a 0.25M solution of CsF (0.25 mmol) in MeOH (1 cm^3) was placed in an n.m.r. tube, which was capped, then kept in a bath at 60 °C and removed at intervals for recording of the ^1H n.m.r. spectrum. From the heights of the Me_3Si peaks for (**1**) and $TsiSi(CH=CH_2)_2F$ at δ 0.35 and 0.28, respectively, the extents of reaction at various times were judged to be: 20%, 6 h; 38.5%, 18 h; 48%, 25 h; 60%, 36 h; 73%, 50 h; 85%, 76 h; 86%, 80 h; and 89%, 85 h. The data gave a good first-order plot with $t_{\frac{1}{2}} = 28$ h. After 120 h the solvent was evaporated and the residue shown by ^1H n.m.r. spectroscopy to be exclusively $TsiSi(CH=CH_2)_2F$.

(*k*) The procedure described under (*j*) was repeated but with $TsiSiMe_2Cl$ in place of (**1**). A good first-order plot was obtained, with $t_{\frac{1}{2}}$ = *ca.* 38.5 h. The product was $TsiSiMe_2F$.

Treatment of $TsiSi(CH=CH_2)_2X$ ($X = N_3$, NCO, *or* NCS) *with* MeOH.—The $TsiSi(CH=CH_2)_2X$ (50 mg) was dissolved in a little CCl_4 (*ca.* 0.02 cm^3) in an n.m.r. tube and MeOH (1 cm^3) was added. The tube was capped, shaken, placed in a bath at 60 °C, and removed at intervals for recording of the ^1H n.m.r. spectrum. In all cases there was no change during 7 days, and the starting materials were recovered unchanged.

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