Low-temperature reactions of dihalogenosilylenes, SiX_2, with I_2 or ICl in toluene yielding dihalogenoiodo(methylphenyl)silanes

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The gaseous silylenes, SiX_2 (X = F, Cl, Br or I), have been condensed into solutions of I_2 or ICl in toluene at −90 °C to give a range of new compounds of formula $SiX_2I(C_6H_4Me)$, demonstrating the generality of a type of reaction of silylenes first observed with SiO. All the products were mixtures of *ortho*, *meta* and *para* isomers but with an uncommonly high proportion of the *ortho* isomer in some cases. As the same iodosilane derivatives were obtained using I_2 or ICl as reagents, it is proposed that the reactions involve electrophilic attack of silylium ions, SiX_2I^+, on the arene.

In an earlier communication, Rowlands and Timms reported on the reaction of silicon monoxide with cold solutions of iodine in toluene which gave polysiloxanes with tolyl, iodo and hydrido substituents.[1,2] The silicon was bonded to the aromatic ring in *ortho*, *meta* and *para* positions. This novel silylene chemistry was tentatively ascribed to electrophilic attack on the toluene by $SiIO^+$. We reported some extensions of this work at a conference.[3] In this paper we show that all dihalogenosilylenes will behave similarly in attacking toluene in the presence of iodine or iodine monochloride at low temperatures to give good yields of dihalogenoiodo(methylphenyl)silanes. We believe the research adds another facet to the chemistry of silylium ions which is of considerable current interest.[4–6]

Results

The silylenes SiF_2, $SiCl_2$ and $SiBr_2$ were formed under vacuum by high-temperature gas–solid reactions of SiF_4, $SiCl_4$ or Br_2 respectively with Si.[7] For one experiment, $SiCl_2$ was prepared by flash thermolysis of Si_2Cl_6.[3] The preparation of SiI_2[8] proved more difficult. It was not formed in appreciable yield by passing iodine or SiI_4 vapours over silicon heated at 900–1100 °C but it was formed in low yield by passing iodine vapour through a mixture of silicon and 'silicon monoxide', the black, coke-like granular solid sold for vacuum evaporation and condensation of SiO gas.

In all cases, the silylenes were condensed into well stirred near-saturated solutions of iodine or iodine monochloride in toluene at −90 °C under vacuum. The resulting solution was then allowed to warm towards room temperature and the toluene was pumped away to leave the product contaminated with any excess of iodine and involatile polymers. With careful distillation under high vacuum it was possible to separate the desired organosilicon products from the iodine and from the involatile, polymeric products. In a few cases, diethyl ether was added at low temperatures which had the effect of converting species containing Si–I bonds into the corresponding Si–OEt species which were much less moisture-sensitive products.

The products from the reaction of $SiCl_2$ and $SiBr_2$ were easily obtained fairly pure as mixtures of isomers of $SiCl_2I(C_6H_4Me)$ **1** and $SiBr_2I(C_6H_4Me)$ **2** respectively. As summarised in Table 1, ^1H, ^{13}C and ^{29}Si NMR spectra of these mixed isomers showed three signals corresponding to the *ortho*, *para* and *meta* isomers. With the ^1H NMR spectra, the methyl proton peak to lowest field was assigned to the *ortho* isomer and the peak to highest field to the *meta* isomer. Isomer ratios, *o*:*p*:*m*, were 10:4:3 for **1** and 5:2:2 for **2**. These ratios were determined first from the areas of the methyl protons in the ^1H NMR spectra but were checked from the relative areas of the group of peaks to lowest field amongst the aromatic protons associated with the protons adjacent to the SiX_2I substituent.

In the analogous reaction with SiF_2 condensed into iodine in toluene, the main product was identified by mass spectrometry and by ^1H, ^{13}C, ^{19}F and ^{29}Si NMR as a mixture of isomers of $SiF_2I(C_6H_4Me)$ **3** with an *o*:*p*:*m* ratio of 3:1:1. In an attempted preparation of the silane **3** using toluene which had not been fully dried, mass spectrometry and ^{19}F NMR spectroscopy indicated the presence of the partial hydrolysis product $[SiF_2(C_6H_4Me)]_2O$ in addition to **3**.

Condensation of $SiBr_2$ into a toluene solution of iodine monochloride gave the same product (**2**) as was obtained with iodine with essentially the same relative abundance of *ortho*, *para* and *meta* isomers. There was no analytical evidence for any product containing a Si–Cl bond although NMR spectroscopy and mass spectrometry showed that there was slight contamination of the product from isomers of iodotoluene arising from acid-catalysed attack of ICl on toluene.

The comparable reaction of SiI_2 was observed by condensing it into a solution of ICl in toluene. Two things complicated the analysis of the products. First, as stated above, detectable amounts of SiI_2 were only obtained from I_2 reacting with silicon plus solid 'silicon monoxide' which generated some SiO gas together with SiI_2. This gave products contaminated with small amounts of the tolyl- and iodo-substituted polysiloxanes reported by Rowlands.[1,2] Secondly, more extensive attack of the ICl on the toluene occurred than from the comparable reaction with toluene, $SiBr_2$ and ICl, giving large amounts of chloro- and iodo-ring-substituted toluenes which also contaminated the product. The result was that although the mass spectrum of the product showed $C_7H_7SiI_3^+$ and $C_7H_7SiI_2^+$ as the dominant high mass peaks, the ^1H NMR spectrum was so complicated in the methylaryl and C–H aromatic regions that peaks for $SiI_3(C_6H_4Me)$ could not be unambiguously assigned.

Ethylbenzene could be used as reactant and solvent for iodine in place of toluene but the solubility of iodine at low temperatures in xylenes or cumene proved much lower and reactions with these solvents were not pursued. Condensation of $SiCl_2$ into a solution of iodine in ethylbenzene at −90 °C followed by addition of diethyl ether and warming to room temperature gave isomers of $SiCl_2(OEt)(C_6H_4Et)$ (complexed by diethyl ether). From the signals for the aromatic protons in the ^{1}H NMR spectrum, the *o*:*p*:*m* isomer ratio was estimated as 4:2:3.

Discussion

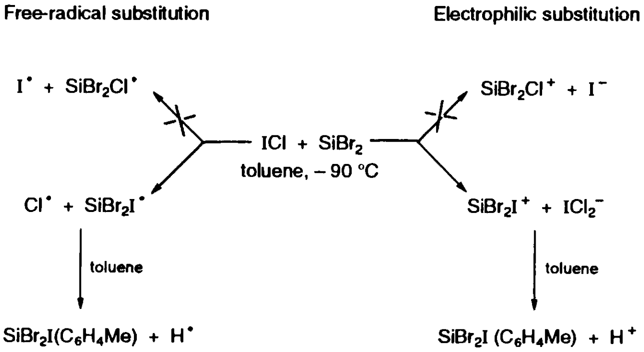
Attempts to react silylenes with aromatic compounds in the absence of I_2 either fail to give any organosilicon products ($SiCl_2$ and $SiBr_2$) or succeed by addition across the multiple bonds to give 1,4-disilacyclohexa-2,5-diene derivatives (SiF_2 and SiO).[7,9] With SiO, but not with any other silylene, products are also obtained in low yield involving insertion of the silylene into either aromatic or alkyl-substituent C–H bonds to give organosilicon products containing Si–H bonds.[9]

The reactions of silylenes with toluene in the presence of I_2 take a completely different path. There is no evidence for addition to multiple bonds or any attack on the methyl group. The only molecular products arise from substitution of aromatic hydrogen atoms and the substitution shows a variable but quite strong bias towards the *ortho* isomer with lesser amounts of the *para* and *meta* isomers. Calculated from ^{1}H NMR peak integrations, the relative proportions of *o*:*p*:*m* isomers are 3:1:1 for SiF_2, 10:4:3 for $SiCl_2$, 5:2:2 for $SiBr_2$ and 6:3:1 for SiO.[1,2] Despite the low temperature (−90 °C), the reactions must occur very fast otherwise further addition of iodine (or ICl) to the silylene would occur to give tetrahalogenosilanes or, as reported for SiO and I_2 in iodoethane solution, silicon oxoiodides.[1,2]

In considering what mechanism could account for the observed substitution reactions, three options seem plausible: (*i*) a free-radical mechanism involving attack by a $SiX_2I^{\bullet}$ species on the toluene, (*ii*) an electrophilic substitution mechanism involving attack by a free or solvent-associated SiX_2I^+ species on toluene or (*iii*) a process of acid-catalysed iodination of toluene, followed by insertion of the silylene into the aromatic C–I bond. Option (*iii*) is least probable as insertion of SiO, one of the most reactive of all silylenes, into carbon–halogen bonds of alkyl or aryl halides has been shown either not to occur or to occur with very low efficiency.[1,2,9] By contrast, the SiO–I_2–toluene reaction is much more efficient.[1,2] However, two observations make us favour option (*ii*) more strongly than option (*i*). First, attack on the toluene methyl protons in the presence of I_2 has not been detected in any of the current reactions or in the earlier work with SiO.[1,2] Secondly, in reaction with $SiBr_2$ or SiI_2, when ICl was used in place of I_2 in solution in toluene, no product containing Si–Cl bonds could be detected. The products were the silane **2**, identical to that obtained from $SiBr_2$ reacting with I_2 in toluene, and $SiI_3(C_7H_7)$ which was not obtained from SiI_2, I_2 and toluene. A similar observation was made by Rowlands[2] on the reaction of SiO with a solution of ICN in toluene, which gave the same products as were obtained from iodine in toluene and no species containing Si–CN bonds. For the $SiBr_2$–ICl–toluene system, possible (and impossible) reaction pathways are shown in Scheme 1. It is very probable electronically that $SiBr_2I^+$ would be formed in preference to $SiBr_2Cl^+$ in the electrophilic-substitution pathway, but there is no obvious reason why $SiBr_2I^{\bullet}$ should be formed in preference to $SiBr_2Cl^{\bullet}$ when the latter would be thermodynamically favoured. Hence our belief that an electrophilic-substitution reaction is more probable. However, it is very unlikely in light of the known properties of silylium ions[4–6] that the SiX_2I^+ ions are really free in the solution. They will be transitory species with a strong tendency to associate with the arene solvent and the counter anions. As the I_2 or ICl molecules will be loosely bound within stacked charge-transfer complexes with the arene,[10] the silylium ions will be formed within the stack creating an ideal environment for their reaction with the arene.

There may also be an effect on the isomer ratios if the sandwiched I_2 molecules are not bound symmetrically to toluene but more towards the methyl substituent. Positive *ortho*-directing may result and this may explain the high *o*:*p* isomer ratios observed in the formation of compounds **1**–**3**.[11] The lower proportion of the *ortho* isomer observed using ethylbenzene rather than toluene with $SiCl_2$, indicates that steric factors easily reduce the availability of the *ortho* position. With the toluene, I_2, SiO reaction, the low proportion of the *meta* isomer (*o*:*p*:*m* ratio 6:3:1) suggests that an electrophile of lower activity than in the other reactions is attacking the toluene. The species $SiIO^+$, postulated in the earlier paper,[1] could have an activity lower than SiX_2I^+ because there are fewer electron-withdrawing groups on the silicon. However, there is a strong possibility, in light of the known instability of silicon–oxygen double bonds towards polymerisation, that the situation is complicated by dimerisation or trimerisation of Si=O occurring at the moment of condensation of the monomeric SiO gas in the toluene.[12]

We are not aware of the $SiX_2I(R)$ (R = aryl) reaction products having been reported previously. Mixtures of isomers of the compounds can be prepared by our methods in gram quantities and they have some potential as synthetic reagents because the Si–I bond is very reactive. We are exploring the possibility that other silylenes, SiR_2, where R=H, alkyl or aryl, will also undergo similar low-temperature iodine-mediated electrophilic-substitution reactions with toluene. However, the reactivity of the intermediate silylium ions $SiIR_2{}^+$ must be



Scheme 1

Table 1 NMR chemical shifts[a] for compounds **1**–**3**

	$\delta(^1H)$		$\delta(^{13}C)$		
Compound	Methyl	Aromatic	Methyl	Aromatic	$\delta(^{29}Si)$
1 $SiCl_2I(C_6H_4Me)$	2.51 (1.8 H), 2.20 (0.5 H, 2.18 (0.7 H)	7.67–6.95 (4 H)	23.19 (*o*), 22.46, 22.33	143.64–126.05	−31.93, −32.08, −35.12 (*o*)
2 $SiBr_2I(C_6H_4Me)$	2.54 (1.65 H), 2.15 (0.7 H), 2.12 (0.65 H)	7.74–6.90 (4 H)	20.92 (*o*), 20.36, 20.18	140.94–123.57	−58.61, −58.99, −62.85 (*o*)
3 $SiF_2I(C_6H_4Me)$[b]	2.55 (1.8 H), 2.38 (0.6 H), 2.36 (0.6 H)	7.70–7.00 (4 H)	21.43 (*o*), 21.11, 20.70	144.11–119.72	−47.03, −50.95, −51.22 (*o*)

[a] Proton, ^{13}C and ^{29}Si NMR spectra recorded in CD_2Cl_2 (^{1}H NMR chemical shifts in C_6D_6 were *ca.* 0.2 ppm to higher field). [b] $\delta(^{19}F)$ (CD_2Cl_2) −108.72, −110.48 and −110.76.

lowered by electron-releasing R groups and addition of iodine to form SiI_2R_2 may become dominant over any electrophilic attack on toluene.

Experimental

Some work on the generation and condensation of silylenes was carried out in a simpler apparatus[3] but the best results for synthesising and reacting silylenes were obtained with the apparatus shown in Fig. 1. A gaseous source of halogen was treated with granular silicon (99.9% pure) at 1000–1300 °C in a 12 mm outside-diameter quartz tube heated by passing current through windings of 0.5 mm molybdenum wire around the tube. For the SiF_2 preparation, SiF_4 was bled in from an external gas burette. For $SiCl_2$ or $SiBr_2$, the vapour over liquid $SiCl_4$ or Br_2 respectively was bled in through a Teflon needle valve. For SiI_2, the cooler bottom part of the quartz tube was packed with granular silicon and the hot-zone part with equal weights of a mixture of granular silicon and 'silicon monoxide' (Merck, Patinal); solid iodine was evaporated from a heated extension at the bottom of the tube so that I_2 vapour passed first over silicon at temperatures up to 700 °C and then over the Si–SiO mixture at temperatures up to 1100 °C.

The furnace was mounted inside a 10 l Pyrex flask which could be evacuated to $< 10^{3}$ Pa with an oil-diffusion pump while being rotated at 60 r.p.m. During an experiment, the flask contained a solution of I_2 (or ICl) in dry toluene cooled to −90 °C by rotation through a bowl of very cold light petroleum (b.p. 30–40 °C). The silylene condensed in the solution. At the end of an experiment the furnace was allowed to cool and the flask was filled with N_2. The toluene solution containing product and any excess of the reactants was transferred out of the flask through 3 mm polyethene tubing to a 1 l flask; the product was then worked up by conventional vacuum line–greaseless Schlenk-line techniques. All apparatus, solvents and reagents used in the work were dried very carefully as the reaction products were extremely water sensitive.

Proton, ^{13}C and ^{29}Si NMR spectra were run in sealed tubes in C_6D_6 or CD_2Cl_2 on JEOL GX400 or GX270 spectrometers and ^{19}F NMR on a JEOL FX90Q spectrometer. Chemical shifts are reported relative to $SiMe_4$ (^1H, ^{13}C and ^{29}Si) or external CCl_3F (^{19}F). Mass spectra were recorded using AEI MS902 or VG Autospec instruments.

$SiCl_2$, I_2 and toluene or ethylbenzene

Tetrachlorosilane (2.2 g, 13 mmol) (Aldrich, 99.5% pure) was passed through the furnace in Fig. 1 heated to 1300 °C over 45 min and the off-gases were condensed into a solution of I_2 (5.6 g, 22 mmol) in toluene (150 cm^3). Product work-up yielded 1.0 g (3.1 mmol) of $SiCl_2I(C_6H_4Me)$ **1** (Found: C, 26.15; H, 2.50. $C_7H_7Cl_2ISi$ requires C, 26.50; H, 2.25%). Mass spectrum (^{35}Cl): *m/z* 316 (20, M^+), 281 (35, $M^+ - Cl$) and 189 (97, $M^+ - I$).

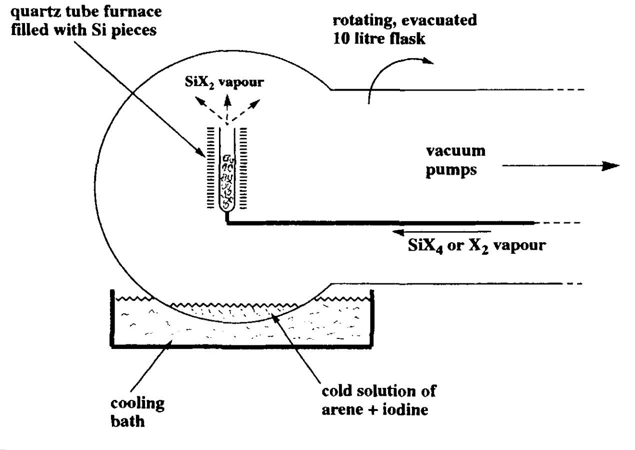


Fig. 1 Apparatus for preparing silylenes and treating them with solutions of I_2 in toluene

In another experiment lasting 1.5 h, Si_2Cl_6 (5.5g, 20 mmol) (Aldrich, 96%) was decomposed by flash pyrolysis[3] through a quartz tube at 1100 °C and the off-gases were condensed under high vacuum into a well stirred solution of I_2 (2 g, 7.9 mmol) in ethylbenzene (100 cm^3) cooled to −90 °C. At the end of the run, diethyl ether (10 cm^3) was added slowly and then the solvents were pumped away leaving a mass of solid and oil from which 0.5 g of a colourless oil was obtained by distillation under high vacuum. This oil could not be freed entirely from complexed diethyl ether so that elemental analysis proved variable, but the mass and ^1H NMR spectra (for labelling see Fig. 2) indicated the formula $SiCl_2(OEt)(C_6H_4Et){\cdot}xEt_2O$. Mass spectrum ($^{35}Cl$): *m/z* 248 ($C_{10}H_{14}Cl_2OSi^+$, 20%), 233 ($C_9H_{11}Cl_2OSi^+$, 9), 219 ($C_{10}H_{14}ClOSi^+$, 10), 213 ($C_8H_9Cl_2OSi^+$, 7), 203 ($C_8H_9Cl_2Si^+$, 15) and 105 ($C_8H_9^+$, 100). ^1H NMR (C_6D_6): δ 0.87 [t, 10 H, J = 7, $(CH_3CH_2)_2O$], 0.97–1.13 (m, 18 H, $C{-}CH_2CH_3$ + $SiCl_2OCH_2CH_3$), 2.32–2.50 (m, 6 H, $C{-}CH_2CH_3$), 3.70 [q, 7 H, J = 7, $(CH_3CH_2)_2O$], 3.86 (q, 6 H, J = 7, $SiCl_2OCH_2CH_3$), 6.96–7.24 (m, 8 H, H_a, H_b, H_c, H_e, $H_{e'}$, H_i, H_j), 7.55 (m, 1.3 H, H_h), 7.62 (br s, 0.7 H, H_g), 7.65 (d, 1.4 H, J = 8, H_f and $H_{f'}$) and 7.84 (dd, 1.4 H, J = 8, 1.5 Hz, H_d).

$SiBr_2$, I_2 or ICl and toluene

Bromine vapour (2 g, 12.7 mmol) was passed over granular silicon at 1300 °C over 40 min and the resulting $SiBr_2$ was condensed into a solution of I_2 (3.5 g, 14 mmol) in toluene (160 cm^3) at −90 °C; the iodine colour in the solution was faint by the end of the run. Pumping off the toluene left a brown tar from which short-path distillation under high vacuum gave as condensate 1.4 g (3.4 mmol) of faintly purple, oily $SiBr_2I(C_6H_4Me)$ **2** (Found: C, 20.40; H, 1.75; I, 31.65. $C_7H_7Br_2ISi$ requires C, 20.70; H, 1.75; I, 31.25%). Mass spectrum (^{81}Br): *m/z* 408 (M^+, 20%), 327 ($M^+ - Br$, 12), 317 ($M^+ - C_7H_7$, 13) and 281 ($M^+ - I$, 100).

In a similar experiment, Br_2 (2.5 g, 16 mmol) was passed through granular silicon at 1300 °C over 1 h and the resulting $SiBr_2$ was condensed into a solution of ICl (4.3 g, 27 mmol) in toluene (160 cm^3) at −90 °C (this solution had been dried over 3A molecular sieves before use). Removal of excess of ICl and the toluene solvent left a mixture of oil and solid from which a slightly brown oil was distilled under high vacuum. Mass spectrum (^{81}Br): *m/z* 406 ($C_7H_7Br_2ISi^+$, 21.4%), 325 ($C_7H_7BrISi^+$, 8.5), 315 (Br_2ISi^+, 14.0), 279 ($C_7H_7Br_2Si^+$, 100) and 218 ($C_7H_7I^+$, 61.2). NMR: ^{29}Si (CD_2Cl_2) as for **2** (Table 1); ^1H and ^{13}C as for **2** plus peaks for *o*-, *m*- and *p*-iodotoluene.[13]

SiF_2, I_2 and toluene

Tetrafluorosilane (11, 42 mmol) (99.5% pure) was passed through silicon at 1300 °C over 1 h and the off-gases were condensed into a solution of I_2 (7.8 g, 31 mmol) in toluene (200 cm^3) at −90 °C in the apparatus displayed in Fig. 1. The final solution was straw colour. Pumping off the toluene at −30 °C left a yellow oil from which 0.7 g of $SiF_2I(C_6H_4Me)$ **3** was recovered by distillation (Found: C, 28.95; H, 2.30. $C_7H_7F_2ISi$

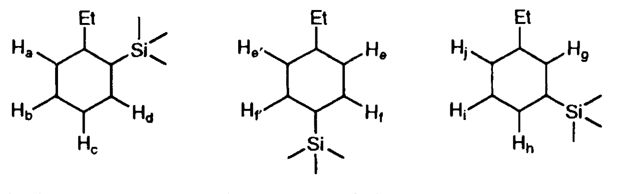


Fig. 2 Aromatic proton labelling for $SiCl_2(OEt)(C_6H_4Et)$

requires C, 29.60; H, 2.50%). Mass spectrum: *m*/*z* 284 (M^+, 100%), 193 ($M^+ - C_7H_7$, 5) and 157 (M^+ − I, 98).

In another experiment, SiF_4 (700 cm^3, 29 mmol) was passed through silicon at 1200 °C over 1 h and the off-gases were condensed into a well stirred solution of I_2 (5 g, 20 mmol) in toluene (50 cm^3); the toluene had been distilled from sodium but had not been dried further with 3A molecular sieves. After work up, the volatile product (0.5 g) looked similar to that above but proved to be a mixture of isomers of **3** and $[SiF_2(C_6H_4Me)]_2O$. Mass spectrum: *m*/*z* 330 ($C_{14}H_{14}F_4OSi_2^+$, 17%), 284 ($C_7H_7F_2ISi^+$, 64), 239 ($C_7H_7F_4OSi_2^+$, 9), 238 [$C_7H_6F_4OSi_2^+$ (cyclic-rearrangment ion), 17], 193 (SiF_2I^+, 3), 176 ($C_7H_7SiF_3^+$, 17) and 157 ($C_7H_7SiF_2^+$, 70). ^{19}F NMR (CD_2Cl_2): δ −108.72 [8752, $SiF_2I(C_6H_4Me$-*o*)], −110.48 [4951, $SiF_2(C_6H_4Me$-*p*)], −110.76 [6766, $SiF_2I(C_6H_4Me$-*m*)], −134.71 [4486, $SiF_2(C_6H_4Me$-*o*)O], −137.31 [2064, $SiF_2(C_6H_4Me$-*p*)O] and −137.50 [2269, $SiF_2(C_6H_4Me$-*m*)O].

SiI_2, I_2 or ICl, and toluene

The vapour from I_2 (3.5 g, 13.8 mmol) was passed through the quartz-furnace tube of the apparatus in Fig. 1 with the lower part of the tube filled with powdered silicon heated to 600–900 °C and the middle part of the tube filled with granular 'silicon monoxide' heated to 900–1100 °C. The off-gases were condensed into a solution of I_2 (3 g, 11.8 mmol) in toluene (100 cm^3) over 40 min. Evaporation of toluene from the resulting solution left a mixture of oil and solid which, on short-path distillation at room temperature under high vacuum yielded first I_2 and then SiI_4 (identified by IR and mass spectroscopy) but no other volatiles. On heating, the residual oil gave a mass spectrum similar to that previously observed from the SiO, I_2, toluene reaction with peaks *m*/*z* > 1000.[1,2]

The above experiment was repeated using a solution of ICl (3.75 g, 23 mmol) in toluene (100 cm^3). After the condensation the toluene, I_2 and ICl were removed under vacuum to leave a sticky brown oil from which a small amount of nearly colourless liquid was obtained by short-path distillation under high vacuum at room temperature. Mass spectrum (intensities corrected to 100% ^{35}Cl): *m*/*z* 500 ($C_7H_7I_3Si^+$, 8.2%), 373 ($C_7H_7I_2Si^+$, 100), 374 ($C_7H_7I_2Si^+$, 12.49), 375 ($C_7H_7I_2Si^+$, 3.90) [$C_7H_7I_2Si^+$ requires *m*/*z* 374 (12.73) and 375 (3.63)], 344 ($C_7H_6I_2^+$, 14.4), 320 ($C_7H_4Cl_3I^+$, 52), 286 ($C_7H_5Cl_2I^+$, 83.3), 251 ($C_7H_5ClI^+$, 17.5) and 193 ($C_7H_4Cl_3^+$, 44.5). The ^1H NMR spectrum showed about 25 peaks in the range δ 1.8–2.6 plus many peaks in the aromatic region, the relative integration of the two regions being 19:17.

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