The Reaction of the Carbene 1,2,2-Trifluoroethylidene with Si-H and Si-Halogen Bonds

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Summary 1,2,2-Trifluoroethylidene readily inserts into the Si–H bond of trialkylsilanes, but insertion into the Si–Cl bonds of silicon tetrachloride or methylchlorosilanes is more difficult; with certain silanes containing Si–H and Si–Cl bonds both types of insertion take place.

1,2,2-TRIFLUOROETHYLIDENE (I), prepared by the standard route,[1]

$$\begin{tikzcd}
\mathrm{CF_2{:}CF_2 + SiHCl_3} \arrow[r, "\mathrm{u.v.}"] & \mathrm{CHF_2{\cdot}CF_2{\cdot}SiCl_3} \arrow[d, "\mathrm{SbF_3}"] \\
\text{(I)}\ \mathrm{CHF_2{\cdot}\ddot{C}F + SiF_4} & \mathrm{CHF_2{\cdot}CF_2{\cdot}SiF_3} \arrow[l, "150^\circ"']
\end{tikzcd}$$

has been shown to insert into C–H bonds.[2] We report the insertion at 150° of (I) into Si–H and Si–halogen bonds in compounds containing only Si–H or Si-halogen bonds and in compounds containing both Si–H and Si–Cl bonds.

The products were separated and purified by g.l.c. and were characterised by ^{1}H and ^{19}F n.m.r., i.r., mass spectrometry, and elemental analysis.

The formation of the product $\mathrm{CHF_2{\cdot}CDF{\cdot}SiMe_3}$ and not of $\mathrm{CHDF{\cdot}CF_2{\cdot}SiMe_3}$ from trimethyldeuteriosilane indicates that the reaction products arise by carbene insertion and not by rearrangement of (I) to trifluoroethylene in an excited state, and subsequent reaction of the diradical with the silane by radical abstraction of deuterium followed by rapid radical combination:

$$\begin{aligned}\mathrm{{\cdot}CHF{\cdot}CF_2{\cdot} + Me_3SiD} &\longrightarrow \mathrm{CHDF{\cdot}CF_2{\cdot} + Me_3Si{\cdot}} \\ &\longrightarrow \mathrm{CHDF{\cdot}CF_2{\cdot}SiMe_3}\end{aligned}$$

Since the yields of insertion products are based on the amount of the carbene (I) formed during the reaction, the overall yields of insertion products are a measure of the ease of insertion of (I). Thus insertion into the Si–H bonds of trialkylsilanes proceeds readily (90—99%) whereas insertion into the Si–Cl bonds of chlorosilanes, or the Si–Br bond of bromotrimethylsilane is more difficult (2—15% yield, based on carbene available). Reactivity towards Si—Cl insertion decreases in the series $\mathrm{Me_2SiCl_2} > \mathrm{MeSiCl_3} > \mathrm{Me_3SiCl}$, $\mathrm{SiCl_4}$ and the position of $\mathrm{Me_3SiCl}$ is apparently anomalous.

Insertions into Si–halogen bonds have only been studied with diazoalkanes, particularly in the presence of a copper catalyst,[3,4] but it has been suggested that the copper-catalysed reactions of diazoalkanes do not involve free carbene intermediates.[5] In contrast to the present results, the reactivities of various chlorosilanes with diazomethane in the presence of a copper catalyst were found[3] to be in the order $\mathrm{SiCl_4} > \mathrm{RSiCl_3}$ or $\mathrm{R_2SiCl_2}$, where R includes methyl.

Both the overall yield of the $\mathrm{CHF_2{\cdot}\ddot{C}F}$ insertion products and the ratio of Si–H : Si–Cl insertion decreases sharply in the series $\mathrm{Me_2ClSiH} > \mathrm{MeCl_2SiH} > \mathrm{Cl_3SiH}$ (yield 98%, 58%, and 53%, respectively; insertion ratio Si–H : Si–Cl, ∞, 2·0 : 1, and 0·7 : 1, respectively), and it is interesting to note that with the silane $\mathrm{Me_2ClSiH}$ only Si–H insertion was observed and the silane was as reactive towards insertion as the trialkylsilanes. The copper-catalysed reaction of diazomethane with trichlorosilane gives only the Si–Cl insertion product, $\mathrm{CH_2Cl{\cdot}SiHCl_2}$,[4] in contrast to the present observation that (I) inserts into both the Si–H and Si–Cl bonds of trichlorosilane.

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