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Preliminary communication

Novel thermal rearrangements involving interchange between groups on silicon and those on its α-carbon

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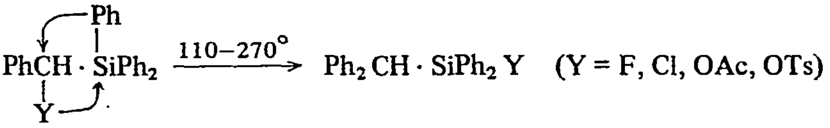
In a recent communication it was reported[1] that α-substituted benzylsilanes undergo thermal rearrangement:



$$\underset{Y}{PhCH} \cdot \overset{Ph}{Si}Ph_2 \xrightarrow{110-270^\circ} Ph_2CH \cdot SiPh_2Y \quad (Y = F, Cl, OAc, OTs)$$

We wish to point out that rearrangements of this type in which there is an interchange of a group attached to silicon with one attached to its α-carbon were demonstrated by us some time ago and reported briefly[2]. The present communication summarises the current position.

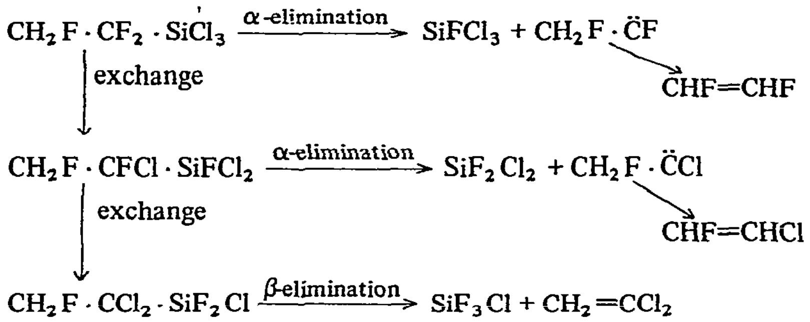
Pyrolysis of silanes of the type $RCF_2 \cdot SiF_3$ results in α-elimination with the formation of silicon tetrafluoride and a carbene which, if not trapped, rearranges to an olefin, *e.g.*[3]:

$$CHF_2 \cdot CF_2 \cdot SiF_3 \xrightarrow{150^\circ} SiF_4 + CHF_2 \cdot \ddot{C}F \rightarrow CF_2{=}CHF$$

Pyrolysis of the corresponding polyfluoroalkyltrichlorosilanes requires a higher temperature (ca. 225°) and the presence of the chloro-olefins in the products *e.g.*[4]:

$$CH_2F \cdot CF_2 \cdot SiCl_3 \xrightarrow{225^\circ} \underset{(19\%)}{CHF{=}CHF} + \underset{(7\%)}{CHF{=}CHCl} + \underset{(60\%)}{CH_2{=}CCl_2} + SiFCl_3$$

cannot be explained on the basis of an exclusive α-elimination reaction involving the reactant silane. The olefins $CHF{=}CHCl$ and $CH_2{=}CCl_2$ are in fact formed via rearrangement reactions involving exchange of chlorine on silicon for fluorine on carbon, *i.e.*:



$$\begin{tikzcd}
CH_2F\cdot CF_2\cdot SiCl_3 \arrow[r, "\alpha\text{-elimination}"] \arrow[dd, "\text{exchange}"] & SiFCl_3 + CH_2F\cdot\ddot{C}F \arrow[d] \\
 & \ddot{C}HF{=}CHF \\
CH_2F\cdot CFCl\cdot SiFCl_2 \arrow[r, "\alpha\text{-elimination}"] \arrow[dd, "\text{exchange}"] & SiF_2Cl_2 + CH_2F\cdot\ddot{C}Cl \arrow[d] \\
 & \ddot{C}HF{=}CHCl \\
CH_2F\cdot CCl_2\cdot SiF_2Cl \arrow[r, "\beta\text{-elimination}"] & SiF_3Cl + CH_2{=}CCl_2
\end{tikzcd}$$

Useful information was obtained by pyrolysis of the polyfluoroalkyltrichlorosilanes (Ia)[2], (Ib)[5], and (II)[5] at temperatures (100–160°) below those at which α-elimination occurs to give carbenes (ca. 225°).

$RCF_2\cdot SiCl_3$	$RCFCl\cdot SiCl_3$
(Ia) $R = Me$	(II) $R = CHF_2$
(Ib) $R = CH_2Cl$	

At 100° (2 h) the silane (Ia) was converted into the rearranged silane, $CH_3\cdot CCl_2\cdot SiF_2Cl$ (99%), which at 235° (16 h) decomposed (77%) by an α-elimination reaction to give vinyl chloride and a mixture of chlorofluorosilanes.

$$CH_3\cdot CF_2\cdot SiCl_3 \xrightarrow{100^\circ} CH_3\cdot CCl_2\cdot SiF_2Cl \xrightarrow{235^\circ} SiF_2Cl_2 + CH_3\cdot\ddot{C}Cl \rightarrow CH_2{=}CHC$$

The intermediate product $CH_3\cdot CFCl\cdot SiFCl_2$ was not detected, even by NMR analysis of the products at varying intervals of time, so the first chlorine-fluorine exchange is rate-determining.

$$CH_3\cdot CF_2\cdot SiCl_3 \xrightarrow{\text{slow}} CH_3\cdot CFCl\cdot SiFCl_2 \xrightarrow{\text{fast}} CH_3\cdot CCl_2\cdot SiF_2Cl$$

The replacement of chlorine on silicon by fluorine should render the silicon more susceptible to nucleophilic attack and so the second exchange would be expected to occur at a faster rate than the first exchange.

The progress of the reaction at 100° was determined at various intervals of time by NMR analysis, and a plot of time against $\log_{10}$(unchanged reactant) gave a straight line (first-order reaction) from which the half life of the reaction was approx. 21 min.

Silane (Ib) in which a hydrogen atom in (Ia) has been replaced by a bulkier chlorine atom rearranged more slowly than (Ia) even at 140° (half life approx. 50 min.) to give the silane $CH_2Cl\cdot CCl_2\cdot SiF_2Cl$ (88%). Similarly silane (II) rearranged to the product $CHF_2\cdot CCl_2\cdot SiFCl_2$ (85%) at 160°.

These exchange reactions are considered to involve a cyclic transition state, e.g.:

The exchange of phenyl on silicon for Y on α-carbon (Y = F, Cl, OAc, OTs)[1] thus usefully broadens the scope of the original observations[2] by showing that aryl groups can migrate as well as halogen.

REFERENCES

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