The Reaction of Silyldiazoalkanes with Acids. The Thermal Rearrangement of α-Substituted Benzyltriphenylsilanes

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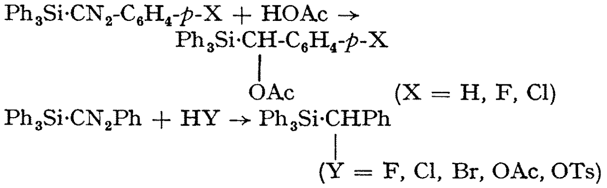
Summary Silylaryldiazo-alkanes react with acids to give α-substituted benzylsilanes, which undergo a novel rearrangement on heating.

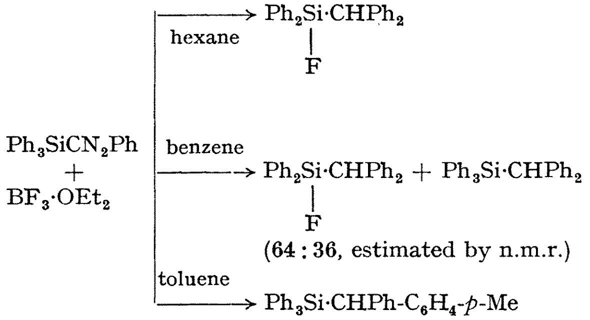
A VARIETY of silyldiazoalkanes are now available *via* the decomposition of the lithium salt of acylsilane toluene-*p*-sulphonylhydrazones.[1] The reaction of the silylaryldiazoalkanes with a number of acids has been found to give α-substituted benzylsilanes in good (*ca.* 80%) yields.



$$Ph_3Si{\cdot}CN_2\text{-}C_6H_4\text{-}p\text{-}X + HOAc \rightarrow Ph_3Si{\cdot}\underset{OAc}{\underset{|}{CH}}\text{-}C_6H_4\text{-}p\text{-}X \qquad (X = H, F, Cl)$$

$$Ph_3Si{\cdot}CN_2Ph + HY \rightarrow Ph_3Si{\cdot}\underset{Y}{\underset{|}{C}}HPh \qquad (Y = F, Cl, Br, OAc, OTs)$$

In none of the above cases did the intermediate α-silyl carbonium ion rearrange or give Friedel–Crafts substitution with an aromatic solvent. However, such processes did occur in the reaction of triphenylsilylphenyldiazomethane with boron trifluoride etherate.



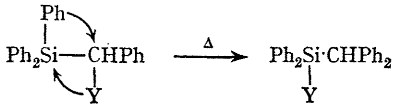
$$Ph_3SiCN_2Ph + BF_3{\cdot}OEt_2 \xrightarrow{\text{hexane}} Ph_2\underset{F}{\underset{|}{Si}}{\cdot}CHPh_2$$

$$Ph_3SiCN_2Ph + BF_3{\cdot}OEt_2 \xrightarrow{\text{benzene}} Ph_2\underset{F}{\underset{|}{Si}}{\cdot}CHPh_2 + Ph_3Si{\cdot}CHPh_2 \quad (64:36, \text{ estimated by n.m.r.})$$

$$Ph_3SiCN_2Ph + BF_3{\cdot}OEt_2 \xrightarrow{\text{toluene}} Ph_3Si{\cdot}CHPh\text{-}C_6H_4\text{-}p\text{-}Me$$

These last results closely resemble those found in the α-silylcarbinol–boron trifluoride system.[2]

The α-substituted benzyltriphenylsilanes undergo a novel thermal rearrangement involving migration of the substituent on carbon to silicon accompanied by shift of a phenyl group from silicon to carbon.



$$Ph_2Si(Ph){-}CHPh(Y) \xrightarrow{\Delta} Ph_2Si(Y){\cdot}CHPh_2$$

(Y=F,Cl, OAc, OTs)

Rearrangement of the fluoro-compound was complete after 14 hr. at 110° whereas the other compounds were completely rearranged after 1 hr. at 250—270°. In all cases none of the starting material could be detected and the benzhydrylsilane appeared to be the sole reaction product. These represent the first examples of such a thermal rearrangement, although similar migrations have been observed using Lewis acid catalysts.[3]

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[3] C. Eaborn, "Organosilicon Chemistry," Butterworth, London, 1960, p. 434.