Preliminary communication

Carbon-functional organosilicon compounds containing an α -hetero substituent

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The synthesis of halomethylsilanes, R_3SiCHX_2 , via halomethyl metal compounds has been developed by Seyferth et al. 1. Recently it was reported that $Ph_3SiCH(Ph)OMe$ is formed when $Ph_3Si \cdot C(OMe)_2Ph$ and Ph_3SiH are heated together at 190° and the intermediacy of $(Ph \cdot C \cdot OMe)$ in this and other reactions was established 2. A more general approach to the synthesis of compounds of the type $R_3Si \cdot CH(R)Y$ (R = alkyl, aryl; Y = OR, NR_2 etc.) is desirable in view of current interest in the electronic effects of α -metalloalkyl groups 3 and their thermolysis 4.

We report that heterocarbenoid compounds of the transition metals provide a suitable source of carbene fragments for insertion into Si-H bonds, and describe the synthesis of some α -alkoxy- and α -cycloalkylamino-benzylsilanes. The addition of [I] (Ph·C·OMe) from a similar source to the double bond of *trans*-methyl crotonate has been reported⁵.

In a typical reaction triethylsilane (4.5 mmole), pyridine (6.7 mmole) and the compound (CO)₅ Cr · C(Ph)NC₄H₈ (3.2 mmole)⁶ are heated in refluxing hexane under argon. The progress of the reaction is indicated by the steady precipitation of the complex py₃Cr(CO)₃ and the evolution of carbon monoxide. After 24 hours the liquid phase contained unreacted starting materials and the compound Et₃Si · CH(Ph)NC₄H₈ (1.3 mmole, 59% yield of pure material based on heterocarbenoid complex consumed (2.2 mmole); b.p. 90°/0.1 mm). Gas chromatography and elemental analysis established the purity of the reaction product. The NMR spectrum of the material in CCl₄ solution (internal TMS; 60 MHz) shows the following δ -values (ppm): 0.62, 15H, Et₃Si; 1.70, 4H, β -CH₂; 2.50, 4H, α -CH₂; 2.94, 1H, CH; 7.23, 5H, C₆H₅. The mass spectrum (70 eV) shows the molecular ion, M⁺(m/e 275) with relative abundance 1% and (M-Et)⁺ 2%, while the most abundant ion, at m/e 160, corresponds to PhCHNC₄H₈⁺.

By using similar procedures we have isolated other compounds of this type of which the following are examples (yield, %; $\delta(CH)$ ppm in CCl_4 solution): Et₃Si·CH(Ph)NC₂H₄ (41; 2.07), Et₃Si·CH(Ph)OMe (82; 3.96), Ph₃SiCH(Ph)OMe (40; 4.64). The last mentioned compound has physical characteristics identical to those reported earlier². The absence both of heterocarbene dimers⁷, [Ph·C·Y]₂ (Y = OR, NR₂), and of hydrogenated materials⁸ of the type Ph·CH₂·Y from among the major products of

these reactions, together with the moderate to good yields of insertion product, provide an index of the specificity of the insertion process under these conditions. A full report of work currently in progress on the synthesis and reactivity of compounds of this type will be made shortly.

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