

Generation and Some Reactions of the Bis(trimethylsilyl)aminyl Radical

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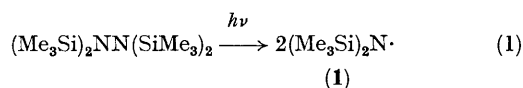
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Summary The radical $(\text{Me}_3\text{Si})_2\text{N}\cdot$, generated by u.v. photolysis of $(\text{Me}_3\text{Si})_2\text{NN}(\text{SiMe}_3)_2$ or of $(\text{Me}_3\text{Si})_2\text{NOSiMe}_3$, readily abstracts hydrogen from hydrocarbons, adds to ethylene, to phosphorus(III) compounds, and to t-butyl isocyanide, and is hence much more reactive than the dimethylaminyl radical.

THERE is considerable interest at present in the changes in properties of organic compounds which are brought about by substitution of silicon for carbon atoms at key positions in the molecule.¹ Dialkylaminyl radicals are less reactive than alkoxy radicals. For example, dimethylaminyl radicals abstract hydrogen from C-H groups much less readily than do alkoxy radicals,² and this difference can be associated

in part with the weaker N-H bond (398 kJ mol^{-1}) in Me_2NH compared with the O-H bond in ROH (439 kJ mol^{-1} in MeOH).³ We now report that the bis(trimethylsilyl)aminyl radical (**1**) exhibits reactivity similar to that of an alkoxy radical and different from that of $\text{Me}_2\text{N}\cdot$.

The radical (**1**) was generated by u.v. photolysis of tetakis(trimethylsilyl)hydrazine⁴ (TTH) [equation (1)] or (along with the trimethylsiloxy radical) of tris(trimethylsilyl)hydroxylamine⁵ (**2**).†



† The mercury compound $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Hg}$ also underwent photochemical cleavage to give (**1**), although this source was generally less convenient than TTH or (**2**).

