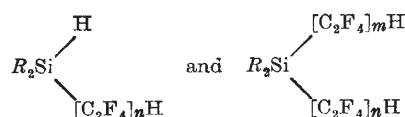


### Free Radical Reactions with Inorganic Covalent Hydrides: a Route to Polyfluoroalkyl Silicon Compounds

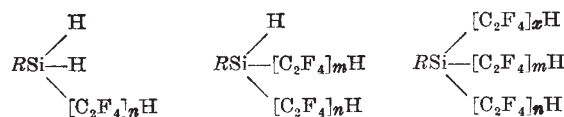
THE reactions of hydrocarbon free radicals are reasonably well established, but much less is known about the reactions of inorganic free radicals based on elements such as bismuth, silicon, germanium, lead, zinc, phosphorus, arsenic, tin or aluminium. The relative stabilities of some of these radicals can be predicted with reasonable certainty. The  $\text{SiCl}_3$  radical, for example, should be similar in type to the  $\text{CF}_3$  or  $\text{CCl}_3$  radical, and it is not surprising that trichlorosilane reacts with olefins<sup>1,2</sup> to give  $\text{SiCl}_3\text{[olefin]}_n\text{H}$ ; thus tetrafluoroethylene<sup>2</sup> yields  $\text{SiCl}_3\text{[CF}_2\text{.CF}_2\text{]}_m\text{H}$ , where  $m = 1-4$ .

Alkylsilyl radicals should be more reactive than trihalogenosilyl radicals, and a general study of their chemistry has been initiated. In particular, their reactions with olefins provide a useful new route for the synthesis of silicon compounds, and especially of polyfluoroalkyl silicon compounds.

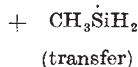
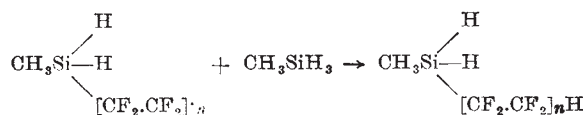
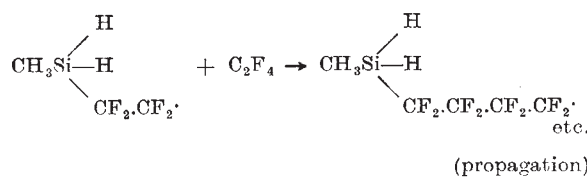
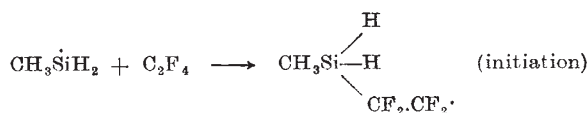
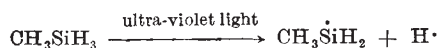
The free radical addition of a compound containing more than one Si—H bond to an olefin occurs with great ease. Thus with tetrafluoroethylene, dialkylsilanes,  $\text{R}_2\text{SiH}_2$ , yield the compounds



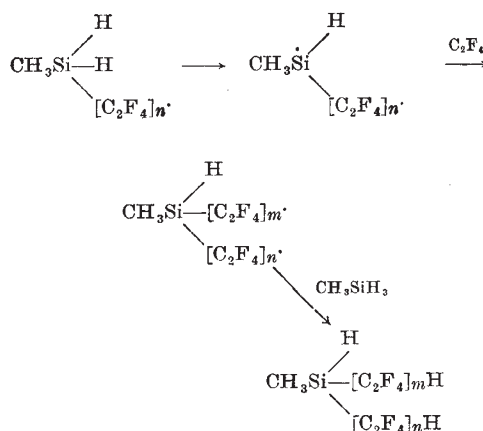
and alkylsilanes,  $\text{RSiH}_3$ , yield the compounds



by very rapid quantitative chain reactions; for example:

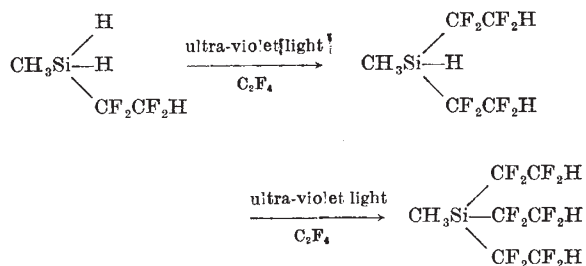


The value of  $n$  can be controlled by the ratio of reactants used, and the compound where  $n = 1$ , for example, has been obtained in 63 per cent yield. It is noteworthy that under normal conditions the above propagation step proceeds in preference to initiation of new chains involving the second or third Si—H bonds:



Compounds containing more than one polyfluoroalkyl group attached to silicon are produced by the further reaction of the initial product  $\text{CH}_3\text{SiH}_2\text{[C}_2\text{F}_4\text{]}_n\text{H}$  with tetrafluoroethylene; that is, mixed carbon-silicon di-radicals are not involved in the reaction.

The compound in which  $n = 1$  can be made to react further with the same or a different olefin, so that a wide variety of silicon compounds can be obtained by this method; for example:



It is evident that such facile free-radical reactions are not restricted to silicon, and many other inorganic free radicals derived from covalent inorganic hydrides can be predicted to react with olefins such as tetrafluoroethylene. Compounds such as  $\text{P}(\text{CF}_2\text{.CF}_2\text{H})_3$ ,  $\text{Me}_2\text{BCF}_2\text{.CF}_2\text{H}$ ,  $\text{MeAl}(\text{CF}_2\text{.CF}_2\text{H})_2$ ,  $\text{Me}_3\text{PbCF}_2\text{.CF}_2\text{H}$ , and  $\text{Zn}(\text{CF}_2\text{.CF}_2\text{H})_2$  should be capable of synthesis by this general method, although it is equally clear that certain of these will be stable only at relatively low temperatures.

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July 2.

<sup>1</sup> Sommer, Pietrusza and Whitmore, *J. Amer. Chem. Soc.*, 67, 188 (1945); 70, 484 (1948).

<sup>2</sup> Haszeldine and Marklow, *J. Chem. Soc.*, 962 (1956).