The Sulfuryl Chloride Chlorination of Alkyl Silanes. The Electronic Effect of Some Silyl Groups

By Yoichiro NAGAI, Noboru MACHIDA and Toshihiko MIGITA
Department of Chemistry, Gunma University, Kiryu, Gunma

(Received December, 24, 1965)

The free radical halogenation of alkylsilanes is one of the most convenient methods of introducing functional groups into the organic substituents attached to silicon. While much of the work in this field has been expended for synthetic purposes,[1] relatively little is known about the effect of changes in the structure of the silanes on the reactivities of each position of the alkyl groups.[2]

In order to obtain quantitative data on the effect of silyl groups in directing substitution, the sulfuryl chloride chlorination of ethyltrichloro-, ethylmethyldichloro-, ethyldimethylchloro-, *n*-propyltrichloro- and *n*-butyltrichloro-silane has been studied competitively in the presence of toluene.

Table I lists the relative reactivities per hydrogen atom at each carbon atom of those silanes, the aliphatic hydrogen atom in toluene being taken as unity.

TABLE I.[a] THE RELATIVE REACTIVITIES OF C–H BONDS IN THE SULFURYL CHLORIDE CHLORINATION OF SILANES

CH_3–CH_2SiCl_3	0.17 0.15
CH_3–$CH_2SiMeCl_2$	0.35 0.41
CH_3[b]–CH_2SiMe_2Cl	— 0.82
CH_3–CH_2–CH_2SiCl_3	0.27 0.57 0.19
CH_3–CH_2–CH_2–CH_2SiCl_3	0.25 1.1 0.49 0.09

a) All the experiments were carried out in carbon tetrachloride at the reflux temperature. Product analyses were made by means of vapor-phase chromatography (QF-1, Silicone Grease).

b) The β-chloroethyl compound has not yet been positively characterized.

It may be seen from the table that the values for the methyl groups of *n*-propyltrichlorosilane and *n*-butyltrichlorosilane are very similar, indicating that the trichlorosilyl group exerts only the slightest influence, if any, on the γ- and δ-carbon atoms. Therefore, it follows that the β-position of ethyltrichlorosilane is less reactive, and that of ethylmethyldichlorosilane is more reactive, than ordinary primary hydrogens. From the electrophilic character of chlorination,[2] it is, then, obvious that the trichlorosilyl group is electron-withdrawing and that the methyldichlorosilyl group is electron-releasing. This seems to be the first comment to have been made concerning the electronic effects of those groups.

Another notable feature of the table is the marked decrease in the reactivity of hydrogens on carbons alpha to silicon. In fact, the reactivity ratio of α-methylene to an ordinary methylene is 0.14 (0.15/1.1), 0.37 (0.47/1.1) and 0.75 (0.82/1.1) for ethyltrichlorosilane, ethylmethyldichlorosilane and ethyldimethylchlorosilane respectively. It should be noted, however, that these methylene groups on silicon have only three adjacent C–H bonds capable of stabilizing the incipient α-radicals by hyperconjugation.

There are indications in the literature that radical formation at the alpha position of alkylsilanes is quite difficult relative to that at the beta position. For example, the chlorination of 1, 1-dichlorosilacyclopentane under radical conditions produces more beta than alpha.[3] Similarly, the sulfuryl chloride chlorination of ethylmethyldichlorosilane yields the chloroethyl compounds only, no substitution occurring at the methyl group alpha to silicon.[4]

The reduced possibilities of alpha radicals for hyperconjugation are apparently responsible for these observations.

---

[1] C. Eaborn, "Organosilicon Compounds," Butterworths Scientific Publications, London (1960), p. 379.

[2] C. Walling, "Free Radicals in Solution," John Wiley & Sons, New York (1957), p. 369.

[3] R. A. Benkeser, Y. Nagai, J. L. Noe, R. F. Cunico and P. H. Gund, *J. Am. Chem. Soc.*, **86**, 2446 (1964).

[4] D. T. Hurd, ibid., **67**, 1813 (1945).