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Abstraction of Methyl Hydrogen of Organosilicon Compounds by *t*-Butoxy Radicals

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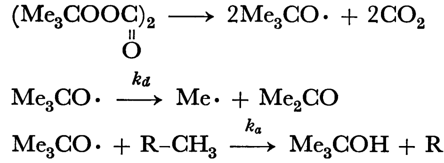
It has been known that in photochlorination of organosilicon compounds with chlorine in the liquid phase a large amount of dichloromethyl derivatives is produced as a by-product, along with the chloromethyl compounds.2) On the other hand, although 1,2-phenyl migration readily takes place in the system of $Ph_3CCH_2\cdot$,3) the similar migration does not occur for $Ph_3SiCH_2\cdot$,4) instead triphenylmethylsilane being formed. Such differences in the chemical behavior of silicon- and carbon-substituted radicals may be attributed to the former being larger in size than the latter, the electronegativity being lower for silicon as compared with carbon, and the availability of empty *d*-orbitals in silicon, which are absent in carbon.

In this connection, it seemed interesting to investigate the relative reactivity of organosilicon compounds towards free radicals in solution. Studies of the radical chemistry of organosilicon compounds are not ample and most of the reported investigations are related to synthesis.5) Recently, a kinetic information in the gas phase has been reported in this field.6) Nagai *et al.* also reported the relative reactivities of some alkylsilanes in the liquid phase photochlorination.7) The reactions described here were concerned with reactivities of *t*-butoxy radicals in hydrogen abstraction of methylsilicon compounds.

TABLE 1. RELATIVE REACTIVITIES OF ONE METHYL HYDROGEN OF ORGANOSILICON COMPOUNDS TOWARDS *t*-BUTOXY RADICALS AT 45.0°C IN 1,1,2-TRICHLOROTRIFLUOROETHANE

Substrate	k_a/k_d	Substrate	k_a/k_d
$Si(CH_3)_4$	0.29	$C_6H_5C(CH_3)_3$	0.21
$C_6H_5Si(CH_3)_3$	0.27	$(C_6H_5)_3CCH_3$	0.52
$(C_6H_5)_2Si(CH_3)_2$	0.33	$C_6H_5OCH_3$	1.99
$(C_6H_5)_3SiCH_3$	0.54	$C_6H_5SCH_3$	8.66
p-$ClC_6H_4Si(CH_3)_3$	0.29	$C_6H_5N(CH_3)_2$	very large
m-$ClC_6H_4Si(CH_3)_3$	0.33	$C_6H_5CH_3$	2.19
$(CH_3)_3SiSi(CH_3)_3$	0.60		
$Ph(CH_3)_2SiSi(CH_3)_2Ph$	0.52		

By the application of the quantitative method described in the previous papers,8,9) the reactivities of one methyl hydrogen atom of methylsilanes towards the abstraction by *t*-butoxy radicals have been investigated in 1,1,2-trichlorotrifluoroethane (Freon 113) at 45.0°C. Di-*t*-butyl peroxyoxalate10) was used as a source of *t*-butoxy redicals. The results are given in Table 1 along with the reactivities of compounds of the type of C_6H_5-$M(CH_3)_n$, in which M stands for a carbon atom or a heteroatom, O, N, and S. It is apparent that, for the attack by the *t*-butoxy radicals, the relative reactivities (k_a/k_d), which show the ratio of rate constant of hydrogen abstraction to that of decomposition of *t*-butoxy radicals to acetone and methyl radicals, are identical within an experimental error, for the substituted phenyltrimethylsilanes.



$$(Me_3CO\underset{\overset{\|}{O}}{O}C)_2 \longrightarrow 2Me_3CO\cdot + 2CO_2$$

$$Me_3CO\cdot \xrightarrow{k_d} Me\cdot + Me_2CO$$

$$Me_3CO\cdot + R\text{-}CH_3 \xrightarrow{k_a} Me_3COH + R\text{-}CH_2\cdot$$

The reactivities of methyl hydrogen in organosilicon compounds are little larger than those of the corresponding carbon analogs. Since the transition state of hydrogen abstraction, especially by electrophilic radicals such as *t*-butoxy radicals, resembles the initial state of the reaction, the polar effect is exerted mainly on the reactivities of abstraction, unless overthrowing strong conjugation effect is present. Therefore, the fact that the reactivities of organosilicon compounds do not differ considerably from those of the corresponding carbon analogs shows that the free redical formed by hydrogen abstraction is little stabilized by vacant 3*d*-orbitals of silicon, but the reactivities depend on the electron density of the C–H bond. It may be concluded also that pentamethyldisilanyl group is more electron-releasing than trimethylsilyl group.11)

It might be considered that the reactivities of the compounds containing one of the other hetero-atoms such as O, S, and N are very large, since these atoms have the electron-releasing effect due to lone pair electrons.

In conclusion, the α-silyl radicals formed by hy-

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drogen abstraction is little stabilized by a conjugation between 3*d*-orbitals on silicon and an odd electron on carbon.

Experimental

Materials. Di-*t*-butyl peroxyoxalate was prepared by the method of Bartlett *et al.*[10] Freon-113 was commercially available and used after distillation. *t*-Butylbenzene, anisole, thioanisole, dimethylaniline, and toluene were commercial samples and were used after purification by the usual way. All of the organosilicon compounds and 1,1,1-triphenylethane were prepared by the Grignard reaction.

Procedure for Kinetic Runs. The procedure for kinetics was carried out in a similar way to that described previously[8,9] at 45.0°C in Freon-113. *t*-Butyl alcohol/acetone ratios were determined by glc on a column packed with polyethylene glycol 1500 using helium as a carrier gas at 90.0°C. The ratios of *t*-butyl alcohol/acetone *vs.* concentration of the substrates were calculated by the method of least squares.