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Silyl Radicals. XV. Stereochemical Course of Chlorine Abstraction by 1-Methyl-4-*t*-butyl-1-silacyclohexyl Radicals from Polychloroalkane*

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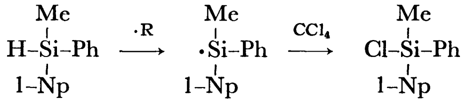
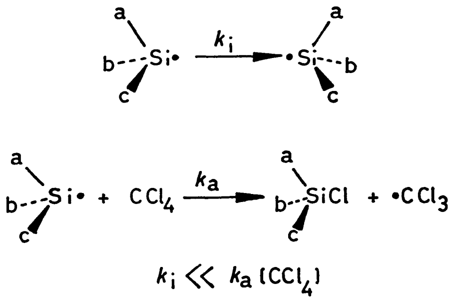
The isomerically pure *cis* and *trans* 1-methyl-4-*t*-butyl-1-silacyclohexane were subjected to the free radical chlorination with carbon tetrachloride in the presence of a catalytic amount of benzoyl peroxide under UV irradiation at 0 °C, affording the corresponding chlorosilanes with retention of configuration. With less reactive polyhalocarbons, however, less stereospecific products were obtained. A mechanism that inversion of silyl radicals competes with chlorine abstraction is proposed. Relative rates of each reaction were analyzed with a steady-state assumption.

During the course of the study on the Group IVB free radicals,[2] we have found that the silyl radical produced from an optically active hydrosilane undergoes chlorine-abstraction reaction mostly with retention of configuration.[3] The chiral silyl radical exists in a pyramidal form with considerable configurational stability, and retains the asymmetry prior to the abstraction of chloride from carbon tetrachloride.



$$\text{H-}\underset{\text{1-Np}}{\overset{\text{Me}}{\text{Si}}}\text{-Ph} \xrightarrow{\cdot\text{R}} \cdot\underset{\text{1-Np}}{\overset{\text{Me}}{\text{Si}}}\text{-Ph} \xrightarrow{\text{CCl}_4} \text{Cl-}\underset{\text{1-Np}}{\overset{\text{Me}}{\text{Si}}}\text{-Ph}$$

This observation has been amply supported by both other chemical[4-6] and ESR studies.[7-12] The inversion process must be slow, relative to the abstraction process, for retention of configuration to be observed.



The reactivity of each enantiomeric radical generated from optically active compounds is energetically identical, because both steric and electronic environments around the radical center are equal in each enantiomeric radical. On the contrary, when a cyclic radical such as a silacyclohexyl radical is produced, it should exist as an equilibrium mixture of conformers and then reacts through energetically different pathways. Introduction of a *t*-butyl group on the ring prevents the ring inversion, then two steric courses of the reaction, *i.e.* axial and equatorial approaches to the radical become distinguishable if inversion around the radical center on silicon is slow enough for product-forming chlorine abstraction.

In this paper stereochemical course of the chlorine abstraction from polychloroalkanes by silyl radicals, which were generated from conformationally stable hydrosilanes, is discussed.

Results and Discussion

The reaction of *cis*- or *trans*-4-*t*-butyl-1-methyl-1-silacyclohexane** (Ia, Ib)[13,14] with carbon tetrachloride in the presence of dibenzoyl peroxide under UV irradiation at 0 °C proceeded stoichiometrically to give the corresponding chlorosilanes. Interestingly as observed in the chlorination of the optically active hydrosilane, the configuration of the hydrosilanes was retained in resulting 4-*t*-butyl-1-methyl-1-chloro-1-silacyclohexane (II) as evidenced by NMR spectra. Figure 1 (a) shows the NMR spectra of the reaction mixture derived from the *trans*-hydrosilane (Ib). Thus, two methyl signals corresponding to *trans*- and *cis*-chlorosilane (IIb and IIa) appeared at δ 0.38 (singlet) and 0.42 (singlet), respectively, in a ratio of 94/6 in addition to the methyl signal of the unreacted *trans*-hydrosilane (Ib) at δ 0.07 (doublet). This means that the reaction proceeds with 94% retention of configuration. The *cis*-hydrosilane (Ia) gave a similar result but slightly less stereospecifically

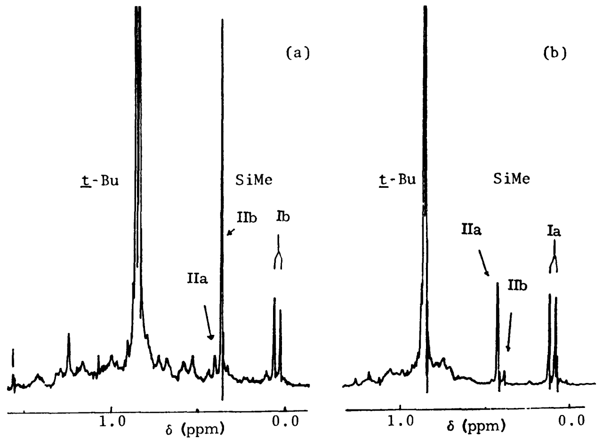


Fig. 1. NMR spectra of the reaction mixture of (a) the chlorination of (Ib) with CCl$_4$ and (b) the chlorination of (Ia) with CCl$_4$.

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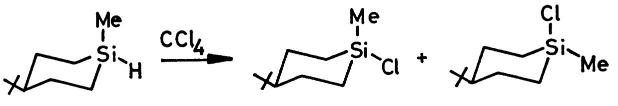
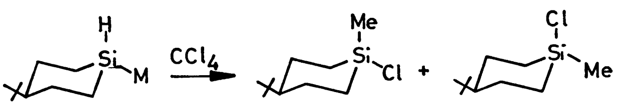
* For part XIV, see Ref. 1.

** Throughout the paper, *cis* and *trans* are defined with respect to 4-*t*-butyl and 1-methyl groups. Suffix a is added to the *cis* compounds and b to the *trans*.

(87%), as seen in Fig. 1(b). Namely, the silyl radical obtained from (Ia) or (Ib) exists in pyramidal form and retains mostly its configuration prior to the abstraction of chlorine from carbon tetrachloride as in the case of the chiral silyl radical obtained from optically active hydrosilane[3,6] and acylsilane.[4]

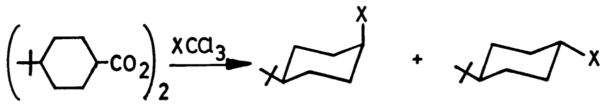


(Ia) (IIa) 87 % (IIb) 13 %



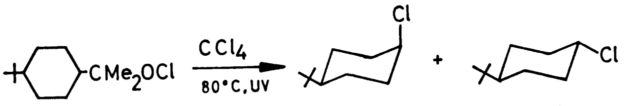
(Ib) (IIa) 6 % (IIb) 94 %

These results are in striking contrast to those observed for cyclohexyl radical.[15] Thus, *cis*- and *trans*-4-*t*-butylcyclohexane carbonyl peroxides, decomposed in carbon tetrachloride or bromotrichloromethane at 30 °C, give rise to the same products irrespective of the configuration of the starting materials.[16]



73% (X=Cl) 27% (X=Cl)
69% (X=Br) 31% (X=Br)

Similar results were reported in the decomposition of 1-(*cis* or *trans*-4-*t*-butylcyclohexyl)-1-methylethyl hypochlorite.[17]



or 67 % 33 %

These facts requires the formation of a common intermediate from both starting substances. This is likely to be the 4-*t*-butylcyclohexyl radical which evidently reacts with a halogen donor from the two sides. The reason why the intermediate 4-*t*-butylcyclohexyl radical gives rise to the thermodynamically less favored product is ascribable either to a twist-boat conformation in the transition state[17] or, more likely, to a torsional effect at the product-forming process.[18] In any event, the intermediate cyclohexyl radicals are in a planar form or in a rapidly-equilibrated state.

Similar reactions of (I) were carried out with pentachloroethane ($CHCl_2-CCl_3$), 1,1,1,2-tetrachloroethane ($CH_2Cl-CCl_3$) and chloroform ($HCCl_3$). The resulting chlorosilane (II) systematically lost its configurational purity in the following order of solvent (reactants), $CCl_4 < CHCl_2CCl_3 < CH_2ClCCl_3 < HCCl_3$. In the case

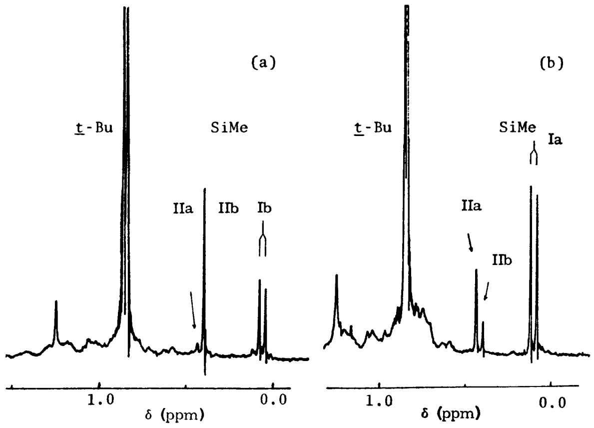


Fig. 2. NMR spectra of the reaction mixture of (a) the chlorination of (Ib) with $CHCl_2CCl_3$ and (b) the chlorination of (Ia) with $CHCl_2CCl_3$.

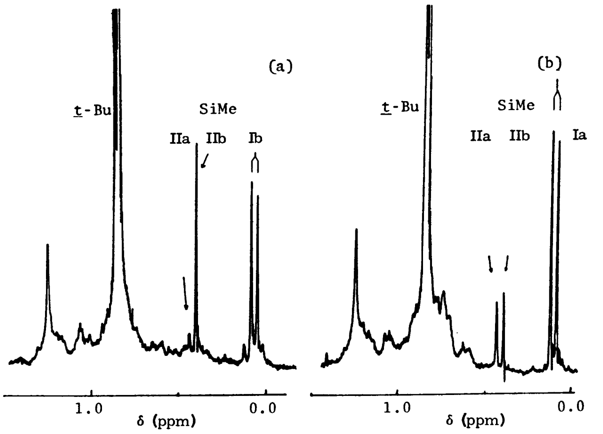
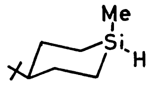
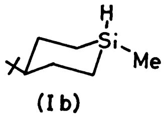


Fig. 3. NMR spectra of the reaction mixture of (a) the chlorination of (Ib) with CH_2ClCCl_3 and (b) chlorination of (Ia) with CH_2ClCCl_3.

TABLE 1. REACTION OF (I) WITH POLYHALOALKANES IN THE PRESENCE OF BENZOYL PEROXIDE AT 0°C

Starting material	Reactant	Reaction time (h)	Conversion (%)	Product(II)		
				cis(IIa)	:	*trans*(IIb)
 (Ia)	$Cl-CCl_3$	3	41	87	:	13
	$CHCl_2-CCl_3$	4	45	75	:	25
	$CH_2Cl-CCl_3$	4	23	57	:	43
	$H-CCl_3$	4.5	28	39	:	61
 (Ib)	$Cl-CCl_3$	3	55	6	:	94
	$CHCl_2-CCl_3$	4	55	12	:	88
	$CH_2Cl-CCl_3$	6	24	18	:	82
	$H-CCl_3$	4	54	25	:	75

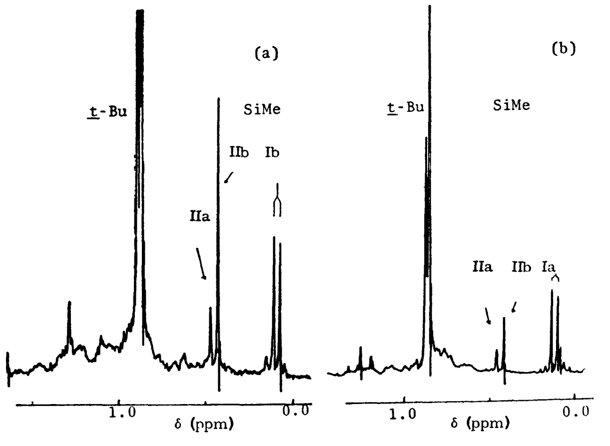


Fig. 4. NMR spectra of the reaction mixture of (a) the chlorination of (Ib) with ZCHCl$_3$ and (b) the chlorination of (Ia) with CHCl$_3$.

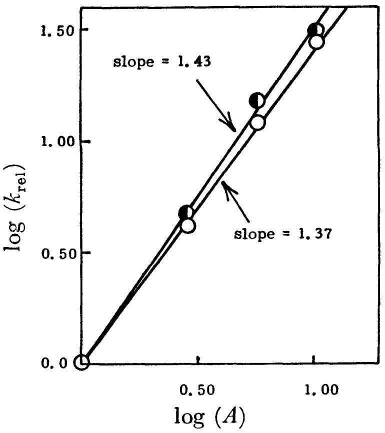
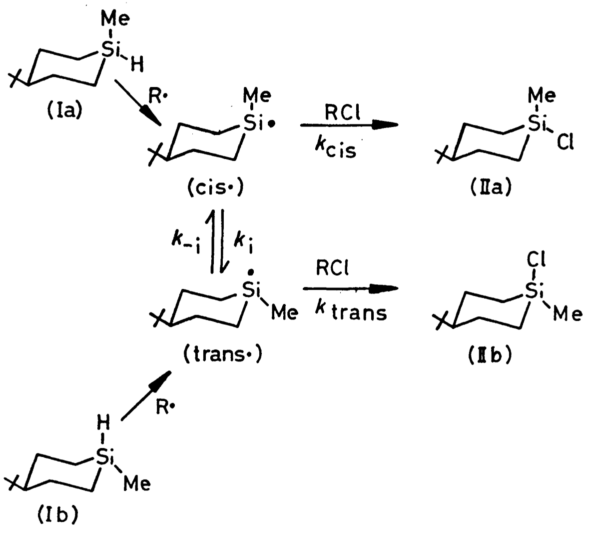


Fig. 5. Correlation between the logarithum of the relative reactivities of both *cis*- (◐) and *trans*- (○) silacyclohexyl radicals (vertical), and logarithum of the relative reactivities of triethylsiyl radicals (horizontal) in chlorine abstraction.

starting from the *cis*-hydrosilane (Ia), intensities of the methyl signal of the *cis*-chlorosilane (IIa) decrease gradually from in carbon tetrachloride to in chloroform. A similar trend can be seen for the case of *trans*-hydrosilane (Ib). These trends can be seen well qualitatively in Figs. 2—5. Quantitative determination of ratios of two isomeric chlorosilanes was performed by integrating the expanded NMR spectra. Generally, it is not easy to get precise integration for two near-by peaks on NMR, although fairly good reproducibility was observed in this particular case (Table 1). Therefore, care must be taken for detailed discussion, but the present data are still pertinent to an approximate kinetic analysis as shown in the next section.

The rate of abstraction of a chlorine atom from carbon tetrachloride is fast compared to the rate of inversion of silyl radicals.[6] On the contrary, the rate of abstraction of a chlorine atom from chloroform may be comparative to the rate of inversion of the same silyl radicals. Therefore, net stereochemistry depends on both relative rates of chlorine abstraction and conformational stabilities of silacyclohexyl radicals as shown in the following scheme.



From this scheme using the relevant rate constants shown above, the *cis*/*trans* product ratio (c/t) can be expressed by the formula

$$(c/t) = (k_{cis}/k_{trans})([cis\cdot]/[trans\cdot]), \qquad (1)$$

where $[cis\cdot]$ and $[trans\cdot]$ are the concentrations of *cis* and *trans* radicals, respectively. The *cis*/*trans* product ratio from *cis* hydrosilane (Ia), $(c/t)_{cis}$, can be derived as follows by assuming the steady-state concentration of the *trans* radical.

$$d[trans\cdot]/dt = k_i[cis\cdot] - k_{-i}[trans\cdot] - k_{trans}[trans\cdot][\mathrm{RCl}] = 0, \qquad (2)$$

$$[cis\cdot]/[trans\cdot] = (k_{-i}/k_i) + (k_{trans}/k_i)[\mathrm{RCl}],$$

$$(c/t)_{cis} = (k_{cis}/k_{trans})(k_{-i}/k_i) + (k_{cis}/k_i)[\mathrm{RCl}]. \qquad (3)$$

Similarly one can obtain the *trans*/*cis* product ratio from *trans* hydrosilane (Ib), $(t/c)_{trans}$, by assuming the steady-state of the *cis* radical derived from *trans*-hydrosilane (Ib).

$$(t/c)_{trans} = (k_{trans}/k_{cis})(k_i/k_{-i}) + (k_{trans}/k_{-i})[\mathrm{RCl}]. \qquad (4)$$

Combination of Eqs. 3 and 4 yields

TABLE 2. RELATIVE RATE CONSTANTS[a)]

Reactant	concn (mol/l)	K	k_{trans}/k_{-i}	k_{cis}/k_i	A[b)]
Cl-CCl$_3$	10.6	2.2	1.3(27)	0.59(33)	11.4
CHCl$_2$-CCl$_3$	8.31	2.1	0.63(13)	0.30(17)	6.18
CH$_2$Cl-CCl$_3$	9.45	2.4	0.23(4.8)	0.096(5.3)	3.07
H-CCl$_3$	12.4	2.4	0.048(1.0)	0.018(1.0)	1.00
			$\rho^*=0.46$[c)]		$\rho^*=0.29$[c)]

a) For definition of the symbols, see text. b) Relative reactivities of polyhaloalkanes in the chlorine abstraction by the triethylsilyl radical, see text. c) Reaction constants in the Taft equation.

$$K = (k_{trans}/k_{cis})(k_{i}/k_{-i}) = \frac{1+(t/c)_{trans}}{1+(c/t)_{cis}}.$$

Then values of $K=(k_{trans}/k_{cis})(k_{i}/k_{-i})$, (k_{trans}/k_{-i}) and (k_{cis}/k_{i}) can be calculated from the respective product ratios. These are listed in Table 2. Since it is reasonable to assume that the rate constants of inversion process are invariant regardless of the nature of the solvents used in this study, (k_{trans}/k_{-i}) and (k_{cis}/k_{i}) indicate the relative reactivities of both *trans* and *cis* radicals toward polyhalomethanes, respectively. These relative reactivities are also listed in parenthases in Table 2. Values of *cis* radicals agree with those of *trans* radicals within a possible experimental error.

Nagai and co-workers[19] reported that the reaction of the triethylsilyl radical with polychloroalkanes, X–CCl_3, where X stands CH_3, H, CH_2Cl, $CHCl_2$, CCl_3, and Cl, proceeded stoichiometrically to give X–CCl_2H, and that the relative reactivities increase in this order. For particular polyhaloalkanes such as $HCCl_3$, CH_2ClCCl_3, $CHCl_2CCl_3$, and CCl_4, they reported values of relative reactivity (k_{X-CCl_3}/k_{HCCl_3}) of chlorine abstraction toward the triethylsilyl radical at 80 °C to be 1.00, 3.07, 6.18 and 11.4, respectively. These relative reactivities derived from competitive experiments were treated by the Taft equation[20] with ρ^* values ranged from 0.26 to 0.29.[19]

The logarithms of relative reactivities toward silacyclohexyl radicals obtained in this study can be correlated strikingly well (correlation coefficient=0.999) with those toward triethylsilyl radicals as shown in Fig. 5. Higher selectivities of silacyclohexyl radicals than triethylsilyl radicals can be attributed to the temperature difference in the extent of 80 °C between two experiments which is reflected in a larger ρ^* value of the Taft equation of 0.46 in the present study.

The K $[K=(k_{trans}/k_{cis})(k_{i}/k_{-i})]$ values are almost constant irrespective of the solvents, as can be seen in Table 2. Since k_i and k_{-i} are unimolecular rate constants and must be invariant in a series of similar solvents, k_i/k_{-i} should be constant in the present case. Nagai *et al.* have also demonstrated that the reactivity of silyl radicals toward chlorine abstraction is rather insensitive to the structure of the radicals at the fixed condition.[19] Therefore, it seems to be reasonable to get constant K values.

As a conclusion, the remarkable configurational stability of silyl radicals is again demonstrated not only qualitatively but also semi-quantitatively.

Experimental

Materials. The required samples of *cis* and *trans*-4-*t*-butyl-1-methyl-1-silacyclohexane (Ia and Ib), and *cis*- and *trans*-4-*t*-butyl-1-methyl-1-chloro-1-silacyclohexane (IIa and IIb) were prepared as described in the previous paper.[13,14] Pentachloroethane ($CHCl_2$–CCl_3), 1,1,1,2-tetrachloroethane (CH_2Cl–CCl_3) and dibenzoyl peroxide were commercially available materials of the reagent grade.

Reaction of cis- *or* trans-*4-*t*-Butyl-1-methyl-1-silacyclohexane (Ia or Ib) with Polyhaloalkanes in the Presence of Dibenzoyl Peroxide (BPO).* Appropriate solutions (*ca.* 5%) of (Ia) or (Ib) in polyhaloalkanes (CCl_4, $CHCl_2CCl_3$, CH_2ClCCl_3, and $CHCl_3$) were prepared in NMR tubes. These were bubbled and filled with dry nitrogen and sealed with stoppers. These tubes were irradiated with a high-pressure mercury arc lamp (450 W, with a Pyrex filter) in an ice bath.

The color of the reaction mixtures changed to pale yellow. From the NMR spectra and GLC, the reaction mixture contained only 4-*t*-butyl-1-methyl-1-chloro-1-silacyclohexane (II) as a single product and the unchanged (I) as silicon-containing materials. The product and unchanged silane were identified by the way of NMR spectra and retention times of GLC by comparing with those of authentic samples.

The ratio of (II) and unchanged (I), and the conformational isomer ratio of each material were determined by means of NMR integration of Si–Me signals.

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