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Stereochemistry of a Chiral Germyl Radical in the Reaction of Carbon Tetrachloride

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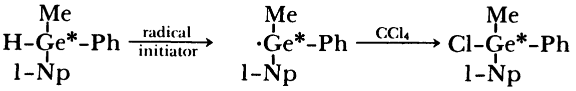
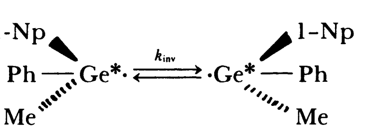
A chiral germyl radical produced from an optically active hydrogermane, 1-NpPhMeGe*H, abstracted a chlorine atom from CCl_4 to give the corresponding chlorogermane with retention of configuration. Progressive dilution of CCl_4 with cyclohexane demonstrated that the chiral germyl radical could also undergo inversion. A mechanism in which inversion of the chiral germyl radical competed with chlorine abstraction was proposed and the relative rate of chlorine abstraction to inversion (k_{Cl}/k_{inv}) of the chiral germyl radical was found to be $(0.52\pm0.13)\ mol^{-1}dm^3$ at 80 °C. The rate constant for the chlorine abstraction (k_{Cl}) by germyl radicals with CCl_4 was determined to be $(6.6\pm1.0)\times10^8\ s^{-1}mol^{-1}dm^3$ by laser-photolysis experiments. By using this rate constant, the k_{inv} value for the chiral germyl radical was estimated to be ca. $2\times10^9\ s^{-1}$.

In a former paper, we have reported that 1-naphthylphenylmethylgermyl radical, 1-NpPhMeGe$\dot{*}$, produced from an optically active 1-NpPhMeGe*H undergoes chlorine abstraction mostly with retention of configuration.[1)] Thus, the chiral germyl radical exists in a pyramidal form which is in harmony with ESR parameters[2–6)] and IR data[7–10)] of germyl radicals, and retains asymmetry for the abstraction of a chlorine atom with CCl_4.

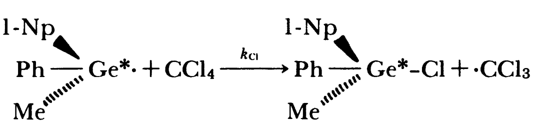


$$\mathrm{H\text{-}\overset{Me}{\underset{1\text{-}Np}{Ge^*}}\text{-}Ph} \xrightarrow[\text{initiator}]{\text{radical}} \mathrm{\cdot\overset{Me}{\underset{1\text{-}Np}{Ge^*}}\text{-}Ph} \xrightarrow{CCl_4} \mathrm{Cl\text{-}\overset{Me}{\underset{1\text{-}Np}{Ge^*}}\text{-}Ph} \qquad (1)$$

The inversion process of this germyl radical must be slow in comparison with the chlorine abstraction from CCl_4 since the germyl radical undergoes retention.



(2)



(3)

$$k_{inv} < k_{Cl}[CCl_4]$$

However, racemic or partially racemized products may be obtained from the chiral germyl radical, if product-forming chlorine abstraction is slow enough for the inversion process.

In this paper, we report the benzoyl peroxide (BPO)-catalyzed and uncatalyzed chlorination of optically active 1-NpPhMeGe*H with CCl_4 and the capacity of the chiral germyl radical produced from the optically active hydrogermane in the reaction (1) to invert under conditions of progressively greater dilution of CCl_4 with cyclohexane. Laser-photolysis studies of the photochemical primary processes of hydrogermanes are also described. A mechanism that induces inversion of the chiral germyl radical competes with chlorine abstraction is discussed, and the k_{inv} value for the chiral germyl radical is estimated by using the rate constant for chlorine abstraction, k_{Cl} obtained by laser-photolysis experiments.

Results and Discussion

BPO-Catalyzed Chlorination of an Optically Active Hydrogermane, (+)-1-NpPhMeGe*H. The reaction of (+)-1-NpPhMeGe*H (≡(+)-R_3Ge^*H), $[\alpha]_{589}$ +27.0± 0.9° (*c* 4.3, cyclohexane),[11)] with CCl_4 diluted cyclohexane at various concentrations was carried out in sealed and degassed tubes using BPO as an initiator at 80 °C The optically active hydrogermane, (+)-R_3Ge^*H, afforded the corresponding chlorogermane quantitatively in all reactions. The products, obtained after evaporation of CCl_4 and cyclohexane followed by recrystallization from pentane, was identified by comparing IR and NMR spectra, and retention time on GLC (SE30 5% 1 m) with those of the racemic R_3Ge^*Cl compound. The results are summarized in Table 1. The (+)-R_3Ge^*H and (−)-R_3Ge^*Cl have the same stereochemical configuration, since optical rotation correlated with the configuration of the optically active hydrogermane, R_3Ge^*H, and the optically active chlorogermane, R_3Ge^*Cl.[12)] Therefore, it can be concluded that the free-radical chlorination of the optically active hydrogermane, (+)-R_3Ge^*H, with CCl_4 without dilution should proceed with retention of configuration.

$$(+)\text{-}R_3Ge^*H \xrightarrow[\text{BPO, 80 °C}]{CCl_4} (-)\text{-}R_3Ge^*Cl \xrightarrow{LiAlH_4} (-)\text{-}R_3Ge^*H \qquad (4)$$

$$[\alpha]_{589}+27.0\pm0.9° \quad [\alpha]_{589}-4.6\pm1.1° \quad [\alpha]_{589}-17.8\pm1.2°$$

The optical purity of the product (−)-R_3Ge^*Cl, $[\alpha]_{589}$ −4.6±1.1° (*c* 3.9, cyclohexane)[12)], was about 73%. Furthermore, (−)-R_3Ge^*Cl was converted to (−)-R_3Ge^*H, $[\alpha]_{589}$−17.8±1.2°, again by reduction with lithium aluminum hydride. Thus, the rate of abstraction of a chlorine atom from CCl_4 with the chiral germyl radical is fast in the reaction of the

Table 1. Effects of Cyclohexane Dilution on the Stereospecificity of Reaction of (+)-R_3Ge^*H with CCl_4 at 80 °C

Run	Reactant[a]			Reaction time/h	Product, R_3Ge^*Cl	
	(+)-R_3Ge^*H (mmol)	CCl_4 ($mmol \cdot dm^{-3}$)	BPO (mmol)		Yield/%[b]	$[\alpha]_{589}$
1	1.12	10.4	0.08	5	100	−4.6±1.1
2	1.21	8.17	0.06	5	100	−3.4±0.4
3	1.10	6.06	0.04	5	99	−2.0±0.5
4	1.08	0.90	0.04	5	95	0

a) A value of $[\alpha]_{589}$ of the (+)-R_3Ge^*H is $[\alpha]_{589}$+27.0±0.9°. b) Isolated yield.

optically active R_3Ge^*H with CCl_4. However, the optical purity of the product (−)-R_3Ge^*Cl was decreased as CCl_4 was diluted with cyclohexane as shown in Table 1. Thus, the rate of chlorine abstraction competes with the rate of inversion under conditions of dilution of CCl_4 with cyclohexane.

Optically active hydrosilanes[13,14] and hydrostannane[15] also react stereoselectively with CCl_4 to give the corresponding chlorides, respectively, with retention of configuration.

Uncatalyzed Chlorination of an Optically Active Hydrogermane, (+)-1-NpPhMeGe*H. The reaction of (+)-R_3Ge^*H, $[\alpha]_{589}$+27.0±0.9° (*c* 4.3, cyclohexane), with CCl_4 was carried out without any catalyst in a sealed and degassed tube at 80 °C for 5 h. The product, $[\alpha]_{589}$+11.9±1.0°, (*c* 4.3, cyclohexane), obtained after evaporation of CCl_4, contained unreacted hydrogermane. The conversion of the hydrogermane to the chlorogermane was determined to be 40% by GLC by an internal standard method. The (+)-R_3Ge^*H and (−)-R_3Ge^*Cl have the opposite optical rotation in spite of the same configuration.[12] The value of $[\alpha]_{589}$ of the product, a mixture of (+)-R_3Ge^*H and (−)-R_3Ge^*Cl, by accounting for the concentration of the unreacted optically active hydrogermane is estimated to be +20°, if all the chlorogermane racemizes completely. A test of the optical stability of the R_3Ge^*Cl will be discussed in the next section. From the observed $[\alpha]_{589}$ of the product, the value of the optical rotation of (−)-R_3Ge^*Cl produced in this uncatalyzed chlorination is estimated to be about −6.0°. Therefore, uncatalyzed chlorination of the optically active hydrogermane proceeded mostly with retention of configuration. Since the free-radical mechanism for uncatalyzed chlorination of hydrogermanes with CCl_4 has been established,[16] this result is consistent with that for BPO-catalyzed chlorination of the optically active hydrogermane.

A Test of the Optical Stability of a Chlorogermane, (+)-1-NpPhMeGe*Cl. The optical stability of (+)-R_3Ge^*Cl was investigated in CCl_4, cyclohexane, and $CHCl_3$ under the reaction conditions.

The optically active chlorogermane, (+)-R_3Ge^*Cl, $[\alpha]_{589}$+6.0±1.0° (*c* 4.3, cyclohexane), was heated in CCl_4 in a sealed and degassed tube at 80 °C for 5 h. The value of $[\alpha]_{589}$ of the optically active chlorogermane, (+)-R_3Ge^*Cl, recovered after evaporation of CCl_4 followed by recrystallization from pentane, was +6.0±1.0°. Therefore, no change in the optical purity was observed. Similarly, the optically active chlorogermane, (+)-R_3Ge^*Cl, was heated in both cyclohexane and $CHCl_3$ at 80 °C for 5 h. The optical purity of the chloride, (+)-R_3Ge^*Cl, was also unchanged within experimental error. Thus, the optically active chlorogermane, R_3Ge^*Cl, is configurationally stable in CCl_4, cyclohexane, and $CHCl_3$ under the reaction conditions.

Laser-Photolysis Study of a Hydrogermane, 1-NpPhMeGeH. Laser-photolysis (ca. 0.1 $mol \cdot dm^{-3}$) in a mixture of benzene and di-*t*-butyl peroxide (DTBP) was carried out at 28.5±2 °C.[17] The laser-photolysis apparatus and measuring system were similar to those published elsewhere.[18] As expected, the rise of the absorption due to the germyl radical was observed in R_3GeH solution. As an example, the time dependence of the probe light intensity, *I*(*t*), observed in the R_3GeH solution at 400 nm is shown by curve (a) in Fig. 1. This curve shows the initial rise and the following slow decay of $R_3Ge\cdot$. The time-resolved absorption spectrum corresponding to the rise of $R_3Ge\cdot$ was also measured. The spectrum observed at 50 and 150 ns after excitation of the R_3GeH solution is shown in Fig. 2. As shown in Fig. 2, the transient spectrum observed with the solution of R_3GeH has a peak at 390 nm.

As is shown by curve (a) in Fig. 1, the decay of $R_3Ge\cdot$ was found to be slow. In the presence of CCl_4, how-

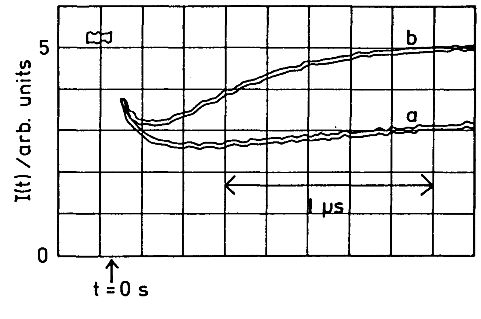


Fig. 1. Ocsilloscope traces of the *I*(*t*) curves observed at 400 nm for 1-NpPhMeGeH (0.1 $mol \cdot dm^{-3}$) in a mixture of benzene and DTBP (a) in the absence and (b) presence of CCl_4 (3.35×10^{-3} $mol \cdot dm^{-3}$).

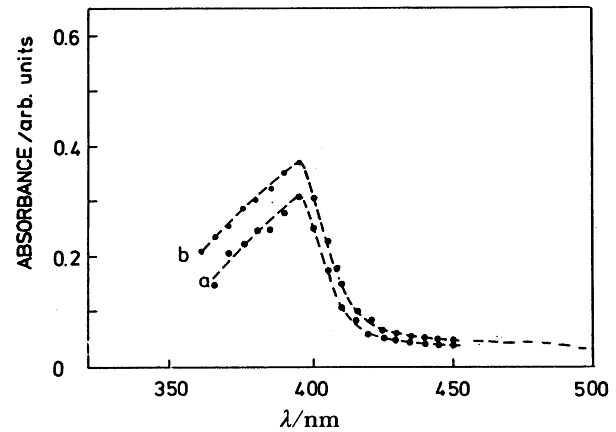


Fig. 2. Transient absorption spectra of 1-NpPhMeGeH (0.1 mol dm^{-3}) in a mixture of benzene and DTBP observed at (a) 50 ns and (b) 150 ns and after excitation with an N_2 laser.

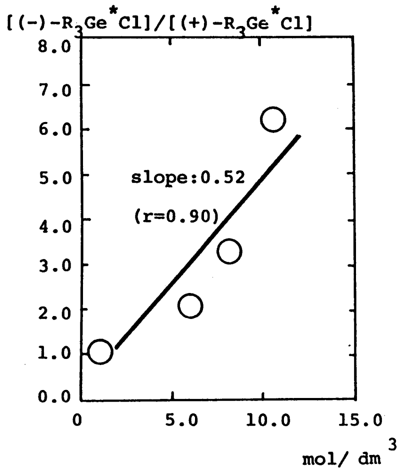
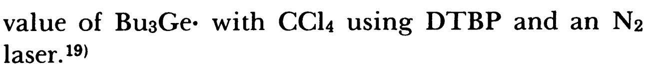


Fig. 3. Correlation between the product ratio and concentrations of CCl_4.

ever, the decay became fast. $R_3Ge\cdot$ was observed to decay with first-order kinetics in the presence of CCl_4, and the rate constant of chlorine abstraction (k_{Cl}) was obtained to be $(6.6\pm1.0)\times10^8$ s^{-1} mol^{-1} dm^3. The k_{Cl} value in a mixture of cyclohexane–DTBP was not changed within experimental error. Recently, Ingold and co-workers have also obtained a similar k_{Cl} value of $Bu_3Ge\cdot$ with CCl_4 using DTBP and an N_2 laser.[19)]

Stereochemistry of a Chiral Germyl Radical in the Reaction with CCl_4. The chiral germyl radical produced from an optically active hydrogermane, (+)-R_3Ge^*H, abstracts a chlorine atom from CCl_4 to give the (−)-R_3Ge^*Cl predominantly with retention of configuration. However, the optical purity of the product, (−)R_3Ge^*Cl, decreased as the CCl_4 is diluted with cyclohexane. Since (−)-R_3Ge^*Cl is configurationally stable under these conditions, optically active chlorogermane was produced. Thus, the loss of optical activity in the product must be due to the fact that the rate of abstraction of a chlorine atom from CCl_4 diluted with cyclohexane may be comparable to the rate of inversion of the germyl radical.

Net stereochemistry of the chiral germyl radical with CCl_4 depends on relative rates of chlorine abstraction (k_{Cl}) and inversion (k_{inv}) as shown in the following scheme.



$$\begin{array}{ccccc} (+)\text{-}R_3Ge^*H \rightarrow & (+)\text{-}R_3Ge^*\cdot & \xrightleftharpoons{k_{inv}} & (-)\text{-}R_3Ge^*\cdot & \leftarrow (-)\text{-}R_3Ge^*H \\ & k_{Cl}\Big\downarrow CCl_4 & & k_{Cl}\Big\downarrow CCl_4 & \\ & (-)\text{-}R_3Ge^*Cl & & (+)\text{-}R_3Ge^*Cl & \end{array}$$

From this scheme using the relevant rate constants shown above, the product ratio can be expressed by the formula

$$d[(-)\text{-}R_3Ge^*Cl]/d[(+)\text{-}R_3Ge^*Cl] = [(+)\text{-}R_3Ge^*\cdot]/[(-)\text{-}R_3Ge^*\cdot] \quad (5)$$

where $[(+)\text{-}R_3Ge^*\cdot]$ and $[(-)\text{-}R_3Ge^*\cdot]$ are the concentrations of each chiral germyl radical, respectively. The product ratio from (+)-R_3Ge^*H can be derived as following by assuming the steady state concentration of (−)-$R_3Ge^*\cdot$ radical.

$$d[(-)\text{-}R_3Ge^*\cdot]/dt = k_{inv}[(+)\text{-}R_3Ge^*\cdot] - k_{inv}[(-)\text{-}R_3Ge^*\cdot] - k_{Cl}[(-)\text{-}R_3Ge^*\cdot][CCl_4] = 0 \quad (6)$$

Combination of Eqs. 5 and 6 yields

$$[(-)\text{-}R_3Ge^*Cl]/[(+)\text{-}R_3Ge^*Cl] = 1 + (k_{Cl}/k_{inv}) \times [CCl_4]. \quad (7)$$

Thus, the product ratio depends on the concentration of CCl_4.[20,21)]

The relationship between the product ratio and concentrations of CCl_4 are shown in Fig. 3. The k_{Cl}/k_{inv} value was calculated to be (0.52±0.13) mol dm^3.

Taking the k_{Cl} value at 28.5 °C into consideration, it may be assumed that the k_{Cl} value at 80 °C for $R_3Ge^*\cdot$ is less than 1×10^9 s^{-1} mol^{-1} dm^3. Thus the k_{inv} value for $R_3Ge^*\cdot$ at 80 °C may be less than 2×10^9 s^{-1}. If we assume that inversion at the germanium center has a normal pre-exponential factor (i.e., ca. $10^{13.3}$ s^{-1}), it is possible to estimate the activation barrier for the inversion process as ca. 5.7 kcal · mol^{-1}. This value is almost the same as that of the silyl radical inversions previously reported.[22)]

In conclusion, the rate of inversion of the chiral germyl radical is comparable to that of chlorine abstraction from CCl_4 and the remarkable configurational stability of the chiral germyl radical in the reaction resulted partly from the rapid chlorine abstraction.

Experimental

Polarimetric analyses of optically active organogermanium compounds were carried out on a Hitachi EPU-2A photoelectric Spectrometer. Laser-photolysis experiments were performed on degassed solutions using a Molectron UV-24 N_2 laser (337 nm, pulse width 10 ns) as an exciting light source.

Materials. Optically active 1-naphthylphenylmethylgermane, R_3Ge^*H, and 1-naphthylphenylmethylchlorogermane, R_3Ge^*Cl, were prepared according to the literature.[11,16] (+)-R_3Ge^*H, $[\alpha]_{589}+27.0\pm0.9°$, mp 74—75 °C; (−)-$R_3Ge^*H$, $[\alpha]_{589}-26.6\pm0.9°$, mp 74—75 °C. (+)-$R_3Ge^*Cl$, $[\alpha]_{589}+6.0\pm1.0°$, mp 67—69 °C.

Reaction of (+)-R_3Ge^*H with CCl_4 at Various Concentrations. A representative example is described. In a small Pyrex tube were placed 0.36 g (1.21 mmol) of (+)-R_3Ge^*H, $[\alpha]_{589}+27.0\pm0.9°$, 2.51 g (16.3 mmol) of CCl_4, and 0.02 g (0.06 mmol) of BPO. The reaction mixture was diluted with cyclohexane to 4.0 dm^3. The Pyrex tube was degassed, sealed and immersed in an oil bath kept at 80 °C for 5 h. After completion of the reaction, volatile materials were removed. The chlorogermane, $[\alpha]_{589}-3.4\pm0.4°$, was purified by recrystallization from pentane. The chlorogermane was identified by comparing IR and NMR spectra and the retention time on GLC (SE30 5% 1 m) with those of an authentic sample.

A Test of Optical Stability of (+)-R_3Ge^*Cl under the Reaction Conditions. In a small Pyrex tube were placed 0.40 g (1.22 mmol) of (+)-R_3Ge^*Cl, $[\alpha]_{589}+6.0\pm1.0°$, and 4.0 dm^3 of CCl_4. The tube was degassed, sealed and immersed in an oil bath kept at 80 °C for 5 h. After removal of CCl_4, the chlorogermane, $[\alpha]_{589}=6.0\pm1.0°$ was recovered and purified by recrystallization from pentane.

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