Reactivities of Stable Rotamers. XVI. Tributylstannane Reduction and Electron-impact Mass Spectra of Rotamers of 1,2,3,4-Tetrachloro-9-(2-chloro-1,1-dimethylethyl)triptycene and 1,2,3,4-Tetrachloro-9-(2-chloro-1-chloromethyl-1-methylethyl)triptycene[1]

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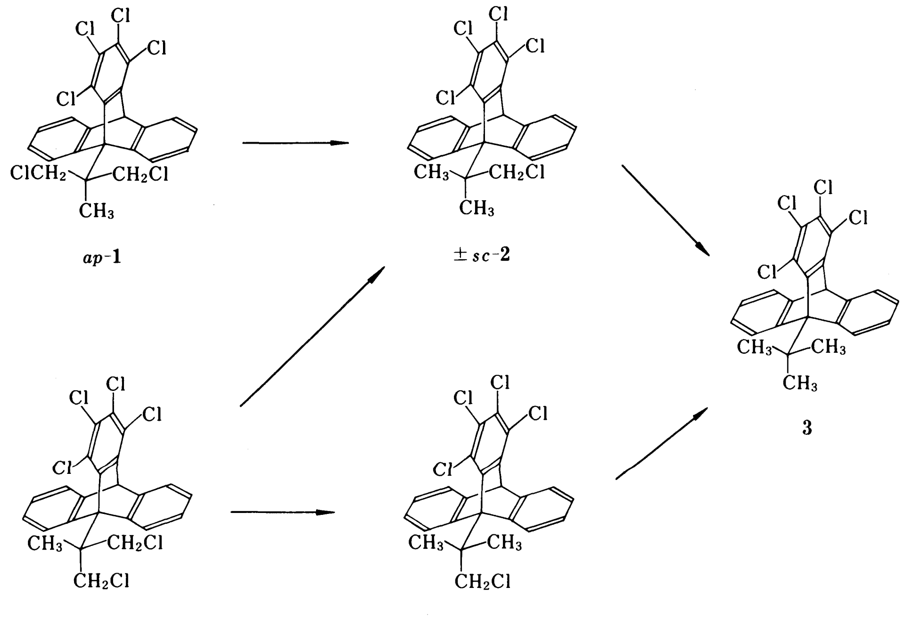
1,2,3,4-Tetrachloro-9-(2-chloro-1-chloromethyl-1-methylethyl)triptycene (**1**) and 1,2,3,4-tetrachloro-9-(2-chloro-1,1-dimethylethyl)triptycene (**2**) were reduced with tributylstannane in the presence of azobisisobutyronitrile in benzene. **1** was reduced to **2** which was further converted to a 9-*t*-butyltriptycene under the conditions. The chloromethyl group *sc* to the *peri*-chloro substituent was found to be *ca.* 7 times more reactive than the *ap* in *sc*-**1**. *sc*-**2** was consumed 1.7 times more rapidly than *ap*-**2**. The results are attributed to the participation of the *peri*-chloro substituent in the chlorine abstraction. Electron impact mass spectra of these compounds reveal that they give different intensities at a number of peaks. The difference is again attributed to the chloro participation in stabilizing the cation formed.

In one of the previous papers of this series, we pointed out that a radical reaction, chlorination of the methyl groups of the *t*-butyl group in 9-*t*-butyl-1,2,3,4-tetrachlorotriptycene (**3**), can be accelerated by the participation of the 1-chloro substituent.[2] Since there are varieties of radical reactions known, the transition states of which should vary from the product-like to substrate-like, the degree of enhancement by the participation of the chloro substituent must be different from reaction to reaction. Alternatively, the degree of the chloro participation could tell the earliness or the lateness of the transition state of a reaction, if a common radical intermediate is to be formed by a variety of reactions.

The rotational barriers in 1,2,3,4-tetrachloro-9-(2-chloro-1-chloromethyl-1-methylethyl)triptycene (**1**) and 1,2,3,4-tetrachloro-9-(2-chloro-1,1-dimethylethyl)triptycene (**2**) are known to be high enough so that any mixing of rotational isomers can be neglected during the course of reactions.[2] The barrier to rotation of the radicals produced in the reaction may be assumed to be high as well from the results in the radical halogenations.[2] To support this assumption, we may cite a fact that 9-*t*-alkyltriptycenes which possess the 9-substituent of a *t*-butyl type, one of the methyls of which is replaced by an sp^2 group, show high barriers as well.[3] Therefore, any contamination by the contribution of other rotamer(s) during the



Scheme 1.

reaction may be neglected in this system, if the reaction is run in the vicinity of 100 °C for a week or so.

At an outset of investigations of other radical reactions, we chose reduction of rotamers of **1** and **2** with tributylstannane. The tributylstannane reduction of organic halides, which can be initiated by azobisisobutyronitrile, is known to proceed with radical intermediates: the rate-determining step is the abstraction of a halogen from the organic halides by tributylstannyl radicals.[4)]

Compound **1** was prepared according to the method described before and separated into rotational isomers, *ap*-**1** and ±*sc*-**1**, by chromatography.[2)] Although separation of *ap*-**2** and ±*sc*-**2** from the mixture of the two was reported to be tedious, as is shown in Scheme 1, if the tributylstannane reduction is successful for *ap*-**1**, it should give mixtures of ±*sc*-**2** and 9-*t*-butyl-1,2,3,4-tetrachlorotriptycene (**3**) in addition to the unreacted starting material, if any, of which separation by chromatography is not too difficult. Indeed, by this method, we could obtain sufficient quantity of ±*sc*-**2** for chracterization and some reactions.

The reaction of the halogen compounds with tributylstannane was generally carried out in benzene solutions, unless otherwise stated. The competitive reactions and determination of the relative rates of reactions were carried out as follows. Nearly equimolar mixtures of *ap*-**2** and ±*sc*-**2** or *ap*-**1** and ±sc-**1** were dissolved in benzene together with a reference compound, either 4-methoxytoluene or 1-methoxy-3,5-dimethylbenzene. Azobisisobutyronitrile was added to the mixture and then tributylstannane (equimolar with the mixture of the substrate) under a nitrogen atmosphere, and the mixture was heated at three temperatures. The decrease in the substrate was monitored by ^{1}H NMR spectroscopy and/or high pressure liquid chromatography (HPLC).

Although we wished to be quantitative, the reactions of **1** were not clean by any means: we found a number of peaks, though small, in HPLC charts in addition to the starting materials and the desired products, **2** and **3**. Especially the peak due to **3** was often in the midst of many small peaks which prevented us from obtaining reliable data of **2**. The yields of compound **2** (±*sc* and *ap*) from compound **1** were *ca.* 50% based on the consumed substrates. These results may be attributed to the strain of the molecules, which could make the aromatic chlorine substituents susceptible to the attack of the tributylstannyl radicals, and force us to be semiquantitative in discussion. The results of the reductions of *ap*-**1** and ±*sc*-**1** are compiled in Tables 1 and 2.

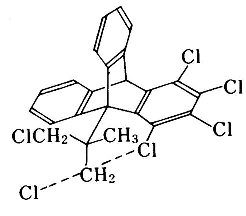
Table 1. Competitive reduction of the *sc* and *ap* chloromethyl groups in ±*sc*-**1**

Temperature/ °C	Conversion/ %	*ap*-**2**/ *sc*-**2**	Reaction time/ h
80	53	6.7	3
69	21	5.8	3
69	13	8	1.5
69	7	6	0.5

Table 2. Results of competitive reactions of ±*sc*-**1** and *ap*-**1** with tributylstannane after 3 h

Temperature/°C	Conversion/%		Product ratio
	±*sc*-**1**	*ap*-**1**	(*sc*-**2**/*ap*-**2**)
100	57	63	2.8
80	57	63	2.4
69	28	31	2.3

Though the reaction is not clean, we may take the ratio *ap*-**2**/*sc*-**2** in the reaction of ±*sc*-**1** as indicating the reactivity of the *sc* and the *ap*-chloromethyl groups in ±*sc*-**1**. Examination of the data in Table 1 reveals that the chloromethyl group *sc* to the *peri*-substituent is about 7 times more reactive than the *ap* group. By reducing the conversion ratio of ±*sc*-**1**, we should be able to expect that the consumption of ±*sc*-**2** is negligible. Yet the ratio *ap*-**2**/*sc*-**2** is almost constant. Thus the reactivity of the *sc*-chloromethyl group is indeed higher than that of the *ap*. This should be attributed to the participation of the *peri*-chloro substituent (**4**), which stabilizes the transition state of the reaction. This type of participation of a chlorine atom in stabilizing radicals has been reported.[5)]



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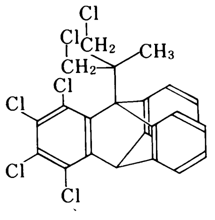
It is also noted that the relative reactivity of the *sc* chloromethyl group to that of the *ap* found in ±*sc*-**1** is much larger than that (1.6) in the radical chlorination of **3** with sulfuryl chloride.[2)] The results will mean that the bond lengthening (C–Cl and C–H, respectively) in the transition states in these reactions are different to a considerable extent.

The data for the competitive reduction of *ap*-**1** and ±*sc*-**1**, shown in Table 2, indicate that the *ap*-form is a little more reactive than the *sc* and the product ratio (*ap*-**2**/*sc*-**2**) is larger than 2. If the two chloromethyl groups in *ap*-**1** had the same reactivity with the *sc*-chloromethyl group in ±*sc*-**1**, the followings could be expected. Since there are two *sc*-chloromethyl groups in *ap*-**1**, the overall rates of reduction of either one of the groups are twice of that of the *sc*-chloromethyl group in ±*sc*-**1**. That means that ±*sc*-**2** is produced from *ap*-**1** with a factor of *ca.* 14 relative to the reduction of the *ap*-chloromethyl group in ±*sc*-**1**. Since the relative rate of formation of ±*sc*-**2** from ±*sc*-**1** is small, the formation of *sc*-**2** *via* this route may be neglected. Then the formation ratio (*ap*-**2**/*sc*-**2**) in the competitive reaction should be 2, if the reactivities of the *sc*-chloromethyl groups in *ap*-**1** and ±*sc*-**1** were the same. The observed ratios are significantly larger than 2 to indicate that the chloromethyl group in *ap*-**1** is more reactive than that in ±*sc*-**1** which is *sc* to the 1-chloro substituent for some reasons. The enhanced rates of decreasing in *ap*-**1** relative to those in *sc*-**1** may be also taken as supporting evidence for the above conclusion.

In the ground state, there are two $\mathrm{Cl\cdots CH_2Cl}$ interactions[6] in *ap*-**1**, whereas there is only one such interaction in ±*sc*-**1**. This will necessarily make the $\mathrm{Cl\cdots CH_2Cl}$ interactions in *ap*-**1** weaker than that in ±*sc*-**1**. The results then may show that this less stabilization in the ground state in *ap*-**1** is important. It may also be pointed out that three C–Cl dipoles are parallel in *ap*-**1** in close proximity (**5**) but one of them is more distant in ±*sc*-**1**: this should result in higher ground state energy of *ap*-**1** than that in ±*sc*-**1**. In addition, probably the steric congestion in *ap*-**1** is more effectively relieved than that in ±*sc*-**1** by the formation of transition state, because the congestedness in this molecule is expected to be greater than that in ±*sc*-**1**. Diagnosis of contributions of these factors awaits further investigations.



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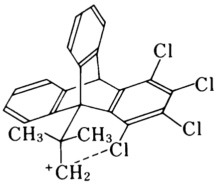
The reduction of ±*sc*-**2** and *ap*-**2** were not clean as well. The competitive reactions of ±*sc*-**2** and *ap*-**2** indicated that the *sc*-form was consumed 1.5, 1.6, and 2.0 times faster than *ap*-**2** at 100, 80, and 61 °C, respectively, after 3 h heating. We cannot postulate directly from the results that ±*sc*-**2** is more vulnerable to the attack of the tributylstannyl radicals than *ap*-**2** because of the complex nature of the reaction, but nonetheless it is tempting to consider so from the results with ±*sc*-**1** and *ap*-**1**. The interesting point here is that the difference in reactivities between the *sc*-chloromethyl group and the *ap* in **2** seems to be diminished considerably from the values observed in ±*sc*-**1**. We do not have good explanations for this finding but it could be postulated that the stabilization due to the $\mathrm{Cl\cdots CH_2Cl}$ interaction, the congestedness, Coulombic interactions, and the enhanced electronegativity of the chloromethyl group in *ap*-**1** relative to that in ±*sc*-**2** are responsible.

Having had two rotamers of compound **2** in hand, we can now compare some properties of the rotamers of **2**, which cannot be examined as a mixture. As one of such examples we have taken the electron-impact mass spectra of the rotamers. Although there are ample reports which describe different fragment patterns of diastereomeric isomers,[7] those of rotational isomers are limited.[8] Therefore, it will be worthwhile to acquire mass spectral data of rotational isomers of **2** as well as **1**, because the mass spectra are usually obtained as a mixture of possible rotamers of a compound. We also expected that, from the results of ionization reactions of these isomers that showed significant stabilization of the *sc*-carbocation by the participation of the 1-chloro substituent in **2**,[9] the fragment species **6** should be more abundant than the fragment **7** in which no special stabilization is expected.



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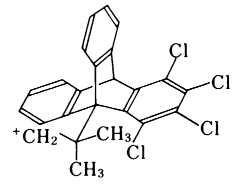

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Sets of typical results are shown in Table 3. Since vaporization of the samples took place at 180—210 °C, we can assume that internal rotation is negligibly slow during the measurement. The intesities of the peaks varied from one measurement to another but the trends in intensities discussed below were reproducible. As expected, we observed a number of peaks in the mass spectra of which relative intensities were different from a rotamer to another. We will discuss the peaks corresponding to species which bear $^{35}\mathrm{Cl}$ atoms only for the sake of simplicity and the absence of ambiguity in the discussion.

Base peaks in both ±*sc*-**2** and *ap*-**2** were mostly at *m/z* 356 which correspond to the loss of the 9-substituent and a chlorine atom with the gain of two hydrogen atoms. The loss is reasonable since removal of the 9-substituent and/or the chlorine atom at the 1-position relieves the strong steric strain. The features noticed in comparison of the two spectra due to ±*sc*-**2** and *ap*-**2** are that the relatively large molecular ion peak for the *ap*, the relatively large peak corresponding to $[M-35]^+$ for the *sc*, and

Table 3. Typical sets of mass spectral data of compounds **1** and **2**[a)]

Assignment	Compound **1**			Compound **2**		
	m/z	±*sc*	*ap*	*m/z*	±*sc*	*ap*
M^+	514	8.5	10.0	480	14.5	20.0
$[M-Cl]^+$	479	10.5	10.0	445	20.5	8.0
$[M-HCl]^+$	478	4.5	10.5	444	38.0	2.5
$[M-(Cl+HCl)]^+$	443	12.7	38.0			
$[M-2HCl]^+$	442	7.0	27.0			

a) Relative intensities to the base peaks which were at *m/z* 356 in all the cases shown here.

the relatively large peak corresponding to $[M-36]^+$ in the *sc*. The first two features both speak for the stabilization of $[M-35]^+$ species in the *sc* form which can be assigned to structure **6**. A part of the reasons for the less abundance of the M^+ peak for the ±*sc*-isomer must be attributed to the more intense peaks corresponding to $[M-35]^+$ and $[M-36]^+$. Since it is known that, if once the cationic species **6** is formed, it undergoes reactions, cyclization and olefin-formation,[9)] this peak may be assigned to the cationic species formed after these reactions. Therefore, the abundance of $[M-36]^+$ peak in the mass spectra of the ±*sc*-form is also evidence for the stabilization of **6**.

In Table 3, are also included the electron impact mass spectra of ±*sc*-**1** and *ap*-**1**. Here again the base peaks were generally *m/z* 356. The features of the mass spectra of *ap*-**2** and ±*sc*-**2** are reproduced here again. Since both rotamers of **1** bear at least one *sc*-chloromethyl group to the *peri*-chloro, it may be fair to compare the results which correspond to the loss of the second chlorine atom. Although we could not observe a $[M-2Cl]^+$ peak, the peaks corresponding to $[M-(Cl+HCl)]^+$ and $[M-2HCl]^+$ are more abundant in the *ap* form than in the *sc*.[10)] The anchimeric assistance in the fragmentation in mass spectra is again important.

Experimental

Substrates were prepared as reported previously,[2)] except for ±*sc*-1,2,3,4-tetrachloro-9-(2-chloro-1,1-dimethylethyl)-triptycene (**2**), of which method of preparation is given below. The products were identified by comparison of their ^1H NMR spectra and retention times in HPLC.

Competitive Reactions. A nearly equimolar amount (*ca.* 5 mg or *ca.* 0.01 mmol) each of *ap* and ±*sc* isomers of **1** was weighed and dissolved in 1.3 mL of benzene. A small amount of azobisisobutyronitrile was added to the solution together with 60 μL of 1-methoxy-3,5-dimethylbenzene or 4-methoxytoluene. After purging of the air by nitrogen, 5.4 μL (0.02 mmol) of tributylstannane was added and the solution was sealed in a tube. The tube was heated at 100, 80, or 69 °C for 3 h by immersing the tube into a boiling bath of water, benzene, or hexane. Averages of 3 runs are given in Table 1. Competitive reactions between *ap*-**2** and ±*sc*-**2** were carried out similarly. A small amount of products which were derived by reduction of the aromatic chlorine atom(s) was detected but these were neglected in analyses.

Analysis of the Unreacted Materials and Products. Analysis was carried out with the use of a Waters HPLC apparatus equipped with a UV detecter at 254 nm, a microporasil column being used. Typical retention times for these compounds were as follows, when the flow rate of hexane was 1.5 mL min^{-1}: **3** 8.4 min, *ap*-**2** 11.5 min, ±*sc*-**2** 11.9 min, *ap*-**1** 14.7 min, ±*sc*-**1** 21.3 min. Intensities were measured by the weight method except for compound **2**, for which special care was taken because of the overlap of the corresponding peaks in HPLC. A calibration curve was drawn by comparing the intensities of the peaks due to the substrates and the products in HPLC with those of ^1H NMR spectra in the former case. The peak heights were used in the case of **2** and a calibration curve was drawn as well.

Mass Spectrometry. The electron-impact mass spectra were recorded on a JEOL-JMS-D300 mass spectrometer with 70 eV electrons. The temperature required for obtaining high enough vapor pressure for the measurement ranged from 180 to 210 °C. The intensities of peaks of interest changed from a measurement to another. Those data given in Table 3 are sets of typical values of which trends were reproducible.

±sc-*1,2,3,4-Tetrachloro-9-(2-chloro-1,1-dimethylethyl)-triptycene (2).* A solution of 110 mg (0.22 mmol) of *ap*-**1** in 12 mL of toluene was heated with 59 μL (0.22 mmol) of tributylstannane and a small amount of azobisisobutyronitrile under reflux for 6 h. The solvent was evaporated and the residue was chromatographed on a silica-gel plate with hexane–dichloromethane as an eluent. The desired product was obtained as crystals, mp 185.0—186.0 °C, in 16% yield. Found: C, 59.38; H, 3.71; Cl, 37.34%. Calcd for $C_{24}H_{17}Cl_5$: C, 59.72; H, 3.55; Cl, 36.73%. ^1H NMR ($CDCl_3$), $\delta=2.13$ (3H, s), 2.32 (3H, s), 4.87 and 4.95 (2H, ABq, $J=11.6$ Hz), 6.06 (1H s), 6.9—7.2 (4H, m), 7.3—7.5 (2H, m), 7.8—8.0 (2H, m).

Although it was possible to increase the amount of ±*sc*-**2** in this reaction by increasing the reducing reagent, products derived by the reduction of aromatic chlorine atom(s) increase in its amount as well. Thus the above procedure is the optimum so far we have achieved. *ap*-**1** could be recovered in *ca.* 80% yield on an average.

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10) In one measurement, the peak at m/z 444 appeared as a very strong one. This peak involves contributions of the fragment $[M-2^{35}\mathrm{Cl}]^+$ from $C_{24}H_{17}{}^{35}Cl_5$ and that $[M-2H^{35}\mathrm{Cl}]^+$ from $C_{24}H_{17}{}^{35}Cl_4{}^{37}Cl$. However, this peak is omitted from the discussion for the following reasons. Firstly, the cause for the stabilization of $[M-2\mathrm{Cl}]^+$ is difficult to find and, secondly, division of the contributions by the two kinds of fragments is not tried in this work.