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Reactivities of Stable Rotamers. VI. Manifestation of Differential Reactivities of the Methyls in a *t*-Butyl Group in Radical Halogenations[1,2)]

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The methyls in a *t*-butyl group are shown to exhibit different reactivities in radical halogenations, if rotation about a $(CH_3)_3C$–CXY_2 bond is frozen. Barriers to rotation of halogenated 9-*t*-butyl-1,2,3,4-tetrachlorotriptycenes are obtained as $\Delta H^{\neq}$ *ca.* 32 kcal/mol. The cause of the selectivity in chlorination with sulfuryl chloride was discussed by obtaining reactivity data with a variety of compounds and halogenating reagents. It is concluded that the neighboring group participation of the peri-halo substituent is responsible for the observed selectivity.

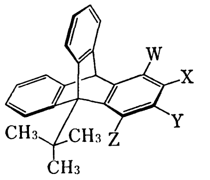
Reactivities of rotamers drew attention of some investigators. Curtin and Hammett³⁾ discussed the problem from the product ratio and Winstein and Holness⁴⁾ from the reaction rates, when the reaction and the equilibration of rotamers are represented by Eq. 1.

$$A_1 \xleftarrow{k_{21}} A_2 \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} A_3 \xrightarrow{k_{34}} A_4 \qquad (1)$$

Eliel and Ro discussed the matter from the similar stand point⁵⁾ and Zefirov *et al.* elaborated further.⁶⁾ Although the scheme was mathematically treated by Seeman and Farone,⁷⁾ the solution gives some ambiguities because the rate constants, k_{21} and k_{34}, are both arbitrary. As far as the reactivity of a single rotamer is not known, this arbitrariness is always involved in the discussion. Winstein and Holness used a diastereomeric pair of 4-*t*-butylcyclohexyl derivatives as models of rotamers.⁴⁾ It may be assumed that a remote *t*-butyl group should not affect the reaction rate to a large extent. The assumption will succeed, if we are discussing the rule of thumb, but will fail in discussion with quantitative aspects. Therefore, in understanding the reactivities of rotamers, which are so often present in nonrigid organic molecules, the knowledge on the reactivities of respective rotamers is absolutely necessary.

Since we have been able to isolate stable rotamers of triptycene and 9-arylfluorene derivatives,⁸⁾ we have felt that comparison of the reactivities will produce useful information about those of rapidly exchanging systems. Furthermore, the merit of using these systems instead of using 1-substituted 4-*t*-butylcyclohexanes is the possibility of introducing a wide variety of substituents. Under these expectations, we decided to launch a project of studying the reactivities of triptycene and 9-arylfluorene systems.

As the beginning of the study in the triptycene system, we focussed our attention to the reactivities of the methyls in a *t*-butyl group. Chemically idential ligands in a group of local C_{3v} symmetry, such as the methyls in a *t*-butyl group, are usually treated nondistinguishable in organic chemistry, because they are usually interchanged rapidly on the laboratory time scale by rotation. However, if the rotation of a *t*-butyl group is frozen on the laboratory time scale, three methyls in a molecule of $(CH_3)_3C$–$CXYZ$ type are all diastereomeric. In a molecule of $(CH_3)_3C$–CXY_2 type, two methyls are enantiotopic and another is diastereotopic with any of the enantiotopic pair of methyls. In principle, the diastereomeric and diastereotopic methyls should show different reactivities if the rotation is frozen. This paper reports the manifestation of the differential reactivities of the diastereotopic methyls in 9-*t*-butyl-1,2,3,4-tetrachlorotriptycene (**1**) and related compounds in radical halogenation reactions.



(**1**): W=X=Y=Z=Cl
(**2**): W=X=Y=Z=Br
(**3**): W=Z=H, X=Y=Cl
(**4**): W=X=Y=H, Z=Cl
(**5**): W=X=Y=Z=H

Experimental

Spectral Measurement. ¹H NMR spectra were obtained on a Hitachi R-20B spectrometer operating at 60 MHz or a Varian EM 390 spectrometer operating at 90 MHz.

9-t-Butyl-1,2,3,4-tetrachlorotriptycene (1). *(a)*: To a suspension of hexachlorobenzene (5.7 g or 20 mmol) in 350 mL of dry ether was added a hexane solution of butyllithium (20 mmol) under a dry nitrogen atmosphere below −30 °C. To the mixture, which was stirred for 2 h at −30—−20 °C, was added 2.34 g (10 mmol) of crystalline 9-*t*-butylanthracene⁹⁾ and the whole was heated under reflux for 3 h. Lithium chloride was filtered off and the filtrate was evaporated. Chromatography of the residue on alumina, using hexane–benzene (10:1) as an eluent, gave 3.3 g (72%) of the desired compound, mp 283.5—284.5 °C. Found: C, 64.07; H, 4.03; Cl, 31.83%. Calcd for $C_{24}H_{18}Cl_4$: C, 64.31; H, 4.05; Cl, 31.64%. ¹H NMR ($CDCl_3$, δ): 2.20 (3H, s), 2.31 (6H, s), 6.09 (1H, s), 6.90—7.15 (4H, m), 7.30—7.45 (2H, m), 7.82—8.15 (2H, m).

(b): To a boiling mixture of 1.0 g (4.3 mmol) of 9-*t*-butylanthracene and 1 mL of isopentyl nitrite in 50 mL of dichloromethane was added a solution of 2.5 g (5.0 mmol) of tetrachloroanthranilic acid¹⁰⁾ in 20 mL of acetone over a period of 2 h. Additional 1.0 mL of isopentyl nitrite was added in 2 portions with intervals of 30 min. The mixture was heated for further 30 min and evaporated. Chromatography of the residue on alumina with 10:1 hexane–benzene as an eluent afforded 700 mg (36%) of the desired compound.

9-t-Butyltriptycene (5), mp 241—241.5 °C, was prepared similarly from 9-*t*-butylanthracene and anthranilic acid in 76% yield. Found: C, 93.07; H, 7.24%. Calcd for $C_{24}H_{22}$: C, 92.86; H, 7.14%. ¹H NMR ($CDCl_3$, δ): 2.06 (9H, s), 5.23 (1H, s), 6.85—7.10 (6H, m), 7.27—7.48 (3H, m), 7.70—8.93 (3H, m).

*1,2,3,4-Tetrabromo-9-*t*-butyltriptycene (2)*, mp 287—288 °C, was similarly prepared from 9-*t*-butylanthracene and tetrabromoanthranilic acid[11] in 8% yield. Found: C, 46.23; H, 2.83; Br, 50.78%. Calcd for $C_{24}H_{18}Br_4$: C, 46.05; H, 2.90; Br, 51.06%. ^{1}H NMR ($CDCl_3$, δ): 1.98 (3H, s), 2.46 (6H, s), 6.22 (1H, s), 6.97—7.20 (4H, m), 7.37—7.58 (2H, m), 7.92—8.15 (2H, m).

*9-*t*-Butyl-2,3-dichlorotriptycene (3)*, mp 184.5—185.5 °C, was similarly prepared from 9-*t*-butylanthracene and 4,5-dichloroanthranilic acid[12] in 39.7% yield. Found: C, 76.28; H, 4.77; Cl, 19.20%. Calcd for $C_{24}H_{20}Cl_2$: C, 75.99; H, 5.31; Cl, 18.69%. ^{1}H NMR ($CDCl_3$, δ): 1.99 (9H, s), 5.05 (1H, s), 6.65—7.03 (4H, m), 7.03—7.35 (2H, m), 7.39 (1H, s), 7.78 (1H, s), 7.46—7.90 (2H, m).

*Reaction between 9-*t*-Butylanthracene and Lithiated* m*-Dichlorobenzene.* To a solution of 3.54 g (24.1 mmol) of *m*-dichlorobenzene in dry ether was added 25.6 mmol of butyllithium in hexane at −40 °C in 40 min and the mixture was stirred for 1 h. 9-*t*-Butylanthracene (15.2 mmol) was added and the temperature was allowed to rise. After the mixture was refluxed for 2 h, it was treated as usual and the product was separated by careful chromatography. The following compounds were obtained (given by the order of elution from an alumina column by hexane).

*9-*t*-Butyl-4-chlorotriptycene*: Mp 273 °C, yield 21%. Found: C, 83.76; H, 6.08; Cl, 10.40%. Calcd for $C_{24}H_{21}Cl$: C, 83.58; H, 6.14; Cl, 10.28%. ^{1}H NMR (CCl_4, δ): 2.06 (3H, s), 2.08 (6H, s), 5.76 (1H, s), 6.7—7.1 (6H, m), 7.1—7.5 (2H, m), 7.5—7.8 (3H, m).

*9-*t*-Butyl-2(and/or 3)-chlorotriptycene*: Mp 258—268 °C, yield 11%. ^{1}H NMR (CCl_4, δ): 2.07 (9H, s), 5.43 (1H, s), 6.7—7.1 (3H, m), 7.1—7.4 (2H, m), 7.4—7.9 (6H, m).

*9-*t*-Butyl-1-chlorotriptycene (4)*: Mp 260.0—260.5 °C, yield 47%. Found: C, 83.54; H, 6.50; Cl, 10.96%. Calcd for $C_{24}H_{21}Cl$: C, 83.58; H, 6.14; Cl, 10.28%. ^{1}H NMR (CCl_4, δ): 2.03 (3H, s), 2.29 (6H, s), 5.05 (1H, s), 6.6—7.05 (6H, m), 7.05—7.4 (3H, m), 7.6—8.0 (2H, m).

The assignment of the structures bases on the NMR spectral data and the consideration that the lithiation of *m*-dichlorobenzene should be preferred in 2-position. Namely, 3-chlorobenzyne should be the main intermediate in this reaction to lead to 1-chloro- and 4-chlorotriptycene derivatives. Of these major products, the chemical shift difference between the methyls of the *t*-butyl group should be larger in the 1-chloro derivative than in the 4-chloro derivative.

*Chlorination of 9-*t*-Butyl-1,2,3,4-tetrachlorotriptycene (1) with Sulfuryl Chloride.* A solution of 200 mg (0.45 mmol) of **1** and 1.2 mL (14 mmol) of sulfuryl chloride in 20 mL of chlorobenzene containing 10 mg of dibenzoyl peroxide was heated under reflux for 1 h. The solvent was evaporated and the residue was subjected to dry-column chromatography on silica gel, using hexane–dichloromethane (20:1) as an eluent, to give fractions containing the starting material (R_f 0.4), a ±*sc*-*ap* mixture of monochlorinated compounds (R_f 0.3), *ap* isomer of dichlorinated compound (R_f 0.25), and ±*sc* isomer of the dichlorinated compound (R_f 0.2). The yields were 5, 28, 27, and 26%, respectively in a typical run. These compounds were purified by recrystallization from tetrahydrofuran–ethanol.

1,2,3,4-Tetrachloro-9-(2-chloro-1,1-dimethylethyl)triptycene. It was not possible to obtain pure isomers by chromatography on silica gel. Chromatography on alumina partially decomposed the ±*sc* form and the *ap* fraction afforded pure *ap* form, mp 251.5—252.5 °C, on recrystallization from chloroform–ethanol. Found: C, 60.02; H, 3.41; Cl, 36.89%. Calcd for $C_{24}H_{17}Cl_5$: C, 59.72; H, 3.55; Cl, 36.73%. ^{1}H NMR ($CDCl_3$, δ): 2.42 (6H, s), 4.58 (2H, s), 6.12 (1H, s), 7.00—7.21 (4H, m), 7.35—7.63 (2H, m), 7.77—8.13 (2H, m).

By subtracting the NMR signals of the *ap* form, the following ^{1}H NMR data ($CDCl_3$, δ) were obtained for the ±*sc* form: 2.14 (3H, s), 2.33 (3H, s), 4.97 (2H, br. s), 6.12 (1H, s), 7.00—7.21 (4H, m), 7.35—7.63 (2H, m), 7.77—8.13 (2H, m).

1,2,3,4-Tetrachloro-9-(2-chloro-1-chloromethyl-1-methylethyl)triptycene. *ap* form, mp 210.5—211.5 °C. Found: C, 55.51; H, 2.97; Cl, 40.89%. Calcd for $C_{24}H_{16}Cl_6$: C, 55.75; H, 3.12; Cl, 41.14%. ^{1}H NMR ($CDCl_3$, 60 MHz, δ): 2.19 (3H, s), 5.01 (4H, q, $\Delta\delta_{AB}$=50.0 Hz, J_{AB}=12.4 Hz), 6.12 (1H, s), 7.03—7.22 (4H, m), 7.35—7.63 (2H, m), 7.82—8.17 (2H, m).

±*sc* form, mp 221.0—221.5 °C. Found: C, 55.87; H, 2.97; Cl, 41.43%. Calcd for $C_{24}H_{16}Cl_6$: C, 55.75; H, 3.12; Cl, 41.14%. ^{1}H NMR ($CDCl_3$, 60 MHz, δ): 2.48 (3H, s), 4.65 (2H, q, $\Delta\delta_{AB}$=12.2 Hz, J_{AB}=12.4 Hz), 5.00 (2H, q, $\Delta\delta_{AB}$=15.2 Hz, J_{AB}=12.2 Hz), 6.12 (1H, s), 7.03—7.22 (4H, m), 7.35—7.63 (2H, m), 7.76—8.03 (2H, m).

*Chlorination of Other 9-*t*-Butyltriptycenes with Sulfuryl Chloride.* The reaction was carried out similarly and the following results were obtained.

(a): Chlorination of 9-*t*-butyl-1-chlorotriptycene (**4**) gave a mixture of *ap* and ±*sc* forms of monochlorinated compounds, of which separation was tedious. However, assignment of the structure and determination of the ratio of the products were straightforward because the ^{1}H NMR spectroscopic features of the rotamers were similar with others. The following ^{1}H NMR data (CCl_4, 60 MHz, δ) were obtained. *ap*: 2.37 (6H, s), 4.55 (2H, s). ±*sc*: 2.13 (3H, br. s), 2.28 (3H, s), 4.97 (2H, q, $\Delta\delta_{AB}$=16.6 Hz, J_{AB}=11.9 Hz).

(b): Chlorination of 9-*t*-butyl-2,3-dichlorotriptycene (**3**) gave a 1:2 mixture of *ap* and ±*sc* forms. Chromatography of the product showed some enrichment of the respective forms but the final separation was not possible. The following ^{1}H NMR data were obtained at 60 MHz. *ap* (CCl_4, δ): 2.12 (6H, s). *ap* (C_6D_6, δ): 1.82 (6H, s). ±*sc* (CCl_4, δ): 2.12 (6H, s), 4.65 (2H, q, $\Delta\delta_{AB}$=14 Hz, J_{AB}=12 Hz). ±*sc* (C_6D_6, δ): 1.92 (3H, s), 1.85 (3H, s).

(c): Chlorination of 9-*t*-butyltriptycene (**5**) afforded a mixture of the starting material, 9-(2-chloro-1,1-dimethylethyl)triptycene and a dichlorinated compound in a 9:70:21 ratio. The mixture was chromatographed on a TLC plate using hexane–benzene (20:1) as a developing solvent. The chromatography afforded a mixture of *ca.* 10:1 monochlorinated compound and the starting material. Recrystallization of the mixture from acetone–hexane yielded pure 9-(2-chloro-1,1-dimethylethyl)triptycene, mp 201—202 °C. Found: C, 83.54; H, 5.88; Cl, 10.63%. Calcd for $C_{24}H_{21}Cl$: C, 83.58; H, 6.14; Cl, 10.28%. ^{1}H NMR ($CDCl_3$, δ): 2.15 (6H, s), 4.70 (2H, s), 5.22 (1H, s), 6.85—7.10 (6H, m), 7.25—7.48 (3H, m), 7.56—7.80 (3H, m). The following ^{1}H NMR data at 60 MHz were obtained for 9-(2-chloro-1-chloromethyl-1-methylethyl)triptycene from the spectrum of a mixture of mono- and dichlorinated compounds ($CDCl_3$, δ): 2.27 (3H, s), 4.71 (4H, q, $\Delta\delta_{AB}$=15.7 Hz, J_{AB}=12.2 Hz), 5.22 (1H, s).

(d): Chlorination of 9-*t*-butyl-1,2,3,4-tetrabromotriptycene (**2**) afforded a mixture of various products. It was not possible to isolate the desired product.

*Bromination of 9-*t*-butyl-1,2,3,4-tetrachlorotriptycene (1).* A solution of 100 mg (0.22 mmol) of the triptycene and 160 mg (1.0 mmol) of bromine in 50 mL of carbon tetrachloride was irradiated with tungsten lamps at room temperature. The reaction mixture was worked up as usual and the products were submitted to dry-column chromatography on silica gel or TLC. Elution with 20:1 hexane–dichloromethane afforded a mixture of *ap*- and ±*sc*-9-(2-bromo-1,1-dimethylethyl)-1,2,3,4-tetrachlorotriptycene (R_f 0.3), *ap*-9-(2-bromo-1-bromomethyl-1-methylethyl)-1,2,3,4-tetrachlorotriptycene (R_f 0.2), and the ±*sc* isomer (R_f 0.15) of the latter. The ±*sc* form of the monobrominated compound was concentrated up to 90% (as judged by ^{1}H NMR spectra) by the chromatography and the following ^{1}H NMR data ($CDCl_3$, δ) were obtained for the two forms. *ap*: 2.40 (6H, s), 4.53 (2H, s), 6.10 (1H, s), 6.95—7.16 (4H, m), 7.35—7.60 (2H, m), 7.80—8.15 (2H, m). ±*sc*: 2.14 (3H, s), 2.36 (3H, s), 4.93 (2H, br. s), 6.10 (1H, s), 6.95—7.16 (4H, m), 7.36—7.60 (2H, m), 7.80—8.15 (2H, m). Elemental analyses of the 10:1 mixture, mp 168—169 °C, gave the following data: C, 54.51; H, 3.08; Br, 15.02; Cl, 26.65%. Calcd for $C_{24}H_{17}BrCl_4$: C, 54.69; H, 3.25; Br, 15.16; Cl, 26.90%.

The following ^{1}H NMR data were obtained for the dibrominated compounds ($CDCl_3$, 60 MHz, δ). *ap*: 2.23 (3H, s), 4.97 (4H, q, $\Delta\delta_{AB}=43.0$ Hz, $J_{AB}=11.9$ Hz), 6.12 (1H, s), 7.02—7.23 (4H, m), 7.36—7.60 (2H, m), 7.85—8.10 (2H, m). ±*sc*: 2.53 (3H, s), 4.58 (2H, q, $\Delta\delta_{AB}=14.1$ Hz, $J_{AB}=11.9$ Hz), 4.96 (2H, q, $\Delta\delta_{AB}=14.0$ Hz, $J_{AB}=12.0$ Hz), 6.11 (1H, s), 7.02—7.23 (4H, m), 7.36—7.60 (2H, m), 7.75—7.99 (2H, m).

Bromination of 9-*t*-butyltriptycene afforded *9-(2-bromo-1,1-dimethylethyl)triptycene*, mp 212—213 °C. Found: C, 74.24; H, 5.34; Br, 20.88%. Calcd for $C_{24}H_{21}Br$: C, 74.04; H, 5.44; Br, 20.52%. ^{1}H NMR ($CDCl_3$, δ): 2.18 (6H, s) 4.67 (2H, s), 5.23 (1H, s), 6.83—7.10 (6H, m), 7.27—7.48 (3H, m), 7.55—7.90 (3H, m).

*Bromination with Bromine–*N*-Bromosuccinimide.* This reaction was carried out similarly with the photobromination except that the equimolar *N*-bromosuccinimide to bromine was added. The reaction was faster than that in the absence of *N*-bromosuccinimide but the products were the same as the photobromination.

Bromination of 9-*t*-butyl-1,2,3,4-tetrabromotriptycene with bromine–*N*-bromosuccinimide gave a *ca.* 10:1 mixture of ±*sc* and *ap* forms of a monobrominated compound of which separation was not possible. The compound was very labile, being decomposed even in chromatography on Florisil, and decomposed on standing at room temperature. The following ^{1}H NMR data ($CDCl_3$, 60 MHz, δ) were obtained. *ap*: 2.51 (6H, s), 4.48 (2H, s), 6.22 (1H, s). ±*sc*: 2.08 (3H, s), 2.48 (3H, s), 5.03 (2H, q, $\Delta\delta_{AB}=15.0$ Hz, $J_{AB}=11.1$ Hz), 6.22 (1H, s).

Photochlorination was carried out by irradiating a solution of 50 mg of a substrate in 50 mL of carbon tetrachloride containing 0.1 mmol of chlorine by tungsten lamps for 10—15 min. The products were identical with those obtained by chlorination with sulfuryl chloride.

Competitive Halogenation. It was carried out using the same conditions as described in the foregoing paragraphs except that equimolar amounts of *t*-butyltriptycene and a halotriptycene were dissolved in carbon tetrachloride or chlorobenzene. Analyses of the products were performed by ^{1}H NMR spectra.

Determination of the Rotational Barrier. *(a)*: A solution was prepared by dissolving 50 mg of 9-(2-chloro-1,1-dimethylethyl)triptycene (±*sc*/*ap*=*ca.* 3) in 0.5 mL of 1-chloronaphthalene. The solution was placed in an NMR sample tube and the tube was sealed after purging the air by nitrogen. The tube was immersed in a boiling solvent bath and the ±*sc*/*ap* ratio was checked by ^{1}H NMR spectra at appropriate intervals. The solvents (boiling points) used for the study were naphthalene (218.5 °C), nitrobenzene (208.0 °C), ethylene glycol (197.0 °C), and *trans*-decalin (187.0 °C). The data were treated as the first order reversible reaction: consideration of Eqs. 2 and 3 gave rate constants given in Table 1.

Table 1. Rate constants for the exchange between and equilibrium constants of ±*sc* and *ap* isomers of 1,2,3,4-tetrachloro-9-(2-chloro-1,1-dimethylethyl)triptycene

T/°C	$k_{sc\to ap}/10^{-4}\ s^{-1}$	$K(\pm sc/ap)$
218.5	2.39	0.96
208.0	1.27	0.96
197.0	0.589	0.96
187.0	0.259	0.96

Table 2. Rate constants for the exchange between and equilibrium constants of ±*sc* and *ap* isomers of 1,2,3,4-tetrachloro-9-(2-chloro-1-chloromethyl-1-methylethyl)triptycene

T/°C	$k_{sc\to ap}/10^{-4}\ s^{-1}$	$K(\pm sc/ap)$
218.5	2.20	1.84
208.0	0.939	1.80
197.0	0.434	1.80
187.0	0.202	1.80

$$K=\frac{2\,k_{ap\to sc}}{k_{sc\to ap}} \tag{2}$$

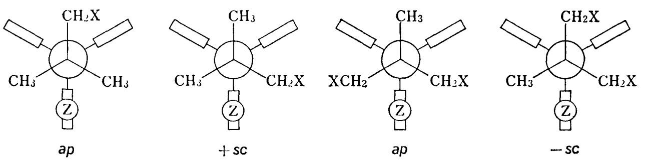
$$\log\left[1-\left(1+\frac{1}{K}\right)\frac{x}{a}\right]=-\frac{k}{2.303}\left(1+\frac{1}{K}\right)t, \tag{3}$$

where a and x are the molar concentrations at time 0 and t, respectively. From the results shown in Table 1, the Eyring plot produced $\Delta H^*_{sc\to ap}=32\pm5$ kcal/mol (1 cal= 4.18 J) and $\Delta S^*=-10\pm13$ e. u. $\Delta H^*_{ap\to sc}$ and ΔS^* were obtained as 32 ± 5 kcal/mol and -12 ± 13 e. u., respectively. The compound tended to decompose at high temperatures on prolonged heating. This seems to cause errors to some extent.

(b): Similarly the rates of isomerization of 9-(2-chloro-1-chloromethyl-1-methylethyl)-1,2,3,4-tetrachlorotriptycene were determined and the data shown in Table 2 were obtained. These data produced $\Delta H^*_{ap\to sc}$ 31 ± 0 kcal/mol and $\Delta S^*-13\pm0$ e. u., respectively. We may have to admit errors as large as those for the monochlorinated compound, although the errors in the least squares treatment were small. Decomposition of the substrate on prolonged heating occurred to some extent.

Results and Discussion

Assignment of the Stereochemistry of the Halogenation Products. The assignment is straightforward because, if it is an *ap* isomer of the monohalogenated compound, the signal due to two methyl groups appears as a singlet and the methylene protons give a singlet as well, as can be seen from the Newman projections. In contrast, ±*sc* forms give two signals for the methyl protons and an AB quartet for the methylene protons, if it is a monohalogenated compound. Similarly, in dihalogenated compounds, *ap* forms give a set of AB quartet because the methylene protons are diastereotopic, whereas the ±*sc* 2 sets of AB quartet for the methylene protons.



monohalogenated dihalogenated

Barriers to Rotation and Population Ratios. From the enthalpies and entropies of activation for rotation, we can calculate the life times of the respective rotamers at a given temperature. At the highest temperature, boiling point of chlorobenzene, we have used, it takes about two weeks for effecting the conversion of 5% of one conformer to another, the amount being considered as the error limit for detection of the change by integration of the NMR spectra. Thus we may neglect the isomerization, since the reaction is over within 1 h. Although not determined, other rotamers must also be stable since even 9-(2-phenyl-1,1-dimethylethyl)-2,3-dichlorotriptycene, a model for compound **2**, has a high barrier to rotation.[12] This assures that we are directly observing the reactivities of respective methyls by comparing the product ratios.

Population ratios of the rotamers are also interesting. At the equilibrium, the population ratio of 9-(2-chloro-1,1-dimethylethyl)-1,2,3,4-tetrachlorotriptycene is very close to unity. Since the statistical value must be ±*sc*/*ap*=2.0, the ±*sc* form is disfavored to some extent. Probably the steric factor dominates. In contrast, 9-(2-chloro-1-chloromethyl-1-methylethyl)-1,2,3,4-tetrachlorotriptycene gives ±*sc*/*ap* values of *ca.* 1.80 which are very close to the statistical value. This is probably caused by the fact that at least one chloromethyl group always flanks the peri-chloro group irrespective of the conformation.

Comparison of the Reactivities of Methyl Groups. The following results are the mean values of 3—5 runs. Reproducibility of the results was good.

At the outset, we looked at the reactivities of methyls in 9-*t*-butyl-1,2,3,4-tetrachlorotriptycene (**1**) with sulfuryl chloride. The ±*sc*/*ap* ratio was 3.2±0.2. Since there are two ±*sc* methyls and one *ap* methyl, the relative reactivity of the ±*sc* methyl is 1.6 if we take the *ap* methyl as a standard. The formation ratio *ap*/±*sc* of dichlorinated product is in conformity with this relative reactivity also: if we assume the relative reactivities of 1.6 and 1.0 for the remaining ±*sc* and *ap* methyls in the monochlorinated compounds, the calculated ratio of *ap*/±*sc* for the dichlorinated compounds is 0.8, which is in good agreement with the observed. The difference in reactivity must be caused by the presence of the peri-chloro group, because chlorination of 9-*t*-butyl-2,3-dichlorotriptycene gave a 2:1 mixture of ±*sc* and *ap* isomers.

Two reasons may be considered for the apparent enhancement of the reactivity of the ±*sc* methyls. Since the molecular structure of 9-*t*-butyl-1,2,3,4-tetrachlorotriptycene (**1**) studied by X-ray crystallography[13] reveals that the peri-chloro and the *t*-butyl groups are tilted away from each other, the *ap* methyl may be pushed into the triptycene skeleton to make it less exposed to the external attack of radicals. Or else, the peri-chloro group may stabilize the transition state for abstraction of hydrogen by radicals. Although the extent of neighboring participation of the chloro group in radical reactions is not large, yet it definitely exists.[14] In order to establish the cause for the selectivity, we took advantage of three techniques: changing halogenation reagents to examine the change in selectivity, changing the peri-substituent to change the extent of neighboring group participation, and competitive halogenation between 9-*t*-butyltriptycene (**5**) and a halogen-substituted 9-*t*-butyltriptycene.

Table 3. Effects of the halogenating reagent on the ±*sc*/*ap* ratios of 9-(2-halo-1,1-dimethylethyl)-1,2,3,4-tetrachlorotriptycenes

Reagent	1/2(±*sc*/*ap*)
SO_2Cl_2	1.6±0.1
Cl_2	1.0±0.05
Br_2	3.1±0.06
Br_2-NBS	1.5±0.1

The effects of changing the halogenation reagent on the ±*sc*/*ap* ratio are summarized in Table 3. The rate determining step in radical halogenations is the hydrogen abstraction.[15] Chlorination with sulfuryl chloride is known to be a little more selective than that with chlorine.[15,16] The product ratio in the chlorination with chlorine indicates that the ±*sc* and *ap* forms are formed almost statistically. If the steric reason had dominated, even chlorine would have given some selectivity, because the *ap* methyl should be protected sterically. Thus the results favor the chloro-participation. The neighboring group participation is further supported by the fact that bromination with bromine gives a very large ±*sc*/*ap* ratio, since the bromination is known to proceed with high selectivity.[17] The large ±*sc*/*ap* ratio suggests lowering the energy of the transition state because of the chloro-participation. If it were the steric reasons that preferred the ±*sc* form in the SO_2Cl_2-chlorination, the ratio should not have changed to a large extent. *N*-Bromosuccinimide is often used to trap hydrogen bromide in photobromination of hydrocarbons.[16] Usually *N*-bromosuccinimide is assumed to not participate in the halogenation reaction but in trapping hydrogen bromide. However, the present results suggest that succinimido radicals participate in hydrogen abstraction because the selectivity is inferior to the photobromination in the absence of *N*-bromosuccinimide. Skell reported recently that succinimido radicals sometimes participate in hydrogen abstraction,[18] and this is another example of such a kind. It is also interesting to note that sulfuryl chloride does give selectivity to some extent, although Russel observed that the difference in selectivity between chlorine and sulfuryl chloride chlorinations vanished in aromatic solvents and suggested that a complex between the aromatic molecule and the chlorine atom was a true attacking species.[19] It seems that chlorosulfonyl radicals participate in hydrogen abstraction in this case.

Now that the bromo group is known to give better assistance in radical formation,[17] if we introduce a bromo substituent in the peri-position, the reactivity of the ±*sc* methyls should be enhanced. In fact, the ±*sc*/*ap* ratio of 9-(2-bromo-1,1-dimethylethyl)-1,2,3,4-tetrabromotriptycene rose to >10 in bromine–*N*-bromosuccinimide bromination. Thus the results support again that the enhancement of the reactivity of the ±*sc* methyls must be attributed to the neighboring group participation of the peri-substituent.

The results of competitive halogenations are given in Table 4. The ±*sc*/*ap* ratios observed in the individual halogenations of the respective compounds were reproduced in these reactions. The results suggest that, while the reactivities of the *ap* methyls are uniformly suppressed to some extent, those of the ±*sc* methyls vary widely: while chlorination gives generally smaller values than unity, bromination gives larger values than that. It is especially noteworthy that the 1,2,3,4-tetrabromo compound (**2**) gives a value as high as 4. This is again the indication that the participation of the peri-substituent is important.

The less reactivity of the tetrachloro compound (**1**) in chlorination is confusing if one simply assumes the neighboring group participation. This phenomenon together with the suppressed reactivity of the *ap* methyls in all halogenations may be attributed to the inductive effect: since the halogenating radicals are known to be electron-demanding,[20] the tetrachloro substituents on a benzeno bridge should suppress the reactivity. We have had such an experience in bromination of 9-allyl-1,2,3,4-tetrachlorotriptycene.[21]

To give further support to this discussion, we have carried out halogenations of 9-*t*-butyl-1-chlorotriptycene (**4**) which should give less electron-withdrawing effect than the tetrahalo compounds. The results are given in Table 5, where ±*sc*/*ap* ratios are taken from the reactions carried out individually. Apparently the reactivity of the *ap* methyl is raised relative to the tetrahalo compounds. The results suggest that the inductive effect is important. It is also interesting to note that the ±*sc*/*ap* ratios are raised relative to the tetrachloro compound (**1**) except the chlorination with chlorine. Probably the higher electron-donating ability of the monochlorobenzeno bridge than the tetrachlorobenzo moiety[22] is responsible for the phenomenon.

TABLE 4. RELATIVE REACTIVITIES OF METHYLS IN *t*-BUTYLTRIPTYCENES RELATIVE TO ONE OF THE METHYLS IN 9-*t*-BUTYLTRIPTYCENE

Halogenating reagent	Substituents	Relative reactivities	
		±*sc*	*ap*
SO_2Cl_2	1,2,3,4-Cl_4	0.95±0.05	0.60±0.03
Cl_2	1,2,3,4-Cl_4	0.84±0.02	0.83±0.05
Br_2	1,2,3,4-Cl_4	2.78±0.3	0.89±0.04
Br_2-NBS	1,2,3,4-Cl_4	1.16±0.08	0.82±0.04
Br_2-NBS	1,2,3,4-Br_4	4.1±0.8	0.8±0.2

TABLE 5. ±*sc*/*ap* RATIOS AND RELATIVE REACTIVITIES OF METHYLS IN 9-*t*-BUTYL-1-CHLOROTRIPTYCENE RELATIVE TO ONE OF THE METHYLS IN 9-*t*-BUTYLTRIPTYCENE

Halogenation reagent	±*sc*/*ap*	Relative reactivities	
		±*sc*	*ap*
Cl_2	2.1±0.1	0.94±0.03	0.92±0.03
Br_2	7.8±0.3	4.2±0.2	1.05±0.02
SO_2Cl_2	3.80±0.04	—	—

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