Bull. Chem. Soc. Jpn., 73, 2563—2569 (2000)


# Reactivities of Stable Rotamers. XLIII. Diazotization of 2-Methyl-2-(1,2,3,4-tetrachloro- and 1,4-dimethoxy-9-triptycyl)propylamine Rotamers[1,2]

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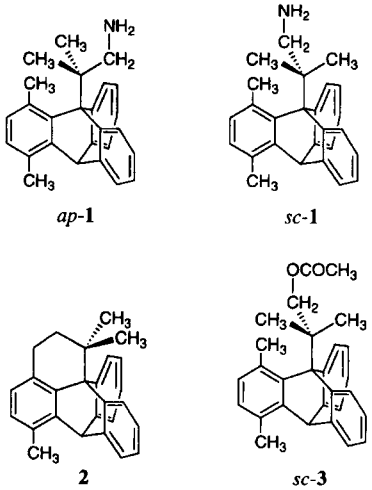
(Received June 5, 2000)

The title amines were prepared from the corresponding rotamers of carboxylic acids via azides and isocyanates. Diazotization of these amines with isopentyl nitrite and organic acids commonly afforded olefins, that are derived from Wagner–Meerwein type rearrangement of the intervening cation followed by deprotonation. Other products included a cyclic compound derived by the attack of the carbocation on an unsubstituted benzeno bridge and esters derived from the acid which was used for diazotization. These two compounds are the products from the cation prior to the rearrangement. The *sc*-tetrachloro compound afforded the esters of the organic acids as almost an exclusive product and the *sc*-dimethoxy compound afforded a cyclized compound which is derived from the nucleophilic reaction of the 1-methoxy group with the cation, followed by demethylation of the resulting oxonium ion. These features are attributed to the strong interaction of the 1-substituent with the intermediate carbocations. In agreement with this interpretation, the formation of the corresponding ester is decreased with decreasing the nucleophilicity of the acid used for the diazotization of the *sc*-tetrachloro compound.

In one of the papers of this series, we have reported that *ap*- and *sc*-2-(1,4-dimethyl-9-triptycyl)-2-methylpropylamine rotamers (**1**) showed interesting differences in reactivities in diazotization with a nitrite in benzene.[3] The focal point was that the *sc*-form afforded a cyclic compound **2**, which was derived by a carbocation-insertion to a C–H bond of the 1-methyl group, and an increase in the yield of the acetate *sc*-**3** derived from the carbocation (Scheme 1 and Table 1). That is, the results prove that even C–H sigma electrons can participate in stabilization of a carbocation.

Although a chloro substituent in organic compounds is not commonly recognized as a nucleophile, we have shown




*ap*-**1** *sc*-**1** **2** *sc*-**3**

Scheme 1.

Table 1. Yields (%) of Products in Diazotization of *sc*-Amines

| Amines | **7** | **8** | **9** | **10** | *sc*-**11** | **15** | **2** |
|---|---|---|---|---|---|---|---|
| *sc*-**4a** | 2 | 8 | 3 | 3 | 59 | — | — |
| *sc*-**4a**[a)] | 10 | 35 | 8 | 2 | 13[b)] | — | — |
| *sc*-**4b** | 0 | 0 | 0 | 0 | 3 | 89 | — |
| *sc*-**1**[c)] | 9 | 5 | 11 | 8 | 18[d)] | — | 36 |

a) Trifluoroacetic acid was used instead of acetic acid. b) This should be read as trifluoroacetate instead of acetate. c) Taken from Ref. 3. Substituents in products are X = $CH_3$ and Y = H. d) Identical with *sc*-**3**.

that molecular interactions between a carbonyl group and a chloro substituent are possible in an extreme case,[4] and that those between a chloro group and a $RCH_2X$ group, where X is a leaving group, do exist.[5] Since the basicity of the sigma electrons of a C–H bond should be lower than that of the lone pair electrons of the chloro substituent, it is expected that the participation of a chloro group in stabilization of carbocations should be stronger than that of the methyl group. Indeed, a cation-forming reaction was accelerated when a chloro substituent existed near the cation.[6] Still stronger should be the participation of the methoxy-oxygen, because ethers often form stable adducts with strong Lewis acids and anchimeric assistance of a methoxy group is known to be stronger than that of a chloro group.[7]

Prompted by these considerations, we decided to see the participation effects on the product distributions in diazotization of *ap*- and *sc*-2-(1,2,3,4-tetrachloro- or 1,4-dimethoxy-9-triptycyl)-2-methylpropylamine rotamers (**4**). This

paper is to report and discuss the results.

## Results and Discussion

The preparation of the amines **4** were carried out in the following ways from the corresponding carboxylic acids **5** (Scheme 2), which were obtained as separate entities.[8,9] Due to high barriers to rotation,[10] these compounds do not undergo internal rotation to give rotational isomers during the reaction. The acids were converted to acid azides, of which Curtius rearrangement afforded isocyanates **6**. The isocyanate **6** was converted to an amine tosylate by heating it in acetonitrile with *p*-toluenesulfonic acid hydrate and the tosylate salt was basified to afford the desired amine.

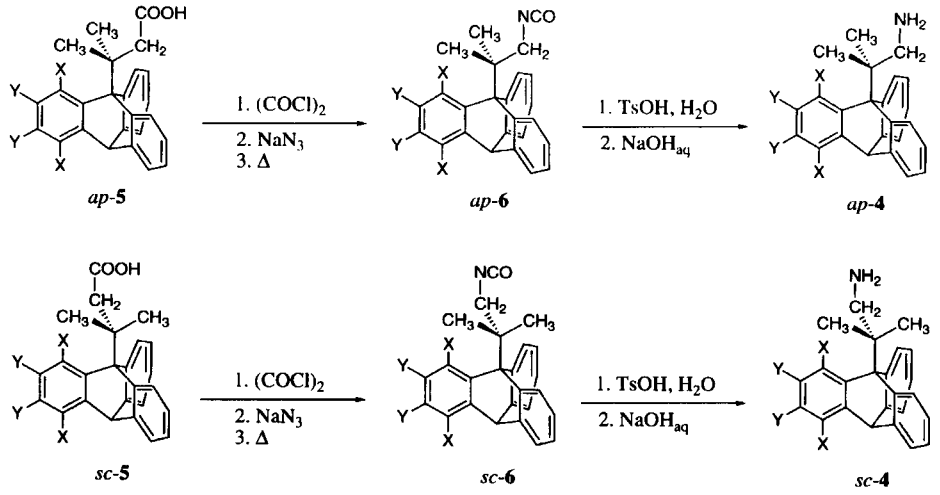
**2-Methyl-2-(1,2,3,4-tetrachloro-9-triptycyl)propylamines (4a).** These amines were diazotized with isopentyl nitrite (*i*-PenONO) in the presence of acetic acid in benzene. The main products from the *ap*-amines are olefins (**7a—9a**) together with a cyclized compound (**10a**) and a small amount of acetate (*ap*-**11a**) (Scheme 3). Besides these products, a small amount of an amide (*ap*-**12a**) was formed. Because the amide is derived from the amine directly, rather than as a result of diazotization, the amide is excluded from the products and the yields of the products are shown in Table 2. Identification of these products was performed by comparing their $^1$H NMR spectra with those reported.

The olefins **7a—9a** must be derived from a carbocation **14a** which is the product of rearrangement of the originally formed cation *ap*-**13a** by diazotization (Scheme 4). The reason for the formation of the cation by migration of a methanide group rather than 9-triptycenide group has been discussed in the previous paper.[3] We have failed to detect

Table 2. Yields (%) of Products in Diazotization of *ap*-Amines

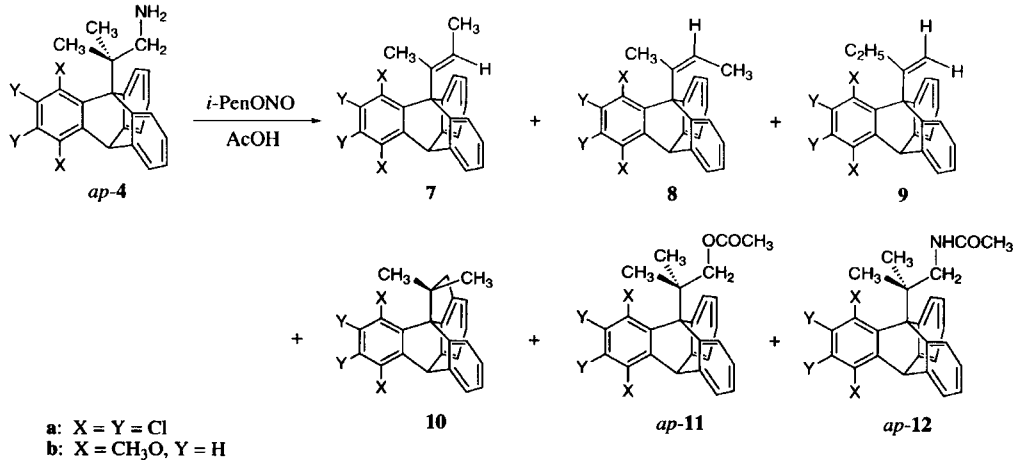
| Amines | 7 | 8 | 9 | 10 | *ap*-11 |
|---|---|---|---|---|---|
| *ap*-**4a** | 46 | 10 | 20 | 4 | 3 |
| *ap*-**4b** | 22 | 25 | 22 | 7 | 4 |
| *ap*-**1**[a)] | 40 | 7 | 20 | 10 | 2 |

a) Taken from Ref. 3. Substituents in products are X = $CH_3$ and Y = H.



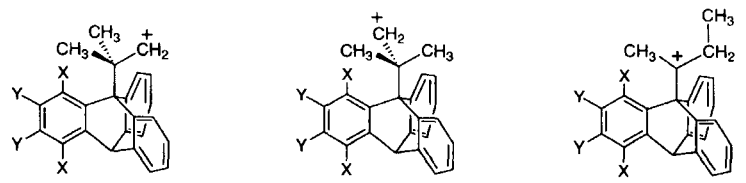

**a**: X = Y = Cl
**b**: X = $CH_3O$, Y = H

Scheme 2.




**a**: X = Y = Cl
**b**: X = $CH_3O$, Y = H

Scheme 3.



*ap*-**13** *sc*-**13** **14**

**a**: X = Y = Cl
**b**: X = $CH_3O$, Y = H

Scheme 4.

any olefins that could be formed if the triptycenide group migrated in the Wagner–Meerwein rearrangement. The cation **14a** loses its original stereochemistry because the barrier to internal rotation in the cation is low.[11]

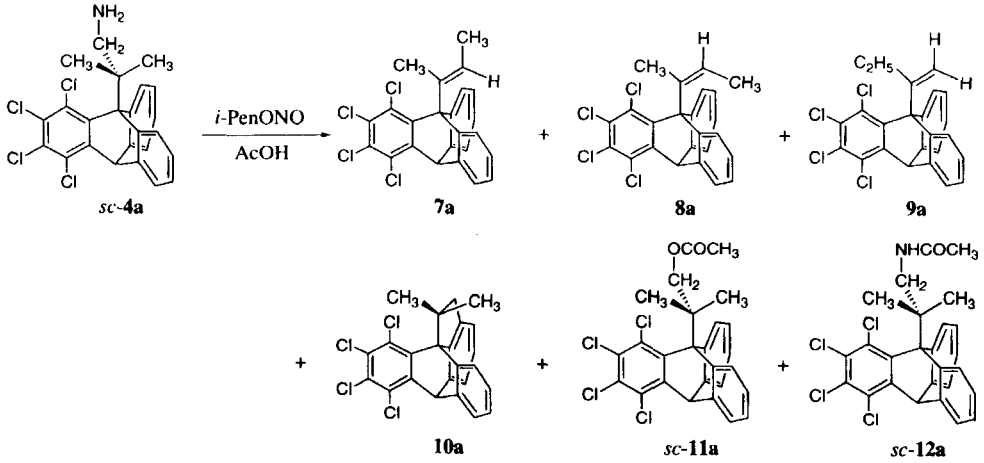
Products **10a** and *ap*-**11a** are the ones derived from unrearranged cation *ap*-**13a**: The attack of the cationic center on the unsubstituted benzeno bridge, which is located close to it, followed by deprotonation, should produce **10a**. The reaction of the cation with the acetate anion which is in the system should produce *ap*-**11a**.

The reaction of the cation *ap*-**13a** with the benzeno bridge or with an acetate anion is rather slow and the Wagner–Meerwein rearrangement to produce **14a** is fast. We attribute such results to steric effects. The cation is protected by the two flanking benzeno bridges to render the reaction with acetate anion slow and the formation of the benzenonium ion by the reaction of the cationic center with the benzeno bridge must be also slow, even though the cation and the benzeno bridge are close, because of the increase in the steric strain.

The results of the diazotization of *sc*-**4a** are strikingly different from those of *ap*-**4a** (Scheme 5 and Table 1). Although a small amount of acetamide from *sc*-**4a** was obtained in this case as well, the main product was the corresponding acetate *sc*-**11a**. The olefins **7a**—**9a** are now minor products and the cyclized product **10a** was also obtained in a very poor yield. The product distribution must be controlled by competition between the rearrangement of and the nucleophilic attack of the acetate anion on the cation *sc*-**13a**. Because the latter reaction can be considered almost unaffected by the rotational positions of the cation, the results must be attributed to the stabilizing effect of the 1-chloro substituent on the carbocation in *sc*-**13a**: the only difference between *ap*-**4a** and *sc*-**4a** is the absence or the presence of the substituent in proximity of the cationic center. The long lifetime of the carbocation attained by the chloro-participation suppresses the rearrangement and the cation can survive until it reacts with the acetate ion.

It is interesting to note that no product which should be derived by the attack of the cation on the tetrachloro benzeno bridge has been detected, though the similar attack on the 1,4-dimethylbenzeno ring took place in another case.[12] This time, the electronic effects should be a strong factor, which prevents the Friedel–Crafts type cyclization, although some steric effects should also operate.

In order to confirm our postulate that the participation of the chloro group is responsible to the results, we tried to use thioacetic acid, which is a stronger nucleophile than acetic acid:[13] The stronger nucleophile should produce the corresponding ester more than the case of acetic acid. However, the reaction of thioacetic acid with *sc*-**4a** was so fast that only the formation of the acetamide *sc*-**12a** was observed. Trifluoroacetic acid is known to be a very weak nucleophile, and thus should afford a trifluoroacetate of the type of **11a** in a poorer yield than acetic acid.[14] As expected, the yield of the trifluoroacetate *sc*-**11a′** (a trifluoroacetoxy group in place of the acetoxy group in **11a**) was reduced and the yields of olefins and the cyclized compound increased instead, when trifluoroacetic acid was used for diazotization, results being




*sc*-**4a** **7a** **8a** **9a**

**10a** *sc*-**11a** *sc*-**12a**

Scheme 5.

compared in Table 1.

**2-(1,4-Dimethoxy-9-triptycyl)-2-methylpropylamine (4b).** The results of diazotization of *ap*-**4b** are shown in Table 2. This reaction also produces olefins **7b**—**9b** as main products together with the cyclized product **10b**, the acetate *ap*-**11b**, and the amide *ap*-**12b** in minor amounts (Scheme 3). The substituent which is located *ap* with respect to the amine moiety has nothing to do electronically, even though it can affect the degree of tilting of the 9-substituent into the notch of the triptycene skeleton.[15]

By contrast, the methoxy group at the 1-position played a major role in controlling the products from the diazotization of *sc*-**4b**. The products were the corresponding acetate *sc*-**11b** and a cyclic ether, of which structure was determined as **15** by elemental analyses and $^1$H NMR spectra, the latter being major, if not exclusive. The acetamide *sc*-**12b** was also formed in small amounts. No olefins **7b**—**9b** were detected among the products (Scheme 6).

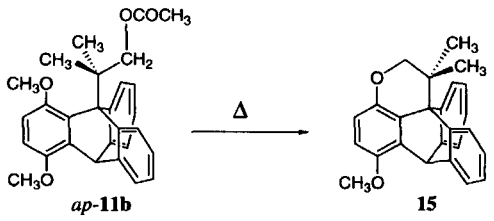
The facile formation of the cyclic ether **15** is interesting. The mechanism must involve formation of the cation *sc*-**13b**, followed by attack of the 1-methoxy group to produce an oxonium ion **16**, of which the methyl group is removed by a nucleophilic attack to produce **15** (Scheme 7). Indeed, we recognized that the 1-methoxy group in the triptycene series undergoes similar reactions very easily.[16,17] Similar results are reported when a carbocation is produced in proximity to a methoxyl group.[18]

**Differences in Reactivities of Rotamers.** Comparing the results of *ap*-amines (*ap*-**4**), we notice that the formation of the cyclic compound **10** is significantly increased in the case of *ap*-**4b** from that of *ap*-**4a**. From the X-ray structures of the similar compounds,[15] the tilting of the 9-substituent by the 1-substituent is most effective when the substituent is a methoxyl group. It is likely that the cationic part is more effectively pushed into the triptycene notch by the 1-methoxyl group than by the 1-chloro group. However, the differences are small and we conclude that the results for the *ap* compounds are very similar, irrespective of the kind of the 1-substituent. Similar results have been obtained in the diazotization of 2-(1,4-dimethyl-9-triptycyl)-2-methylpropylamine, as are compiled in Table 2 as well.[3]

The situation of the *sc* conformations is completely different from that of the *ap*. The fate of the intermediate cation **13** is affected strongly by the substituent. As was expected, the participation of the methoxyl group was much stronger than that of a chloro group.[7] Indeed, the participation was so strong that the methoxyl group acted as a reacting species rather than giving the acetate, *sc*-**11b**, in ample amounts. If we can place a carbocation near other substituents than those described here or elsewhere,[3] we anticipate a chance of finding interesting molecular interactions which are hitherto unknown.

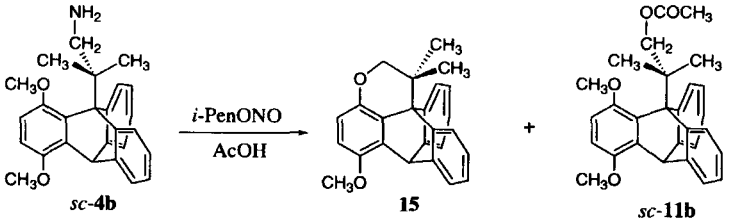
**Facile Formation of Compound 15.** In connection to the strong interaction of the 1-methoxyl group with the carbocation, we wish to report another experience of facile formation of compound **15**. We reported the syntheses of 9-*t*-butyltriptycenes which contain an oxygen substituent in the 9-*t*-butyl group.[19] We introduced the oxygen-containing *t*-butyl group to anthracene before formation of triptycenes. As a result, the *ap*-conformer was produced as a main product because of the steric effect[20] in the addition of a benzyne to an anthracene. To obtain the *sc*-isomer, it was necessary to isomerize the *ap*-compound into the *sc*. During that experiment, we found that heating the acetate *ap*-**11b** for isomerization caused not an equilibrium between the rotamers *ap*- and *sc*-**11b** but it caused formation of compound **15** in an excellent yield (Scheme 8). No acetate *sc*-**11b** was observed under the condition (heating at > 200°C in 1-chloronaphthalene).

The results are interpreted as follows: although the *sc*-



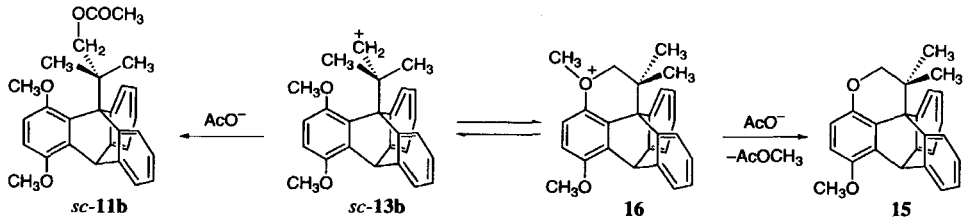

*ap*-**11b** **15**

Scheme 8.




*sc*-**4b** **15** *sc*-**11b**

Scheme 6.




*sc*-**11b** *sc*-**13b** **16** **15**

Scheme 7.

form is formed under the conditions, it reacts also to form the oxonium ion **16**, of which methyl group is removed by the acetate anion that exists in the system. Even the alcohol *sc*-**17b** yielded **15** when it was treated with trichloroacetamide and boron trifluoride. This means that in the presence of the Lewis acid, even the alcohol **17b** can react to form the oxonium ion **16**.

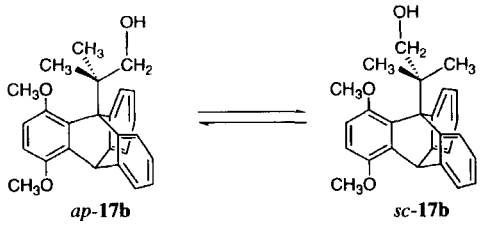
Consideration of the mechanisms of the formation of the cyclic ether **15** suggests that, if we use a poorer leaving group than an acetoxyl group, isomerization should proceed smoothly. Thus we submitted the free *ap*-alcohol (*ap*-**17b**) to isomerization by heating. This worked out satisfactorily (Scheme 9), though heating longer than 6 h also showed the presence of the cyclic ether **15** among the products. The results mean that even the OH group in a primary alcohol can act as a leaving group under the conditions. Thus this cyclization is proved to be an extremely facile reaction. This must be due to the close proximity of the groups concerned.

## Experimental

$^1$H NMR and IR spectra were determined on a Varian Gemini-300 machine, which operated at 300.1 MHz, and a Hitachi I-2000 spectrophotometer, respectively. Elemental analyses were performed with a Perkin-Elmer 240C analyzer. HPLC was carried out with a 30 mm$\phi$ × 250 mm column packed with Intersil PREP-SIL of GL Sciences, the pump being a GL Sciences PU 616. Melting points are not corrected.

**Chromatographic Separation of Rotational Isomers.** We reported separation of rotational isomers of the series of tetrachlorotriptycenes and those of dimethoxytriptycenes with use of silver nitrate-impregnated silica gel chromatography of olefinic compounds and normal silica gel chromatography of the acetonides of diols, respectively.[8,9] We now find that high performance liquid chromatography of the corresponding aldehydes on silica gel can be conveniently used for separation of isomers. The following data were obtained for 3-methyl-3-(1,2,3,4-tetrachloro-9-triptycyl)butanal and 3-(1,4-dimethoxy-9-triptycyl)-3-methylbutanal. *3-Methyl-3-(1,2,3,4-tetrachloro-9-triptycyl)butanal:* 1 : 1 hexane–dichloromethane eluent, flow rate 40 mL min$^{-1}$, 20 kg cm$^{-2}$ pressure, retention times 24 min (*ap*) and 26 min (*sc*). *3-(1,4-Dimethoxy-9-triptycyl)-3-methylbutanal:* 15 : 15 : 1 hexane–dichloromethane–ethyl acetate eluent, flow rate 15 mL min$^{-1}$, 8 kg cm$^{-2}$ pressure, retention times 19 min (*ap*) and 23 min (*sc*).

**3-Methyl-3-(1,2,3,4-tetrachloro-9-triptycyl)butanoyl Chloride.** To a solution of 511 mg (1.04 mmol) of the tetrachlorocarboxylic acid (**5a**)[8] in 40 mL of benzene, was added 1.43 mL (15.6 mmol) of oxalyl dichloride and the mixture was stirred for 2 h. The solvent and other volatile materials were removed in vacuo and the resulting chloride was submitted to the next reaction. The following $^1$H NMR ($CDCl_3$) data were recorded. *ap*: $\delta$ = 2.44 (6H, s), 4.25 (2H, s), 6.08 (1H, s), 7.03—7.13 (4H, m), 7.47—7.49 (2H, m), 7.82—7.85 (2H, m). *sc*: $\delta$ = 2.23 (3H, s), 2.42 (3H, s), 4.47 and 4.83 (2H, ABq, $J$ = 18.8 Hz), 6.10 (1H, s), 7.06—7.12 (4H, m), 7.43—7.50 (2H, m), 7.81—7.86 (2H, m).




*ap*-**17b** *sc*-**17b**

Scheme 9.

**3-Methyl-3-(1,2,3,4-tetrachloro-9-triptycyl)butanoyl Azide.** To a solution of 531 mg (1.04 mmol) of the chloride in 35 mL of acetone was added 67.6 mg (1.04 mmol) of sodium azide in 250 μL of water with ice cooling. The mixture was stirred for 15 min at that temperature and then poured into water. Organic materials were extracted with benzene and the extract was dried over magnesium sulfate. Usually this benzene solution was used for the next reaction directly, but the following spectral data were obtained for the azide in one case. *ap*: $^1$H NMR ($CDCl_3$) $\delta$ = 2.46 (6H, s), 3.57 (2H, s), 6.08 (1H, s), 7.09—7.12 (4H, m), 7.46—7.49 (2H, m), 7.86—7.89 (2H, m); IR ($CHCl_3$): 2136 and 1706 cm$^{-1}$. *sc*: $^1$H NMR ($CDCl_3$) $\delta$ = 2.21 (3H, s), 2.42 (3H, s), 3.80 and 4.17 (2H, ABq, $J$ = 16.2 Hz), 6.09 (1H, s), 7.07—7.13 (4H, m), 7.41—7.49 (2H, m), 7.88—7.96 (2H, m). IR ($CHCl_3$) 2132 and 1708 cm$^{-1}$.

**2-Methyl-2-(1,2,3,4-tetrachloro-9-triptycyl)propyl Isocyanate (6a).** The benzene solution obtained in the preceding procedure was heated under reflux for 2 h and the solvent was evaporated in vacuo. The residue showed the following spectral data. *ap*: $^1$H NMR ($CDCl_3$) $\delta$ = 2.37 (6H, s), 4.33 (2H, s), 6.07 (1H, s), 7.05—7.12 (4H, m), 7.45—7.48 (2H, m), 7.82—7.85 (2H, m). IR ($CHCl_3$) 2272 cm$^{-1}$. *sc*: $^1$H NMR ($CDCl_3$) $\delta$ = 2.09 (3H, s), 2.26 (3H, s), 4.68 and 4.71 (2H, ABq, $J$ = 13.8 Hz), 6.09 (1H, s), 7.05—7.12 (4H, m), 7.43—7.48 (2H, m), 7.89—7.93 (2H, m). IR ($CHCl_3$) 2272 cm$^{-1}$.

**2-Methyl-2-(1,2,3,4-tetrachloro-9-triptycyl)propylamine (4a) Tosylate.** To a solution of 38 mg (0.20 mmol) of *p*-toluenesulfonic acid hydrate in a mixture of 4 mL of acetonitrile and 1 mL of water, was added slowly a solution of the isocyanate obtained from 0.10 mmol of the azide in 4 mL of acetonitrile. The whole was heated under reflux for 4 h. The mixture was allowed to cool, during which process crystals separated from the solution. They were collected and the following $^1$H NMR ($CDCl_3$) spectra were recorded. The yields from the carboxylic acids were ca. 40% in total. *ap*-**4a** tosylate: $\delta$ = 2.11 (3H, s), 2.37 (6H, s), 3.98—4.01 (2H, br s), 6.04 (1H, s), 6.83 (2H, t, $J$ = 8.1 Hz), 6.98 (2H, d, $J$ = 8.1 Hz), 7.01—7.06 (2H, m), 7.43 (2H, d, $J$ = 6.4 Hz), 7.82 (2H, d, $J$ = 8.1 Hz), 7.87 (2H, d, $J$ = 8.2 Hz), 8.35 (3H, br s). *sc*-**4a** tosylate: $\delta$ = 1.96 (3H, s), 2.21 (3H, s), 2.27 (3H, s), 4.18—4.46 (2H, m), 6.05 (1H, s), 6.82—7.07 (6H, m), 7.39—7.44 (2H, m), 7.79—7.92 (4H, m), 8.36—8.42 (3H, br s).

**2-Methyl-2-(1,2,3,4-tetrachloro-9-triptycyl)propylamine (4a).** The amines were generated from the stored amine tosylates (102 mg or 0.206 mmol) with 50 mL of 5% aqueous sodium hydroxide and 5 mL of ether and extracted with dichloromethane. The extract was dried over magnesium sulfate and the solvent was evaporated. The amines were used directly as such, because no impurities were detected in $^1$H NMR spectra. *ap*-**4a**: $^1$H NMR ($CDCl_3$) $\delta$ = 1.51 (2H, br s), 2.22 (6H, s), 3.59 (2H, s), 6.00 (1H, s), 6.96—7.01 (4H, m), 7.36—7.39 (2H, m), 7.80—7.83 (2H, m). *sc*-**4a**: $^1$H NMR ($CDCl_3$) $\delta$ = 1.60 (2H, br s), 2.04 (3H, s), 2.13 (3H, s), 3.92 (2H, br s), 6.08 (1H, s), 7.02—7.10 (4H, m), 7.42—7.46 (2H, m), 7.97—8.03 (2H, m). The amines were characterized as acetamides. *ap*-Acetamide (*ap*-**12a**). This compound was prepared from the amine (*ap*-**4a**) and acetic anhydride and purified by recrystallization from dichloromethane, mp 279.5—280.5 °C. Found: C, 61.85; H, 4.19; N, 2.95%. Calcd for $C_{26}H_{21}Cl_4NO$: C, 61.80; H, 4.19; N, 2.77%. $^1$H NMR ($CDCl_3$) $\delta$ = 2.17 (3H, s), 2.30 (6H, s), 4.38 (2H, d, $J$ = 6.6 Hz), 5.97 (1H, br m), 6.08 (1H, s), 7.09—7.14 (4H,

m), 7.45—7.48 (2H, m), 8.05—8.08 (2H, m). *sc*-Acetamide (*sc*-**12a**). This compound was prepared from *sc*-**4a** and acetic anhydride and recrystallized from tetrahydrofuran-hexane, mp 189—191 °C. Found: C, 61.98; H, 4.24; N, 2.79%. Calcd for $C_{26}H_{21}Cl_4NO$: C, 61.81; H, 4.19; N, 2.77%. $^1$H NMR ($CDCl_3$) $\delta$ = 2.07 (3H, s), 2.15 (3H, s), 2.19 (3H, s), 4.07 and 5.18 (2H, AB of ABX, $J_{AB}$ = 14.5 Hz, $J_{AX}$ = 8.9 Hz, $J_{BX}$ = 4.8 Hz), 5.99 (1H, br m), 6.09 (1H, s), 7.04—7.17 (4H, m), 7.43—7.47 (2H, m), 7.89—7.92 (1H, m), 8.24 (1H, d, $J$ = 7.1 Hz).

**Diazotization of *ap*-4a with Acetic Acid.** A solution of 94.0 mg (0.203 mmol) of the *ap*-**4a** in 15 mL of benzene was mixed with 23.2 μL (0.406 mmol) of acetic acid and 27.3 μL (0.203 mmol) of isopentyl nitrite and the mixture was heated under reflux for 1 h. The mixture was cooled; the contents were mixed with water, and this solution was extracted with dichloromethane. The extract was dried over magnesium sulfate and filtered. After evaporation of the solvent, the residue was submitted to preparative TLC with a 3 : 2 dichloromethane–hexane eluent. A mixture of compounds that carry hydrocarbon substituent at the 9-position gave a spot at $R_f$ 0.7, an acetoxy compound at $R_f$ 0.3, and an amide at $R_f$ ca. 0. The data given in Table 2 are the averages of three runs. The composition of the mixture which moved most easily in the TLC was determined by $^1$H NMR spectra by comparison with those of the authentic samples. The spectrum ($CDCl_3$, $\delta$) of the mixture was consistent with the assumption that the following compounds were the composites. The yields were 40%, 10%, 20%, and 4% for **7a**, **8a**, **9a**, and **10a**, respectively. The $^1$H NMR spectra of these compounds were identical with those reported.[11,21] The second fraction contained an ester which was identified as *ap*-2-methyl-2-(1,2,3,4-tetrachloro-9-triptycyl)propyl acetate (*ap*-**11a**) by comparison of the $^1$H NMR spectra with the authentic specimen.[19] The yield was 3%. The third fraction contained 9% of a compound which was identical in all aspects with the authentic specimen of *N*-acetyl-9-(2-amino-1,1-dimethylethyl)-1,2,3,4-tetrachlorotriptycene (*ap*-**12a**), mp 251—253 °C, prepared above.

**Diazotization of *sc*-4a with Acetic Acid.** This reaction was carried out similarly to that for *ap*-**4a**. The following compounds were identified. The halogenated hydrocarbon mixture that contained **7a**, **8a**, **9a**, and **10a** was obtained by TLC as above. The yields of **7a**, **8a**, **9a**, and **10a** were deduced to be 2%, 8%, 3%, and 3%, respectively.

*sc*-2-Methyl-2-(1,2,3,4-tetrachloro-9-triptycyl)propyl acetate (*sc*-**11a**) was obtained in 59% yield. It was recrystallized from hexane–dichloromethane, mp 206—207 °C. Found: C, 61.59; H, 4.04%. Calcd for $C_{26}H_{20}Cl_4O$: C, 61.68; H, 3.98%. $^1$H NMR ($CDCl_3$) $\delta$ = 2.01 (3H, s), 2.24 (3H, s), 2.31 (3H, s), 5.18 and 5.26 (2H, ABq, $J$ = 12.0 Hz), 6.08 (1H, s), 6.97—7.18 (4H, m), 7.42—7.50 (2H, m), 7.90—8.02 (2H, m). Lit. mp 216.5—218.0 °C.[19] Heating a solution of *sc*-**11a** in 1-chloronaphthalene for 12 h afforded ca. 1 : 2 mixture of the *ap* and *sc* isomers. They were separated by HPLC (30 : 1 hexane–dichloromethane eluent). The following $^1$H NMR ($CDCl_3$) data were recorded for *ap*-**11a**: $\delta$ = 2.24 (3H, s), 2.33 (6H, s), 5.04 (2H, s), 6.07 (1H, s), 7.03—7.14 (4H, m), 7.42—7.50 (2H, m), 7.89—7.98 (2H, m). It was identical with the authentic specimen.[19] The *sc*-amide *sc*-**12a**, mp 185—187 °C, was obtained in 4% yield. It was identical with the authentic specimen described above.

**Diazotization of *sc*-4a with Trifluoroacetic Acid.** This reaction was carried out similarly using 79.5 mg (0.172 mmol) of *sc*-**4a** with 26.3 μL (0.344 mmol) of trifluoroacetic acid and 23.1 μL (0.172 mmol) of isopentyl nitrite in 15 mL of benzene. Chlorinated hydrocarbons, **7a**, **8a**, **9a**, and **10a**, were obtained in 10%, 35%, 8%, and 2% yields, respectively. A fraction at $R_f$ 0.3 afforded a compound in 13% yield which was almost pure 2-methyl-2-(1,2,3,4-tetrachloro-9-triptycyl)propyl trifluoroacetate (*sc*-**11a′**). This product tended to be hydrolyzed in silica gel chromatography and thus only spectral data were collected. $^1$H NMR ($CDCl_3$) $\delta$ = 2.08 (3H, s), 2,34 (3H, s), 5.46 and 5.55 (2H, ABq, $J$ = 12.0 Hz), 6.10 (1H, s), 7.05—7.15 (4H, m), 7.34—7.51 (2H, m), 7.78—7.83 (1H, m), 7.92—7.97 (1H, m). IR ($CHCl_3$): 1784 cm$^{-1}$. The compound was characterized by converting it to the corresponding alcohol (*sc*-**17a**).

**2-Methyl-2-(1,2,3,4-Tetrachloro-9-triptycyl)-1-propanol (*sc*-17a).** The trifluoroacetate *sc*-**11a′** (22 mg or 0.039 mmol) was dissolved in 4 mL of ether and treated with 1.5 mg (0.039 mmol) of lithium tetrahydridoaluminate in 2 mL of ether. The excess $LiAlH_4$ was decomposed with ethanol and the mixture was acidified with hydrochloric acid. The product was obtained in 83% yield and recrystallized from hexane–dichloromethane, mp 214.5—215.5 °C. This compound was identical in all respects with the authentic specimen of the corresponding alcohol *sc*-**17a**.[19] $^1$H NMR ($CDCl_3$) $\delta$ = 2.04 (3H, s), 2.25 (3H, s), 4.73 (2H, br s), 6.08 (1H, s), 7.07—7.09 (4H, m), 7.44—7.46 (2H, m), 8.00—8.08 (2H, m). The hydroxylic proton signal was not detected.

**3-(1,4-Dimethoxy-9-triptycyl)-3-methylbutanoyl Azide.** This compound was prepared in a process similar to that used for the tetrachloro compound described above. The use of 174 mg (0.419 mmol) of the dimethoxy-carboxylic acid (**5b**)[9] and 0.50 mL (5.73 mmol) of oxalyl dichloride gave the acid chloride which, was treated with a solution of 27.3 mg (0.420 mmol) of sodium azide in 100 μL of water. The total yield was 75%. The following spectral data were recorded. *ap*: $^1$H NMR ($CDCl_3$) $\delta$ = 2.18 (3H, s), 2.21 (3H, s), 3.59 (2H, s), 3.79 (3H, s), 3.80 (3H, s), 5.88 (1H, s), 6.59 and 6.62 (2H, ABq, $J$ = 9.0 Hz), 6.97—7.04 (4H, m), 7.40—7.44 (2H, m), 7.80 (2H, app dd, $J$ = 3.4 and 5.6 Hz). IR ($CHCl_3$): 1710 and 2132 cm$^{-1}$. *sc*: $^1$H NMR ($CDCl_3$) $\delta$ = 2.17 (3H, s), 2.18 (3H, s), 3.66 and 4.09 (2H, ABq, $J$ = 15.5 Hz), 3.76 (3H, s), 3.82 (3H, s), 5.89 (1H, s), 6.59 and 6.65 (2H, ABq, $J$ = 9.0 Hz), 6.95—7.01 (4H, m), 7.37—7.43 (2H, m), 7.77—7.85 (2H, m). IR ($CHCl_3$): 1708 and 2132 cm$^{-1}$.

**2-(1,4-Dimethoxy-9-triptycyl)-2-methylpropyl Isocyanate (6b).** A benzene solution of the foregoing azide, concentrated to 50 mL, was heated under reflux for 2 h. Then the solvent was evaporated. The residue showed the following spectral data. *ap*: $^1$H NMR ($CDCl_3$) $\delta$ = 2.14 (6H, s), 3.74 (3H, s), 3.80 (3H, s), 4.39 (2H, s), 5.88 (1H, s), 6.59 and 6.62 (2H, ABq, $J$ = 8.9 Hz), 6.96—7.02 (4H, m), 7.40—7.43 (2H, m), 7.72—7.75 (2H, m). IR ($CHCl_3$): 2272 cm$^{-1}$. *sc*: $^1$H NMR ($CDCl_3$) $\delta$ = 2.04 (3H, s), 2.08 (3H, s), 3.75 (3H, s), 3.80 (3H, s), 4.48 and 4.63 (2H, ABq, $J$ = 13.8 Hz), 5.89 (1H, s), 6.61 and 6.63 (2H, ABq, $J$ = 9.0 Hz), 6.95—7.01 (4H, m), 7.37—7.42 (2H, m), 7.70 (1H, app dd, $J$ = 2.7 and 6.3 Hz), 7.81 (1H, app dd, $J$ = 3.2 and 5.8 Hz). IR ($CHCl_3$) 2276 cm$^{-1}$.

**2-(1,4-Dimethoxy-9-triptycyl)-2-methylpropylamine (4b).** The tosylates of these amines were prepared similarly to the case of the tetrachloro compounds. The following $^1$H NMR data were recorded. *ap*-**4b** tosylate: $^1$H NMR ($CDCl_3$) $\delta$ = 2.03 (3H, s), 2.17 (6H, s), 3.56 (3H, s), 3.78 (3H, s), 4.03 (2H, br s), 5.83 (1H, s), 6.55 and 6.58 (2H, ABq, $J$ = 9.0 Hz), 6.73—6.78 (2H, m), 6.89—6.94 (4H, m), 7.36 (2H, d, $J$ = 6.0 Hz), 7.78 (2H, d, $J$ = 7.9 Hz), 7.88 (2H, d, $J$ = 8.2 Hz), 8.27 (3H, br m). *sc*-**4b** tosylate: $^1$H NMR ($CDCl_3$) $\delta$ = 2.01 (3H, s), 2.10 (3H, s), 2.20 (3H, s), 3.74 (3H, s), 3.83 (3H, s), 4.25 (2H, br d), 5.87 (1H, s), 6.51 and 6.64 (2H, ABq, $J$ = 9.1 Hz), 6.79—6.84 (1H, m), 6.91—6.98 (4H, m), 7.35—7.39

(2H, m), 7.76—7.85 (4H, m), 8.14 (3H, br m).

The tosylates were converted to the free amine, as is described for the tetrachloro compound **4a**, and used directly as such, because no impurities were detected in the $^1$H NMR spectra. *ap*-**4b**: $^1$H NMR ($CDCl_3$) $\delta$ = 1.55 (2H, br s), 2.05 (6H, s), 3.72 (5H, s), 3.80 (3H, s), 5.87 (1H, s), 6.57 and 6.61 (2H, ABq, $J$ = 8.9 Hz), 6.91—7.00 (4H, m), 7.37—7.41 (2H, m), 7.95—7.98 (2H, m). *sc*-**4b**: $^1$H NMR ($CDCl_3$) $\delta$ = 1.53 (2H, br s), 1.93 (3H, s), 2.03 (3H, s), 3.74 (2H, s), 3.77 (3H, s), 3.82 (3H, s), 5.89 (1H, s), 6.58 and 6.64 (2H, ABq, $J$ = 9.0 Hz), 6.92—7.00 (4H, m), 7.37—7.41 (2H, m), 7.82—7.89 (2H, m). These amines were characterized as acetyl derivatives. The acetamides **12b** were prepared by treating the amine with acetic anhydride and the product from diazotization was compared. The acetamides were recrystallized from dichloromethane–hexane. *ap*-**12b**: mp 299—300 °C. Found: C, 78.45; H, 6.70; N, 3.59%. Calcd for $C_{28}H_{29}NO_3$: C, 78.66; H, 6.84; N, 3.28%. $^1$H NMR ($CDCl_3$) $\delta$ = 2.04 (6H, s), 2.16 (3H, s), 3.72 (3H, s), 3.80 (3H, s), 4.43 (2H, d, $J$ = 6.4 Hz), 5.87 (1H, s), 5.96 (1H, br t, $J$ = 6.5 Hz), 6.57 and 6.61 (2H, ABq, $J$ = 8.9 Hz), 6.95—7.04 (4H, m), 7.39—7.42 (2H, m), 7.95—7.98 (2H, m). *sc*-**12b**: mp 297.0—298.5 °C. Found: C, 78.68; H, 6.75; N, 3.18%. Calcd for $C_{28}H_{29}NO_3$: C, 78.66; H, 6.84; N, 3.28%. $^1$H NMR ($CDCl_3$) $\delta$ = 1.94 (3H, s), 2.07 (3H, s), 2.17 (3H, s), 3.80 (3H, s), 3.82 (3H, s), 4.08 and 4.80 (2H, AB of ABX, $J_{AB}$ = 13.9 Hz, $J_{AX}$ = 8.4 Hz, $J_{BX}$ = 4.9 Hz), 5.89 (1H, s), 5.96 (1H, br m), 6.60 and 6.65 (2H, ABq, $J$ = 8.9 Hz), 6.94—7.05 (4H, m), 7.37—7.40 (2H, m), 7.79—7.84 (1H, m), 8.03—8.06 (1H, m).

**Diazotization of 4b with Acetic Acid.** A mixture prepared by adding 18.1 μL (0.316 mmol) of acetic acid and 21.2 μL (0.158 mmol) of isopentyl nitrite into a solution of 60.9 mg (0.158 mmol) of **4b** was heated at 80 °C for 1 h. The mixture was allowed to cool and then washed with water. The water layer was extracted with dichloromethane and the extracts were combined with the benzene solution. The combined solution was dried, filtered, and evaporated. $^1$H NMR spectra were determined at this stage to estimate the formation ratios of various products. Chromatography of the product on silica gel (1 : 2 dichloromethane–hexane eluent) gave a mixture of the olefins **7b**—**9b** and the cyclized product **10b**, (a cyclic ether in the case of *sc*), the acetate **11b**, and acetamide **12b** (15% for *ap* and 21% for *sc*). The yields of the products except the acetamides are shown in Table 1 as normalized values for the *ap* form. These olefins,[11] the cyclized product,[21] and the acetate[19] gave identical $^1$H NMR spectra to those reported. From the sc form, **15** and *sc*-**11b** were obtained in 95 : 5 ratio. The cyclic ether **15** was recrystallized from hexane–dichloromethane, mp 251—252 °C. Found: C, 84.42; H, 6.34%. Calcd for $C_{25}H_{22}O_2$: C, 84.71; H, 6.26%. $^1$H NMR ($CDCl_3$) $\delta$ = 1.68 (3H, s), 1.99 (3H, s), 3.81 (3H, s), 3.88 and 4.41 (2H, ABq, $J$ = 10.3 Hz), 5.70 (1H, s), 6.46 and 6.55 (2H, ABq, $J$ = 8.7 Hz), 6.82—6.91 (2H, m), 7.01—7.08 (2H, m), 7.29 (1H, dd, $J$ = 1.4 and 7.2 Hz), 7.47 (1H, dd, $J$ = 2.2 and 6.3 Hz), 7.52 (1H, d, $J$ = 7.5 Hz), 7.77 (1H, dd, $J$ = 1.7 and 7.7 Hz).

**Attempted Isomerization of *ap*-Acetate (*ap*-11b).** Heating a solution of *ap*-**11b** in 1-chloronaphthalene for 12 h afforded the cyclized compound **15**, mp 249—251 °C, which was identical with the compound described above. Isomerization of the alcohol *ap*-**17b** was already reported.[19] No anomaly was noticed in the isomerization of *ap*-**17b** unless the heating period was more than 6 h.

This work was partially supported by a Special Fund for Cooperative Research which was administered by Japan Private School Promotion Foundation.

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