  Bull. Chem. Soc. Jpn., 55, 1514—1521 (1982) [Vol. 55, No. 5

Reactivities of Stable Rotamers. VIII. Difference in Reactivities of 1,2,3,4-Tetrachloro-9-(2-halo-1,1-dimethylethyl)triptycene Rotamers in Lewis Acid-catalyzed Reactions[1,2]

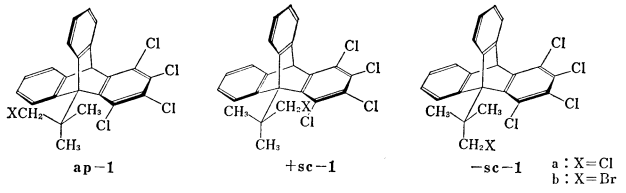
Hiromi KIKUCHI, Shigetaka SEKI, Gaku YAMAMOTO, Tsutomu MITSUHASHI, Nobuo NAKAMURA, and Michinori ŌKI*

Department of Chemistry, Faculty of Science, The University of Tokyo, Bunkyo-ku, Tokyo 113

(Received July 30, 1981)

±*sc*-1,2,3,4-Tetrachloro-9-(2-chloro-1,1-dimethylethyl)triptycene was found to react in the presence of titanium(IV) chloride at room temperature to give an isomeric mixture of 1,2-dimethyl-7,8,9,10-tetrachloro-1,2,6,10b-tetrahydro-6,10b-*o*-benzenoaceanthrylenes. The structure of the latter was confirmed by independent syntheses. In contrast, the *ap* conformer of the former did not give any sign of the reaction under the same conditions but reacted when antimony(V) chloride was added to give the same mixture. Careful examination of the reaction mixture suggests that the starting material was rapidly converted to (*E*)-1,2,3,4-tetrachloro-9-(1-methyl-1-propenyl)triptycene and cyclization followed. Action of silver nitrate on ±*sc*-9-(2-bromo-1,1-dimethylethyl)-1,2,3,4-tetrachlorotriptycene afforded a mixture of the stereoisomers of the olefin while the *ap* form remained intact.

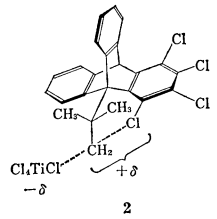
Since we were able to show recently that methyls in a *t*-butyl group could behave differently in radical halogenations, when the rotation of the *t*-butyl group was frozen,[3] we naturally wished to extend the work on the reactivities of rotamers to see those of the halogenated compounds. Because 9-(2-halo-1,1-dimethylethyl)triptycenes possess the structure of neopentyl halide, their S_N2 type substitution was expected to be very slow.[4] However, we happened to find that the ±*sc* conformer of 1,2,3,4-tetrachloro-9-(2-chloro-1,1-dimethylethyl)triptycene (**1a**) was partially destroyed if purification was attempted by chromatography on alumina, whereas the *ap* form was eluted intact.[3] This suggests that ionization reactions of the halide may be facile in general, especially in the ±*sc* conformation. Thus we decided to investigate the reactivities of ±*sc*- and *ap*-**1a** in ionization reactions. This paper reports the difference in reactivities of the rotamers, when they are treated with a Lewis acid. The structure of the products was confirmed by independent syntheses. The possible mechanisms of the reaction are also discussed.



Results and Discussion

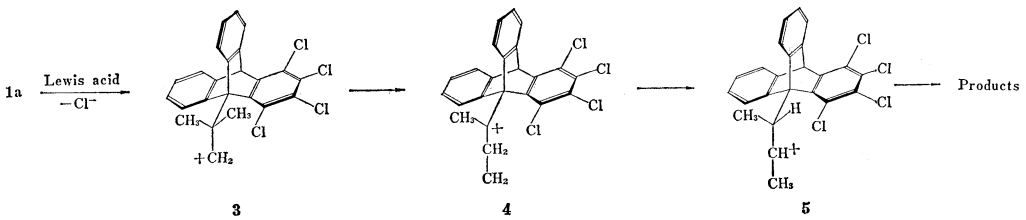
*Reactivities of 1,2,3,4-Tetrachloro-9-(2-chloro-1,1-dimethylethyl)triptycene (**1a**) Rotamers.* Since the barrier to rotation of the 2-chloro-1,1-dimethylethyl group about the C_9–C_{subst} bond is known to be *ca.* 37 kcal/mol (1 cal=4.18 J),[3] it is certain that we are looking at the reactivity of each isomer. The treatment of a mixture of **1a** rotamers with a large excess of titanium(IV) chloride caused the reaction of the ±*sc* form but the *ap* form remained unreacted. The pseudo-first order reaction rate constant for the ±*sc* form was obtained as 5.3×10^{-4} s^{-1} at 41 °C. Under the same conditions, the *ap* form did not give any sign of the reaction even after 164 h. This indicates that the rate constant of the reaction of *ap*-**1a** under the conditions is 8.7×10^{-8} s^{-1} at the most. (We took 5% of the material reacted since the error in integration of ^{1}H NMR spectra may be estimated at this level.) Then the relative reaction rate of ±*sc*-**1a** is $>6\times10^3$ if that of *ap*-**1a** is unity. The pseudo-first order rate constant of *ap*-**1a** in the presence of antimony(V) chloride was 8.8×10^{-4} s^{-1} at 39.8 °C, whereas the reaction of ±*sc*-**1a** was too fast to measure the rate by conventional methods under the conditions.

This large difference in reactivities of ±*sc*-**1a** and *ap*-**1a** must be derived by the presence of a chloro group in a peri-position. Since titanium(IV) chloride and antimony(V) chloride act as Lewis acids, it is expected that these coordinate with the chloro group in the 9-substituent and help ionization of the compound. Then the developed cation (**2**) can be stabilized by the presence of a chloro group in proximity in the ±*sc* conformation, since neighboring participation of the chloro group is well documented[5]

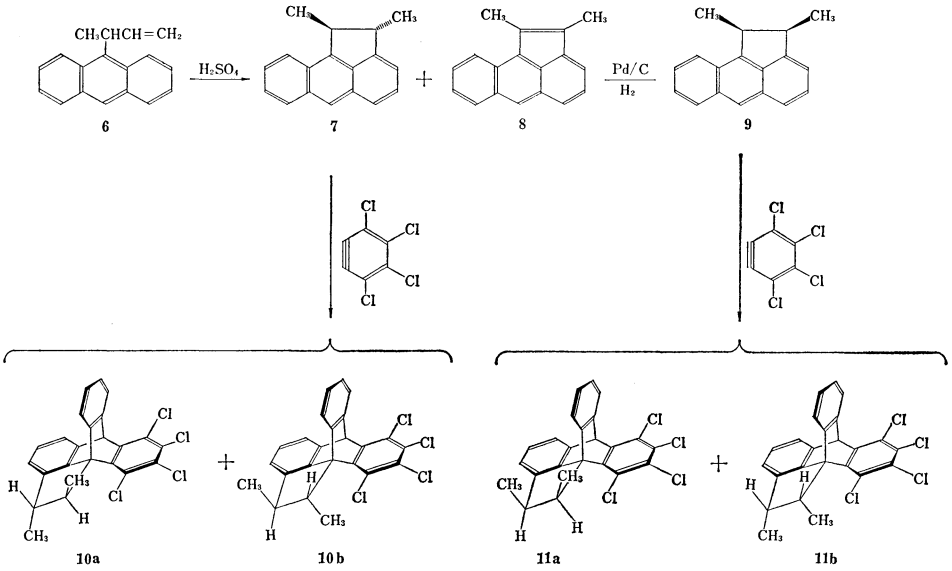


2

and chloronium ion is also known.[6] There is a possibility that the ground state of this molecule is so congested that the steric acceleration of ionization[7] ensues. However, if it were the main cause, the *ap*-form as well as the ±*sc* form should have ionized with comparable rates. It is especially noteworthy that titanium(IV) chloride, which is known to be a weak catalyst for the Friedel-Crafts reaction of primary organic halides,[8] does cause the reaction under mild conditions: Participation of the chloro group seems strong in this case. Indeed, several examples of strong participation of the peri-chloro group in triptycenes have been reported.[9] Another interesting



Scheme 1.



Scheme 2.

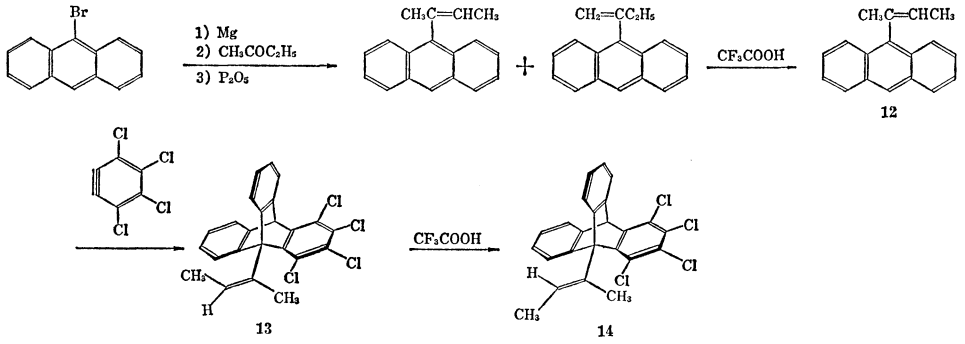
point is that the intermolecular Friedel-Crafts reaction with the solvent molecule has not been detected. This is probably because the intermolecular reaction is prohibited due to the steric factor.

Antimony(V) chloride is known to be a stronger Lewis acid than titanium(IV) chloride.[10] Therefore it is reasonable that this reagent caused the reaction of even *ap*-**1a**.

Structures of the Products. Both of the reactions catalyzed by Lewis acids afforded almost the identical mixture of the products. On standing, a part of the product solidified. After purification, the solid product showed ^{1}H NMR signals of two kinds of methyls, each coupled with a proton. A mass spectrum of the compound indicated that a molecule of hydrogen chloride was eliminated from the starting material. These results suggest that an extensive rearrangement has taken place in the 9-substituent of **1a**. Since the cation (**3**) originally formed from **1a** can undergo a series of Wagner-Meerwein rearrangements and finally the cation undergoes intramolecular cyclization (Scheme 1),[11,12] the most probable structure of the pure material seemed to be one of possible isomers of **10** and **11**.

It is not possible to assign the structure of the solid product from ^{1}H NMR spectral data only, because there are four possible stereoisomers. Thus independent syntheses of the products were performed (Scheme 2). 9-(1-Methyl-2-propenyl)anthracene (**6**) was treated with concentrated sulfuric acid to afford a mixture of *trans*-1,2-dimethylaceanthrene (**7**), 1,2-dimethylaceanthrylene (**8**), and a small amount of *cis*-1,2-dimethylaceanthrene (**9**). Compound **8** was separated by chromatography and hydrogenated over palladium–charcoal to afford **9**. The *cis*-dimethylaceanthrene **9** was treated with tetrachlorobenzyne to afford two isomers (**11**) which were formed by the different directions of attack by the benzyne. One of the products crystallized out and it was found to be identical with the solid product which was obtained above. Another isomer was purified by high pressure liquid chromatography to give a solution of the almost pure substance. Thus the original solid product has a *cis*-structure at the newly formed 5-membered ring. Likewise, *trans*-1,2-dimethylaceanthrene (**7**) was treated with tetrachlorobenzyne to give a mixture of stereoisomers of **10**. One of the products crystallized out from the mixture. Thus ^{1}H NMR spectra of two isomers each of **10** and **11** have become available.

The next step for the identification is to assign structures **10a** and **10b**, and structures **11a** and **11b**. We took advantage of two pieces of information available from the ^{1}H NMR spectra. The first is the chemical shift of the aromatic protons. Since 9-substituted triptycenes are highly congested, strong van der Waals interactions are due between the 9-substituent and the peri-proton. Accumulated data in this laboratory suggest that if the substituent in the 9-position is tertiary, the peri-proton gives rise to a multiplet signal at a far downfield of the aromatic region. The data may further be interpreted that if a proton in the peri-position is flanked by two methyl



Scheme 3.

groups, it gives a signal at a considerably low field. Indeed, we have succeeded in assigning stereostructures of adducts between 9-(1,1-dimethyl-2-phenylethyl)anthracene and dimethyl acetylenedicarboxylate by this method.[13] Inspecting the molecular models, we notice that **10a** and **11a** possess a peri-hydrogen which is very close to a methyl, whereas **10b** and **11b** have that which is far from any of methyls. Therefore, if one of the two isomers of **10** and **11** gives an aromatic proton signal at a low field apart from others, then it is very likely to be **10a** and **11a**. Inspection of the NMR data suggests that, of the trans isomers, that which was obtained as crystals gives a low field signal and is likely to be **10a**. In contrast, a cis isomer which was obtained as crystals has no such low-field signal for the aromatic protons but that obtained as a solution exhibited a low-field signal. Thus the crystalline compound of the cis configuration is assigned to **11b**. These assignments are further confirmed by NOE experiments. An NOE experiment of the crystalline form of **10**, irradiating the methyl signal at δ 2.19 and observing the intensity of the signal at δ 7.90 showed 19% increase in intensity. Likewise, irradiation of the methyl proton signal at δ 2.11 of the isomer of **11**, which was obtained as a solution, showed 23% increase in intensity of the aromatic proton signal at δ 7.87, whereas no such enhancement of the signal was observed in the NOE experiment of the crystalline product of *cis*-structure or the crystalline product of the original cyclization reaction. Thus the structural assignment is now confirmed as follows.

10a: A crystalline product from the Diels-Alder reaction of *trans*-1,2-dimethylaceanthrene.

10b: Another product from the above reaction which was not purified completely.

11a: A compound which was obtained as an almost pure solution by high pressure liquid chromatography from the product of the Diels-Alder reaction of *cis*-1,2-dimethylaceanthrene.

11b: A crystalline product from the above reaction and also a crystalline product from the treatment of **1a** with Lewis acids.

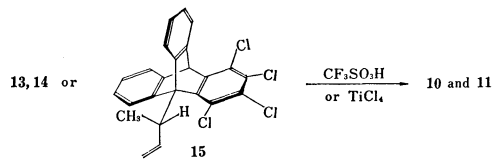
Using the ^{1}H NMR signals of these compounds, we can now analyze the composition of the products obtained by the reactions of $\pm$*sc*-**1a** and *ap*-**1a**. The ratios were constant at **10a**:**10b**:**11a**:**11b**=45:$\approx$0:10:45 within the error of $\pm$5%.

Mechanisms of the Reaction. If we neglect the presence of a counterion, the mechanisms of cyclization may be shown as those in Scheme 1 as a first approximation. However, there are a few points we wish to mention here. The first is the intervention of an olefin (**13** and/or **14**). While, when a large excess of titanium(IV) chloride was used in the reaction of $\pm$*sc*-**1a** for a long time, only the cyclized products were detected, an olefin was a major product together with a small amount of the cyclized products when the reaction was conducted for a shorter period in the presence of a relatively small excess of the catalyst.

The structure of the olefin was determined by independent syntheses as follows (Scheme 3). A Grignard reagent prepared from 9-bromoanthracene was added to 2-butanone and the resulted alcohol was dehydrated with phosphorus(V) oxide to give a mixture of olefins. Treatment of the mixture of olefins with trifluoroacetic acid yielded a mixture of (*Z*)- and (*E*)-9-(1-methyl-1-propenyl)anthracene (**12**) in which the *Z*-form predominated. Treatment of the mixture of *Z*- and *E*-forms with tetrachlorobenzyne followed by chromatography gave (*Z*)-1,2,3,4-tetrachloro-9-(1-methyl-1-propenyl)triptycene (**13**). Isomerization of **13** to its *E*-isomer (**14**) was effected by trifluoroacetic acid.

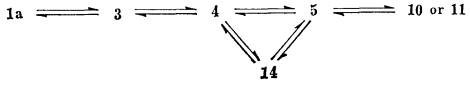
The structures of olefins of the triptycenes (**13** and **14**) and those which were found during the synthesis of the former were elucidated by considering the ring current effect of the benzene rings in ^{1}H NMR spectra. Of the two 9-(1-methyl-1-propenyl)anthracenes, one gives a methyl signal at δ 1.98 and the other at δ 1.23. The space-filling models of these compounds suggest that, as are expected from analogy of mesitylene derivatives,[14] the two planes made by the olefin and the anthracene cannot be coplanar. Thus the methyl group at the far end in the *Z*-olefin is located over the anthracene ring. In contrast, in the *E*-form, the methyl is far from the anthracene. Therefore, it is reasonable to assign the *Z*-structure for a compound which shows its NMR signal of the methyl group at a higher field than the counterpart. Similarly, the *E* and *Z* structures of the olefin in triptycenes (**13** and **14**) were assigned by taking advantage of the geometry of molecules which is suggested by molecular models: in the *Z*-conformation of the olefinic triptycene, the methyl group at the end of the 9-sub-

stituent should be in the shielding zone of the flanking benzeno bridges, whereas it is in the deshielding zone of the benzeno bridges in the *E*-conformation. The fact that, while the anthracene gave a mixture of *Z* and *E* forms of the olefin on equilibration, the triptycenes gave the almost pure *E*-olefins on equilibration, may be rationalized by considering the steric factor: Since the end-methyl group directs inside of the triptycene skeleton in the *Z*-conformation, its thermodynamic stability must be low.



Cyclization of olefins (**13** and **14** as well as **15**) gives almost the identical mixture of isomers of the cyclized products (**10** and **11**) when they were treated with titanium(IV) chloride or trifluoromethanesulfonic acid. This may be taken as evidence that the cation (**4** and/or **5**) are really involved in the process of the cyclization. An interesting point is that, although the cyclization did occur under these conditions, no cyclization was observed if trifluoroacetic acid was used. The acid must be a strong one for the cyclization to occur. The failure of cyclization in the presence of sulfuric acid may be ascribed to the presence of a basic solvent molecule (CD_3CN). This will mean that the concentration of the protonated species **5** must be high for the cyclization to occur which is rather slow. The slow cyclization can be expected since the formation of the 5-membered ring proceeds in the conformation in which the fully eclipsed interactions between the benzo groups and the methyl or the hydrogen of the forming 5-membered ring develop.

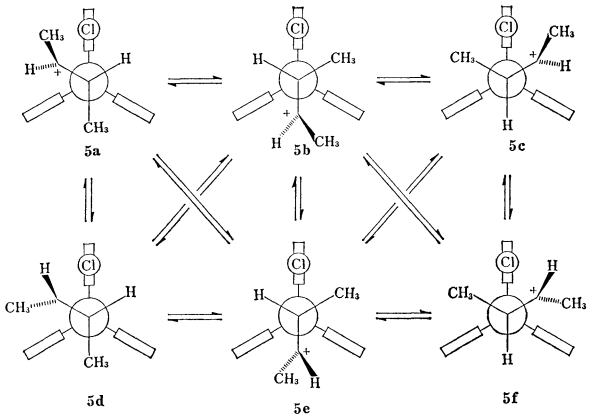
It is questionable to say that the olefin (**13** or **14**) is the real intermediate of the reaction which gives the cyclized products (**10** and **11**), whereas it is certain that the cyclization which affords **10** and **11** is slow and the olefin is formed rapidly from the halogen compound (**1a**), because, should the cation be formed, it will rearrange rapidly to **4** to release the strain. We see that there are two possibilities (Scheme 4): One is that the reaction proceeds in the sequential manner where the olefin **14** is formed from either **4** or **5**, but on protonation, the olefin goes back to the cation (**4** and **5**). An alternative is the sequence



Scheme 4.

in which **14** becomes a real intermediate which on protonation gives the cation **5**. We cannot rule out any of the two processes at present. Probably the both processes contribute to the total reaction.

It is interesting that both *ap*-**1a** and ±*sc*-**1a** reacted to give almost identical mixtures of the cyclized products, although their reactivities differed to a great



Scheme 5.

extent. This must mean that, although the ionization reaction of isomers of **1a** differes in their rates, the subsequent steps should involve at least a same intermediate. In addition, we could not find any of the intermediates other than the olefin **14** when the Lewis acids were used. The results can be accommodated if the Wagner-Meerwein rearrangement is fast: it is reasonable to assume so because the Wagner-Meerwein rearrangements were known to be very fast in various systems,[15] and the steric strain in the cation **3**, which is close to 1,2,3,4-tetrachloro-9-*t*-butyltriptycene[16] or 1,2,3,4-tetrachloro-9-(1-cyano-1,1-dimethylethyl)triptycene,[17] must be the driving force for the rearrangement, as discussed above (see also note 12). Thus the isomers of **3** are formed from *ap*- and ±*sc*-**1a** but they are transformed into **4** very rapidly. There are rotational isomers of **4** also. Therefore isomers of **4** may be formed from the rotamers of **1a**. However, the barriers to rotation of triptycenes carrying an sp^2-hybridized carbon at the bridgehead are known to be rather low.[18] The common intermediate is probably formed in this stage, although there is a possibility that, in the olefin **14**, the stereochemistry is scrambled. The final intermediate (**5**) should have a high barrier to rotation since its analogous compound, 1,2,3,4-tetrachloro-9-(1-methyl-2-propenyl)triptycene, has a high barrier and the rotation occurs slowly at room temperature.[19]

Since the cation **5** is the direct precursor for the cyclization, the discussion of the possible conformation leading to **10** and **11** may deserve further mention. There are various conformations possible for **5** (Scheme 5).[20] Since the conformational energy of C^+–CH_3 inside forms (**5d**—**f**) are very high from the steric grounds,[21] their concentrations should be very low. In addition, the reactivities of the C^+–CH_3 inside forms are not apparently higher than the C^+–CH_3 outside conformations (**5a**—**c**). Thus the reaction paths through C^+–CH_3 inside conformations (**5d**—**f**) may be neglected. Of the important conformations (**5a**—**c**), **5a** leads to **11a** when it cyclizes and **5c** to **10b**, whereas **5b** conformation gives rise to **10a** and **11b**. On the grounds of the interaction between a cation and a peri-substituent (chloro group in this case),[9] the conformations **5a** and **5c** are considered to be more stable than **5b**. However, in

practice, **10b** has not been observed in the products. We may have to assume that the cyclization from conformation **5c** is extremely unfavorable. In contrast, **11a** was formed, although the yield was lower than those of **10a** and **11b**. This is probably attributed to two factors. The first is the fact that, in the transition state for the cyclization, the methyl and the chloro groups are eclipsing with each other for the formation of **10b**, whereas the eclipsing is between the chloro and hydrogen for the formation of **11a**. The second factor is that the conformation **5c** is so energy-rich, because two bulky groups are flanking the chloro group in the peri-position, that its population is scarce.[22] Conformation **5b**, on the other hand, is not stabilized by any of the apparent intramolecular interaction. Since the products which are led from this intermediate are main, the reaction rates of **5b** should be very large relative to others.

*Reactions of 1,2,3,4-Tetrachloro-(2-bromo-1,1-dimethylethyl)triptycene (**1b**) Rotamers.* Although a bromo compound is known to be a little more reactive than a corresponding chloro compound in substitution reactions, the *ap* form of **1b** also failed to give any reaction product when it was treated with titanium(IV) chloride. ±*sc*-**1b** reacted normally to give the *E*-olefin (**14**) and cyclized products (**10** and **11**). The reaction is considered to proceed as was discussed in that of **1a**.

Likewise, a reaction of *ap*-**1b** with silver nitrate in acetonitrile failed to give any product after heating at 50—60 °C for 3 h, whereas ±*sc*-**1b** was completely converted to olefins (**13** and **14**) under the conditions. It is interesting to note that an almost 1:1 mixture of *E* and *Z* olefins was formed by the action of silver nitrate on **1b**, whereas the action of titanium(IV) chloride afforded the *E*-olefin exclusively. The cause for this phenomenon is not well understood at the moment but the weak basicity[23] and the bulkiness of the pentachlorotitanate anion must be responsible for the observed results. In contrast the smaller size and the stronger basicity[23] of the nitrate anion in addition to the higher temperature used for the reaction would give less selectivity of the reaction.

Experimental

*9-(1-Methyl-1-propenyl)anthracene (**12**).* A solution of 10 g (39 mmol) of 9-bromoanthracene and 7.7 g (41.2 mmol) of 1,2-dibromoethane in 150 mL of ether was added 2.95 g (123 mmol) of magnesium, activated by iodine, in 20 mL of ether. The addition required 24 h. The reaction mixture was boiled for further 24 h and then a solution of 2.9 g (40.3 mmol) of 2-butanone in ether was added to the mixture over a period of 4 h. The mixture was stirred for 24 h and decomposed with aqueous ammonium chloride. The organic layer was separated, washed, dried, and then evaporated. After removing anthracene by taking up the mixture in benzene, the soluble part was chromatographed on silica gel (10:1 hexane–benzene) to afford 9-(1-hydroxy-1-methylpropyl)anthracene in 20.3% yield. ^{1}H NMR ($CDCl_3$, δ): 0.89 (3H, t, J=7.4 Hz), 1.95 (3H, s), 2.12 (1H, s), 0.98—2.02 (2H, m), 7.08—7.46 (4H, m), 7.65—8.06 (2H, m), 8.19 (1H, br s), 8.61—8.95 (2H, m).

The crude alcohol (1.0 g or 4.0 mmol) was heated with 1.0 g of phosphorus(V) oxide in 50 mL of carbon tetrachloride. The mixture was filtered and the filtrate was evaporated. The residue (0.75 g) consisted of 33:22:45 (*E*)- and (*Z*)-9-(1-methyl-1-propenyl)anthracenes and 9-(1-ethylvinyl)anthracene, as judged from a ^{1}H NMR spectrum. The mixture in 50 mL of carbon tetrachloride was boiled with 1 mL of trifluoroacetic acid for 2 d, washed with water and then with aqueous sodium hydrogencarbonate, and dried over magnesium sulfate. Evaporation of the solvent gave a 3.7:1 mixture of (*Z*)- and (*E*)-9-(1-methyl-1-propenyl)-anthracene (**12**), recrystallization of which from tetrahydrofuran–hexane afforded a 1.6:1 mixture of the *Z*- and *E*-olefins, mp 70—73 °C. Found: C, 93.24; H, 6.70%. Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94%. The following ^{1}H NMR data ($CDCl_3$, δ) have been recorded. *E*-isomer: 1.98 (3H, d, J=7.1 Hz), 2.14 (3H, d, J=1 Hz), 5.62 (1H, dq, J=7.1 and 1 Hz), 7.3—7.6 (4H, m), 7.8—8.3 (4H, m), 8.32 (1H, s). *Z*-isomer: 1.23 (3H, br d, J=7.0 Hz), 2.07 (3H, d, J=1 Hz), 6.08 (1H, dq, J=7.0 and 1 Hz), 8.35 (1H, s) and other aromatic protons (8H). The following ^{1}H NMR data of 9-(1-ethylvinyl)anthracene were obtained by subtracting the data of *E*- and *Z*-olefins from those of the mixture ($CDCl_3$, δ): 1.15 (3H, t, J=7.5 Hz), 2.55 (2H, br q, J=7.5 Hz), 5.18 (1H, m), 5.78 (1H, m), and aromatic protons (8H).

trans-*1,2-Dimethylaceanthrene (**7**) and 1,2-Dimethylaceanthrylene (**8**).* A mixture of 20 mL of concentrated sulfuric acid and a solution of 3.95 g of 9-(1-methyl-2-propenyl)anthracene[19] in 50 mL of carbon tetrachloride was stirred at room temperature for 1 h. The organic layer was washed with water and then with aqueous sodium hydrogencarbonate, and evaporated. The residue was chromatographed on silica gel with the use of hexane as an eluent. Crude *trans*-1,2-dimethylaceanthrene (**7**), which was contaminated by a small amount of *cis*-isomer, and 1,2-dimethylaceanthrylene (**8**) were obtained in 28.4 and 18.9% yields, respectively.

trans-*1,2-Dimethylaceanthrene (**7**).* High resolution MS exhibited a molecular ion peak at *m/e* 232.1247. $C_{18}H_{16}$ requires 232.1248. ^{1}H NMR ($CDCl_3$, δ): 1.29 (3H, d, J=7 Hz), 1.42 (3H, d, J=7 Hz), 3.18 (1H, q, J=7 Hz), 3.59 (1H, q, J=7 Hz), 8.10 (1H, s), 6.9—8.2 (7H, m).

*1,2-Dimethylaceanthrylene (**8**).* Mp 112.5—113.0 °C. Found: C, 93.94; H, 5.85%. Calcd for $C_{18}H_{14}$: C, 93.87; H, 6.12%. ^{1}H NMR ($CDCl_3$, δ): 2.32 (3H, d, J=1 Hz), 2.64 (3H, d, J=1 Hz), 8.25 (1H, s), 7.2—8.6 (7H, m).

cis-*1,2-Dimethylaceanthrene (**9**).* A solution of 0.7 g of 1,2-dimethylaceanthrylene (**8**) in 30 mL of ethyl acetate was shaken with 50 mg of 5% palladium on charcoal under a hydrogen atmosphere. The theoretical amount of hydrogen was absorbed within 3 h. The mixture was filtered and the filtrate was evaporated. Recrystallization of the residue from ethanol–hexane gave pure product, mp 79—80 °C, in 65% yield. Found: C, 93.06; H, 6.85%. Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94%. ^{1}H NMR ($CDCl_3$, δ): 1.26 (3H, d, J=7 Hz), 1.45 (3H, d, J=7 Hz), 3.77 (1H, quintet, J=7 Hz), 4.07 (1H, quintet, J=7 Hz), 8.09 (1H, s), 7.0—8.1 (7H, m).

9-(1-Methyl-1-propenyl)triptycene. A solution of 360 mg (2.0 mmol) of anthranilic acid in 10 mL of acetone was added in 1 h to 9-(1-methyl-1-propenyl)anthracene (Z/E=1.6) and 0.5 mL of isopentyl nitrite in 20 mL of dichloromethane under a nitrogen atmosphere. The solvents were removed by evaporation and 5 mL of ethanol was added to induce crystallization. The crystals were recrystallized from acetone–hexane. The product, mp 185—192 °C, consisted of 1:1.6 of *E* and *Z* isomers. Found: C, 93.49; H, 6.32%. Calcd for $C_{24}H_{20}$: C, 93.46; H, 6.54%. The

following ^{1}H NMR ($CDCl_3$, δ) spectral data were obtained. *E*-isomer: 2.07 (3H, br d, J=6.9 Hz), 2.25 (3H, br s), 5.29 (1H, s), 6.55 (1H, br q, J=6.9 Hz), 6.78—7.10 (6H, m), 7.25—7.63 (6H, m). *Z*-isomer: 0.95 (3H, dq, J=6.9 and 1 Hz), 2.73 (3H, br s), 5.27 (1H, s), 6.18 (1H, br q, J=6.9 Hz), 6.83—7.10 (6H, m), 7.22—7.73 (6H, m).

*(Z)-1,2,3,4-Tetrachloro-9-(1-methyl-1-propenyl)triptycene (**13**).* A similar treatment of 9-(1-methyl-1-propenyl)anthracene with tetrachlorobenzyne, generated from tetrachloroanthranilic acid,[24] afforded the crude triptycene. Column chromatography on alumina (10:1 hexane–dichloromethane) followed by recrystallization of the eluted product from acetone–hexane gave 100 mg of pure (*Z*)-1,2,3,4-tetrachloro-9-(1-methyl-1-propenyl)triptycene, mp 239.5—240.5 °C. Found: C, 64.39; H, 3.34; Cl, 31.87%. Calcd for $C_{24}H_{16}Cl_4$: C, 64.61; H, 3.61; Cl, 31.78%. ^{1}H NMR ($CDCl_3$, δ): 0.91 (3H, br d, J=7.2 Hz), 2.68 (3H, br s), 5.89 (1H, s), 6.09 (1H, br q, J=7.2 Hz), 6.77—7.12 (4H, m), 7.22—7.51 (2H, m), 7.60—7.90 (2H, m).

*trans-1,2-Dimethyl-7,8,9,10-tetrachloro-1,2,6,10b-tetrahydro-6,10b-o-benzenoaceanthrylene (**10**).* This compound was prepared similarly from *trans*-1,2-dimethylaceanthrene (**7**) and tetrachlorobenzyne. After rough chromatography, the product consisted of 6:5 (1*SR*,2*SR*,10b*SR*) and (1*RS*,2*RS*,10b*SR*) isomers. Out of the mixture, one isomer crystallized out on standing. It was purified by recrystallization from hexane–ethanol. The pure compound, mp 265—266 °C, was assigned a (1*SR*,2*SR*,10b*SR*)-structure (**10a**) due to the NOE experiment. Found: C, 64.82; H, 3.42%. Calcd for $C_{24}H_{16}Cl_4$: C, 64.60; H, 3.62%. High resolution MS (M^+): 444.0011, 445.9942, 447.9951, 449.9950. $C_{24}H_{16}Cl_4$ requires 444.0002, 445.9973, 447.9943, and 449.9914. Intensities of the peaks agreed well with those calculated from natural abundance of ^{35}Cl and ^{37}Cl. ^{1}H NMR ($CDCl_3$, δ): 1.50 (3H, d, J=7 Hz), 2.19 (3H, d, J=7 Hz), 3.21 (1H, q, J=7 Hz), 3.83 (1H, q, J=7 Hz), 5.97 (1H, s), 6.8—7.5 (6H, m), 7.90 (1H, m). The (1*RS*,2*RS*,10b*RS*)-isomer (**10b**) could not be separated even by high performance liquid chromatography because its R_f value was too close to that of the (1*SR*,2*SR*,10b*SR*)-isomer. ^{1}H NMR ($CDCl_3$, δ): 1.40 (3H, d, J=7 Hz), 2.00 (3H, d, J=7 Hz), 6.05 (1H, s).

*cis-1,2-Dimethyl-7,8,9,10-tetrachloro-1,2,6,10b-tetrahydro-6,10b-o-benzenoaceanthrylene (**11**).* This compound was prepared as described in the preparation of the *trans*-isomer (**10**). One of the products crystallized out from the mixture, purified by recrystallization from hexane–ethanol and found to be (1*RS*,2*SR*,10b*SR*)-isomer (**11b**), mp 272.5—274.5 °C. Found: C, 64.63; H, 3.37; Cl, 31.68%. Calcd for $C_{24}H_{16}Cl_4$: C, 64.60; H, 3.62; Cl, 31.78%. ^{1}H NMR ($CDCl_3$, δ): 1.40 (3H, d, J=7 Hz), 1.55 (3H, d, J=7 Hz), 3.35 (1H, quintet, J=7 Hz), 3.83 (1H, quintet, J=7 Hz), 5.90 (1H, s), 6.8—7.6 (7H, m). The structural assignment based on the NOE experiment. The (1*SR*,2*RS*,10b*SR*)-isomer (**11a**) was separated as above and obtained as a solution of an almost pure material. ^{1}H NMR ($CDCl_3$, δ): 1.12 (3H, d, J=7 Hz), 2.11 (3H, d, J=7 Hz), 3.63 (1H, quintet, J=7 Hz), 4.48 (1H, quintet, J=7 Hz), 6.02 (1H, s), 6.8—7.5 (6H, m), 7.87 (1H, m). The original reaction mixture contained 3:2 (1*RS*,2*SR*,10b*SR*)- and (1*SR*,2*RS*,10b*SR*)-isomers.

Isomerization of 9-(1-Methyl-1-propenyl)triptycenes. A solution of 30 mg of 9-(1-methyl-1-propenyl)triptycene and 1 mmol of trifluoroacetic acid in 0.5 mL of chloroform-*d* was heated in a sealed tube at 90 °C. The isomerization was followed by ^{1}H NMR to show that the content was almost pure *E*-form after 50 h. The solvent was evaporated and the residue was purified by TLC (silica gel, 20:1 hexane–dichloromethane) to afford the pure *E*-form, mp 228 °C. Found: C, 93.28; H, 6.27%. Calcd for $C_{24}H_{20}$: C, 93.46; H, 6.54%.

Similarly the isomerization of (*Z*)-1,2,3,4-tetrachloro-9-(1-methyl-1-propenyl)triptycene (**13**) was carried out. It took 30 days to obtain *E*/*Z* ratio of 10. The *E*-isomer (**14**) was obtained as a pure form on recrystallization from the tetrahydrofuran–hexane, mp 222—223 °C. High resolution MS (M^+): 443.9990, 445.9969, 447.9919, 449.9889. $C_{24}H_{16}Cl_4$ requires 444.0002, 445.9973, 447.9943, and 449.9914. Intensity ratios of these peaks were in good agreement with those calculated from the natural abundance of ^{35}Cl and ^{37}Cl. ^{1}H NMR ($CDCl_3$, δ): 2.00 (3H, br d, J=6.9 Hz), 2.11 (3H, br s), 5.85 (1H, s), 6.50 (1H, br q, J=6.9 Hz), 6.8—7.1 (4H, m), 7.2—7.5 (2H, m), 7.6—7.9 (2H, m).

*Reaction of 1,2,3,4-Tetrachloro-9-(2-chloro-1,1-dimethylethyl)triptycene (**1a**) Rotamers in the Presence of a Large Excess of Lewis Acids.* To a solution of 0.13 mmol of a mixture of ±*sc*- and *ap*-**1a** in 10 mL of benzene was added 0.2 mL (3.3 mmol) of titanium(IV) chloride and the mixture was left to stand for 18 h. The mixture was washed with water and the solvent was evaporated. A ^{1}H NMR spectrum of this residue showed that, whereas the ±*sc* form had completely reacted, the *ap* form remained almost unaltered. The residue was purified by thin layer chromatography on silica gel, hexane being used as an eluent, to give a mixture of stereoisomers of 1,2-dimethyl-7,8,9,10-tetrachloro-1,2,6,10b-tetrahydro-6,10b-*o*-benzenoaceanthrylene (**10** and **11**) in 52% yield. On standing the product fraction, a part solidified which was purified by recrystallization from hexane–ethanol, mp 272.5—274.5 °C. MS showed M^+ peaks at *m*/*e* 452, 450, 448, 446, and 444 to indicate that a hydrogen chloride molecule was lost from the starting material. It was identical with (1*RS*,2*SR*,10b*SR*)-1,2-dimethyl-7,8,9,10-tetrahydro-1,2,6,10b-tetrahydro-6,10b-*o*-benzenoaceanthrylene (**11b**). The original mixture of the product contained 45:≈0:10:45 **10a**, **10b**, **11a**, and **11b** as judged from its ^{1}H NMR spectrum.

ap-**1a** was treated similarly with an excess of antimony(V) chloride in benzene. The cyclized product was obtained in 71% yield and the composition of isomers was very close to, if not identical with, that obtained from the ±*sc* form of **1a**. Antimony(V) chloride also effected the same reaction of a mixture of ±*sc* and *ap*-**1a** to give the same mixture.

*Reaction of 1,2,3,4-Tetrachloro-9-(2-chloro-1,1-dimethylethyl)triptycene (**1a**) with Relatively Small Excess of Lewis Acid.* A mixture (3:1) of ±*sc*- and *ap*-**1a** (60 mg or 0.12 mmol) in 0.4 mL of benzene-d_6 was mixed with 0.07 mL (1.1 mmol) of titanium(IV) chloride and the reaction was followed by ^{1}H NMR. It took 100 min for the reaction of ±*sc* form to proceed almost completely at room temperature under the conditions. The main product of the reaction was (*E*)-1,2,3,4-tetrachloro-9-(1-methyl-1-propenyl)triptycene (**14**) in addition to a small amount of cyclized compounds (**10** and **11**).

*Reaction of 1,2,3,4-Tetrachloro-9-(2-bromo-1,1-dimethylethyl)triptycene (**1b**) with Lewis Acids.* A mixture of ±*sc*- and *ap*-**1b** (25.6 mg, *sc*/*ap* 6.0) in 10 mL of benzene was treated overnight with 0.05 mL of titanium(IV) chloride as above. The reaction gave the *E*-olefin (**14**) in addition to a small amount of the cyclized compounds (**10** and **11**). The *ap* form of **1b** was recovered over 90%.

A mixture (50 mg or 0.095 mmol) of ±*sc*- and *ap*-**1b** with 0.17 mmol of silver nitrate in 0.05 mL of acetonitrile-d_3 was heated at 50—60 °C for 3 h because the reaction

was slow at room temperature. The reaction mixture gave the olefins (**13**/**14**=1) and recovered *ap*-**1b**.

Cyclization of Olefins with Acids. A mixture (30 mg) of (*E*)- and (*Z*)-1,2,3,4-tetrachloro-9-(1-methyl-1-propenyl)-triptycene was dissolved in 0.4 mL of chloroform-*d* and 0.05 mL of trifluoromethanesulfonic acid was added to the solution. The reaction was followed by ^{1}H NMR to show that it was complete within 5 min at room temperature. The product was a mixture of cyclized compounds (**10** and **11**) and the composition was quite similar with those obtained by other methods. The yield was *ca.* 70%.

Similarly 1,2,3,4-tetrachloro-9-(1-methyl-2-propenyl)triptycene (**15**) was treated with trifluoromethanesulfonic acid to afford 67% cyclized products (**10** and **11**). Titanium(IV) chloride could also effect cyclization of the olefin to give 71% cyclized products.

However, treatment of (*Z*)-1,2,3,4-tetrachloro-9-(1-methyl-1-propenyl)triptycene with trifluoroacetic acid resulted in formation of the *E*-form as stated above but failed to give cyclized products. Sulfuric acid-d_2 also failed to give cyclization products, although a mixture of the olefin and sulfuric acid-d_2 in $CDCl_3$–CD_3CN (3:1) was heated up to 90 °C.

Determination of Rates of Reactions. Reactions of 1,2,3,4-tetrachloro-9-(2-chloro-1,1-dimethylethyl)triptycene (**1a**) were carried out similarly as were described above, except using benzene-d_6 as a solvent and dioxane in a capillary tube as an external standard. Decrease in the amount of the starting material was followed by ^{1}H NMR spectroscopy. The data were treated by assuming that the reaction was of pseudo-first order since a large excess of the catalyst was employed.

Spectral Measurements. The normal ^{1}H NMR spectra were measured on either a Hitachi R-20B or Varian EM 390 spectrometer, operating at 60 and 90 MHz, respectively. With dilute solutions, a JEOL FX60 machine was used which was equipped with the FT facilities. For the NOE measurements of ordinary concentrations, the EM 390 spectrometer was used. A sample (25 mg) was dissolved in 0.3 mL of chloroform-*d*. Air in the sample tube was replaced by argon. The methyl signal appearing at a lower field was irradiated and the integration of a signal which was at the lowest field of the aromatic region was carried out. The integrated area was compared with that due to bridgehead proton appearing at δ *ca.* 6. For dilute solutions, data were accumulated for 500 times. Mass spectra were obtained with a Hitachi RMU-6L instrument and high resolution mass spectra with a JEOL JMS-D300.

High Pressure Liquid Chromatography. It was carried out with a Waters Model 6000A apparatus equipped with a UV detector. A microporasil column of 4 mm×30 cm was used. The eluent was hexane. Although the peaks due to two isomers of **11** were not separated clearly, it was possible to shave the front part to give almost pure **11a**, as far as ^{1}H NMR spectra concerned. The overlap of peaks due to two isomers of **10** was so severe that it was impossible to concentrate **10b** by this method.

This work was supported by a grant from Toray Science Foundation to which our thanks are due.

References

1) For Part VII, see M. Ōki and R. Saito, *Chem. Lett.*, **1981**, 649.

2) A preliminary note has been published: H. Kikuchi, T. Mitsuhashi, N. Nakamura, and M. Ōki, *Chem. Lett.*, **1980**, 209.

3) T. Morinaga, S. Seki, H. Kikuchi, G. Yamamoto, and M. Ōki, *J. Am. Chem. Soc.*, **102**, 1173 (1980); S. Seki, T. Morinaga, H. Kikuchi, T. Mitsuhashi, G. Yamamoto, and M. Ōki, *Bull. Chem. Soc. Jpn.*, **54**, 1465 (1981).

4) F. C. Whitmore and G. H. Fleming, *J. Am. Chem. Soc.*, **55**, 4161 (1933); F. C. Whitmore, E. L. Wittle, and A. H. Popkin, *ibid.*, **61**, 1586 (1939).

5) A. Streitwieser, Jr., *Chem. Rev.*, **56**, 571 (1956).

6) P. E. Peterson and E. V. P. Tao, *J. Am. Chem. Soc.*, **86**, 4503 (1964); G. A. Olah and P. E. Peterson, *ibid.*, **90**, 4675 (1968).

7) H. C. Brown and R. S. Fletcher, *J. Am. Chem. Soc.*, **71**, 1845 (1949).

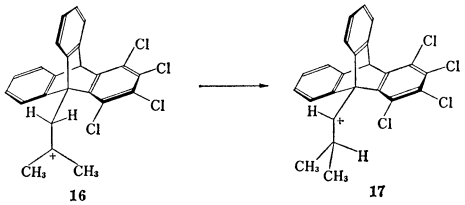
8) a) N. M. Cullinane and D. M. Leyshon, *J. Chem. Soc.*, **1954**, 2942; b) P. Mastagli, P. Lambert, and C. Hirigoyen, *C. R. Acad. Sci.*, **249**, 1964 (1959); c) G. A. Olah, S. Kobayashi, and M. Tashiro, *J. Am. Chem. Soc.*, **94**, 7448 (1972).

9) G. Izumi, G. Yamamoto, and M. Ōki, *Bull. Chem. Soc. Jpn.*, **54**, 3064 (1981).

10) O. C. Dermer, D. M. Wilson, and V. H. Dermer, *J. Am. Chem. Soc.*, **63**, 2881 (1941); Ref. 8c.

11) σ-Participation in isomerization of neopentyl type cation now seems to be established: T. Ando, H. Yamataka, H. Morisaki, J. Yamawaki, J. Kuramochi, and Y. Yukawa, *J. Am. Chem. Soc.*, **103**, 430 (1981); V. J. Shiner, Jr., and J. J. Tai, *ibid.*, **103**, 436 (1981). However, we show the scheme with classical cations for the sake of simplicity.

12) The possibility that the triptycyl group migrates at the first stage cannot be ruled out, since **1a** takes most probably, the conformation in which the chloro group in the 9-substituent takes an outward position of the triptycyl group and a group anti to the leaving group is prone to migration in Wagner-Meerwein rearrangement. However, this is not our first choice for the mechanism for the following reasons. If it is the case the cation formed at the initial stage may be approximated by **16** which does not easily cyclize because of the steric effect of the *gem*-dimethyl group but isomerizes to **17** and then to **5**. If **16** were to intervene, there should be a strong possibility that a proton is lost from one of the methyls to lead to 9-(2-methyl-2-propenyl) compound, which was not actually found in the olefinic products.



16 17

13) G. Yamamoto and M. Ōki, *Bull. Chem. Soc. Jpn.*, **48**, 3686 (1975).

14) L. L. Ingraham, "Steric Effects on Certain Physical Properties," in "Steric Effects in Organic Chemistry," ed by M. S. Newman, John Wiley & Sons, New York (1956), pp. 479—522.

15) M. Saunders, P. von R. Schleyer, and G. A. Olah, *J. Am. Chem. Soc.*, **86**, 5680 (1964); D. M. Brouwer, C. MacLean, and E. L. Mackor, *Discuss. Faraday Soc.*, **39**, 129 (1965); G. J. Karabatsos, R. A. Mount, D. O. Rickter, and S. Meyerson, *J. Am. Chem. Soc.*, **88**, 5651 (1966); M. Saunders and M. R. Kates, *ibid.*, **100**, 7082 (1978).

16) M. Mikami, K. Toriumi, M. Konno, and Y. Saito, *Acta Crystallogr., Sect. B*, **31**, 2427 (1975).

17) S. Otsuka, T. Mitsuhashi, and M. Ōki, *Bull. Chem. Soc. Jpn.*, **52**, 3663 (1979); S. Otsuka, G. Yamamoto, T. Mitsuhashi, and M. Ōki, *ibid.*, **53**, 2095 (1980).

18) M. Nakamura and M. Ōki, *Bull. Chem. Soc. Jpn.*, **48**, 2106 (1975).
19) H. Kikuchi, S. Hatakeyama, G. Yamamoto, and M. Ōki, *Bull. Chem. Soc. Jpn.*, **54**, 3832 (1981).
20) For the sake of simplicity of the scheme, some of the possible paths of interconversion were omitted.
21) M. Ōki, G. Izumi, G. Yamamoto, and N. Nakamura, *Bull. Chem. Soc. Jpn.*, **55**, 159 (1982); G. Yamamoto and M. Ōki, *ibid.*, **54**, 481 (1981); N. Nogami, Ph. D. Thesis, The University of Tokyo (1978).
22) F. Suzuki, M. Ōki, and H. Nakanishi, *Bull. Chem. Soc. Jpn.*, **47**, 3114 (1974).
23) Direct evidence that the proton affinity of pentachlorotitanate anion is less than that of nitrate anion is not available in literature. However, the relative acidity is apparent if one considers the strong reactivity of a complex between acetyl chloride and titanium(IV) chloride (A. Bertrand, *Bull. Soc. Chim. Fr.*, **1880**, 403: Gmelins Handbuch der Anorganischen Chemie, Titan, p. 320) and acetyl nitrate which is more or less covalent (H. Burton and P. F. G. Praill, *J. Chem. Soc.*, **1955**, 729).
24) V. Villiger and L. Blangey, *Ber.*, **42**, 3549 (1909).