© *1988 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn., 61, 4309—4314 (1988)*

Reactivities of Stable Rotamers. XXIV. Formation of Isomeric Ketones by Cyclization of Rotameric 3-Methyl-3-(1,2,3,4-tetrahalo-9-triptycyl)butanoyl Chloride and Barriers to Isomerization of the Ketones[1)]

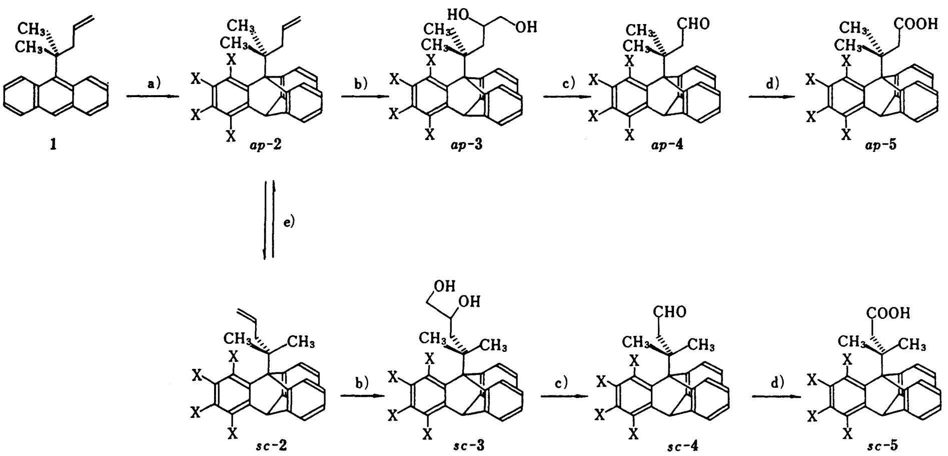
Michinori Ōki,*,† Toshihiro Tanuma, Yasuhiro Tanaka, and Gaku Yamamoto
Department of Chemistry, Faculty of Science, The University of Tokyo, Bunkyo-ku, Tokyo 113
(Received March 29, 1988)

Rotational isomers of 3-methyl-3-(1,2,3,4-tetrahalo-9-triptycyl)butanoic acid, where the halo is either fluoro or chloro have been prepared. Cyclization of their acid chlorides afforded *ap*- and *sc*-ketones from *ap*- and *sc*-isomers, respectively. The barriers to isomerization were 29.9 and 26.8 kcal mol^{-1} at 363 K, for the fluoro and the chloro ketones, respectively, for the $ap \rightarrow \pm sc$ process. The equilibrium constants (sc/ap) at 363 K were 2.34 and 18.5 for the fluoro and the chloro compounds respectively. The barriers to isomerization and the relative stabilities of the isomeric ketones were discussed based on the MMP2(NONPLANAR) calculation results and the steric congestion in the ground state.

While we have reported interesting differences in reactivities of 3-(1,4-disubstituted 9-triptycyl)-3-methylbutanoyl chloride rotamers, when they were treated with Lewis acids, and isomerization kinetics of the ketones obtained from the respective rotamers,[2)] it is hoped to increase the number of data to discuss the general trends in reactivities, equilibrium constants, and barriers to isomerization. We thus prepared 3-methyl-3-(1,2,3,4-tetrahalo-9-triptycyl)butanoic acid rotamers, and then examined their reactivities, the barriers to isomerization of the ketones derived from them, and the equilibrium constants of the ketones. This paper reports and discusses results of such investigations.

The 3-methyl-3-(1,2,3,4-tetrahalo-9-triptycyl)butanoic acid rotamers (**5**) were prepared in the following ways. Addition of tetrahalobenzyne to 9-(1,1-dimethyl-3-butenyl)anthracene (**1**)[2)] afforded a mixture of rotamers of 9-(1,1-dimethyl-3-butenyl)-1,2,3,4-tetrahalotriptycene (**2**) which contained *ap*-rotamers predominantly. The mixture was heated in boiling 1-chloronaphthalene to enrich *sc*-isomers by isomerization and the resulted mixture of rotamers was separated by chromatography on silver nitrate-impregnated silica gel. The olefins were oxidized with trimethylamine oxide in the presence of osmium tetraoxide[3)] to produce the corresponding diols (**3**) which were further oxidized with periodic acid to afford the aldehydes (**4**).[4)] The aldehydes were finally oxidized with potassium permanganate to produce the desired carboxylic acids (**5**).

The individual rotamers of the carboxylic acids were converted to the corresponding acid chlorides (**6**) by the treatment with oxalyl dichloride, and the acid chlorides were treated with titanium(IV) chloride to produce the ketones (**7**). As expected, due to the low



Scheme 1. Synthetic routes to 3-methyl-3-(1,2,3,4-tetrahalo-9-triptycyl)butanoic acid rotamers: a series X=F, b series X=Cl. a) Tetrahalobenzyne, b) OsO_4-$(CH_3)_3NO$, c) HIO_4, e) heating and chromatography on SiO_2–$AgNO_3$. Only one of the *sc*-forms is shown.

---

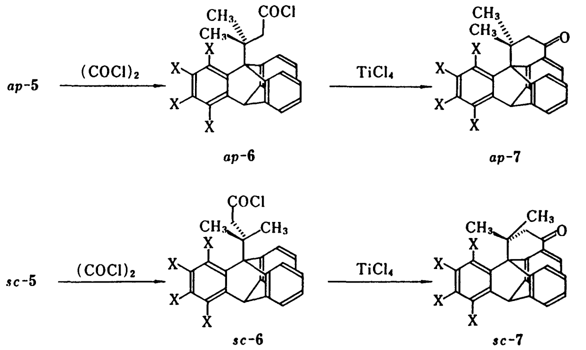
† Present address: Department of Chemistry, Faculty of Science, Okayama University of Science, Ridaicho, Okayama 700.

electron density at the 1-position of these compounds (**6**), no ipso attack by the intervening acylium cation was apparent. The corresponding ketones (**7**) were the exclusive products: even the *sc*-isomers afforded **7** only, though in other instances *sc*-isomers gave products of different types.

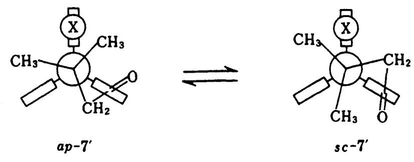
Although the difference in the reactivities of the rotamers of the chloro compound (**6b**) was not apparent, we noticed a difference in the fluoro compound (**6a**): whereas the reaction of **6b** with titanium(IV) chloride in benzene for 3 hours at room temperature afforded the corresponding cyclic ketones (**7**) of both isomers in good yields, the same treatment of *sc*-**6a** for 4 hours gave back some unreacted compound which was recovered as *sc*-**5a** in addition to the ketone (**7**) (31 and 58% yields, respectively). The incomplete reaction of *sc*-**6a** under the conditions was not due to the hydrolysis of *sc*-**6a** to *sc*-**5a** but slowness of the cyclization reaction. This was checked in two ways. Firstly, ^{1}H NMR spectra did not show any signals due to the hyrolyzed product in the reaction mixture. Secondly, treatment of (*sc*-**6a**) for 6 hours gave the ketones as sole products and no acid *sc*-**5a** was recovered.

It may be argued that the formation of a cation in the vicinity of the fluoro substituent was slow because, in cases where a chloronium or fluoronium ion of a three-membered ring could be formed in competition, only the former was formed.[6,7] However, we believe the results are better interpreted by considering the fact that there are two benzene rings in the *ap*-form (*ap*-**6a**) to react with the acylium ion, whereas there is only one such ring in *sc*-**6a**, because *ap*-**6a** gave 10% recovered acid after 2 hour treatment. The slow reaction in both isomers in **6a** relative to **6b** may be attributed to the stronger electron-withdrawing effect of the fluorine atom than the chlorine.

Ketones, *ap*-**7′** and *sc*-**7′**, obtained from *ap*-**6** and *sc*-**6**, respectively, were different compounds and could be isomerized with each other on heating. The barriers to the isomerization and the equilibrium constants between the isomers are listed in Tables 1 and 2, for the fluoro and the chloro compounds, respectively. The interesting trends seen in these tables are that the isomerization is easier in the chloro compound than in the fluoro compound and the equilibrium constant (*sc*/*ap*) is larger in the chloro compound than in the fluoro compound.



Scheme 2. Formation of isomeric ketones from rotamers of **5**.



Scheme 3. Isomerization of the ketones (**7**).

Table 1. Rate Constants for Isomerization, *ap*→*sc*, Equilibrium Constants, Thermodynamic Parameters, and Kinetic Parameters for Compound **7a** in Toluene-d_8

Temperature/°C	$k\times10^5$/s^{-1}	$K(sc/ap)$
81	0.287	2.39
90	0.729	2.34
100	2.40	2.29
110	6.61	2.25

$\Delta H^{\neq}=28.7\pm3.1$ kcal mol^{-1},[a] $\Delta S^{\neq}=-3\pm9$ cal mol^{-1} K^{-1},
$\Delta H^{\circ}=0.6\pm0.1$ kcal mol^{-1}, $\Delta S^{\circ}=0.2\pm0.2$ cal mol^{-1} K^{-1}.

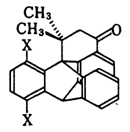
a) 1 cal=4.184 J.

Table 2. Rate Constants for Isomerization, *ap*→*sc*, Equilibrium Constants, Thermodynamic Parameters, and Kinetic Parameters for Compound **7b** in Toluene-d_8

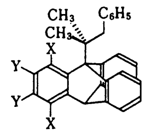
Temperature/°C	$k\times10^5$/s^{-1}	$K(sc/ap)$
60	2.27	22.6
70	7.02	21.2
80	21.8	20.4
90	52.8	18.5

$\Delta H^{\neq}=24.8\pm2.8$ kcal mol^{-1},[a] $\Delta S^{\neq}=-6\pm8$ cal mol^{-1} K^{-1},
$\Delta H^{\circ}=-1.4\pm0.1$ kcal mol^{-1}, $\Delta S^{\circ}=2\pm3$ cal mol^{-1} K^{-1}.

In order to see the effects of the 1-substituent on the barriers to isomerization and on the equilibrium constants, the data are summarized in Table 3 together with those of 8,11-dimethyl and 8,11-dimethoxy compounds (**8**). Generally speaking, the bulkier the 1-substituent, the lower the barrier to isomerization and the larger the equilibrium constant. This means that the ground state energy is more effectively raised than the transition state energy for isomerization by introducing a bulky substituent at the 11-position. It is especially so for the *ap*-ketones. The trend observed in the barriers to isomerization is parallel to that observed in 1,2,3,4-tetra- or 1,4-disubstituted 9-(1,1-dimethyl-2-phenylethyl)triptycenes (**9**),[8] open-chain analogs of the ketones.



8 a : X=CH_3O
b : X=CH_3



9

Table 3. Comparison of Free Energies of Activation for Isomerization, *ap* → *sc*, and Equilibrium Constants of Ketones in Toluene-d_8 at 90 °C

Compound	1-Substituent	$\Delta G^{\ddagger}_{363}$ / kcal mol^{-1}	K(sc/*ap*)	Reference
8b	CH_3	26.0	17.2	2
7b	Cl	27.0	18.5	This work
8a	CH_3O	29.4	6.0	2
7a	F	29.8	2.29	This work

Table 4. Steric Energies and Dissected Energies of Ketones as Calculated by MMP2(NONPLANAR) Method

Conformation		**7a**		**7b**	
		ap	*sc*	*ap*	*sc*
Steric energy		36.375	35.584	49.337	47.896
Compression		3.463	3.358	5.291	5.489
Bending		12.363	12.446	14.138	15.432
Stretch-Bend		0.040	0.024	0.128	0.143
van der Waals	a)	21.574	21.596	27.186	27.677
	b)	−2.600	−2.737	−1.938	−0.763
Torsional		−9.027	−9.690	−4.659	−9.315
Dipole		10.561	10.588	9.192	9.234

a) 1,4 energy. b) Others.

Since single crystals of these compounds have not been obtained yet, we performed molecular mechanics MMP2(NONPLANAR) calculations, in order to get further into insight. The results are shown in Table 4. This program seems to yield more realistic results than MM2 or MMP2 programs, of which results were previously reported.[2,9)] As were the cases previously reported, the total energies indicate that *sc*-**7** is always more stable than *ap*-**7** and the main difference in the total energies is attributed to the difference in the torsion terms: *ap*-**7** suffers from severer torsion than the *sc* form and the difference is larger in the case of a bulky 11-substituent than in the case of a less bulky substituent.

Although the reliability of the MM2 calculation results for this kind of highly congested molecules might be argued, we believe, as discussed in the previous paper,[2)] that the results are supported by the following ^{1}H NMR data. Namely, there is a methyl group, of which protons give a ^{1}H NMR signal at a considerably high magnetic field, in each of the isomers of **7a** and **7b**. These signals show coupling with a small coupling constant to indicate that there is a long range coupling with a proton. MMP2(NONPLANAR) calculations show that the −*sc*-methyl in *ap*-**7′** and the *ap*-methyl in *sc*-**7′** are located in the shielding zone of the distorted benzene ring. The *ap*-methyl in *sc*-**7′** suffers from additional shielding of the carbonyl moiety. These methyl groups are exactly antiperiplanar with one of the methylene protons, thus forming a W-letter skeleton that is favorable for the long range coupling.[10)]

The spin-couplings between the 1-fluorine and the methyl-protons in *ap*- and *sc*-**7a** are also consistent with the calculated structures. The *ap*-methyl-protons in *sc*-**7′** fail to show coupling with the fluorine but there is a distinct coupling observed with the methylene proton. The distance between the +*sc*-methyl and 1-F in *sc*-**7′** and that between the +*sc*-methyl and 1-F in *ap*-**7′**, 2.73 and 2.71 Å, respectively, are almost the same in agreement with almost the same F-H coupling constants, 7.9 and 8.1 Hz, respectively, for the former and the latter. The distance between the −*sc*-methyl and the 1-F in *ap*-**7′** is much longer than that between the +*sc*-methyl and the 1-F in *ap*-**7′**, 2.99 and 2.71 Å, respectively, justifying the observed coupling constants of 2.6 Hz for the former and 8.1 Hz for the latter. These distances between the methyls and the 1-F would not have been expected from the molecular models.

Experimental

^{1}H NMR spectra were recorded with a JEOL GX-270 spectrometer and infrared spectra with a Hitachi IR-260-30 spectrometer. Freshly distilled benzene was used for the Friedel-Crafts reaction. Others were of commerical origin.

1,2,3,4-Tetrafluoro-9-(1,1-dimethyl-3-butenyl)triptycene (2a). To a solution of 9.92 g (49.1 mmol) of chloropentafluorobenzene in 100 mL of dry ether, cooled with Dry Ice-acetone, was added slowly 32.6 mL (49.1 mmol) of butyllithium in hexane under a nitrogen atmosphere and the mixture was stirred at that temperature for 6 h. To this mixture was added 2.55 g (9.81 mmol) of 9-(1,1-dimethyl-3-butenyl)anthracene (**1**)[2)] in 10 mL of ether from a syringe. The whole was stirred for 2 h at −78 °C, for 2 h at 0 °C, and then for 60 h at 13 °C. The reaction was completed by heating under reflux for 2 h and the mixture was washed with dilute hydrochloric acid and then with water. The ether layer was dried over magnesium sulfate and the solvent was evaporated. Chromatography of the residue on silica gel (hexane eluent) afforded a mixture of *ap*-**2a** and *sc*-**2a**, which was contaminated with a 1,4-adduct of the benzyne to the anthracene. The ratio of *ap*-**2a**, *sc*-**2a**, and the 1,4-adduct was 7 : 3 : 1.

The mixture, which weighed 2.5 g at this stage, was dissolved in a small amount of 1-chloronaphthalene and heated under reflux for 50 h under a nitrogen atmosphere. Rough chromatography of the product on silica gel (hexane eluent) afforded a mixture which contained *ap*-**2a** and *sc*-**2a** in 1 : 2 ratio. The mixture was separated by chromatography on silica gel impregnated ca. 10% silver nitrate with the use of 5 : 1 hexane–dichloromethane as an eluent. The order of elution was *sc*-**2a**, *ap*-**2a**, and the 1,4-adduct.

***ap*-2a**, mp 163—164 °C, yield, 3.6%. It was recrystallized from hexane. Found: C, 76.54; H, 5.00%. Calcd for $C_{26}H_{20}F_4$: C, 76.46; H, 4.94%. ^{1}H NMR ($CDCl_3$) δ=2.00 (6H, d, J=8.9 Hz), 3.29 (2H, d, J=7.1 Hz), 5.20—5.36 (2H, m), 5.69 (1H, d. J=1.0 Hz), 6.18—6.37 (1H, m), 7.00—7.12 (4H, m), 7.38—7.48 (2H, m), 7.81—7.90 (2H, m).

***sc*-2a**, caramel, yield 6.7%. ^{1}H NMR ($CDCl_3$) δ=1.93 (3H, d, J=8.1 Hz), 2.05 (3H, s), 3.01 (1H, dd, J=14.5 and 7.2 Hz), 3.31 (1H, dd, J=14.5 and 6.8 Hz), 5.20—5.36 (2H, m), 5.69 (1H, d, J=1.0 Hz), 6.15—6.35 (1H, m), 6.99—7.12 (4H, m), 7.36—7.48 (2H, m), 7.79—7.95 (2H, m).

1,2,3,4-Tetrachloro-9-(1,1-dimethyl-3-butenyl)triptycene (2b). This compound was prepared similarly as described above for the tetrafluoro compound (**2a**) from **1** and hexachlorobenzene, except the followings. The lithiation of hexachlorobenzene was carried out at −30 °C and the generation of the benzyne by stirring for 5—6 h with gradual raise of temperature to −10 °C and then stirring overnight in an ice-bath, during which time the temperature was allowed to rise to room temperautre. A product which contained *ap*-**2b**, *sc*-**2b**, and a 1,4-adduct in 7 : 3 : 5 ratio was obtained in ca. 20% yield. The *ap*-olefin could be isolated by recrystallization of the mixture from hexane–dichloromethane. The separation of the *sc*-isomer from others was carried out by chromatography on SiO_2–$AgNO_3$, after isomerization by heating a 1-chloronaphthalene solution for 20 h, which gave a ca. 1 : 1 *ap*-**2b** and *sc*-**2b** mixture.

ap-**2b**, mp 230.5—231.0 °C. Found: C, 65.99: H, 4.10; Cl, 29.85%. Calcd for $C_{26}H_{20}Cl_4$: C, 65.85; H, 4.25; Cl, 29.90%. ^{1}H NMR ($CDCl_3$) δ=2.29 (6H, s), 3.24 (2H, d, J=7 Hz), 5.22—5.28 (2H, m), 6.07 (1H, s), 6.17—6.32 (1H, m), 7.03—7.11 (4H, m), 7.44—7.47 (2H, m), 7.92—7.95 (2H, m).

sc-**2b**, caramel. ^{1}H NMR ($CDCl_3$) δ=2.60 (3H, s), 2.18 (3H, s), 3.49 (1H, dd, J=15.2 and 6.2 Hz), 3.65 (1H, dd, J=15.2 and 8.1 Hz), 5.26—5.32 (2H, m), 6.09 (1H, s), 6.19—6.34 (1H, m), 7.03—7.11 (4H, m), 7.42—7.48 (2H, m), 7.93—7.98 (1H, m), 8.02—8.05 (1H, m).

***ap*-4-Methyl-4-(1,2,3,4-tetrafluoro-9-triptycyl)-1,2-pentanediol (3a).** To a solution of 251 mg (0.615 mmol) of the olefin (**2a**) in 50 mL of *t*-butyl alcohol, were added 3.76 g (33.8 mmol) of trimethylamine oxide dihydrate, 2 mL of pyridine, and 15 mL of water. To the solution under an argon atmosphere, was added ca. 20 mg of osmium tetraoxide in 1 mL of *t*-butyl alcohol, and the whole was heated for 24 h. The mixture was treated with 20 mL of 20% aqueous sodium hydrogensulfite and then most of *t*-butyl alcohol was evaporated. The residue was extracted with dichloromethane or ether and the extract was washed with saturated aqueous sodium chloride and dilute hydrochloric acid. Evaporation of the solvent afforded the desired product as caramel, which was used directly for the next reaction. The following ^{1}H NMR data ($CDCl_3$, δ) were recorded: 2.03 (3H, d, J=8.1 Hz), 2.13 (3H, d, J=8.8 Hz), 2.66 (1H, dd, J=15.1 and 2.7 Hz), 2.89 (1H, dd, J=15.1 and 7.5 Hz), 3.59 (1H, t, J=8.0 Hz), 4.27 (1H, dd, J=8.0 and 6.0 Hz), 4.63—4.79 (1H, m), 5.69 (1H, br s), 7.02—7.11 (4H, m), 7.39—7.47 (2H, m), 7.69—7.76 (1H, m), 8.03—8.09 (1H, m).

The *sc*-diol (*sc*-**3a**) was prepared similarly and used for the next reaction. The crude product contained two diastereomers due to the presence of a new chiral center in addition to the chirality of being the *sc* form. Due to the complexity of the ^{1}H NMR spectra, only the signals due to methyl protons were recorded ($CDCl_3$, δ): 2.02 (3H, d, J=7.0 Hz), 2.11 (3H, d, J=7.7 Hz), 2.12 (3H, s), 2.24 (3H, s). The formation ratio of the two isomers was 4 : 3.

***ap*-4-Methyl-4-(1,2,3,4-tetrachloro-9-triptycyl)-1,2-pentanediol (3b).** This compound was prepared similarly as above. ^{1}H NMR ($CDCl_3$) δ=2.34 (3H, s), 2.48 (3H, s), 2.63—2.73 (1H, m), 3.45—3.54 (1H, m), 3.68—3.77 (1H, m), 4.33—4.47 (1H, m), 6.07 (1H, s), 7.03—7.10 (4H, m), 7.43—7.46 (2H, m), 7.75—7.79 (1H, m), 8.06—8.10 (1H, m). In addition, a very broad peak at δ 2.1—2.6 was observed.

***sc*-Diol (*sc*-3b).** ^{1}H NMR ($CDCl_3$, δ): *sc*-**3b**(I), 2.20 (3H, s) and 2.25 (3H, s); *sc*-**3b**(II), 2.08 (3H, s) and 2.38 (3H, s). The ratio of *sc*-**3b**(I) and *sc*-**3b**(II) was 4 : 3.

***ap*-3-Methyl-3-(1,2,3,4-tetrafluoro-9-triptycyl)butanal (4a).** The product obtained by the dihydroxylation described above was dissolved in 10 mL of tetrahydrofuran and stirred with 0.46 g (2.0 mmol) of periodic acid dihydrate in 3 mL of water for 3 h at room temperature. The mixture was diluted with 100 mL of water and extracted with dichloromethane. Evaporation of the solvent afforded a crude product which was used directly for the next reaction. The following ^{1}H NMR data ($CDCl_3$, δ) were recorded: 2.22 (6H, d, J=9.2 Hz), 3.66 (2H, d, J=2.2 Hz), 5.70 (1H, d, J=1.0 Hz), 7.04—7.13 (4H, m), 7.42—7.49 (2H, m), 7.75—7.83 (2H, m), 10.23 (1H, t, J=2.6 Hz).

sc-**4a**. ^{1}H NMR ($CDCl_3$) δ=2.19 (3H, d, J=7.9 Hz), 2.25 (3H, d, J=0.7 Hz), 3.47 (1H, br dd, J=16.5 Hz), 3.63 (1H, br dt, J=16.5 and 2.9 Hz), 5.70 (1H, d, J=1.3 Hz), 7.02—7.11 (4H, m), 7.38—7.48 (2H, m), 7.73—7.84 (2H, m), 10.22 (1H, t, J=2.1 Hz).

***ap*-3-Methyl-3-(1,2,3,4-tetrachloro-9-triptycyl)butanal (4b).** This compound was prepared similar as above. ^{1}H NMR ($CDCl_3$) δ=2.49 (6H, s), 3.64 (2H, d, J=2.0 Hz), 6.08 (1H, s), 7.04—7.11 (4H, m), 7.45—7.49 (2H, m), 7.84—7.88 (2H, m), 10.16 (1H, t, J=2.0 Hz).

sc-**4b**. ^{1}H NMR ($CDCl_3$) δ=2.28 (3H, s), 2.42 (3H, s) 3.72 (1H, dd, J=17.0 and 1.8 Hz), 4.16 (1H, dd, J=17.0 and 2.9 Hz), 6.10 (1H, s), 7.07—7.10 (4H, m), 7.44—7.49 (2H, m), 7.83—7.92 (2H, m), 10.20 (1H, dd, J=2.9 and 1.8 Hz).

***ap*-3-Methyl-3-(1,2,3,4-tetrafluoro-9-triptycyl)butanoic Acid (5a).** The aldehyde (*ap*-**4a**) obtained above was dissolved in 22 mL of acetone and stirred for 2 h with 0.29 g (1.8 mmol) of potassium permanganate in 5 mL of water and a small amount of sodium hydrogencarbonate at room temperature. The mixture was acidified with dilute sulfuric acid and the excess of the permanganate was destroyed with 20% aqueous sodium hydrogensulfite. The mixture was extracted with dichloromethane and the solvent was evaporated. The residue was purified by preparative TLC on silica gel (11 : 1 dichloromethane–ether eluent). An analytical sample was obtained by recrystallization of the product from tetrahydrofuran–pentane, mp 282—284 °C (decomp). The yield was 68% based on the olefin (*ap*-**2a**). Found: C, 70.20; H, 4.07%. Calcd for $C_{25}H_{18}F_4O_2$: C, 70.42; H, 4.25%. ^{1}H NMR ($CDCl_3$) δ=2.21 (6H, d, J=8.4 Hz), 3.62 (2H, s), 5.71 (1H, br s), 7.05—7.17 (4H, m), 7.41—7.50 (2H, m), 7.80-7.95 (2H, m), 10.4—11.1 (1H, br s).

sc-**5a**, mp 285—287 °C (decomp), was prepared similarly from the corresponding aldehyde and purified by recrystallization from dichloromethane–hexane. The yield was 67% based on the olefin (*sc*-**2a**). Found: C, 70.14; H, 4.37%. Calcd for $C_{25}H_{18}F_4O_2$: C, 70.42; H, 4.25%. ^{1}H NMR ($CDCl_3$) δ=2.20 (3H, d, J=8.1 Hz), 2.25 (3H, s), 3.46 (1H, dd, J=15.3 and 2.0 Hz), 3.70 (1H, d, J=15.3 Hz), 5.71 (1H, br s), 7.02—7.17 (4H, m), 7.37—7.50 (2H, m), 7.77—7.88 (1H, m), 7.88—7.98 (1H, m), 10.8—11.8 (1H, br s).

***ap*-3-Methyl-3-(1,2,3,4-tetrachloro-9-triptycyl)butanoic Acid (5b).** This compound was prepared similarly as above, the yield being 70% based on the olefin (*ap*-**2b**), and purified by recrystallization from dichloromethane–hexane. The melting point was 254—256 °C (decomp). This compound failed to give correct analytical data but the corresponding methyl ester did. ^{1}H NMR ($CDCl_3$) δ=3.49 (6H, s), 3.60 (2H, s), 6.09 (1H, s), 7.09—7.13 (4H, m), 7.46—7.50 (2H, m), 7.92—7.97 (2H, m).

The methyl ester, mp 209—211 °C. Found: C, 61.75; H, 4.11; Cl, 28.08%. Calcd for $C_{26}H_{20}Cl_4O_2$: C, 61.69; H, 3.98; Cl, 28.01%. ^{1}H NMR ($CDCl_3$) δ=2.44 (6H, s), 3.51 (2H, s), 3.82 (3H, s), 6.08 (1H, s), 7.08—7.13 (4H, m), 7.43—7.50 (2H, m), 7.91—7.95 (1H, m), 8.01—8.05 (1H, m).

sc-**5b**, mp 286—287 °C (decomp), was similarly prepared in 65% yield based on the olefin (*sc*-**2b**) and purified by recrystallization from dichloromethane-hexane. This compound failed to give correct analytical data but the methyl ester did. ^{1}H NMR ($CDCl_3$) δ=2.24 (3H, s), 2.46 (3H, s), 3.84 and 4.22 (2H, ABq, J=15 Hz), 6.10 (1H, s), 7.07—7.13 (4H, m), 7.43—7.50 (2H, m), 7.91—7.95 (1H, m), 8.01—8.05 (1H, m).

The methyl ester, mp 206—208 °C. Found: C, 61.49; H, 4.28; Cl, 27.98%. Calcd for $C_{26}H_{20}Cl_4O_2$: C, 61.69; H, 3.98; Cl, 28.01%. ^{1}H NMR ($CDCl_3$) δ=2.15 (3H, s), 2.40 (3H, s), 3.84 (3H, s), 3.76 and 4.14 (2H, ABq, J=15.2 Hz), 6.08 (1H, s), 7.06—7.11 (4H, m), 7.42—7.48 (2H, m), 7.90—7.93 (1H, m), 8.03—8.06 (1H, m).

Intramolecular Friedel-Crafts Reaction of the Acid Chloride (6) Derived from 5. The typical reaction is described with the use of *ap*-**5a**. To a solution of 52 mg (0.12 mmol) of *ap*-**5a** in 10 mL of benzene was added 0.1 mL (1.2 mmol) of oxalyl dichloride under a nitrogen atmosphere and the whole was stirred for 4 h at room temperature. The excess of oxalyl dichloride and the solvent were removed in vacuo. The residue showed the following signals in ^{1}H NMR ($CDCl_3$, δ): 2.20 (6H, d, J=9.2 Hz), 4.26 (2H, s), 5.71 (1H, br s), 7.04—7.16 (4H, m), 7.41—7.51 (2H, m). 7.72—7.81 (2H, m). The residue was taken up in 10 mL of benzene and was mixed with 0.2 mL (1.8 mmol) of titanium(IV) chloride. The mixture was stirred for 3 h at room temperature and then treated with water. The organic layer was separated and the aqueous layer was extracted with dichloromethane. The combined organic layers were dried over magnesium sulfate and the solvent was evaporated. The residue was purified by preparative TLC on silica gel (dichloromethane eluent) to give 78% *ap*-8,9,10,11-tetrafluoro-1,1-dimethyl-1,2-dihydro-7*H*-7,11b-*o*-benzeno-3*H*-benz[*dl*]anthracen-3-one (**7a**). The pure sample, mp 176—177 °C, was obtained by recrystallization from hexane. Found: C, 73.62; H, 3.99%. Calcd for $C_{25}H_{16}F_4O$: C, 73.53; H, 3.95%. ^{1}H NMR ($CDCl_3$) δ=1.63 (3H, dd, J=2.6 and 1.4 Hz), 2.03 (3H, d, J=8.1 Hz), 2.78 (1H, d, J=15 Hz), 3.36 (1H, dd, J=15 and 1.4 Hz), 5.76 (1H, d, J=1.5 Hz), 6.95—7.11 (2H, m), 7.15—7.29 (1H, m), 7.33—7.41 (1H, m), 7.58—7.72 (1H, m), 7.77—7.85 (1H, m). IR (Nujol mull): 1695 cm^{-1}. The same treatment for 2 h gave 65% *ap*-**7a** and 10% recovered *ap*-**5a**.

The following ^{1}H NMR data ($CDCl_3$, δ) of *sc*-**6a** were recorded: 2.17 (3H, d, J=8.6 Hz), 2.25 (3H, s), 4.06 (1H, dd, J=18.1 and 4.3 Hz), 4.34 (1H, d, J=18.1 Hz), 5.71 (1H, br d, J=1.3 Hz), 7.01—7.16 (4H, m), 7.38—7.52 (2H, m), 7.70—7.81 (2H, m).

sc-**7a**, mp 196—197 °C was similarly prepared from the acid chloride (*sc*-**6a**) and purified by recrystallization from hexane. However, the reaction of the acid chloride was slow in this case: after 4 h stirring at room temperature, the ketone was obtained in 58% yield, whereas 31% acid *sc*-**5a** was recovered. When the reaction was continued for 6 h, the ketone was obtained in 87% yield and no acid was recovered. Found: C, 73.78; H, 4.24%. Calcd for $C_{25}H_{16}F_4O$: C, 73.53; H, 3.95%. ^{1}H NMR ($CDCl_3$) δ=1.68 (3H, d, J=1.3 Hz), 2.06 (3H, d, J=7.9 Hz), 2.75 (1H, d, J=15.8 Hz), 3.55 (1H, br d, J=15.8 Hz), 5.81 (1H, d, J=1.3 Hz), 7.13—7.25 (3H, m), 7.50—7.57 (1H, m), 7.58—7.64 (1H, m), 7.67—7.74 (1H, m), 7.86—7.93 (1H, m). IR (Nujol mull): 1690 cm^{-1}.

ap-8,9,10,11-Tetrachloro-1,1-dimethyl-1,2-dihydro-7*H*-7,11b-*o*-benzeno-3*H*-benz[*dl*]anthracen-3-one (**7b**), mp 257—259 °C, when recrystallized from dichloromethane-hexane, was similarly obtained from the corresponding tetrachloro acid (*ap*-**5b**) in 70% yield. Since this compound failed to give the correct analytical data, high resolution mass spectrum was recorded. Found: m/z 471.9970, 473.9988, 475.9924, and 477.9817. Calcd for $C_{25}H_{16}{}^{35}Cl_4O$, $C_{25}H_{16}{}^{35}Cl_3{}^{37}ClO$, $C_{25}H_{16}{}^{35}Cl_2{}^{37}Cl_2O$, and $C_{25}H_{16}{}^{35}Cl^{37}Cl_3O$: 471.9955, 473.9926, 475.9897, and 477.9865. The intensity ratios of the signals agreed with those expected from the natural abundances of ^{35}Cl and ^{37}Cl. ^{1}H NMR ($CDCl_3$) δ=1.83 (3H, d, J=1.5 Hz), 2.34 (3H, s), 2.78 (1H, d, J=15 Hz), 3.31 (1H, dd, J=15 and 1.5 Hz), 6.09 (1H, s), 7.00—7.12 (2H, m), 7.18—7.23 (1H, m), 7.38—7.41 (1H, m), 7.63—7.66 (1H, m), 7.67—7.71 (1H, m), 7.87—7.90 (1H, m). IR (KBr disc): 1690 cm^{-1}.

sc-**7b**, mp 258—260 °C, was similarly prepared from the corresponding acid (*sc*-**5b**) in 70% yield. Recrystallization of the compound from dichloromethane-hexane afforded the analytical sample. Found: C, 63.36; H, 3.51; Cl, 29.61%. Calcd for $C_{25}H_{16}Cl_4O$: C, 63.32; H, 3.40; Cl, 29.90%. ^{1}H NMR ($CDCl_3$) δ=1.64 (3H, d, J=1.5 Hz), 2.31 (3H, s), 2.78 (1H, d, J=16 Hz), 4.20 (1H, dd. J=16 and 1.5 Hz), 6.14 (1H, s), 7.15—7.23 (3H, m), 7.53—7.56 (1H, m), 7.63—7.66 (1H, m), 7.74—7.77 (1H, m), 7.90—7.93 (1H, m). IR (KBr disc): 1690 cm^{-1}.

Kinetics of Isomerization of Ketones (7). The *ap*-ketone was dissolved in toluene-d_8 to make up a ca. 20 mmol L^{-1} solution. The sample solution was placed in a thermostatted bath, except for one case where a boiling benzene bath was used. The rates of isomerization were followed by the change in intensities of ^{1}H NMR signals due to the methyl protons or the 7-proton. The data were treated by assuming the reversible first order reactions. The rate constants thus obtained were put into the Eyring equation to produce kinetic parameters.

Comparison of the Kinetic and Thermodynamic Parameters. The parameters shown in Table 3 were obtained by extrapolation of the thermodynamic and kinetic parameters obtained in the temperature ranges other than the given temperature. The thermodynamic parameters may include large errors, especially for those which give large K values.

Molecular Mechanics Calculations. Molecular mechanics calculations were performed using the MMP2(82) program[11] at the Computer Center of the University of Tokyo, assuming a "nonplanar" π-system for each compound. As the force field does not contain parameters for halogen atoms attached to an sp^2 carbon atom, several necessary parameters were added. The equilibrium bond length (Å) and stretching force constant (md Å^{-1}) for C(sp^2)-X were assumed to be 1.715 and 2.66, respectively, when X=Cl, and 1.330 and 5.10, respectively, when X=F. The equilibrium bond angle (deg) and bending force constant (md Å rad^{-2}) were 120.0 and 0.40, when X=Cl, for C(sp^2)-C(sp^2)-X, and 120.0 and 0.65, respectively, for X=F. Torsional constants, V_1 and V_2, of −0.93, and 9.0 kcal mol^{-1}, respectively, for X-C(sp^2)-R, where R is any atom, were used. The out-of-plane bending parameter of 0.05 md Å rad^{-1} was used for both the cases where X=Cl and F.

This work was supported by a Grant-in-Aid (No.

62124035) for Fundamental Scientific Research of the Ministry of Education, Science and Culture.

References

1) For Part XXIII of the series, see M. Ōki, J. Tsukahara, Y. Sonoda, K. Moriyama, and N. Nakamura, *Bull. Chem. Soc. Jpn.*, **61**, 4303 (1988).

2) T. Tanaka, K. Yonemoto, Y. Nakai, G. Yamamoto, and M. Ōki, *Bull. Chem. Soc. Jpn.*, **61**, 3239 (1988).

3) R. Ray and D. S. Matteson, *Tetrahedron Lett.*, **21**, 449 (1980).

4) E. L. Jackson, *Org. React.*, **2**, 341 (1944).

5) R. Adams and L. H. Ulich, *J. Am. Chem. Soc.*, **42**, 599 (1920).

6) G. A. Olah and J. M. Bollinger, *J. Am. Chem. Soc.*, **90**, 947 (1968).

7) A referee suggested that, since addition of a cation to fluoro-olefins was much easier than to chloro-olefins [G. A. Olah and Y. K. Mo, *Adv. Fluorine Chem.*, **7**, 69 (1973): W. S. Johnson, G. W. Daub, T. A. Lyle, and M. Niwa, *J. Am. Chem. Soc.*, **102**, 7800 (1980)], the argument would not hold. However, the results of Ref. 6 clearly indicates that a three-membered fluoronium ion is very reluctantly formed. We believe these two cases must be considered separately.

8) G. Yamamoto, M. Suzuki, and M. Ōki, *Bull. Chem. Soc. Jpn.*, **56**, 306 (1983).

9) K. Yonemoto, Y. Nakai, G. Yamamoto, and M. Ōki, *Chem. Lett.*, **1985**, 1739.

10) K. B. Wiberg, G. M. Lampman, R. P. Ciura, D. S. Connor, P. Schertler, and J. Lavanish, *Tetrahedron*, **21**, 2749 (1965) and papers cited therein.

11) N. L. Allinger and H. L. Flanagan, *J. Comput. Chem.*, **4**, 399 (1983).