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Reactivities of Stable Rotamers. XXIII. Some Addition Reactions toward the Vinyl Group in 9-(2-Vinyl-1-naphthyl)fluorene Rotamers[1)]

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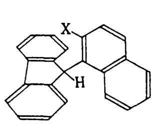
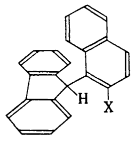
Addition reactions to the vinyl group of the *ap* and the *sp* rotamers of 9-(2-vinyl-1-naphthyl)fluorene were carried out. Whereas action of sulfuric acid on the *sp* rotamer caused a cyclization reaction, the *ap* isomer was recovered under the conditions. While addition of bromine afforded normal products for both the isomers, reaction of chlorine afforded chlorine-substituted products (chloro olefins) in addition to the normal adduct, the formation of the former being predominant, in the *sp* form. The slightly enhanced reactivity of the *sp* form relative to the *ap* in bromination together with the formation of the chloro olefin and the behavior of the *sp* form in the treatment with sulfuric acid are attributed to the stabilization of the intermediates by the π-participation of the fluorene ring. Other addition reactions, epoxidation, hydrogenation, hydroboration, osmium tetraoxide oxidation, chlorination with (dichloroiodo)benzene, and diimide reduction, which are believed to proceed through a cyclic transition state, have also been studied to show that the rates of the reactions of one isomer are not much different from those of another. Spectroscopic data suggest that the conformation of the vinylnaphthalene portion in both isomers are similar. Little difference in the reaction rates of the two rotamers are attributed to the possible transition state conformation which may not be affected by the steric hindrance of the fluorene ring.

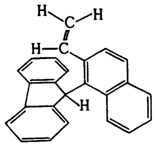
In previous papers of this series, we have pointed out that, in 9-(2-substituted 1-naphthyl)fluorene derivatives (**1**), reactions which occur over the fluorene ring with bulky transition states can be much slower than those which occur in the remote sites from the fluorene moiety.[2,3)] Thus the reactions that occur in the X group of the *ap* conformer (*ap*-**1**) are much slower than those occurring in the X of the *sp* conformer (*sp*-**1**), the k_{sp}/k_{ap} values exceeding 30 in some cases.

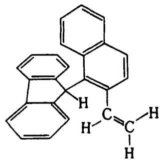

ap-1


sp-1

(if X precedes C₈ₐ of naphthalene in the sequence rule)

Based on these generallizations, we see that addition reactions of 9-(2-formyl-1-naphthyl)fluorenes (**1**: X=CHO) are on the border line, because the following relative rates, k_{sp}/k_{ap}, are obtained: sodium tetrahydroborate reduction 7.6, oxime formation 3.7, addition of Gringard reagents ca. 1.8.[2)] In view of these results, it will be worthwhile to examine some other reactions that would give similar situations in the transition states of reactions to that of the aldehyde. Since a vinyl group has a similar bulkiness with a formyl group as far as we consider the CH= group that should give important steric interactions with the fluorene moiety, 9-(2-vinyl-1-naphthyl)fluorene (**2**) is a good model to further the understanding of the steric effects in some reactions of this type of compounds. In addition, various types of addition reactions to an olefin which proceed with cyclic and consequently bulky transition states are known. This paper discusses the results of some addition reactions of **2**.


sp-2


ap-2

Rotational Barriers and Equilibrium Constant. In order to avoid complexity arising from isomerization of one rotamer to another, it is desirable to run reactions under conditions that do not permit contamination of one isomer by another produced by isomerization. Thus at the outset of the investigation we undertook the measurement of the rates of isomerization of these isomers. *ap*-**2** in toluene-d_8 exhibited the equilibrium constant (*sp*/*ap*) of 0.47 and the rate constant of isomerization of $8.48\times10^{-6}\,\mathrm{s}^{-1}$ at 80 °C. Similarly, the *sp* isomer gave the following results: *ap*/*sp* 2.1, *k*(isomerization) $1.95\times10^{-5}\,\mathrm{s}^{-1}$. These results agree quite well. The free energy ef activation for rotation is 28.9 kcal mol^{-1} (1 cal=4.184 J) for the *ap*→*sp* process, and is 28.4 kcal mol^{-1} for the *sp*→*ap* process at 80 °C.

The barriers to rotation in these olefins are appreciably higher than those in the aldehyde (**1**: X=CHO), 26.8 kcal mol^{-1} at 80 °C.[2)] The equilibrium constant, 2.1, is significantly larger than the corresponding value, 1.5, for the aldehyde.[2)] The difference cannot be attributed to the difference in the ground state conformations, because both the aldehyde[4)] and the olefins (**2**), for which evidence is described in Experimental section, are coplanar with the naphthalene nucleus.

We attribute the difference in the equilibrium con-

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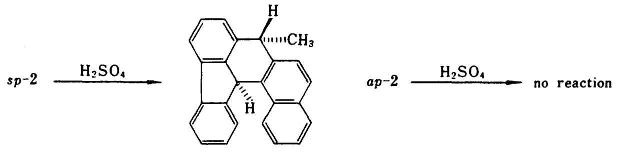
stants between the aldehyde (**1**: X=CHO) and the olefin (**2**) to the difference in the solvents, hexachlorobutadiene for the aldehyde and toluene-d_8 for the olefin.

Addition Reactions of Cationic Species. Treatment of *sp*-**2** with concentrated sulfuric acid afforded *trans*-8-methyl-8,14c-dihydrodibenz[*a,l*]aceanthrylene (**3**) smoothly which was identical with the authentic specimen reported in a previous paper.[5] The result unambiguously shows that the benzylic cation formed by addition of a proton to the vinyl group can attack the aromatic ring of the fluorene moiety if the conformation of the starting olefin is *sp*. By contrast, we recovered *ap*-**2** after the same treatment for 60 days. Thus it is extremely difficult to get a cyclized product from a cation produced in the benzylic position of *ap*-**2**, as reported for another case of dehydration reaction of *sp*-9-[2-(1-hydroxyethyl)-1-naphthyl]fluorene.[6]



3

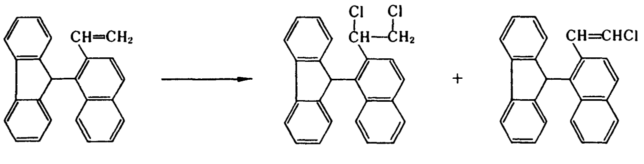
Addition of bromine to the olefinic bond is usually assumed to proceed through a bridged bromonium ion because of the stereospecificity of the reaction.[7] However, the stereospecificity is lost in the addition of bromine to *cis*- and *trans*-1-propenylbenzene.[8] Since the compounds we are concerned here are styrene derivatives, the reaction might be assumed to follow the path where an open-chain cation intervenes. If the intermediate is distinctly a cation, then we might expect to obtain a cyclized product from *sp*-**2** as was the case for the sulfuric acid treatment.

In the actual reaction, no anomaly was observed not only for *ap*-**2** but also for *sp*-**2**: normal addition reaction products (**4**) were obtained. This would mean that the cationic species formed during the reaction is not a naked cation but is stabilized by the participation of the bromine atom beta to the cationic center. The nonstereospecificity of the bromine addition[8] is not inconsistent with this interpretation but would mean that, due to the weak participation of the bromine atom, the bond between the cationic center and the bromine atom breaks and reforms rapidly under the conditions, when stereochemistry is reversed. This result is consistent with the finding that, in the addition reaction of bromine to 1-propenylbenzene, partial stereoselectivity is observed.[8,9]

The relative rate (k_{ap}/k_{sp}) of the bromine addition was 0.80 in carbon tetrachloride. It is rather surprising to note that the reaction which occurs at a crowded site is faster than that in a less crowded site. It is especially so when we compare the results with those of addition reactions to the formyl group: although the relative rates vary from reaction to reaction, the reactions that occur in a less crowded site are always faster than those in a crowded site.[2] We wish to attribute this apparently anomalous relative rate to the participation of the π-system of the fluorene ring. Namely the cationic species formed by addition of a cationic bromine is partly stabilized by the π-participation. In agreement with this interpretation, we found that the same reaction in acetonitrile prefers the *ap*-olefin, although the degree of the preference is rather small, k_{ap}/k_{sp}=1.2. It has been found that solvation shell around the cationic species formed over the fluorene ring is completed by involving the participation of the fluorene ring.[6] Thus, if the solvent molecules are good nucleophiles, the cation formed from *ap*-**2** must be more stable than that from *sp*-**2**, because the solvation shell is completed by solvent molecules alone in the *ap*-**2** case.

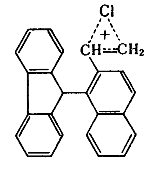
2 **4**

The reactions of the olefin (**2**) with chlorine were rather surprising: while the *ap*-form afforded the chlorine-addition product (**5**), as the normal olefin, in addition to a small amount of an unidentified material, the ratio of the addition product (**5**) to a chlorine-substitution product (**6**) was 1.0 : 1.4 in the case of *sp*-**2**. Compound **6** is not the secondary product from **5**, because the formation ratio, **5**/**6**, at the later stage of the reaction was the same with that at the earlier stage and **6** was not converted practically to **5** under the reaction conditions in a separate experiment.



2 **5** **6**

The mechanism of the formation of **6** is assumed to be that the intervening cation (**7**) which is stabilized, though weak, by the participation of the chlorine atom in the β-position suffers from deprotonation more preferably than the attack of the chloride ion at the α-position. The preferred formation of **6** in the case of *sp*-**2** must be derived from the facts that the vinyl group is situated in the sterically more hindered site and that the ionic character of the intervening **7** is more significant than that of the *ap*-form because of the π-participation. It might be argued that the chloronium ion is possible only in aliphatic β-chloro carbocations and not for the benzylic cation.[10] In the addition of chlorine to an olefinic bond in compounds of styrene type, open-chain β-chloro cations which form ion-pairs are postulated.[11] However, the postulate cannot accommodate the difference in the reactivities of the rotamers observed here. We prefer, therefore, that the chlorine participation is significant in this case, though the C-Cl bond may break and form rapidly because the participation is weak. The formation of the chloro-olefin which is also observed in other cases is attributed to deprotonation from either the weakly chloro-participated **7** or transitionally formed open-chain cation.



7

Addition Reactions with Cyclic Transition States. Relative rates (k_{ap}/k_{sp}) are given in Scheme 1 for various addition reactions of which transition states are cyclic, together with some related reactions.

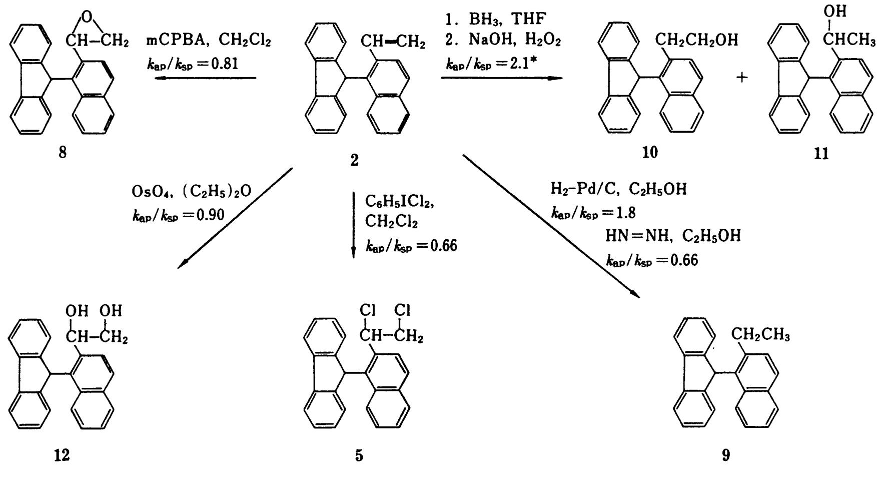
Epoxidation of olefins with peroxycarboxylic acids is known to proceed stereospecifically.[12] Even *cis*-stilbene gives a stereospecific addition product, *cis*-2,3-diphenyloxirane.[13] Thus in the formation of epoxides, the transition state may be unequivocally assumed to be a three-membered cycle. Both *ap*-**2** and *sp*-**2** reacted smoothly with *m*-chloroperbenzoic acid to give epoxides (**8**). The relative rate was very close to unity but the reaction of *sp*-**2** was significantly favored over that of *ap*-**2**.

Four-membered cyclic transition states are assumed for catalytic hydrogenation[14] and addition of borane.[15] Hydrogenation of *ap*-**2** and *sp*-**2** over palladium on carbon proceeded smoothly to afford *ap*- and *sp*-9-(2-ethyl-1-naphthyl)fluorene (**9**), respectively. The relative rate was ca. 2. Addition of borane to *sp*-**2** in tetrahydrofuran, followed by oxidation with alkaline hydrogen peroxide, afforded 9-[2-(2-hydroxyethyl)-1-naphthyl]fluorene (**10**) and 9-[2-(1-hydroxyethyl)-1-naphthyl]fluorene (**11**) in 7:3 ratio, whereas *ap*-**2** afforded the corresponding **10** and **11** in 5:2 ratio. This poor regioselectivity in the borane addition was also reported in the literature for the case of styrene.[15,16] Strictly speaking, therefore, we observed two reactions, which differ in the rate constants, to make the comparison of the reactivities of the rotamers very difficult. However, since the product ratios due to the regiochemically different additions in both rotamers are not far from each other and the rates of the additions to the two olefinic substrates are comparable, we may compare the reactivity of the rotamers, as a rule of thumb, by taking the rates of decrease in the amount of the starting materials, *sp*-**2** and *ap*-**2**. These results are shown in Scheme 1. This reaction is the one among those examined in this work, that shows the highest reactivity of the *ap*-isomer relative to the *sp*. Although we tried to add 9-borabicyclo[3.3.1]nonane, which should give distinct steric effects,[17] to the olefin, isomers failed to give products.

Cis-addition, though not exclusive, of chlorine to olefins was first established by Barton and Miller[18] when (dichloroiodo)benzene was used. Although this addition reaction has a complicated nature,[19] it will be worthwhile to try the reaction as an example of a five-membered cyclic transition state. The reaction of (dichloroiodo)benzene with *ap*-**2** and *sp*-**2** proceeded smoothly to give the corresponding dichlorides (**5**). The relative rate was 0.66. Although this reaction can involve ionic, radical, and cyclic intermediates (or transition state), details are not known. However, the results suggest that the mechanism of the reaction of **2** with this reagent is different from the addition reaction of chlorine, because the product ratios were different.

A five-membered cyclic transition state is also expected for the oxidation of the olefin with osmium tetraoxide.[20] Addition of the reagent gave the corresponding diols (**12**). The relative rate was 0.90.

Diimide addition to olefins is also stereospecific and



Scheme 1. Reactions of *ap*- and *sp*-9-(2-vinyl-1-naphthyl)fluorene rotamers, products, and relative reactivities (k_{ap}/k_{sp}).
* For k_{ap}/k_{sp} here, see the text.

a six-membered cyclic transition state is involved.[21] Since the isomerization of the rotamers of **2** can occur under the alkaline conditions, we used the method of generation of diimide under neutral conditions.[22] The reduction of **2** took place smoothly to afford 9-(2-ethyl-1-naphthyl)fluorene (**9**). The relative reactivity is less than unity to mean that the vinyl group over the fluorene ring is more vulnerable to the reaction.

Summarizing these results, we notice that the rates of addition reactions of various reagents to the olefinic bond of compound **2** do not differ to a large extent from the *ap* to the *sp* rotamer, even though we selected various space-demanding reactions with cyclic transition states from a three membered to a six-membered ring.

Although the ground state conformations of the vinylnaphthalene moieties are planar, the rotamers cannot react in the conformations as such, because the bulky transition state must be taken that should strongly interfere with the fluorene ring in the *sp* rotamer. Therefore, a strong possibility is that the vinyl group rotates from the naphthalene plane to permit the access of the reagent. This rotation will occur in both conformers, *ap*-**2** and *sp*-**2**, because the reactions of *ap*-**2**, especially those which are not electron-demanding, must be faster than those of *sp*-**2**, to an extent that is determined by the energy required for the rotation, if *ap*-**2** reacts in the planar conformation. Though the electron density in the vinyl group should increase by taking the nonplanar structure, this effect on the reaction rate may be neglected.

If the vinyl group takes the nonplanar conformation invoked above, in the transition state of addition reactions where the benzylic carbon must approach the sp^3-hybridized geometry, the hydrogen on the benzylic carbon will direct toward the fluorene moiety to make the steric interaction energy minimum. We conclude therefore, that in this kind of transition state conformations the steric hindrance is minimum and the transition state energy is by and large the same for the two rotamers to make the relative reaction rates close to unity.

Close examination of the results in Scheme 1 reveals that in nonpolar solvent the reactions in which electron-demanding reagents are used tend to give smaller values of k_{ap}/k_{sp} than unity except for hydroboration. Although we should not overlook solvent effects, it is tempting to consider that the π-participation from the fluorene system is accelerating the reactions of *sp*-**2**.

Borane will not be an adding species as such: it should be accompanied by solvent molecule(s) because of its high Lewis acidity. This steric effect may be the reason why borane gives a k_{ap}/k_{sp} value of more than one. We do not have a good explanation for the results of diimide reduction at present. Probably the solvent effect is important because we used strongly polar and hydrogen-bonding ethanol as a solvent.

Coming back to the situation of addition reactions to the aldehyde (**1**: X=CHO), we now believe that, since the steric situation of it is very close to the olefin (**2**), the k_{sp}/k_{ap} value which is close to unity is normal. Those reactions which give large k_{sp}/k_{ap} values for the aldehyde may involve factors of solvation.

Experimental

^{1}H NMR spectra were recorded on either a Varian EM390 spectrometer which operates at 90 MHz or a JEOL GX270 machine which operates at 270 MHz. Melting points are not corrected.

Infrared Spectra. They were recorded on a Hitachi IR-260-30 spectrophotometer with a thalium(I) chloride cell of 0.1 mm path length. The solutions were prepared by dissolving the sample in carbon tetrachloride to make up 1.04 mol L^{-1} solutions for both isomers. Both isomers exhibited absorptions due to C=C stretching at the identical wavenumber, 1620 cm^{-1}.

Ultraviolet Absorption Spectra. They were recorded on a Hitachi-UV-340 spectrophotometer with a silica cell of 1.0 cm in length. Samples were dissolved in methanol and the concentrations of **2** were ca. 1×10^{-5} mol L^{-1} for the short wavelength region (<300 nm) and ca. 6×10^{-4} mol L^{-1} for the long wavelength region (>300 nm). The spectrum of 2-vinylnaphthalene was recorded for only the long wavelength region with 7.79×10^{-4} mol L^{-1} concentration in methanol because absorptions at the shorter wavelength region have been reported.[23] The following absorption maxima were recorded (wavelength in nm and log ε parentheses given):

sp-**2**:[5] 249 (4.59), 293 (4.09), 303 (4.09), 328 (sh), 346 (1.86).
ap-**2**:[5] 242 (4.65), 267 (sh), 280 (sh), 290 (4.19), 302 (4.17), 320 (sh), 344 (1.69).
2-vinylnaphthalene: 323 (2.69), 331 (2.41), 340 (2.50).

***trans*-8-Methyl-8,14c-dihydrodibenz[*a*,*l*]aceanthrylene (3).** A solution of 1.0 g of *sp*-**2** in 10 mL of 1,2-dimethoxyethane was mixed with a mixture of 30 mL of 1,2-dimethoxyethane and 30 mL of concentrated sulfuric acid and stirred overnight at room temperature. The mixture was poured into water and extracted with ether. The ethereal extract was washed with aqueous sodium hydrogencarbonate and dried over magnesium sulfate. The solvent was evaporated and the residue was chromatographed on silica gel (hexane eluent) to afford the cyclic compund (**3**), mp 173.0—174.0 °C, in 90% yield. The compound was identical with that previously reported.[5]

9-[2-(1,2-Dibromoethyl)-1-naphthyl]fluorene (4). A solution of 1.0 g (3.1 mmol) of the *ap*-olefin in 150 mL of carbon tetrachloride was mixed with 510 mg (3.2 mmol) of bromine in 50 mL of carbon tetrachloride, by adding the latter gradually at 0 °C. The solvent was evaporated after 30 min and the residue was chromatographed through a short column of silica gel. The *sp*-dibromide was obtained in 1.4 g (93%) yield, mp 173.0—174.0 °C. Found: C, 62.64; H, 3.80; Br, 33.83%. Calcd for $C_{25}H_{18}Br_2$: C, 62.77; H, 3.80; Br, 33.43%. ^{1}H NMR ($CDCl_3$) δ=4.1—4.6 (2H, m), 5.81 (1H, s), 6.0—6.3 (1H, m), 6.4—8.0 (14H, m).

Similarly the *sp*-olefin gave *ap*-dibromide, mp 137.5—138.5 °C. Found: C, 62.69; H, 3.67; Br, 33.71%. Calcd for $C_{25}H_{18}Br_2$: C, 62.77; H, 3.80; Br, 33.43%. ^{1}H NMR ($CDCl_3$) δ=3.2—3.5 (2H, m), 4.0—4.3 (1H, m), 6.17 (1H, s), 7.0—8.0

(13H, m), 8.4—8.6 (1H, m).

Reaction of Olefin 2 with Chlorine. A solution of 50 mg (0.16 mmol) of the olefin (**2**) in 50 mL of carbon tetrachloride was mixed with 8.3 mL of ca. 20 mmol L^{-1} solution of chlorine in carbon tetrachloride at 0 °C and the mixture was stirred for 3.5 h at the temperature. From the reaction mixture, the solvent and other volatile materials were evaporated and the residue was chromatographed on silica gel with 5 : 1 hexane-dichloromethane as an eluent.

ap-**2** afforded the dichloride (*sp*-**5**), mp 150—151 °C, and a small amount of an unidentified by-product. Found: C, 77.41; H, 4.76; Cl, 17.92%. Calcd for $C_{20}H_{18}Cl_2$: C, 77.13; H, 4.66; Cl, 18.21%. ^{1}H NMR ($CDCl_3$) δ=4.25—4.42 (2H, m), 5.83 (1H, s), 5.96—6.06 (1H, m), 6.46—8.00 (14H, m).

sp-**2** afforded the dichloride (*ap*-**5**) and the olefin (*sp*-**6**) in 1.0 : 1.4 ratio. *ap*-**5** was identical with the product obtained from the reaction of *sp*-**2** with (dichloroiodo)benzene which is described later but decomposed on standing to give *sp*-**2** and *sp*-**6**. The olefin originally contained ca. 11 : 1 trans and cis olefins as judged by ^{1}H NMR spectra and gave trans-olefin (*sp-trans*-**6**) on recrystallization from ethanol, mp 134.0—135.0 °C. Found: C, 85.25; H, 5.03%. Calcd for $C_{25}H_{17}Cl$: C, 85.10; H, 4.86%. ^{1}H NMR ($CDCl_3$) δ=5.68 (1H, d, *J*=14 Hz), 5.90 (1H, d, *J*=14 Hz), 6.14 (1H, s), 7.11—7.98 (13H, m), 8.53—8.60 (1H, m). The following ^{1}H NMR data ($CDCl_3$, δ) for the *cis*-chloro olefin (*sp-cis*-**6**) were collected: 5.38 (1H, d, *J*=9 Hz), 5.46 (1H, d, *J*=9 Hz), 6.12 (1H, s), 7.11—7.98 (13H, m), 8.53—8.60 (1H, m).

9-[2-(1,2-Epoxyethyl)-1-naphthyl]fluorene (8). To a solution of 150 mg (0.47 mmol) of the *ap*-olefin (**2**) in 30 mL of chloroform, was added 110.0 mg (0.64 mmol) of *m*-chloroperbenzoic acid which had been washed with a buffer solution of pH 7.6 to remove any acidic materials.[24] The mixture was stirred for a week at room temperature and the mixture was directly submitted to chromatography on silica gel with 1 : 1 hexane-dichloromethane eluent to give 95% *sp*-epoxy compound. The compound was purified by recrystallization from benzene-hexane, mp 144.0—145.0 °C. Found: C, 89.55; H, 5.16%. Calcd for $C_{25}H_{18}O$: C, 89.79; H, 5.43%. ^{1}H NMR ($CDCl_3$) δ=2.95—3.32 (2H, m), 4.55—4.60 (1H, m), 5.90 (1H, s), 6.40—8.00 (14H, m).

Similar treatment of the *sp*-olefin with stirring for 22 h afforded 70% *ap*-epoxy compound (*ap*-**8**), mp 134.0—135.0 °C, after recrystallization from benzene-hexane. Found: C, 89.67; H, 5.14%. Calcd for $C_{25}H_{18}O$: C, 89.79; H, 5.43%. ^{1}H NMR ($CDCl_3$) δ=1.83—1.95 (2H, m), 2.64—2.68 (1H, m), 6.17 (1H, s), 7.05—8.05 (13H, m), 8.46—8.55 (1H, m). The yield was not improved after stirring for 7 d: unreacted material was detected.

Hydroboration of 2. A solution of 100 mg (0.31 mmol) of *ap*-**2** in 40 mL of tetrahydrofuran, which was freshly distilled from lithium tetrahydridoaluminate, was mixed with 1.4 mL of 1 mol L^{-1} solution of borane in tetrahydrofuran and the mixture was stirred for 2.5 h under a nitrogen atmosphere. To the reaction mixture diluted with 50 mL of tetrahydrofuran, were added 1.5 mL of 30% hydrogen peroxide and 1.5 mL of 3 mol L^{-1} aqueous sodium hydroxide and the whole was stirred for 1.5 h under a nitrogen atmosphere. The mixture was poured into water and extracted with ether. The ether layer was dried over magnesium sulfate and the solvent was evaporated. Chromatography of the residue on silica gel under medium pressure, with 1 : 4 hexane-ether eluent, afforded 1.0 : 2.5 *sp*-1-ol (**11**) and *ap*-2-ol(**10**). The former was identical with that reported[2,5] and the latter was recrystallized from dichloromethane-pentane, mp 110.0—111.5 °C. High resolution MS: *m/z* 336.1553. Calcd for $C_{25}H_{20}O$: M, 336.1515. ^{1}H NMR ($CDCl_3$) δ=3.44 (2H, t, *J*=9 Hz), 4.13 (2H, t, *J*=9 Hz), 5.77 (1H, s), 6.40—7.98 (14H, m). The OH proton was not detected.

Similarly the *sp*-olefin gave 42% *sp*-2-ol (**10**) and 18% *ap*-1-ol (**11**), which was identical with authentic specimen.[2,5]

sp-2-Ol (**10**), mp 115.5—117.5 °C. Found: C, 89.16; H, 6.23%. Calcd for $C_{25}H_{20}O$: C, 89.25; H, 5.99%. ^{1}H NMR ($CDCl_3$) δ=1.91 (2H, t, *J*=7 Hz), 3.00 (2H, t, *J*=7 Hz), 6.15 (1H, s), 7.0—8.0 (13H, m), 8.4—8.6 (1H, m). The OH proton was not detected.

9-(2-Ethyl-1-naphthyl)fluorene (9). a) Catalytic Hydrogenation of 2. A solution of 60 mg of the *sp*-olefin in 80 mL of ethanol was added to 10 mg of 5% palladium on carbon, which was activated by shaking with hydrogen and 20 mL of ethanol, and the whole was stirred under a hydrogen atmosphere. The hydrogen absorption was completed after 20 h. The product was recrystallized from ethanol, mp 118.8—119.5 °C. The yield was 99%. Found: C, 93.46; H, 6.11%. Calcd for $C_{25}H_{20}$: C, 93.71; H, 6.29%. ^{1}H NMR ($CDCl_3$) δ=0.48 (3H, t, *J*=7 Hz), 1.65 (2H, q, *J*=7 Hz), 6.15 (1H, s), 7.12—7.97 (13H, m), 8.52 (1H, m).

Similarly *ap*-**9**, mp 107.5—108.0 °C, was obtained in 99% yield. Found: C, 93.41; H, 6.19%. Calcd for $C_{25}H_{20}$: C, 93.71; H, 6.29%. ^{1}H NMR ($CDCl_3$) δ=1.40 (3H, t, *J*=8 Hz), 3.10 (2H, q, *J*=8 Hz), 5.69 (1H, s), 6.35—7.92 (14H, m).

b) Diimide Reduction of 2. A solution of 100 mg (0.31 mmol) of *sp*-**2** in 100 mL of ethanol was mixed with 0.5 mL (8.6 mmol) of hydrazine hydrate and 1 drop of 1% aqueous copper(II) sulfate. To the mixture was slowly added 2.0 mL (17 mmol) of 30% aqueous hydrogen peroxide with ice-cooling. After 30 min, the mixture was poured into water and extracted with ether. The ethereal extract was dried over magnesium sulfate and the solvent was evaporated to give 95% *sp*-**9** which was identical with the compound obtained above.

Similarly *ap*-**2** afforded *ap*-**9**, identical with the compound described above, in almost quantitative yield.

Reaction of (Dichloroiodo)benzene with 2. To a solution of 40 mg (0.12 mmol) of *ap*-**2** in 35 mL of dichloromethane was added 35 mg (0.12 mmol) of (dichloroiodo)benzene[25] and the mixture was stirred for 23 h at room temperature. The solvent and the volatile materials were removed by distillation in vacuo and the residue was recrystallized from hexane to give *sp*-**5** in almost quantitative yield.

Similarly, the reaction of *sp*-**2** with (dichloroiodo)benzene afforded *ap*-**5**, mp 90—95 °C (decomp). This compound decomposed on attempted recrystallization from pentane to yield *sp*-**2** and *sp*-**6**, though it was stable at 0 °C. It also decomposed slowly at room temperature even in the solid state on standing. The yield was ca. 80%. High resolution MS: *m/z* 388.0742 and 390.0701. Calcd for $C_{25}H_{16}{}^{35}Cl_2$ and $C_{25}H_{16}{}^{35}Cl^{37}Cl$: M, 388.0784 and 390.0754. ^{1}H NMR ($CDCl_3$) δ=3.05—3.40 (2H, m), 4.04—4.12 (1H, m), 6.22 (1H, s), 7.08—8.02 (13H, m), 8.52—8.64 (1H, m).

Reaction of 2 with Osmium Tetraoxide. To a solution of 70 mg (0.22 mmol) of **2** in 50 mL of ether, was added a solution of ca. 60 mg (0.24 mmol) of osmium tetraoxide in 4.0 mL of ether under an argon atmosphere and the whole was stirred for 24 h at room temperature. To the solution was added 2.5 g of sodium hydrogensulfite, 10 mL of water and 10 mL of ethanol and the mixture was heated at 60 °C with stirring for 24 h. The mixture was poured into water and the ether layer was separated. The aqueous layer was extracted with ether and the combined extracts were dried over magnesium sulfate. The solvent was evaporated to give the diol (**12**) in ca. 70% yields. The following ^{1}H NMR data were collected ($CDCl_3$, δ). *sp*-**12**: 3.91—4.15 (2H, m), 5.63—5.72 (1H, m), 5.79 (1H, s), 6.40—8.02 (14H, m). The OH protons were not detected. *ap*-**12**: 2.60—3.24 (2H, m), 3.70—3.80 (1H, m), 6.20 (1H, s), 7.13—8.01 (13H, m), 8.52—8.59 (1H, m).

These diols were characterized by converting them to acetonides through treatment of the diols with acetone and *p*-toluenesulfonic acid.

***sp*-Diol Acetonide:** Mp 151.5—152.0 °C, after recrystallization from hexane. High resolution MS: m/z 392.1741. Calcd for $C_{28}H_{24}O_2$: M, 392.1775. ^{1}H NMR ($CDCl_3$) δ=1.54 (3H, s), 1.67 (3H, s), 3.96—4.58 (2H, m), 5.64 (1H, s), 5.90—5.96 (1H, m), 6.41—7.95 (14H, m).

***ap*-Diol Acetonide:** oil. High resolution MS: m/z 392.1739. Calcd for $C_{28}H_{24}O_2$: M, 392.1775. ^{1}H NMR ($CDCl_3$) δ=0.80 (3H, s), 1.37 (3H, s), 2.56—3.07 (2H, m), 4.07—4.12 (1H, m), 6.18 (1H, s), 7.04—7.97 (13H, m), 8.53—8.56 (1H, m).

Competitive Addition Reactions. Two rotational isomers (10 mg each or 0.03 mmol) of **2** were dissolved in an appropriate solvent with a small amount of fluorene which served as a reference. The appropriate reagent (0.03 mmol or less) in an appropriate solvent was added to the solution and the decrease in the amount of each rotamer was recorded with the use of either integration of ^{1}H NMR signals or calibration curves for the amounts of the olefins drawn by using the UV absorption at 254 nm which was used for the detection in HPLC. The reaction conditions were similar to those described above for the individual rotamers except for the addition of bromine and chlorine, when a dilute solution (ca. 0.1 mmol L^{-1}) of the halogen in carbon tetrachloride was added to the solution of **2**. The results given in Scheme 1 are averages of 2—3 runs which were terminated before 50% completion of the reactions.

Determination of Barriers to Rotation in 9-(2-Vinyl-1-naphthyl)fluorene (2). A solution of 40 mg of the *ap* isomer in 0.5 mL of toluene-d_8 was sealed in an NMR tube. The tube was immersed in a boiling benzene bath. The rotation was quenched by cooling rapidly with an ice-water bath at a given time and the isomer ratio was determined by ^{1}H NMR spectroscopy. The equilibrium constant was obtained by heating the sample tube as above for 48 h. The isomer ratio did not change after heating for further 12 h. The data were treated by assuming a first order reversible reaction.

The *sp*-isomer was treated similarly. It gave the same equilibrium constant that was obtained form the *ap* isomer.

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