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Reactions of *ap*- and *sp*-1-(9-Fluorenyl)-2-(1-methylethenyl)naphthalene Rotamers with Bromine Chloride or Iodine Chloride and Unusual Populations of the Corresponding 1-(9-Fluorenyl)-2-[(*E*)-2-halo-1-methylethenyl]naphthalene Rotamers [#,1]

Michinori Ōki,* Takanori Hirose, Kiyoka Maeda, Maki Yanagawa, Yasukazu Kataoka,

Hiroharu Kojima, Nobuhiro Morita, and Shinji Toyota

Department of Chemistry, Faculty of Science, Okayama University of Science, Ridaicho, Okayama 700

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Reactions of bromine chloride and iodine chloride with the olefinic bond in 1-(9-fluorenyl)-2-(1-methylethenyl)-naphthalene rotamers were carried out to examine the product distributions. In the case of the *ap*-isomer bromine chloride yielded some bromo-olefins in addition to the addition product, whereas the yield of (8*R**,14c*S**)-8-bromomethyl-8-methyl-8,14c-dihydrodibenzo[*a.l*]aceanthrylene from the *sp*-isomer diminished with respect to the case of the reaction between bromine and the *sp*-isomer. The results are attributed to the low nucleophilicity and high proton affinity of the chloride ion. Iodine chloride afforded more addition product for the *ap*-isomer than the case of bromine chloride, whereas the *sp*-isomer reacted with iodine chloride to give a better yield of a cyclized compound, (8*R**,14c*S**)-8-iodomethyl-8-methyl-8,14c-dihydrodibenzo[*a,l*]aceanthrylene, than that of the cyclized compound from bromine chloride. Such results are attributed to the better stabilizing effects of an iodo substituent on a β-carbocation than a bromo one. Populations of *ap* and *sp* rotamers of 1-(9-fluorenyl)-2-[(*E*)-2-halo-1-methylethenyl]naphthalenes at equilibrium were unusual in the sense that the *ap*-isomer of the sterically more crowded iodo compound was favored relative to the less crowded chloro compound. UV absorption spectra were not conclusive for charge transfer interactions but X-ray crystallography of these compounds revealed that the olefinic carbons in the ethenyl group were attracted to the fluorene ring significantly.

Reactions of the olefinic bond in 1-(9-fluorenyl)-2-(1-methylethenyl)naphthalene rotamers (*ap*-**1** and *sp*-**1**) revealed some interesting phenomena from one rotamer to another and from one reagent to others. A change in the anionic part X in BrX changed the ratios of substituted olefins to addition products when the rotamer is *ap* and changed the ratios of substituted olefins to the cyclized compound in the case of *sp*.[2,3] Poor yields of the addition product of chlorine reflected the low stabilizing ability of the chloro substituent for the β-chloro carbocation.[4] Less nucleophilicity of the chloride ion than of the bromide ion in addition reactions and stronger proton affinity of the chloride ion than of the bromide ion in deprotonation are reflected to the product ratios. Proton affinity of the anionic species produced from BrX played an important role in determining the product ratios as well.[3]

Solvent effects on the product ratios were also important in reactions of halogens with compound **1**.[4] It will be more informative if we can fix the solvent of a reaction as well as the halogen which acts as a positive species or the halogen which acts as a negative species in reactions of XY with the olefinic bond of the title compound. Although we carried out the reaction of bromine with the compound, in which both positive and negative species are bromine, we cannot expect a wide variety of reagents if we fix the anion as bromide. In contrast, if we fix the anion as chloride, it will be possible to use a variety of halogen compounds, including chlorine of which results have been reported.[4]

This paper is to report results of reactions of BrCl and ICl to compare them with those of the Cl_2 case, and to discuss the effects of the positive species on the product distributions. It will be seen that the positive species in these reactions exhibit strong effects on the product distributions. We confine ourselves to a limited number of solvents, carbon tetrachloride and nitromethane, to facilitate discussion of the results.

Results

Reaction of bromine chloride with *ap*-**1** in carbon tetrachloride afforded *sp*-2-[1-(bromomethyl)ethenyl]-1-(9-fluorenyl)naphthalene (*sp*-**2**: X = Br), *sp*-2-[(*E*)-2-bromo-1-methylethenyl]-1-(9-fluorenyl)naphthalene (*sp*-**3**: X = Br), and *sp*-2-(2-bromo-1-chloro-1-methylethyl)-1-(9-fluorenyl)-naphthalene (*sp*-**4**: X = Br) in 38, 3, and 44% yields, respectively (Scheme 1 and Table 1). We immediately notice that the addition product *sp*-**4** (X = Br) increased with respect to the reaction with chlorine but the formation of olefins (*sp*-**2** and *sp*-**3**: X = Br), which were not detected in the bromine addition reaction, is significant.[2] The formation of the olefins

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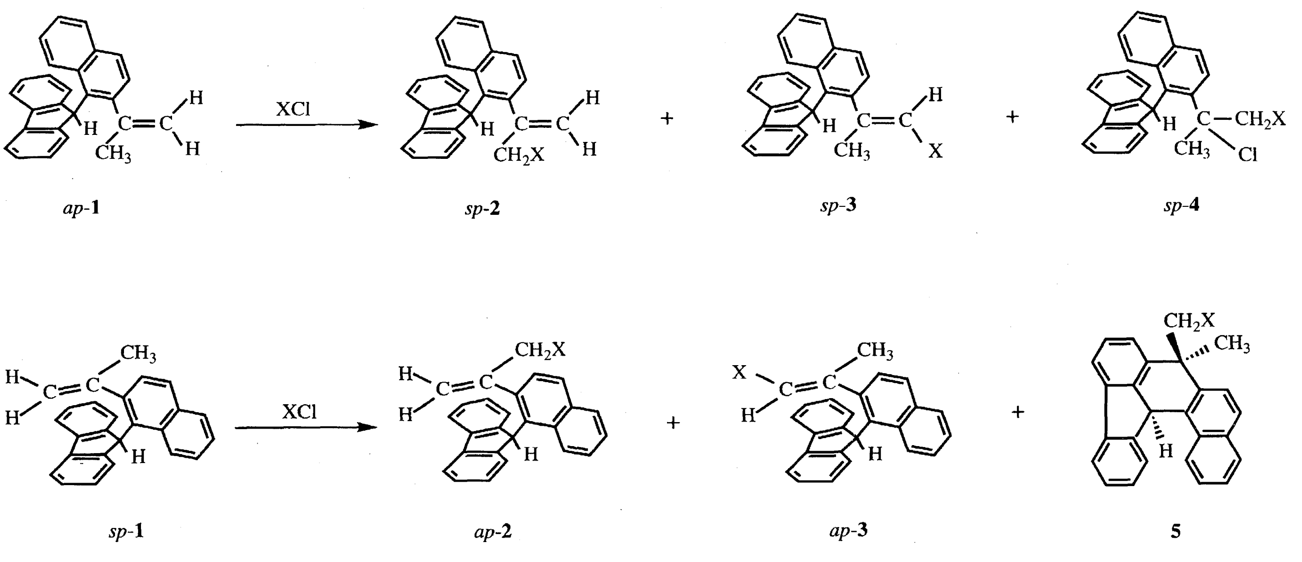
[#] This paper is dedicated to Professor Waldemar Adam on his 60th birthday.



Scheme 1.

Table 1. Product Distributions from the Reactions of *ap*-**1** and Halogen Chlorides (% Normalized to 100%) and Solvent Effects on the Distribution

X of XCl	Solvent	*sp*-**2**	*sp*-**3**	*sp*-**4**
Cl	CCl_4	84	8	8
	CH_3NO_2	37	42	21
Br	CCl_4	45	3	52
	CH_3NO_2	7	5	88
I[a]	CCl_4	18	2	80
	CH_3NO_2	11	0	89

a) In addition, 10% and 2% *sp*-**2** (X = Cl) were detected in the product mixture in CCl_4 and CH_3NO_2, respectively.

Table 2. Product Distributions from the Reactions of *sp*-**1** and Halogen Chlorides (% Normalized to 100%) and Solvent Effects on the Distribution

X of XCl	Solvent	*ap*-**2**	*ap*-**3**	**5**
Cl	CCl_4	94	6	—
	CH_3NO_2	25	18	57
Br	CCl_4	63	28	9
	CH_3NO_2	5	9	86
I[a]	CCl_4	—	41	59
	CH_3NO_2	—	14	86

a) In addition, 32 and 5% *ap*-**2** (X = Cl) were detected in the product mixture in CCl_4 and CH_3NO_2, respectively.

must be the reflection of strong proton affinity of the chloride ion relative to the bromide ion.

Reaction of bromine chloride with *sp*-**1** in carbon tetrachloride afforded *ap*-2-[1-(bromomethyl)ethenyl]-1-(9-fluorenyl)naphthalene (*ap*-**2**: X = Br), *ap*-2-[(*E*)-2-bromo-1-methylethenyl]-1-(9-fluorenyl)naphthalene (*ap*-**3**: X = Br), and (8*R**,14c*S**)-8-bromomethyl-8-methyl-8,14c-dihydrodibenzo[*a*,*l*]aceanthrylene (**5**: X = Br) in 53, 24, and 8% yields, respectively (Scheme 1 and Table 2). The features of the product distribution are that the yield of the cyclic compound **5** (X = Br) decreased and the yields of the bromo-olefins (*ap*-**2** and *ap*-**3**: X = Br) increased with respect to the cases of the bromine reaction. Again, high proton affinity of the chloride ion, with respect to the bromide ion, must be responsible for the increased yields of olefins and the decreased amount of the cyclized product **5**.

While bromine chloride is known to be in equilibrium with a mixture of bromine and chlorine to a small extent[5] and the addition of chlorine[6] to the olefinic bond is known to be much faster than bromine in general, although the mechanisms are different,[7—9] chlorine addition products were not detected in reactions of bromine chlorine with normal olefins.[10] Our case was no exception. This must be attributed to the minute amount of chlorine in the equilibrium.

Reaction of iodine chloride with *ap*-**1** in carbon tetrachloride proceeded smoothly to afford *sp*-1-(9-fluorenyl)-2-[1-(iodomethyl)ethenyl]naphthalene (*sp*-**2**: X = I), *sp*-1-(9-fluorenyl)-2-[(*E*)-2-iodo-1-methylethenyl]naphthalene (*sp*-**3**: X = I), *sp*-2-(1-chloro-2-iodo-1-methylethyl)-1-(9-fluorenyl)naphthalene (*sp*-**4**: X = I), and *sp*-2-[1-(chloromethyl)ethenyl]-1-(9-fluorenyl)naphthalene (*sp*-**2**: X = Cl) in 15, 2, 66, and 10% yields respectively (Table 1).

Here a product containing chlorine (*sp*-**2**: X = Cl) was detected. However, we believe *sp*-**2** (X = Cl) is not the primary reaction product of *ap*-**1** with chlorine but is a secondary product: Iodine chloride is known to react with organic iodides to give the corresponding chlorides[11] and the equilibrium between iodine chloride and iodine-chlorine is barely detectable only in dilute solutions.[12] Indeed, when an excess of iodine chloride was used, the yields of the chloro compounds increased substantially. The rates of addition of iodine to a double bond are much smaller[13,14] than those of chlorine, although the mechanisms are shown to be different from each other. Therefore, if the reaction of chlorine, which is produced by the equilibrium, were important, chloro-olefins (*sp*-**2** and *sp*-**3**: X = Cl) would have increased in their amounts considerably when an excess of iodine chloride was used.

The feature of the product distribution is that an addition product *sp*-**4** (X = I) was increased significantly in its amount from the bromine chloride case at the expense of *sp*-**2** (X = I). The formation of *sp*-**3** (X=I) was little affected by the cationic part, if one compares the result with those of the bromine chloride addition.

Reaction of iodine chloride with *sp*-**1** was rather slow and afforded 23% *ap*-1-(9-fluorenyl)-2-[(*E*)-2-iodo-1-methylethenyl]naphthalene *ap*-**3** (X = I) and 33% cyclized compound, (8*R**,14c*S**)-8-iodomethyl-8-methyl-8,14c-dihydrodibenzo-[*a,l*]aceanthrylene (**5**: X = I) (Table 2). No *ap*-1-(9-fluorenyl)-2-[1-(iodomethyl)ethenyl]naphthalene (*ap*-**2**: X = I) was detected, but *ap*-2-[1-(chloromethyl)ethenyl]-1-(9-fluorenyl)naphthalene (*ap*-**2**: X = Cl) was obtained in ca. 32% yield.

The features of the product distribution are that the yield of **5** (X = I) increased significantly form the case of bromine chloride reaction, whereas the formation of *ap*-**2** (X = I) was not detected. The last result makes a striking contrast to the case of bromine, bromine chloride, and chlorine reactions, where this type of compounds *ap*-**2** (X = Br or Cl) is main in the olefinic products. This is probably because the allylic iodide type compound (*ap*-**2**: X = I) was easily transformed to the corresponding chloride under the conditions.

The stereochemistry of compounds *ap*-**3** and *sp*-**3** was assigned by analogy with other compounds. The negative NOE on the vinyl proton signal in its ^{1}H NMR spectrum, when the methyl-proton signal was irradiated, supports the conclusion. The X-ray structure of *ap*-**3**, as discussed later, also supports this assignment. The structure of the cyclized compound **5** (X = I) was confirmed by NOE experiments.

When the solvent is switched from carbon tetrachloride to nitromethane, increases in the yields of the addition products (**4**) in the case of the reaction of *ap*-**1** and those of the cyclized compound (**5**) in the case of *sp*-**1** are noticed (Tables 1 and 2). The results are in line with those obtained for the chlorine cases[4] but the increases are not so pronounced as were the cases in the chlorine reaction. In nitromethane, increases in the yields of compound **3** are commonly observed, except for one case, at the expense of **2**, the phenomena being also observed in chlorine and bromine reactions.[4]

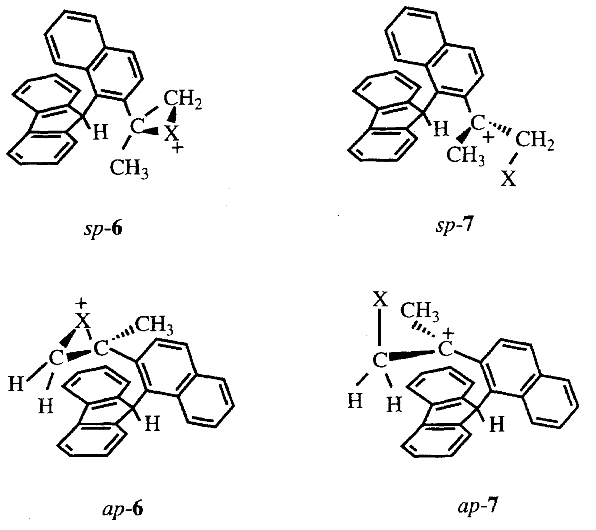
The results are summarized in Tables 1 and 2, compiling the results for bromine chloride and iodine chloride, as well as results of the chlorine case which were published earlier.[4]

Discussion

Reactions in Carbon Tetrachloride. The electrophilic addition reactions of halogens are believed to proceed via a three-membered ring, halonium ion,[15,16] which is formed by addition of a cationic species to the double bond of an olefinic compound. The stability of the three-membered rings is dependent on the size of the atom,[17,18] which is the cationic center of the electrophile, as well as on the ionization potential and the electronegativity of the atom. Polarizability of the central atom may also be important. Thus chloronium ion is believed to be the least stable among the halonium ions[19,20] except fluoronium ion, if it really exists in solution.[21—25] It is more meaningful to discuss the results obtained for halogen chlorides because comparison of the data among halogens can avoid certain complexities (Tables 1 and 2).

We have invoked an idea that the closed halonium ion produces adducts whereas open-cations produce halo-olefins.[4] Of course, because pure S_N2 type reactions of these halonium ions should give different regioselectivity from what is commonly observed, the halonium ring must open or nearly open to form the products in the former case. We will use the term, halonium ion, with this implication. It also deserves mention that there should be a rapid equilibrium between the halonium ion and the open β-halo carbocation. Let us see whether this model can account for the results obtained with bromine chloride and iodine chloride.

Effect of X of XCl in Reactions of *ap*-1. In the addition reactions of chlorine to *ap*-**1**, we must take into account the weak participation in the stabilization of the carbocation by a β-chloro substituent, which is made by electrophilic addition of a chlorine cation to a π-bond, as well as weak nucleophilicity and strong proton affinity of the chloride ion. These characteristics of the chloride ion will lead to preferred formation of olefins rather than the addition product in the case of *ap*-**1**. Another point we should take into account when we discuss the reaction mechanisms is that the bridged carbocation (*sp*-**6**), if it is to be formed to any extent, must be formed at a site where the steric hindrance is very severe. Thus the intermediate should be very close to an open-chain β-chloro carbocation (*sp*-**7**) rather than to a symmetrically bridged form (*sp*-**6**) (Scheme 2). In the open-chain cation, when it is formed from the halonium ion, the least sterically hindered proton is one of those in the methyl group, because the halogen should be closely located to the cationic center even in the open form, relatively speaking. If the cation reacts with the chloride ion before internal rotation takes place, then the most vulnerable protons to the attack of the anion must be those of the methyl group. The reaction of chlorine with *ap*-**1** thus gives the lowest yield of the addition product *sp*-**4** (X = Cl) and the best yield of the chloromethyl



Scheme 2.

compound *sp*-**2** (X = Cl) along with the chloro-olefin *sp*-**3** (X = Cl).

When the addend is bromine chloride, the attacking electrophile is a bromine cation which forms a *β*-bromo carbocation. The latter cation is usually more stable than the corresponding chloro counterpart and the lifetime can be very long in special cases.[26—28] Therefore, although the steric situation is not favorable for forming this bridged cation in the case from *ap*-**1**, at least an unsymmetrical bromonium ion *sp*-**6** will be formed. Then the cation can survive until it is attacked by a chloride ion to form *sp*-**4** (X = Br). However, because of the poor nucleophilicity of the chloride ion, the yield of the adduct *sp*-**4** (X = Br) is lower than the case of the bromine addition when the attacking anion to *sp*-**6** is bromide ion. We believe a portion of the intermediate exists as an open cation *sp*-**7** and this is attacked by the chloride ion to lose the proton. Because the cation is open, even though a bromo group is rather close to the cation center, it can undergo internal motion to make the bromomethyl proton open to the attack of the chloride ion. This is the reason for the increased yield of *sp*-**3** (X = Br) relative to the case of the reaction with chlorine. The bromonium ion has some open isomers but its reaction with bromide ion to lose a proton is rather slow, so we did not notice the bromo-olefins in the reaction of bromine with *ap*-**1**.

The feature of the results in the iodine chloride reaction with *ap*-**1** is the increase in the yield of *sp*-**4** (X=I). This must again be attributed to the stabilization of the bridged cation *sp*-**6** due to the facts that the iodine atom has a large atomic radius and its ionization potential is the lowest among the halogens examined here. The three-membered ring cation *sp*-**6** is so effectively stabilized that it can survive until the poor nucleophile, chloride ion, attacks the carbocationic center. It is also true that partial neutralization of the charge on the *β*-carbon atom by an iodo substituent retards the deprotonation reaction.

Effect of X of XCl in Reactions of *sp*-1. In the case of the reaction of chlorine with *sp*-**1**, chlorine cation adds to the olefinic bond but the cationic carbon is very reluctant to take an sp^3-hybridized structure *ap*-**6** because of the steric effect. This is demonstrated by the very sparce population of *ap*-9-(2-*t*-butylphenyl)fluorene relative to the *sp*-counterpart.[29] Thus the intermediate cation should exist as an open-chain cation *ap*-**7** rather than the bridged *ap*-**6**. The open-chain cation has another advantage by being stabilized by π-participation of the fluorene ring. This open-chain carbocation should lose a proton very easily from the methyl group because the chloromethyl protons are sterically protected at the initial stage when it is formed, whereas the cyclization to form **5** (X = Cl) should be slow compared to the deprotonation because the distance between the olefinic π-system and the fluorene π-system is ca. 3Å[2] and the steric congestion together with geometric requirement to form the ring retards such a reaction. Thus the main product in the reaction of *sp*-**1** with chlorine is *ap*-**2** (X = Cl).

In the case of the bromine chloride reaction with *sp*-**1**, a similar open-chain cation *ap*-**7** (X = Br) will be formed. Nucleophilic attack by the chloride ion on the carbocation is very slow due to steric reasons. Thus most of the cations lose their protons to form the bromo-olefins (*ap*-**2** and *ap*-**3**: X = Br). Evidently the yield of the bromomethyl compound *ap*-**2** decreased, whereas that of *ap*-**3** increased. Although the cyclized product **5** (X = Br) is a minor product because of the strong proton affinity of the chloride ion, its existence is clearly noted. All of these results indicate that bromine is better at stabilizing the cation *ap*-**7** than the chlorine case (see below).

The same reasoning will apply to the better yield of the cyclized compound **5** (X=I) in the reaction of iodine chloride with *sp*-**1**. Although the intervening carbocation is reluctant to take an sp^3-hybridized structure (*ap*-**6**), thanks to the large atomic radius of the iodine atom, it can still participate in stabilizing the cation *ap*-**7**.[30] The participation neutralizes the charge on the *β*-carbon in *sp*-**7** to make the protons less vulnerable to the attack of the chloride ion and to allow the *β*-cation to have a long enough lifetime to approach the benzene ring to form **5** (X = I).

We may add the yields of the chloro compounds (*ap*- and *sp*-**2**) to those of **2** (X = I) because the former compounds

Table 3. Population Ratios of the Rotamers of **3** in Toluene-d_8

X	H[a,b]	Cl	Br[a]	I
Population (*sp*/*ap*)	15.6	2.43	2.33	1.81

a) Taken from the published data.[2] b) Here the population ratio is *ap*/*sp* due to reversal of designation by the CIP rule.

Table 4. UV Absorption Maxima of *ap*- and *sp*-1-(9-Fluorenyl)-2-[(*E*)-2-halo-1-metylethenyl]naphthalenes and Their Parent Compounds

Substituent	Compound	Absorptions (nm) with log ε in parentheses						
H	*ap*-**1**	299.5 (4.10)	289.0 (4.20)	265.5 (4.46)		224.0 (5.00)		206.5 (5.00)
	sp-**1**	302.0 (4.04)		269.0 (4.33)		227.0 (4.89)	219.5 (4.88)	200.0 (4.95)
Cl	*sp*-**3**	299.5 (4.24)	288.5 (4.34)	265.5 (4.60)		225.0 (5.09)		209.5 (5.10)
	ap-**3**	300.5 (4.07)			251.0 (4.47)		221.5 (4.93)	201.0 (4.98)
Br	*sp*-**3**	299.5 (4.02)	289.0 (4.12)	265.5 (4.39)	255.5 (4.37)	223.5 (4.93)		
	ap-**3**	301.0 (4.06)			253.0 (4.47)	224.0 (4.91)		199.0 (4.95)
I	*sp*-**3**	299.5 (4.20)	288.5 (4.30)	262.0 (4.56)	255.5 (4.56)	229.0 (5.05)		205.5 (5.05)
	ap-**3**	301.0 (4.24)			255.0 (4.62)	227.0 (5.05)		202.0 (5.08)

Table 5. Atomic Coordinates and Equivalent Isotropic Thermal Parameters of Non-Hydrogen Atoms in 2-[(*E*)-2-Chloro-1-methylethenyl)-1-(9-fluorenyl)naphthalene (*ap*-**3**: X = Cl)[a]

Atom	*x*	*y*	*z*	B_{eq}[b]
Cl(1)	0.5166(2)	0.1831(3)	0.6761(1)	6.91(1)
C(1)	0.3383(6)	−0.3321(9)	0.6054(4)	5.1(2)
C(2)	0.4206(7)	−0.372(1)	0.5751(5)	7.2(3)
C(3)	0.4468(6)	−0.276(1)	0.5244(5)	7.3(3)
C(4)	0.3921(6)	−0.138(1)	0.5030(4)	6.7(2)
C(4a)	0.3123(6)	−0.0938(9)	0.5335(4)	5.1(2)
C(4b)	0.2447(6)	0.0464(9)	0.5242(4)	4.9(2)
C(5)	0.2384(7)	0.174(1)	0.4783(4)	6.9(2)
C(6)	0.1643(8)	0.292(1)	0.4802(5)	8.0(3)
C(7)	0.0982(8)	0.282(1)	0.5256(5)	7.4(2)
C(8)	0.1036(6)	0.1538(9)	0.5710(4)	5.8(2)
C(8a)	0.1773(6)	0.0367(8)	0.5704(4)	4.5(2)
C(9)	0.1947(5)	−0.1189(8)	0.6100(3)	3.9(1)
C(9a)	0.2837(5)	−0.1919(8)	0.5843(4)	4.4(2)
C(1′)	0.2138(5)	−0.1210(8)	0.6956(3)	3.7(1)
C(2′)	0.2758(5)	−0.0110(7)	0.7449(4)	3.8(1)
C(3′)	0.2818(6)	−0.0120(9)	0.8228(4)	4.9(2)
C(4′)	0.2332(6)	−0.1255(9)	0.8507(4)	5.0(2)
C(4a′)	0.1750(5)	−0.2463(9)	0.8043(4)	4.5(2)
C(5′)	0.1273(6)	−0.369(1)	0.8342(4)	5.7(2)
C(6′)	0.0706(4)	−0.482(1)	0.7889(5)	6.5(2)
C(7′)	0.0614(7)	−0.486(1)	0.7122(5)	6.5(2)
C(8′)	0.1054(6)	−0.3690(9)	0.6814(4)	5.0(2)
C(8a′)	0.1652(5)	−0.2443(8)	0.7258(4)	3.8(1)
C(1″)	0.3430(5)	0.1094(8)	0.7211(4)	4.4(2)
C(2″)	0.4259(5)	0.0624(8)	0.7019(4)	4.4(2)
C(3″)	0.3165(7)	0.275(1)	0.7310(6)	7.3(3)

a) Values in parentheses are estimated standard deviations.
b) $B_{\mathrm{eq}}/\text{Å}^2 = (8\pi^2/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \boldsymbol{a}_i \cdot \boldsymbol{a}_j$.

Table 6. Atomic Coordinates and Equivalent Isotropic Thermal Parameters of Non-Hydrogen Atoms in 2-[(*E*)-2-Bromo-1-methylethenyl]-1-(9-fluorenyl)naphthalene (*ap*-**3**: X = Br)[a]

Atom	*x*	*y*	*z*	B_{eq}[b]
Br(1)	0.97813(4)	0.18594(6)	0.82677(3)	5.69(1)
C(1)	1.1672(4)	−0.3316(5)	0.8957(3)	4.9(1)
C(2)	1.0854(4)	−0.3700(7)	0.9257(3)	6.0(1)
C(3)	1.0586(4)	−0.2707(7)	0.9752(3)	6.3(1)
C(4)	1.1125(4)	−0.1308(6)	0.9957(3)	5.5(1)
C(4a)	1.1940(3)	−0.0891(5)	0.9659(2)	4.25(9)
C(4b)	1.2613(3)	0.0516(4)	0.9753(2)	4.26(9)
C(5)	1.2687(4)	0.1845(6)	1.0197(3)	5.7(1)
C(6)	1.3411(5)	0.3005(6)	1.0168(3)	6.9(1)
C(7)	1.4059(5)	0.2889(6)	0.9723(3)	6.3(1)
C(8)	1.4001(4)	0.1550(5)	0.9279(2)	5.3(1)
C(8a)	1.3271(3)	0.0396(4)	0.9294(2)	3.96(8)
C(9)	1.3097(3)	−0.1179(4)	0.8902(2)	3.79(9)
C(9a)	1.2200(3)	−0.1904(4)	0.9158(2)	3.96(8)
C(1′)	1.2891(3)	−0.1224(4)	0.8047(2)	3.43(8)
C(2′)	1.2269(3)	−0.0107(4)	0.7559(2)	3.66(8)
C(3′)	1.2196(3)	−0.0112(5)	0.6783(2)	4.50(10)
C(4′)	1.2670(3)	−0.1253(5)	0.6499(2)	4.6(1)
C(4a′)	1.3257(3)	−0.2477(5)	0.6965(2)	3.98(9)
C(5′)	1.3712(4)	−0.3701(6)	0.6666(3)	5.3(1)
C(6′)	1.4268(4)	−0.4880(6)	0.7112(3)	6.0(1)
C(7′)	1.4406(4)	−0.4892(6)	0.7886(3)	5.7(1)
C(8′)	1.3972(3)	−0.3718(5)	0.8193(3)	4.5(1)
C(8a′)	1.3384(3)	−0.2456(4)	0.7754(2)	3.65(8)
C(1″)	1.1597(3)	0.1101(4)	0.7784(2)	4.01(9)
C(2″)	1.0769(3)	0.0578(5)	0.7986(2)	4.02(9)
C(3″)	1.1839(6)	0.2783(6)	0.7705(5)	6.7(2)

a) Values in parentheses are estimated standard deviations.
b) $B_{\mathrm{eq}}/\text{Å}^2 = (8\pi^2/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \boldsymbol{a}_i \cdot \boldsymbol{a}_j$.

are most likely be formed from **2** (X = I) by electrophilic coordination of the iodine in iodine chloride, followed by S_N2 type reactions of the chloride ion or its complex.[31] Then it is apparent that the formation of the olefins was more favored in the nonpolar CCl_4 solvent than the polar CH_3NO_2 solvent from *ap*-**1**. For *sp*-**1**, the same tendency is observed, in addition to the favored formation of *ap*-**3** (X = I) over *ap*-**2**.

We note that the ratios of *ap*-**2** to *ap*-**3** change to a significant extent as the halogens change. This is reasonable because, as the halogen becomes large, the lifetime of the intervening cation *ap*-**7** is lengthened by participation of the β-halo substituent[23] and the cation undergoes internal rotation, by which the proton on the halomethyl group becomes exposed to the attack of the chloride ion.

Solvent Effects on Product Distributions. Outstanding solvent effects on the product distribution in the reactions of bromine and chlorine with *ap*- and *sp*-**1** were observed.[4] It is interesting to examine also the solvent effects on the reactions of the bromine chloride and iodine chloride.

Apparently, nitromethane enhances formation of the addition product *sp*-**4** from *ap*-**1** and the cyclized compound **5** from *sp*-**1**. This has been attributed to the stabilizing effects of the polar solvent on the open-chain cation.[4] By solvating the cationic center of the carbocation, solvent molecules retard the deprotonation reactions so that the nucleophilic reactions at the carbocation are encouraged. Close examination of the product distributions reveal, however, that the solvent effects are drastic in the case of the reaction of chlorine but tend to saturate as we descend the periodic table.

Another feature observed in the case of chlorine was the increase in the yield of *sp*- or *ap*-**3** in nitromethane. However, this effect tends to saturate also in the cases of bromine chloride and iodine chloride. This result may be in part due to the fact that the olefin formation is not major any more in these reactions and is partly attributed to the stabilizing effects already present by the large halogens. At any rate, the polar solvent increases the lifetime of the open cation, *ap*-**7** or *sp*-**7**. The longer lifetime of **7** increases the chance for the cation to be attacked by halide anions or by the π-system.

Unusual Rotamer Populations of Compound 3. Because *sp*-**3** was obtained in a very poor yield, we prepared it by allowing internal rotation of *ap*-**3**. It was during this process that we found that halogenated olefins **3** showed unusual populations. Because halogens are larger than hydrogen and the (*E*)-2-haloethenyl group is supposed to be located upon

Table 7. Atomic Coordinates and Equivalent Isotropic Thermal Parameters of Non-Hydrogen Atoms in 1-(9-Fluorenyl)-2-[(*E*)-2-iodo-1-methylethenyl]naphthalene (*ap*-**3**: X = I)[a]

Atom	x	y	z	B_{eq}[b]
I(1)	−0.14280(3)	−0.18834(4)	−0.66904(2)	4.85(1)
C(1)	−0.2821(5)	0.3257(7)	−0.6051(3)	4.6(1)
C(2)	−0.1722(6)	0.3623(8)	−0.5766(4)	6.1(2)
C(3)	−0.0968(5)	0.2647(9)	−0.5287(3)	5.5(2)
C(4)	−0.1289(5)	0.1268(8)	−0.5085(3)	5.1(2)
C(4a)	−0.2387(4)	0.0855(6)	−0.5360(3)	3.8(1)
C(4b)	−0.2949(4)	−0.0543(6)	−0.5265(3)	3.8(1)
C(5)	−0.2568(5)	−0.1862(7)	−0.4830(3)	5.3(2)
C(6)	−0.3306(7)	−0.3024(8)	−0.4857(4)	6.3(2)
C(7)	−0.4389(6)	−0.2898(7)	−0.5296(4)	6.1(2)
C(8)	−0.4779(5)	−0.1591(7)	−0.5729(3)	4.9(1)
C(8a)	−0.4048(4)	−0.0433(5)	−0.5717(3)	3.5(1)
C(9)	−0.4283(4)	0.1121(6)	−0.6106(3)	3.4(1)
C(9a)	−0.3147(4)	0.1848(5)	−0.5849(3)	3.5(1)
C(1′)	−0.4915(3)	0.1150(5)	−0.6954(2)	3.0(1)
C(2′)	−0.4758(4)	0.0048(5)	−0.7431(3)	3.3(1)
C(3′)	−0.5432(4)	0.0056(7)	−0.8200(3)	3.9(1)
C(4′)	−0.6175(4)	0.1178(7)	−0.8488(3)	4.3(1)
C(4a′)	−0.6307(4)	0.2389(6)	−0.8039(4)	3.7(1)
C(5′)	−0.7045(4)	0.3626(8)	−0.8337(4)	4.9(2)
C(6′)	−0.7160(5)	0.4786(8)	−0.7898(4)	5.7(2)
C(7′)	−0.6553(5)	0.4792(7)	−0.7137(4)	5.5(2)
C(8′)	−0.5827(4)	0.3632(6)	−0.6826(3)	4.3(1)
C(8a′)	−0.5682(3)	0.2381(5)	−0.7253(2)	3.2(1)
C(1″)	−0.3854(4)	−0.1114(5)	−0.7202(3)	3.3(1)
C(2″)	−0.2858(4)	−0.0590(6)	−0.7010(3)	3.4(1)
C(3″)	−0.4155(6)	−0.2791(8)	−0.7275(5)	6.2(2)

a) Values in parentheses are estimated standard deviations.
b) $B_{eq}/\text{Å}^2 = (8\pi^2/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \boldsymbol{a}_i \cdot \boldsymbol{a}_j$.

Table 8. Dihedral Angles Made by Planes Involved in the Olefinic Moiety and the Benzene Ring in *ap*-1-(9-Fluorenyl)-2-[(*E*)-2-halo-1-methylethenyl]naphthalenes (*ap*-**3**)[a]

Halogen	Planes-1-2	Planes-1-3	Planes-2-3
H[b]		30.8	
Cl	5.6	28.8	34.2
Br	3.8	28.3	32.0
I	4.3	27.0	31.3

a) Plane 1 is defined by atoms halogen, C(1″), and C(2″), plane 2 by C(1″), C(2″), and C(3″), and plane 3 by C(4b), C(5), C(6), C(7), C(8), and C(8a). b) Plane 1 is defined by C(1″), C(2′), C(2″), and C(3″), and plane 3 by C(4a), C(4b), C(5), C(6), C(7), C(8), C(8a), and C(9). Recalculated from the published data.[2)]

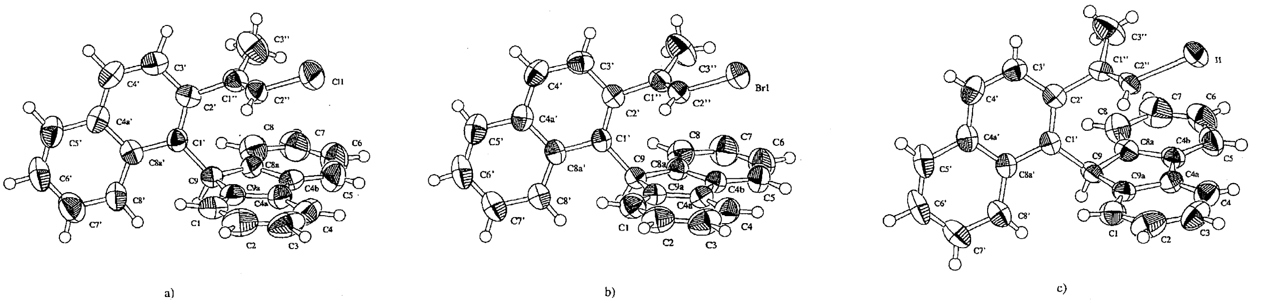
Table 9. Selected Nonbonding Distances in *ap*-2-(9-Fluorenyl)-1-[(*E*)-2-halo-1-methylethenyl]naphthalenes (*ap*-**3**)

Substituent	H[a]	Cl	Br	I
X–C(4a)		3.874(7)	3.907(4)	3.956(5)
X–C(4b)		3.873(6)	3.958(4)	4.022(5)
C(1″)–C(4a)	3.800(1)	3.80(1)	3.787(5)	3.750(6)
C(1″)–C(4b)	3.566(1)	3.496(9)	3.507(5)	3.468(6)
C(1″)–C(8)	3.488(2)	3.420(9)	3.441(6)	3.415(7)
C(1″)–C(8a)	3.027(1)	2.972(8)	2.993(5)	2.959(6)
C(1″)–C(9)	3.025(2)	3.028(9)	3.040(5)	3.022(7)
C(1″)–C(9a)	3.463(2)	3.54(1)	3.534(5)	3.512(6)
C(2″)–C(1)	3.745(2)	3.84(1)	3.789(6)	3.785(8)
C(2″)–C(4)	3.988(2)	3.97(1)	3.906(6)	3.854(8)
C(2″)–C(4a)	3.345(2)	3.275(9)	3.241(5)	3.214(7)
C(2″)–C(4b)	3.487(2)	3.356(8)	3.370(5)	3.338(7)
C(2″)–C(8a)	3.444(2)	3.320(8)	3.347(5)	3.315(6)
C(2″)–C(9)	3.388(2)	3.283(9)	3.289(5)	3.275(7)
C(2″)–C(9a)	3.219(2)	3.207(9)	3.169(5)	3.159(7)
C(3″)–C(7)	3.920(2)	3.92(1)	3.91(1)	3.85(1)
C(3″)–C(8)	3.433(2)	3.47(1)	3.481(9)	3.45(1)
C(3″)–C(8a)	3.539(2)	3.58(1)	3.574(8)	3.545(9)

a) The data were recalculated with the use of published data.[2)]

the fluorene group as in the unsubstituted compound,[2)] consideration of the steric effects would predict that *ap*-halo-olefins **3** would be less stable, relatively speaking to the *sp*-counterpart, than the unsubstituted one (*sp*- and *ap*-**1**). Thus this tendency would be enhanced by going from the chloro compound to the iodo compound. However, the observation is contrary to the prediction: While all the halogen compounds favored the *sp*-isomer with respect to the *ap*, the *ap*-iodo compound is most stable relative to the *sp*-isomer among the compounds examined and the *sp*/*ap* ratio changed from 15.6 of the parent compound **1** to 1.81 in the iodo compound **3** (X = I) (Table 3).

It may be argued that the conformation of 2-halo-1-methyl-*E*-ethenyl group is not the same with that in the parent compound, but the very similar chemical shifts of the methyl protons in ^{1}H NMR spectra of these compounds with that of



a) b) c)

Fig. 1. ORTEP drawings of *ap*-2-(9-fluorenyl)-1-[(*E*)-2-halo-1-methylethenyl]naphthalenes with thermal ellipsoids at 50% probability: a) chloro compound, b) bromo compound, c) iodo compound.

Table 10. Crystal Data of *ap*-2-(9-Fluorenyl)-1-[(*E*)-2-halo-1-methylethenyl)naphthalenes (*ap*-**3**)

Substituent	Cl	Br	I
Empirical formula	$C_{26}H_{19}Cl$	$C_{26}H_{19}Br$	$C_{26}H_{19}I$
Formula weight	366.89	411.34	458.34
Crystal dimension/mm^3	0.05 × 0.05 × 0.08	0.15 × 0.15 × 0.20	0.15 × 0.12 × 0.12
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a/Å	12.766(2)	12.910(1)	13.007(1)
b/Å	8.625(2)	8.559(1)	8.663(2)
c/Å	18.549(2)	18.680(1)	16.8812(9)
α/°	90	90	90
β/°	109.030(10)	109.331(6)	110.163(5)
γ/°	90	90	90
V/Å^3	1930.8(5)	1947.6(3)	1997.1(4)
Z	4	4	4
D_c/g cm^{-3}	1.262	1.403	1.524
μ(Cu $K\alpha$)/cm^{-1}	17.80	29.08	126.26
No. of reflections	3257	3273	3359
No. of observations	2015	2396	2784
A value	0.84	1.00	0.94
R	0.098	0.043	0.039
R_w	0.086	0.049	0.036

the parent compound strongly suggest that the conformation is the same.

The reason for the phenomenon must be either destabilization of the *sp*-isomer or stabilization of the *ap*-isomer, relatively speaking. However, it is difficult to envisage destabilization factor(s) for the *sp*-isomers. This leads to an assumption that the *ap*-isomer is stabilized relative to the *sp*-counterpart. We, therefore, examined the UV-vis spectra of these compounds to find evidence for the charge-transfer interactions. The data are shown in Table 4. Although the machine read absorptions for both *ap*- and *sp*-isomers of **3** at ca. 255 nm, except for the *sp*-isomer of the chlorine compound, there was always a larger protuberance in absorptions for the *ap*-isomer than that for the *sp*. This can be seen also as slightly enhanced absorptions for the *ap*-isomers relative to the *sp*-isomers in Table 4 in the 255 nm region. We might attribute the absorptions at 255 nm to charge transfer interactions and thus the stabilization to the charge-transfer interactions between the haloethenyl group and the fluorene moiety. However, the absorptions are so weak that we reserve a definite conclusion at the moment.

To get further insight into the interaction, X-ray structures of *ap*-2-(9-fluorenyl)-1-[(*E*)-2-halo-1-methylethenyl]naphthalenes (*ap*-**3**) were determined. The atomic coordinates are given in Tables 5, 6, and 7 and ORTEP drawings in Fig. 1. Since the skeletons of 1-(9-fluorenyl)naphthalene did not show significant differences, the main interests lie in the structures of the olefinic part of the molecules. The dihedral angles made by the olefinic part and the fluorene moiety are shown in Table 8 and the nonbonding distances shorter than 4Å, except one case, between the nonhydrogen atoms in the olefinic part and the fluorene system are shown in Table 9. Those of the parent compound *sp*-**1** were recalculated from the stored[2)] data and corrected for the fact that the data were for the enantiomeric compound with respect to those described in this paper, if there were a halogen atom in the olefinic moiety.

We expected that the nature of the interactions could be diagnosed from at least three phenomena in the structural characteristics. The first is the dihedral angles of the olefinic bond and the fluorene ring. The completely parallel conformation should favor the interaction because of the good overlap of the orbitals concerned. The second is the charge-transfer interactions between the halogen and the fluorene moiety. If it is the case, the halogen-fluorene distance should be closer than the sum of the van der Waals radii of the two groups. The third is the π–π interactions[32,33)] of the two groups. If this is the case, the two π systems should approach each other to make a closer contact than the sum of the van der Waals radii.

The dihedral angles compiled in Table 8 clearly show that the halogens are distorted from the plane made by the olefinic carbons but the extent of the distortion is rather small. The dihedral angles made by the olefin plane and the benzene ring are again almost the same, though there is a tendency that, when one goes from chlorine to iodine, the dihedral angles become slightly smaller. Comparing the dihedral angles in unsubstituted compound with those of the halogenated compounds suggests that the change in the dihedral angles cannot be the main cause for the interaction. Thus we conclude that the interactions between the two moieties are unlikely to be governed by the dihedral angles concerned.

The nonbonding atomic distances shown in Table 9 reveal that halogens are situated more distantly from the nearest carbons than the sum of the van der Waals radii of the atoms concerned. It is not possible to attribute the interactions to those between the halogen and the fluorene moiety.

In contrast, the olefinic carbons are attracted to the fluorene system when the compound carries a halogen atom with respect to the unsubstituted compound, whereas the distances between the olefinic carbons and the saturated carbon (C9) are almost the same irrespective of the substitution. This tendency of short nonbonding distances continues when one goes from the chloro compound to the iodo compound. C(2″) in particular seems to be attracted to the fluorene moiety as the size of the halogen becomes large: In the special cases, the distance between C(2″) and C(4) and that between C(2″) and C(4a) decrease by about 0.13 Å by going from the nonsubstituted compound to the iodo compound. Clearly the attraction is the cause for the relative stabilization of the *ap*-forms to the *sp*-forms in these compounds.

The nature of the attractive interactions observed here is either charge transfer or π–π interactions[32,33] but is not well understood at the moment: The effects of the halogen imply that the large atomic size is important for the interactions to occur. It probably is caused by the polarizability or dispersion force effects. The theoretical study for understanding this interaction is in progress.

Experimental

The product distribution was determined by ^{1}H NMR spectra, which were measured with use of a Varian Gemini 300 machine that operated at 300.1 MHz, before separation of the products. The product ratios shown in Tables 1 and 2 are averages of three runs. Identification of the products was carried out by comparing the ^{1}H NMR spectra with authentic specimen, when known, or by elemental analyses together with ^{1}H NMR spectra, when unknown. Melting points are not corrected.

Reaction of *ap*-1-(9-Fluorenyl)-2-(1-methylethenyl)naphthalene (*ap*-1) with Bromine Chloride in Carbon Tetrachloride. Bromine chloride was prepared by adding an equivalent amount of bromine to a chlorine solution in carbon tetrachloride. An equimolar amount of bromine chloride solution was added to a solution of *ap*-**1** (100 mg or 0.301 mmol)[2] in 5.7 mL of carbon tetrachloride with ice-cooling. The mixture was stirred for 1 h and washed with 5% aqueous sodium hydrogencarbonate. The product distribution was determined at this stage by ^{1}H NMR spectrum. The solvent was removed in vacuo and the residue was submitted to preparative TLC on silica gel (6 : 1 hexane–dichloromethane eluent) to afford the starting material, *ap*-**2**, *sp*-**3**, and *sp*-**4**, with R_f′s of 0.58, 0.43, 0.48, and 0.49, respectively. The formation ratios are given in Table 1. The starting material was detected only in a trace amount.

sp-2-[(*E*)-2-Bromo-1-methylethenyl]-1-(9-fluorenyl)naphthalene (*sp*-**3**: X = Br) and *sp*-2-[1-(bromomethyl)ethenyl]-1-(9-fluorenyl)-naphthalene (*sp*-**2**: X = Br) were found to be identical with the known compounds by comparing their ^{1}H NMR spectra.[2]

sp-2-(2-Bromo-1-chloro-1-methylethyl)-1-(9-fluorenyl)naphthalene (**4**: X = Br), mp 172.0—173.0 °C, was purified by recrystallization from acetone. Found: C, 69.63; H, 4.42%. Calcd for $C_{26}H_{20}BrCl$: C, 69.74; H, 4.50%. ^{1}H NMR (CDCl$_3$) $\delta = 2.54$ (3H, s), 4.14 and 4.68 (2H, ABq, $J = 10.4$ Hz), 6.50 (1H, d, $J = 8.9$ Hz), 6.65 (1H, s), 6.81 (1H, ddd, $J = 1.4$, 6.8, and 8.3 Hz), 7.18—7.26 (4H, m), 7.31 (1H, d, $J = 7.4$ Hz), 7.39—7.46 (2H, m), 7.70—7.83 (3H, m), 7.94 (1H, d, $J = 5.8$ Hz), 7.98 (1H, d, $J = 6.6$ Hz).

Reaction of *sp*-1-(9-Fluorenyl)-2-(1-methylethenyl)naphthalene (*sp*-1) with Bromine Chloride in Carbon Tetrachloride. The reaction was carried out similarly to the above and the products were separated by preparative TLC (6 : 1 hexane–dichloromethane eluent). The R_f values were 0.63, 0.39, 0.52, and 0.28 for the starting material, *ap*-**2** (X = Br), *ap*-**3** (X = Br), and 8-bromomethyl-8-methyl-8,14c-dihydrodibenzo[*a*,*l*]aceanthrylene (**5**: X = Br), respectively. The starting material was recovered in ca. 5% yield.

ap-**2** (X = Br), *ap*-**3** (X = Br), and **5** (X = Br) were identified by the ^{1}H NMR spectra on comparison with those of the authentic specimens.[2]

Reaction of Iodine Chloride with *ap*-1 in Carbon Tetrachloride. This reaction was carried out similarly to the above with use of 100 mg (0.301 mmol) of *ap*-**1** and iodine chloride (0.360 mmol) in 5 mL of carbon tetrachloride at 0 °C. The reaction was quenched after 2 h. ^{1}H NMR spectra indicated the presence of *sp*-**2** (X = Cl), *sp*-**2** (X = I), *sp*-**3** (X = I), and *sp*-**4** (X = I) with other minor compounds, the ratio being 10, 15, 2, and 66, respectively, together with 7% of the unreacted compound. The products were separated by TLC (6 : 1 hexane–dichloromethane). The starting material, *ap*-1-(9-fluorenyl)-2-[1-(iodomethyl)ethenyl]naphthalene (*sp*-**2**: X = I), *sp*-1-(9-fluorenyl)-2-[(*E*)-2-iodo-1-methylethenyl]naphthalene (*sp*-**3**: X = I), *sp*-2-(1-chloro-2-iodo-1-methylethyl)-1-(9-fluorenyl)-naphthalene (*sp*-**4**: X = I), and *sp*-2-[1-(chloromethyl)ethenyl]-1-(9-fluorenyl)naphthalene (*sp*-**2**: X = Cl) exhibited R_f values of 0.60, 0.42, 0.61, 0.48, and 0.46, respectively.

***sp*-2 (X = I):** Recrystallized from dichloromethane–hexane, mp 147—148 °C. Found; C, 67.95; H, 4.21%. Calcd for $C_{26}H_{19}I$: C, 68.13; H, 4.17%. ^{1}H NMR (CDCl$_3$) $\delta = 4.43$ (2H, s), 5.49 (1H, s), 5.74 (1H, s), 5.79 (1H, d, $J = 1.1$ Hz), 6.44 (1H, dd, $J = 1.0$ and 8.9 Hz), 6.84 (1H, ddd, $J = 1.5$, 6.9 and 8.4 Hz), 7.18—7.23 (5H, m), 7.38—7.43 (2H, m), 7.49 (1H, d, $J = 8.7$ Hz), 7.73 (1H, d, $J = 8.1$ Hz), 7.80 (1H, d, $J = 8.4$ Hz), 7.94 (2H, d, $J = 7.3$ Hz).

***sp*-3 (X = I)** was produced in such a low yield that it was identified by ^{1}H NMR spectra by comparing with that of the authentic specimen. For preparation of this compound, see the "equilibration" section.

***sp*-4 (X = I):** Recrystallized from dichloromethane-hexane, mp 137.0—137.5 °C. Found: C, 63.23; H, 4.07%. Calcd for $C_{26}H_{20}ClI$: C, 63.11; H. 4.03%. ^{1}H NMR (CDCl$_3$) $\delta = 2.58$ (3H, s), 4.10 and 4.65 (2H, ABq, $J = 10.1$ Hz), 6.49 (1H, dd, $J = 0.8$ and 8.9 Hz), 6.63 (1H, s), 6.81 (1H, ddd, $J = 1.4$, 6.7, and 8.8 Hz), 7.18—7.24 (4H, m), 7.37 (1H, dd, $J = 0.7$ and 7.7 Hz), 7.40—7.47 (2H, m), 7.72 (1H, d, $J = 8.9$ Hz), 7.72 and 7.81 (2H, ABq, $J = 8.8$ Hz), 7.97 (2H, t, $J = 7.8$ Hz).

sp-2-[1-(Chloromethyl)ethenyl]-1-(9-fluorenyl)naphthalene (*sp*-**2**: X = Cl) was identical in every respect with the authentic specimen.[4]

Reaction of Iodine Chloride with *sp*-1 in Carbon Tetrachloride. This reaction was similarly carried out as described above. The reaction proceeded only to 79% completion after 2 h, as judged from the presence of the starting material. ^{1}H NMR spectrum of the products indicated the presence of *sp*-**1**, an iodo-olefin *ap*-**3**, the cyclized compound **5** (X = I), and a chloro-olefin *ap*-**2** (X = Cl) in a 21, 32, 21, and 26 ratio. No signals attributable to *ap*-**2** (X = I) were detected. TLC of the products (6 : 1 hexane–dichloromethane) gave four fractions, R_f being 0.66, 0.57, 0.48, and 0.37 for the starting material, *ap*-**3** (X = I), *ap*-**2** (X = Cl), and **5** (X = I), respectively.

***ap*-3 (X = I):** Recrystallized from ether–hexane, mp 132—133 °C. Found: C, 68.39; H, 4.12%. Calcd for $C_{26}H_{19}I$: H, 68.13; H, 4.17%. ^{1}H NMR (CDCl$_3$) $\delta = 1.33$ (3H, d, $J = 1.1$ Hz), 4.71 (1H, q, $J = 1.1$ Hz), 5.99 (1H, s), 7.02 (1H, d, $J = 8.5$ Hz), 7.17—7.25 (4H, m), 7.39 (2H, t, $J = 7.7$ Hz), 7.60 (1H, ddd, $J = 1.2$, 6.9, and 8.0 Hz), 7.69 (1H, ddd, $J = 1.5$, 6.8, and 8.3 Hz), 7.77 (1H, d, $J = 8.3$ Hz), 7.90 (2H, d, $J = 7.7$ Hz), 7.95 (1H, dd, $J = 1.6$ and 8.2 Hz), 8.60 (1H, d, $J = 8.6$ Hz).

5 (X = I): Recrystallized from THF–hexane, mp 122—130 °C (decomp). Found: C, 68.30; H, 4.26%. Calcd for $C_{26}H_{19}I$: H, 68.13; H, 4.17%. ^{1}H NMR (CDCl$_3$) $\delta = 1.84$ (3H, s), 4.17 (2H, s), 5.37 (1H, s), 7.34—7.50 (6H, m), 7.53 (1H, dd, $J = 0.8$ and 7.7 Hz), 7.62 (1H, d, $J = 8.8$ Hz), 7.74 (1H, dd, $J = 0.8$ and 7.4 Hz), 7.86—7.89 (2H, m), 8.08 (1H, dd, $J = 0.8$ and 8.2 Hz), 8.73 (1H, dd, $J = 1.5$ and 7.9 Hz).

ap-2-[1-(Chloromethyl)ethenyl]-1-(9-fluorenyl)naphthalene was identified by comparing its ^{1}H NMR spectrum with that of the authentic specimen.[4)]

Reactions of 1 in Nitromethane. The nitromethane solvent was purified by distillation, followed by treatment with chlorine to remove any impurity which might react with halogen halide. The redistilled solvent was used for the reactions. The results are shown in Tables 1 and 2.

Equilibration of 3. The general method is described by taking the iodo compound as an example. A sample (166 mg) of *ap*-**3** (X = I) in 20 mL of toluene was heated under reflux for 2 h. The solution was cooled and the solvent evaporated in vacuo. The ratio of the rotamers was determined at this point. The residue was submitted to TLC (3 : 1 hexane–dichloromethane eluent) and 35.6 mg and 104 mg of pure *ap*-**3** and *sp*-**3** were obtained, respectively. The population ratios were determined by ^{1}H NMR. The results of these isomerizations are summarized in Table 3.

sp-**3** (X = I) was recrystallized from ether-hexane, mp 167—168 °C. Found: C, 68.40; H, 4.22%. Calcd for $C_{26}H_{19}I$: C, 68.13; H, 4.17%. ^{1}H NMR (CDCl$_3$) $\delta = 2.43$ (3H, d, $J = 1.3$ Hz), 5.61 (1H, s), 6.43 (1H, dd, $J = 0.8$ and 8.6 Hz), 6.52 (1H, q, $J = 1.3$ Hz), 6.85 (1H, ddd, $J = 1.4$, 6.9, and 8.5 Hz), 7.11 (2H, dd, $J = 0.8$ and 7.6 Hz), 7.20 (2H, dt, $J = 1.1$ and 7.5 Hz), 7.21 (1H, ddd, $J = 1.1$, 6.8, and 8.0 Hz), 7.36 (1H, d, $J = 8.4$ Hz), 7.42 (2H, tt, $J = 1.1$ and 7.5 Hz), 7.72 (1H, d, $J = 7.4$ Hz), 7.78 (1H, d, $J = 8.2$ Hz), 7.94 (1H, d, $J = 7.6$ Hz).

X-Ray Crystallography. Crystals suitable for X-ray crystallography were grown from dichloromethane–hexane. X-ray data were obtained on a Rigaku AFC7R four circle diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.54178$ Å). The scan mode was the 2θ method in the range of $2\theta < 120°$, the scan rate being 16, 10, and 10° min^{-1} for the chloro, bromo, and iodo compounds respectively. The scan range was calculated by $A° + 0.35° \tan\theta$, where the values A are given in Table 10. The weak reflections were scanned three times. The structures were solved by the direct method and refined by the full-matrix least-square method by using the teXsan program. Anisotropic and isotropic thermal parameters were employed for non-hydrogen and hydrogen atoms, respectively. Some hydrogen atoms were refined but most of them were included in fixed positions. Azimuthal scans of several reflections indicated no need for an absorption correction. The data were corrected for Lorentz and polarization effect. A correction for secondary extinction was applied. The function minimized was $\sum[w(|F_o| - |F_c|)^2]$ where $w = (\sigma_c^2|F_o|)^{-1}$. Additional crystal and analysis data are listed in Table 10.

The complete F_o—F_c data have been deposited as Document 70011 at the Office of the Editor of Bull. Chem. Soc. Jpn.

UV Absorption Spectra. These were recorded on a Hitachi U-2000 spectrophotometer for solutions of compound **3** in hexane. The concentrations were 2.21×10^{-5} mol L^{-1}.

NOE Experiments. The difference NOE spectra were recorded on a JEOL GSX-400 NMR spectrometer which operated at 399.8 MHz. The standard technique NOEDIF, provided with the spectrometer, was used with the following parameters: Irradiation time 5 s, irradiation power IRATN 350, pulse delay 3 s. A degassed solution of ca. 10 mg of a sample in CDCl$_3$ was used at ambient temperature. While irradiation of the methyl proton signal of compound *sp*-**3** (X = I) and *ap*-**3** (X = I) did not show any significant enhancement of the olefinic proton signal, that of the methyl proton signal in compound **5** (X = I) enhanced the 14c-H signal by 20%.

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30) It may be argued that the stabilization is not due to participation of the β-halo substituent but due to hyperconjugation.

However, our preliminary results with sulfenyl chlorides suggest that the alkyl(aryl)thio group does not stabilize the cation. Because the alkyl(aryl)thio cation must be stable with respect to the halogen cations, we believe the bulkiness together with ionization potentials of halogens is responsible to the stabilization. The results of the reaction of chalcogenyl halides with compound **1** will be a subject of another paper which should be published in due course.

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