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Reactivities of Stable Rotamers. XLI. Reactions of 1-(9-Fluorenyl)-2-(1-methylethenyl)naphthalene Rotamers with Chalcogenyl Halides and Observation of Coloration During the Reaction of Methanesulfenyl Chloride and the *ap*-Rotamer[1)]

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Reactions of *p*-toluenesulfenyl chloride with the title olefins in carbon tetrachloride afforded an addition product and *sp*-1-(9-fluorenyl)-2-[1-(*p*-tolylthiomethyl)ethenyl]naphthalene in the case of *ap*, whereas the only product was *ap*-1-(9-fluorenyl)-2-[1-(*p*-tolylthiomethyl)ethenyl]naphthalene in the case of *sp*. No cyclized compounds, which are commonly observed in the reactions of the *sp*-isomer with halogens or halogen chloride, were detected. Various unsuccessful attempts, including use of methanesulfenyl chloride to take advantage of different sulfur acidity, use of a soft anion to retard deprotonation or a polar solvent to accelerate cyclization by stabilizing the intervening cations, have been made to find conditions for formation of the cyclized compound. Similar unsuccessful results were obtained with benzeneselenenyl halides. Such results are attributed to the effective participation of a chalcogen atom in stabilizing a β-carbocation, which opens momentarily but is less vulnerable to the S_N2 type attack of the existing nucleophile. Coloration was observed in the reaction of the *sp* form with methanesulfenyl chloride.

Reactions of various halogen chlorides,[2,3)] as well as other positive halogen compounds,[4,5)] with the olefinic bond in *sp*- and *ap*-1-(9-fluorenyl)-2-(1-methylethenyl)naphthalenes (**1**) were examined to show interesting differences in the reactivities of the rotamers. Since sulfenyl chlorides are known to add across a double bond with a stable thiiranium intermediate,[6,7)] which is analogous to halonium ions, it will be interesting to see the effects of stabilization of the thiiranium ion for the product distribution.

There is another point of interest about the thiiranium ions: If thiiranium ions are as unstable as the halonium ions, due to the steric effects in one of the rotamers, it provides an example of an open β-thio cation. The fate of this cation should be intriguing. In our cases of the rotamers of compound **1**, we have demonstrated that the three-membered halonium ion is produced in the case from *ap*-**1**, but its formation is disfavored from *sp*-**1** because of the severe steric hindrance. Thus our systems could provide a probe to see the reactivity differences of the open and closed cations if the latter is stable in the *sp*-position. We have selected *p*-toluenesulfenyl chloride and methanesulfenyl chloride as representatives for such addend. Here we disclose the results with some discussion of the possible reasons for the observations.

In the preceding paper of this series,[2)] we reported reactions of halogen chlorides with *ap*- and *sp*-1-(9-fluorenyl)-2-(1-methylethenyl)naphthalene (**1**) rotamers. The results were discussed on the standpoint that the halogen effectively contributes to stabilization of the intervening carbocation as the size of the halogen becomes large. However, argument can be made that the stabilization of the intervening β-halo carbocation can be the result of the stabilization due to hyperconjugation because the larger the halogen atom, the more stable the halogen cation. In this respect, it will be interesting to see the results of the reactions of *ap*-**1** and *sp*-**1** with sulfenyl chlorides, because the stability of the sulfenyl cation is considered to be higher than the halogen cation, at least for the chlorine and bromine cases.

Selenenyl halides are also known to add across a double bond to form seleniranium intermediates.[8,9)] In analogy of the halonium ions, the seleniranium ions should be more stable than thiiranium ions. Although this has not been proven, anchimeric assistance of a selenium atom is known to be stronger than that of a sulfur atom.[10)] This consideration leads to a prediction that alkane(arene)selenenyl halides should favor formation of an addition product in the case of *ap*-**1** and formation of a cyclized compound from *sp*-**1**. Thus we explored the reactions of selenenyl halides with **1**. The results have been contrary to the expectation.

Results

Reaction of *p*-toluenesulfenyl chloride with *ap*-**1** in a 1 : 1.1 chloroform–carbon tetrachloride mixture was rather slow and afforded 59% *sp*-2-[1-chloro-1-methyl-2-(*p*-tolylthio)ethyl]-1-(9-fluorenyl)naphthalene (*sp*-**3**: R = *p*-$CH_3C_6H_4$, Y = S)

and 8% *sp*-1-(9-fluorenyl)-2-[1-(*p*-tolylthiomethyl)ethenyl]-naphthalene (*sp*-**2**: R = *p*-$CH_3C_6H_4$, Y = S) after 1 h at 0 °C (Scheme 1). There were no other signals attributable to *sp*-1-(9-fluorenyl)-2-[(*E*)-1-methyl-2-(*p*-tolylthio)ethenyl]naphthalene (*sp*-**4**: R = *p*-$CH_3C_6H_4$, Y = S), which was expected to form from the analogy of the reactions of compound *ap*-**1** with halogens or halogen chlorides.[2—5]

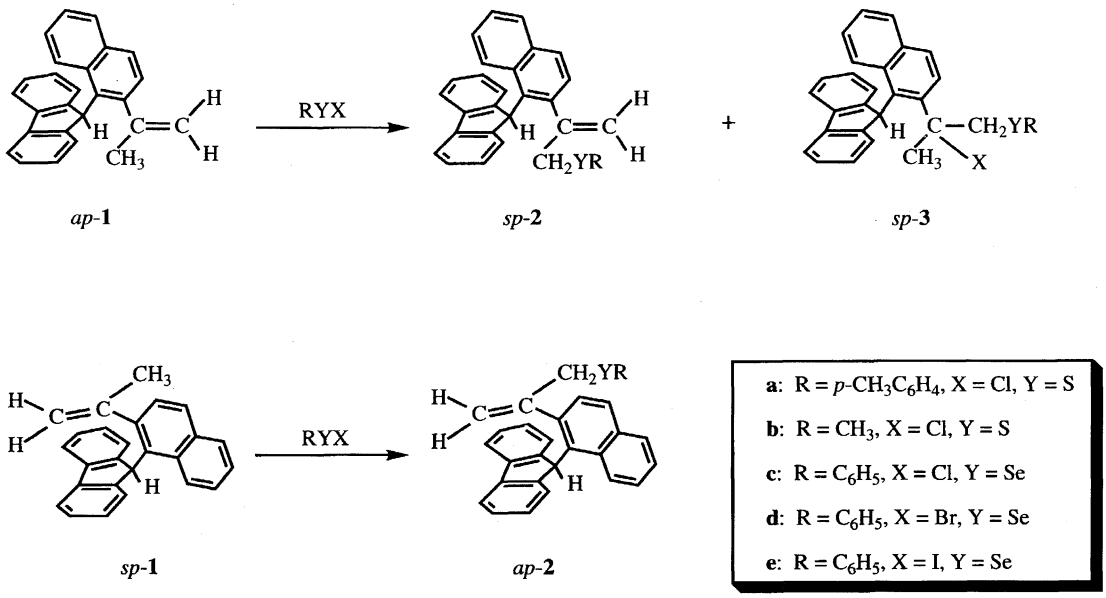
The yield of *sp*-**2** (R = *p*-$CH_3C_6H_4$, Y = S) increased from 6 to 76% at the expense of *sp*-**3** (R = *p*-$CH_3C_6H_4$, Y = S) after 44 h at 0 °C, indicating that the main part of *sp*-**2** (R = *p*-$CH_3C_6H_4$, Y = S) is secondary at this temperature after several hours. The ratio of *sp*-**3** to *sp*-**2** was almost constant at 7 : 1 at 0 °C, when it was examined at intervals of ca. 10 min for 1 h for the reactions in chloroform–carbon tetrachloride solutions.

Reaction of *p*-toluenesulfenyl chloride with *sp*-**1** was also slow and yielded *ap*-1-(9-fluorenyl)-2-[1-(*p*-tolylthiomethyl)ethenyl]naphthalene (*ap*-**2**: R = *p*-$CH_3C_6H_4$, Y = S) as an exclusive product. Neither a cyclization product, 8-methyl-8-(*p*-tolylthiomethyl)-8,14c-dihydrodibenzo[*a*,*l*]aceanthrylene (**5**: R = *p*-$CH_3C_6H_4$, Y = S) nor *ap*-1-(9-fluorenyl)-2-[(*E*)-1-methyl-2-(*p*-tolylthiomethyl)ethenyl]naphthalene (*ap*-**4**: R = *p*-$CH_3C_6H_4$, Y = S) was formed (Scheme 2).

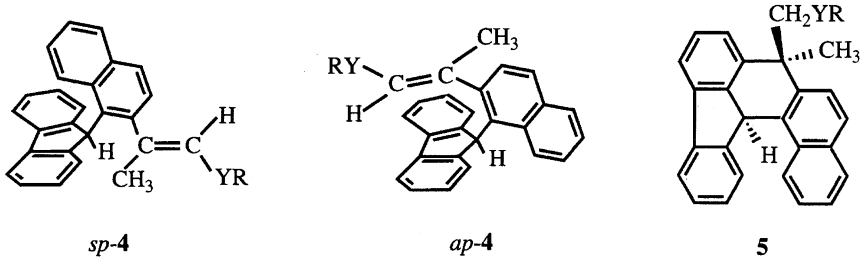
Methanesulfenyl chloride behaved in much the same way with *p*-toluenesulfenyl chloride, though it was expected that the sterically small and electron-donating methyl group could give different results from those of the reaction with *p*-toluenesulfenyl chloride: The main products from the *ap*-isomer **1** were the adduct (*sp*-**3**: R = CH_3, Y = S) and the methylthio olefin (*sp*-**2**: R = CH_3, Y = S) and an exclusive product from *sp*-**1** was the methylthio olefin (*ap*-**2**: R = CH_3, Y = S).

The addition product (*sp*-**3**) of methane(*p*-toluene)sulfenyl chloride to *ap*-**1** was unstable and lost hydrogen chloride on standing or on chromatography. The structures of these compounds were confirmed by converting them to the corresponding hydroxy compound (*sp*-**6**) by hydrolysis or to sulfones (*sp*-**8**) by oxidation. In the latter treatment, a sulfone (*sp*-**7**) was also obtained from the dehydrochlorinated product.

Reaction of *sp*-**1** with methanesulfenyl chloride afforded *ap*-**2** (R = CH_3, Y = S) only, very similar with the reaction of *p*-toluenesulfenyl chloride: No **5** was detected. Although



Scheme 1.



Scheme 2. Compounds which were not detected, though expected to form.

the increase in the yield of the cyclized compound **5** was attempted by using nitromethane or acetonitrile as a solvent, which was successful for the cases of chlorine and bromine, no such product was formed within the limit of the detecting method used in this study. Finally, to examine whether the cyclized compound could be obtained by using a weak protonophile, methanesulfenyl bromide was used for the reaction of *sp*-**1**. No difference was found, however.

We have been successful in increasing the yields of **5** by using a large halogen atom. In this respect, benzeneselenenyl chloride would produce more favorably the cyclized compound **5** than the case of *p*-toluenesulfenyl chloride. However, this expectation was not materialized: The only product observed was 1-(9-fluorenyl)-2-[1-(phenylselenomethyl)ethenyl]naphthalene (*ap*-**2**: R = C_6H_5, Y = Se). To seek other favorable conditions for formation of **5** (R = C_6H_5, Y = Se), we used benzeneselenenyl bromide and iodine–diphenyl diselenide complex, which is known to act as if it is benzeneselenenyl iodide,[11] in chlorinated methanes and in nitromethane. None of these reactions produced **5**, however.

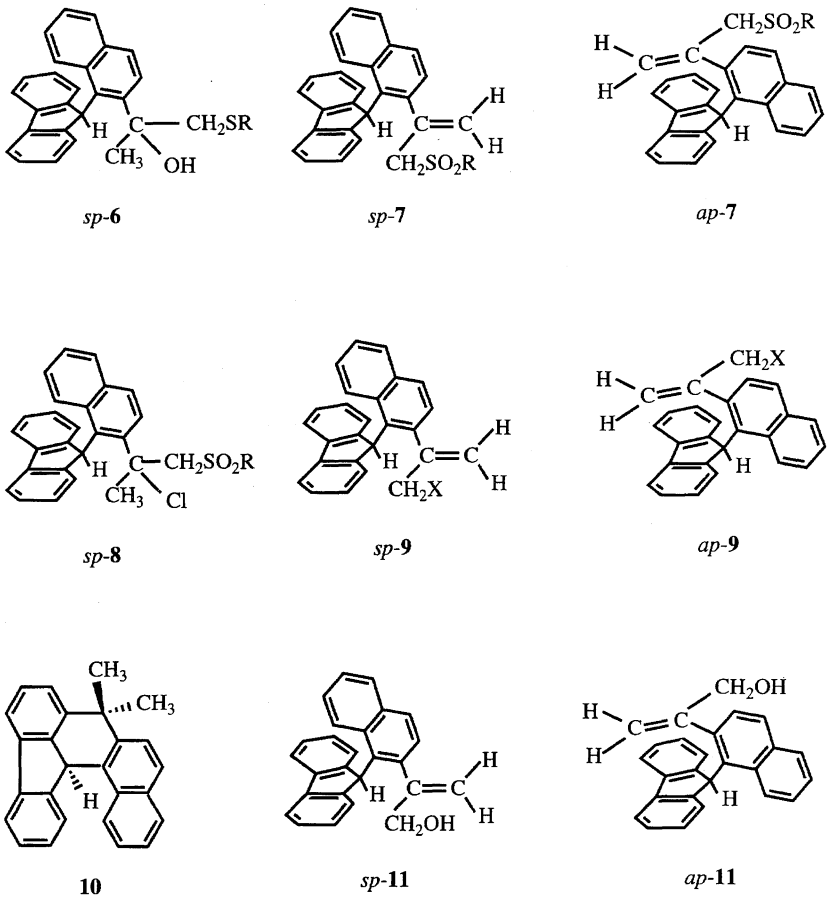
An interesting point in the reactions of benzeneselenenyl halides with *ap*-**1** is that no addition product (*sp*-**3**: R = C_6H_5, Y = Se, X = Cl or Br) was detected. The reaction exclusively produces compound *sp*-**2** (R = C_6H_5, Y = Se). Although these reactions give corresponding halogen compounds (**9**) (Scheme 3), these are considered to be secondary as will be discussed in the following section.

Iodine-diphenyl diselenide reacted slowly with both *sp*-**1** and *ap*-**1** in carbon tetrachloride. Thus the reaction had to be carried out in chloroform to get reasonable rates of reactions. Surprisingly, *sp*-**1** reacted with this reagent to form 8,8-dimethyl compound (**10**) without showing any detectable formation of *ap*-**2**. The structure of **10** could be confirmed by the fact that it was also produced by treatment of *sp*-**1** with hydrogen bromide.

The structures of compound **2** (R = C_6H_5, Y = Se) were confirmed by oxidizing them to the corresponding allylic alcohols (**11**) with mCPBA. This type of reaction is well documented in the literature.[12]

Discussion

Addition of Sulfenyl Chlorides. The sulfur participation in the β-thiocation is known to be very strong[13] and a sulfur and a chloro substituent exchange their sites through the three-membered cyclic cation.[6] But we observed only one addition product in this case. In order to prove the structure of *sp*-**3** (R = *p*-$CH_3C_6H_4$, Y = S), we oxidized the sulfur atom in *sp*-**3** with mCPBA to the corresponding sulfone, the method being successfully used for structure determination by X-ray crystallography.[14] The oxidation of the products produced both the corresponding sulfone (*sp*-**8**) and the dehydrochlorinated sulfone (*sp*-**7**) (Scheme 3). The chemical



sp-**6** *sp*-**7** *ap*-**7**

sp-**8** *sp*-**9** *ap*-**9**

10 *sp*-**11** *ap*-**11**

Scheme 3.

shifts of the AB protons due to the methylene group in compound *sp*-**8** shifted downfield, relative to the original compound *sp*-**3**. 2-Aryl(alkyl)thio-1-hydroxy compound (*sp*-**6**), which was prepared by hydrolysis of *sp*-**3** (R = *p*-$CH_3C_6H_4$ or CH_3, X = Cl, Y = S), exhibited the chemical shifts of the methylene and the methyl protons upfield. These indicate that the methylene group is attached to the sulfur atom.

While the β-alkylthio chloride (*sp*-**3**, Y = S) ionizes back to the episulfonium chloride, the attack of the chloride ion on the primary carbon seems to be very slow, thus producing a single compound on addition of the sulfenyl chloride across the double bond of *ap*-**1**. Though the reasons for this slow attack by the chloride ion on the thiiranium ion are not well understood, we tentatively attribute the results to the steric effects, which retard the formation of an sp^3 carbon with large substituents, due to the presence of the 9-fluorenyl group at the 1 position of the naphthalene ring. Because of the stable nature of the cation, being tertiary benzylic and carrying a β-sulfur atom, the cation will open easily but is protected from the attack of the chloride ion both by the fluorene group and by the sulfur atom which should be located closely to the cationic center in its stable form.

The mechanisms of formation of *sp*-**2** (R = *p*-$CH_3C_6H_4$, Y = S) deserve discussion. There are two alternative ways: Direct conversion of the thiiranium ion into *sp*-**2** during the reaction or the formation of *sp*-**2** from the thiiranium ion which is formed from compound *sp*-**3** (R = *p*-$CH_3C_6H_4$, X = Cl, Y = S). Although it is not completely proven, the constant ratios of *sp*-**2** (R = *p*-$CH_3C_6H_4S$, Y = S) to the adduct (*sp*-**3**: R = *p*-$CH_3C_6H_4$, Y = S) during the early stage of the reaction at low temperatures strongly suggest that these compounds are directly formed from the intermediate by kinetic control. Thus the ratio of the adduct to the olefin is ca. 7 : 1 in the case of *ap*-**1** when the reaction was carried out in chloroform–carbon tetrachloride. However, the system of *sp*-**2** and hydrogen chloride is thermodynamically more stable than *sp*-**3**; *sp*-**2** increases in its amount in the later stage of the reaction, especially when the system is open.

In contrast, *sp*-**1** afforded only *ap*-**2** (R = *p*-$CH_3C_6H_4$, Y = S). Neither addition product nor cyclized product **5** (R = *p*-$CH_3C_6H_4$, Y = S) was formed even under conditions which should favor this type of products. The absence of the addition product is ascribed to the steric effects that make the presence of a tertiary carbon above the fluorene ring prohibitively unstable.

There are two possible reasons for the absence of the cyclized compound **5**. One is that the intermediate cation remains open, because the characteristic three-membered cationic species is of high energy in the case of the intermediate from *sp*-**1**. Because a sulfur atom is small and its ionization potential is relatively large, when formation of the three-membered species is prohibited, it may destabilize a β-cation like a chlorine atom. However, this possibility is less likely because sulfur comprises a more strongly participating substituent than oxygen.[15]

The other reason is that the carbocation is stabilized due to sulfur participation. Although the thiiranium ion might not be formed due to the steric conditions, the cation is still stabilized by a rather remote participation of the sulfur and thus because of its stability it survives until the reaction mixture is quenched. This possibility seemed to be supported by the color of the solution which was reddish violet. We thus examined the ^{1}H NMR spectra of the reaction mixture. However, all the observed signals were assignable to the starting materials and products even at -50 °C. Although the color is likely to indicate the presence of intermediate(s), the quantity was so minute that it did not allow detection by ^{1}H NMR.

Taking into consideration the fact that the oxirane compound, in which the RS^+ group in the thiiranium ion is replaced by an oxygen, was isolated as a stable compound,[16] together with the discussions described above, it is tempting to consider that the thiiranium ion or an intermediate close to it really exists in this case and survives until it is deprotonated. Because of the cationic charge on the tertiary carbon in the open β-thiocation, the deprotonation should take place either from the methyl group or the thiomethyl group. The preferential deprotonation from the methyl group is tentatively attributed to the steric effects given by the fluorenyl group: Due to the steric effects, the methylene protons are forced to take positions which are just above the fluorene ring. Because the partial opening of the thiiranium ion will make the methyl-proton vulnerable to abstraction by the chloride ion, the deprotonation occurs preferentially on the methyl group.

Addition of Selenenyl Halides. Selenenyl halide is known to add across a double bond in a *trans* fashion[17,18] and thus a seleniranium ion[8,9] is commonly accepted as an intermediate. It would be natural to expect that, from the analogy of halogens,[19] a selenium atom would form a more stable three-membered ring than a sulfur atom. This expectation is supported by the fact that the neighboring participation of a selenium atom is more effective than a sulfur.[8]

The exclusive formation of *sp*-**2**, the absence of *sp*-**3**, in the reaction of *ap*-**1** with selenenyl halides is rather surprising, if one considers the selenium participation, which is expected to be better than that of sulfur. We wish to attribute the results tentatively to the effective participation of the selenium: The participation of a selenium atom is so effective that the formation of the adduct *sp*-**3** is slow, especially in sterically hindered cases such as the present one. The rates of reaction of selenenyl halide with olefins are known to be large with respect to sulfenyl halide.[20,21] This is contradictory with our observation that the addition of the selenenyl halides was slower than the sulfenyl halides. This is probably due to the steric situation of the compounds concerned. It is possible that the seleniranium ion or an intermediate close to it survives until it is deprotonated by a halide ion or water. Thus deprotonation from seleniranium ion or incipient seleniranium ion takes place directly and this reaction overwhelms the attack of the halide ion on the cationic center, which should form the adduct. Further studies to shed light on this problem are in progress.

Selenenyl halides, the selenium atom in which had been

expected to stabilize the β-seleno cation intermediate, also failed to give any cyclized compound **5** from *sp*-**1**. This was true even though the bromide or iodide, which have less affinity to proton, was used. We attribute the results to the high stability of the seleniranium ion or the incipient seleniranium ion. Because of the strong participation of the selenium atom, the positive charge on the benzylic carbon is so sparse that the attack of the carbocation on the fluorene ring cannot take place.

The formation of the halogen compound (**9**) in treatment of the olefin **1** with benzeneselenenyl halide is interesting. We wish to attribute the formation of these halo compounds to a secondary reaction of compound **2** with the corresponding selenenyl halide. Evidence follows. When 0.5 mol of benzeneselenenyl chloride was used for 1.0 mol of *sp*-**1**, the ratio of *ap*-**9** (X = Cl) to *ap*-**2** (R = C_6H_5, Y = Se) was ca. 1 : 3, which should be compared to a ratio of 4.5 : 1 when an equivalent amount of benzeneselenenyl chloride was used. When 2 mol of benzeneselenenyl chloride was used for 1 mol of *sp*-**1**, the only product was *ap*-**9** (X = Cl): No *ap*-**2** (R = C_6H_5, Y = Se) was detected. Furthermore, treatment of *ap*-**2** (R = C_6H_5, Y = Se) with benzeneselenenyl chloride afforded *ap*-**9** (X = Cl).

This type of reaction was reported some 30 years ago on sulfur compounds: When sulfides were treated with sulfenyl chlorides, disulfides and chlorides were formed.[22,23] We therefore interpret the results as indicating that *ap*-**2** (R = C_6H_5, Y = Se) was attacked by selenenyl halides and the diselenides formed with a positive selenium atom were cleaved by the halide ion either by S_N2 type or S_N2' type reactions. Diphenyl diselenide is obtained in these reactions, the amount of which was in accord of the reaction mechanism mentioned. The experimental results also suggest that the selenium in *ap*-**2** (R = C_6H_5, Y = Se) is more easily attacked by the selenenyl halide than the olefinic bond.

The formation of the dimethyl compound **10** in the reaction of *sp*-**1** with the iodine–diphenyl diselenide complex should be attributed to the reaction initiated by proton addition to the double bond. To confirm this assumption, we have carried out reactions in various solvents. The results are shown in Table 3.

The reactions are anomalous if one only takes into account polarity of the solvent. However, if one takes both polarity and the basicity of the solvent into consideration, it seems a natural consequence. Namely, proton formation is favored in polar solvent and thus the formation of compound **10** is generally fast in polar solvent. However, if the polar solvent scavenges protons, namely is basic, the reaction is retarded. Acetonitrile is a typical example. This postulate necessarily requires formation of a proton. Probably a cationic intermediate is formed in a minute amount by addition of the selenenyl moiety which provides a proton either by deprotonation to form *ap*-**2** or less likely by cyclization to produce **5** followed by deprotonation. These products could not be detected because the extent of the formation is so limited. Then the proton acts as a catalyst to form the cation and then the cyclized compound **10**. The addition of a proton to the double bond in *sp*-**1** is much faster than that of phenylselenenyl cation which should be formed from the iodine–diphenyl diselenide complex.

General Discussion. As to the mechanism of addition of the chalcogenyl halides, two points are worthy of note.

Although Hammett plots of the rates of addition of arenesulfenyl halides across double bonds produce a good straight line,[24] the plots of addition to substituted styrenes are not linear.[25] Therefore the original proposal of intervention of a thiiranium formation at the rate-limiting step[26] is reexamined[27] and the general consensus seems to point to a modified transition state that involves sulfurane character.[20] Namely these anomalous results are attributed to intervention of an intermediate, which is on the spectrum between chalcogeniranium ion at one end and chalcogenurane at the another.[20,21] However, the chalcogenurane intermediate does not explain the formation of the substituted olefins *ap*-**2**. We therefore wish to discuss the results by assuming that the β-thio or β-seleno carbocation intervenes in these reactions.

There is another possibility. The difference in the three-membered ring cation with a chalcogen atom from that with a halogen atom is the fact that the chalcogen atom carries a substituent and two pairs of electrons, whereas the halogen carries three unshared pairs of electrons only. Because the substituent on the chalcogen atom is much larger than the lone pair electrons,[28,29] there could be steric hindrance when the molecule takes a structure which is required for neighboring participation. Indeed, although any of the two electron pairs on the chalcogen can be used for participation, the substituent on the chalcogen has to be eclipsing the C–H bond involving the originally terminal olefinic carbon to which the chalcogen is attached, whereas it is a pair of electrons which eclipse the C–H bond in the case of halogens. Thus the participation is disfavored in the chalcogen cases.

It is hard to decide which is the major reason for the outcome. However, there is one clear point. That is, the chalcogeniranium ion must be an intermediate, because otherwise the formation of the olefins **2** cannot be explained. Even if the chalcogenurane is the intermediate, it should change to the chalcogeniranium ion in the next step. The chalcogeniranium ion can open to a β-chalcogeno cation to a small degree due to the stability of the cation, which is tertiary and benzylic, and the slightly open cation leads to the product. The main difference between the sulfur and the selenium compounds is that the seleniranium ion is more stable than the thiiranium ion; this difference leads to the absence of the adducts in the case of selenenyl halides.

Generally solvent effects are very small for the reactions of **1** with chalcogenyl halides, especially for selenenyl halides (Tables 1 and 2). This makes a sharp contrast to the case of reactions of halogens.[2,3] It is further noted that as one descends the periodic table of chalcogens, the solvent effects tend to diminish. While the convincing explanation for these results needs further evidence, the results might support the intermediacy of the chalcogenurane especially for the selenium cases.

Finally, the absence of the cyclized compound **5** in the

Table 1. Product Distributions (% Normalized to 100%) in Reactions of *ap*-1-(9-Fluorenyl)-2-(1-methylethenyl)-naphthalene (*ap*-**1**) with Chalcogenyl Halides[a)]

Reactant	Solvent	Recovered *ap*-**1**	*sp*-**2**	*sp*-**3**	*sp*-**9**
p-$CH_3C_6H_4SCl$	CCl_4	—	26	74	—
	CH_3NO_2	10	25	65	—
CH_3SCl	CCl_4	85	7	8	—
	CH_3NO_2	25	19	56	—
C_6H_5SeCl	$CHCl_3$	63	7	—	30
	CH_3NO_2	50	39	—	11
C_6H_5SeBr	$CHCl_3$	87	—	—	13
	CH_3NO_2	91	—	—	9
$(C_6H_5Se)_2 \cdot I_2$[b)]	$CHCl_3$	100	—	—	—
	CH_3NO_2	100	—	—	—

a) Reaction conditions: 0 °C, 30 min except for the last entry.
b) 70 °C, 20 min.

Table 2. Product Distributions (% Normalized to 100%) in Reactions of *sp*-1-(9-Fluorenyl)-2-(1-methylethenyl)-naphthalene (*sp*-**1**) with Chalcogenyl Halides[a)]

Reactant	Solvent	Recovered *sp*-**1**	*ap*-**2**	*ap*-**9**	**10**
p-$CH_3C_6H_4SCl$	CCl_4	37	63	—	—
	CH_3NO_2	20	80	—	—
CH_3SCl	CCl_4	85	15	—	—
	CH_3NO_2	45	55	—	—
CH_3SBr	CH_3NO_2	58	42	—	—
C_6H_5SeCl	$CHCl_3$	62	7	31	—
	CH_3NO_2	82	4	14	—
C_6H_5SeBr	$CHCl_3$	93	—	7	—
	CH_3NO_2	90	—	10	—
$(C_6H_5Se)_2 \cdot I_2$[b)]	$CHCl_3$	12	—	—	88
	CH_3NO_2	100	—	—	0

a) Reaction conditions: 0 °C, 30 min except for the last entry.
b) Reaction conditions: 70 °C, 20 min.

Table 3. Solvent Effects on the Reaction of Diphenyl Diselenide–Iodine Complex with *sp*-**1** as Revealed by Yields of **10**

Solvent	ε[a)]	Reaction conditions	Recovered *sp*-**1**	**10**
CCl_4	2.238	Reflux, 20 min	81	19
C_6H_6	2.283	Reflux, 20 min	100	—
$CHCl_3$	4.9	70 °C, 20 min	12	88
C_6H_5Cl	5.6493	70 °C, 20 min	50	50
CH_3NO_2	35.87	70 °C, 20 min	100	—
CH_3CN	37.5	70 °C, 20 min	100	—

a) Dielectric constants.

product from *sp*-**1** rejects the hypothesis that the increase in the yield of the cyclized compound in the series of halogens is not due to hyperconjugation: The formation of the cyclized compound must be attributed to an anchimeric assistance of the halogen when its atomic size is large.

Coloration During the Reaction of *sp*-1 with Methanesulfenyl Chloride. During the reaction of *sp*-**1** with methanesulfenyl chloride, we noticed that greenish color developed for a short time and finally the color changed to reddish purple. UV-vis absorption spectroscopy at low temperatures revealed that the absorption had a maximum at ca. 610 nm with absorbance of ca. 0.055. The absorption of the reaction mixture at the final stage had a maximum at 540 nm with absorbance of 0.315.

^{1}H NMR spectra measured at low temperatures showed that no signals attributable to the reaction intermediate were observed but there were signals due to the starting materials and the products. Thus the origin of the absorption at 540 nm is unknown.

Stopped flow measurement of the reaction mixture showed that the absorption at 620 nm increases to the maximum after ca. 16 s at 25 °C and decreases until after ca. 60 s when it again increases. This is because the weak band at ca. 610 nm unfortunately overlaps with the skirts of the intense absorption at 540 nm; as a consequence it is impossible to analyze the increase and the decrease in the intermediate. Thus, the present paper reports only the observation of the coloration. Though the coloration is likely to indicate the presence of a charge-transfer intermediate, the establishment of the nature of the absorption needs further study.

In order to see whether this phenomenon could be observed in other cases, the mixtures of *ap*-**1** and methanesulfenyl chloride, *sp*-**1** and benzeneselenenyl chloride, and *ap*-**1** and benzeneselenenyl chloride were submitted to the search of the charge-transfer intermediates. To the limit of our instrument, we could not detect any evidence for the existence of any absorption in the longer wavelength. This is an indication either that there are no such intermediates involved in these mixtures or that the lifetime of the intermediate is too short for the detection by the instrument.

Although charge-transfer intermediates are reported in the cases of olefin–halogen mixtures[30)] and are supported by theoretical calculations,[31,32)] no such report for the addition of chalcogenyl halides has been published to the best of our knowledge. Study to clarify whether this generally occurs or this is an exceptional case is in progress.

Experimental

The product distribution was determined by ^{1}H NMR spectra, which were measured with use of a Varian Gemini 300 spectrometer that operated at 300.1 MHz, before separation of the products. The product ratios shown in Tables 1, 2, and 3 are averages of 3 runs. Identification of the product was carried out by comparing the ^{1}H NMR spectra with authentic specimens, when known, or by elemental analysis or high resolution mass spectra together with ^{1}H NMR spectra, when unknown. High resolution mass spectra were obtained on a JEOL MStation-700 spectrometer. Melting points are not corrected.

Reaction of *ap*-1-(9-Fluorenyl)-2-(1-methylethenyl)naphthalene (*ap*-1) with *p*-Toluenesulfenyl Chloride in Carbon Tetrachloride. To a solution of 141 mg (0.425 mmol) of *ap*-**1**[2)] in 15 mL of carbon tetrachloride was added a solution of 0.638 mmol of *p*-toluenesulfenyl chloride[33)] in 3 mL of carbon tetrachloride with ice-cooling. The mixture was allowed to react for 15 min with stirring at that temperature, washed with saturated aqueous sodium hydrogencarbonate, and dried over magnesium sulfate. The solvent was evaporated in vacuo and a part of the residue was submitted to analysis of the products by ^{1}H NMR spectroscopy. The main

part of the product was submitted to preparative TLC on silica gel (4 : 1 hexane–ethyl acetate eluent) and the starting material, *sp*-1-(9-fluorenyl)-2-[1-(*p*-tolylthiomethyl)ethenyl]naphthalene (*sp*-**2**: R = *p*-$CH_3C_6H_4$, Y = S), and crude *sp*-2-[1-chloro-1-methyl-2-(*p*-tolylthio)ethyl]-1-(9-fluorenyl)naphthalene (*sp*-**3**: R = *p*-$CH_3C_6H_4$, X = Cl, Y = S) were separated, the R_f of *sp*-**2** being 0.78. Compound *sp*-**3** (R = *p*-$CH_3C_6H_4$, X = Cl, Y = S) was easily decomposed on chromatography and could not be purified further. On standing *sp*-**3** (R = *p*-$CH_3C_6H_4$, X = Cl, Y = S) lost hydrogen chloride slowly to afford *sp*-**2** (R = *p*-$CH_3C_6H_4$, Y = S). Thus this compound was identified by hydrolysis to afford the stable hydroxy compound and by oxidation to a corresponding sulfone which was also stable. See the following sections.

***sp*-2 (R = *p*-$CH_3C_6H_4$, Y = S):** Recrystallized from dichloromethane–hexane, mp 50—51 °C. Found: C, 87.42; H, 5.71%. Calcd for $C_{33}H_{26}S$: C, 87.18; H, 5.76%. ^{1}H NMR ($CDCl_3$) δ = 2.25 (3H, s), 4.05 (2H, s), 5.39 (1H, d, J = 1.4 Hz), 5.56 (1H, d, J = 1.4 Hz), 5.68 (1H, s), 6.42 (1H, dd, J = 0.8 and 8.7 Hz), 6.83 (1H, ddd, J = 1.3, 6.8, and 8.4 Hz), 6.97 (2H, d, J = 7.9 Hz), 7.11—7.25 (5H, m), 7.37—7.44 (3H, m), 7.72 (1H, d, J = 7.5 Hz), 7.55 (1H, d, J = 6.9 Hz), 7.78 (2H, d, J = 8.2 Hz), 7.93 (2H, d, J = 7.6 Hz).

***sp*-3 (R = *p*-$CH_3C_6H_4$, X = Cl, Y = S):** ^{1}H NMR ($CDCl_3$) δ = 2.30 (3H, s), 2.47 (3H, s), 3.89 and 4.38 (2H, ABq, J = 12.6 Hz), 6.49 (1H, d, J = 8.8 Hz), 6.73 (1H, s). Other aromatic proton signals were not identified.

Time Dependence of the Formation Ratios of *sp*-2 to *sp*-3. A solution of 18.5 mg (5.56×10^{-5} mol) of *ap*-**1** in 0.50 mL of chloroform-*d* containing 0.05% TMS was mixed with the same mole amount of *p*-toluenesulfenyl chloride in 0.543 mL of carbon tetrachloride at 0 °C in an NMR sample tube: The progress of the reaction was monitored by ^{1}H NMR spectrum at the same temperature. The following ratios, *sp*-**3**/*sp*-**2**, were observed (time in min given in parentheses): 6.7 (10), 6.6 (20), 5.6 (30), 7.5 (60). The same reaction at 24 °C showed the decrease of the ratio to 2.0 after 60 min and 1/15 after 10 h.

***sp*-1-(9-Fluorenyl)-2-[1-hydroxy-1-methyl-2-(*p*-tolylthio)ethyl]naphthalene (*sp*-6: R = *p*-$CH_3C_6H_4$).** The reaction products obtained as above from 1.72 g of *ap*-**1**[2] were treated with acetonitrile to remove difficultly soluble *ap*-**1** and other materials derived from *p*-toluenesulfenyl chloride. The solvent was evaporated in vacuo to yield 1.67 g of a product mixture, which was taken up in 40 mL of tetrahydrofuran. The solution was stirred for 15 h after adding 4 mL of water to it. The solvent was evaporated and the residue was treated with aqueous sodium hydrogencarbonate. The mixture was extracted with ethyl acetate and the extract dried over magnesium sulfate. After evaporation of the solvent, the residue was submitted to TLC on silica gel with 25 : 1 hexane–ethyl acetate eluent, when 9% of the hydroxy compound (*sp*-**6**: R = *p*-$CH_3C_6H_4$) and 48% *sp*-**2** (R = *p*-$CH_3C_6H_4$, Y = S) were obtained. The desired compound melted at 154.5—155.5 °C after recrystallization from dichloromethane–hexane. Found: C, 83.68; H, 6.03%. Calcd for $C_{33}H_{28}OS$: C, 83.68; H, 5.97%. ^{1}H NMR ($CDCl_3$) δ = 2.00 (3H, s), 2.28 (3H, s), 3.40 (1H, s), 3.60 and 4.10 (2H, ABq, J = 13.2 Hz), 6.44 (1H, dd, J = 0.8 and 8.7 Hz), 6.72 (1H, s), 6.78 (1H, ddd, J = 1.4, 6.7, and 8.7 Hz), 7.00 (2H, dd, J = 0.8 and 8.6 Hz), 7.11—7.20 (5H, m), 7.27—7.31 (2H, m), 7.36—7.43 (2H, m), 7.69 (1H, dd, J = 0.9 and 8.0 Hz), 7.75 and 7.79 (2H, ABq, J = 8.9 Hz), 7.95 (2H, dd, J = 0.9 and 7.5 Hz).

Oxidation of the Products from *ap*-1 and *p*-Toluenesulfenyl Chloride. The reaction mixture obtained as above from 517 mg (1.56 mmol) of *ap*-**1** was treated with acetonitrile. The soluble part (193 mg) was taken up in 30 mL of dichloromethane after evaporating the acetonitrile. A solution of 414 mg (2.04 mmol) of mCPBA in 30 mL of dichloromethane was added and the mixture was stirred for 30 min at room temperature. The reaction mixture was washed with aqueous sodium hydrogencarbonate and dried over magnesium sulfate. The solvent was evaporated and the residue was submitted to TLC on silica gel with 4 : 1 hexane–ethyl acetate eluent, when 13% chloro–sulfone (*sp*-**8**: R = *p*-$CH_3C_6H_4$) and 12% ene-sulfone (*sp*-**7**: R = *p*-$CH_3C_6H_4$) were obtained, the R_f's being 0.59 and 0.50 respectively.

***sp*-2-[1-Chloro-1-methyl-2-(*p*-tolylsulfonyl)ethyl]-1-(9-fluorenyl)naphthalene (*sp*-8: R = *p*-$CH_3C_6H_4$):** Recrystallized from dichloromethane–hexane, mp 153—154 °C. Found: C, 75.91; H, 5.18%. Calcd for $C_{33}H_{27}ClO_2S$: C, 75.77; H, 5.20%. ^{1}H NMR ($CDCl_3$) δ = 2.35 (3H, s), 2.78 (3H, s), 4.29 and 4.38 (2H, ABq, J = 14.0 Hz), 6.34 (1H, s), 6.44 (1H, d, J = 8.6 Hz), 6.78 (1H, ddd, J = 1.4, 6.7, and 8.3 Hz), 7.12—7.25 (7H, m), 7.29—7.46 (2H, m), 7.69 (2H, d, J = 8.5 Hz), 7.72 (1H, d, J = 7.7 Hz), 7.84 and 7.90 (2H, ABq, J = 8.8 Hz), 7.92 and 7.96 (2H, ABq, J = 7.7 Hz).

***sp*-1-(9-Fluorenyl)-2-[1-(*p*-tolylsulfonylmethyl)ethenyl]naphthalene (*sp*-7: R = *p*-$CH_3C_6H_4$):** Recrystallized from dichloromethane-hexane, mp 135.5—136.5 °C. Found: C, 81.48; H, 5.35%. Calcd for $C_{33}H_{26}O_2S$: C, 81.45; H, 5.39%. ^{1}H NMR ($CDCl_3$) δ = 2.38 (3H, s), 4.34 (2H, s), 5.46 (1H, s), 5.71 (1H, s), 5.72 (1H, s), 6.39 (1H, d, J = 9.1 Hz), 6.83 (1H, ddd, J = 1.4, 6.8, and 8.3 Hz), 7.09 (2H, d, J = 7.5 Hz), 7.15—7.25 (5H, m), 7.39 (1H, d, J = 7.4 Hz), 7.42 (2H, d, J = 8.5 Hz), 7.71 (1H, d, J = 7.9 Hz), 7.75 (1H, d, J = 6.9 Hz), 7.78 (2H, d, J = 8.3 Hz), 7.93 (2H, d, J = 7.7 Hz).

Reaction of *sp*-1-(9-Fluorenyl)-2-(1-methylethenyl)naphthalene with *p*-Toluenesulfenyl Chloride in Carbon Tetrachloride. The reactions were carried out similarly to the methods described for the reactions of the *ap*-isomer. The only product obtained was *ap*-1-(9-fluorenyl)-2-[1-(*p*-tolylthiomethyl)ethenyl]naphthalene (*ap*-**2**: R = *p*-$CH_3C_6H_4$: Y = S) together with the recovered starting material, the R_f's being 0.50 and 0.62, respectively, after silica-gel TLC with 4 : 1 hexane–ethyl acetate eluent. It melted at 44 °C after recrystallization from dichloromethane–hexane. Found: C, 87.45; H, 5.62%. Calcd for $C_{33}H_{26}S$: C, 87.18; H, 5.76%. ^{1}H NMR ($CDCl_3$) δ = 2.26 (3H, s), 2.76 (2H, s), 3.80 (1H, app s), 4.34 (1H, d, J = 1.3 Hz), 6.10 (1H, s), 6.98 (4H, app s), 7.15—7.25 (5H, m), 7.28—7.40 (2H, m), 7.59 (1H, ddd, J = 1.1, 6.9, and 8.1 Hz), 7.67 (1H, ddd, J = 1.4, 6.8, and 8.3 Hz), 7.77 (1H, d, J = 7.8 Hz), 7.78 (2H, d, J = 7.5 Hz), 7.95 (1H, dd, J = 1.1 and 7.9 Hz), 8.60 (1H, d, J = 8.5 Hz).

Reaction of *ap*-1-(9-Fluorenyl)-2-(1-methylethenyl)naphthalene with Methanesulfenyl Chloride in Carbon Tetrachloride. The reaction was carried out similarly with use of 139 mg of *ap*-**1** and 0.502 mmol of methanesulfenyl chloride[34,35] in 10 mL of carbon tetrachloride. The mixture of the reaction products was submitted to silica-gel TLC (4 : 1 hexane–ethyl acetate) to afford *sp*-1-(9-fluorenyl)-2-[1-(methylthiomethyl)ethenyl]naphthalene (*sp*-**2**: R = CH_3, Y = S) and *sp*-2-[1-chloro-1-methyl-2-(methylthio)ethyl]-1-(9-fluorenyl)naphthalene (*sp*-**3**: R = CH_3, X = Cl, Y = S) together with the recovered starting material, R_f of *sp*-**2** (R = CH_3, Y = S) being 0.75. Chromatography of the mixture decomposed *sp*-**3** (R = CH_3, X = Cl, Y = S) easily, mainly affording *sp*-**2** (R = CH_3, Y = S).

***sp*-2 (R = CH_3, Y = S):** Recrystallized from dichloromethane-hexane, mp 126 °C. Found: C, 85.87; H, 5.72%. Calcd for $C_{27}H_{22}S$: C, 85.67; H, 5.86%. ^{1}H NMR ($CDCl_3$) δ = 2.09 (3H, s), 3.66 (2H, s), 5.45 (1H, d, J = 1.7 Hz), 5.51 (1H, d, J = 1.4 Hz), 5.81 (1H, s), 6.43 (1H, dd, J = 0.8 and 8.6 Hz), 6.83 (1H, ddd, J = 1.4,

6.8, and 8.6 Hz), 7.16—7.23 (5H, m), 7.38—7.43 (2H, m), 7.44 (1H, d, J = 8.6 Hz), 7.72 (1H, d, J = 8.2 Hz), 7.78 (1H, d, J = 8.3 Hz), 7.94 (2H, d, J = 7.6 Hz).

***sp*-3 (R = CH_3, Y = S):** This compound was unstable and could not be purified to the analytical level. The following ^{1}H NMR data were recorded ($CDCl_3$) δ = 2.23 (3H, s), 2.52 (3H, s), 3.47 and 4.01 (2H, ABq, J = 13.0 Hz), 6.49 (1H, d, J = 8.7 Hz), 6.74 (1H, s). The aromatic proton signals were not identified.

Hydrolysis to Afford 1-(9-Fluorenyl)-2-[1-hydroxy-1-methyl-2-(methylthio)ethyl]naphthalene (*sp*-6: R = CH_3). The reaction mixture obtained from 1.01 mmol of *ap*-**1** was dissolved in 20 mL of tetrahydrofuran and stirred with 5 mL of water at room temperature for 12 h. After the same treatment described for compound *sp*-**6** (R = *p*-$CH_3C_6H_4$, Y = S), the products were separated by TLC on silica gel (2 : 1 hexane–dichloromethane eluent), R_f's being 0.78, 0.59, and 0.19 for compounds *ap*-**1**, *sp*-**2** (R = CH_3), and *sp*-**6** (R = CH_3), respectively. The desired compound was obtained in 20% yield and was recrystallized from dichloromethane–hexane, mp 121—122 °C. Found: C, 81.79; H, 6.03%. Calcd for $C_{27}H_{24}OS$: C, 81.78; H, 6.10%. ^{1}H NMR ($CDCl_3$) δ = 1.99 (3H, s), 2.18 (3H, s), 3.17 and 3.72 (2H, ABq, J = 13.4 Hz), 3.48 (1H, s), 6.44 (1H, dd, J = 1.0 and 9.0 Hz), 6.78—6.80 (1H, m), 6.79 (1H, s), 7.14—7.22 (5H, m), 7.37—7.43 (2H, m), 7.68 (1H, dd, J = 1.6 and 8.5 Hz), 7.74 and 7.78 (2H, ABq, J = 8.7 Hz), 7.96 (2H, dd, J = 0.9 and 7.6 Hz).

Oxidation of the Reaction Products from *ap*-1 and Methanesulfenyl Chloride. This was carried out similarly as described for oxidation of the products from *ap*-**1** and *p*-toluenesulfenyl chloride. The mixture of the reaction products was separated by TLC on silica gel (2 : 1 hexane–ethyl acetate eluent) to afford 5% chloro sulfone (*sp*-**8**: R = CH_3), 25% ene-solfone (*sp*-**7**: R = CH_3), and 19% *ap*-**1**, R_f's being 0.44, 0.52, and 0.78, respectively.

2-[(1-Chloro-1-methyl-2-(methylsulfonyl)ethyl]-1-(9-fluorenyl)naphthalene (*sp*-8: R = CH_3): Recrystallized from dichloromethane–hexane, mp 156—157 °C. Found: C, 72.28; H, 5.20%. Calcd for $C_{32}H_{23}ClO_2S$: C, 72.55; H, 5.19%. ^{1}H NMR ($CDCl_3$) δ = 2.75 (3H, s), 2.94 (3H, s), 4.27 and 4.39 (2H, ABq, J = 14.1 Hz), 6.47 (1H, d, J = 8.8 Hz), 6.57 (1H, s), 6.81 (1H, ddd, J = 1.5, 6.8, and 8.9 Hz), 7.17—7.25 (5H, m), 7.40—7.48 (2H, m), 7.72 (1H, dd, J = 1.3 and 8.2 Hz), 7.85 (2H, s), 7.99 (2H, t, J = 8.5 Hz).

1-(9-Fluorenyl)-2-[1-(methylsulfonylmethyl)ethenyl]naphthalene (*sp*-7: R = CH_3): Recrystallized from dichloromethane–hexane, mp 154 °C. Found: C, 79.11; H, 5.28%. Calcd for $C_{27}H_{22}O_2S$: C, 79.00; H, 5.40%. ^{1}H NMR ($CDCl_3$) δ = 2.94 (3H, s), 4.31 (2H, s), 5.68 (1H, s), 5.86 (1H, d, J = 0.9 Hz), 5.90 (1H, d, J = 0.9 Hz), 6.44 (1H, dd, J = 0.8 and 8.7 Hz), 6.86 (1H, ddd, J = 1.3, 6.8, and 8.5 Hz), 7.13—7.23 (5H, m), 7.40—7.45 (2H, m), 7.57 (1H, d, J = 8.5 Hz), 7.73 (1H, d, J = 8.2 Hz), 7.83 (1H, d, J = 8.5 Hz), 7.95 (2H, d, J = 7.6 Hz).

Reaction of *sp*-1-(9-Fluorenyl)-2-(1-methylethenyl)naphthalene with Methanesulfenyl Chloride in Carbon Tetrachloride. This reaction was carried out similarly to the methods described for the *ap*-isomer. ^{1}H NMR spectra of the reaction products indicated that there were only two compounds, one of which was the starting material. These were isolated by TLC on silica gel with 4 : 1 hexane–ethyl acetate, R_f's being 0.62 and 0.82 for *ap*-**2** (R = CH_3, Y = S) and *sp*-**1**, respectively.

***ap*-2 (R = CH_3, Y = S):** It was an oil. HRMS Found: m/z 379.1542. Calcd for $C_{27}H_{23}{}^{32}S$: $(M+1)^+$, 379.1520. The following ^{1}H NMR data were collected ($CDCl_3$) δ = 1.74 (3H, s), 2.36 (2H, s), 3.84 (1H, d, J = 1.4 Hz), 4.35 (1H, d, J = 1.4 Hz), 6.11 (1H, s), 7.16—7.22 (4H, m), 7.25 (1H, d, J = 8.4 Hz), 7.35—7.40 (2H, m), 7.58 (1H, ddd, J = 1.0, 6.8, and 7.9 Hz), 7.67 (1H, ddd, J = 1.5, 6.8, and 8.3 Hz), 7.78 (1H, d, J = 8.5 Hz), 7.79 (2H, d, J = 7.6 Hz), 7.95 (1H, dd, J = 1.4 and 8.0 Hz), 8.60 (1H, d, J = 8.6 Hz).

Oxidation of the Reaction Product: This was carried out similarly as above with use of mCPBA. The reaction mixture was separated by TLC on silica gel with 2 : 1 hexane–ethyl acetate eluent, R_f being 0.22 for *ap*-**7** (R = CH_3). Compound *ap*-**7** (R = CH_3) was purified by recrystallization from dichloromethane-hexane, mp 155 °C. Found: C, 79.08; H, 5.44%. Calcd for $C_{27}H_{22}O_2S$: C, 79.00; H, 5.40%. ^{1}H NMR ($CDCl_3$) δ = 2.43 (3H, s), 2.73 (2H, s), 4.36 (1H, s), 4.78 (1H, s), 6.16 (1H, s), 7.21—7.25 (4H, m), 7.39—7.44 (2H, m), 7.43 (1H, d, J = 8.3 Hz), 7.62 (1H, ddd, J = 1.3, 6.9, and 8.1 Hz), 8.70 (1H, ddd, J = 1.5, 6.8, and 8.4 Hz), 7.83 (3H, d, J = 8.0 Hz), 7.97 (1H, dd, J = 1.3 and 7.6 Hz), 8.61 (1H, d, J = 8.5 Hz).

Reaction of Compound 1 with *p*-Toluenesulfenyl Chloride or Methanesulfenyl Chloride in Nitromethane. These reactions were carried out similarly to the methods described for carbon tetrachloride solutions. The typical procedure follows. To a solution of 96.4 mg (0.290 mmol) of *ap*-**1** in 5 mL of nitromethane was added 0.435 mmol of *p*-toluenesulfenyl chloride. The mixture was allowed to react for 15 min at 0 °C. The solvent was removed in vacuo and the residue was separated by TLC on silica gel. The results are summarized in Tables 1 and 2.

Reaction of *sp*-1 with Methanesulfenyl Bromide. To a solution of 102 mg (0.307 mmol) of *sp*-**1** in 6 mL of nitromethane was added 0.368 mmol of methanesulfenyl bromide[36] in 1 mL of nitromethane at 0 °C. The mixture was allowed to react at the temperature for 15 min. The results are shown in Table 2.

Reaction of *sp*-1 with Benzeneselenenyl Chloride. To a solution of 120 mg (0.359 mmol) of *sp*-**1** in 5 mL of chloroform was added 0.400 mmol of benzeneselenenyl chloride in 7 mL of chloroform at 0 °C. The mixture was allowed to react for 30 min at that temperature. The mixture was washed with aqueous sodium hydrogencarbonate and the solution was dried over anhydrous magnesium sulfate. The solvent was evaporated and the residue was submitted to TLC on silica gel with 8 : 1 dichloromethane–hexane eluent. *ap*-**2** (R = C_6H_5, Y = Se), *ap*-**9** (X = Cl), and *sp*-**1** exhibited R_f values of 0.24, 0.35, and 0.44, respectively.

ap-**9** (X = Cl) was identical with the authentic specimen[3] in every respect.

ap-1-(9-Fluorenyl)-2-[1-(phenylselenomethyl)ethenyl]naphthalene (*ap*-**2**: R = C_6H_5, Y = Se) was obtained as an oil. HRMS (FAB) Found: m/z 489.1159. Calcd for $C_{32}H_{25}{}^{80}Se$: $(M + 1)^+$, 489.1121. ^{1}H NMR ($CDCl_3$) δ = 2.77 (2H, s), 3.82 (1H, d, J = 1.3 Hz), 4.29 (1H, d, J = 1.2 Hz), 6.10 (1H, s), 7.10—7.21 (9H, m), 7.31 (1H, d, J = 8.4 Hz), 7.33—7.38 (2H, m), 7.57 (1H, ddd, J = 1.2, 6.8, and 8.0 Hz), 7.65 (1H, ddd, J = 1.5, 6.8, and 8.4 Hz), 7.76 (1H, d, J = 8.2 Hz), 7.78 (2H, dd, J = 1.0 and 7.6 Hz), 7.91 (1H, dd, J = 1.4 and 8.0 Hz), 8.59 (1H, d, J = 8.6 Hz).

When 2 molar amounts of benzeneselenenyl chloride were used, no *ap*-**2** (R = C_6H_5, Y = Se) was observed but *ap*-**9** (X = Cl) only, whereas when 0.5 molar amount of benzeneselenenyl chloride was used, the reaction yielded 63% unreacted *sp*-**1**, 9% *ap*-**9** (X = Cl), and 28% *sp*-**2** (R = C_6H_5, Y = Se). In addition to these compounds, diphenyl diselenide was always obtained. The R_f values in TLC with 8 : 1 hexane–dichloromethane eluent are 0.57, 0.47, 0.39, and 0.28 for diphenyl diselenide, *sp*-**1**, *ap*-**9** (X = Cl), and *ap*-**2** (R = C_6H_5, Y = Se), respectively.

Reaction of *ap*-2 (R = C_6H_5, Y = Se) with Benzeneselenenyl Chloride. To a solution of 46.9 mg (0.0962 mmol) of *ap*-**2**

(R = C_6H_5, Y = Se) in 3 mL of chloroform was added 0.115 mmol of benzeneselenenyl chloride in 1.5 mL of chloroform. The mixture was allowed to react for 15 min with heating under reflux. After the usual treatment, 26.1 mg of diphenyl diselenide and 32.5 mg of *ap*-**9** (X = Cl) were obtained.

Reaction of *ap*-1 with Benzeneselenenyl Chloride. This reaction was similarly carried out. TLC of the products with 8 : 1 hexane–dichloromethane afforded diphenyl diselenide, *ap*-**1**, *sp*-**9** (X = Cl), and *sp*-1-(9-fluorenyl)-2-[1-(phenylselenomethyl)ethenyl]naphthalene (*sp*-**2**: R = C_6H_5, Y = Se), the R_f's being 0.53, 0.36, 0.23, and 0.17, respectively. *sp*-**9** (X = Cl) was identical with the authentic specimen.[3] *sp*-**2** (R = C_6H_5, Y = Se), oil. HRMS (FAB) Found: *m/z* 489.1179. Calcd for $C_{32}H_{25}{}^{80}Se$: $(M+1)^+$, 489.1121. ^{1}H NMR ($CDCl_3$) δ = 4.09 (2H, s), 5.31 (1H, d, J = 1.3 Hz), 5.42 (1H, d, J = 1.3 Hz), 5.75 (1H, s), 6.42 (1H, d, J = 8.6 Hz), 6.83 (1H, ddd, J = 1.3, 6.9, and 8.5 Hz), 7.10—7.23 (8H, m), 7.37—7.49 (5H, m), 7.73 (1H, dd, J = 0.8 and 8.1 Hz), 6.79 (1H, d, J = 8.2 Hz), 7.93 (2H, d, J = 7.6 Hz).

Reaction of *sp*-1 with Benzeneselenenyl Bromide. The reaction was carried out similarly to the procedures described in the reactions of benzeneselenenyl chloride with one exception: The solution was heated under reflux for 15 min. *sp*-**1** afforded *ap*-2-[1-(bromomethyl)ethenyl]-1-(9-fluorenyl)naphthalene (*ap*-**9**: X = Br) as an exclusive product, which was identified by comparing the ^{1}H NMR spectra with the authentic specimen.[2] The reaction was very slow at 0 °C (See Table 2) and, even at refluxing temperature of chloroform, only 39% *ap*-**9** (X = Br) was detected after 20 min, while 61% unreacted *sp*-**1** was recovered.

Reaction of *ap*-1 with Benzeneselenenyl Bromide. This reaction was carried out as above, starting with 59.2 mg of *ap*-**1** and 0.214 mmol of benzeneselenenyl bromide. *sp*-**9** (X = Br) was obtained in 13% yield with 87% recovery of the starting material.

Reaction with Iodine–Diphenyl Diselenide Complex with 1. To a solution of 107 mg of *sp*-**1** in 3 mL of chloroform was added 0.388 mmol of iodine–diphenyl diselenide complex in 3 mL of chloroform. The mixture was heated under reflux for 15 min. The solution was washed with aqueous sodium hydrogencarbonate and dried over magnesium sulfate. After evaporation of the solvent, the residue was submitted to TLC on silica gel with 8 : 1 hexane–dichloromethane eluent. Neither 1-(9-fluorenyl)-2-[1-(iodomethyl)ethenyl]naphthalene (*ap*-**9**: X = I) nor 1-(9-fluorenyl)-2-[1-(phenylselenomethyl)ethenyl]naphthalene (*ap*-**2**: R = C_6H_5, Y = Se) was detected, but the exclusive product was 8,8-dimethyl-8,14c-dihydrodibenzo[*a*,*l*]aceanthrylene (**10**). The R_f values under the conditions were 0.59, 0.44, and 0.39 for diphenyl diselenide, *sp*-**1**, and compound **10**, respectively. Compound **10** was recrystallized from THF–hexane, mp 148—150 °C. Found: C, 93.75; H, 6.11%. Calcd for $C_{26}H_{20}$: C, 93.94; H, 6.06%. ^{1}H NMR ($CDCl_3$) δ = 1.66 (3H, s), 2.01 (3H, s), 5.38 (1H, s), 7.33—7.51 (6H, m), 7.80 and 7.84 (2H, ABq, J = 8.8 Hz), 7.81—7.85 (1H, m), 7.89 (1H, dd, J = 1.5 and 6.9 Hz), 8.16 (1H, d, J = 7.6 Hz), 8.80 (1H, dd, J = 0.8 and 8.5 Hz).

To examine the solvent effect, an appropriate solvent was used in the same amount as described above. The results are summarized in Table 3. For benzene and carbon tetrachloride, the reaction mixture was heated under reflux for 20 min, while solutions were heated at 70 °C for 20 min for acetonitrile, chlorobenzene, and chloroform solvent.

Reaction of *sp*-1 with Hydrogen Bromide. A solution of *sp*-**1** (380 mg or 1.14 mmol) in 10 mL of benzene containing 1.71 mmol of hydrogen bromide was allowed to stand a week at room temperature and then was washed with aqueous sodium hydrogencarbonate. After removal of the solvent, the residue was submitted to TLC with hexane eluent; two spots were obtained. The first spot (R_f 0.39) was recovered *sp*-**1** and the second (R_f 0.26) was 8,8-dimethyl-8,14c-dihydrodibenzo[*a*,*l*]aceanthrylene (**10**). It was identical with the compound obtained by treatment of *sp*-**1** with the iodine–diphenyl diselenide complex.

Oxidation of 2 (R = C_6H_5, Y = Se) with *m*-Chloroperoxybenzoic Acid. To a solution of 41.8 mg of *ap*-**2** (R = C_6H_5, Y = Se) in 6 mL of dichloromethane was added a solution of 18.6 mg (0.108 mmol) of mCPBA. The mixture was stirred for 30 min at room temperature. The mixture was washed with aqueous sodium hydrogencarbonate and dried over magnesium sulfate. The solvent was evaporated and the residue was submitted to TLC on silica gel with 4 : 1 hexane–ethyl acetate to separate the desired compound from the starting material. The R_f values for *sp*-**11** and *ap*-**2** (R = C_6H_5, Y = Se) were 0.36 and 0.74, respectively. The yield was 63% with 29% recovery of the starting material. Compound *sp*-**11** was purified by recrystallization from dichloromethane–hexane, mp 199.5–200.5 °C. Found: 89.67; H, 5.87%. Calcd for $C_{26}H_{20}O$: C, 89.62; H, 5.79%. ^{1}H NMR ($CDCl_3$) δ = 0.17 (1H, t, J = 7.0 Hz), 3.60 (2H, br s), 3.71 (1H, dd, J = 1.5 and 2.9 Hz), 4.45 (1H, dd, J = 1.8 and 3.2 Hz), 6.09 (1H, s), 7.02 (1H, d, J = 8.4 Hz), 7.21—7.27 (4H, m), 7.39—7.44 (2H, m), 7.60 (1H, ddd, J = 1.2, 6.8, and 8.0 Hz), 7.69 (1H, ddd, J = 1.5, 6.8, and 8.4 Hz), 7.77—7.38 (3H, m), 7.96 (1H, dd, J = 1.4 and 8.0 Hz), 8.61 (1H, d, J = 8.6 Hz).

Similar oxidation of *sp*-**2** (R = C_6H_5, Y = Se) afforded 81% hydroxy compound (*sp*-**11**), which was purified by TLC, the eluent being 4 : 1 hexane–ethyl acetate. The R_f values were 0.71 and 0.41 for *sp*-**2** (R = C_6H_5, Y = Se) and *sp*-**11**, respectively. It was an oil and its identity was established by isomerization by rotation to *ap*-**11**. HRMS(FAB) Found: *m/z* 349.1586. Calcd for $C_{26}H_{21}O$: $(M+1)^+$, 349.1593. ^{1}H NMR ($CDCl_3$) δ = 1.72 (1H, br s), 4.60 (2H, br s), 5.45 (1H, dd, J = 1.4 and 2.9 Hz), 5.66 (1H, dd, J = 1.2 and 3.4 Hz), 5.79 (1H, s), 6.45 (1H, dd, J = 0.8 and 8.6 Hz), 6.85 (1H, ddd, J = 1.4, 6.8, and 8.5 Hz), 7.13—7.24 (5H, m), 7.38—7.43 (2H, m), 7.43 (1H, d, J = 8.6 Hz), 7.73 (1H, d, J = 8.0 Hz), 7.79 (1H, d, J = 8.5 Hz), 7.94 (2H, d, J = 7.7 Hz).

Thermal Isomerization of 2 and 11. A solution of 118 mg of *ap*-**2** (R = CH_3, Y = S) in 25 mL of toluene was heated under reflux for 7 h. After the usual treatment, the product was analyzed by ^{1}H NMR which showed the population ratio, *sp*/*ap*, of 14 : 1. These mixtures could be separated to respective rotamers by TLC with 4 : 1 hexane–dichloromethane, R_f's being 0.42 and 0.37 for *ap* and *sp* isomers respectively. Isomerization of the hydroxy compound (**11**) and phenylselenenyl compound (**2**: R = C_6H_5, Y = Se) was similarly carried out and the population ratios, *sp*/*ap*, of 14 : 1 and 13 : 1 were obtained, respectively. Isomerization of **2** (R = *p*-$CH_3C_6H_4$, Y = S) was carried out as carbon tetrachloride solutions by heating for 27 h under reflux. Under these conditions, the same population ratios, *sp*/*ap* = 19 : 1, were obtained by starting from either of the two isomers.

UV-vis Absorptions and Stopped Flow Measurements. UV-vis spectra at low temperatures were measured on a Hitachi U-3000 spectrometer equipped with an Oxford Cryostat DN1704 and rapid scan spectra on a Union Giken RA-401 Rapid Reaction Analyzer (Stopped Flow/Rapid Scan).

A 47.5 mmol L^{-1} solution of *sp*-**1** in nitromethane and a 46.9 mmol L^{-1} solution of methanesulfenyl chloride in the same solvent were prepared. Equal volumes of these solutions were mixed at −20 °C. The mixture showed an absorption with a maximum at ca. 610 nm after 4 min, with an absorbance of ca. 0.055. Although intensity of this absorption was almost the same after 6 min of the

mixing, the color began to fade after 8 min and became invisible after 60 min. A new absorption maximum was observed at 540 nm; it was persistent until the mixture was quenched with water and its absorbance was 0.315. The absorption at 610 nm was not due to *sp*-**1**, which is transparent above 350 nm, nor due to methanesulfenyl chloride which absorbs at 359 nm.

For the measurement on the RA-401 Analyzer, the solutions of the same concentrations were used. The measurement was carried out at 25 °C. The wavelength of the measurement was set at 620 nm to avoid the effects of the band at 540 nm as much as possible. However, it was not possible to avoid the effect of the band on that at 620 nm due to the weakness of the latter. The results are described in the Discussion.

Because evidence for the existence of intermediates for the mixtures of *sp*-**1** and benzeneselenenyl chloride, *ap*-**1** and methanesulfenyl chloride, and *ap*-**1** and benzeneselenenyl chloride, by the naked eye or by the UV-vis spectra at −20 °C was not available, the wavelength region of 405—790 nm was scanned with the RA-401 with 10 ms intervals at 0 °C. No evidence for the extra absorption was obtained, however.

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