Reactivities of Stable Rotamers. XXXVIII. Reaction of Chlorine with 1-(9-Fluorenyl)-2-(1-methylethenyl)naphthalene Rotamers: Outstanding Solvent Effects on Product Distribution and Ritter Type Reactions in Acetonitrile[1)]

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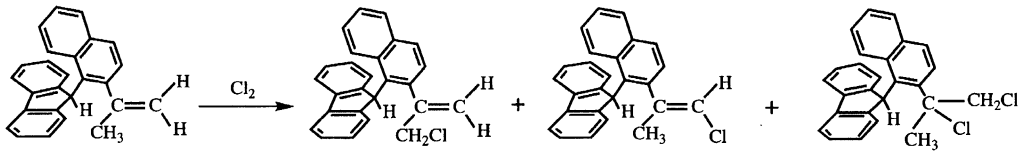
Reactions of the olefinic moiety of the title compounds with chlorine were done as carbon tetrachloride, nitromethane, and acetonitrile solutions. The *ap*-isomer afforded a mixture of the corresponding addition product and olefins that are derived by deprotonation of the intervening chloro-carbocation. The product distribution was strongly affected by the solvents, although chlorinated olefins are the main products in carbon tetrachloride. The *sp*-isomer yielded the chloro-olefins that are rotationally isomeric with these compounds in carbon tetrachloride. No cyclized compound, which is expected if the attack of the intermediate cation on a benzene ring closely located to it takes place, was detected under these conditions. By contrast, the reaction in nitromethane resulted in formation of the cyclized compound as a major product from the *sp* isomer. In acetonitrile, the reaction afforded the cyclized compound in a fair yield from the *sp*, but that of the *ap* isomer gave products that were derived by the Ritter type reactions, in addition to those observed in other solvents. The results are attributed to the stability of the intervening cations in these solvents. In the Ritter type reaction, the first evidence that deprotonation from the intervening acetonitrilium ion to produce a ketene imine was obtained. The bromine addition to the olefinic bond in the *sp*-isomer of the title compound revealed that the solvent seriously affects the yields of the cyclic compound as well as the ratios of two bromo-olefins.

Addition of bromine to the olefinic bond in 1-(9-fluorenyl)-2-(1-methylethenyl)naphthalene rotamers (*ap*-**1** and *sp*-**1**) has been reported.[2)] It showed very different properties of the rotamers toward the reaction: The rotamer gave an addition product in the case of *ap*, but the products were bromo-olefins and a cyclized product, which was derived by the attack of the intervening bromomethyl cation on the benzene ring, that was located closely, in the case of *sp*. The results were attributed to the structure of the intervening cation from the *sp*, which could not take the normal 3-membered bromonium ion structure due to the steric effects in the position where it was formed, and to the high instability of the addition product, if it were formed.

The same type of reaction of chlorine to the same double bond would be interesting for several reasons. First, a 3-membered ring chloronium ion is known to be less stable than the corresponding bromonium ion ring.[3)] Second, chloride ion, which should be the next attacking species in the reaction, is less nucleophilic toward carbocations but has more proton affinity than bromide ion. This should change the product distribution in the reaction from the bromine addition. Indeed, we had observed that even *ap*-2-ethenyl-1-(9-fluorenyl)naphthalene, which lacked the methyl group of compound **1**, yielded some olefins in the chlorination reaction.[4)] This paper reports the results of reactions of chlorine with compound **1** together with interesting solvent effects on the product distributions.

Reaction of Chlorine in Carbon Tetrachloride. Treatment of *ap*-**1** with chlorine in carbon tetrachloride afforded a mixture of *sp*-2-[1-(chloromethyl)ethenyl]-1-(9-fluorenyl)-naphthalene (*sp*-**2**), *sp*-2-(2-chloro-1-methyl-*E*-ethenyl)-1-(9-fluorenyl)naphthalene (*sp*-**3**), and the addition compound *sp*-2-(1,2-dichloro-1-methylethyl)-1-(9-fluorenyl)naphthalene (*sp*-**4**) in 84, 8 and 8% yields, respectively (Scheme 1). The feature is the low yield of the addition product and the high yield of compound *sp*-**2**. These may be attributed to the steric effects as well as the high proton affinity of the chloride ion. If the intervening cation takes a 3-membered ring chloronium ion structure, the steric effects make the energy state rather high. Together with the fact that the chloronium ion is not as stable as bromonium ion even in circumstances of less steric effects, the steric effects most likely cause opening of the chloronium ion (open β-chloro carbocation) or to force the intermediate to take a close structure to the open β-chloro carbocation, which makes the deprotonation main in the next step, because chloride ion is also known to be less nucleophilic but with more proton affinity than bromide ion to produce *sp*-**4**.

Treatment of *sp*-**1** with chlorine in carbon tetrachloride afforded 94% *ap*-2-[1-(chloromethyl)ethenyl]-1-(9-fluorenyl)-



ap-**1** *sp*-**2** *sp*-**3** *sp*-**4**

Scheme 1. Reaction of *ap*-**1** with chlorine.

naphthalene (*ap*-**2**) and 6% *ap*-2-(2-chloro-1-methyl-*E*-ethenyl)-1-(9-fluorenyl)naphthalene (*ap*-**3**) but the presence of (8*R**,14c*S**)-8-chloromethyl-8-methyl-8,14c-dihydrodibenzo[*a*,*l*]aceanthrylene (**5**) was not detected (Scheme 2). These results may again be attributed to the unfavorable steric conditions for formation of the chlorine-adduct and low nucleophilicity together with high proton affinity of the chloride ion. These conditions should make the lifetime of the intermediate cation so short that the intermediate cannot survive until it reacts with a nearby benzene ring.

We assumed that the intervening carbocation from *sp*-**1** and bromine could not be stabilized by bromine participation, because if it were to take place, the carbon atom would have to take an sp^3 hybridized structure, which would be too unstable in this position.[2] As a corollary the cation most probably exists as an open cation, which should be highly reactive. Deprotonation is an easy reaction to take place in the presence of chloride ion for this open cation, but cyclization to afford the cyclized compound **5** is slow because the cation must approach the π-system of the benzene ring: The distance between the olefinic π-system and that of the benzene ring is known to be about 3 Å by the X-ray study but the carbocation has to move to add to C_4 of the fluorene ring irrespective of the steric congestion.[2]

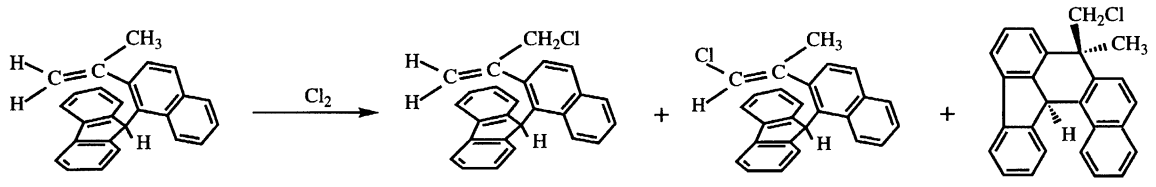
Solvent Effects on the Reaction Between *sp*-1 and Bromine. We hoped that by stabilizing the intervening carbocation, the cyclized compound (**5**) could be formed to a measurable extent. Thus we decided to examine solvent effects on the product formation. In the case of bromine, we observed formation of all three possible products, two olefins (*ap*-**6** and *ap*-**7**) and the cyclized product **8**, for *sp*-**1** (Scheme 3). We thought, therefore, it would be a reasonable starter to observe the solvent effects on the product formation for the reaction of *sp*-**1** with bromine. The results are shown in Table 1.

Two features can be pointed out from the results with various solvents. As we go from a solvent of low polarity to one of high polarity, the ratio of *ap*-2-[1-(bromomethyl)-ethenyl]-1-(9-fluorenyl)naphthalene (*ap*-**6**) to *ap*-2-(2-bromo-1-methyl-*E*-ethenyl)-1-(9-fluorenyl)naphthalene (*ap*-**7**) changes gradually, the former becoming less favored. The most dramatic solvent effects are found in the highly polar

Table 1. Solvent Effects on the Production Ratios of Olefins and the Cyclized Compounds in Treatment of *sp*-**1** with Bromine

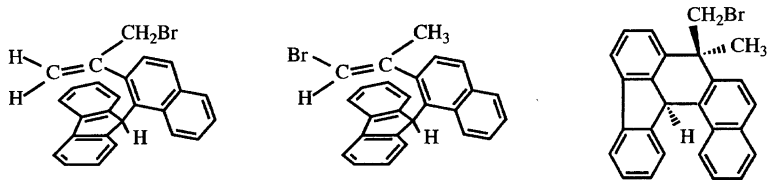
Solvent	ε[a]	*ap*-**6**	*ap*-**7**	**8**
CCl_4	2.23	58	30	12
$CH_3CO_2C_2H_5$	6.02	35	56	9
CH_3CO_2H	6.17	24	60	16
CH_2Cl_2	8.93	25	60	15
o-$Cl_2C_6H_4$	9.93	40	50	10
$ClCH_2CH_2Cl$	10.37	9	66	25
CH_3OH	32.66	24	60	16
CH_3NO_2	35.94	4	12	84
CH_3CN	35.94	7	15	78

a) Dielectic constant of solvent.



sp-**1** *ap*-**2** *ap*-**3** **5**

Scheme 2. Reaction of *sp*-**1** with chlorine.



ap-**6** *ap*-**7** **8**

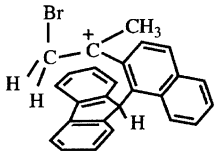
Scheme 3. Products from the reaction of bromine with *sp*-**1**.

solvents. That is, in acetonitrile and in nitromethane, the main product is now the cyclized compound, (8*R**,14c*S**)-8-bromomethyl-8-methyl-8,14c-dihydrodibenzo[*a*,*l*]aceanthrylene (**8**). The tendency of the ratio of *ap*-**6** to *ap*-**7** is held in these two polar solvents.

We wish to attribute these results to stabilization of the intervening cation **9** (Scheme 4). When we go from a less polar solvent to a more polar one, the lifetime of the open cation should increase. In a very nonpolar solvent such as carbon tetrachloride, the lifetime of the intermediate is so short that it may not have enough time to undergo internal rotation. When a bromine cation adds to the double bond of *sp*-**1**, it naturally comes from the least sterically hindered direction to produce a cation that has two bromomethyl hydrogens very close to the fluorene moiety. This makes a sterically protected situation for the bromomethyl hydrogens. Therefore, if the lifetime of the cation is very short, deprotonation will take place from the methyl group rather than from the bromomethyl group. Because the bromide anion has less proton affinity than chloride anion, deprotonation by the bromide anion should be slow, relatively speaking. Thus the intermediate has a chance to interact with the π-system of the fluorene ring to produce the cyclic compound **8**. When the solvent becomes polar, the lifetime of the intermediate becomes significantly long to make the internal rotation possible. This rotation makes the bromomethylene hydrogens more vulnerable to the attack of the bromide anion.

When the solvent is very polar, the positive charge originally placed on the β-carbon atom in **9** will be dispersed to the solvent molecules and the hydrogens in both the methyl and the bromomethyl groups become less vulnerable to the attack of the base. This makes the formation of the olefins, *ap*-**6** and *ap*-**7**, less favorable and the soft carbocation now has more affinity toward the soft π-base to favor the formation of the cyclic compound **8**.

Interpretation of the Results of Reactions of Chlorine with 1. From this standpoint, the chlorine case can be interpreted as follows. The intermediate from *sp*-**1** and a chlorine cation will be analogous to **9**. Thus we write the structure of the intermediate as **10** (Scheme 5). The chloride ion that reacts with the methyl or the chloromethyl hydrogens to produce the olefins is much more reactive than the bromide ion. Therefore, the lifetime of the intermediate **10** is still shorter than the case of **9** and bromide. Thus in carbon tetrachloride, the intermediate **10** almost exclusively produces the chloromethyl compond *ap*-**2**, which is a deprotonation product from the methyl group in **10**. As was discussed, the intermediate from *ap*-**1** can be a chloronium ion **11** or an open chain cation **11′** (Scheme 5). Although it is possible to argue that the intermediate will be an unsymmetrical 3-membered ring chloronium ion, if we consider both **11** and **11′**, it will mean that these extreme cases could cover the intermediate case, as has been done in the literature.[5]



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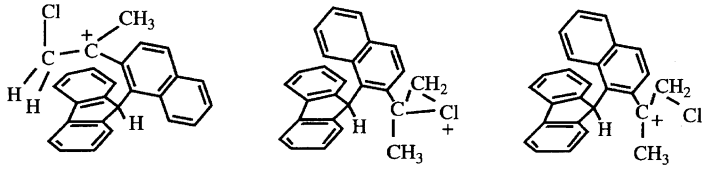
Scheme 4. Oversimplified intermediate of the reaction of bromine with *sp*-**1**.

We propose to assume that the chloronium ion **11** gives the addition product (*sp*-**4**), and the open cation **11′** does the olefins.[6] This assumption is supported by two facts. One is that the addition of bromine to *ap*-**1** gives the adduct as an exclusive product. This is interpreted as the result of the stable bromonium ion. Although we cannot rule out the presence of the open cation to a small extent, because its lifetime is short and the bromide ion is a poor protonophile, the open cation **9** gives olefins even in the case where the anion is bromide in the event of *sp*-**1**. The results presented in this paper suggest that the equilibrium between **11** and **11′** is in favor of the open cation in the chlorine case. This is reasonable because of the weak participation of the chloro group and the steric effects that disfavor the formation of the 3-membered ring chloronium ion.

Reaction of Chlorine in Polar Solvents. The results of the solvent effects on the product distribution from *sp*-**1** and bromine suggests that a very polar solvent could change the product distribution drastically even in the case of chlorine addition. Thus we did the reaction of chlorine with *ap*-**1** and *sp*-**1** in nitromethane and in acetonitrile. The results are shown in Tables 2 and 3. Although it might be argued that chlorine can react with acetonitrile, there is a report of this type of treatment in the literature,[7] which used a pretreatment of the solvent with chlorine. The results of the reactions in our cases show that the conversion of the substrate cannot reach 100% and there remains some unreacted compound.

Reaction of Chlorine in Nitromethane Solvent. The feature of the reaction of *ap*-**1** with chlorine in nitromethane is that the yield of the chloromethyl-olefin *sp*-**2** is considerably reduced, while that of the chloro-olefin *sp*-**3** is increased, and



10 **11** **11′**

Scheme 5. Possible intermediates in the reaction of chlorine with *sp*-**1** and *ap*-**1**.

Table 2. Solvent Effects on the Formation Ratio of Products in the Reaction of Chlorine with *ap*-**1**

Solvent	ε	*sp*-**2**	*sp*-**3**	**4**
CCl_4	2.23	84	8	8
CH_3NO_2	35.94	37	42	21
CH_3CN[a)]	35.94	42	19	6

a) There were four compounds, *sp*-**12**, *sp*-**13**, *sp*-**14**, and *sp*-**15**, in addition to those listed in the Table in 19,6,3, and 5% ratios, respectively.

Table 3. Solvent Effects on the Formation Ratio of Products in the Reaction of Chlorine with *sp*-**1**

Solvent	ε	*ap*-**2**	*ap*-**3**	**5**
CCl_4	2.23	94	6	0
CH_3NO_2	35.94	25	18	57
CH_3CN	35.94	20	20	60

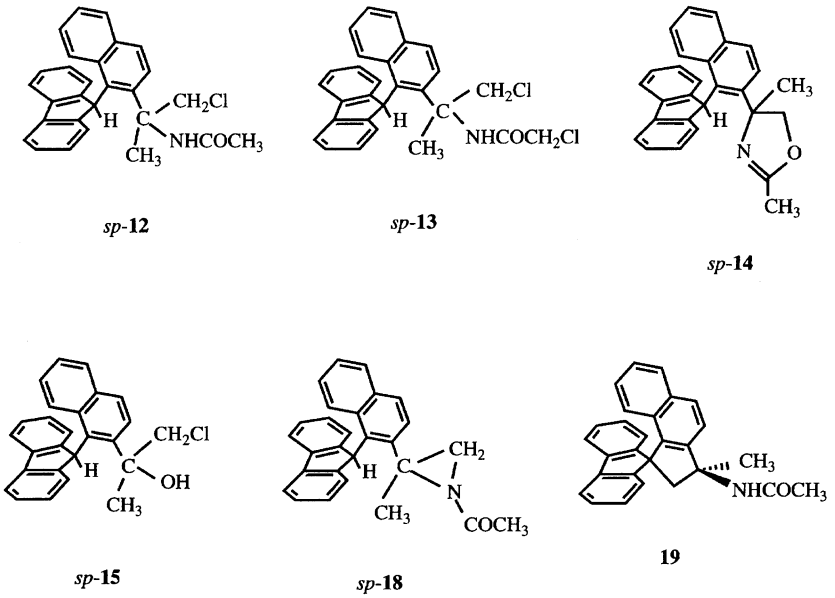
that of the addition product **4** increased significantly. These trends were what we expected from the results of the reaction of bromine in nitromethane, if we assume a rapid equilibrium between the chloronium ion and the open cation. The polar solvent increased the lifetime of the intermediate cations, especially the open one **11′**, and increased the chance of the reaction of the chloronium ion **11** with the chloride ion to form the adduct *sp*-**4**. The increase in the yield of *sp*-**3** and the decrease in that of *sp*-**2** are also reflections of the increased lifetime of the intermediate **11′**, which allows internal rotation before the reaction takes place. This is because the long lifetime of the open cation means that the cation has chances to go back to the chloronium ion and to undergo internal rotation by which the chance of the deprotonation reaction from the chloromethyl group increases relative to that in the methyl group.

In the case of *sp*-**1**, the yield of the chloromethyl compound *ap*-**2** drastically decreased, while that of the chloroolefin *ap*-**3** increased to a considerable extent. In addition, the cyclic compound, (8*R**,14c*S**)-8-chloromethyl-8,14c-dihydrodibenzo[*a*,*l*]aceanthrylene (**5**), is now a major product. These results are also understood by considering the stabilization of the open cation by solvation, as was discussed for the case of the reaction of bromine. It is worthy of note that chances of deprotonaiton decreased to such an extent that the cyclic compound **5** overwhelms even though the deprotonation reaction of the chloride anion is a fast reaction.

Reaction of Chlorine in Acetonitrile. These reactions are straightforwad for the case of *sp*-**1**, while they are complicated in the case of *ap*-**1** because of the occurrence of the Ritter reaction.

sp-**1** afforded almost the same distribution of the products as that in nitromethane as are seen in Table 3. This is reasonable because acetonitrile and nitromethane have almost the same dielectric constant and their stabilization of the cation by solvation is expected to be very similar in addition to the fact that the acetonitrile adduct to the intermediate cation **10** cannot be formed due to the steric reasons.

ap-**1**, in contrast to *sp*-**1**, afforded three nitrogen-containing compounds and a chlorohydrin *sp*-**15** in addition to normal olefins, *sp*-**2** and *sp*-**3**, and the chlorine-adduct (**4**) (Scheme 6). The formation of the chlorohydrin can be attributed to the presence of a minute amount of water which could not be removed by our technique. The structures of the nitrogen-containing compounds were determined, by spectroscopic data as well as others, as the acetamide derivative *sp*-**12**, a chloroacetamido compound *sp*-**13**, and an oxazoline derivative *sp*-**14**. If we count these nitrogen-containing compounds and the chlorohydrin *sp*-**15**, products derived from the intervening cation and the chloride ion or with the solvent molecule amounts to 39%. Therefore, although the yield of the adduct *sp*-**4** itself is low, we can conclude that



Scheme 6. Structure of products and related compounds.

the intermediate cation is well stabilized in acetonitrile also.

Structure Determination of Nitrogen-Containing Compounds and Reaction Mechanisms. The most abundant product contained an acetamido group judged from the elemental analysis and spectroscopic data, both IR and ^{1}H NMR. The formation of this compound is rationalized, if we consider the Ritter reaction,[8] in which the intermediate carbocation **11′** reacts with a molecule of solvent acetonitrile. The intermediate **16** will react with a molecule of water to produce the acetamido compound *sp*-**12** (Scheme 7).

The second compound showed similar ^{1}H NMR and IR spectra but one signal due to the methyl protons in its NMR spectra was missing. Instead there was a methylene group. Elemental analysis of the compound showed that it contained two chlorine atoms rather than one.

Since the formation of *sp*-**13** in a Ritter reaction was so unusual from the mechanistic view, we tried to see the structure by X-ray crystallography. Unfortunately, the crystals seemed to contain some anomalies and we could not obtain the residual factor better than 15%, unless we assumed that two molecules existed in the crystal, which had different configurations at the chiral center. This is probably because there is chirality about the $C_{9'}$–C_1 bond in addition to the presence of the chiral center. There could exist diastereomers in crystals. Thus we solved the structures by assuming that there are equal populations of two molecules in which the methyl and the chloromethyl groups, which are attached to the chiral center, are exchanged. Then we were able to obtain 0.085 and 0.081 residuals and weighted residuals, respectively. In Fig. 1 is shown an ORTEP drawing of one of the isomers thus obtained.

Although we cannot discuss the structure in detail from

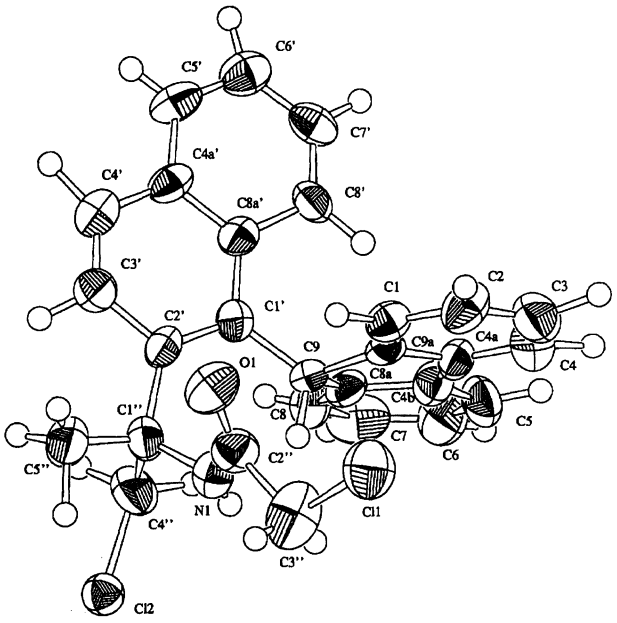
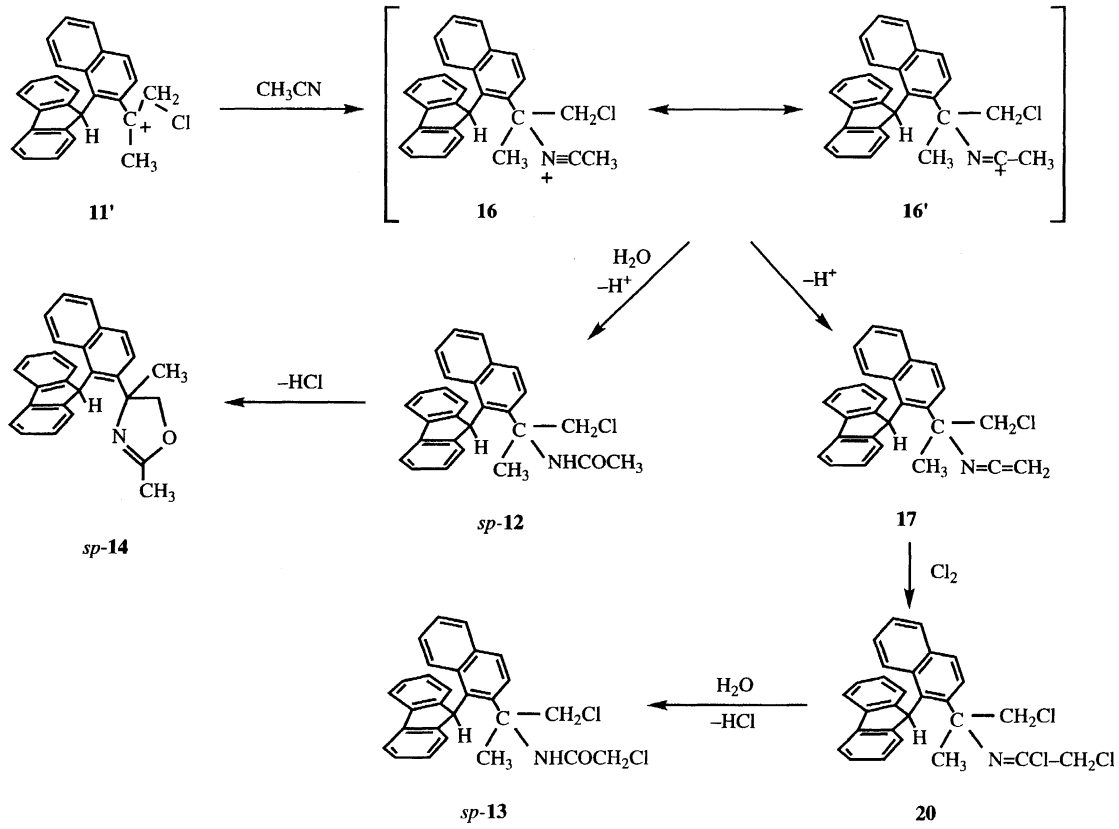


Fig. 1. ORTEP drawing of *sp*-2-[2-chloro-1-(chloroacetamido)-1-methylethyl]-1-(9-fluorenyl)naphthalene (*sp*-**13**) with thermal elipsoids at 50% probability.



Scheme 7. Reaction paths to products in the reaction of chlorine with *ap*-**1** in acetonitrile.

the X-ray data, yet we believe the gross structure (Fig. 1) is reliable. It is clear that the compound contained a chloroacetyl group instead of the acetyl in compound *sp*-**12**. The atomic coordinates for the isomer in Fig. 1 are given in Table 4. This structure (*sp*-**13**) is in conformity with all other relevant data.

The formation of this compound *sp*-**13** must be rationalized as is shown in Scheme 7. That is, deprotonation takes place from the intermediate **16** of the Ritter reaction to afford a ketene imine **17**. When addition of chlorine to the ketene imine takes place to produce **20**, it is hydrolyzed in the treatment of the product, the chloroacetamido compound *sp*-**13** being produced. Or the addition of chlorine cation to the C=C bond of **17** to produce the intermediate, which has a chloromethyl group instead of the the methyl of the intermediate **16**, is an alternative.

To the best our knowledge, deprotonation from the intermediate of type **16** has not been known in the Ritter reactions. This is probably due to two factors. Since the Ritter reaction has usually been done in strongly acidic media, the anion in the system had very poor proton affinity. Secondly even though deprotonation might take place, protonation which reproduces the adduct of type **16**, is rapid because the proton concentration in the system is high. The chlorination reported in this paper has provided a unique system that provides us insight into the Ritter reaction.

Table 4. Atomic Coordinates and Equivalent Isotropic Thermal Parameters of Non-Hydrogen Atoms in 1-(9-Fluorenyl)-2-[2-chloro-1-(chloroacetamido)-1-methylethyl]naphthalene [a)]

Atom	*x*	*y*	*z*	B_{eq} [b)]
Cl(1)	0.5293(3)	0.2110(1)	0.2015(3)	5.46(7)
Cl(2)	0.3275(4)	0.2026(2)	0.8573(4)	3.08(8)
O(1)	0.6678(6)	0.2443(3)	0.4789(7)	4.4(2)
N(1)	0.4681(7)	0.2469(3)	0.5936(7)	3.3(2)
C(1)	0.5140(8)	0.3574(3)	0.3095(9)	3.1(2)
C(1′)	0.5098(8)	0.3743(3)	0.6464(8)	2.7(2)
C(1″)	0.5090(9)	0.2699(3)	0.7324(9)	3.3(2)
C(2)	0.5067(9)	0.3670(4)	0.1655(9)	4.2(2)
C(2′)	0.5655(8)	0.3319(3)	0.7215(8)	2.9(2)
C(2″)	0.5493(9)	0.2327(3)	0.4878(10)	3.6(2)
C(3)	0.404(1)	0.3944(4)	0.1061(10)	4.6(2)
C(3′)	0.6814(9)	0.3430(4)	0.8054(9)	3.3(2)
C(3″)	0.475(1)	0.1976(5)	0.376(1)	5.6(3)
C(4)	0.2996(10)	0.4144(4)	0.1928(10)	4.4(2)
C(4′)	0.7325(8)	0.3943(4)	0.8216(10)	3.6(2)
C(4″)	0.388(1)	0.2732(4)	0.8271(10)	4.6(3)
C(4a)	0.3021(8)	0.4053(3)	0.3370(8)	2.9(2)
C(4a′)	0.6744(8)	0.4408(4)	0.7488(9)	3.1(2)
C(4b)	0.2146(8)	0.4214(4)	0.4494(9)	3.3(2)
C(5)	0.0944(9)	0.4511(4)	0.4476(10)	4.0(2)
C(5′)	0.7252(9)	0.4956(4)	0.7601(10)	4.0(2)
C(5″)	0.614(1)	0.2291(4)	0.793(1)	5.8(3)
C(6)	0.0323(9)	0.4652(4)	0.576(1)	4.6(3)
C(6′)	0.6729(9)	0.5389(4)	0.6882(10)	3.8(2)
C(7)	0.0876(9)	0.4484(4)	0.702(1)	4.8(3)
C(7′)	0.5686(9)	0.5288(4)	0.5970(9)	3.5(2)
C(8)	0.2047(9)	0.4161(4)	0.7040(9)	3.7(2)
C(8′)	0.5138(9)	0.4783(3)	0.5817(8)	3.1(2)
C(8a)	0.2668(7)	0.4024(3)	0.5805(9)	2.9(2)
C(8a′)	0.5660(7)	0.4304(3)	0.6594(8)	2.8(2)
C(9)	0.3876(8)	0.3663(3)	0.5549(9)	2.9(2)
C(9a)	0.4090(8)	0.3756(3)	0.3923(8)	2.9(2)

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

The ^{1}H NMR spectra of the third compound showed very similar patterns to those of compound *sp*-**12** but the NH proton was missing. Elemental analysis showed that the compound contained no chlorine atom. There are two candidates with structures that conform with these data. They are 2-(1-acetyl-2-methylaziridin-2-yl)-1-(9-fluorenyl)naphthalene (*sp*-**18**) and 2-(2,4-dimethyl-2-oxazolin-4-yl)-1-(9-fluorenyl)-naphthalene (*sp*-**14**) (Scheme 6). According to the literature, *N*-(2-haloethyl)acylamides undergo rearrangement to 2-alkyl(aryl)-2-oxazolines on treatment with base,[9—14] while the same compounds are obtained also by rearrangement of 1-acylaziridines under various conditions.[10,15—24] We tried the syntheses of *sp*-**14** by the reaction of *sp*-**12** with a base but it resulted in the formation of a spiro compound (**19**) due to facile deprotonation at the 9-position of the fluorene system followed by an intramolecular S_N2 type reaction. Likewise, application of the method of syntheses of acylaziridines by addition of iodine isocyanate[25] followed by reduction[26] and acetylation to produce *sp*-**18** failed because of an extremely slow reaction of iodine isocyanate with *ap*-**1**, probably due to steric effects.

The key to the structural assginment comes from the chemical properties: 2-Oxazoline is known to be basic and the compound is found to be basic. It forms a salt with perchloric acid and its ^{1}H NMR spectrum showed strong downfield shifts of signals due to both of the methyl groups and the methylene group. This suggests delocalization of a positive charge and is consistent with structure *sp*-**14** for the compound. The structure was thus assigned to a 2-methyl-2-oxazoline derivative *sp*-**14**. This cyclization occurred even by heating the acetamide *sp*-**12** in solution. This compound is also formed when the acetamide was treated with hydrogen chloride under these reaction conditions. Therefore, we believe this is a secondary product from the primary ones.

The formation of 2-oxazoline from 2-halo-1-acylamidoethane under acidic conditions is a hitherto unknown reaction. The mechanism must involve protonation on the chloro substitutent followed by intramolecular nucleophilic attack on the carbon that bears the chloro group by the oxygen of the acetamide group. Probably the special steric situation is the cause for the facile reaction of *sp*-**12** to *sp*-**14**.

Experimental

Melting points are not corrected. 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 Table 1 through 3 are averages of three runs. Identification of the products was done by comparing the ^{1}H NMR spectra with an authentic specimen, when known, or by elemental analyses together with

^{1}H NMR spectra and other relevant data, when unknown. Elemental analyses were done on a Perkin–Elmer 240C Analyzer. Elemental analysis of chlorine was done at the Analytical Center, Department of Chemistry, The University of Tokyo. IR spectra were recorded on a Hitachi I-2000 spectrometer.

Reaction of Chlorine with *ap*-1-(9-Fluorenyl)-2-(1-methylethenyl)naphthalene (*ap*-1). Carbon Tetrachloride Solvent. To a solution of 100 mg (0.304 mmol) of the *ap*-olefin in 5.00 mL of carbon tetrachloride, was gradually added 21.4 mg (0.304 mmol) of chlorine in carbon tetrachloride with ice cooling. The mixture was stirred for 1.5 h and washed with water. The solvent was evaporated and the formation ratio of *sp*-**2** : *sp*-**3** : *sp*-**4** was found to be 84 : 8 : 8. The residue was submitted to TLC with 1 : 3 dichloromethane–hexane eluent.

A fraction, of which R_f was 0.52, contained two materials. The richer material was purified by recrystallization from hexane-dichloromethane. This compound was identified as *sp*-2-[1-(chloromethyl)ethenyl]-1-(9-fluorenyl)naphthalene (*sp*-**2**), mp 130—131 °C, recrystallized from ether–hexane. Found: C, 85.32; H, 5.28%. Calcd for $C_{26}H_{19}Cl$: C, 85.12; H, 5.22%. ^{1}H NMR ($CDCl_3$) δ=4.56 (2H, s), 5.56 (1H, s), 5.77 (2H, s), 6.45 (1H, d, J = 8.7 Hz), 6.85 (1H, t, J = 8.5 Hz), 7.15—7.25 (5H, m), 7.39—7.47 (3H, m), 7.74 (1H, d, J = 8.2 Hz), 7.80 (1H, d, J = 8.4 Hz), 7.94 (2H, d, J = 7.7 Hz).

This fraction also contained the simple addition compound, *sp*-2-(1,2-dichloro-1-methylethyl)-1-(9-fluorenyl)naphthalene (*sp*-**4**), which was identified by comparing the ^{1}H NMR spectra with the authetic specimen (see blow).

The second fraction, R_f 0.69, afforded *sp*-2-(2-chloro-1-methyl-*E*-ethenyl)-1-(9-fluorenyl)naphthalene (*sp*-**3**), mp 159—160 °C, which was recrystallized from ether–hexane. Found: C, 85.14; H, 5.30%. Calcd for $C_{26}H_{19}Cl$; C, 85.12; H, 5.22%. ^{1}H NMR ($CDCl_3$) δ = 2.36 (3H, s), 5.64 (1H, s), 6.34 (1H, s), 6.45 (1H, d, J = 8.7 Hz), 6.85 (1H, t, J = 8.5 Hz), 7.11 (2H, d, J = 7.9 Hz), 7.17—7.24 (3H, m), 7.37—7.44 (3H, m), 7.72 (1H, d, J=8.2 Hz), 7.79 (1H, d, J=8.3 Hz), 7.95 (2H, d, J = 7.7 Hz).

Nitromethane Solvent. The reaction was done similarly as described above with the use of nitromethane, which was distilled after dissolving chlorine. The formation ratio of *sp*-**2** : *sp*-**3** : *sp*-**4** was 37 : 42 : 21. The products were separated by a Sanki Centrifugal Liquid–Liquid Partition Chromatograph with a 5 : 4 : 1 hexane–acetonitrile–chloroform system, when *sp*-**2**, *sp*-**4**, and *sp*-**3** were eluted in this order. It was also possible to separate them by TLC with 1 : 4 ethyl acetate–hexane eluent, R_f's being 0.65, 0.74, and 0.70, respectively for *sp*-**2** : *sp*-**3** : *sp*-**4**. *sp*-2-(1,2-Dichloro-1-methylethyl)-1-(9-fluorenyl)naphthalene (*sp*-**4**), mp 190—191 °C, was purified by recrystallization from dichloromethane–hexane. Found: C, 77.16; H, 4.97%. Calcd for $C_{26}H_{20}Cl_2$: C, 77.40; H, 5.00%. ^{1}H NMR ($CDCl_3$) δ = 2.50 (3H, s), 4.24 and 4.72 (2H, ABq, J = 10.8 Hz), 6.50 (1H, dd, J = 8.9 and 0.8 Hz), 6.63 (1H, s), 6.81 (1H, app t, J = 9.3 Hz), 7.19—7.24 (5H, m), 7.41—7.44 (2H, m), 7.70—7.81 (3H, m), 7.96—8.00 (2H, m).

Acetonitrile Solvent. This reaction was done similarly after treating the solvent with chlorine. The formation ratio was 42, 19, 6, 5, 19, 6, and 3% for *sp*-**2**, *sp*-**3**, *sp*-**4**, *sp*-**15**, *sp*-**12**, *sp*-**13**, and *sp*-**14**, respectively. The mixture was separated by TLC with 9 : 1 hexane–ethyl acetate eluent, R_f's being 0.65, 0.74, 0.70, 0.53, 0.18, 0.38, 0.28, respectively, for *sp*-**2**, *sp*-**3**, *sp*-**4**, *sp*-**15**, *sp*-**12**, *sp*-**13**, and *sp*-**14**.

sp-2-(1-Acetamido-2-chloro-1-methylethyl)-1-(9-fluorenyl)-naphthalene (*sp*-**12**), mp 198—206 °C (decomp), was purified by recrystallization from chloroform–hexane. Found: C, 78.64; H, 5.58; N, 3.29%. Calcd for $C_{28}H_{24}ClNO$: C, 78.94; H, 5.68; N, 3.29%. ^{1}H NMR ($CDCl_3$) δ = 1.88 (3H, s), 2.16 (3H, s), 4.28 and 4.79 (2H, ABq, J = 10.9 Hz), 6.11 (1H, br s), 6.39 (1H, d, J = 8.8 Hz), 6.41 (1H, s), 6.78 (1H, app t, J = 7.0 Hz), 7.07 (2H, d, J = 6.7 Hz), 7.17—7.21 (2H, m), 7.38—7.44 (3H, m), 7.70—7.75 (2H, m), 7.85 (1H, d, J = 8.8 Hz), 7.96 (2H, dd, J = 7.7 and 2.9 Hz). IR (Nujol) 1650, 3324 cm^{-1}.

sp-2-(2-Chloro-1-hydroxy-1-methylethyl)-1-(9-fluorenyl)naphthalene (*sp*-**15**), mp 106—108 °C, was purified by recrystallization from hexane. Found: C, 81.30; H, 5.52%. Calcd for $C_{26}H_{21}ClO$: C, 81.12; H, 5.50%. ^{1}H NMR ($CDCl_3$) δ = 2.04 (3H, s), 2.94 (1H, s), 4.10 and 4.42 (2H, ABq, J = 11.3 Hz), 6.45 (1H, d, J = 8.8 Hz), 6.70 (1H, s), 6.79 (1H, app t, J = 8.5 Hz), 7.11 (1H, d, J = 8.0 Hz), 7.17—7.22 (4H, m), 7.39—7.44 (2H, m), 7.68—7.82 (3H, m), 7.97 (2H, d, J = 6.8 Hz).

sp-2-[2-Chloro-1-(chloroacetamido)-1-methylethyl]-1-(9-fluorenyl)naphthalene (*sp*-**13**), mp 204—206 °C, was purified by recrystallization from THF–hexane. Found: C, 72.95; H, 5.07; N, 3.12; Cl, 15.67%. Calcd for $C_{28}H_{23}Cl_2NO$: C, 73.05; H, 5.04; N, 3.04; Cl, 15.67%. ^{1}H NMR ($CDCl_3$) δ = 2.21 (3H, s), 3.89 (2H, s), 4.23 and 4.78 (2H, ABq, J = 11.4 Hz), 6.23 (1H, s), 6.37 (1H, dd, J = 8.7 and 0.7 Hz), 6.78 (1H, app t, J = 7.2 Hz), 7.02—7.06 (2H, m), 7.15—7.25 (4H, m), 7.40—7.46 (2H, m), 7.70—7.77 (2H, m), 7.86 (1H, d, J = 9.1 Hz), 7.96 (2H, dd, J = 7.7 and 2.9 Hz). IR (Nujol) 1670, 3360 cm^{-1}.

sp-2-(2,4-Dimethyl-2-oxazolin-4-yl)-1-(9-fluorenyl)naphthalene (*sp*-**14**), mp 141—142 °C, was purified by recrystallization from 2-propanol–ether. Found: C, 86.26; H, 6.01; N, 3.59%. Calcd for $C_{28}H_{23}NO$: C, 86.34; H, 5.95; N, 3.60%. ^{1}H NMR ($CDCl_3$) δ = 1.89 (3H, s), 2.13 (3H, s), 4.64 and 4.76 (2H, ABq, J = 8.2 Hz), 5.56 (1H, s), 6.39 (1H, dd, J = 8.3 and 0.9 Hz), 6.76 (1H, app t, J = 5.3 Hz), 7.09—7.23 (5H, m), 7.43 (2H, t, J = 7.0 Hz), 7.70 (1H, d, J = 8.6 Hz), 7.81 (1H, d, J = 8.9 Hz), 7.97 (2H, app d, J = 8.0 Hz), 8.15 (1H, d, J = 8.8 Hz). IR (Nujol) 1680 cm^{-1}. The perchlorate salt of *sp*-**14** was prepared by treating a solution of *sp*-**14** in ether with 60% perchloric acid. It crystallized with 1.5 molecules of water of crystallization and decomposed at 191—211 °C. Found: C, 65.40; H, 4.95; N, 2.56%. Calcd for $C_{28}H_{24}NO_5 \cdot 3/2H_2O$: C, 65.05; H, 5.26; N, 2.71%. ^{1}H NMR ($CDCl_3$) δ = 1.62 (3H, br s), 2.33 (3H, s), 2.85 (3H, s), 4.83 (1H, s), 5.35 and 5.54 (2H, ABq, J = 9.3 Hz), 6.40 (1H, d, J = 8.8 Hz), 6.86 (1H, ddd, J = 8.5, 7.0, and 1.3 Hz), 7.04 (2H, t, J = 7.6 Hz), 7.18—7.30 (3H, m), 7.46 and 7.51 (2H, ABq, J = 7.2 Hz), 7.72 (1H, d, J = 8.7 Hz), 7.77 (1H, d, J = 7.9 Hz), 8.00 (3H, t, J = 8.8 Hz), 13.00 (1H, br s).

Reaction of Chlorine with the *sp*-Olefin. Carbon Tetrachloride Solvent. This reaction was done similarly as above. The formation ratio of *ap*-**2** : *ap*-**3** was 94 : 6. No **5** was detected. TLC with 1 : 3 dichloromethane–hexane eluent gave 2 spots, R_f's being 0.52 and 0.69.

The first fraction afforded *ap*-2-[1-(chloromethyl)ethenyl]-1-(9-fluorenyl)naphthalene (*ap*-**2**), mp 116—119 °C, which was purified by recrystallization from ether–hexane. Found: C, 85.32; H, 5.28%. Calcd for $C_{21}H_{19}Cl$: C, 85.12; H, 5.22%. ^{1}H NMR ($CDCl_3$) δ=3.26 (2H, s), 3.88 (1H, s), 4.60 (1H, s), 6.60 (1H, s), 7.18—7.23 (6H, m), 7.35—7.44 (2H, m), 7.58—7.72 (2H, m), 7.80 (2H, d, J = 9.0 Hz), 7.96 (1H, d, J = 8.5 Hz), 8.61 (1H, d, J = 7.5 Hz).

The second fraction afforded *ap*-2-(2-chloro-1-methyl-*E*-ethenyl)-1-(9-fluorenyl)naphthalene (*ap*-**3**), mp 121—122 °C. Found: C, 85.14; H, 5.30%. Calcd for $C_{26}H_{19}Cl$: C, 85.12; H, 5.22%. ^{1}H NMR ($CDCl_3$) δ = 1.55 (3H, s), 4.42 (1H, d, J = 1.5 Hz), 6.03 (1H, s), 7.05 (1H, d, J = 8.4 Hz), 7.18—7.26 (5H, m), 7.39 (2H, app dt, J = 5.5 and 3.0 Hz), 7.59 (1H, t, J = 7.0 Hz), 7.70 (1H, t, J = 7.0

Hz), 7.78 (2H, d, J = 7.8 Hz), 7.88 (1H, d, J = 8.6 Hz), 8.60 (1H, d, J = 8.4 Hz).

Nitromethane Solvent. The products from this reaction gave 4 spots in TLC with 1 : 4 ethyl acetate–hexane eluent, R_f's being 0.80, 0.76, 0.80, and 0.40 for *sp*-**1**, *ap*-**2**, *ap*-**3**, and **5**, respectively. The distribution ratio of *sp*-**1**, *ap*-**2**, *ap*-**3**, and **5** was thus 9 : 23 : 16 : 52%, respectively. The mixture of *sp*-**1** and *ap*-**3** thus obtained could be separated by preparative TLC with 100 : 1 hexane–ether eluent.

(8R^*,14cS^*)-8-Chloromethyl-8-methyl-8,14c-dihydrodibenzo-[*a*,*l*]aceanthrylene (**5**), mp 155—165 °C (decomp), was purified by recrystallization from THF–hexane. Found: C, 85.08; H, 5.22%. Calcd for $C_{26}H_{19}Cl$: C, 85.12; H, 5.22%. ^{1}H NMR ($CDCl_3$) δ = 1.67 (3H, s), 4.55 (2H, s), 5.36 (1H, s), 7.37—7.54 (6H, m), 7.68—7.74 (2H, m), 7.85—7.90 (3H, m), 8.12 (1H, d, J = 7.7 Hz), 8.80 (1H, dd, J = 8.1 and 1.2 Hz). The stereochemistry of **5** was determined by NOE experiments. Irradiation of the signal due to the 8-methyl protons increased the intensity of the signal due to 14c-H by 23.5%, but that of the methylene proton signal did not show a significant increase of the 14c-H signal.

Acetonitrile Solvent. This reaction afforded unreacted *sp*-**1**, *ap*-**2**, *ap*-**3**, and **5** in a 6 : 19 : 19 : 56 ratio. The separation of these products was done as is described above and their identity was established by comparing the ^{1}H NMR spectra with an authentic specimen.

Reaction of Bromine with *sp*-1 in Vaious Solvents. Solvents used in these reactions were purified by distillation before use. To a solution of *ap*-**1** (103 mg or 0.31 mmol) in 10.0 mL of an appropriate solvent was added bromine (55 mg or 0.34 mmol) in the same solvent. The reaction mixture was treated similarly as described for the reaction of chlorine. Identification of the products was done by comparing the ^{1}H NMR spectra with those reported.[2)]

Reaction of *sp*-12 with Potassium Hydroxide. To a solution of 216.3 mg (0.508 mmol) of *sp*-**12** in 30 mL of ethanol, was added a solution of 0.33 g (6.2 mmol) of potassium hydroxide in 20 mL of water and the mixture was heated under reflux for 36 h. After the usual treatment, 3-acetamido-3-methylspiro[benzo[*g*]-indane-1,9′-fluorene] (**19**) was obtained in 142.5 mg or 72% yield. It was recrystallized from dichloromethane–hexane, mp 218—230 °C (decomp). Found: C, 86.12; H, 5.89; N, 3.52%. Calcd for $C_{28}H_{23}NO$: C, 86.34; H, 5.95; N, 3.60%. ^{1}H NMR ($CDCl_3$) δ = 2.01 (6H, s), 2.80 and 3.35 (2H, ABq, J = 14.5 Hz), 5.95 (1H, br s), 6.50 (1H, dd, J = 8.5 and 1.0 Hz), 6.93 (1H, ddd, J = 8.3 6.9, and 1.3 Hz), 7.07 (1H, dd, J = 7.6 and 1.0 Hz), 7.14—7.20 (2H, m), 7.24 (1H, ddd, J = 8.1 6.9, and 1.1 Hz), 7.33—7.40 (3H, m), 7.59 (1H, d, J = 8.5 Hz), 7.77 (1H, d, J = 8.1 Hz), 7.82—7.89 (3H, m). IR (Nujol) 3236, 1634 cm^{-1}.

X-Ray Crystallography. Crystals used for the X-ray diffraction were grown from THF and hexane. A crystal of 0.20×0.20×0.30 mm size was mounted on a Rigaku AFC7R four circle diffractometer with Cu $K\alpha$ radiation (λ = 1.54178 Å). The scan mode was the ω–2θ method in the range of 2θ <120.1°, the scan rate being 16° min^{-1} and the scan width (1.42 + 0.30 tan θ)°. A total of 1972 reflections was collected and 1833 reflections were used for calculation. The structures were solved by the direct method and refined by the full-matrix least-square method by using the teXsan program. Some non-hydrogen atoms were refined anisotropically, while the rest were refined isotropically. Hydrogen atoms were included but not refined. The linear absorption coefficient, μ, for Cu $K\alpha$ radiation was 27.4 cm^{-1}. An empirical absorption correction based on azimuthal scans of several reflections was applied, which resulted in transmission factors from 0.82 to 1.00. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coefficient = 1.44014e−06). The function minimized was $\Sigma[w(|F_o| - |F_c|)^2]$ where $w = (\sigma_c^2|F_o|)^{-1}$. The following crystal data were obtained: Empirical formula $C_{28}H_{23}Cl_2NO$, F.W. 460.40, crystal system orthorhombic, a = 10.099(2), b = 23.784(2), c = 9.423(2) Å, V = 2263.4(5) Å^3, space group $P2_12_12_1$, Z = 4, D_{calcd} = 1.351 g cm^{-3}, R = 0.085, R_w = 0.081.

The complete $F_o - F_c$ data have been deposited as Document No. 69066 at the Office of the Editor of Bull. Chem. Soc. Jpn.

References

1) For the previous paper of this series, see: S. Toyota and M. Ōki, *Bull. Chem. Soc. Jpn.*, **69**, 177 (1996).

2) M. Ōki, K. Shionoiri, K. Otake, M. Ono, and S. Toyota, *Bull. Chem. Soc. Jpn.*, **66**, 589 (1993).

3) R. C. Fahey, *Top. Stereochem.*, **3**, 237 (1968).

4) M. Ōki, J. Tsukahara, Y. Sonoda, K. Moriyama, and N. Nakamura, *Bull. Chem. Soc. Jpn.*, **61**, 4303 (1988).

5) M.-F. Ruasse, *Acc. Chem. Res.*, **23**, 87 (1990).

6) If an open cation is produced, it is rather unstable in nonpolar solvents and deprotonation takes place very rapidly. Deprotonation from the chloronium ion can be considered rather slow because the cationic charge is not adjacent to the methyl or the chloromethyl group. Indeed, chloro-olefins are not formed in addition reactions of chlorine to normal olefins, in which the cyclic chloronium ion intermediate is proposed. When there is a rapid equilibrium between the open and the ring cations, the long lifetime in polar solvents means that the open-cation has chances to go back to the cyclic one, where the reaction takes place to produce the adduct. Solvation of the open cation in polar solvents also retards deprotonation by neutralizing the positive charge on the carbon and, when the solvent molecule leaves the cationic center, the movement being required for formation of the adduct, the rapid deprotonation takes place rather than the attack of the chloride ion on the cation.

7) R. M. Keefer and L. J. Andrew, *J. Am. Chem. Soc.*, **81**, 1063 (1959).

8) L. I. Krimen and D. J. Cota, *Org. React.*, **17**, 213 (1969).

9) A. A. Goldberg and W. Kelly, *J. Chem. Soc.*, **1948**, 1919.

10) S. S. Skorokhodov, S. G. Ershova, N. V. Mikhailova, and A. A. Vansheidt, *Zh. Obshch. Khim.*, **31**, 3626 (1961); *Chem. Abstr.*, **57**, 8555f (1962).

11) H. Cassebaum and K. Uhlich, *J. Prakt. Chem.*, **315**, 1057 (1973).

12) F. Franco and J. M. Muchowski, *J. Heterocycl. Chem.*, **17**, 1613 (1980).

13) J. Sicher, M. Tichy, F. Sipos, and M. Pankova, *Collect. Czech. Chem. Commun.*, **26**, 2418 (1961).

14) S. Winstein and R. Boschan, *J. Am. Chem. Soc.*, **72**, 4669 (1950).

15) H. E. Heine, *Angew. Chem.*, **74**, 772 (1962); *Angew. Chem., Int. Ed. Engl.*, **1**, 528 (1962).

16) C. U. Pitman, Jr., and S. P. McManus, *J. Org. Chem.*, **35**, 1187 (1970).

17) T. A. Folgia, L. M. Gregory, and G. Maerker, *J. Org. Chem.*, **35**, 3779 (1970).

18) P. Thyrum and A. R. Day, *J. Med. Chem.*, **8**, 107 (1965).

19) R. D. Guthrie and D. Murphy, *J. Chem. Soc.*, **1965**, 3828.

20) P. E. Fanta and E. N. Walsh, *J. Org. Chem.*, **31**, 59 (1965).

21) P. E. Fanta, R. J. Smat, and J. R. Krikau, *J. Heterocycl. Chem.*, **5**, 419 (1968).

22) P. E. Fanta and E. N. Walsh, *J. Org. Chem.*, **30**, 3574 (1964).

23) H. W. Heine, D. C. King, and L. A. Portland, *J. Org. Chem.*, **31**, 2662 (1966).
24) P. G. Mente, H. W. Heine, and G. R. Scharoubin, *J. Org. Chem.*, **33**, 4547 (1968).
25) A. Hassner and C. Heathcock, *Tetrahedron.*, **20**, 1037 (1964).
26) A. Hassner, M. E. Loeber, and C. Heathcock, *J. Org. Chem.*, **32**, 540 (1967).