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Dedicated to Full Member of the Russian Academy of Sciences I. P. Beletskaya on occasion of her jubilee
Michinori Oki appreciates continuous friendship of I. P. Beletskaya both in science and in IUPAC activities.

Reactivities of Stable Rotamers: XLIV. Ring-Opening Reactions of 1-(9-Fluorenyl)-2-(2-methyl-2-oxiranyl)naphthalene Rotamers With Acids and the Structure of Oxiranes

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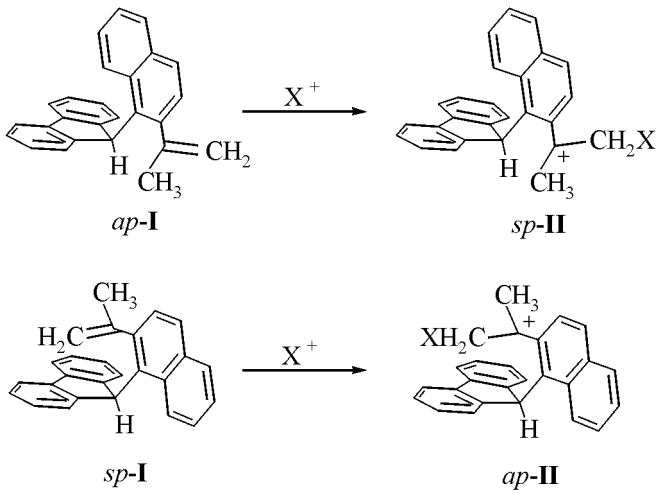
Abstract—X-ray crystallography of the *ap*-form of the 1-(9-fluorenyl)-2-(2-methyl-2-oxiranyl)naphthalene has revealed that the carbon atom of the oxirane which is connected to the naphthyl group in this compound is almost planar. The specific structural features of the epoxy ring in this compound are caused by sterical effects and by the presence of a π-system in the immediate vicinity of the oxirane ring. Certain differences have been found also in reactivity of rotational isomers of 2-X-substituted 1-[1-(9-fluorenyl)-2-naphthyl]-ethyl cations (X = O, S, Se). At X = O arose more deprotonation product from the α-position of the oxygen than in reactions of sulfur and selenium-containing analogs. Reactions of epoxides with zinc chloride almost exclusively gave the corresponding aldehydes.

The difference in reactivity showed by rotational isomers of 1-(9-fluorenyl)-2-(1-methylethenyl)-naphthalene (**I**) revealed in variation of structures and yields of products obtained therefrom is undoubtedly of great theoretical interest. The electrophilic additions to the double bond in alkene (**I**) is considered to afford β-substituted ethyl cations (**II**), the fate of which is determined by the stability of cation, the influence of substituent **X**, and the anions present in the system (Scheme 1). We have examined the reactions in the cases of β-X-substituted cations where **X** was bromine [3–5], chlorine [5], other halogen [7], sulfur [7], and selenium [7]. The feature of the reactions is that *ap*-rotamers (**I**) often afforded addition products whereas the *sp*-rotamers (**I**) never gave rise to addition products. The latter occurs because of the steric effects: In the space provided by the fluorene ring and the ethenyl group a quadri-coordinated carbon cannot be accommodated comfortably unless one of the four atoms attached to the carbon is hydrogen.

We thought it would be interesting to examine the effects of heteroatom where X is oxygen. Although it might not be easy to generate (*sp*-**II**) or (*ap*-**II**) where X is oxygen by direct method from **I**, the ring-opening reactions in oxiranes **IV** with proton acid should afford that kind of intermediates (**II**, X = O, or **III**) (Scheme 2) [8].

Thus we decided to prepare epoxides (*ap*-**IV**) and (*sp*-**IV**) by direct oxidation of olefins (**I**). Although

Scheme 1.



Rotamers of alkenes (**I**) and carbocations (**II**) arising in their reactions with $\mathbf{X}^+$.

* Preliminary communication see [1]. For preceding communication see [2].

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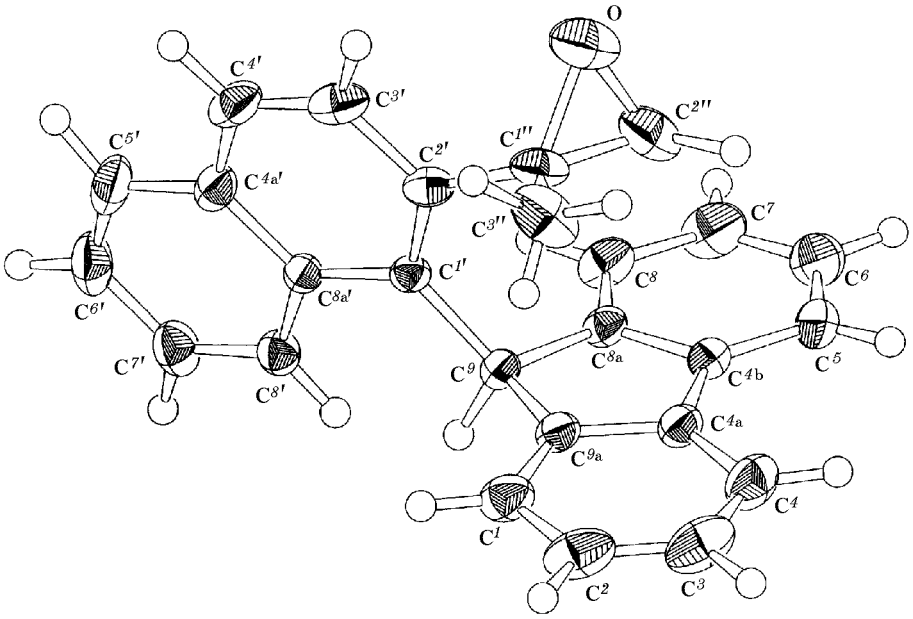
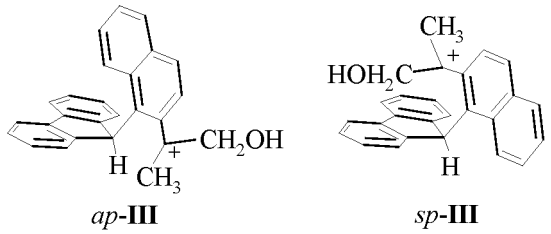


Fig. 1. Spatial arrangement of *ap*-1-(9-fluorenyl)-2-(2-methyl-2-oxyranyl)naphthalene (*ap*-**IV**).

some difficulties in preparing the *ap*-epoxide (*ap*-**IV**) were expected because of the steric effects described above, to our surprise, the reactions were smooth and the rates of formation (*ap*-**IV**) were even a little larger than those of formation of (*sp*-**IV**) (Scheme 3). However this does not mean that rotamer (*ap*-**IV**) is as stable as (*sp*-**IV**), because thermal equilibration results in (*sp*-**IV**)/(*ap*-**IV**) ratio equal to 36 : 1.

In order to find reasons for facile oxidation of alkene (*sp*-**I**) we first obtained X-ray structure of epoxide (*ap*-**IV**). The results of X-ray study of (*ap*-**IV**) are shown in Fig. 1 and in Table 1. In the structure we found that the oxirane carbon $C^{1''}$ which is attached to the naphthalene group forms an almost planar carbon which possesses four substituents excluding the ring oxygen atom. Planar quadri-coordinated carbons are not odd these days, as can be illustrated by a fact that there is even a review [9] which compiles these atoms, but these carbons are either very special or very difficult to prepare.

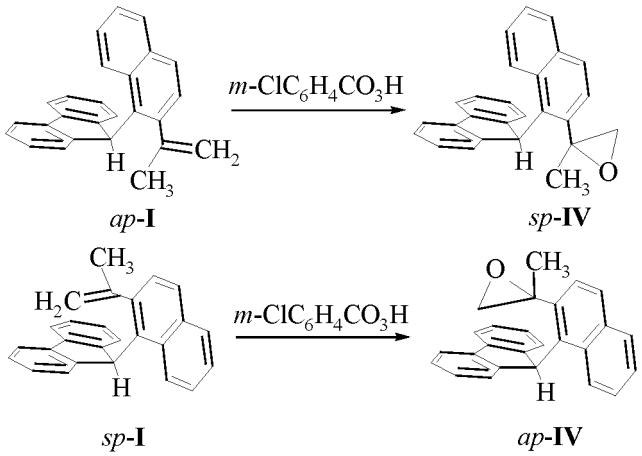
Scheme 2.



ap-**III** *sp*-**III**

It seems that we had single crystals of (*sp*-**IV**) as well, but unfortunately it was not possible to solve the X-ray diffraction patterns: We had an experience before, in the same series, that there were diastereomers possible for the *sp*-compound [5] because of the presence of chirality due to the fact that the naphthyl group does not bisect the fluorene but is tilted from the bisecting plane of the fluorene ring and the oxirane ring has a chiral center at C^{1}. In contrast, (*ap*-**IV**) though it has the same stereochemical elements as (*sp*-**IV**) has to take one conformation only with respect to the bisecting plane of the fluorine, due to the steric reasons which will be discussed later in this paper. We have taken care of

Scheme 3.



ap-**I** *sp*-**IV**

sp-**I** *ap*-**IV**

Table 1. Some structural parameters of epoxide (*ap*-**IV**)

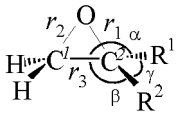
Bond	*l*, Å
$C^{1''}$-$C^{2''}$	1.483 (4)
$C^{1''}$-O	1.486 (3)
$C^{2''}$O	1.396 (4)
$C^{1''}$-$C^{3''}$	1.487 (4)
$C^{1''}$-$C^{2'}$	1.509 (3)
Bond anglea	**ω, deg**
$OC^{1''}C^{2''}$	56.1 (2)
$OC^{1''}C^{3''}$	112.4 (2)
$OC^{1''}C^{2'}$	113.1 (2)
$C^{2''}C^{1''}C^{3''}$	119.1 (2)
$C^{2''}C^{1''}C^{2'}$	120.5 (2)
$C^{3''}C^{1''}C^{2'}$	118.2 (2)
$C^{1''}OC^{2''}$	61.9 (2)
$OC^{2''}C^{1''}$	62.1 (2)
Nonbonding distance	***l*, Å**
$C^{1''}\cdots C^{1}$	3.766 (3)
$C^{1''}\cdots C^{4a}$	3.504 (3)
$C^{1''}\cdots C^{8a}$	3.468 (3)
$C^{1''}\cdots C^{9a}$	3.146 (3)
$C^{2''}\cdots C^{4a}$	3.355 (4)
$C^{2''}\cdots C^{4b}$	3.065 (4)
$C^{2''}\cdots C^{8a}$	3.132 (4)
$C^{2''}\cdots C^{9a}$	3.552 (4)

[a] The sum of three bond angles at $C^{1''}$ is equal to 357.8 (119.1+120.5+118.2).

these possibilities in trails to solve the structure, but were unable to obtain unique structure for this compound. This forced us to approach the problem by searching the literature or by calculation.

The Cambridge Structural Database [10] contains 172 oxirane derivatives. We have found that most of the compounds have the carbon atom with a structure very close to planar: Of 172 compounds, 169 showed the angles of 350° or more when we add angles made by the substituents of the oxirane ring and another carbon center (angles α, β, and γ in Scheme 4). Thus the structure of oxiranes seems to be unique in that the carbon takes a configuration which is almost planar exept the oxygen atom. Moreover, we found that even the simplest compound, oxirane, has also a carbon atom which carries two hydrogens [11] and another oxirane carbon in almost a plane (Table 3).

Scheme 4.



Designation of bond lengths and bond angles in oxirane and its derivatives.

We calculated the geometry of oxirane by Hartree Fock method (RHF/6-31G*), and the results are compiled in Table 2 In Table 3 are also compiled experimental data obtained by literature search. Because the structural parameters obtained by calculation were satisfactory, we extended our calculations to see the substituent effects and to see whether the different lengths of C–O bond and the flat carbon in (*ap*-**IV**) could be produced by the substituents. While calculation reproduces the structure of oxiranes satisfactorily as far as the bond angles are concerned, the different lengths of C–O bonds in (*ap*-**IV**) is not reproduced by calculation. We introduced a methyl and/or a phenyl group to the same carbon atom of oxirane to see whether this operation can produce different lengths of the C–O bonds. As shown in Table 2, this operation does not produce different C–O bond lengths, however. The agreement of the calculated structure with the experimental data (see Table 3) was satisfactory, but we could not produce the unique structure of the oxirane ring in (*ap*-**IV**) by this method.

The distance between the $C^{1''}$ and the π-system of fluorene is within the sum of van der Waals radii, as seen in Table 1. To see whether the elongation of the O–C bond is caused by the influence of the π-system we placed an ethene molecule in the following fashion in the vicinity of oxirane: The C=C bond of ethene was placed orthogonally to the C^2–C^1 bond of oxirane, with both carbon atoms of ethene 3 Å apart below C^2 atom, and the angle $C^1C^2C_{ethene}$ was set at 100°. The calculation results are shown in Table 4 together with other relevant data. This operation caused the different C–O bond lengths but the angle α + β + γ is not particularly enlarged. Thus we decided to explore the effects of bulkiness of substituents in addition to the effects of the π-system. Although the data are not included in Table 4, if we place an ethane molecule at the same position relative to 2,2-dimethyloxirane the angle α + β + γ becomes 359.4°, while C^2–O and C^1–O are 1.451 and 1.383 Å respectively.

The effects of π-system are clear. The calculation results imply that the steric effects of substituents as well as electronic effects of the π-system are

Table 2. Structural parameters of oxiranes calculated by RHF/6-31G* (Scheme 4)

R^1	R^2	α, deg	β, deg	γ, deg	(α + β + γ), deg	r^1, Å	r^2, Å	r^3, Å
H	H	119.9	119.9	115.3	355.1	1.400	1.400	1.452
Me	H	122.5	117.4	115.3	355.2	1.404	1.405	1.454
Me	Me	119.9	119.9	115.7	355.5	1.409	1.406	1.455
Ph	H	122.4	117.3	114.9	354.6	1.400	1.403	1.458
Ph	Me	119.3	119.9	116.4	355.6	1.406	1.405	1.459

Table 3. Experimental structural parameters of oxirane and its derivatives (Scheme 4)[a]

R^1	R^2	α, deg	β, deg	γ, deg	(α + β + γ), deg	r^1, Å	r^2, Å	r^3, Å	Ref.
H	H	119.7	119.7	116.6	356.0	1.431	1.431	1.466	[11]
Me	H	121.6	118.2	113.3	353.1	1.416	1.436	1.451	[12]
Me	Me	120.8	120.8	114.4	356.0	1.419	1.437	1.444	[13]
Ar[b]	H	122.4	119.0	114.0	354.7	1.434	1.430	1.448	[14]

[a] Unless otherwise mentioned, the structures were obtained by microwave spectroscopy. [b] Ar = 4-$NO_2C_6H_4$, X-ray analysis.

Table 4. Comparison of calculated and observed structural parameters of oxiranes

Mthods	α, deg	β, deg	γ, deg	(α + β + γ), deg	r^1, Å	r^2, Å	r^3, Å
Microwave spectroscopy	119.7	119.7	116.6	356.0	1.431	1.431	1.466
Calcd.[a]	120.2	120.0	115.4	355.6	1.409	1.402	1.447
X-ray, *ap*-**IV**	119.1	120.5	118.2	357.8	1.487	1.396	1.509

[a] Ethene was placed close to the O–C bond. For position of ethene see text.

important in forming the observed structure of the oxirane ring in (*ap*-**IV**). One of the C–O bonds is lengthened and the oxirane carbon concerned becomes flatter. Thus the carbon is rather quinqui-coordinated, approaching a so-called hypervalent carbon which was reported recently [15].

These results lead us to conclude that the special structures of the oxirane ring in (*ap*-**IV**) (long $C^{1''}$–O bond and a sum of bond angles α + β + γ close to 360°) owe to the general structural feature of the oxirane ring and participation of the π-system which is placed closely to the C–O bond; π···C–O interactions and steric effects are responsible for the observed structure of the oxirane ring in (*ap*-**IV**): The $C^{1''}$–O is lengthened by the O–C···π interaction.

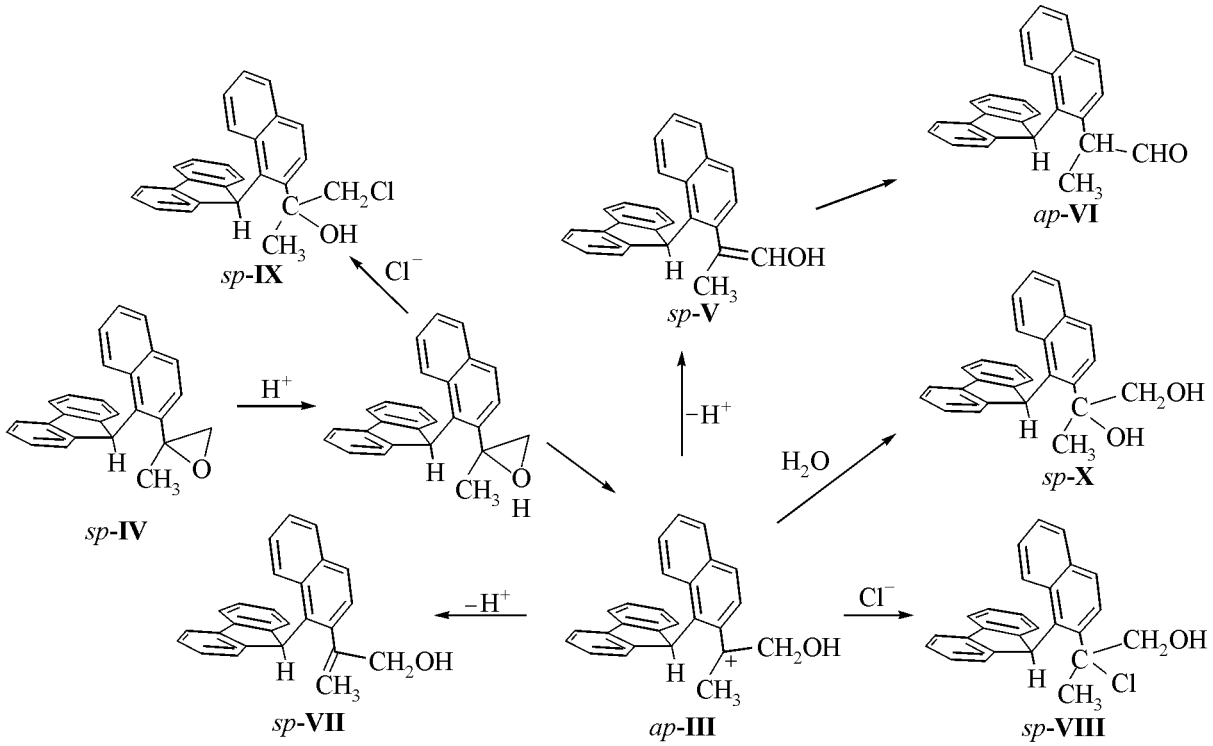
The equilibration experiment indicates that, although (*ap*-**IV**) is more easily formed than (*sp*-**IV**), the former is not particularly stable. We interpret the results in the following way. The oxidation with *m*-chloroperbenzoic acid occurs easier with (*sp*-**IV**) than with (*ap*-**IV**) because of the participation of the π-system of fluorene* while (*ap*-**IV**) is unstable relative to (*sp*-**IV**) because of the steric effects. The equilibrium constant of 36 : 1 is rather a normal value for this kind of systems [3, 6].

Expected products from reactions of epoxide (*sp*-**IV**) with hydrochloric acid in THF are shown in Scheme 5. The reaction of (*sp*-**IV**) with hydrochloric acid will induce protonation of the oxirane ring which subsequently opens to afford (*ap*-**III**) carbocation.

The intermediate can undergo the following reactions. When deprotonation takes place from the methylene part of the $HOCH_2$ group, it will produce the enol form (*sp*-**V**) of aldehyde (*ap*-**VI**). The former will ultimately rearrange into (*ap*-**VI**). If the deprotonation take place from the methyl group, it will produce an allyl alcohol derivative (*sp*-**VII**). The

* According to X-ray diffraction study in the initial compound (*sp*-**I**) the distance between $C^{1''}$ and C^{8a} is only 3.0 Å [3].

Scheme 5.



Possible transformation paths of (*ap*-**III**) intermediate and (*sp*-**IV**) epoxide.

cation (*ap*-**III**) can also react with nucleophiles in the system. If the reaction of (*ap*-**III**) with chloride ion takes place, (*sp*-**VIII**) is produced, and hydration can afford diol (*sp*-**X**).

The expected compounds were all found among the products. However there was an unexpected product from (*ap*-**III**). This is 2-(1-hydroxy-1-methylethyl-2-chloro)-1-(9-fluorenyl)naphthalene (*sp*-**IX**), the formation of which deserves further comment. If the intermediate (*ap*-**III**) is formed, it is unlikely that compound (*sp*-**IX**) is formed.

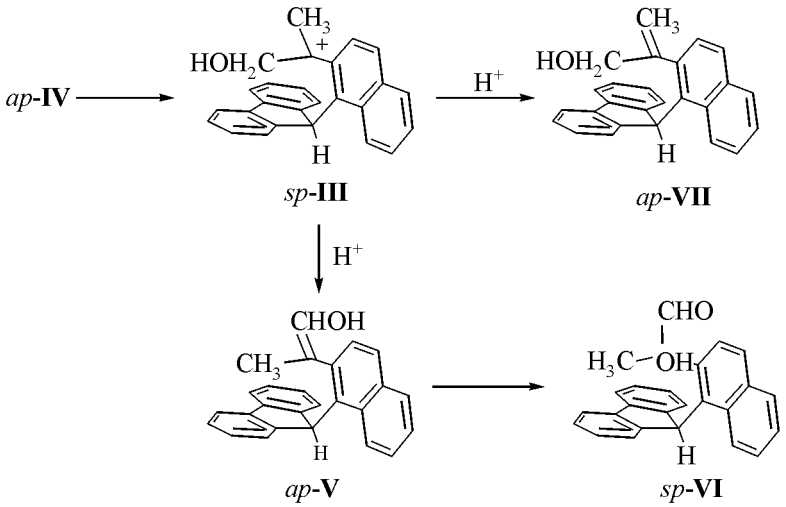
There are several studies of the ring opening reactions of oxiranes with chloride ions in the presence of acid [16, 17]. We must assume that compound *sp*-**IX** is formed without intermediacy of *ap*-**III**. Rather, *sp*-**IX** will be formed via S_N2-type attack on the protonated epoxy ring in *sp*-**IV**. Indeed, those reports which deal with reactions of chloride with epoxides in the presence of acid indicate that the S_N2-type reactions are rather fast and under certain conditions they become main reactions [16, 17]. Undoubtedly, the reaction rates are enhanced by the presence of proton which coordinates the oxirane oxygen increasing the ability of the leaving group. We attribute the formation of *sp*-**IX** to this kind of reactions. Distribution of the reaction products are compiled in Table 5.

Table 5. Product distribution (%) in reactions of epoxide *sp*-**IV** with hydrochloric acid (A) and anhydrous hydrogen chloride (B) in THF

Added HCl[a]	A				B			
	ap-**VI**	*sp*-**VII**	*sp*-**VIII**	*sp*-**IX**	*sp*-**X**	*ap*-**VI**	*sp*-**VII**	*sp*-**VIII**
1.2	10	12	14	60	–	78	3	11
6.0	24	11	14	42	6	64	10	12
12	28	10	12	29	18	48	14	14

[a] Amount of HCl is given as moles of hydrogen chloride per 1 mol of substrate.

Scheme 6.



Possible transformation paths of *sp*-**III** intermediate.

Table 5 indicates that, when more hydrochloric acid is used per unit amount of *sp*-**IV**, more diol *sp*-**X** is produced. This is reasonable, because more water means the increase in the chance of reaction of *ap*-**III** with water. Interesting is the fact that, when the amount of hydrochloric acid is minimal, the formation of *sp*-**IX** is maximal and the yields of *sp*-**IX** are decreased when the amount of water is increased, even though the amount of chlorine ion increases. The reasons for these results are not well understood, but we wish to attribute the results to the change of nucleophilicity of the chloride ion. When the amount of water is minimal, hydration of the chloride ion will be minimal and the nucleophilicity of the ion is maximal: This is in agreement with that the yield of *sp*-**IX** is decreased when water is increased. Although the concentration of chloride ion increases, this effect seems to be counterbalanced by the low reactivity of chloride ion in water to make the influence of the increase in the chloride ion small.

Reaction of epoxide (*ap*-**IV**) with hydrochloric acid in THF affords intermediate carbocation *sp*-**III** the fate of which canbe similarly expected (Scheme 6) except one point: Because of the steric effects discussed above the formation of compounds that carry a chloro or a hydroxy substituent on the α-carbon, rotamers *sp*-**VIII**, *sp*-**IX**, *sp*-**X**, will not be possible.

As expected, there were *sp*-**VI** and *ap*-**VII** in the products, but none of the other products were detected except one, which we were able to separate and showed the presence of olefinic protons in its ^{1}H NMR spectrum. Because it seemed difficult to identify the product from the NMR spectrum only, we decided to carry out X-ray crystallography. The results are shown in Fig. 2 as an ORTEP drawing. It was 3-methyl[3,4-*a*]naphthalino-3a,8b-(1,3-butadieno)-3,3a,4,8b-tetrahydro-2*H*-indeno[1,2-*b*]furan (**XI**).

The products distribution is summarized in Table 6.

The formation of compound **XI** from cation (*sp*-**III**) may be rationalized in the following way (Scheme 7). Because, as X-ray structure of the starting compound *ap*-**IV** indicates, the cationic center in *sp*-**III** is very close to the *9a* position of the fluorine ring, an ipso-attack by the carbocation site of *sp*-**III** at this position will take place to produce **XII** in which partial positive charges should develop at *1*, *3* and *4a* positions. The reaction of positive charge at *4a* position with the oxygen atom of the hydroxymethyl group will form a cyclic oxonium ion **XIII** which on deprotonation should afford compound **XI**. Though

Table 6. Product distributions (%) in reaction of epoxide (*ap*-**IV**) with hydrochloric acid (A) and anhydrous hydrogen chloride (B) in THF

Amount of HCl[a]	A			B	
	sp-**VI**	*ap*-**VII**	**XI**	*sp*-**VI**	*ap*--**VII**
1.2	45	55	–	94	6
6.0	57	41	2	94	6
12	52	11	37	95	5

[a] Amount of HCl is given as moles of hydrogen chloride per 1 mol of substrate.

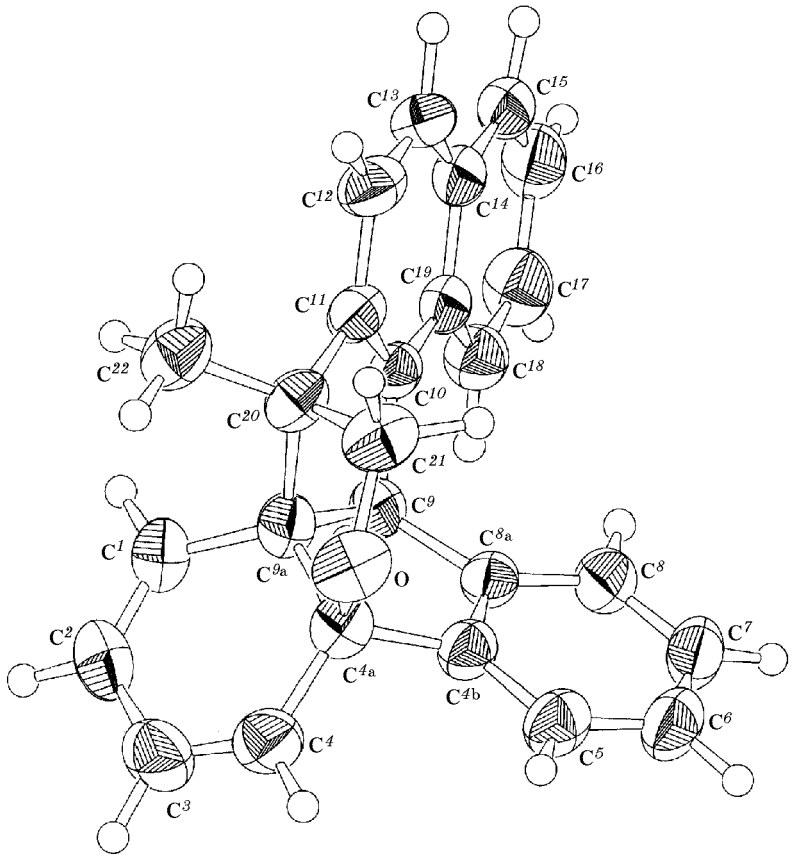


Fig. 2. Spatial arrangement of 3-methyl[3,4-*a*]naphthalino-3a,8b-(1,3-butadieno)-3,3a,4,8b-tetrahydro-2*H*-indeno[1,2-*b*]-furan (**XI**).

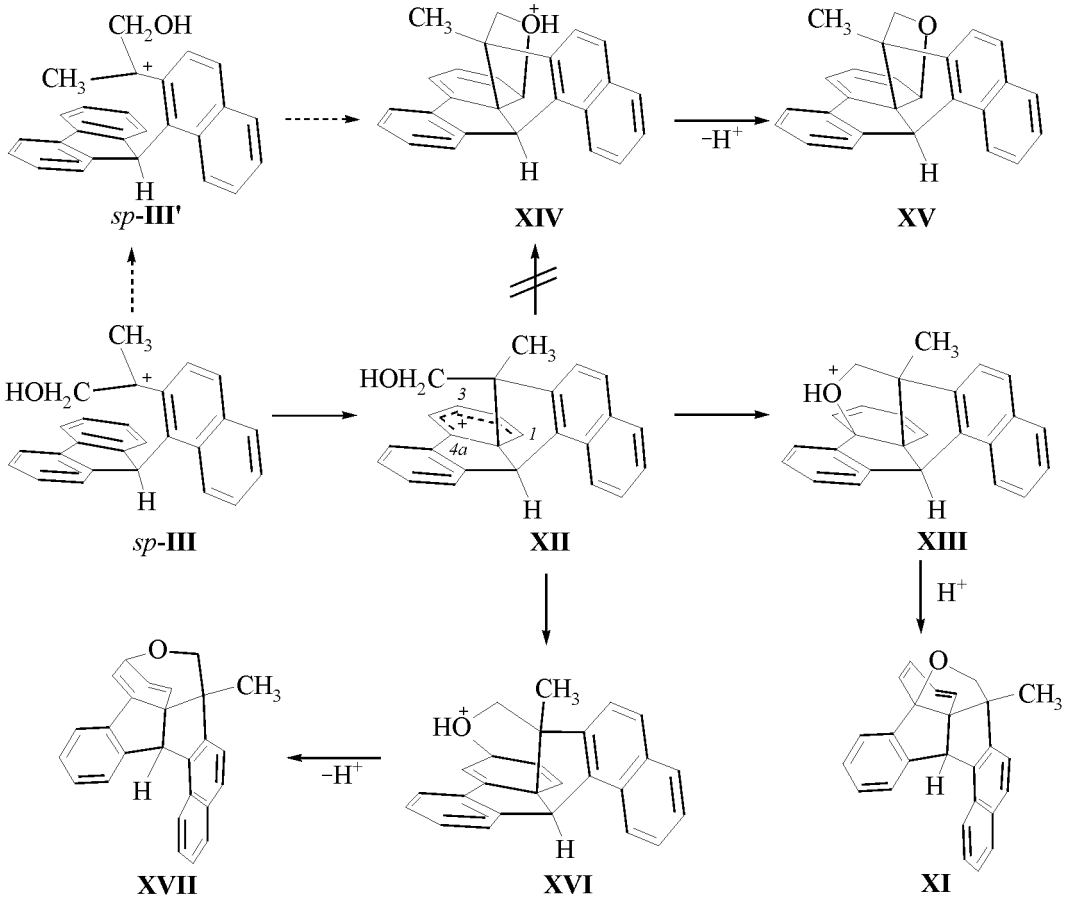
the yield of **XI** was nil when 1.2 mol of hydrochloric acid is used the result is not due to to the deficiency of hydrochloric acid: By adding water in addition to 1.2 mol of hydrochloric acid, the formation of **XI** was enhanced and its yield increased as more water was added indicating that water is necessary to produce **XI** from *sp*-**III**.

It should be noted that we had experience of reaction with *ipso*-attack when alkene (*ap*-**I**) was treated with *N*-bromosuccinimide in aqueous dioxane, but never observed an ipso-attack in anhydrous media: *ipso*-attack has never occurred though attack on C^1 of the fluorene ring is observed from time to time under anhydrous conditions [3–6]. Thus the *ipso*-attack occurs only in the presence of water. Though the details are not known, it is tempting to consider that for the *ipso*-attack to occur stabilization of the intermediate cation by hydration is important.

Nucleophilic attack of a hydroxy group on arenonium ion **XII** may occur not only at position C^{4a} yielding cation **XIII** but also at positions C^1 and C^3 affording intermediates **XIV** and **XVI** that in their turn would yield cyclization products **XV** and **XVII**. However neither **XV** nor **XVII** were obtained, and the exclusive cyclization product was **XI**. Why cyclization to form intermediate **XIII** takes place but not those to produce **XIV** and **XVI**? This is a serious question, because both **XIII** and **XIV** are formed to give a five-membered ring although **XVI** involves a seven-membered ring and is expected to be less easily formed than **XIII** and **XIV**.

We believe that the reason for the absence of **XV** is due to the steric effects from the following experience we have encountered in the past [3]. Firstly, it is the structure of alkene **I**. The methyl group there never takes position above the fluorene ring: Rather it takes position over the rim of the fluorene group as confirmed both by calculation and by X-ray crystallography [3, 6]. This happens because being a slightly larger group than the π-system the methyl group takes a position where it is more comfortable on the ground of steric repulsion. In contrast to this situation the $HOCH_2$ group in **XII** has to take a position over

Scheme 7.



Possible cyclization paths of carbocation (*sp*-**III**).

the inside of the fluorine ring, that is energetically less favorable than **XI** but necessary for cyclization affording cation **XIII**. Though the structure of **XII** is energetically disfavored as far as the steric congestion of the $HOCH_2$ group concerns this situation is included in the activation energy for forming **XII**. Secondly, for the formation of **XV** the methyl group has to take the position inside the fluorene ring which is of high energy. In order to support the above discussion we calculated the relative energies of compounds **XI, XV,** and **XVII** as models for transition states in cyclization by the PM3 method [18]: 0 (**XI**), 55.98 (**XV**), 15.58 (**XVII**) kcal mol^{-1}.

As seen, the relative energy of **XI** is the lowest and that **XV** is more than that of **XI** by 50 kcal mol^{-1}. Similarly **XVII** is less stable than **XI** by 15 kcal mol^{-1}. While the results clearly indicate that formation of **XIII** is a preferred process and other pathways will not take place, there is another factor we should not forget. That is, the positions of the methyl and hydroxymethyl groups are to be exchanged for formation of **XV**. This exchange is possible only when rotation about the $C^{1''}$–$C_{naphthyl}$ bond in *sp*-**III** takes place. In *sp*-**III** this exchange requires huge energy because the methyl or hydroxymethyl group has to pass over the fluorene ring. This energy for rotation could be even larger than the values calculated for model compounds **XI, XV**, and **XVII**. We conclude that formation of **XV** and **XVII** is not likely to occur on these grounds.

Reactions of epoxide **IV** rotamers with anhydrous hydrogen chloride were carried out in THF to test the effect of water on the reactions. The results are summarized in Tables 5 and 6. By comparing the product distributions obtained from *sp*-**IV** using hydrochloric acid in THF with that obtained under anhydrous conditions, one notices that the yields of the aldehyde, *ap*-**VI**, increases while those of the allylic alcohol, *sp*-**VII**, and the chlorohydrin, *sp*-**VIII**, are not affected greatly. These results may be interpreted by considering the limited mobility of the chloride ion in the system. Though the chloride ions are not likely

to be produced under the conditions in significant quantities, the formation of *sp*-**VIII** is difficult to interpret without the chloride ions. Also the formation of *ap*-**VI** and *sp*-**VII** are more easily understood by assuming the presence of chloride ion than the absence of it. Because of the absence of water the ion pairs in THF may be very tight and not be able to move easily. Then the deprotonation from the site which is close to the ion pair becomes the predominant process. The reactions of *ap*-**IV** are similar to those of *sp*-**IV**. The main product is the aldehyde *sp*-**VI**.

The results of reaction of epoxide **IV** rotamers with zinc chloride are described below. Epoxide *sp*-**IV** afforded aldehyde *ap*-**VI** and alcohol *sp*-**VII** in 96 : 4 ratio, its rotamer *ap*-**IV** gave aldehyde *sp*-**VI** as almost an only product. Probably in this case as well the mobility of ionic species is important.

In summary, the reactions of *ap*-**IV** with hydrochloric acid showed interesting differences from those of *sp*-**IV**. The main cause for the differences is attributed to the steric effects which prevent formation of rotamers of *sp*-**VIII**, *sp*-**IX**, *sp*-**X**. Another important factor is that the α-carbon which is attached to the naphthalene ring is very close to the *9a* position of the fluorene ring to make it possible for the cationic center in *sp*-**III** to attack the *9a* position to form compound **XI**, if water is present.

Finally we wish to compare the results of the present study on cations **III** with those obtained for analogous sulfur and selenium-containing cations (**II**, X = S or Se). The feature of the results obtained with the latter is that the yield of compounds that correspond to deprotonation from α-position of S or Se are lower than those of aldehydes when **X** is oxygen. This reminds us the effect of substituents in benzene series: Although a fluoro group is electron-donating, a chloro group is electron-withdrawing. This is often ascribed to the low efficiency of overlaps of 2*p*- and 3*p*-orbitals in the case of chloro substituent whereas that of 2*p*–2*p* orbitals overlap efficiently to make the fluoro substituent electron-donating. Though there are some exceptions for this generaslization, the similar results are also observed for halogen compounds **II** (X = halogen).

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were obtained on Varian Gemini-300 or a JEOL Lamda-300 spectrometers, IR spectra on a Nicolet AVATAR 320 FT-IR spectrometer. The elemental analyses were performed on a Perkin Elmer 240C machine. The melting points are not corrected. High resolution mass spectra were obtained on JEOL MStation 700 mass spectrometer.

***sp*-2-(2-Methyl-2-oxiranyl)-1-(9-fluorenyl)-naphthalene (*sp*-IV).** To a solution of 178 mg (0.51 mmol) of alkene (*ap*-**I**) [3] in 20 ml of dichloromethane was added 175 mg (1.01 mmol) of *m*-chloroperbenzoic acid in 5 ml of dichloromethane. The reaction mixture was stirred for 20 h at room temperature till reaction was complete. The mixture was washed with aqueous sodium hydrogen carbonate and dried over magnesium sulfate. After evaporation of the solvent the residue was submitted to TLC on silica gel with 2 : 1 hexane–dichloromethane eluent. The desired product was recrystallized from 2-propanol hexane, the yield being 89%, mp 133–134°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.91 s (3H), 3.15 and 3.24 AB-quartet (2H, *J* 5.2 Hz), 5.93 s (1H), 6.42 d (1H, *J* 8.6 Hz), 6.84 d.d.d (1H, *J* 1.4, 6.9, 8.6 Hz), 7.06 d (1H, *J* 6.9 Hz), 7.16–7.24 m (4H), 7.40–7.45 m (2H), 7.72 d (1H, *J* 8.1 Hz), 7.73 and 7.82 AB-quartet (2H, *J* 8.2 Hz), 7.97 d.d (2H, *J* 0.9, 7.6 Hz). Found, %: C 89.83; H 5.8. $C_{26}H_{20}O$. Calculated, %: C 89.62; H 5.79.

***ap*-2-(2-Methyl-2-oxiranyl)-1-(9-fluorenyl)-naphthalene (*ap*-IV)** was prepared similarly from alkene (*sp*-**I**) as above. The reaction was completed after 16 h and the desired compound *ap*-**IV** was obtained in 83% yield, mp 142–143°C (from dichloromethane–hexane). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.71 d (3H, *J* 0.6 Hz), 1.63 d.d (1H, *J* 0.6 and 4.5 Hz), 1.78 d (1H, *J* 4.5 Hz), 6.31 s (1H), 7.14–7.31 m (4H), 7.40–7.46 m (2H), 7.60 d (1H, *J* 8.5 Hz), 7.60 d.d.d (1H, *J* 1.2, 6.8, 8.0 Hz), 7.68 d.d.d (1H, *J* 1.6, 6.8, 8.4 Hz), 7.85 d (1H, *J* 8.8 Hz), 7.89 d.d (2H, *J* 1.7, 7.7 Hz), 7.96 d.d (1H, *J* 1.5, 8.0 Hz), 8.63 d (1H, *J* 8.7 Hz). Found, %: C 89.60; H 5.71. $C_{26}H_{20}O$. Calculated, %: C 89.62; H 5.79.

Equilibration of rotamers (*sp*-IV) and (*ap*-IV). Epoxide (*sp*-**IV**) (15.6 mg) was dissolved in 5 ml of toluene-d_8, and the solution was heated under reflux for 2 h. After cooling the *ap/sp* ratio was determined from the intensities of the methyl signals in the ^{1}H NMR spectrum. The (*ap*-**IV**)/(*sp*-**IV**) ratio was 1 : 36.

Reaction of epoxide (*sp*-IV) with hydrochloric acid. The hydrochloric acid used in the reaction was commercially available 1.0 M hydrochloric acid from Wako. To a solution of 100 mg (0.287 mmol) of (*sp*-**IV**) in 5.0 ml of THF was added 0.344 ml (0.344 mmol) of the hydrochloric acid, and the mixture was stirred at room temperature for 7 h when completion of the reaction was confirmed.

The mixture was poured into water and extracted with dichloromethane. Then the extract was washed with aqueous sodium hydrocarbonate and dried. The ratio of reaction products was determined at this stage by ^{1}H NMR spectra.

The reactions with the use of larger amounts of hydrochloric acid were carried out similatly. The used hydrochloric acid was 1.72 ml (0.17 mmol) of 1 M hydrochloric acid solution when 6 equiv of hydrochloric acid is indicated, and for 12 equiv 3.44 ml of hydrochloric acid solution was used. Reaction products roughly purified by GPC were submitted to TLC on silica gel with 4:1 hexane–ethyl acetate eluent, and fractions were obtained at *Rf* of 0.67, 0.55, 0.53, 0.35, and 0.21. These products were identified as aldehyde (*ap*-**VI**), chlorohydrin (*sp*-**VIII**), its isomer (*sp*-**IX**), an allylic alcohol (*sp*-**VII**), and diol (*sp*-**X**) respectively. The results are summarized in Table. 5. The compounds obtained were characterized by elemental analyses, ^{1}H NMR spectra and sometimes by IR and mass spectra.

***sp*-1-(9-Fluoreneyl)-2-(1-formylethyl)naphthalene (*ap*-VI),** mp 63–65°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.69 d (3H, *J* 7.7 Hz), 4.41 q (1H, *J* 7.7 Hz), 5.65 s (1H), 6.45 d (1H, *J* 8.7 Hz), 6.82 t (1H, *J* 7.7 Hz), 7.09 t (1H, *J* 7.7 Hz), 7.15–7.20 m (4H), 7.27 d (1H, *J* 6.7 Hz), 7.40 t (2H, *J* 7.7 Hz), 7.70 d (1H, *J* 6.7 Hz), 7.91 d (1H, *J* 6.7 Hz), 7.98 d (2H, *J*7.7 Hz), 10.05 s (1H). IR spectrum: 1730 cm^{-1} (C=O). Found, %: C 89.64; H 5.73. $C_{26}H_{20}O$. Calculated, %: C 89.62; H 5.79.

***sp*-2-[1-(Hydroxymethyl)ethenyl]-1-(9-fluorenyl)naphthalene (*sp*-VII).** This compound was identical to the authentic specimen reported earlier [7]. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.62 br.s (1H), 4.59 s (2H), 5.45 d.d (1H, *J* 1.4 and 2.9 Hz), 5.66 d.d (1H, *J* 1.2, 2.9 Hz), 5.79 s (1H), 6.44 d (1H, *J* 8.6 Hz), 6.85 d.d.d (1H, *J* 1.4, 6.8, 8.6 Hz), 7.12-7.24 m (5H), 7.36-7.44 m (3H), 7.73 d (1H, *J* 6.6 Hz), 7.78 d (1H, *J* 6.6 Hz), 7.94 d (1H, *J* 7.7 Hz).

***sp*-2-[(2-Hydroxy-1-methyl-1-chloro)ethyl]-1-(9-fluorenyl)naphthalene (*sp*-VIII**), mp 197–199°C. This compound was identical to the authentic specimen (lit. mp 199–200.5°C [7]). M^+ 385.1333 (FAB). Calculated for $C_{26}H_{21}ClO$: 385.1359. ^{1}H NMR spectrum (CDCl3), δ, ppm: 2.31 s (3H), 2.94 s (1H), 4.22 and 4.62 AB-quartet (2H, *J* 11.3 Hz), 6.48 d (1H, *J* 8.8 Hz), 6.69 s (1H), 6.79 t (1H, *J* 8.5 Hz), 7.11 d (1H, *J* 8.0 Hz), 7.18–7.23 m (4H), 7.40–7.45 m (2H), 7.68–7.82 m (3H), 7.97 d (2H, *J* 6.8 Hz).

***sp*-2-[(1-Hydroxy-1-methyl-2-chloro)ethyl]-1-(9-fluorenyl)naphthalene (*sp*-IX**), mp 107–110°C. This compound was identical to the authentic specimen (lit. mp 106–108°C [5]). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.04 s (3H), 2.94 s (1H), 4.10 and 4.42 AB-quartet (2H, *J* 11.4 Hz), 6.46 d (1H, *J* 8.8 Hz), 6.70 s (1H), 6.79 t (1H, *J* 8.5 Hz), 7.11 d (1H, *J* 8.0 Hz), 7.18–7.23 m (4H), 7.40–7.45 m (2H), 7.68–7.82 m (3H), 7.97 d (2H, *J* 6.8 Hz).

***sp*-2-(1,2-Dihydroxy-1-methylethyl)-1-(9-fluorenyl)naphthalene (*sp*-X).** Colorless oil. $[MH]^+$ 367.1669 (FAB). Calculated for $C_{26}H_{22}O_2$: 367.1698. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.92 s (3H), 2.09 br.m (1H), 2.99 s (1H), 3.99 d.d (1H, *J* 5.7, 11.1 Hz), 4.42 d (1H, *J* 11.1 Hz), 6.46 d (1H, *J* 8.7 Hz), 6.74 s (1H), 6.79 d.d.d (1H, *J* 1.5, 6.8, 8.6 Hz), 7.10–7.23 m (5H), 7.40 t (2H, *J* 7.2 Hz), 7.69 d (1H, *J* 7.8 Hz), 7.72 d (1H, *J* 8.9 Hz), 7.80 d (1H, *J* 8.8 Hz), 7.96 d (2H, *J* 7.7 Hz).

Reaction of epoxide (*ap*-IV) with hydrochloric acid was carried out similarly with that described for *sp*-rotamer. TLC of reaction mixture on silicagel (eluent hexane-ethyl acetate, 4:1) afforded three spots at R_f 0.68, 0.65, and 0.35. These were identified as the aldehyde (*sp*-**VI), the cyclized product XI**, and the allylic alcohol (*ap*-**VII) (Table 6).**

***sp*-1-(9-Fluorenyl)-2-(1-formylethyl)naphthalene (*sp*-VI**), mp 67–69°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.63 d (3H, *J* 7.7 Hz), 2.61 q (1H, *J* 7.7 Hz), 6.20 s (1H), 6.97 d (1H, *J* 8.5 Hz), 7.15–7.27 m (4H), 7.37–7.45 m (2H), 7.57–7.69 m (2H), 7.82 s (1H), 7.85–7.89 m (2H), 7.91 d (1H, *J* 7.8 Hz), 8.53 d (1H, *J* 8.7 Hz), 8.73 s (1H). IR spectrum: 1735 cm^{-1} (C=O). Found, %: C 89.98; H 5.95. $C_{26}H_{20}O$. Calculated, %: C 89.62; H 5.79.

***ap*-2-[1-(Hydroxymethyl)ethenyl]1-(9-fluorenyl)-naphthalene (*ap*-VII**), mp 197–199°C. This compound was identical to the authentic specimen (lit. mp 199–200.5°C [6]). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.17 d (1H, *J* 8.6 Hz), 3.59 br.s (2H), 3.71 d.d (1H, *J* 1.5, 3.1 Hz), 4.45 d.d (1H, *J* 1.5, 3.1 Hz), 6.09 s (1H), 7.02 d (1H, *J* 8.6 Hz), 7.12–7.24 m (4H), 7.36–7.44 m (2H), 7.60 d.d.d (1H, *J* 1.2, 6.6, 8.0 Hz), 7.69 d.d.d (1H, *J* 1.2, 6.6, 8.0 Hz), 7.78–7.83 m (3H), 7.94 d.d (1H, *J* 1.4, 7.7 Hz), 8.61 d (1H, *J* 8.6 Hz).

3-Methyl[3,4-a]naphthalen°-3a,8b-(1,3-butadieno)-3,3a,4,8b-tetrahydro-2*H*-indeno[1,2-b]furan

(**XI)**, mp 177–178°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.43 s (3H), 3.33 and 3.63 AB-quartet (2H, *J* 8.6 Hz), 5.06 s (1H), 6.01 m (2H), 6.13 d.t (1H, *J* 9.6, 3.2 Hz), 6.31 d (1H, *J* 9.3 Hz), 7.12 t (1H, *J* 7.6 Hz), 7.20–7.29 m (2H), 7.42 d (1H, *J* 7.7 Hz), 7.49 t (1H, *J* 8.1 Hz), 7.56 d (1H, *J* 7.7 Hz), 7.63 d.t (1H, *J* 1.3, 7.6 Hz), 7.77 d (1H, *J* 8.4 Hz), 7.87 d (1H, *J* 8.2 Hz), 8.27 d (1H, *J* 8.4 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 21.1, 61.5, 63.1, 68.9, 75.4, 89.6, 119.9, 121.9, 122.8, 124.2, 124.0, 125.0, 125.4, 125.8, 126.4, 128.3, 128.7, 128.8, 128.9, 129.9, 130.1, 133.8, 138.9, 143.8, 144.3, 144.5. Found, %: C 89.97; H 5.82. $C_{26}H_{20}O$. Calculated, %: C 89.62; H 5.79.

Reactions of epoxides IV with anhydrous hydrogen chloride in THF. THF used for the reactions was purified by distillation after thoroughly drying over calcium hydride. Hydrogen chloride gas was introduced to the THF. A portion (1.00 ml) of the solution was pipetted and was poured into 20 ml of water to titrate against 0.100 M sodium hydroxide. The solution of known concentration was used by taking the necessary amount with a microsyringe. To a solution of 5.00 mg (14.3 mol) of rotamer (*sp*-**IV**) in 10 ml of THF was added 17.2 mol of hydrogen chloride in 90.1 l of THF and the whole was stirred for 10 min at room temperature till reaction was completed. The rest of the handling procedure was the same as described for the reacrion of epoxide (*sp*-**IV**) with hydrochloric acid in THF. The results are compiled in Table 5. The reaction of rotamer (*ap*-**IV**) with anhydrous hydrogen chloride was carried out similarly. The results are compiled in Table 6.

Reactions of epoxides IV with zinc chloride in THF. Zinc chloride was thoroughly dried by heating for 5 h at 110°C. To a solution of 5.00 mg (14.2 mol) of compound **IV** in 0.25 ml of THF was added 9.79 mg (71.7 mol) of zinc chloride, and the whole was stirred for 20 h at room temperature when the reaction was completed.

X-ray diffraction study. Crystals suitable for X-ray diffraction study were grown from hexane dichloromethane mixture.

Compound (*ap*-IV). Monoclinic crystal, space group *P*21/n, a 12.5012 (8), b 8.5771 (3), c 17.3006 (9) Å, β 94.665 (1)°, *V* 1848.9 (2) A3, Z 4, ρ_{calc} 1.252 g cm^{-3}, μ(MoK_α) 0.74 cm^{-1}. A crystal having dimensions of $0.40 \times 0.30 \times 0.20$ mm was mounted. The data were collected on a Rigaku RAXIS-IV imaging plate diffractometer (MoK_α radiation, λ 0.71070 Å, $2\theta_{max}$ 54.9°) at –120°C. The reflection data were corrected for the Lorentz-polarization effects and secondary extinction (coefficient 9.1943×10^{-7}). The structure was solved by the direct method and refined by the full-matrix least-squares method by using teXsan program on a Comtec O2 workstation. The nonhydrogen atoms were refined anisotropically. Some hydrogen atoms were refined isotropically, and the rest were included in fixed positions. Among 4083 observed reflections, 3569 reflections with $I > 2(I)$ were used for the refinement of 296 structural parameters. R(F) [$I > 2\sigma(I)$] 0.068, $wR(F^2)$ 0.064, GOF 3.97.

Compound XI. $C_{26}H_{20}O$, Mr 348.44, monoclinic crystal. Space group *P*21/n, *a* 9.011 (2), *b* 19.132 (1), *c* 11.404 (1) Å, β 109.595 (9)°, V 1852.3(4) Å3, *Z* 4, ρ_{calc} 1.249 g cm^{-3}, μ(CuK_α) 5.74 cm^{-1}. A single crystal having dimensions of $0.13 \times 0.13 \times 0.08$ mm was investigated on a Rigaku AFC7R diffractometer (CuK_α radiation, λ 1.54178 Å, $2\theta_{max}$ 120.2°) at room temperature. The structure was solved as above. Among 3022 observed reflections 2173 with $I > 2.0\sigma(I)$ were used for the refinement of 325 structural parameters. $R(F)$ [$I > 2\sigma(I)$] 0.043, $wR(F_2)$ 0.067, GOF 1.38.

MO calculations. The PM3 calculations [18] of compounds **XI, XV**, and **XVII** were performed by MOPAC program integrated in Chem3D Pro program on a Mac G3 computer. The input structure was roughly optimized by MM2, and then by PM3 method. *Ab initio* calculations were performed by Gaussian 98 program [19] on a Tempest-3 workstation.

REFERENCES

1. Hirose, T., Morita, N., Toyota, S., and Oki, M., *Tetrahedron Lett.*, 1997, vol. 38, p. 4575.
2. Oki, M., Yoshida, S., Taguchi, Y., Minato, I., Nobuoka, K., Fukada, N., Toyota, S., Tanaka, T., Tanaka, Y., and Yamamoto, G., *Bull. Chem. Soc. Jpn.*, 2000, vol. 73, p. 2563.
3. Oki, M., Shionoiri, K., Otake, K., Ono, M., and Toyota, S., *Bull. Chem. Soc. Jpn.*, 1993, vol. 66, p. 589.
4. Oki, M., Maeda, K., Akinaga, T., Kataoka, Y., and Toyota, S., *Bull. Chem. Soc. Jpn.*, 1994, vol. 67, p. 2825.
5. Oki, M., Hirose, T., Aki, M., Morita, N., Nose, E., Kataoka, Y., Ono, M., and Toyota, S., *Bull. Chem. Soc. Jpn.*, 1996, vol. 69, p. 3345.
6. Oki, M., Hirose, T., Maeda, K., Yanagawa, M., Kataoka, Y., Kojima, H., Morita, N., and Toyota, S., *Bull. Chem. Soc. Jpn.*, 1997, vol. 70, p. 859.
7. Oki, M., Hirose, T., Kataoka, Y., Ogata, T., Kita-

hara, K., Toyota, S., Matsuo, T., Kawai, Y., and Ohno, A., *Bull. Chem. Soc. Jpn.*, 1999, vol. 72, p. 63.
8. Gritter, R.J., *The Chemistry of the Ether Linkage*, Patai, S., Ed., London: Interscience Publishers, 1967.
9. Rottger, D. and Erker, G., *Angew. Chem., Int. Ed.*, 1997, vol. 36, p. 812.
10. *The Cambridge Structural Database, Version 5.22*, January 2002, Cambridge Crystallographic Data Centre, 12, Union Road. Cambridge. CB2 1EZ. UK.
11. Hirose, C., *Bull. Chem. Soc. Jpn.*, 1974, vol. 47, p. 1311.
12. Imachi, M. and Kuczkowski, R. L., *J. Mol. Struct.*, 1982, vol. 96, p. 55.
13. Hartwig, H. and Dreizler, H., *J. Mol. Struct.*, 1997, vol. 406, p. 1.
14. Williams, D.J., Crotti, P., Macchia, B., and Macchia, F., *Tetrahedron*, 1975, vol. 31, p. 993.
15. Akiba, K.-Y., Yamashita, M., Yamamoto, Y., and Nagase, S., *J. Am. Chem. Soc.*, 1999, vol. 121, 10644.
16. Addy, J.K. and Parker, K.E., *J. Chem. Soc.*, 1963, p. 915.
17. Addy, J.K. and Parker, K.E., *J. Chem. Soc.*, 1965, p. 644.
18. Stewart, J.I.P., *J. Comp. Chem.*, 1989, vol. 10, p. 209.
19. *Gaussian 98 (Revision A.1)*, Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Zakrzewski, V.G., Montgomery, J.A., Stratmann, R.E., Burant, J.C., Dapprich, S., Millam, J.M., Daniels, A.D., Kudin, K.N., Strain, M.C., Farkas, O., Tomasi, J., Barone, V., Cossi, M., Cammi, R., Men-nucci, B., Pomelli, C., Adamo, C., Clifford, S., Ochterski, J., Petterson, G.A., Ayala, P.Y., Cui, Q., Morokuma, K., Malick, D.K., Rabuck, D.A., Raghavachari, K., Foresman, J.B., Cioslowski, J., Ortiz, J.V., Stefanov, V.V., Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., Gomperts, R., Martin, R.L., Fox, D.J., Keith, T., Al-Laham, M.A., Peng, C.Y., Nanayakkara, A., Gonzalez, C., Challacombe, M., Gill, P.M.W., Johnson, B.G., Chen, W., Wong, M.W., Andres, J.L., Head-Gordon, J., Replogle, E.S., Pople, J.A., Pittsburgh: Gaussian, Inc., 1998.