Reactivities of Stable Rotamers. XXXIII. Addition of Positive Bromine Compounds to the Olefinic Moiety of 1-(9-Fluorenyl)-2-(1-methylethenyl)naphthalene Rotamers and Facile Benzene Ring Cleavage in One of the Intermediates from the *sp*-Form[1)]

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Addition of positive bromine compounds to the title olefins was carried out with use of *N*-bromosuccinimide–water and *t*-butyl hypobromite and the results are compared with the case of bromine addition. In the case of the *ap*-isomer, the reactions reported here all produce bromo-olefins in addition to an addition product, in contrast to the case of bromine which gives only an addition product. The *sp*-isomer afforded the same products as was observed for the bromine-addition but with different proportions of the products. The anionic species of more proton affinity and consequently of less affinity toward carbocations caused a decrease in formation of the addition product and an increase in formation of bromo-olefins in the case of the *ap*-isomer. The ratios of products, bromo-olefins to a cyclized compound, were affected by the anionic species in the case of *sp*-isomer: Both *N*-bromosuccinimide–water and *t*-butyl hypobromite yielded about the same amounts of the two olefins, but the yields of the cyclized compound varied significantly. The results are not explained in a straightforward manner. Probably solvent effects are important. In addition, the reaction of the *sp*-form with *N*-bromosuccinimide in tetrahydrofuran-water afforded (7*R**,7a*S**,12b*S**)-7-bromomethyl-8-[(*E*)-bromomethylene]-7-methyl-7a-[(*Z*)-3-oxo-1-propenyl]-7,7a,8,12b-tetrahydrobenzo[5,6]pentaleno[1,2-*a*]naphthalene, a compound which is derived by cleavage of a benzene ring. The structural features of the last compound are also discussed.

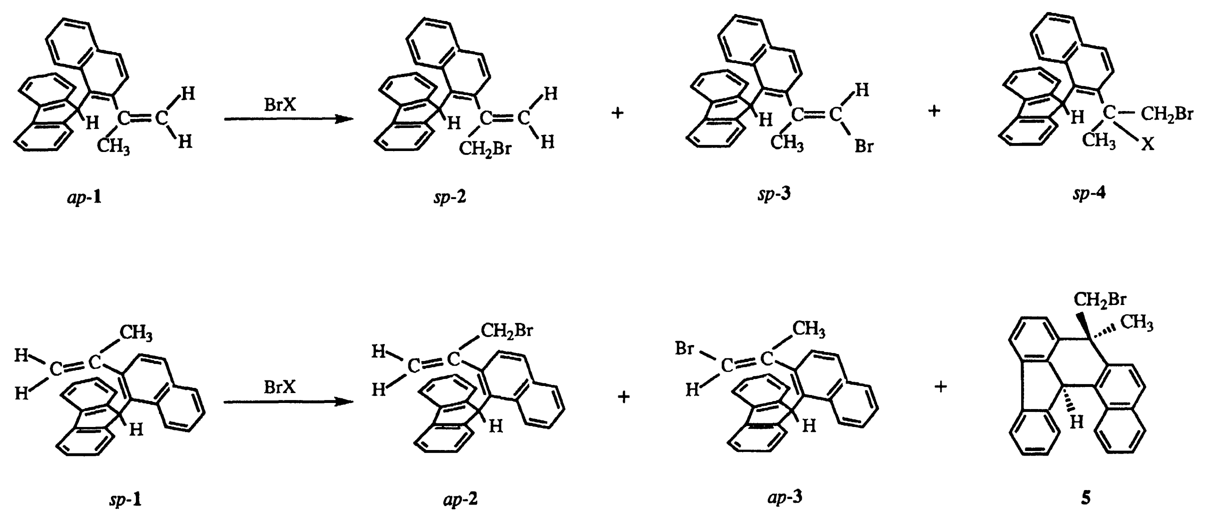
Addition of bromine to the olefinic bond in 1-(9-fluorenyl)-2-(1-methylethenyl)naphthalene rotamers (*sp*-**1** and *ap*-**1**) produced the normal addition product (**4**: X=Br) in the case of the *ap*-isomer, whereas the *sp*-isomer could not afford the normal addition product but gave olefins (*ap*-**2** and *ap*-**3**) and a cyclized product (**5**).[2)] No bromo-olefins (*sp*-**2** and *sp*-**3**) which are rotationally isomeric to *ap*-**2** and *ap*-**3** were detected from *ap*-**1** (Scheme 1).

Addition of bromine to an olefinic bond is believed to proceed via a bridged bromonium ion,[3)] if the corresponding open β-bromo-carbocation is not stable. In the case of *ap*-**1**, it is possible to form such a bromonium ion (*sp*-**6**) because there is a room for formation of such an intermediate, whereas it is impossible to form such an intermediate (*ap*-**6**) for the *sp*-isomer: If such an intermediate were to be formed above the fluorene ring in the *ap* form, the steric effects due to the fluorenyl system should be profound, as is observed for the conformational equilibria for *sp*- and *ap*-9-(*o*-*t*-butylphenyl)fluorene, in which the *ap*-form was not detected.[4)] Therefore, we assume that the bridged bromonium ion (*ap*-**6**) is not formed from *sp*-**1**, but an open-cation (*ap*-**7**) is formed instead. The formation of the olefins and the cyclized compound proceeded via *ap*-**7** which underwent deprotonation reactions to give *ap*-**2** and *ap*-**3** or a Friedel–Crafts type cyclization to give **5**.

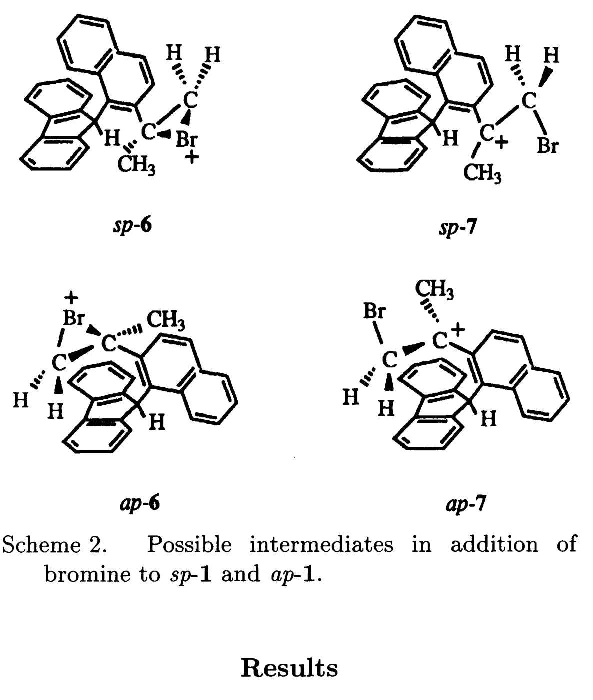
In general we may assume in an oversimplified way that there is an equilibrium between the bridged bromonium ion (**6**) and an open β-bromo-carbocation (**7**), the stability of the two cations depending on the substituents and the environment. The partial loss of stereochemistry in the addition of bromine to 1-methyl-1-propenylbenzene[5)] should be attributed to the substituent effects which favor the open cation at least to some extent owing to the electronic and/or the steric effects of the substituents, the effects being substantiated by ^{13}C NMR spectra.[6)] Our case is an example in which the steric effects of the substituents predominate (Scheme 2).

We have reported the chlorine addition to 9-(2-vinyl-1-naphthyl)fluorene, which lacks the methyl group in the substituent with respect to the compound in question here, where formation of chloro-olefins in addition to an adduct even in the *ap*-case was observed.[7)] The results suggest that we may have a chance to observe formation of bromo-olefins from the *ap*-isomer, if we can control the addition of the anionic species to the intermediate, bromonium ion (*sp*-**6**). Consequently if we find formation of bromo-olefins from *ap*-**1**, it may lend support for postulating the presence of the open-cation (*sp*-**7**) even for the *ap*-**1** case. This postulate bases on the fact that the steric effects are fairly strong, as observed by models, when the bromonium ion (*sp*-**6**) is formed.

Thus we were interested in examining the effects of the anion, which should vary in their proton affinity as well as carbon-nucleophilicity. We selected oxygen-anions in these examinations. This paper is to report the results, which as expected, show that bromo-olefins are formed even from *ap*-**1**, and to describe an unexpectedly facile benzene-ring cleavage which occurred when an ipso attack of the carbocation (*ap*-**7**) intramolecularly to the 8a (or 9a) position of the fluorene ring takes place. The possible mechanisms of this facile benzene-ring cleavage are also discussed.



Scheme 1. Reaction of positive bromine compounds with *ap*-**1** and *sp*-**1**.



Scheme 2. Possible intermediates in addition of bromine to *sp*-**1** and *ap*-**1**.

Table 2. Product Distribution in the Reaction of *sp*-**1** with Positive Bromine Compounds (% Normalized to 100%)

BrX	*ap*-**2**	*ap*-**3**	**5**
Br_2[a)]	58	30	12
NBS·H_2O[b)]	30	35	35
t-BuOBr·EtOH	42	45	13

a) Data from Ref. 2. b) Normalized after subtraction of 12% of compound **8**.

Results

The results are summarized in Tables 1 and 2.

Treatment of *ap*-**1** with *N*-bromosuccinimide in THF–water afforded *sp*-2-[(1-bromomethyl)ethenyl]-1-(9-fluorenyl)naphthalene (*sp*-**2**) and *sp*-2-(2-bromo-1-hydroxy-1-mehylethyl)-1-(9-fluorenyl)naphthalene (*sp*-**4**: X=OH) in 35 and 65% yields, respectively. The same reaction for *sp*-**1** yielded *ap*-2-[(1-bromomethyl)ethenyl]-1-(9-fluorenyl)naphthalene (*ap*-**2**), *ap*-2-[(*E*)-2-bromo-1-methylethenyl]-1-(9-fluorenyl)naphthalene (*ap*-**3**), and 8-bromomethyl-8-methyl-8,14c-dihydrodibenz[*a*.*l*]-aceanthrylene (**5**) in 26, 31, and 31% yields, respectively.

Table 1. Product Distribution in the Reaction of *ap*-**1** with Positive Bromine Compounds in Carbon Tetrachloride (% Normalized to 100%)

BrX	*sp*-**2**	*sp*-**3**	*sp*-**4**
Br_2[a)]	—	—	100
NBS·H_2O	35	—	65
t-BuOBr·EtOH	12	3	85

a) Data from Ref. 2.

In addition, the reaction of *sp*-**1** afforded an unexpected product (**8**), of which structure determination is discussed below, in 12% yield. Elemental analysis of **8** indicated that its molecular formula was $C_{26}H_{20}Br_2O$. Compound **8** showed spectral data which suggested the presence of an α,β-unsaturated aldehyde moiety in addition to a possible olefinic proton. These spectral data were so unusual that we could not assign a structure to the product from these. Thus X-ray analysis was performed on this compound. Although the compound was rather sensitive toward radiation, it was possible to obtain satisfactory results.

The atomic coordinates and an ORTEP drawing are given in Table 3 and Fig. 1, respectively. The results unambiguously show that the structure of the compound is (7*R**,7a*S**,12b*S**)-7-bromomethyl-8-[(*E*)-bromomethylene]-7-methyl-7a-[(*Z*)-3-oxo-1-propenyl]-7,7a,8,12b-tetrahydrobenzo[5,6]pentaleno[1,2-*a*]naphthalene. Clearly, one of the benzene rings in the original fluorene moiety was cleaved to form the unusual product.

Treatment of *ap*-**1** with *t*-butyl hypobromite in ethanol afforded 12% *sp*-**2**, 3% *sp*-**3**, and 85% addition product (*sp*-**4**: X=OC_2H_5), whereas the *sp*-form of **1**

Table 3. Atomic Coordinates and Equivalent Isotropic Thermal Parameters in (7*R**,7a*S**,12b*S**)-7-Bromomethyl-8-[(*E*)-bromomethylene]-7-methyl-7a-[(*Z*)-3-oxo-1-propenyl]-7,7a,8,12b-tetrahydrobenzo[5,6]pentaleno[1,2-*a*]naphthalene (**8**)

Atom	*x*	*y*	*z*	*B*(eq)
Br(1)	0.20756(5)	0.98644(5)	0.04504(3)	5.03(1)
Br(2)	−0.11611(6)	1.18842(6)	0.26108(3)	6.78(2)
O	−0.0577(6)	0.8129(6)	0.4046(3)	12.1(2)
C(1)	−0.0818(6)	0.4592(5)	0.1148(3)	5.1(1)
C(2)	−0.0937(7)	0.3424(5)	0.0865(3)	6.0(2)
C(3)	0.0044(8)	0.2982(6)	0.0546(3)	6.3(2)
C(4)	0.1166(7)	0.3678(5)	0.0507(2)	5.3(1)
C(4a)	0.1359(5)	0.4906(4)	0.0794(2)	4.4(1)
C(5)	0.2513(6)	0.5661(5)	0.0775(2)	5.0(1)
C(6)	0.2671(5)	0.6838(5)	0.1048(3)	4.5(1)
C(6a)	0.1659(4)	0.7333(4)	0.1352(2)	3.8(1)
C(7)	0.1609(4)	0.8624(4)	0.1656(2)	3.8(1)
C(7a)	0.0538(5)	0.8393(4)	0.2111(2)	4.1(1)
C(8)	−0.0424(5)	0.9498(4)	0.2115(2)	4.2(1)
C(8a)	−0.1709(5)	0.9219(4)	0.1622(2)	4.1(1)
C(9)	−0.2825(6)	0.9996(6)	0.1356(3)	5.3(1)
C(10)	−0.3879(6)	0.9512(7)	0.0871(3)	6.0(2)
C(11)	−0.3856(6)	0.8319(7)	0.0634(3)	5.6(2)
C(12)	−0.2740(5)	0.7532(6)	0.0896(2)	4.8(1)
C(12a)	−0.1672(4)	0.7988(5)	0.1384(2)	4.2(1)
C(12b)	−0.0400(5)	0.7299(4)	0.1756(2)	4.1(1)
C(12c)	0.0524(4)	0.6627(4)	0.1376(2)	3.8(1)
C(12d)	0.0332(5)	0.5375(4)	0.1114(2)	4.0(1)
C(13)	0.0979(5)	0.9588(5)	0.1110(3)	4.3(1)
C(14)	0.3012(6)	0.9155(6)	0.2036(3)	5.7(2)
C(15)	0.1278(6)	0.7895(5)	0.2792(2)	5.3(1)
C(16)	0.0879(7)	0.7810(6)	0.3349(3)	6.1(2)
C(17)	−0.0395(8)	0.8170(7)	0.3484(3)	7.3(2)
C(18)	−0.0065(6)	1.0479(6)	0.2520(3)	5.0(1)

yielded 42% *ap*-**2**, 45% *ap*-**3**, and 13% 8-bromomethyl-8-methyl-8,14c-dihydrodibenz[*a*,*l*]aceanthrylene (**5**).

The features of the product distributions are, 1) reduced formation of the adduct (*sp*-**4**) for the reagents reported here together with increased formation of olefins (*sp*-**2** and *sp*-**3**) with respect to treatment with bromine in the case of *ap*-**1** and 2) formation of about the same amounts of two olefins *ap*-**2** and *ap*-**3** and varying amounts of the cyclic compound (**5**) in the case of *sp*-**1**. Facile benzene ring cleavage in formation of **8** from *sp*-**1** may also be cited, although the yield is only ca. 10%. The details of differences are mentioned in the Discussion section.

Discussion

In order to facilitate comparison, the results are summarized in Tables 1 and 2 which also incorporate the results of bromine addition reactions. A mixture of *N*-bromosuccinimide and water is often used as a substitute for hypobromic acid,[8] which is a source of positive bromine in electrophilic addition reactions to an olefinic bond. *t*-Butyl hypobromite behaves similarly.[9]

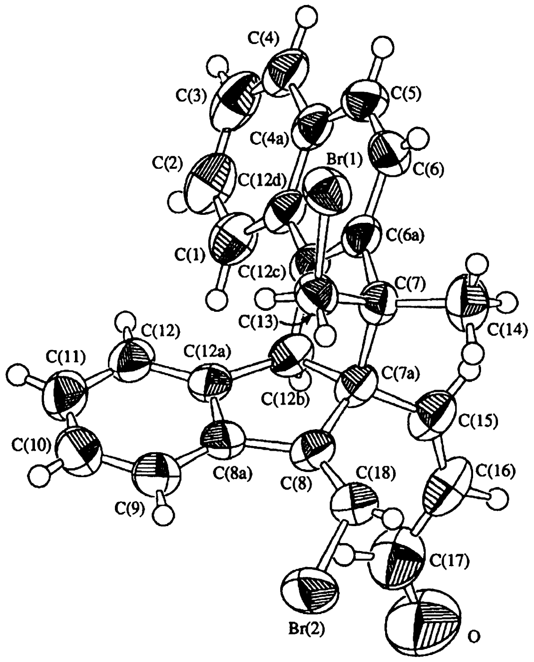


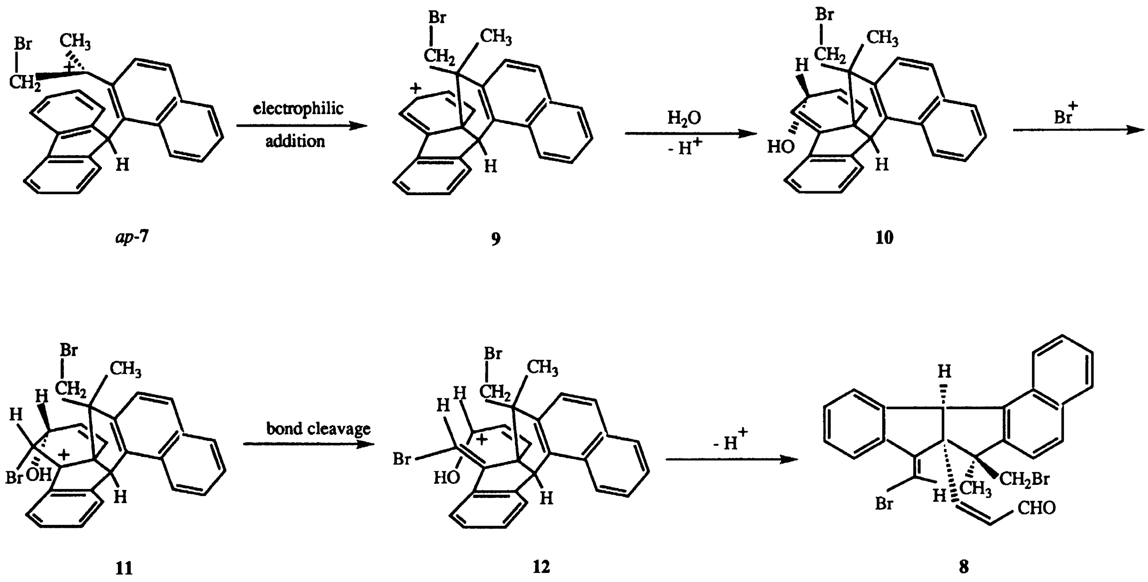
Fig. 1. An ORTEP drawing of (7*R**,7a*S**,12b*S**)-7-Bromomethyl-8-[(*E*)-bromomethylene]-7-methyl-7a-[(*Z*)-3-oxo-1-propenyl]-7,7a,8,12b-tetrahydrobenzo-[5,6]pentaleno[1,2-*a*]naphthalene (**8**).

Clearly, the most obvious difference between the bromine addition and the positive bromine compounds reported in this paper is the formation of olefins for *ap*-**1**. Whereas bromine gives the simple addition product quantitatively from *ap*-**1**, both *N*-bromosuccinimide–water and *t*-butyl hypobromite in ethanol give bromo-olefins (*sp*-**2** and *sp*-**3**) in addition to the addition products (**4**). More abundant formation of the adduct (**4**) in the case of *t*-butyl hypobromite than in the case of hypobromic acid (from NBS and water) can be attributed to the better nucleophilic nature of ethoxide (or ethanol) with respect to that of hydroxide (or water). As a corollary, bromo-olefins (*sp*-**2** and *sp*-**3**) are formed more abundantly in the reaction with hypobromic acid than in that with the hypobromite.

In the case of *sp*-**1**, the formation ratios of the bromo-olefins (*ap*-**2** and *ap*-**3**) to the cyclized compound (**5**) are difficult to explain from simple consideration of proton affinity: Because water and ethanol are weak acids, the corresponding anion should have strong proton-affinity with respect to bromide ion, yet the olefins are formed in practically the same ratios. The reason for

Table 4. Selected Bond Distances in Compound **8** with Standard Deviations in Parentheses

Atom	Atom	Distance/Å	Atom	Atom	Distance/Å
C(6a)	C(7)	1.507(6)	C(7)	C(7a)	1.594(6)
C(7)	C(13)	1.548(6)	C(7a)	C(8)	1.511(6)
C(7a)	C(12b)	1.563(6)	C(8)	C(8a)	1.479(6)
C(8)	C(18)	1.331(7)	C(12a)	C(12b)	1.513(6)
C(12b)	C(12c)	1.515(6)			



Scheme 3. Possible reaction paths for the formation of **8** from *sp*-**1**.

Table 5. Selected Bond Angles in Compound **8** with Standard Deviations in Parentheses

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C(6a)	C(7)	C(7a)	101.5(3)	C(6a)	C(7)	C(13)	109.5(4)
C(6a)	C(7)	C(14)	115.5(4)	C(7a)	C(7)	C(13)	108.6(3)
C(7a)	C(7)	C(14)	113.6(4)	C(13)	C(7)	C(14)	107.9(4)
C(7)	C(7a)	C(8)	113.3(4)	C(7)	C(7a)	C(12b)	104.0(3)
C(7)	C(7a)	C(15)	110.5(4)	C(8)	C(7a)	C(12b)	105.1(3)
C(8)	C(7a)	C(15)	115.8(4)	C(12b)	C(7a)	C(15)	107.1(4)
C(7a)	C(8)	C(8a)	107.1(4)	C(7a)	C(8)	C(18)	121.5(4)
C(8a)	C(8)	C(18)	131.4(5)	C(12a)	C(12b)	C(12c)	119.8(4)
C(7a)	C(12b)	C(12a)	103.2(4)	C(7a)	C(12b)	C(12c)	102.9(4)

this anomaly may involve solvent effects, which require further investigation for understanding. The formation ratio of olefins which is almost the same for *N*-bromosucinimide–water and *t*-butyl hypobromite will mean that, because of the high proton affinity of those anions derived from water and ethanol, they abstract a proton from the intervening cation (*ap*-**7**) without discrimination between the bromomethyl group and the methyl group. *N*-Bromosuccinimide–water clearly gives more cyclization products than others. The reason for the high yield is not well understood but it may also be connected with the difference in solvation of the intervening cation.

Formation of the unexpected product (**8**) may be rationalized in the following way (Scheme 3 in which stereochemistry of compound **8** is reversed from those of intermediates *ap*-**7** through **12** for the convenience of drawing and of nomenclature). It is known that the cationic center (*ap*-**7**) which is created by addition of the bromine cation to the olefinic bond in *sp*-**1** is closely located to $C_1(C_8)$ and $C_{9a}(C_{8a})$.[2] Compound **5** is formed when the cation adds to the benzene ring at the 1 position and then deprotonation follows. Adding the cation to the C_{9a} position is a kind of ipso attack which is known to be common in electron-rich aromatic systems.[10—12] If it occurs, then the intermediate **9** is formed which can be a resonance hybrid of various valence isomers. When the cation **9** is trapped by water, the product will be an alcohol (**10**): This type of reactions are known to occur if water is present in a not too acidic system.[13] The double bond in **10** may be attacked by a positive bromine species. Here, the attack preferentially occurs at the 4-position because of the formation of a tertiary cation and for the steric reasons. We write structures of the products as in the scheme by considering the steric effects. When the bonding electrons between C(Br) and C(OH) are given to the cationic center, the bond is cleaved to form a C(Br)=C double bond and an α-hydroxy-carbocation (**12**), which loses a proton on the oxygen atom to form the observed product (**8**).

The facile benzene ring cleavage of this type has not been known to the best of our knowledge, but there are several examples of C–C bond cleavage if a β-hydroxy carbocation is formed: Dehydration of 1,3-diols with acid gives rise to fragmentation to a carbonyl compound and an olefin.[14—16] The driving force must be the repulsion of a stable molecule to form a stable

Table 6. Selected Torsion Angles in Compound **8** with Standard Deviations in Parentheses

Atom	Atom	Atom	Atom	Torsion angle/°
C(6)	C(6a)	C(7)	C(13)	84.1(6)
C(6)	C(6a)	C(7)	C(14)	−37.9(7)
C(7)	C(6a)	C(12c)	C(12b)	−5.0(5)
C(12c)	C(6a)	C(7)	C(7a)	20.8(4)
C(6a)	C(7)	C(7a)	C(8)	−141.2(4)
C(6a)	C(7)	C(7a)	C(12b)	−27.7(4)
C(6a)	C(7)	C(7a)	C(15)	86.9(4)
C(13)	C(7)	C(7a)	C(8)	−25.9(5)
C(13)	C(7)	C(7a)	C(12b)	87.6(4)
C(13)	C(7)	C(7a)	C(15)	−157.7(4)
C(14)	C(7)	C(7a)	C(8)	94.1(5)
C(14)	C(7)	C(7a)	C(12b)	−152.3(4)
C(14)	C(7)	C(7a)	C(15)	−37.7(6)
C(7)	C(7a)	C(8)	C(18)	−84.7(5)
C(12b)	C(7a)	C(8)	C(8a)	−16.7(5)
C(15)	C(7a)	C(8)	C(18)	44.5(7)
C(7)	C(7a)	C(12b)	C(12c)	25.3(4)
C(8)	C(7a)	C(12b)	C(12a)	19.2(4)
C(15)	C(7a)	C(12b)	C(12a)	142.9(4)
C(15)	C(7a)	C(12b)	C(12c)	−91.8(4)
C(7a)	C(8)	C(8a)	C(12a)	7.4(5)
C(7a)	C(8)	C(18)	Br(2)	−177.3(4)
C(8a)	C(8)	C(18)	Br(2)	1.6(9)
C(8)	C(8a)	C(12a)	C(12b)	−5.6(5)
C(8a)	C(12a)	C(12b)	C(7a)	−15.6(5)
C(7a)	C(12b)	C(12c)	C(6a)	−13.6(5)

α-hydroxy carbocation. There are also several similar bond cleavages in Beckmann rearrangement of α-hydroxy compounds: Benzoin[17—20)] and other α-hydroxy ketone oximes[21)] undergo facile C–N bond cleavage when Beckmann rearrangement is attempted to give an isonitrile and a carbonyl compound. Although the reaction mechanisms have not been discussed, cleavage of 1-(polymethoxyphenyl)cyclohexene to produce cyclohexanone under acidic conditions may also fall into this category.[22)] A recent report of the facile cleavage of 3-methyl-2-butenyl esters by iodine may be another example of this reaction.[23)] It may be interesting to know whether this unexpectedly facile benzene ring cleavage can occur in general or not. A work on this line is in progress.

It is an unanswered question why this abnormal addition-cleavage product was formed to an extent of ca. 10% yield when *N*-bromosuccinimide–water was used but we do not observe its formation in other cases. There must be several factors which caused this result, including solvent nucleophilicity, stabilization of the intermediate(s) by solvation, and the ease of addition of the positive bromine species to a double bond. At least, solvent effects on the product distribution must be explored to understand the phenomena as well as the formation ratios of various products discussed above.

The structure of compound **8** deserves mention because this is a highly congested molecule (Tables 4, 5, and 6). The points of interests are in the region of the two five-membered rings which are cis-fused. Clearly the fused part is distorted to accommodate the alkyl(alkenyl) groups, as can be seen from the torsion angles concerned. The five-membered ring fusion angle is widely opened at C(7a) and C(12b). Each cyclopentene ring takes a distorted half-chair conformation with respect to the fused aromatic ring. The C(13)–C(7) bond is almost orthogonal to the C(7a)–C(8) and the C(7a)–C(12b) bonds. All the torsion angles involving the C(7)–C(7a) axis are abnormal, because of being a substituted cyclopentene structure: The *cis*-substituents in the five-membered ring C(6a)–C(7)–C(7a)–C(12b)–C(12c) are twisted by ca. 30° from the eclipsing positions to avoid van der Waals interactions. The nonbonding distance between C(14) and C(15) and that between C(15) and C(18) are 2.90 and 3.03 Å, respectively. The stereochemistry of the bromomethylene group which is attached to C(8) clearly takes an *E*-structure and the atoms involved in this olefinic bond are almost in a same plane irrespective of the sterically demanding conditions.

Bond lengths and bond angles are astonishingly normal irrespective to the unusual torsion angles. There are two bonds longer than usual, C(7a)–C(12b) and C(7)–C(7a), which are involved in the highly substituted region. Other bonds are normal as are seen in Table 4. Bond angles are also, by and large, normal except for several cases. For tetrahedral carbons, C(7), C(7a), and C(12b) show some abnormal values, as expected, but the abnormal cases are few. For the sp^2 hybridized carbons, C(8) exhibits some unusual bond angles probably because of the steric effects of the substituents concerned to make the planar structure.

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 MHz, before separation of the products. The product ratios shown in Tables 1 and 2 are average of three runs. Identification of the products was carried out by comparing the ^{1}H NMR spectra with authentic specimen, when known, or by elemental analyses together with ^{1}H NMR spectra, when unknown. Infrared spectra were determined on a Hitachi I-2000 spectrometer.

Reaction of the Olefin Rotamers (1) with *N*-Bromosuccinimide and Water. *ap*-**1** (or *sp*-**1**) (100 mg or 0.300 mmol) was added to a mixture of 56.2 mg (0.316 mmol) of *N*-bromosuccinimide, 5.0 mL of water, and 5.0 mL of tetrahydrofuran. The mixture was stirred for 6 h at room temperature, diluted with water, and extracted with dichloromethane. The dichloromethane solution was dried and the solvent was evaporated. The residue was submitted to thin-layer chromatography on silica gel (4 : 1 hexane–dichloromethane eluent). Only *sp*-**3** and *sp*-2-(2-bromo-1-hydroxy-1-methylethyl)-1-(9-fluorenyl)naphthalene (*sp*-**4**: X = OH) were obtained with R_f values of 0.45 and 0.43, respectively. *sp*-**3** was identical with the authentic specimen.[2)] *sp*-**4** (X=OH) was recrystallized from hexane–dichloromethane, mp 118.5—119.0 °C. Found: C, 72.73; H, 5.14%. Calcd for $C_{26}H_{21}BrO$: C, 72.82; H, 4.94%. ^{1}H NMR ($CDCl_3$) δ=2.08 (3H, s), 2.89 (1H, br s), 4.04 and 4.35 (2H, ABq, J=10.6 Hz), 6.46 (1H, d, J=8.8 Hz), 6.68 (1H, s), 6.77—6.83 (1H, m), 7.10 (1H, d, J=7.7 Hz), 7.17—7.25 (4H, m), 7.39—7.44 (2H, m), 7.69—7.82 (3H, m), 7.95—7.98 (2H, d, J=7.8 Hz).

The similar treatment of *sp*-**1** afforded *ap*-**2**, *ap*-**3**, **5**, and **8** at R_f of 0.60, 0.45, 0.33, and 0.02, respectively.

ap-**2**, *ap*-**3**, and **5** showed the identical ^{1}H NMR spectra with the authentic specimens in the literature.[2)]

Compound **8** was recrystallized from ether–hexane, mp 105—125 °C (decomp). Found: C, 61.24; H, 3.96%. Calcd for $C_{26}H_{20}Br_2O$: C, 61.44; H, 3.97%. ^{1}H NMR ($CDCl_3$) δ=1.80 (3H, s), 2.82 and 3.41 (2H, ABq, J=10.1 Hz), 5.30 (1H, s), 5.93 (1H, dd, J=12.2, 8.2 Hz), 6.48 (1H, s), 7.20 (1H, d, J=12.2 Hz), 7.34—7.59 (5H, m), 7.68 (1H, app. t, J=ca. 7.1 Hz), 7.84 (1H, d, J=8.3 Hz), 7.94 (1H, d, J=8.2 Hz), 8.17 (1H, d, J=8.1 Hz), 8.58 (1H, d, J=7.0 Hz), 9.94 (1H, d, J=8.1 Hz). IR ($CHCl_3$) 1674 cm^{-1}.

Reaction of Olefin Rotamers (1) with *t*-Butyl Hypobromite. To a solution of 100 mg (0.300 mmol) of the *ap*-olefin (*ap*-**1**) in 10 mL of ethanol, was slowly added 35.8 mL (0.315 mmol) of *t*-butyl hypobromite[24)] in 5 mL of ethanol at room temperature. The mixture was allowed to stand for 4 h, poured into water and extracted with dichloromethane. The extract was dried over magnesium sulfate and the solvent was evaporated. The residue was separated by TLC (7 : 2 hexane–dichloromethane eluent) to afford *sp*-**2**, *sp*-**3**, and *sp*-**4** (X=OC_2H_5) showing R_f values of 0.57, 0.45, and 0.33, respectively.

sp-2-(2-Bromo-1-ethoxy-1-methylethyl)-1-(9-fluorenyl)-naphthalene (*sp*-**4**: X=OC_2H_5) was purified by recrystallization from hexane-dichloromethane, mp 147—150 °C. Found: C, 73.52; H, 5.44%. Calcd for $C_{28}H_{25}BrO$: C, 73.60; H, 5.44%. ^{1}H NNR ($CDCl_3$) δ=1.06 (3H, t, J=6.5 Hz), 2.13 (3H, s), 3.65 and 3.74 (2H, ABq coupled with 3H, J=8.4 and 6.5 Hz), 4.10 and 4.02 (2H, ABq, J=10.4 Hz), 6.39 (1H, d, J=10.4 Hz), 6.79 (1H, ddd, J=9.0, 6.8, 1.4 Hz), 6.99 (1H, s), 7.04 (1H, d, J=6.8 Hz), 7.13—7.26 (4H, m), 7.37—7.42 (2H, m), 7.64 (1H, d, J=7.8 Hz), 7.71 (1H, d, J=9.0 Hz), 7.81 (1H, d, J=7.3 Hz), 8.00 (2H, d, J=7.8 Hz).

The reaction of the *sp*-olefin (*sp*-**1**) was carried out similarly. *ap*-**2**, *ap*-**3**, and **5** gave R_f values of 0.60, 0.47, and 0.33, respectively, in TLC with 4 : 1 hexane–dichloromethane eluent. They gave the identical ^{1}H NMR spectra which were described above for each compound.

X-Ray Crystallography.[25)] Crystals suitable for X-ray crystallography were grown from ether–hexane. A sample of 0.20×0.20×0.30 mm^3 size was mounted on an Rigaku AFC7R four circle diffractometer and X-Ray data were collected with graphite monochromated Cu $K\alpha$ (λ=1.54178 Å) radiation. The scan mode was the ω–2θ method to a maximum 2θ value of 120.1°. The structure was solved by the direct method and refined by the full matrix least-squares method by using the teXsan crystallographic software package. Anisotropic thermal parameters were employed for non-hydrogen atoms and isotropic for hydrogens. Reflection data within $|F_o|>2\sigma(F_o)$ were used for the structure determination and refinement. The function minimized was $\sum[w(|F_o|-|F_c|)]^2$, where $w=[\sigma^2(F_o)]^{-1}$. The following crystal data were obtained. Formula $C_{26}H_{20}Br_2O$, F. W. 508.25, scan rate 16.0° min^{-1}, scan range $(1.84+0.30\tan\theta)°$, crystal system monoclinic, sapce group $P2_1/n$, a=9.9607(9), b=10.5575(9), c=20.7460(6) Å, β=102.934(4)°, V=2126.3(3) Å^3, Z=4, D_c 1.59 g cm^{-3}, μ 49.4 cm^{-1}, No. of data collected 3579, No. of data used 3364, R 0.039, R_w 0.046.

References

1) For the preceding paper of this series, see: M. Ōki, Y. Taguchi, T. Okamoto, T. Miyasaka, K. Hamada, S. Toyota, K. Yonemoto, and G. Yamamoto, *Bull. Chem. Soc. Jpn.*, **66**, 3790 (1993).

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

3) I. Roberts and G. E. Kimball, *J. Am. Chem. Soc.*, **59**, 947 (1937).

4) M. Nakamura, N. Nakamura, and M. Ōki, *Bull. Chem. Soc. Jpn.*, **50**, 2986 (1977).

5) J. H. Rolston and K. Yates, *J. Am. Chem. Soc.*, **91**, 1477 (1969).

6) G. A. Olah, R. D. Porter, C. L. Jeuell, and A. M. White, *J. Am. Chem. Soc.*, **94**, 2044 (1972).

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

8) E. E. van Tamelen, A. Storni, E. J. Hessler, and M. Schwartz, *J. Am. Chem. Soc.*, **85**, 3295 (1963).

9) J. -M. Geneste and A. Kergomard, *Bull. Soc. Chim. Fr.*, **1963**, 470.

10) P. B. D. de la Mare, *Acc. Chem. Res.*, **7**, 361 (1974).

11) S. R. Hartshorn, *Chem. Soc. Rev.*, **3**, 167 (1974).

12) B. Moodie and K. Schofield, *Acc. Chem. Res.*, **9**, 287 (1976).

13) P. C. Myhre, *J. Am. Chem. Soc.*, **94**, 7921 (1972).

14) H. E. Zimmerman and J. English, Jr., *J. Am. Chem. Soc.*, **76**, 2285 (1954).

15) H. E. Zimmerman and J. English, Jr., *J. Am. Chem. Soc.*, **76**, 2291 (1954).

16) H. E. Zimmerman and J. English, Jr., *J. Am. Chem. Soc.*, **76**, 2294 (1954).

17) A. Werner and A. Piguet, *Ber. Dtsch. Chem. Ges.*, **37**, 4295 (1904).

18) A. Werner and T. Detscheff, *Ber. Dtsch. Chem. Ges.*, **38**, 69 (1905).

19) J. S. Buck and W. S. Ide, *J. Am. Chem. Soc.*, **53**, 1912 (1931).

20) A. H. Blatt and R. P. Barnes, *J. Am. Chem. Soc.*, **56**, 1148 (1934).

21) J. N. Shah, Y. P. Mehta, and G. M. Shah, *J. Org. Chem.*, **43**, 2078 (1978).

22) J. M. Bruice and F. K. Sutcliffe, *Chem. Ind.* (*London*), **1955**, 745.

23) J. Cossy, A. Albouy, M. Scheloske, and D. G. Pardo, *Tetrahedron Lett.*, **35**, 1539 (1994).

24) C. Walling and A. Padwa, *J. Org. Chem.*, **27**, 2976 (1962).

25) Tables of coodinates for the hydrogen atoms, anisotropic thermal parameters of the non-hydrogen atoms, and complete F_o-F_c data are deposited as Document No. 67060 at the Office of the Editor of Bull. Chem. Soc. Jpn.