Hz, H-1), 8.52 (s, H-11), 11.92 (s, OH-4), 11.84 (s,OH-6). Anal. Calcd for $C_{27}H_{24}O_{10}NF_3$: C, 55.96; H, 4.17. Found: C, 55.69; H, 4.23.

7-Epi-8-demethoxy-7-*O*-(2,3,4-trideoxy-3-(trifluoroacetamido)-α-L-*lyxo*-hexopyranosyl)aranciamycinon (29): 20.0 mg of the *cis*-diol **21** afforded after TLC 3.4 mg (24%) of the polar glycoside **29**: mp 134 °C dec.; IR 3420, 2980, 1710, 1673, 1621, 1593 cm^{-1}; UV/vis 210 (4.38), 239 (4.45), 261 (4.30), 438 nm (4.04); ^1H NMR (400 MHz) δ 1.25 (d, J = 6.7 Hz, H-6'), 1.47 (s, CH_3), 1.94 (m, H-2') 2.30 (dd, J = 15.2, J = 3.9 Hz, H-8), 2.68 (dd, J = 15.2, J = 3.9 Hz, H-8), 3.64 (m, H-4'), 4.13 (s, OH-9), 4.31 (m, H-3'), 4.38 (q, J = 6.7 Hz, H-5'), 5.43 (d, J = 3.5 Hz, H-1'), 5.55 (t, H-7), 6.65 (d, J = 8.4 Hz, NH), 7.37 (dd, J = 8.4, J = 1.0 Hz, H-3), 7.78 (t, H-2), 7.92 (dd, J = 7.6, J = 1.0 Hz, H-1), 8.51 (s, H-11), 11.91 (s, OH-4), 12.83 (s, OH-6).

9-Epi-8-demethoxy-7-*O*-(2,3,6-trideoxy-3-(trifluoroacetamido)-α-L-*lyxo*-hexopyranosyl)aranciamycinon (30). From the less polar zone of the chromatography (see above) 5.0 mg (31%) of glycoside **30** was isolated: mp 147 °C; IR 3460, 3920, 1707, 1672, 1621, 1595 cm^{-1}; UV/vis see **29**; ^1H NMR (400 MHz) δ 1.33 (d, J = 6.5 Hz, H-6'), 1.42 (s, CH_3), 1.87 (dt, J = 12.6, J = 3.6 Hz, H-2_a'), 2.00 (d, J = 8.2 Hz, OH), 2.08 (dd, J = 5.2, J = 3.6 Hz, H-2_e'), 2.47 (dd, J = 14.7, J = 7.0 Hz, H-8), 2.64 (dd, J = 14.7, J = 6.0 Hz, H-8), 3.66 (m, H-4'), 4.25 (q, H-5'), 4.29 (m, H-3'), 5.20 (t, H-7), 5.51 (d, J = 3.6 Hz, H-1'), 6.69 (d, J = 8.4 Hz, NH), 7.37 (dd, J = 8.4, J = 1.1 Hz, H-3), 7.76 (t, H-2), 7.90 (dd, J = 7.6, J = 1.1 Hz, H-1), 8.45 (s, H-11), 11.90 (s, OH-4), 12.81 (s, OH-6).

Registry No. **3**, 106-51-4; **4**, 58274-64-9; **5**, 76695-89-1; **7**, 14787-38-3; **8**, 605-93-6; **9**, 2161-90-2; **10**, 91295-25-9; **11**, 91295-26-0; **12**, 3300-25-2; **13**, 91295-27-1; **14**, 91295-28-2; **15**, 91310-97-3; **16**, 91295-29-3; **17**, 84340-89-6; **18**, 84341-05-9; **19**, 91295-30-6; **20**, 91310-98-4; **21**, 91295-31-7; **22**, 91295-32-8; **24**, 57785-90-7; **25**, 91382-92-2; **26**, 91310-99-5; **27**, 91295-33-9; **28**, 91295-34-0; **29**, 91382-93-3; **30**, 91382-94-4; ethyl acetoacetate, 141-97-9.

The Bromination of 5,8-Diacetoxy-1,4-dihydro-1,4-ethanonaphthalene

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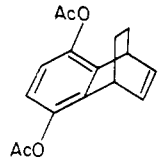
Received March 14, 1984

The bromination of 5,8-diacetoxy-1,4-dihydro-1,4-ethanonaphthalene has been found to give only one product, the dibromide produced via a Wagner–Meerwein rearrangement with accompanying aryl migration. The structure of the product was determined by ^1H–^{13}C correlation NMR and ^{13}C–^{13}C double quantum coherence NMR. The bromine configurations and the molecular conformation were determined by chemical shift considerations coupled with a complete analysis of the proton–proton spin coupling constants. Structures reported in related studies are brought into question by this result which has a bearing also on recent investigations of homoconjugation in 1,4-dihydro-1,4-ethanonaphthalene systems.

The addition of bromine to benzobicyclooctadienes such as 5,8-diacetoxy-1,4-dihydro-1,4-ethanonaphthalene (**1**) may lead to a multiplicity of products. Attack on the



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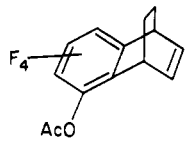

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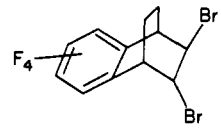

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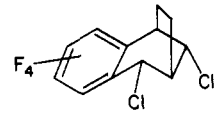
double bond may be syn or anti to the aromatic ring. The intermediate(s), whether bromonium ion or carbocation, may react directly with bromide ion to give nonrearranged product or may undergo Wagner–Meerwein rearrangement involving either the aryl group or the ethano bridge before reacting to give rearranged dibromides. The Barkhash group in Russia have examined the addition of bromine to tetrafluorobenzobicyclooctadiene (**2**).[1] The product was reported as the unrearranged dibromide (**3**). The addition of chlorine gave a mixture of the 1,2-addition product and the rearranged compound (**4**). As a matter for future reference, it may be mentioned that the treatment of the tetrafluorobenzobarrelene (**5**) with *tert*-butyl hypochlorite in acetic acid gave a mixture of rearranged chloroacetates **6** and **7**.[2] The principal method of structure determination in these studies was proton magnetic resonance aided by spin decoupling. If one bears in mind the uncertainties



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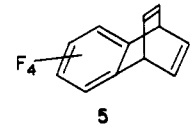

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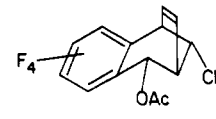

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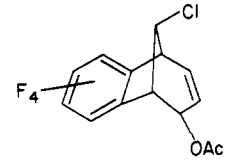

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imposed by the small range of vicinal axial–equatorial and equatorial–equatorial spin–spin coupling constants along with the even greater uncertainties introduced by the effects of electronegative groups such as bromine, chlorine, and acetoxy[3] on these coupling constants, then one feels justified in expressing reservations about structural assignments in such closely related compounds as those encountered in these studies.

Recently, Paquette and co-workers[4] have studied the addition of a series of weak electrophiles to 2-methyl-1,4-dihydro-1,4-ethanonaphthalene and its 5,8-dimethoxy and 5,6,7,8-tetrafluoro analogues. Predominent syn stereoselectivity was observed for photooxygenation, cyclopropanation, oxymercuration, hydroboration, and epoxidation. On the basis of these results a case was made

(1) Provolotskaya, N. N.; Limasova, T. I.; Berus, E. I.; Exner, O.; Barkhash, V. A. *J. Org. Chem. USSR (Engl. Transl.)* **1970**, *6*, 1615.
(2) Vorozlitsov, I. N.; Berus, E. I.; Derendyaev, B. G.; Barkhash, V. A. *J. Gen. Chem. USSR (Engl. Transl.)* **1969**, *39*, 2264.
(3) Jackman, L. M.; Sternhell, S. "Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry"; Pergamon Press: Oxford, 1969.
(4) Paquette, L. A.; Bellamy, F.; Wells, G. J.; Bohm, M. C.; Gleiter, R. *J. Am. Chem. Soc.* **1981**, *103*, 7122.

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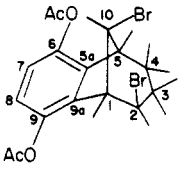
Table I. Proton NMR Parameters for Compound 9



9

H no.[a]	δ	H no.[a]	J,[c] Hz	H no.[a]	J,[c] Hz
1	3.67	1,2	2.6	3a,4s	1.0
2	4.30	1,10	3.9	3s,4a	12.1
3a	1.90	2,3a	1	3s,4s	6.1
3s	2.03	2,3s	6.3	4a,4s	−15.8
4a	1.58	3a,3s	−13.7	4a,5	3.4
4s	2.58	3a,4a	5.6	4s,5	2.0
5	3.28				
7/8	6.97[b]				
	7.03				
10	4.53				

[a] The designations a and s refer to positions anti and syn to the aromatic ring. [b] Not specifically assigned. [c] Estimated to be good to ±0.1 Hz except for $J_{2,3a}$ which is about 0.4 Hz.

for the absence of any significant homoconjugative stabilization by the π-electrons of the aryl group for a developing positively charged transition state in these additions to the double bond. Subsequently, it has been shown[5] that the electrophilic character of *m*-chloroperbenzoic acid can be fine tuned with the aid of hydrogen bonding solvents. Thus as the peracid becomes a weaker electrophile due to increasing involvement in hydrogen bonding to the solvent, the epoxidation of a series of 5,8-disubstituted-1,4-dihydro-1,4-ethanonaphthalenes was shown to lead to increasing amounts of the less sterically favored *anti*-epoxide.

In view of the uncertainties in structure derived from the earlier NMR studies and the interesting questions concerning steric and electronic effects controlling electrophilic additions in the benzobicyclooctadiene system, it seemed of some importance to examine the bromination of 5,8-diacetoxy-1,4-dihydro-1,4-ethanonaphthalene. The results of that study are reported here.

Experimental Section

Conventional proton NMR spectra were taken on a Varian EM-390, and ^{13}C NMRs were acquired on a JEOL FX-60 operating at 15 MHz. All spectra were taken in deuteriochloroform with internal Me_4Si. High field spectra and 2-D experiments were acquired on a prototype GN-300 at General Electric Company, NMR Instruments in Freemont. The synthesis of 5,8-diacetoxy-1,4-dihydro-1,4-ethanonaphthalene was described previously.[5]

Bromination of 5,8-Diacetoxy-1,4-dihydro-1,4-ethanonaphthalene. To a solution of 0.272 g (1 mmol) of the olefin 1 in 5 mL of chloroform was added dropwise and with stirring a solution of 0.17 g (1.06 mmol) of bromine in 2 mL of chloroform. The reaction was allowed to stand for 15 min at room temperature, and the solvent was removed by rotary evaporation. The ^{13}C NMR of the crude material indicated that only one product was formed quantitatively. Initially this material was isolated and purified by preparative thin-layer chromatography and crystallization from hexane, mp 125–126 °C. subsequently, it was found sufficient to recrystallize the crude product several times from ethanol. Yields of isolated, crystalline material were usually around 70%. Anal. Calcd for $C_{16}H_{16}O_4Br_2$: C, 44.47; H, 3.73; Br, 36.99. Found: C, 44.10; H, 3.79; Br, 36.74.

Treatment of ethanol solutions of the dibromide with hot ethanolic silver nitrate slowly gave a curdy, buff precipitate over several hours. A solution of the dibromide in acetone saturated with sodium iodide gave only a light yellow color after the period of a week. A sample (ca. 150 mg) in 10 mL of ethanol was refluxed overnight with 1 g of powdered zinc. Filtration and rotary evaporation gave a crude product which showed two spots on TLC. The more polar spot corresponded in R_f to an authentic sample of 5,8-dihydroxy-1,4-dihydro-1,4-ethanonaphthalene. The ^{13}C NMR of the crude product confirmed this material as the major of two products by comparison with the spectrum of an authentic sample.

The chemical shifts and coupling constants of the dibromide are given in Table I. The latter were derived with the aid of selective proton decoupling experiments of the four methine protons falling between 3.5 and 4.5 ppm. Because of the highly first-order character of the aliphatic portion of the proton spectrum, it was possible to analyze and simulate the spectrum by a subdivision into a series of four, five, and six spin systems using the six spin program available on the FX-60. Protons were assigned to their respective carbons with the aid of a 2-D proton–carbon correlation spectrum.

The ^{13}C chemical shifts are given in Table II along with the relative LIS determined by incremental additions of $Yb(FOD)_3$. The latter were determined by using the FX-60 instrument. The carbon–carbon connectivity scheme was determined by conducting the 2-D double quantum coherence experiment as described by Turner.[6] That portion of the 2-D plot concerning the aliphatic carbons is shown in Figure 1. For this experiment 150 mg of dibromide dissolved in deuteriochloroform was examined in a 5-mm NMR tube. Total data accumulation was 3.5 days.

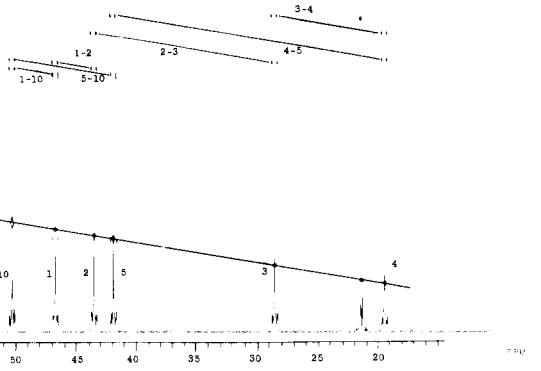


Figure 1. Carbon-13 double quantuum coherence plot for 9 with connectivity lines drawn for the aliphatic carbons in the spectrum.

Table II. ^{13}C Chemical Shifts and Relative LIS for 9

δ	relative LIS	assign
18.91	0.15	4
20.79	0.28	Me's
	0.38	
28.26	0.12	3
42.10	0.20	5
43.53	0.11	2
47.07	0.17	1
50.55	0.12	10
122.54	0.27	8
123.32	0.30	7
135.60	0.26	9a
136.45	0.29	5a
142.81	0.31	9
143.59	0.39	6
169.13	0.67	CO's
	1.00	

Results and Discussion

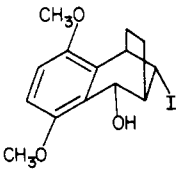
The bromination of olefin 1 gives a single dibromide. Assignment of the structure of the product was made difficult by the observation that there was no reaction with sodium iodide in acetone; yet treatment of the dibromide with zinc in ethanol gave a significant amount of returned starting olefin. These reactions have served as classical

(5) Smith, W. B.; Stock, L.; Cornforth, Sir John *Tetrahedron* **1983**, *39*, 1379.

(6) Turner, D. L. *J. Magn. Reson.* **1983**, *53*, 259.

expectations of vicinal dibromides. However, the Barkhash group[1] observed that the rearranged dibromide, 2-*exo*,7-*anti*-dibromotetrafluorobenzonorborn-5-ene, when treated with magnesium in tetrahydrofuran gave back tetrafluorobenzonorbornene from which the dibromide had originated. It would appear that these reactive, bicyclic dibromides, even when the bromines are not vicinally located, can revert to the original olefin structure.

Consideration was given to the possibility that the product might have rearranged structures analogous to **4** or to **7**. The former has been proposed as one of the products of chlorination of tetrafluorobenzobicyclooctadiene.[1] While the latter has been observed in reactions of the tetrafluorobenzobarrelene system,[2] no analogues have been reported as products of electrophilic additions in the benzobicyclooctadiene system. Recently,[5] it has been reported that 5,8-dimethoxy-1,4-dihydro-1,4-ethanonaphthalene reacts with hypoiodous acid to form **8**. On the basis of these observations, one might be led to favor a dibromide structure analogous to **4**.



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The ambiguities posed by the literature and chemical evidence suggested a more detailed NMR examination of the product. While the 90-MHz proton NMR clearly showed the four methine protons, the overall eight spin system of the aliphatic protons was too tightly coupled for successful analysis even with the aid of proton decoupling. The 15-MHz carbon NMR displayed all of the carbons except that the acetate methyls and carbonyls, respectively, were coincident. Single-frequency off-resonance decoupling allowed assignment of the proton substitution pattern. The relative lanthanide induced shifts (LIS) were measured by incrementing in $Yb(FOD)_3$ while observing changes in the various line frequencies. These are recorded along with the ultimate carbon assignments in Table II. These data show that the lanthanide is not complexing equally with the two acetate carbonyls. Reasonably this is due to a steric blocking of one acetate by the intrusion of a bromine on that side of the molecule. Thus, the unrearranged dibromide structure can be discarded on the basis of both chemical and NMR evidence.

The 2-D proton–carbon correlation spectrum was utilized to assign specific protons by their chemical shifts to their directly bonded carbons. Two points can be made regarding these data. The two downfield aliphatic protons at 4.30 and 4.53 ppm might have been assumed to be associated with the two carbons bearing the bromines which should also be downfield from the other methine bearing carbons. This is not so in fact as the 4.30 ppm proton was found to be attached to the carbon at 43.53 ppm, not the one at 47.07 ppm. Clearly considerations of structure other than electronegativity are affecting the carbon chemical shifts. Secondly, the proton chemical shifts of the set of methylene protons were observed to straddle the other set and were associated with a carbon 9.3 ppm more shielded than its confrere. This carbon and its associated protons must be involved in a strong steric interaction (presumably with a bromine). Even with all this array of chemical and NMR evidence the assignment of the structure is not unambiguous.

The decision on the gross structure was made on the basis of a 2-D ^{13}C–^{13}C double quantum coherence experiment carried out by the method of Turner.[6] The results are shown as a partial plot in Figure 1. The body of this illustration is a two-level contour plot showing pairs of peaks which arise from ^{13}C nuclei which are spin coupled to directly bonded ^{13}C nuclei. Shown at the bottom is a plot of the projected 2-D data. Incomplete suppression of the main ^{13}C–^{12}C peak (normally about 200 times more intense than the ^{13}C–^{13}C peaks) results in the tall signal in the center of each ^{13}C doublet pair. The contours corresponding to these central peaks show up along the main diagonal at the bottom. Additional connectives, not shown, confirm that C-1 and C-5 are the benzylic carbons, and that C-1 and C-5 are bounded to C-9a and C-5a, respectively. It is now possible to assign uniquely the basic carbon structure shown for **9** in Table I. The positioning of the C-10 bromine anti to the aromatic ring follows from chemical shift considerations in the ^{13}C spectrum. Recently the point has been made that substituents bearing lone pair electrons and located on carbons γ to a carbon π-system will induce a shielding interaction in the latter if oriented so that the lone pairs and the π-system can interact.[7] No such interaction is evidenced by the chemical shifts at carbons **5a** and **9a**. However, the proton and carbon chemical shifts at C-4 are clearly indicative of a strong 1,3-interaction with the C-10 bromine. This is augmented by the 1,3-interaction with the bromine at C-2. The latter must be anti to the aromatic ring for the same reason. This corresponds to an inversion by incoming bromide at the migration origin; a result often observed in Wagner–Meerwein rearrangements.

The above proposal of two bromines located 1,3 to each other and both anti to the aromatic ring raises the spectre of a strong diaxial interaction between them. This could be relieved by putting the six-membered ring into a boat conformation. However, this now introduces a flagpole-bowsprit interaction between the bromine at C-10 and the C-3 axial proton. The chemical shift of this proton does not support this conformation.

As pictured for **9** in Table I, the conformation of this ring appears to be a half-chair. The two 1,3-diaxial interactions between the bromines and H_4a are still intact though somewhat lessened. The 1,3-diaxial interaction of the two bromines is also less than in the chair conformation. This conformation is strongly supported by the values of $J_{2,3a}$ and $J_{2,3s}$ of 1 Hz and 6.3 Hz, respectively; values in keeping with dihedral angles of near 90° and 20°, respectively.[3] Furthermore, the bromine at C-2 is now so positioned to provide the steric shielding required by the LIS.

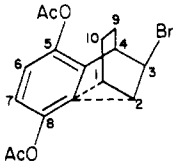
It is pointless to compare the result from this study with those for the addition of bromine and chlorine to tetrafluorobenzobicyclooctadiene. As mentioned above, the structures for the latter study were assigned solely on the basis of an incomplete analysis of proton coupling constants.

Paquette et al.[4] have cited five factors that might contribute to the stereochemical course of electrophic addition to the benzobicyclooctadienes. Principal among these were the steric interactions imposed by the ethano bridge protons, the possibility of homoconjugative interactions of the aryl π-system with the developing positive charge, and the modification of the olefin π-lobes by an interaction with the aryl π-system transmitted through the intevening σ-framework.

It is evident from the bromine configuration in **9** that initial attack by the electrophile has occurred from the

(7) Smith, W. B. *Org. Magn. Reson.* **1983**, *21*, 675.

sterically least favored side of the π-system. Most reasonably the driving force for this mode of addition is supplied by the formation of an aryl-bridged intermediate **10**. The question of whether the transition state leading



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to this intermediate involves homoconjugation with the aryl π-system is a moot point. Attack of bromide on **10** at position 2 would lead to the formation of an energetically unfavorable cis vicinal dibromide. Consequently, the only product of the reaction is formed by attack at position 1. This interpretation is consitent with the observations of Tanida et al.[8] who reported the acetolysis of the benzobicyclo[2.2.2]octen-*anti*-2-yl brosylate to give a mixture of 83% unrearranged *anti*-2-acetate and 17% of benzo[6.7]bicyclo[3.2.1]octen-*anti*-2-yl acetate which they suggested was formed from a aryl-bridged intermediate.

Acknowledgment. Grateful acknowledgement is hereby extended to The Robert A. Welch Foundation for their support of the TCU portion of this work. We thank Dr. Ralph E. Hurd of General Electric Company, NMR Instruments who obtained the 2-D proton–carbon correlation spectrum of the dibromide. Helpful experiments by undergraduate student, Vincent Michaud, are also acknowledged as are discussions with Professors Paul D. Bartlett and Sir John Cornforth.

Registry No. 1, 63350-92-5; 9, 91632-19-8.

(8) Tanida, H.; Tori, K.; Kitahonoki, K. *J. Am. Chem. Soc.* **1967**, *89*, 3212.

Effect of Cholesterol on the Stereoselective Hydrolysis in Artificial Membrane Systems

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Received March 12, 1984

The catalytic efficiency and enantioselectivity for the hydrolysis of *p*-nitrophenyl *N*-dodecanoyl-D(L)-phenylalaninate (**2b**) in the catalytic system of *N*-tetradecanoyl-L-histidyl-L-leucine (**1b**) and didodecyldimethylammonium bromide (**3a**) were enhanced by addition of cholesterol at an optimum temperature (25 °C). Furthermore, it is suggested that the hydrophobic interaction between reactants in the bilayer membrane system (**3a**) might be reduced by adding cholesterol on the basis of the isokinetic temperature. It is concluded from these results that the fluidity of the artificial bilayer matrix (**3a**) varies upon addition of cholesterol.

It is widely known that enzyme catalyses are usually stereospecific. For example, the α-chymotrypsin-catalyzed hydrolysis of *N*-acetyl-D(L)-amino acid *p*-nitrophenyl esters demonstrates the interrelationship between substrate specificity and stereoselectivity.[1] Enzyme-model studies[2-5] have been the subject of continued interest in such areas as the development of stereoselective reaction sites for the hydrolysis of enantiomeric esters and in aiding understanding the origins of stereoselectivity in the above-mentioned proteolytic enzymes.[1]

The stereoselective hydrolysis of N-protected amino acid *p*-nitrophenyl esters catalyzed by *N*-acyl-L-histidines has recently attracted considerable attention.[2] Relatively high stereoselectivity has been attained in the hydrolysis of diastereomeric dipeptide substrates with a thio functionalized surfactant,[3] in the hydrolysis of *N*-acyl amino acid esters with dipeptide L-histidine derivatives in the presence of cationic surfactants,[4] or in that with L-histidine derivatives in the presence of cationic surfactants,[4] or in that with L-histidine derivatives in bilayer systems.[5] On the other hand, the stereoselectivity of proteolytic metalloenzymes has been modeled by micellar systems.[6] Furthermore, we attempted to examine the kinetic origin of high enantioselectivity by measuring substrate-binding properties, activation parameters, and kinetic salt and organic cosolvent effects in the comicellar systems and emphasized the importance of hydrophobicity of the enantiomer substrate for the elevation of enantioselectivity.[7] However, there has been no report of the effect of fluidity of the reaction field on stereoselective hydrolysis in molecular assembly systems.

The purpose of this paper is to explore the cholesterol effect on the enantioselective hydrolytic cleavage (hydrolysis) of *p*-nitrophenyl *N*-dodecanoyl-D(L)-phenylalaninate (**2b**), which bears a long hydrophobic acyl chain, by the bilayer and micellar catalytic systems of L-histidine

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