Exo Stereoselectivity in Electrophilic Attack on Bicyclo[4.3.1]decatetraenyl Anion and in Deprotonation of Tricyclo[4.3.1.0]deca-2,4,7-triene[1]

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Abstract: Bicyclo[4.3.1]decatetraenyl anion (1,5-methano[9]annulenyl anion) (**2**), on quenching with deuterium oxide, gives exclusively 9-*exo*-deuteriotricyclo[4.3.1.0]decatriene (**3**). On the reactions with alkyl halides, carbon dioxide, or bulky trimethylsilyl chloride, **2** shows also an exclusive exo-face incorporation of the electrophiles to give **7–12**. The exact geometrical configuration at the C-9 position of the above reaction products was determined by the ^{1}H NMR spectra of their Diels–Alder adducts with isobenzofuran, by the Eu(fod)$_3$-induced ^{1}H NMR spectra, or by the chemical transformation to correlate with each of epimeric pairs. Treatment of **3** with base left no deuterium in the resulting bicyclo[4.3.1]decatetraenyl anion (**2**). The above-described exo stereoselectivity in electrophilic attack on **2** and in deprotonation of tricyclo[4.3.1.0]deca-2,4,7-triene (**1**) (dedeuteration of **3**) is absolutely opposite to the previously reported Radlick and Rosen's conclusion. The origin of the exo selectivity of **2** has been discussed briefly on the basis of the concept of orbital interaction between the π HOMO of distorted allyl anion moiety, C_7–C_8–C_9, and the vacant orbital of an electrophile as indicated in **25** and **26**. The exo-attack transition state (**25**) is expected to be favored over the endo-attack transition state (**26**), since the former carries the antibonding exo lobe of C-7 located away from the reaction center, while the latter suffers more significant interference due to a closer antibonding endo lobe of C-9. This mechanistic description would give rise to a new view for the stereoselectivity in the reactions of bridged vinylogous ions. Possible participation of the cyclopropane Walsh-type orbitals at C-1 and C-6 of **1** in the exo selectivity of the deprotonation has also been discussed. Additionally, compound **1** and its 9-exo-substituted derivatives underwent Diels–Alder cycloaddition with isobenzofuran in their endo face.

The synthetic and theoretical accessibility of numerous bridged annulenes has given rise to vigorous development. However the stereochemistry of their reactions with electrophiles has never been fully investigated. It has been known that tricyclo[4.3.1.0]-deca-2,4,7-triene (**1**) is deprotonated with dimsyl sodium[2,3] or butyllithium,[4] generating bicyclo[4.3.1]decatetraenyl anion (**2**), which is quantitatively protonated with water regenerating the original **1**. Radlick and Rosen[5] have found that deprotonation of **1** to **2** and deuterium incorporation of **2** to deuterated tricyclo[4.3.1.0]decatriene (**3**) proceed with remarkable stereoselectivity. They indicated an endo (trans to the methylene bridge) selectivity in these reactions because the ^{1}H NMR signal at δ 2.71 of **1** disappeared in the deuterated compound (**3**) and the deuterium was absent in **2**, which was obtained by the treatment of the deuteriotricyclodecatriene (**3**) with a base. They assigned the signal at δ 2.71 to H-9-endo and the one at δ 2.47[6] to H-9-exo by considering that the signal of the exo proton could appear at higher field than that of the endo proton, owing to the cyclopropane ring anisotropy. Indeed the shielding capability of a cyclopropane ring is widely recognized in saturated systems as have been reported so far.[7] However, much caution would be required for the assignment of 9-methylene protons of the tricyclodecatriene (**1**) because olefinic anisotropy is also conceivable[8] in addition to the cyclopropane ring effect.

In order to decide whether the stereoselective reaction proceeds on the exo or endo face, we studied electrophilic reactions of **2** and the stereochemical configuration of the reaction products. The present paper describes herein the efforts to prove a high exo stereoselectivity in the deprotonation of **1** and electrophilic attack on **2**. The results obtained here are absolutely opposite to the Radlick and Rosen consideration, on the basis of which it was long understood that the endo side was preferred for electrophilic attack.[9]

Results

To substantiate further the ^{1}H NMR spectral assignment of the tricyclodecatriene (**1**) and to determine the deuteration mode of **2**, we allowed **1** to react with isobenzofuran to afford a single adduct (**4**), the structural proof of which was based on its ^{1}H NMR data summarized in Table I. The coupling constants J(7,A) and J(8,B) indicated a cis arrangement of these pairs of protons, eliminating the two possible isomeric trans arrangements of the corresponding protons.

Of the two remaining structures (see Scheme I), **4** was preferred to **5** on the basis of the following: (a) The chemical shift of H-10-syn in the adduct was comparable to those of the corresponding protons not shielded by the aromatic ring in tricyclo-[4.3.1.0]deca-2,4-diene[10] and its 8-*endo*-chloro[3] derivative. (b) H-10-anti showed W coupling with H-9 at δ 1.05 (J = 2.0 Hz) but not with H-7. (c) Of the two 9-methylene protons, the one that coupled with H-10-anti resonates at ca. 1.0 ppm higher field than the noncoupled proton. This can be reasonably explained only by structure **4** where H-9-endo is located in the shielding region of the aromatic ring.

Reaction of the monodeuterated triene **3**, obtained from anion **2** by D_2O quenching,[11] with isobenzofuran gave the deuterio adduct **6**. Adduct **6** showed no signal corresponding to H-9-exo (δ 2.01) of **4** and showed signals corresponding to H-9-endo (δ 1.05) and H-8 (δ 2.81) of **4** in a simpler multiplicity (Figure 1).

(1) For a preliminary communication on this subject, see: K. Takahashi, T. Kagawa, and K. Takase, *J. Chem. Soc., Chem. Commun.*, 863 (1979).
(2) W. Grimme, M. Kaufhold, U. Dettmeier, and E. Vogel, *Angew. Chem., Int. Ed. Engl.*, **5**, 604 (1966).
(3) P. Radlick and W. Rosen, *J. Am. Chem. Soc.*, **88**, 3461 (1966).
(4) I. Murata, K. Nakasuji, and T. Morita, *Chem. Lett.*, 743 (1974).
(5) P. Radlick and W. Rosen, *J. Am. Chem. Soc.*, **89**, 5308 (1967).
(6) The chemical shifts δ 2.65 and 2.35 of the 9-methylene protons reported in ref 5 should be corrected as given here.
(7) L. Birladeanu, T. Hanafusa, S. Winstein, *J. Am. Chem. Soc.*, **88**, 2315 (1966); P. Radlick and S. Winstein, *ibid.*, **85**, 343 (1963); P. K. Freeman, F. A. Raymond, and M. F. Grostic, *J. Org. Chem.*, **32**, 24 (1967); L. A. Paquette, O. Cox, M. Oku, and R. P. Henzel, *J. Am. Chem. Soc.*, **96**, 4892 (1974).
(8) The two protons of C-4 methylene in bicyclo[3.1.0]hex-2-ene had nearly identical chemical shifts: P. K. Freeman, M. F. Grostic, and A. F. Raymond, *J. Org. Chem.*, **30**, 771 (1965).
(9) R. J. Hunadi and G. K. Helmkamp, *J. Org. Chem.*, **43**, 1586 (1978); K. Lammertsma and H. Cerfontain, *J. Am. Chem. Soc.*, **100**, 8244 (1978).
(10) H. Günther and T. Keller, *Chem. Ber.*, **103**, 3231 (1970).
(11) Quenching with D_2O, AcOD, or MeOD of solutions of the lithium salt of the anion **2** in THF, the sodium salt in dimethyl sulfoxide, and the potassium salt in 1,2-dimethoxyethane led to the same compound (**3**) in each case.

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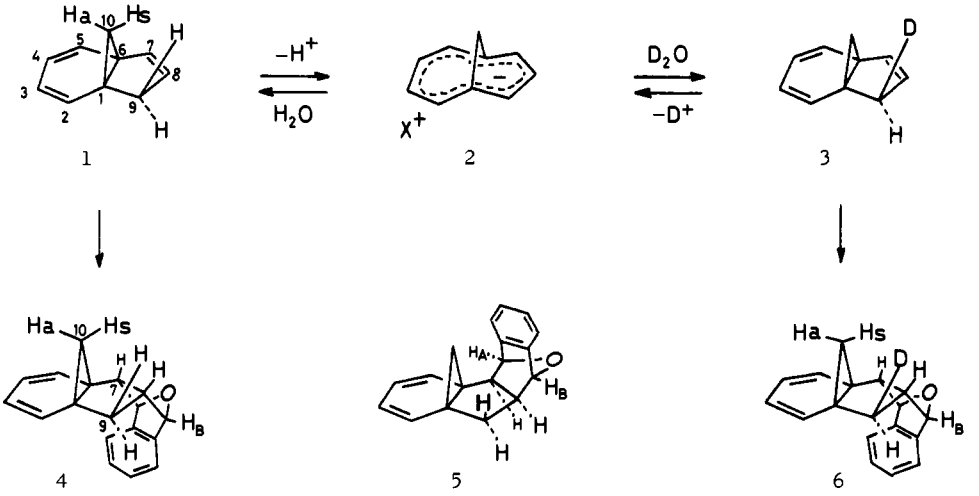
Table I. ^{1}H NMR Data of the Diels–Alder Adducts with Isobenzofuran in $CDCl_3$ at 100 MHz[a,b]

compd	H-10 syn	H-10 anti	H-9 exo	H-9 endo	H-7	H-8	H-A	H-B	H-2,3,4,5	Ph	Me
4	1.20 (d)	−0.48 (dd)	2.01 (dd)	1.05 (ddd)	3.40 (dd)	2.81 (dddd)	5.28 (d)	5.08 (d)	5.20–6.20 (m)	6.98 (br s)	
	J(10a,10s) = 3.5, J(10a,9endo) = 2.0, J(9exo,9endo) = 13.0, J(8,9endo) = 4.8, J(9exo,8) = 9.0, J(8,7) = 9.0, J(8,B) = 6.0, J(7,A) = 5.0										
16	1.45 (d)	−0.45 (dd)		2.26 (dd)	3.03–3.73 (m)		5.35 (d)	5.25 (d)	5.30–6.33 (m)	7.13 (br s)	3.73 (s)
	J(10a,10s) = 4.0, J(10a,9endo) = 1.0, J(8,9endo) = 4.5, J(8,B) = J(7,A) = 5.0										
17	1.34 (d)	−0.24 (dd)		3.08 (dd)	2.69 (d)	2.55 (dd)	5.22 (s)	4.98 (s)	6.28–6.45 5.76–6.10	7.13 (br s)	3.80 (s)
	J(10a,10s) = 4.0, J(10a,9endo) = 1.5, J(8,9endo) = 4.5, J(7,8) = 7.0, J(8,B) = J(7,A) = 0.0										
24	1.32 (d)	−0.50 (dd)		0.42 (dd)	3.32 (dd)	2.68 (ddd)	5.29 (d)	5.04 (d)	5.00–6.18 (m)	7.16 (br s)	0.12 (s)
	J(10a,10s) = 4.0, J(10a,9endo) = 1.7, J(8,9endo) = 6.2, J(7,8) = 10.0, J(8,B) = 5.5, J(7,A) = 6.0										

[a] δ relative to Me_4Si; J values in Hz. [b] Magnitudes of coupling constants and chemical shift assignments were confirmed through spin-decoupling experiments.

Scheme I



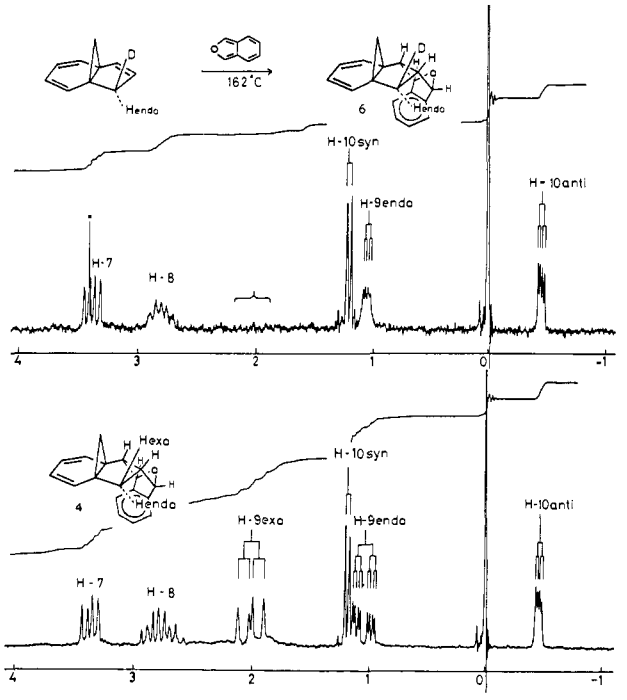


Figure 1. ^{1}H NMR spectra (100 MHz, Me_4Si) of Diels–Alder adducts **4** and **6**.

Irradiation of **6** at H-10-anti (δ −0.48) resulted in simplification of H-9-endo (δ 1.05) and H-10-syn (δ 1.20) to a broad doublet and a singlet, respectively. These observations indicate unequivocally that **6** carries the deuterium at the 9-exo position. Of the two double triplets centered at δ 2.71 and 2.47 for the 9-methylene protons of **1**, the former disappeared in the spectrum of **3** and therefore should be assigned to H-9-exo[12] in accordance with stereospecific exo-face incorporation of deuterium into the 1,5-methano[9]annulenyl anion (**2**).

Table II. LIS Values of Bridge Protons H-10-syn and H-10-anti in 9-Carbomethoxytricyclo[4.3.1.0]decatrienes (13 and 15) in the Presence of Eu(fod)$_3$[a]

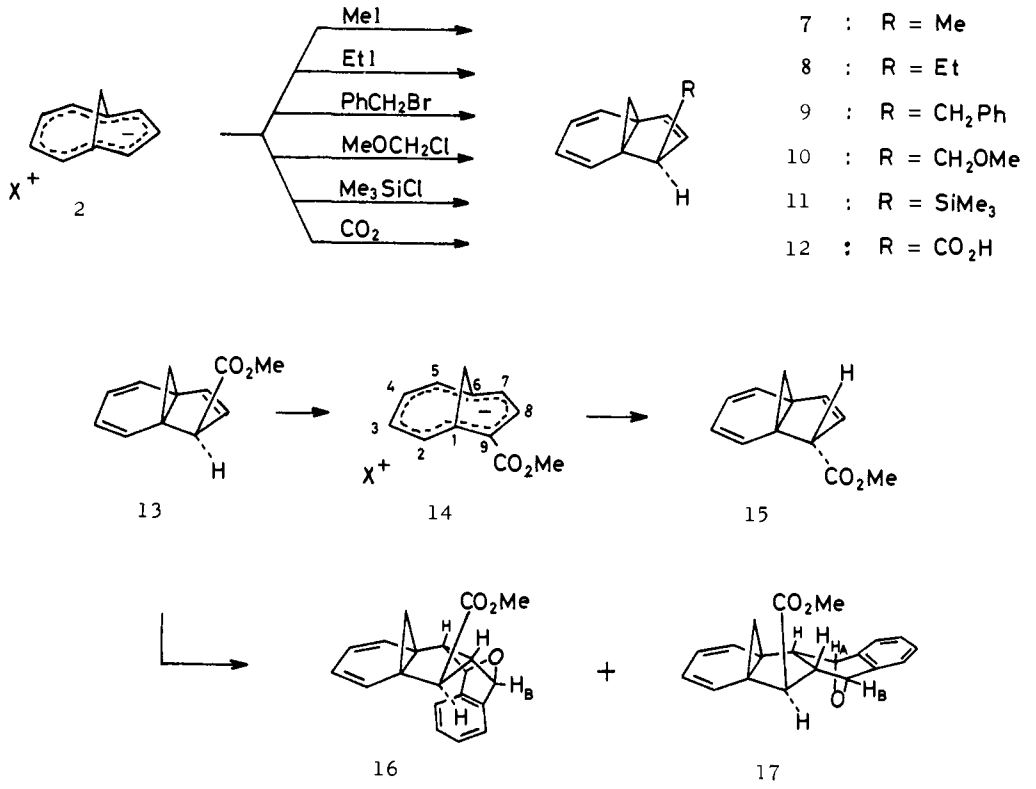
Proton	LIS value 13	LIS value 15
H-10-syn	4.27	1.48
H-10-anti	1.25	1.13

[a] The relative LIS values of H-10-syn to H-10-anti of 13 and 15 are 3.42 and 1.31, respectively.

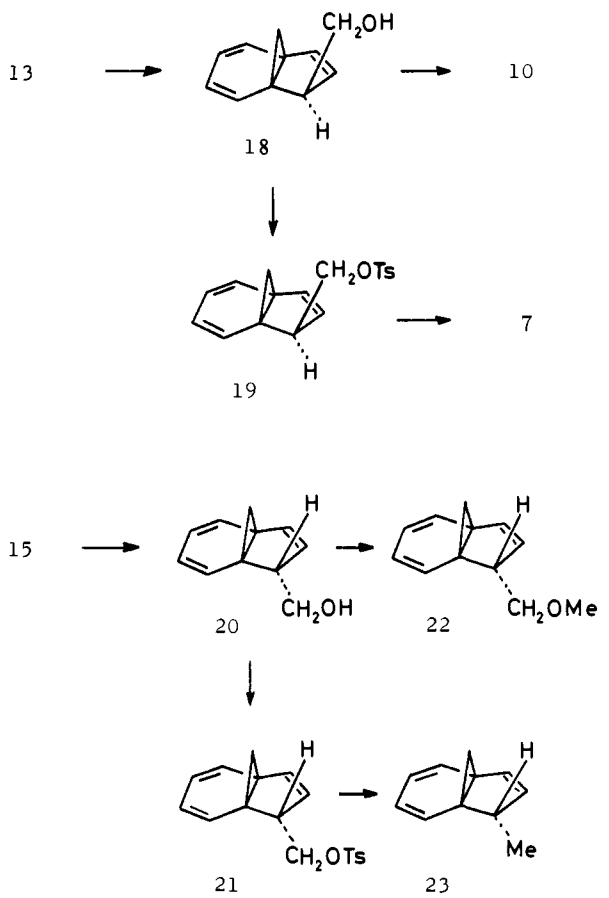
In order to have a more general insight into the stereoselective reaction of **2** with electrophiles, we treated a THF solution of **2** with alkyl halides such as MeI, EtI, $PhCH_2Br$, and $MeOCH_2Cl$ at 0 °C; this resulted in the formation of **7**, **8**, **9**, and **10**, respectively. When **2** was treated with chlorotrimetylsilane at 0 °C and with an excess of carbon dioxide at −78 °C, trimethylsilyl derivative **11** and carboxylic acid **12**, respectively, were obtained. The ^{1}H NMR spectral examination proved that these products are all sterically pure, not being contaminated with any epimeric isomers, because H-10-anti and H-10-syn were observed as a distinct pair of doublets, not accompanied with any other pairs of doublets due to epimeric isomers, in the higher field. Thus, the high stereoselectivity in these reactions can also be manifested, but their ^{1}H NMR coupling parameters furnished no information

(12) An assignment of the ^{1}H NMR signals of **1** has thus been achieved as follows: δ ($CDCl_3$ with Me_4Si) 0.03 (d, J = 3.1 Hz, H-10-anti), 1.47 (d, J = 3.1 Hz, H-10-syn), 2.47 (ddd, J = 17.0, 2.2, and 2.2 Hz, H-9-endo), 2.71 (ddd, J = 17.0, 2.2, and 2.2 Hz, H-9-exo), 5.30 (ddd, J = 6.0, 2.2, and 2.2 Hz, H-8), 6.03 (m, J = 6.0 Hz, H-7), 5.79–5.97 (2 H, m, H-3,4), 6.15–6.40 (2 H, m, H-2,5).

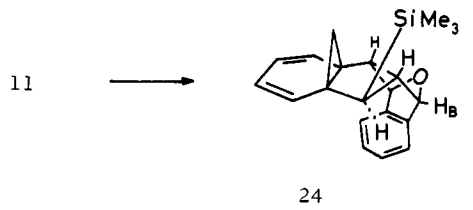
Scheme II



Scheme III



Scheme IV



about the stereochemistry at C-9 of these products. The ester **13**, obtained from **12** by methylation, was treated with LDA to give an anion (**14**) and then protonated with acetic acid to give an epimeric ester (**15**) (Scheme II).

The ^{1}H NMR spectra of **13** and **15** were examined in the presence of Eu(fod)$_3$. The LIS values, the slope of the initial linear portion of a plot of induced chemical shift ($\delta_E - \delta_{ppm}$) vs. molar ratio Eu(fod)$_3$/substrate, for H-10-syn and H-10-anti are listed in Table II. The relative LIS value of H-10-syn to H-10-anti in **13** is larger than that in **15** by a factor of about 2.7, indicating that the ester group is situated closer to the H-10-syn in **13** than in **15**.[13] To get further support for the configuration of the ester group, we allowed **13** to react with isobenzofuran to give adducts **16** and **17**. Vicinal coupling constants, both J(7,A) and J(8,B), were found to be 5.0 Hz in **16** and 0 Hz in **17** (Table I). H-9 in **16** was more shielded by the aromatic ring than the corresponding proton in **17**, while H-10-syn in **16** and the corresponding proton in **17** had much the same chemical shifts. This evidence, together with the value of J(8,9) and the characteristic coupling between H-10-anti and H-9 in **16** and in **17**, demonstrates unequivocally assigned structures **16** and **17** and requires the exo orientation of the ester group in **13**. The epimeric esters **13** and **15** were then converted, by reducing their ester groups, to the corresponding methyl and methoxymethyl derivatives, which made it possible to clarify the C-9 configuration of **7** and **10** obtained by the alkylation from **2**. Lithium aluminum hydride reduction[14] of the exo ester **13** provided an alcohol (**18**) which upon reaction with diazomethane in the presence of boron trifluoride etherate afforded a 9-*exo*-methoxymethyl derivative, identical in all respects

(13) The anion **14** also shows an exo stereoselection in the reaction with alkyl halides, although to a lesser extent than **2**: K. Takahashi, T. Kagawa, and K. Takase, *Chem. Lett.*, 701 (1979).

(14) Lithium aluminum hydride reduction of esters can be utilized for configurational studies: J. A. Dale and H. S. Mosher, *J. Org. Chem.*, **35**, 4002 (1970).

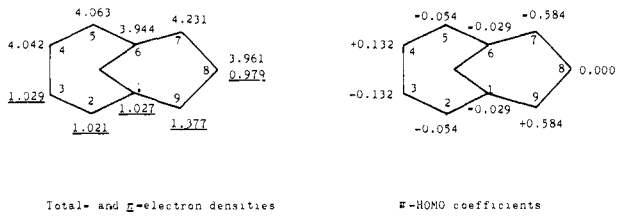


Figure 2. CNDO/2 calculation of bicyclo[4.3.1]decatetraenyl anion (**2**).

with **10** by ^{1}H NMR spectral comparison. Treatment of **18** with *p*-toluenesulfonyl chloride in pyridine provided a tosyl ester (**19**). Upon reduction with lithium aluminum hydride, **19** was transformed into a 9-*exo*-methyl derivative whose ^{1}H NMR spectrum was in complete agreement with that of **7**. A similar transformation was performed on the endo ester **15** via an alcohol (**20**) and a tosyl ester (**21**), providing a 9-*endo*-methoxymethyl derivative (**22**) and a 9-*endo*-methyl derivative (**23**), respectively. These epimers had spectroscopic properties different from those of **10** and **7** (Schemes III and IV).

The exo orientation of the trimethylsilyl group of **11** was confirmed on the basis of ^{1}H NMR analysis of its isobenzofuran adduct (**24**). The adduct **24** showed (Table I) the H-9 signal at higher field as a doublet of doublets (J(9,10-anti) = 1.7 Hz), H-A and H-B signals as doublets (J(7,A) = 6.0, J(8,B) = 5.5 Hz), and the H-10-syn signal without shielding by the aromatic ring, supporting assigned structure **24**. Although the exact stereochemical identification of ethyl (**8**) and benzyl (**9**) derivatives was not achieved,[15] it seemed reasonable to assume exo orientation for them, analogous to the cases of **7** and **10**.

Thus, it has been proved that 1,5-methano[9]annulenyl anion (**2**), even in the reaction with a bulky trimethylsily group, shows an overwhelming tendency for stereospecific exo capture of electrophiles.

The ^{1}H NMR spectrum of **2**, obtained from 9-*exo*-deuteriotricyclodecatriene (**3**) with dimsyl sodium, exhibited a 2 H broad doublet at δ 5.98 due to H-7 and H-9 and a broad triplet at δ 5.58[16] due to H-8, no deuterium residue being detected. In addition, the carbanion solution, produced from **3** with *n*-butyllithium in THF, was quenched with water, affording a tricyclodecatriene whose ^{1}H NMR spectrum was completely identical with that of **1**. Therefore, proton (deuterium) abstraction of **1** (**3**) to **2** also must have proceeded stereoselectively at the exo face.

Discussion

The observed exo capture of the electrophiles cannot be dictated by the steric effect since there must be a larger steric interaction by the methylene bridge in the exo face than in the endo face. The stereoselectivity of **2** was not influenced by the nature of solvents, proton sources used, and counterions of the anion, so that, even if a contact ion pair[17] could be formed on protonation, it would be again not essential for rationalizing the stereoselectivity.

For a more precise definition of the responsible parameters, the observed exo selectivity was theoretically treated according to the concept of orbital interaction. For that purpose the assumed structure of **2** was first constructed by the method of Allinger's molecular mechanics calculation[18] and then adjusted to minimize the total energy by angle variation ($\angle C_1$–C_9–C_8 and $\angle C_6$–C_7–C_8) by using a CNDO/2 approximation.[19] The charge densities and the π-HOMO coefficients thus obtained are listed in Figure 2.

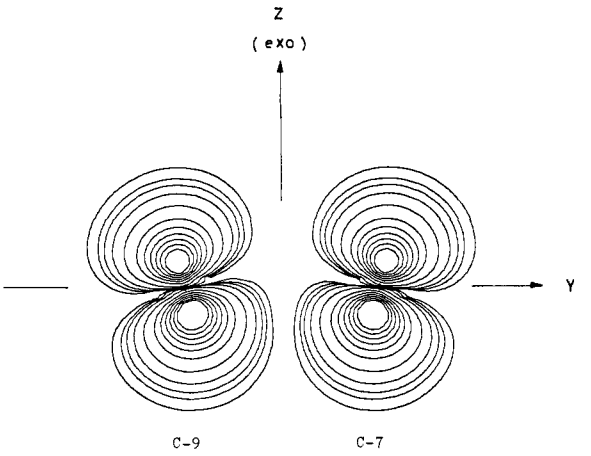


Figure 3. HOMO electron density distributions at C-9 and C-7 of bicyclo[4.3.1]decatetraenyl anion (**2**). Contour lines are from inside to outside; ρ = 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, 0.1, 0.05, 0.03, 0.02, and 0.01.

The π-HOMO lobes located at C-1 and C-6 overlap in phase with the π-HOMO lobes of C-9 and C-7, respectively, which correspond to the terminal π HOMO of the allyl anion moiety.

Exo stereoselection in the reactions of norbornene with electrophiles has recently been attributed to the nonequivalency in frontier π orbital extension;[20] i.e., the π HOMO of norbornene has large coefficients at the exo face as a result of mixing with a high-lying bridged σ orbital(s) in an out-of-phase and with the σ orbital localized at unsaturated carbons in an out-of-phase relation to the bridged σ orbital(s), which causes more electron crowding in the exo region to assist exo-electrophilic attack. The electron density distribution of the π lobes of C-7 and C-9 in the HOMO of **2** calculated by the extended Hückel MO[21] is seen from the contour map depicted on the plane perpendicular to the C_7–C_8–C_9 coplane (Figure 3), where the orbital amplitudes are much the same in exo and endo lobes, indicating very little orbital mixing of $\pi(p_z)$ with the s-atomic orbitals. However, the p_z orbitals mix with the p_y orbitals, causing the p_z lobes to cant outward at the exo face and inward at the endo face. The difference in such a geometrical orientation of modified π orbitals between exo and endo faces can be expected to influence the transition state of electrophilic reactions to **2**; *i.e.*, the π orbitals in C-7 and C-9 are antisymmetric to the plane bisecting the bridgehead–bridgehead axis (x axis), and the relative signs of the terminal AO coefficients are inverted; therefore an electrophile must inevitably experience antibonding interaction with a π lobe in C-7 when it approaches closely to have bonding interaction with the π lobe of C-9. The electrophile can approach the exo lobe of C-9 with less significant interference by the antibonding interaction because the exo lobe of C-7 is located away from the exo lobe of C-9. On the other hand, the endo side approach of the electrophile suffers more significant antibonding interference because the antisymmetric two π lobes are situated in closer proximity at the endo side. Thus exo side approach would result in a decrease of transition energy compared with the endo side one. These features are indicated schematically in **25** and **26**.

(15) Compounds **8** and **9** showed ^{1}H NMR signals of H-9 as complex multiplets perturbed by the methylene protons in ethyl and benzyl groups, preventing a clear stereochemical analysis.

(16) ^{1}H NMR spectrum of **2** was analyzed at 100 MHz in Me_2SO-d_6: δ −1.15 [dtd, J(10-anti,10-syn) = 7.2 Hz, J(10-anti,7) = J(10-anti,9) = 1.3 Hz, J(10-anti,8) = 0.6 Hz, H-10-anti], −0.69 (dt, J(10-*syn*,2) = J(10-syn,5) = 0.5 Hz, H-10-syn), 5.58 (dt, J(8,9) = J(8,7) = 6.0 Hz, H-8), 5.80 (dd, J(3,2) = J(4,5) = 6.0 Hz, J(3,5) = J(4,2) = 2.0 Hz, H-3,4), 5.98 (dd, H-7,9), 6.84 (dd, H-2,5).

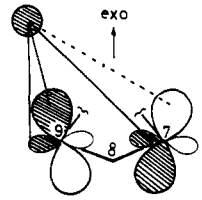
(17) W. D. Kollmeyer and D. J. Cram, *J. Am. Chem. Soc.*, **90**, 1784 (1968) and earlier papers; Y. Pocker and J. H. Exner, *ibid.*, **90**, 6764 (1968); D. J. Cram, "Fundamentals of Carbanion Chemistry", Academic Press, New York, 1965, Chapters 3–5.

(18) The calculation was performed by using the program MMI (program no. 318 of the Quatum Chemistry Program Exchange, Indiana University): N. L. Allinger, J. T. Sprague, and T. Liljerfors, *J. Am. Chem. Soc.*, **96**, 5100 (1974); D. H. Wertz and N. L. Allinger, *Tetrahedron*, **30**, 1579 (1974).

(19) Molecular mechanics calculation was initially carried out for a neutral model compound, bicyclo[4.3.1]deca-1,3,5,7-tetraene, and then C-9 was modified so that the anion has a C_s symmetry. Atomic coordinates of C-8, H-8, H-7, and H-9 were subsequently changed in such a way that the angles $\angle C_1$–C_9–C_8 and $\angle C_6$–C_7–C_8, vary in the range of 202–150°, and the total energy corresponding to the respective angle was calculated by CNDO/2 to search the energetically most favorable geometry of **2**.

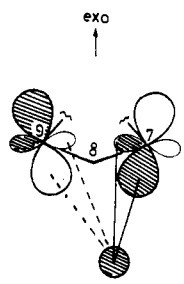
(20) S. Inagaki, H. Fujomoto, and K. Fukui, *J. Am. Chem. Soc.*, **98**, 4054 (1976).

(21) In the CNDO/2 calculation, the overlap integrals are neglected because the normalization condition, $\sum_r C_{ir}^2 = 1$, is included. Such a method, therefore, is not suitable to examine the orbital deformation caused by orbital mixing. This is the reason why we used the extended Hückel method to draw the contour map.



exo-Attack

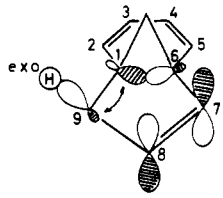
25



endo-Attack

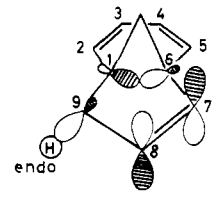
26

The second factor responsible could be the relative orientation of the antibonding molecular orbitals of Walsh type at C-1 and C-6 positions toward the lobes of the reaction center. As in the effect of a cyclopropane ring entering into π-type conjugation with a neighboring π-electron system,[22] there is the net electron transfer from C-1,6 antibonding orbitals to the neighboring sp^2-type reaction center in the reaction of **2** with electrophiles giving **3** and **7–12** and vice versa in the deprotonation of tricyclodecatriene (**1**) giving **2**. In the latter case, the C_9–H_{exo} bond cleaves more readily than the C_9–H_{endo} bond, because the C_9–H_{exo} bond and its sp^3 tail peg are in a parallel arrangement with the C-1 orbital participating in the cyclopropane basal bond, resulting in good overlap of these lobes, while the C_9–H_{endo} bond is envisaged at a perpendicular orientation with the cyclopropane basal bond in C-1 as indicated in **27** and **28**.



C_9-H_{exo} Bond breaking

27



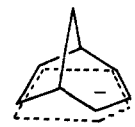
C_9-H_{endo} Bond breaking

28

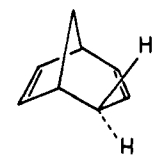
If the protonation of **2** and deprotonation of **1** proceed via an identical transition state, such a mechanism as depicted in **27** could also rationalize the exo selectivity in the reaction of **2** with electrophiles.

To differentiate which is the essential factor of the two described above, it is desirable to know the information regarding stereoselection of the modified allyl anion moiety carrying no cyclopropane residue. Brown and Cain have demonstrated that the quenching of a THF solution of 1,3-bis(homocyclopentadienide) anion (**29**) by syringing it into dimethyl-d_6 sulfoxide results in predominant 4-exo deuterium incorporation (in more than 85% selectivity)[23] and the rates of base-catalyzed hydrogen–deuterium exchange at the 4-position of bicyclo[3.2.1]octa-2,6-diene (**30**) in dimethyl sulfoxide were in the ratio (exo:endo) 6.0:1.[24]

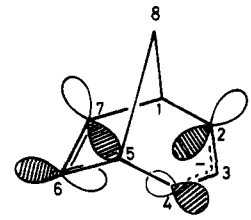
While no precise explanation has been offered so far, we here contend that the exo selectivity in the protonation of **29** is exactly due to the mechanism shown in **25**, since the allylic π HOMO of C-2 and C-4 of **29**, as clarified on the molecular model, should be canted inward at the endo face and outward at the exo face to overlap well with the endo lobes of the π LUMO of C-6 and C-7, as seen in **31**, from which bis(homoaromatic) stabilization[25] originated. On referring to the exo deuteration of **29**, the cyclopropyl participation does not necessarily contribute to the stereoselectivity of electrophilic attack on **2**.[26] The cyclopropyl participation would contribute presumably to the exo deprotonation in **1** because the deprotonation of the cyclopropane-ring-free compound (**30**) appears to occur at the 4-endo position in preference to the 4-exo position.[24]



29

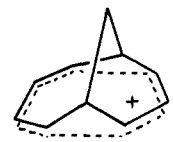


30

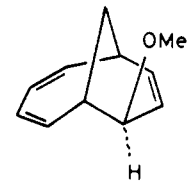


31

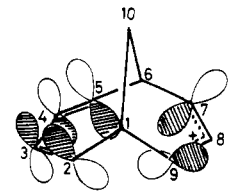
The mechanism shown in **25** could also be applicable to nucleophilic attack on the bridged cations in a similar manner,[29] but with use of the π LUMO of the cationic species. Interestingly, Schröder et al. reported that bicyclo[4.3.1]decatrienyl cation (**32**), one of novel bis(homotropylium) cations, reacted with methanol–sodium acetate at −78 °C to produce stereoselectively 7-*exo*-methoxybicyclo[4.3.1]deca-2,4,7-triene (**33**) in 61% yield.[30]



32



33



34

The allylic π LUMO of C-7 and C-9 of **32** would be canted inward at the endo face and outward at the exo face to overlap

(22) R. Hoffmann, *Tetrahedron Lett.*, 2907 (1970); H. Günther, *ibid.*, 5173 (1970).
(23) J. M. Brown and E. N. Cain, *J. Am. Chem. Soc.*, **92**, 3821 (1970).
(24) J. M. Brown and E. N. Cain, *J. Chem. Soc. B*, 730 (1971).
(25) M. Goldstien, *J. Am. Chem. Soc.*, **89**, 6357 (1967); G. B. Trimitsis and A. Tuncay, *ibid.*, **98**, 1997 (1976); S. Winstien, M. Ogliaruso, M. Sakai, and J. M. Nicholson, *ibid.*, **89**, 3656 (1967).

(26) The allyl anion generated from bicyclo[3.2.1]oct-2-ene showed a 2.3-fold predominant exo deuteration at C-4.[27] A higher exo selectivity was also observed in the reaction of bicyclo[3.2.1]oct-3-en-2-yl radical with *tert*-butyl perbenzoate, resulting in the formation of *exo*-bicyclo[3.2.1]oct-3-en-2-yl benzoate.[28] In these cases, however, nothing can be concluded because a steric effect is not excluded and π-lobe modification in the HOMO of the allyl anion and radical is ambiguous.
(27) A. K. Cheng and J. B. Stothers, *Can. J. Chem.*, **55**, 50 (1977).
(28) H. L. Goering and U. Mayer, *J. Am. Chem. Soc.*, **86**, 3753 (1964).
(29) We thank a reviewer for drawing our attention on this point.
(30) G. Schröder, U. Prange, N. S. Bowman, and J. F. M. Oth, *Terahedron Lett.*, 1970, 3251; G. Schröder, U. Prange, B. Putze, and J. F. M. Oth, *Chem. Ber.*, **104**, 3406 (1971). They have argued that the exo selectivity of **32** is due to the poor electron density at the exo face.

well with the endo lobes of the terminal π HOMO of the butadiene moiety (C-2–C-5), which builds up an aromatic sextet at the endo face of the cation as seen in **34**. Therefore the profound exo selectivity observed on the cation **32** is explained again quite reasonably by the mechanism shown in **25**.

Thus, it can be concluded that in electrophilic attack on bicyclodecatetraenyl anion (**2**) and 1,3-bis(homocyclopentadienide) anion (**29**) and possibly in nucleophilic attack on bicyclodecatrienyl cation (**32**), the antibonding interaction between the attacking species and the canted π lobes associated with the allylic terminals seems to function as a dominant factor for the high exo stereoselection.

Experimental Section

General Procedure. Melting points are uncorrected. ^{1}H NMR spectra were obtained with a Varian HA-100 (a few with a Varian A-60) spectrometer. Coupling constant and chemical shift assignments were confirmed by spin-decoupling experiments. ^{13}C NMR spectra were taken on a Nihondenshi JEOL FX-100 (25 MHz) spectrometer with Me_4Si as an internal standard. Mass spectra were recorded on a Hitachi M-52 spectrometer at an ionization potential of 25 eV. Infrared spectra were determined on a Shimazu IR-27G spectrometer. Microanalyses were performed at Analytical Laboratory, Department of Chemistry, Tohoku University.

Diels–Alder Reaction of 1 with Isobenzofuran. A mixture of **1** (260 mg, 2.0 mmol), 1,2,3,4-tetraphenyl-1,4-carbonyl-9,10-oxido-1,4,9,9a,10,10a-hexahydroanthracene (1.056 g, 2.0 mmol), and diglyme (4.0 mL) was heated at reflux (162 °C) under nitrogen for 15 min. The reaction mixture was cooled, treated with water, and extracted with methylene chloride. The combined extracts were washed with saturated aqueous $NaHCO_3$, dried, and evaporated to leave colorless crystals, to which was added a small amount of methylene chloride, and the resulting solution was transferred to a silica gel column. Elution with 3:1 hexane–ether gave a crude adduct, which was further purified by preparative TLC. There was isolated **4**: 38 mg (8%); mp 73–75 °C; IR (KBr) 3050–2870, 1460, 1350, 970, 910, 850, 750, 730–720 cm^{-1}; ^{1}H NMR, see Table I; mass spectrum, *m/e* (%) 248 (3.7), 130 (100), 118 (75). Anal. ($C_{18}H_{16}O$) C, H.

Deuteration of 2. A THF solution of the lithium salt of **2** prepared by the method of Murata et al.[4] was quenched with D_2O to afford **3**, a colorless oil (72%); ^{1}H NMR ($CDCl_3$) δ 0.06 (d, J = 3.2 Hz, H-10-anti), 1.48 (d, J = 3.2 Hz, H-10-syn), 2.47 (pentuplet, J = 2.2 Hz, H-9-endo), 5.30 (dd, J = 6.0 and 2.2 Hz, H-8), 6.10 (dm, J = 6.0 Hz, H-7), 5.80–5.98 (m, H-3,4), 6.15–6.41 (m, H-2,5); mass spectrum, *m/e* (%) 131 (100). The spectral data were absolutely identical with those of the compound obtained by the D_2O quenching of the sodium salt of **2** in dimethyl sulfoxide solution. AcOD or MeOD quenching of **2** gave the same compound, **3**. When a solution of **1** (130 mg, 1.0 mmol) in dimethoxyethane (2 mL) was added to a stirred suspension of KH (washed previously with dry hexane to remove mineral oil) (120 mg, 3.0 mmol) in dimethoxyethane (3 mL) under nitrogen at 0 °C, a deep violet solution of the potassium salt of **2** was generated. D_2O quenching of this solution afforded **3**.

Diels–Alder reaction of 3 with isobenzofuran was carried out by the method described for the formation of **4** to afford **6** (7%): colorless needles, mp 75–76 °C; IR (KBr) 3050–2870, 1460, 1330, 1020, 1010, 970, 830, 780–690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ −0.48 (dd, J = 2.0 and 3,5 Hz, H-10-anti), 1.05 (br dd, J = 2.0 and 4.0 Hz, H-9-endo), 1.20 (d, J = 3.5 Hz, H-10-syn), 2.81 (ddd, J = 4.0, 6.0, and 9.0 Hz, H-8), 3.40 (dd, J = 9.0 and 5.0 Hz, H-7), 5.12 (d, J = 6.0 Hz, H-B), 5.31 (d, J = 5.0 Hz, H-A), 5.33–6.27 (m, H-2,3,4,5), 7.02 (s, Ph); mass spectrum, *m/e* (%) 249 (1.9), 131 (100), 118 (52).

9-*exo*-Methyltricyclo[4.3.1.0]decatriene (7). To a stirred solution of tricyclo[4.3.1.0]decatriene (**1**) (390 mg, 3.0 mmol) and TMEDA (1.5 mL) in dry THF (15 mL) was added dropwise a solution of *n*-butyllithium in hexane (3.6 mL, 3.6 mmol) at 0 °C under nitrogen. After being stirred for 1 h at 0 °C, the resulting reddish yellow solution of **2** was added to a solution of methyl iodide (2.5 mL) in dry THF (3 mL) at 0 °C. The mixture was stirred for an additional 1 h, acidified with 2 N HCl, and extracted with ether. After neutralization of the organic phase with saturated aqueous $NaHCO_3$ and drying over Na_2SO_4, the solvent was distilled off and the residue was chromatographed on silica gel with hexane as an eluant to give a colorless oil (315 mg, 73%): IR (neat) 3050–2860, 1600, 1535, 1453, 1332, 1020, 1010, 970, 825, 745 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ −0.17 (d, J = 3.5 Hz, H-10-anti), 1.48 (d, J = 3.5 Hz, H-10-syn), 1.20 (d, J = 7.0 Hz, Me), 2.97 (ddq, J = 2.0, 2.0, and 7.0 Hz, H-9-endo), 5.12 (dd, J = 6.0 and 2.0 Hz, H-8), 5.73–6.43 (m, H-7,2,3,4,5); mass spectrum, *m/e* (%) 144 (48), 129 (100), 128 (72), 119 (28), 117 (28). Anal. ($C_{11}H_{12}$) C, H.

Other 9-Exo-Substituted Tricyclo[4.3.1.0]decatrienes. A THF solution of **2** (2.0 mmol), prepared in the same manner as above, was added to a solution of ethyl iodide (1.56 g, 10 mmol), benzyl bromide (1.71 g, 10 mmol), chloromethyl methyl ether (805 mg, 10 mmol), or trimethylsilyl chloride (1.26 mL, 10 mmol) at 0 °C. The usual workup afforded the corresponding substitution products. The carboxylation of **2** in THF solution was carried out by adding exceess dry ice under nitrogen at −78 °C and then stirring for 30 min at room temperature.

9-*exo*-Ethyltricyclo[4.3.1.0]decatriene (8): a colorless oil; 190 mg (60%); IR (neat) 3070–2870, 1600, 1540, 1470, 1370, 1335, 1255, 1020, 975, 860, 800, 750 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ −0.16 (d, J = 3.5 Hz, H-10-anti), 1.50 (d, J = 3.5 Hz, H-10-syn), 2.75 (br dt, J = 2.0 and 7.0 Hz, H-9), 5.17 (dd, J = 6.5 and 2.0 Hz, H-8), 5.70–6.37 (m, H-7,2,3,4,5), 0.90–1.90 (m, Et). Anal. ($C_{12}H_{14}$) C, H.

9-*exo*-Benzyltricyclo[4.3.1.0]decatriene (9): a colorless oil; 277 mg (63%); IR (neat) 3070–2860, 1600, 1540, 1490, 1455, 1330, 1075, 1020, 980, 740 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.04 (d, J = 3.5 Hz, H-10-anti), 1.70 (br d, J = 3.5 Hz, J(10-syn,9) = 0.7 Hz, H-10-syn), 2.75–2.90 (m, CH_2Ph), 3.09–3.31 (H-9), 5.24 (dd, J = 2.0 and 6.0 Hz, H-8), 6.09 (br dd, J = 6.0 and 2.0 Hz, slightly coupled with H-5, H-7), 5.54–6.39 (m, H-2,3,4,5), 7.30 (br s, Ph). Anal. ($C_{17}H_{16}$) C, H.

9-*exo*-Methoxymethyltricyclo[4.3.1.0]decatriene (10): a colorless oil; 237 mg (68%); IR (neat) 3050–2830, 1600, 1540, 1480–1450, 1370, 1340, 1182, 1113, 750 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ −0.14 (d, J = 3.5 Hz, H-10-anti), 1.47 (br d, J = 3.5 Hz, J(10-syn,9-endo) = 0.7 Hz, H-10-syn), 3.33 (s, Me), 3.12 (m, H-9), 3.22–3.66 (m, CH_2O), 5.10 (dd, J = 5.5 and 2.0 Hz, H-8), 5.77 (m, H-3,4), 6.00 (dd, J = 5.5 and 2.0 Hz, H-7), 6.18 (m, H-2,5); mass spectrum, *m/e* (%) 174 (27), 142 (63), 141 (68), 129 (72), 128 (100), 115 (40). Anal. ($C_{12}H_{14}O$) C, H.

9-*exo*-Trimethylsilyltricyclo[4.3.1.0]decatriene (11): a colorless oil; 315 mg (78%); IR (neat) 3060–2820, 1580, 1540, 1240, 1125, 1030, 980, 886, 840, 750 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.02 (d, J = 3.5 Hz, H-10-anti), 0.21 (s, Me), 1.67 (d, J = 3.5 Hz, H-10-syn), 2.17 (t, J = 2.5 Hz, H-9), 5.41 (dd, J = 2.5 and 6.5 Hz, H-8), 5.79–6.48 (m, H-7,2,3,4,5); mass spectrum, *m/e* (%) 202 (7), 129 (17), 128 (56), 115 (12), 102 (5), 73 (100).

9-*exo*-Carboxytricyclo[4.3.1.0]decatriene (12): colorless needles; 243 mg (70%), mp 77–78 °C (from 20:1 hexane–ether); IR (KBr) 3050–2600, 1705, 1400, 1290 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.03 (d, J = 3.5 Hz, H-10-anti), 1.72 (d, J = 3.5 Hz, H-10-syn), 3.80 (dd, J = 2.2 and 2.5 Hz, H-9), 5.27 (dd, J = 6.0 and 2.2 Hz, H-8), 6.16 (br dd, J = 6.0 and 2.5 Hz, H-7), 5.75–5.98 (m, H-3,4), 6.20–6.38 (m, H-2,5). Anal. ($C_{11}H_{10}O_2$) C, H.

9-*exo*-Methoxycarbonyltricyclo[4.3.1.0]decatriene (13) was prepared by treatment of **12** with excess diazomethane in ether. **13**: colorless needles (from petroleum ether), mp 32–33 °C; IR (KBr) 3050–2900, 1735, 1600, 1540, 1435, 1310, 1186, 1182, 1150 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ −0.01 (d, J = 3.0 Hz, H-10-anti), 1.64 (d, J = 3.0 Hz, H-10-syn), 3.72 (s, Me), 3.72 (dd, J = 2.0 and 2.0 Hz, H-9), 5.24 (dd, J = 6.0 and 2.0 Hz, H-8), 5.70–5.90 (m, H-3,4), 6.12 (dd, J = 6.0 and 2.0 Hz, H-7), 6.16–6.32 (m, H-2,5); ^{13}C NMR ($CDCl_3$) δ 23.8 (C-10), 37.2 (C-1), 45.1 (C-6), 57.2 (C-9), 138.1 (C-7), 119.7 (C-3,4), 125.2, 126.5, 127.5 (C-2,5,8). Anal. ($C_{12}H_{12}O_2$) C, H.

9-Methoxycarbonylbicyclo[4.3.1]decatetraenyl Anion (14).[31] **(a)** A mixture of NaH (washed previously with dry hexane to remove oil coating) (54 mg) and dimethyl-d_6 sulfoxide (3 mL) was heated at 70–80 °C for 1 h with stirring under argon and then cooled to room temperature. The resulting clear solution of dimsyl sodium (0.5 mL, ca. 0.37 mmol) was transferred to a dry NMR tube containing **13** (20 mg, 0.11 mmol) via a syringe under argon, producing an orange-red solution of the anion (**14**); ^{1}H NMR (Me_2SO-d_6) δ −0.94 (br d, J = 7.0 and 0.5 Hz, H-10-anti), 0.71 (d, J = 7.0 Hz, H-10-syn), 3.40 (s, Me), 5.76 (br d, J = 7.0 and 0.5 Hz, H-8), 6.06 (dd, J = 7.0 and 8.0 Hz, H-4), 6.21 (dd, J = 8.0 and 7.0 Hz, H-3), 6.56 (d, J = 7.0 Hz, H-7), 6.62 (dd, J = 7.0 and 1.6 Hz, H-5), 7.27 (dd, J = 1.6 and 7.0 Hz, H-2); ^{13}C NMR (Me_2SO-d_6) δ 42.2 (C-10), 48.5 (Me), 104.7 (C-9), 112.3 (C-7), 114.3, 114.9 (C-1,6), 116.8, 120.3, 122.4, 125.3 (C-2,5,3,4), 132.2 (C-8).

(b) To a solution of diisopropylamine (101 mg, 0.96 mmol) in dry THF (1.5 mL) was added dropwise a solution of *n*-butyllithium in hexane (740 μL, 0.9 mmol) under nitrogen at −78 °C. After being stirred for 30 min at 0 °C, the mixture was cooled again to −78 °C and a solution of **13** (150 mg, 0.79 mmol) in dry THF (1.5 mL) was added. The resulting solution was allowed to warm to 0 °C and further stirred for 30 min, affording a bright red solution of the anion (**14**).

9-*endo*-Methoxycarbonyltricyclo[4.3.1.0]decatriene (15). The THF solution of **14** prepared by using **13** (150 mg, 0.79 mmol) and LDA (0.9 mmol) was cooled to −78 °C and added to a solution of acetic acid (959

(31) For ease of comparison the numbering used is based on tricyclo[4.3.1.0]decatriene (**1**).

mg, 15.9 mmol) in dry THF (3.0 mL) at -78 °C. After being stirred for 20 min at -78 °C, the mixture was allowed to warm to 0 °C and worked up as usual to give a colorless oil (96 mg, 64%), which solidified on trituration with petroleum ether. Recrystallization from petroleum ether gave colorless needles: mp 41-42 °C; IR (KBr) 3070-2950, 1740, 1600, 1535, 1430, 1320, 1160 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.14 (d, J = 3.5 Hz, H-10-anti), 1.43 (d, J = 3.5 Hz, J(10-syn,9) = 0.5 Hz, H-10-syn), 3.64 (s, Me), 3.67 (dd, J = 2.0 and 2.0 Hz, H-9), 5.25 (dd, J = 2.0 and 6.0 Hz, H-8), 6.24 (dd, J = 2.0 and 6.0 Hz, H-7), 5.74-5.88 (m, H-3,4), 6.10-6.30 (m, H-2,5). Anal. ($C_{12}H_{12}O_2$) C, H.

Diels-Alder reaction of 13 with isobenzofuran was carried out in the same manner as described for the formation of **4** from **1** to produce a mixture of **17** and **16**, which was separated by preparative TLC using 1:1 hexane-ether elution. **16**: colorless needles (8%); mp 82-83 °C; IR (KBr) 3040-2950, 1730, 1455, 1435, 1340, 1270-1150, 970 cm^{-1}; ^1H NMR, see Table I. Anal. ($C_{20}H_{18}O_3$) C, H. **17**: colorless needles (10%); mp 85-86 °C; IR (KBr) 3050-2960, 1733, 1460, 1435, 1260-1145 cm^{-1}; ^1H NMR (see Table I). Anal. ($C_{20}H_{18}O_3$) C, H.

Diels-Alder reaction of 11 with isobenzofuran was carried out in a similar manner to that described above to give **24**: colorless needles (9.0%); mp 86-87 °C; IR (KBr) 3040-2929, 1460, 1350, 1240, 970, 865, 830 cm^{-1}; ^1H NMR, see Table I; mass spectrum, m/e (%) 320 (3), 215 (14), 202 (57), 129 (32), 128 (68), 118 (66), 73 (100).

Reduction of 13. According to the usual procedure, **13** (150 mg) was treated with LAH (45.4 mg, 1.19 mmol) in dry ether (10 mL) at 0 °C for 1 h to give **18**: colorless oil; 136 mg (100%); IR (neat) 3350, 3060-2870, 1598, 1535, 1333, 1060, 1015, 978, 750 cm^{-1}; ^1H NMR ($CDCl_3$) δ -0.07 (d, J = 3.5 Hz, H-10-anti), 1.60 (d, J = 3.5 Hz, H-10-syn), 2.05 (br s, OH), 3.13 (ddt, H-9), 3.82 (m, CH_2O), 5.23 (dd, J = 6.0 and 2.0 Hz, H-8), 5.78-6.50 (m, H-7,2,3,4,5); mass spectrum, m/e (%) 160 (15), 129 (63), 128 (100).

Derivation of 18 to 10. To a stirred solution of **18** (32 mg, 0.2 mmol) in methylene chloride (4.0 mL) was added boron trifluoride etherate (7.6 μL) at 0 °C; then ethereal diazomethane solution (2.0 mL) was added dropwise. After the solution stirred at 0 °C for 1 h, the precipitate which formed was filtered off and the filtrate was poured into ice water. Extraction with methylene chloride, washing the extract with aqueous $NaHCO_3$, drying (Na_2SO_4), and solvent evaporation left a colorless oil (20 mg, 57%), which was chromatographed on silica gel. The product obtained had spectral data identical with those of **10**.

Derivation of 18 to 7 via 19. A mixture of **18** (148 mg, 1 mmol), pyridine (118.65 mg, 1.5 mmol), tosyl chloride (285.9 mg, 1.5 mmol), and methylene chloride (8 mL) was heated at reflux for 19 h. To this was added again a mixture of tosyl chloride (0.5 mmol) and pyridine (0.5 mmol), and heating was further continued for 12 h at reflux. The reaction mixture was cooled, diluted with water, neutralized with 2 N HCl, and extracted with ether. Ether extracts were washed with aqueous $NaHCO_3$ and dried. Removal of the solvent gave **19** as a colorless oil; 258 mg (85%). A solution of this oil (0.85 mmol) in ether (8 mL) was heated at reflux with LAH (32.26 mg, 0.85 mmol) for 13 h. After the solution cooled to room temperature, excess hydride was destroyed with water and the ether layer was dried (Na_2SO_4). Removal of the solvent and column chromatography of the oily residue gave a colorless oil (75 mg, 61%), which had spectral data identical with those of 7. **19**: ^1H NMR ($CDCl_3$) δ -0.25 (d, J = 3.5 Hz, H-10-anti), 1.30 (d, J = 3.5 Hz, H-10-syn), 2.45 (s, Me), 3.23 (ddt, J = 7.5, 2.0 and 2.0 Hz, H-9), 4.12 (d, J = 7.5 Hz, CH_2O), 5.05 (dd, J = 6.0 and 2.0 Hz, H-8), 5.65-6.35 (m, H-2,3,4,5,7), 7.33 and 7.85 (two AB-type d's, J = 8.0 Hz, Ph).

Reduction of 15 was carried out in the same way as described for the reduction of **13**. **20**: colorless oil (73%); IR (neat) 3350, 3040-2870, 1600, 1535, 1330, 1065, 1020, 970, 750 cm^{-1}; ^1H NMR ($DCCl_3$) δ 0.05 (d, J = 3.5 Hz, H-10-anti), 1.47 (d, H-10-syn), 1.83 (br s, OH), 2.97 (m, H-9), 3.57 (m, CH_2O), 5.20 (dd, J = 6.0 and 2.0 Hz, H-8), 5.70-6.68 (m, H-7,2,3,4,5); mass spectrum, m/e (%) 160 (20), 142 (35), 141 (32), 129 (75), 128 (100), 127 (55), 115 (30), 102 (25).

9-*endo*-Methoxymethyltricyclo[4.3.1.0]decatriene (22). The endo alcohol **20** was methylated by the same method as the formation of **10** from **18** to give **22**: colorless oil (46%); ^1H NMR ($CDCl_3$) δ 0.00 (d, J = 3.0 Hz, H-10-anti), 1.47 (d, J = 3.0 Hz, H-10-syn), 2.97-3.75 (m, H-9 and CH_2O), 3.33 (s, Me), 5.15 (dd, J = 6.0 and 2.0 Hz, H-8), 6.10 (br d, J = 6.0 Hz, H-7), 5.75-6.55 (m, H-2,3,4,5).

9-*endo*-Tosyloxymethyltricyclo[4.3.1.0]decatriene (21) was prepared by the same method as described for the preparation of **19**. **21**: colorless oil (88%); ^1H NMR ($CDCl_3$) δ 0.03 (d, J = 3.0 Hz, H-10-anti), 1.42 (d, H-10-syn), 2.50 (s, Me), 3.10 (m, H-9), 3.51-4.21 (m, CH_2O), 5.08 (dd, J = 6.0 and 2.0 Hz, H-8), 5.70-6.75 (m, H-2,3,4,5,7), 7.10 and 7.87 (two AB-type d's, J = 8.0 Hz, Ph).

9-*endo*-Methyltricyclo[4.3.1.0]decatriene (23) was prepared from **21** by the same method as described for the derivation of 7 from **19**. **23**: colorless oil (61%); ^1H NMR ($CDCl_3$) δ 0.00 (d, J = 3.0 Hz, H-10-anti), 0.93 (d, J = 7.0 Hz, Me), 1.53 (d, J = 3.0 Hz, H-10-syn), 2.88 (ddq, J = 2.0, 2.0, and 7.0 Hz, H-9), 5.27 (dd, J = 6.0 and 2.0 Hz, H-8), 5.68-6.58 (m, H-7,2,3,4,5).

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Long-Range Triplet-Triplet Energy Transfer within Metal-Substituted Hemoglobins

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Abstract: We present a detailed analysis of the long-range (Förster-type) triplet-to-triplet energy transfer between the photoexcited triplet states of the zinc and magnesium protoporphyrin IX chromophores of Zn- and Mg-substituted hemoglobin. The observations of this rarely detected process are made in fluid solution and at ambient temperature by monitoring the time dependence of triplet-triplet absorption subsequent to flash excitation. This appears to be the first time that rate constants have been measured for Förster energy transfer (triplet) between chromophores at crystallographically known distances and orientations. To provide further reference data on chromophore-protein complexes, we have measured the triplet decay rates for zinc myoglobin (k_1 = 70 ± 5 s^{-1}) and magnesium myoglobin (k_1 = 24 ± 1 s^{-1}) and the bimolecular rate constant for quenching the zinc myoglobin triplet by O_2 (k_q = 1.25 × 10^8 M^{-1} s^{-1}) and by dithionite (k_q = 2.4 × 10^6 M^{-1} s^{-1}).

Introduction

Since its elucidation by Förster, about 30 years ago,[1] long-range (dipole-dipole) electronic energy transfer has been extensively studied and widely used in the investigation of photoreactions and the characterization of molecules in their excited state.[2] This energy-transfer process is extremely sensitive to interchromophoric distances, and singlet-energy donors are routinely used to estimate both intra- and intermolecular distances in protein systems. Energy-transfer reactions involving triplet donors can occur by

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