Conclusion

In the case where both reactants are absorbed by the hydrophobic core of the micelle the reacting bonds are forced into a region so that the electronic structure of the transition state differs from that in aqueous solution; the nature of the region, as reflected by the effective charges on the attacking oxygen at the various stages of the reaction path, is not water-like.

Acknowledgment. One of us is grateful to the University of Kuwait for sabbatical leave and financial assistance of the work. (N.Al-A).

Supplementary Material Available: Tables of rate constants from which parameters in Tables II and III are derived (4 pages). Ordering information is given on any current masthead page.

Photolyses of (3-Naphthoxypropyl)-, (4-Naphthylbutyl)-, and (4-Naphthyl-4-oxobutyl)cobaloxime

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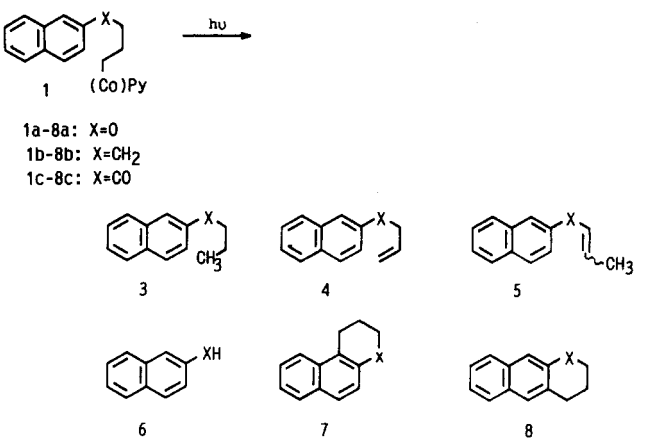
The cobalt–carbon bond of the titled compounds is photochemically cleaved to generate an organoradical and a cobaloxime(II) radical pair. 3-(1- or 2-naphthoxy)propyl, 4-(1- or 2-naphthyl)butyl, and 4-(1- or 2-naphthyl)-4-oxobutyl radicals thus formed undergo three types of reactions: (a) hydrogen abstraction to give a saturated terminal, (b) hydrogen elimination to give a terminal olefin, and (c) substitution on the naphthalene ring. In benzene and radicals follow process b exclusively (the radicals from (3-(2-naphthoxy)propyl)cobaloxime (**1a**), (3-(1-naphthoxy)propyl)cobaloxime (**2a**), and (4-(1-naphthyl)butyl)cobaloxime (**2b**)) or preferentially (the radicals from (4-(2-naphthyl)butyl)cobaloxime (**1b**), (4-(2-naphthyl)-4-oxobutyl)cobaloxime (**1c**), and (4-(1-naphthyl)-4-oxobutyl)cobaloxime (**2c**)). In chloroform, process a becomes important to the extent as the sum of the other two processes. In water–acetonitrile (4:1), process c becomes important and even takes precedence of others for the radicals from **1b** and **1c**. This feature is accounted for by the folding of the side chain of hydrophobic radicals. Encapsulation of the radicals in β-cyclodextrin stimulates process c except for the case of the radical from **2c**. In the case of cobaloxime **2c**, α-cyclodextrin does not affect the partition process of the intermediate radical. This feature is accounted for by the shallow inclusion of the radical due to the hydrogen bonding as depicted in Figure 1d.

We have been concerned with the biomimetic reaction of coenzyme B_{12} using organobis(dimethylglyoximato)(pyridine)cobalt(III), organocobaloxime as a model compound,[1] and have exploited the photolytic cleavage of the alkyl–cobalt bond of organocobaloximes to generate an organoradical and cobaloxime(II) radical pair.[2] In those model studies the organoradicals have phenyl or carbonyl functions at the position β to the radical center. We selected these systems to test the participation of the functional groups in radical rearrangements. Those experiments prompted us to explore the photolysis of alkylcobaloximes having a naphthyl group at the δ-position. The naphthyl group was selected to test the effect of cyclodextrin on the photolyses in an aqueous medium.

Results and Discussion

(3-(2-Naphthoxy)propyl)cobaloxime (**1a**), (4-(2-naphthyl)butyl)cobaloxime (**1b**), (4-(2-naphthyl)-4-oxobutyl)cobaloxime (**1c**), (3-(1-naphthoxy)propyl)cobaloxime (**2a**), (4-(1-naphthyl)butyl)cobaloxime (**2b**), and (4-(1-naphthyl)-4-oxobutyl)cobaloxime (**2c**) were synthesized from the corresponding bromides and cobaloxime(I) anion[3]

Scheme I



in the same manner as reported in earlier papers.[2] Elemental analyses and spectroscopic data fully supported the structures of those organocobaloximes. The UV absorption of organocobaloxime has been well characterized, and its absorption at the longest wavelength appears at 440–460 nm. This absorption band is assigned to a ligand to metal charge transfer and is responsible for the radical rupture of the cobalt–carbon bond of organocobaloximes.[4]

Photolyses of the organocobaloximes gave a variety of products, as shown in Schemes I and II. Products **3a**,[5] **4a**,[6] **6a**, **7a**,[7] **9a**,[5] **9b**,[8] **9c**,[9] **10a**,[10] **12b**,[11] **13a**,[12] **15a**, and **16a**[7]

(1) (a) Halpern, J. B_{12}; Dolphin, D., Ed.; Academic Press: New York, 1982; Vol. 1, Chapter 14. (b) Golding, B. T. *Ibid.* Vol. 1, Chapter 15. (c) Retey, J. *Ibid.* Vol. 2, Chapter 13.

(2) (a) Tada, M.; Miura, K.; Okabe, M.; Seki, S.; Mizutani, H. *Chem. Lett.* **1981**, 33. (b) Okabe, M.; Osawa, T.; Tada, M. *Tetrahedron Lett.* **1981**, *22*, 1899. (c) Tada, M.; Akinaga, S.; Okabe, M. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3939. (d) Tada, M.; Inoue, K.; Sugawara, K.; Hiratsuka, M.; Okabe, M. *Chem. Lett.* **1985**, 1821. (e) Tada, M.; Inoue, K.; Okabe, M. *Ibid.* **1986**, 703. (f) Tada, M.; Nakamura, T.; Matsumoto, M. *Ibid.* **1987**, 409. (g) Tada, M.; Nakamura, T.; Matsumoto, M. *J. Am. Chem. Soc.* **1988**, *110*, 4647.

(3) Shrauzer, G. N. *Inorganic Syntheses*; McGraw-Hill: New York, 1968; Vol. 11, p 65.

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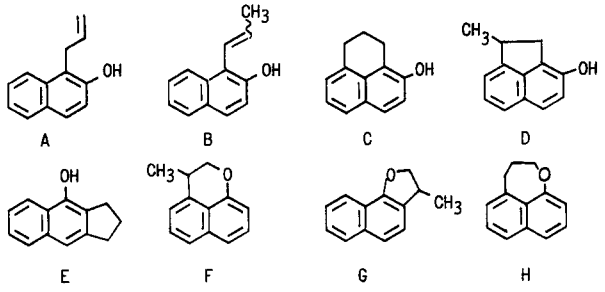
Table I. Product Distribution and Yields of the Photolysis Products of Cobaloxime 1

cobaloxime	X	solvent	additive	irrad time, h	product ratio,[a] %						total yield, %
					3	4	5	6	7	8	
1a	O	$CHCl_3$	none	2.0	51	49	–	–	–	–	99
1a	O	C_6H_6	none	2.0	–	100	–	–	–	–	99
1a	O	CH_3CN-H_2O	none	2.0	8	74	3	+[c]	12	3	*b*
1a	O	CH_3CN-H_2O	β-CDX	2.0	1	60	10	9	20	–	*b*
1b	CH_2	$CHCl_3$	none	1.5	45	52	–	–	3	–	94
1b	CH_2	C_6H_6	none	1.5	–	91	–	–	9	–	93
1b	CH_2	CH_3CN-H_2O	none	2.0	7	32	–	–	61	–	*b*
1b	CH_2	CH_3CN-H_2O	β-CDX	2.0	1	29	–	–	70	–	*b*
1c	CO	$CHCl_3$	none	0.5	55	12	3	–	30	–	77
1c	CO	C_6H_6	none	0.5	2	30	28	–	40	–	70
1c	CO	CH_3CN-H_2O	none	0.5	+[c]	29	11	–	60	–	*b*
1c	CO	CH_3CN-H_2O	β-CDX	0.5	+[c]	16	8	–	76	–	*b*

[a] Relative intensities of gaschromatogram. [b] Not determined. [c] Trace amount (<0.5%).

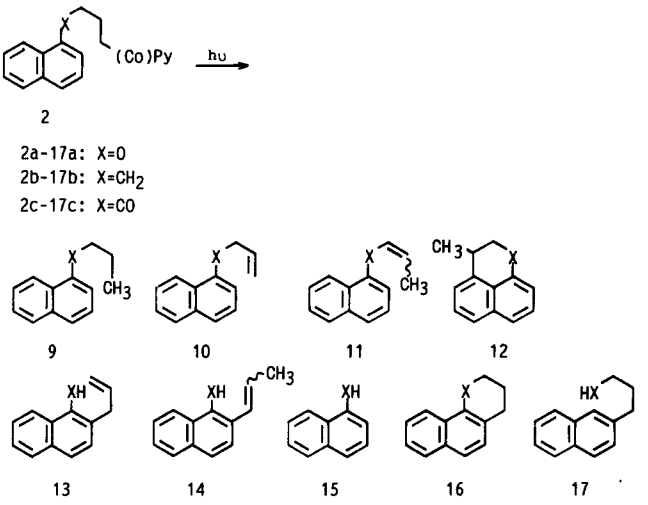
were identified with authentic samples by comparison of gas chromatograms and fragmentation patterns of mass spectra. The structures of products **3b** (=**17b**), **3c**, **7b** (=**16b**), and **16c** were deduced by comparison of the mass spectra with those of the reported data.[13,14] The structures of the other products, **5a**, **8a**, **11b**, **14a**, and **17a**, were deduced by the analyses of the mass spectra.

Product **5a** showed a peak at m/z = 169 (M^+ – 15, 12) which shows the existence of a methyl group. 1-Allyl-2-naphthol (A), 1-(1-propenyl)-2-naphthol (B), 2,3-dihydrophenalen-4-ol (C), and 1-methyl-acenaphthen-3-ol (D) were eliminated as possible structures of **5a** by the absence of mass fragments at m/z = 167 (M^+ – OH) and 166 (M^+ – OH_2), and 165 (M^+ – OH_2 – H), which are characteristic fragments for ortho-substituted phenols[15] (see also Scheme IV for **14a**). These features deduced the



structure **5a** though it has no definite proof. Structure **8a** was deduced from the similarity of its mass spectrum to those of **7a** and **16a**. The fragmentation patterns of **8a** were characterized by the intense retro-Diels–Alder fragment at m/z = 156 as seen in the spectra of **7a** and **16a**. Product **11b** showed mass peaks at m/z = 167 (71), 166 (100), and 165 (83) due to the stepwise elimination of one methyl and two hydrogen atoms from the molecular ion (route a in Scheme III). Other prominent fragment ions from **11b** appeared at m/z = 154 (53), 153 (44), and 152 (49), which were formed by the stepwise loss of ethylene and two hydrogen atoms by route b. These fragmentation

Scheme II



patterns are similar to those of **12b**, which was identified with the authentic sample. Other possible structures for **11b** having a molecular peak at m/z = 182, 1,2,3,4-tetrahydroanthracene, 1-(1-butenyl)naphthalene, and 1,8-tetramethylenenaphthalene, were eliminated by comparison with the authentic sample or by comparison of the reported mass spectral data.[12] The structure of **14a** was assigned by the following reasoning: Of the plausible structure having a molecular peak at m/z = 184 and having a 1-naphthoxy moiety, there remain structures E–H. However, fragmentation peaks at m/z = 169 (M^+ – CH_3), 167 (M^+ – OH), 166 (M^+ – H_2O), and 165 (M^+ – H_2O – H) are hardly accounted for by structures other than **14a**. A reasonable fragmentation pattern is shown in Scheme IV.[16]

Product **17a** with a molecular peak at m/z = 186 contains a naphthalene derivative with a saturated substituent of C_3H_7O. Confirmation of structure **17a** was obtained from fragment ions at m/z = 167 (M^+ – H_2O – H), 155 (M^+ – CH_2OH), and 141 (M^+ – CH_2CH_2OH) which are in contrast to the framentation of **3a**. The structures of products **4b**, **4c**, **5c**, **7c**, **10b**, and **11c** were determined from the NMR and mass spectral data of the isolated products from the photolyses. Products **4b** and **10b** showed similar spectra, intense peaks at m/z = 182 (M^+), 142 (M^+ – CH_2=C=CH_2), and 141 (M^+ – CH_2=$CHCH_2$), and NMR spectra having typical signals due to a vinyl group. Product **7c** showed that an almost identical mass spectrum to **16c**, m/z = 196 (93, M^+), 168 (86, M^+ – CH_2=CH_2), and 140 (100, M^+ – CH_2=CH_2 – CO). Product **7c** lacks a

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(13) (a) *API-Selected Mass Spectral Data*; Thermodynamic Research Center, Texas. (b) *NIST/EPA/MSDC, Mass Spectral Data Base*; Ver. II, National Institute Standards and Technology, Gaintherburg, MD.
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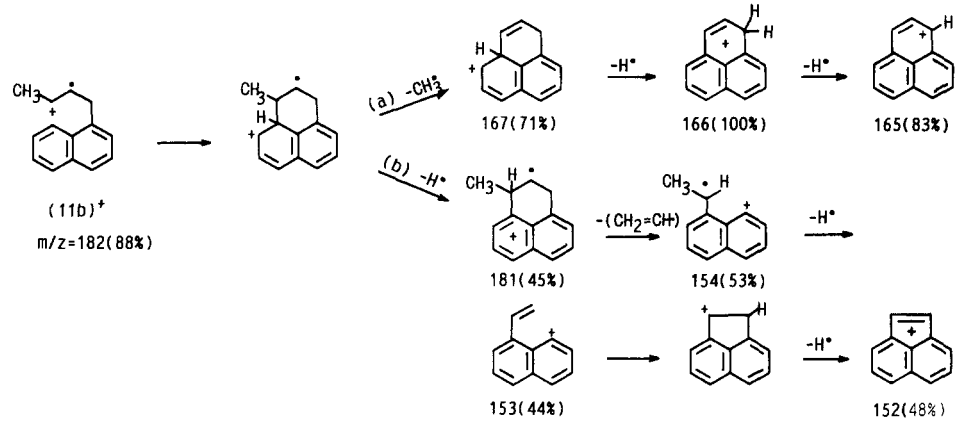
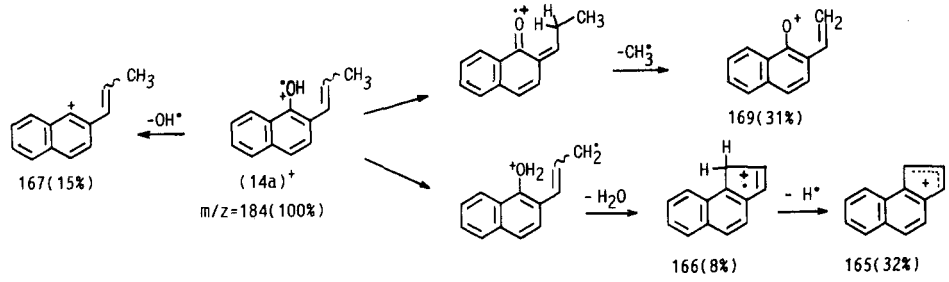
(16) Aczel, T.; Lumpkin, H. E. *Anal. Chem.* **1960**, *32*, 1819.

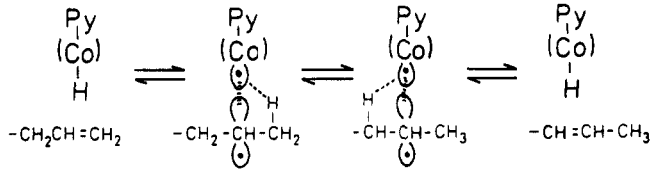
Scheme III



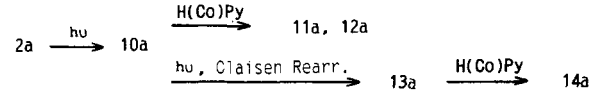
Scheme IV



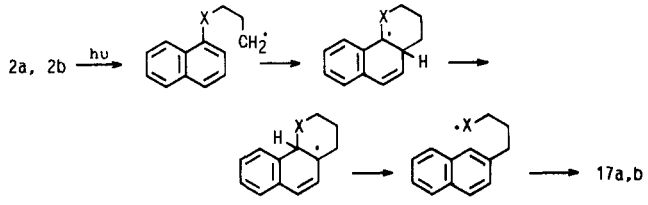
Scheme V



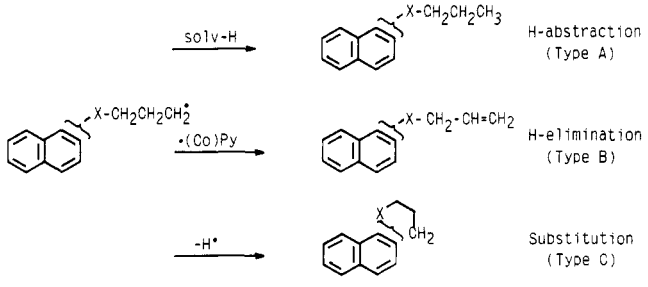
Scheme VI



Scheme VII



Scheme VIII



typical NMR signal due to the C_1 hydrogen on the naphthalene ring having an acyl substituent at the C_2 position, $\delta = 8.61$ for 2-acetylnaphthalene.[17] This feature eliminates another possible structure, 1,2,3,4-tetrahydroanthracen-1-one. Products **4c**, **5c**, and **11c** were further interrelated to **3c** and **9c** by hydrogenation of the olefinic groups.

Tables I and II show the product distributions and the product yields of the photolyses of organocobaloximes **1a–c** and **2a–c**. The product yields in organic solvents are nearly quantitative in most of the cases. It was difficult to obtain the yields in the water–acetonitrile (4:1) system since solubility of the organocobaloximes was poor and only a small amount (5 mg) of the organocobaloximes was photolyzed. The product yields from cobaloxime **2b** were estimated by gas chromatographic analysis of the products mixture using an internal standard. By this method we obtained the total yield of 84% in water–acetonitrile and 40% in the same solvent containing β-cyclodextrin.

Internal olefins **5a** and **11b** must be formed from **4a** and **10b**, respectively, by the double bond migraton mediated by hydridocobaloxime[18] (Scheme V) since the thermal treatment of **4a** and **10b** did not afford **5a** and **11b**. Similarly product **5c**, **11c**, and **14a** must be derived from its β,γ-unsaturated counterpart by the same process or by a thermal allylic rearrangement.

A facile Claisen rearrangement of **10a** accounts for the formation of **13a**, which further rearranges to form product **14a**. In fact, irradiation of the authentic sample of **10a** gave **13a** and **15a** (Scheme VI). In some runs 2-allylnaphthoquinone was formed as a secondary product from **13a**. In contrast to **10a**, 2-(allyloxy)naphthalene (**4a**) was stable under the reaction conditions, and no products from the Claisen rearrangement were detected in the photolysis product.

Alkyl migrations to form **17a** and **17b** are reasonably explained by the hydrogen shift and ring opening of the intermediate (Scheme VII). Conversion of an alkyl radical into an alkoxy radical seems thermodynamically unfa-

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Table II. Product Distribution and Yield of the Photolysis Products of Cobaloxime 2

cobaloxime	X	solvent	additive	irrad time, h	product ratio,[a] %									total yield, %
					9	10	11	12	13	14	15	16	17	
2a	O	$CHCl_3$	none	1.0	68	32	–	–	–	–	–	–	–	78
2a	O	C_6H_6	none	1.0	+[e]	70	–	–	30[b]	–	–	–	–	69
2a	O	CH_3CN-H_2O	none	1.0	6	3	–	–	59	16	10	2	4	[c]
2a	O	CH_3CN-H_2O	β-CDX	1.0	2	2	–	–	61	17	7	7	4	[c]
2b	CH_2	$CHCl_3$	none	1.0	41	59	–	–	–	–	–	–	+[e]	100
2b	CH_2	C_6H_6	none	1.0	–	100	–	–	–	–	–	–	+[e]	100
2b	CH_2	CH_3CN-H_2O	none	2.0	6	66	18	+[e]	–	–	–	7	3	84[d]
2b	CH_2	CH_3CN-H_2O	β-CDX	2.0	2	64	2	4	–	–	–	19	9	40[d]
2c	CO	$CHCl_3$	none	6.0	53	–	19	–	–	–	–	28	–	100
2c	CO	C_6H_6	none	6.0	3	–	81	–	–	–	–	16	–	100
2c	CO	CH_3CN-H_2O	none	4.5	6	–	45	–	–	–	–	49	–	[c]
2c	CO	CH_3CN-H_2O	β-CDX	4.5	5	–	49	–	–	–	–	46	–	[c]

[a] Relative intensities of gaschromatogram. [b] In some runs 2-allylnaphthoquinone was formed by autoxidation. [c] Not determined. [d] Determined by gas chromatography using internal standards. [e] Trace amount (<0.5%).

Table III. Relative Percentage of the Decay Processes of the Intermediate Radical from Organocobaloximes 1a–c and 2a–c

cobaloxime	solvent	ratio of decay process			cobaloxime	solvent	ratio of decay process		
		A	B	C			A	B	C
1a	$CHCl_3$	51	49	–	**2a**	$CHCl_3$	68	32	–
1a	C_6H_6	0	100	–	**2a**	C_6H_6	+[b]	100	–
1a	CH_3CN-H_2O	8	77	15	**2a**	CH_3CN-H_2O	6	88	6
1a	CH_3CN-H_2O[a]	1	79	20	**2a**	CH_3CN-H_2O[a]	2	87	11
1b	$CHCl_3$	45	52	3	**2b**	$CHCl_3$	41	59	–
1b	C_6H_6	0	91	9	**2b**	C_6H_6	0	100	–
1b	CH_3CN-H_2O	7	32	61	**2b**	CH_3CN-H_2O	6	84	10
1b	CH_3CN-H_2O[a]	1	29	70	**2b**	CH_3CN-H_2O[a]	2	70	28
1c	$CHCl_3$	55	15	30	**2c**	$CHCl_3$	53	19	28
1c	C_6H_6	2	58	40	**2c**	C_6H_6	3	81	16
1c	CH_3CN-H_2O	+[b]	40	60	**2c**	CH_3CN-H_2O	6	45	49
1c	CH_3CN-H_2O[a]	+[b]	24	76	**2c**	CH_3CN-H_2O[a]	5	49	46

[a] β-Cyclodextrin was added to the reaction mixture. [b] Trace amount (<0.5%).

vorable, but the hydrogen shift in the intermediate converts the radical into the more stable species which has a more extended conjugate system.

These considerations enable us to classify the primary reaction of the photoyses of organocobaloximes **1a–c** and **2a–c** into three categories, Type A, B, and C (Scheme VIII), and the relative ratio of those reactions are shown in Table III.

Organocobaloximes **1** and **2** gave **3** and **9** by the type A reaction, and **4** and **10** by the type B reaction, respectively. Products **4** and **10** gave **5**, **6**, **11**, **12**, **13**, **14**, and **15** as secondary products. In addition, the type C reaction afforded **7**, **8**, **16**, and **17**.

The photolyses in benzene gave **4** and **10** as the primary products, and isomerization followed in some cases. This finding is a general feature of the photolyses of other classes of organocobaloximes in benzene, a poor hydrogen donor. It has been well established that the photolysis of organocobaloximes generates a pair of organoradicals and cobaloxime(II) radicals,[19,20,21] and the resulting cobaloxime(II) radical abstracts a β-hydrogen of the organoradical to give an olefin.

The photolyses in chloroform, a strong hydrogen donor, gave hydrogen abstraction products, **3** and **9**, in addition to terminal olefins. Our earlier studies[2] showed that the other class of organoradical generated in chloroform preferentially abstracts a hydrogen atom from the solvent to give a saturated product.[2] In the present study, however, the hydrogen elimination by the cobaloxime radical (type B), giving terminal olefins, is competitive with the hydrogen abstraction from the solvent (type A) (Scheme VIII).

The photolyses in aqueous systems gave a complex mixture of products. Isomerization of terminal olefins to internal olefins is accounted for by a radical shift mechanism under the influence of cobaloxime hydride (Scheme V).

In aqueous media hydrogen elimination (type B) and radical substitution (type C) are major reactions. Importance of the type B reaction can be explained by poor hydrogen donation ability of water and the increased life time of the intimate pair of organoradicals and cobaloxime radicals. Both radicals are hydrophobic and do not easily diffuse in aqueous solvent. It is noteworthy that the radical substitution (type C) becomes another important reaction of the radical decay in the aqueous solvent. The type C reaction can be explained on the basis of its conformational effects. Radical intermediates having tetramethylene, or its oxa analogue, are hydrophobic, and the stretched conformation of the side chain must be unfavorable. The structure of solvent cage is considered to be another important factor. Water is a more organized solvent than benzene and may affect the conformation of the side chain. These properties must force a folded conformation of the side chain to minimize the molecular surface of the radical intermediate.[22] This folding effect stimulates initial radical attack on naphthalene and the following process. Type C reaction of organocobaloxime **2** is less important than that of organocobaloxime **1**. This feature is explained by the susceptibility of the α- and β-position of naphthalene to radical substitution.[23] The

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(21) Rao, D. N.; Symons, M. C. R. *J. Chem. Soc., Faraday Trans. I* **1984**, *80*, 432.
(22) Reitz, G. A.; Demons, J. N.; DeGroff, B. A.; Stepheres, E. M. *J. Am. Chem. Soc.* **1988**, *110*, 5051.

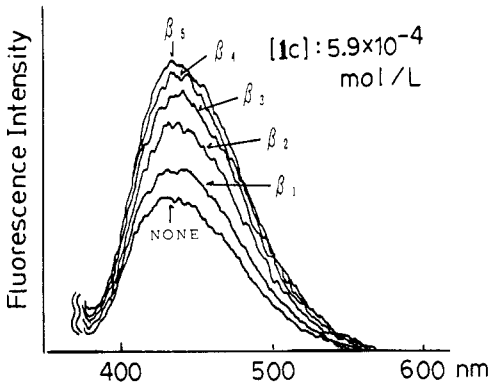

Figure 1. Fluorescence intensities of organocobaloxime **1c** in the presence of β-cyclodextrin. [CD]: β_1, 5.9×10^{-4} mol/L; β_2, 2.2×10^{-3} mol/L; β_3, 4.4×10^{-3} mol/L; β_4, 6.6×10^{-3} mol/L; β_5, 8.8×10^{-3} mol/L.

relative importance of the type C reaction increases in the order of **1a**, **1b**, and **1c** as well as **2a**, **2b**, and **2c**. This fact clearly indicates that the initial radical addition on naphthalene has a latent nucleophilic character as reported.[24]

The effect of β-cyclodextrin on the product distributions must be due to the formation of an inclusion complex. Naphthalene is a good guest molecule for β-cyclodextrin, but cobaloxime is too bulky to be included. Inclusion of the naphthalene moiety is shown by the increased fluorescence intensity from the naphthalene moiety of cobaloximes **1** and **2** on addition of β-cyclodextrin, whereas only a small effect was observed by the addition of α-cyclodextrin (Figure 1). The cavity of α-cyclodextrin is too small to accommodate the naphthalene moiety of the organocobaloximes cited in this paper, and indeed essentially no effect was seen on the photolyses of organocobaloximes in the presence of α-cyclodextrin. Inclusion of organocobaloximes in β-cyclodextrin is expected to decrease the type B reaction due to steric hindrance and increase the relative ratio of the radical substitution (type C) from the organocobaloximes **1** and **2**.

Fluorescence intensities of cobaloximes **1c** and **2c** are intensified by the addition of β-cyclodextrin. The Benesi-Hildebrand equation[25] (eq 1) as to the fluorescence

$$\frac{[\mathrm{Co}][\mathrm{CD}]}{\Delta F} = \frac{1}{\Delta f(K_{\mathrm{assoc}})} + \frac{[\mathrm{Co}] + [\mathrm{CD}]}{\Delta f} \qquad (1)$$

spectra of the organocobaloximes (Co) in the presence of β-cyclodextrin gives the association constant (K_{assoc}). Figure 2 shows the relation of the emission intensities and the concentration of β-cyclodextrin [CD], where ΔF and Δf are the difference in fluorescence intensity and molar fluorescence coefficient, respectively, in the presence and absence of β-cyclodextrin. These analyses provided the association constants for **1c**, 4.3×10^2 M^{-1}, and for **2c**, 1.8×10^2 M^{-1}. This small difference in the association constants cannot explain the different behaviors of **1c** and **2c** by addition of β-cyclodextrin. One of the possible explanation is the difference in the expected geometry of the inclusion complex (Figure 3b).[26] The carbonyl oxygen of **2c** and the hydroxy group on the rim of β-cyclodextrin are expected to form a hydrogen bond, and hence only a shallow inclusion is envisaged.[27] The present study deals with the chemical behaviors of 4-(naphthyl)butyl radical and its oxo and oxa analogues in varying environment, and we must remember the life time of the intermediate radicals. Conformational dynamics are considered to be affected to a limited extent within the short life time.

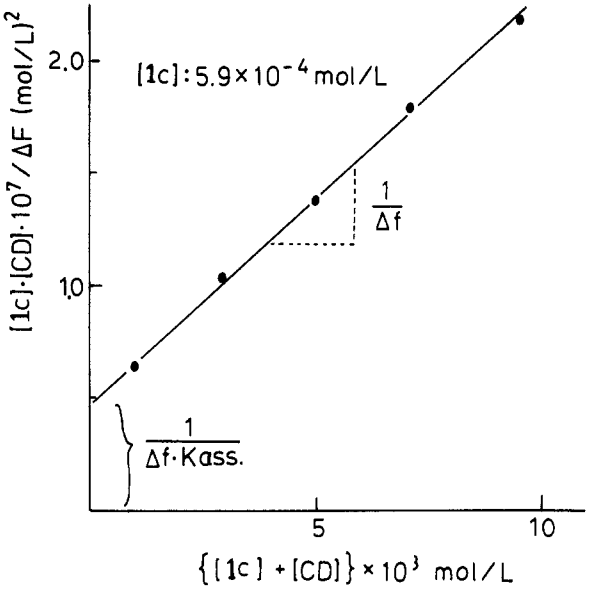

Figure 2. Benesi-Hildebrand plots of the fluorescence from organocobaloxime **1c** in the presence of β-cyclodextrin.

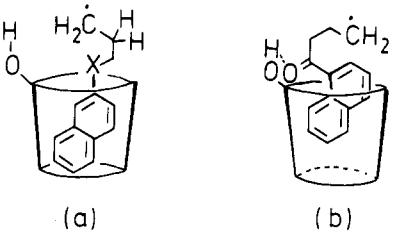

Figure 3. Schematic representation of the inclusion of intermediate radicals.

The observations recorded in this paper indicate that the interaction between an organoradical and a cobalt(II) complex is important in the selection of a partition of the decay process of radical intermediate. This concept must be taken into consideration in the discussion of reaction mechanism of the coenzyme-B_{12} mediated biological processes and its model reactions.[1]

In conclusion the photolyses of (4-naphthylbutyl)- or (3-naphthoxypropyl)cobaloximes gave exclusively terminal olefins in benzene (type B). On the other hand, the products with saturated side chain and terminal olefins (types A and B) are found in comparative yields in chloroform. In an aqueous system, intramolecular radical substitution (type C) becomes more important as a primary process. Inclusion of the naphthalene moiety of the organoradicals in β-cyclodextrin generally stimulates the type C process.

Experimental Section

IR spectra were measured in chloroform solution. NMR spectra were measured in the presence of tetramethylsilane as an internal standard, and chemical shifts and coupling constants are recorded in δ (ppm) and hertz, respectively. Mass spectra were measured by the EI method at the ionization voltage of 70 eV. Product analyses by gas chromatography were carried out by a gas

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chromatograph equipped with a hydrogen flame ionization detector and wide bore columns of Shimazu CBP-W12-100 (0.53 mm (Φ) × 12 m) or CBP20-W12-100 (0.53 mm (Φ) × 12 m).

All solvents used for the photolyses were distilled before use, and commercially available β-cyclodextrin was used without purification.

Syntheses of 3-(1-Naphthoxy)propyl Bromide and 3-(2-Naphthoxy)propyl Bromide. Both bromides were synthesized in a same procedure, and the synthesis of 3-(1-naphthoxy)propyl bromide is described.

A mixture of α-naphthol (4.30 g, 3×10^{-2} mol) and potassium hydroxide (1.87 g, 4.8×10^{-2} mol) in 20 mL of methanol was treated with 1,3-dibromopropane (18.20 g, 9×10^{-2} mol), and the mixture was stirred overnight at room temperature under nitrogen. After evaporation of the solvent, the residue was added with 20 mL of 1 N hydrochloric acid and extracted with chloroform (3 × 30 mL). The chloroform extract was washed with aqueous sodium hydrogen carbonate and water and dried over sodium sulfate. The condensate was distilled at reduced pressure to give 3-(1-naphthoxy)propyl bromide (3.10 g, 40%), bp 113 °C (0.31 mmHg). The sample thus obtained was essentially pure from GLC analysis and the ^{1}H NMR spectrum (supplementary material). ^{1}H NMR ($CDCl_3$): 2.11 (2 H, quint, J = 6.0), 3.40 (2 H, t, J = 6.0), 3.87 (2 H, t, J = 6.0), 6.49 (1 H, double d, J = 2.2 and 8.4), 6.99–7.71 (5 H, m), 7.96–8.25 (1 H, m).

The same procedure using β-naphthol as a starting material gave 3-(2-naphthoxy)propyl bromide[28] in 65% yield, bp 130.5 °C (0.31 mmHg). ^{1}H NMR ($CDCl_3$): 2.18 (2 H, quint, J = 6.0), 3.45 (2 H, t, J = 6.0), 4.00 (2 H, t, J = 6.0), 6.92–7.84 (7 H, m).

Syntheses of 4-(1-Naphthyl)butyl Bromide and 4-(2-Naphthyl)butyl Bromide. 4-(1-Naphthyl)butanoic acid[29] (2.15 g, 1×10^{-2} mol) was reduced by lithium aluminum hydride (1.00 g) in 70 mL of dry ether by stirring overnight at room temperature and refluxing for 1.5 h.

The mixture was treated with 50 mL of 2 N hydrochloric acid, and the ether layer was washed with sodium hydrogen carbonate and dried over magnesium sulfate. 4-(1-Naphthyl)butanol thus obtained was directly brominated by phosphorus tribromide (0.4 mL). The mixture was allowed to stand overnight at room temperature and was treated with 5 mL of cold water followed by stirring for 5 min. Chloroform extract (5 mL × 5) was washed with water and dried over magnesium sulfate. Condensation of the extract and chromatography of the residue on alumina (100–200 mesh, 2.7 (Φ) × 8 cm, benzene) to remove polar materials gave 4-(1-naphthyl)butyl bromide[30] (2.25 g, 85% from 4-(1-naphthyl)butanoic acid. ^{1}H NMR ($CDCl_3$): 1.73–2.18 (4 H, m), 2.56–3.40 (4 H, m), 7.08–7.95 (7 H, m); MS 264 (11, M^+), 262 (10, M^+), 141 (100).

The synthesis of 4-(2-naphthyl)butyl bromide[31] from 4-(2-naphthyl)butanoic acid was carried out in the same manner as the synthesis of 4-(1-naphthyl)butyl bromide mentioned above. Distillation under reduced pressure gave the bromide (40% from the acid), bp 200–215 °C (0.17–0.20 mmHg). ^{1}H NMR (CCl_4): 1.71–2.06 (4 H, m), 2.60–2.93 (2 H, m), 3.27–3.50 (2 H, m), 7.10–7.83 (7 H, m).

Synthesis of 4-(1-Naphthyl)-4-oxobutyl Bromide. 1-Bromonaphthalene (30.2 g, 0.14 mol) in 30 mL of THF was treated with 0.65 mL of n-butyllithium (1.5 mol/L) under cooling in a dry ice–methanol bath at −78 °C, and the mixture was stirred for 10 min at the same temperature. The cooled mixture was then added with copper(I) iodide (95 mg) and stirred at the same temperature for 5 min and at ambient temperature for 10 minutes. The mixture was again cooled to −78 °C and was treated with 4-bromobutanoyl chloride (1.74×10^{-1} mol) in 1 mL of THF. The reaction mixture was stirred overnight at ambient temperature by removing the cooling bath. Addition of saturated aqueous ammonium chloride and ether extraction (2.5 mL × 3) gave the crude product after drying over sodium sulfate and evaporation of the solvent. The residue thus obtained was chromatographed on silica gel (2.0 (Φ) × 6 cm) eluted with benzene to remove polar materials. Kugelrohr distillation gave 4-(1-naphthyl)-4-oxobutyl bromide (30%), bp 175–180 °C (0.15–0.20 mmHg). The sample thus obtained was essentially pure from GLC analysis and the ^{1}H NMR spectrum (supplementary material). ^{1}H NMR (CCl_4): 2.20 (2 H, quint, J = 6.0), 3.04 (2 H, t, J = 6.0), 3.40 (2 H, t, J = 6.0), 7.10–7.98 (6 H, m), 8.44–8.73 (1 H, m). IR (CCl_4): 3060, 1684 cm^{-1}.

Synthesis of 4-(2-Naphthyl)-4-oxobutyl Bromide. Ground aluminum(III) chloride (6.40 g, 4.8×10^{-2} mol) and 60 mL of nitrobenzene placed in a dry reaction vessel was added dropwise with 4-bromobutanoyl chloride (5.1 mL) and naphthalene (5.12 g, 4.0×10^{-2} mol) in 40 mL of nitrobenzene. During the addition (40 min) the reaction mixture was cooled to −5 °C. The mixture was stirred overnight at room temperature and then added with excess of ice. Dichloromethane extract (80 mL × 3) was washed with saturated aqueous sodium hydrogen carbonate and water and then dried over sodium sulfate. Evaporation of the solvent gave the crude product, which was dissolved in 60 mL of benzene and treated with 2 g of active charcoal. After warming for 5 min, the mixture was filtered through a Celite layer to give the crystalline product after evaporation of the solvent. The crystalline product was rinsed with 15 mL of methanol and distilled with a Kugelrohr apparatus to give 4-(2-naphthyl)-4-oxobutyl bromide (38%), bp 180–185 °C (0.15–0.18 mmHg); mp 108.5–110 °C. The sample thus obtained was essentially pure from GLC analysis and the ^{1}H NMR spectrum (supplementary material). ^{1}H NMR ($CDCl_3$): 2.28 (2 H, quint, J = 6.0), 3.20 (2 H, t, J = 6.0), 3.50 (2 H, t, J = 6.0), 7.34–8.10 (6 H, m), 8.36 (1 H, br s). IR (CCl_4): 3065, 1686 cm^{-1}.

Syntheses of Organocobaloxime 1 and 2. Organocobaloximes **1** and **2** were synthesized essentially in the same manner, and a general procedure[2c,3] is described in this section. A mixture of cobalt(II) chloride hexahydrate and 2 equiv of dimethylglyoxime in methanol (1–2 mL for 1 mmol of the cobalt salt) was treated with the mixture of 2 equiv of sodium methoxide (1.0 mol/L) and 1.5 equiv of pyridine in methanol under ice cooling and a nitrogen atmosphere. Methanol was degassed by bubbling argon in an ultrasonic bath before use. To this reaction mixture was added a slight excess (1.1–1.2 equiv) of sodium borohydride in portion, and the mixture was stirred for 30 min in an ice bath to get the dark solution of (dimethylglyoxiomato)cobalt(I)–pyridine. The cobalt(I) complex thus obtained was added with one of the bromides in the neat state or as a concentrated solution in methanol or THF. The solution was stirred overnight in the dark under nitrogen. In the case of organocobaloximes **1c** and **2c**, the reducing agent was replaced by zinc powder to avoid the reduction of the carbonyl groups. The mixture of cobaloxime(II)–pyridine, the corresponding bromide, and excess of zinc powder (activated by treating with hydrochloric acid) was stirred overnight in the same manner. The reaction mixture was filtered through Celite when precipitates were formed and evaporated under reduced pressure. The solid residue thus obtained was passed through a short column of Florisil using chloroform as eluent to remove polar materials. Organocobaloximes thus obtained were recrystallized from benzene or hexane–benzene containing a small amount of pyridine. The organocobaloximes were obtained in 71% (**2a**) to 23% (**2c**) yield from the corresponding bromide.

1a: mp 181.5–185.5 °C dec; ^{1}H NMR ($CDCl_3$) 1.52–1.76 (4 H, m), 2.10 (12 H, s), 3.88–4.12 (2 H, m), 6.65–6.87 (1 H, m), 7.10–7.70 (9 H, m), 8.65 (2 H, d, J = 5.5), 18.20 (2 H, br s); IR ($CHCl_3$) 1607, 1583, 1564, 1451, 1266, 1096 cm^{-1}; UV (EtOH) λ_{max} (log ε) 227 (4.98), 314 (3.90), 328 (3.87), 440 nm (3.04). Anal. Found: C, 56.59; H, 5.89; N, 12.54. Calcd for $C_{26}H_{32}N_5O_5Co$: C, 56.41; H, 5.84; N, 12.65.

1b: mp 164.0–170.5 °C dec; ^{1}H NMR ($CDCl_3$) 0.67–1.87 (6 H, m), 2.05 (12 H, s), 2.95 (2 H, t, J = 7.4), 7.11–8.13 (10 H, m), 8.62 (2 H, d, J = 5.5), 18.14 (2 H, br s); IR ($CHCl_3$) 1604, 1559, 1454, 1088 cm^{-1}; UV (EtOH) λ_{max} (log ε), 225 (5.10), 250 (4.48), 319 (3.80), 448 nm (3.07). Anal. Found: C, 58.90; H, 6.44; N, 12.59. Calcd for $C_{27}H_{34}N_5O_4Co$: C, 58.79; H, 6.23; N, 12.70.

1c: mp 169.5–170.5 °C dec; ^{1}H NMR ($CDCl_3$) 1.32–1.68 (4 H, m), 2.01 (12 H, s), 2.93 (2 H, t, J = 6.8), 7.11–8.03 (9 H, m), 8.37 (1 H, m), 8.54 (2 H, d, J = 5.5), 18.12 (br s); IR ($CHCl_3$) 1681,

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1614, 1566, 1458, 1090 cm^{-1}; UV (EtOH) λ_{max} (log ϵ) 219 (4.95), 247 (4.97), 282 (4.27), 326 (sh, 3.80), 342 (sh, 3.75), 455 nm (4.11). Anal. Found: C, 57.16; H, 5.70; N, 12.37. Calcd for $C_{23}H_{32}N_5O_5Co$: C, 57.35; H, 5.70; N, 12.38.

2a: mp 162.0–166.0 °C dec; ^1H NMR ($CDCl_3$) 1.46–1.68 (4 H, m), 2.10 (12 H, s), 3.89–4.08 (2 H, m), 6.99–7.73 (10 H, m), 8.55 (2 H, d, J = 5.5), 18.24 (2 H, br s); IR ($CHCl_3$) 1631, 1603, 1453, 1090 cm^{-1}; UV (EtOH) λ_{max} (log ϵ) 232 (4.77), 251 (4.48), 294 (4.12), 320 (3.92), 447 nm (3.07). We could not get the satisfactory value of elemental analysis with **2a**, but the sample used for the photolyses was essentially pure from TLC (SiO_2) analysis and the ^1H NMR specrum (supplementary material).

2b: mp 162.5–163.0 °C dec; ^1H NMR ($CDCl_3$) 1.41–1.87 (6 H, m), 1.95 (12 H, s), 2.65 (2 H, t, J = 7.6), 6.96–7.70 (10 H, m), 8.45 (2 H, d, J = 5.5), 18.28 (2 H, br s); IR ($CHCl_3$) 1609, 1560, 1450, 1228, 1085 cm^{-1}; UV (EtOH) λ_{max} (log ϵ) 224 (5.09), 250 (4.57), 271 (4.22), 283 (4.20), 294 (sh, 4.12), 334 (sh, 3.74), 450 nm (3.12). Anal. Found: C, 58.47; H, 6.28; N, 12.41. Calcd for $C_{27}H_{34}N_5O_4Co$: C, 58.79; H, 6.23; N, 12.70.

2c: mp 166.0–167.5 °C dec; ^1H NMR ($CDCl_3$) 1.08–1.73 (4 H, m), 2.06 (12 H, s), 3.15 (2 H, t, J = 6.1), 7.04–8.03 (9 H, m), 8.31 (1 H, m), 8.42 (2 H, d, J = 5.5), 18.30 (2 H, br s); IR ($CHCl_3$) 1673, 1605, 1555, 1448, 1088 cm^{-1}; UV (EtOH) λ_{max} (log ϵ) 218 (4.83), 243 (4.56), 294 (4.11), 448 nm (3.05). Anal. Found: C, 57.66; H, 5.65; N, 12.50. Calcd for $C_{27}H_{32}N_5O_5Co$: C, 57.35; H, 5.70; N, 12.38.

Photolyses of Organocobaloximes. (a) Photolyses in Organic Solvent. One of the organocobaloximes (5.5×10^{-3} mol/L in chloroform and 4.5×10^{-5} mol/L in benzene) was placed in a tube type reaction vessel of Pyrex, and the reaction vessel was capped by a rubber septum. The reaction vessel was dipped in an ultrasonic bath, and the solution was bubbled by argon through a syringe needle to purge dissolved air. The solution of the organocobaloxime was irradiated for 1–2 h with a 450-W high-pressure mercury lamp mounted in a rotary type irradiation apparatus (the distance between the lamp and the reaction vessel was 5 cm). The reaction was monitored by TLC analyses of aliquots, and the irradiation was stopped at disappearance of the starting organocobaloxime. The reaction mixture was condensed and passed through a silica gel column (1.0 (Φ) × 4 cm) eluted by 20 mL of chloroform to separate organic products in the yields of 69–100%. The products, which contained two or more components, were analyzed by gas chromatography, and the ratios recorded in Tables I and II were relative intensities of the gas chromatograms. In the cases of **1a** and **1b**, a large-scale experiment was carried out to isolate the products by using a reaction vessel (150 mL) which was irradiated internally with a 100-W high-pressure mercury lamp through a Pyrex cooling jacket. The products were separated by preparative TLC (SiO_2, 20 × 20 cm) using benzene as an eluent.

(b) Photolyses in Aqueous System. One of the organocobaloximes (6.7×10^{-4} mol/L) in a mixed solution of water and acetonitrile (4:1) was placed in a cylinder type reaction vessel and irradiated in the same manner as described in the part a of this section. The reaction mixture was extracted with ether (20 mL × 5), and the condensate of the ethereal extract was passed through a column of silica gel (1.0 (Φ) × 4.0 cm) with 25 mL of benzene and 5 mL of chloroform. The product mixture thus obtained was analyzed by gas chromatography. The irradiation in the presence of β-cyclodextrin was carried out in the same manner as mentioned above but using the following reaction mixture. Fifteen equivalents of β-cyclodextrin to the organocobaloxime was dissolved in 12 mL of water, and it was added with one of the organocobaloximes in 3 mL of acetonitrile (organocobaloxime: 6.7×10^{-4} mol/L, β-cyclodextrin: 1.0×10^{-2} mol/L). The Pyrex reaction vessel containing the mixture was dipped in an ultrasonic bath and bubbled with argon for 1 h to purge dissolved air and complete the complexation. The mixture was irradiated for 1–3 h in the same manner as described in the part a of this section and extracted with ether (20 mL × 5). In general, the wall of the reaction vessel was deteriorated by covering with insoluble degradation products, and then photolyses did not proceed further. In the case of organocobaloxime **2b**, the yield of the photolysis products was obtained by using an internal standard in gas chromatographic analysis and the value (40%) is much lower than those under other reaction conditions.

Product Identification. Products **3a**,[5] **4a**,[6] **6a**, **7a**,[7] **9a**,[5] **9b**,[8] **9c**,[9] **10a**,[10] **12b**,[11] **13a**,[12] **15a**, and **16a**[7] were identified to the authentic samples, which were prepared in separate methods, by the comparison of MS, NMR, and IR spectra.

Product **3b** (=**17b**),[13] **3c**,[13] **7b** (=**16b**),[13] and **16c**[14] were identified by the comparison of the mass or NMR spectra with those reported.

3b (=**17b**): MS 184 (30, M^+), 155 (23), 153 (13), 142 (50), 141 (100), 128 (34), 115 (31).

3c: MS 198 (18, M^+), 155 (100), 127 (63).

7b (=**16b**): MS 182 (99, M^+), 165 (32), 154 (100), 153 (48), 152 (29), 141 (49), 115 (18).

16c: ^1H NMR ($CDCl_3$) 2.18 (2 H, quint, J = 6.0), 2.79 (2 H, t, J = 6.0), 3.12 (2 H, t, J = 6.0), 7.14–8.00 (5 H, m), 9.41 (1 H, d, J = 8.1); MS 196 (92, M^+), 168 (100), 140 (77), 139 (47).

Structures of products **4b**, **4c**, **5c**, **7c**, **10b**, and **11c** were deduced from MS and ^1H NMR (90 MHz) spectra of the isolated products from the photolyses in organic solvents and discussed in the text. Since the quantity of the isolated products was limited, only MS and FT-NMR spectra were analyzed.

4b: ^1H NMR ($CDCl_3$) 2.26–2.61 (2 H, m), 2.67–3.01 (2 H, m), 4.76–5.15 (2 H, m), 5.48–6.13 (1 H, m), 7.03–7.79 (7 H, m); MS 182 (M^+, 59), 142 (41), 141 (100), 115 (77).

4c: ^1H NMR ($CDCl_3$) 3.89 (2 H, dt, J = 6.6 and 1.3), 4.97–5.12 (1 H, m), 5.33 (1 H, dt, J = 2.4 and 1.3), 5.74–6.62 (1 H, m), 7.33–7.61 (2 H, m), 7.61–7.99 (4 H, m), 8.40 (1 H, d, J = 0.9).

5c: ^1H NMR ($CDCl_3$) 2.05 (3 H, d, J = 5.3), 7.00–7.14 (2 H, m), 7.46–7.72 (2 H, m), 7.72–8.09 (4 H, m), 8.44 (1 H, d, J = 0.7); MS 196 (M^+, 55), 195 (12), 181 (21), 155 (99), 127 (100).

7c: ^1H NMR ($CDCl_3$) 2.30 (2 H, quint, J = 6.0), 2.75 (2 H, t, J = 6.0), 3.39 (2 H, t, J = 6.0), 7.43–7.97 (4 H, m), 8.00–8.23 (2 H, m); MS 196 (M^+, 93), 168 (86), 140 (100), 139 (60).

10b: ^1H NMR (CCl_4) 2.29–2.78 (2 H, m), 3.03–3.29 (2 H, m), 4.85–5.22 (2 H, m), 5.61–6.26 (1 H, m), 7.23–8.05 (7H, m); MS 182 (M^+, 11), 142 (12), 141 (100), 115 (38).

11c: ^1H NMR ($CDCl_3$) 1.97 (3 H, d, J = 5.9), 6.49–7.10 (2 H, m), 7.33–7.70 (4 H, m), 7.70–8.00 (2 H, m), 8.08–8.29 (1 H, m); MS 196 (M^+, 75), 195 (22), 181 (69), 168 (12), 167 (12), 155 (91), 153 (23), 127 (100).

Products **5a**, **8a**, **11b**, **14a**, and **17a** could not be isolated in pure state and were deduced only from mass spectra as discussed in the text.

5a: MS 184 (100, M^+), 183 (10), 169 (12), 156 (11), 152 (10), 141 (22), 128 (71), 115 (11).

8a: MS 184 (100, M^+), 156 (61), 147 (13), 146 (18), 141 (15), 133 (45), 128 (63), 115 (18).

11b: MS 182 (88, M^+), 181 (45), 167 (71), 166 (100), 165 (83), 154 (53), 153 (44), 152 (48), 141 (24), 115 (11).

14a: MS 184 (100, M^+), 169 (31), 167 (15), 166 (8), 165 (32), 157 (31), 153 (21), 152 (21), 141 (26).

17a: MS 186 (35, M^+), 167 (12), 155 (11), 153 (35), 142 (74), 141 (100).

Synthesis of 1-Methyl-2,3-dihydrophenalene (12b) as an Authentic Sample. 2,3-Dihydrophenalen-1-one (86 mg) in 1 mL of ether was added to methyl magnesium iodide in ether (0.5 mL). Conventional workup and chromatography on silica gel (1.6 (Φ) × 7.5 cm) eluted with benzene gave 1-methyl-2,3-dihydrophenalen-1-ol (40 mg, 43%). The product was subjected to hydrogenolysis on Pd/C in ethanol–acetic acid (10:1), 4 days at room temperature, to give 1-methyl-2,3-dihydrophenalene.[10]

^1H NMR ($CDCl_3$) (400 MHz): 1.40 (3 H, d, J = 8.0), 1.82–1.90 (1 H, m), 2.08–2.15 (1 H, m), 3.04–3.11 (1 H, m), 3.16–3.24 (2 H, m), 7.22–7.42 (4 H, m), 7.67 (2 H, d, J = 8.0); MS 182 (88, M^+), 181 (33), 167 (100), 166 (47), 165 (79), 154 (45), 153 (50), 152 (58), 141 (20).

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Supplementary Material Available: NMR spectra of title compounds (12 pages). Ordering information is given on any current masthead page.