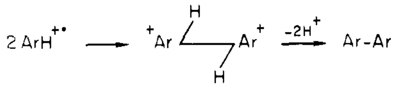
added $AlCl_3$ or Me_4NCl.

It will be noted from the above that for a given arene, the conditions under which the reaction

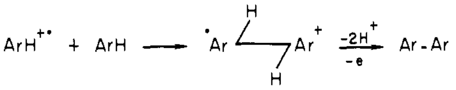
$$\mathrm{ArH} + {}^{1}/_{3}\mathrm{SbCl_3} \rightarrow \mathrm{ArH}^{+}\cdot + {}^{1}/_{3}\mathrm{Sb} + \mathrm{Cl}^{-} \qquad (2)$$

occurs are the same as those under which the self-protonation reactions typified by eq 1 occur. These results, including the isolation of stoichiometric quantities of Sb metal, suggest that the arene radical cation is an important reactive intermediate. Thus, the strong protonic acid responsible for self-protonation may have been derived from the coupling of radical cations[21] as in reaction



$$2\,\mathrm{ArH}^{+\bullet} \longrightarrow {}^{+}\mathrm{Ar}(\mathrm{H})\text{–}(\mathrm{H})\mathrm{Ar}^{+} \xrightarrow{-2\mathrm{H}^{+}} \mathrm{Ar{-}Ar} \qquad (3)$$

3 or from the electrophilic attack of radical cations on yet unreacted arene molecules as in reaction 4.[21]



$$\mathrm{ArH}^{+\bullet} + \mathrm{ArH} \longrightarrow {}^{\bullet}\mathrm{Ar}(\mathrm{H})\text{–}(\mathrm{H})\mathrm{Ar}^{+} \xrightarrow[-e]{-2\mathrm{H}^{+}} \mathrm{Ar{-}Ar} \qquad (4)$$

We have described an unusual arene self-protonation reaction which takes place in an aprotic $SbCl_3$–$AlCl_3$ melt and which is driven by the stoichiometric reduction of $SbCl_3$ to Sb metal. In addition we have presented evidence that the reaction begins with the oxidation of the arene to its radical cation by the solvent, $SbCl_3$, and that the role of the $AlCl_3$ is to enhance the oxidizing power of the $SbCl_3$.

Acknowledgments. We appreciate the assistance of L. L. Brown with the NMR measurements, M. V. Buchanan with the mass spectroscopy measurements, H. L. Yakel with the X-ray diffraction study, and L. O. Gilpatrick with the product separations and identifications. We also appreciate valuable discussions with M. L. Poutsma and J. Brynestad. This research was sponsored by the Office of Basic Energy Sciences, U.S. Department of Energy, under Contract W-7405-eng-26 with the Union Carbide Corp.

---

(21) Wen, Long-Sing; Kovacic, P. *Tetrahedron* **1978**, *34*, 2723, and references cited therein.

Redox-Photosensitized Reactions. 5.[1] Redox-Photosensitized Ring Cleavage of 1,1a,2,2a-Tetrahydro-7*H*-cyclobut[*a*]indene Derivatives: Mechanism and Structure–Reactivity Relationship

Tetsuro Majima, Chyongjin Pac,* and Hiroshi Sakurai

Contribution from The Institute of Scientific and Industrial Research, Osaka University, Suita, Osaka 565, Japan.

Received December 7, 1979

Abstract: The mechanistic aspects of the redox-photosensitized chain cycloreversion of *trans,syn*-indene dimer **1** have been investigated in detail. The π complex of **1** with the cation radical of phenanthrene (and selected other aromatic hydrocarbons) that is generated by photochemical electron transfer with *p*-dicyanobenzene has been shown to be a key intermediate by way of which the cycloreversion of **1** rapidly occurs without the formation of its cation radical; the rate constant for the cycloreversion has been determined to be $1 \times 10^{9}\ \mathrm{s}^{-1}$. Redox photosensitization has been applied to the other related compounds and it has been found that the cyclobutanes which can undergo redox-photosensitized ring cleavage possess the phenyl group at C_2. The importance of through-bond interactions between the two π-electron systems is discussed.

Introduction

Electron transfer is an important photochemical process of exciplex formation systems in polar solvents;[2,3] the chemistry of photogenerated ion radicals has now received considerable attention.[4-7] In a previous paper,[8] we reported that in aromatic hydrocarbon (S)–*p*-dicyanobenzene (DCNB)–acetonitrile systems a novel type of photosensitization occurs which causes ionic reactions of furan and olefins (D). We now call this photosensitization redox photosensitization, since the initiation process is the photochemical electron transfer (photoredox) reaction from S to DCNB[8-10] and since an important intermediate is the cation radical of S ($S^{+}\cdot$) which may act as a redox carrier. The final products would be interpreted to arise from the cation radical of D. However, the redox-photosensitized reactions can occur even in cases where complete hole transfer from $S^{+}\cdot$ to D which gives the cation radical of D is substantially endothermic. Therefore, we assumed the intervention of a π complex formed between $S^{+}\cdot$ and D as a key intermediate.[8]

Thus, redox photosensitization is closely related to the chemical nature of photogenerated $S^{+}\cdot$ and has been applied to other re-

---

(1) Part 4: T. Majima, C. Pac, J. Kubo, and H. Sakurai, *Tetrahedron Lett.*, 377 (1980).

(2) A. Weller, *Pure Appl. Chem.*, **16**, 115 (1968).

(3) M. Ottolenghi, *Acc. Chem. Res.*, **6**, 153 (1973); P. Froelich and E. L. Wehry in "Modern Fluorescence Spectroscopy", Vol. 2, E. L. Wehry, Ed., Plenum Press, New York, 1976, pp 381–6.

(4) C. Pac and H. Sakurai, *Tetrahedron Lett.*, 3829 (1969); K. Mizuno, C. Pac, and H. Sakurai, *J. Chem. Soc., Chem. Commun.*, 553 (1975); K. Mizuno, H. Okamoto, C. Pac, and H. Sakurai, *ibid.*, 839 (1975).

(5) R. A. Neunteufel and D. R. Arnold, *J. Am. Chem. Soc.*, **95**, 4080 (1973); D. R. Arnold and A. J. Maroulis, *ibid.*, **99**, 7355 (1977), and references cited therein.

(6) J. A. Barltrop, *Pure Appl. Chem.*, **33**, 179 (1973).

(7) A. Ledwith, *Acc. Chem. Res.*, **5**, 133 (1972); S. Farid, S. H. Hartman, and T. R. Evans in "The Exciplex", M. Gordon and W. R. Ware, Eds., Academic Press, New York, 1975, p 327; T. R. Evans, R. Wake, and O. Jaeckie, *ibid.*, p 345; K. Mizuno, R. Kaji, H. Okada, and Y. Otsuji, *J. Chem. Soc., Chem. Commun.*, 594 (1978).

(8) C. Pac, A. Nakasone, and H. Sakurai, *J. Am. Chem. Soc.*, **99**, 5806 (1977).

(9) T. Asanuma, T. Gotoh, A. Tsuchida, M. Yamamoto, and Y. Nishijima, *J. Chem. Soc., Chem. Commun.*, 485 (1977).

(10) S. Tazuke and N. Kitamura, *J. Chem. Soc., Chem. Commun.*, 515 (1977).

0002-7863/80/1502-5265$01.00/0

Table I. Dependence of Quantum Yields (ϕ_{IN}) on Concentration of 1 and Light Intensity[a]

	10^3[**1**], M									
light intensity[b]	10	12	16	20	30	34	60	100	∞[c]	10^{-3}(slope),[d] M
2.74×10^{-8}	3.64	3.92	4.69	4.98	6.02	6.04	6.25	7.25		
1.1×10^{-7}	3.68	4.02	4.63	5.03	5.75	5.90	6.33	6.33	8.2	1.54
6.4×10^{-7}	3.60	3.89	4.17	4.81	5.92	6.09	6.58	6.85		

[a] Degassed dry acetonitrile solution; [P] = 0.01 M and [DCNB] = 0.1 M; at 313 nm. [b] Einstein/min. [c] Extrapolated value (ϕ_{IN}^{∞}); see text and Figure 1. [d] Slope of the linear plot in Figure 1.

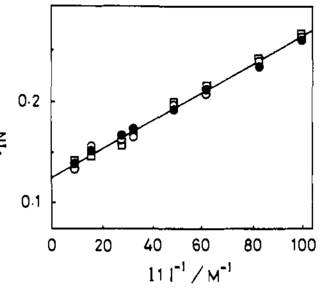
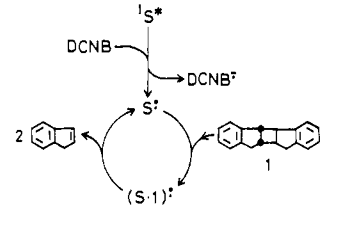


Figure 1. Least-squares plots of ϕ_{IN}^{-1} vs. $[\mathbf{1}]^{-1}$ for 313-nm irradiation: (○) 2.7×10^{-8} einstein/min; (●) 1.2×10^{-7} einstein/min; (□) 6.4×10^{-7} einstein/min. See footnotes in Table I.

actions.[11,12] We have found that redox photosensitization effects the cycloreversion of indene cyclobutane dimers.[13] The suggested mechanism involves catalysis by $S^{+}\cdot$ via a π complex which leads to cleavage of the cyclobutane ring without the formation of the discrete cation radical of the cyclobutanes. Thus, the redox-photosensitized cycloreversion of indene dimers is a novel type of reaction without precedent, being mechanistically different from ring cleavage via the cation radical of cyclobutane compounds.[14-16]



In the present investigation, we have carried out extensive kinetic studies to unveil the mechanism for the redox-photosensitized cycloreversion of *trans*,*syn*-indene dimer **1**; the intermediacy of a π complex [$(S\cdot\mathbf{1})^{+}\cdot$] is strongly suggested. Moreover, redox photosensitization has been applied to 1,1a,2,2a-tetrahydro-7*H*-cyclobut[*a*]indene derivatives **1**–**12** to establish the structure-reactivity relationship in redox-photosensitized ring cleavage.

Results

Preparation of Cyclobutane Compounds. All the cyclobutane compounds were prepared by known methods; the synthetic routes are delineated in Scheme I. The spectral properties of **1**–**12** are in accord with the structures. The endo configuration of the hydroxyl group of **4**, **5**, and **8** was deduced from the well-known fact that hydride reduction[17] and Grignard reactions[18] of bicyclic ketones usually occur by dominant attack of reagents to the sterically less hindered side. Irradiation of a benzene solution containing *trans*-β-nitrostyrene and indene gave **6** in good yield in a manner similar to the photocycloaddition of *trans*-β-nitrostyrene to styrene.[19] The endo location of the phenyl group of **6** and **7** was indicated from NMR spectra; one of aromatic protons shows a signal at an unusually high field.

Table II. Dependence of Quantum Yields (ϕ_{IN}) on Concentration of Phenanthrene[a]

		ϕ_{IN}	
	[P], M	dry soln[b]	wet soln[c]
	0.10	2.41	2.36
	0.09	2.65	
	0.08		2.64
	0.072	2.90	
	0.06	3.67	3.30
	0.045	4.17	
	0.04		3.98
	0.03	4.90	
	0.02	6.25	4.83
	0.01	6.85	5.81
	0.00[d]	9.4	7.6
slope,[e] M^{-1}		3.06	3.02

[a] Degassed acetonitrile solution; [1] = 0.05 M and [DCNB] = 0.1 M; at 313 nm. [b] See Experimental Section. [c] A drop of water was added into 1000 mL of dry acetonitrile. [d] Extrapolated values. [e] Slope of the linear plot in Figure 2.

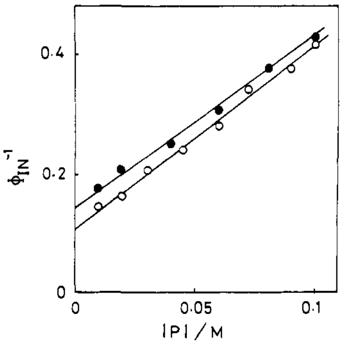


Figure 2. Least-squares plots of ϕ_{IN}^{-1} vs. [P]: (○) dry solutions; (●) wet solutions. See footnotes in Table II.

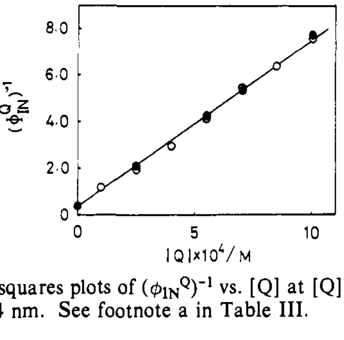


Figure 3. Least-squares plots of $(\phi_{IN}^{Q})^{-1}$ vs. [Q] at [Q] $\leq 10^{-3}$ M: (○) 313 nm; (●) 334 nm. See footnote a in Table III.

Quantum Yield for Indene Formation in Redox-Photosensitized Cycloreversion of 1. For mechanistic investigation, the cycloreversion of *trans*,*syn*-cyclobuta[*a*]diindene **1** using phenanthrene (P) as S was employed as the typical reaction. Irradiation of a dry acetonitrile solution containing P, DCNB, and **1** at 313 nm

---

(11) T. Majima, C. Pac, and H. Sakurai, *Chem. Lett.*, 1133 (1979).

(12) S. Tazuke and N. Kitamura, *Nature (London)*, **275**, 301 (1978).

(13) T. Majima, C. Pac, A. Nakasone, and H. Sakurai, *J. Chem. Soc., Chem. Commun.*, 490 (1978).

(14) P. Bersford, M. C. Lambert, and A. Ledwith, *J. Chem. Soc. C*, 2508 (1970).

(15) A. A. Lamola, *Mol. Photochem.*, 107 (1972).

(16) S. Takamuku and W. Schnabel, private communication.

(17) H. C. Brown and H. D. Deck, *J. Am. Chem. Soc.*, **87**, 5620 (1965).

(18) E. C. Ashby and J. T. Laemmile, *Chem. Rev.*, **75**, 521 (1975).

(19) O. L. Chapman, A. A. Griswald, E. Hoganson, G. Lenz, and J. Reasoner, *Pure Appl. Chem.*, **9**, 585 (1964).

Table III. Dependence of Observed and Calculated Quantum Yields (ϕ_{IN}^{Q}) on Concentration of *p*-Dimethoxybenzene (Q)[a]

$10^2 \times$ [Q], M	ϕ_{IN}^{Q} 334 nm	ϕ_{IN}^{Q} 313 nm	$1/\phi_{IN}^{Q}$ obsd	$1/\phi_{IN}^{Q}$ calcd[b] $\alpha = 0.1$	$\alpha = 0.2$	$\alpha = 0.3$
0.000	3.60	3.62	0.276	0.276	0.276	0.276
0.010		0.89	1.12	1.01	1.01	1.01
0.025	0.51	0.53	1.90	2.11	2.11	2.11
0.040		0.35	2.88	3.22	3.21	3.22
0.055	0.24	0.24_5	4.08	4.33	4.32	4.34
0.070		0.18	5.53	5.43	5.42	5.45
0.085	0.15_5	0.15_6	6.39	6.54	6.54	6.58
0.10	0.130	0.13_3	7.50	7.06	7.65	7.70
0.40		0.32_4	30.9	30.2	30.6	31.2
0.50	0.030					
0.80		0.016	62.2	61.1	63.1	65.32
1.00	0.013					
1.10		0.011_5	87.0	85.2	88.9	93.0
1.30	0.010					
1.40		0.0086	116.1	109.8	115.9	122.5
1.60	0.0078					
1.70		0.0070	143.0	134.6	144.2	153.8
1.80	0.0066					
2.00	0.0056	0.0057	176	161.1	173.7	186.9

[a] Degassed dry acetonitrile solution; [1] = 0.01 M, [P] = 0.01 M, and [DCNB] = 0.1 M. [b] Calculated from eq 21; see text.

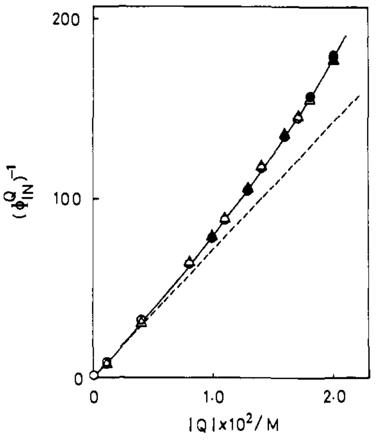


Figure 4. Plots of $(\phi_{IN}^{Q})^{-1}$ vs. [Q] at [Q] ≥ 10^{-3} M: (○) 313 nm; (●) 334 nm; (△) calculated values with $\alpha = 0.2$. See footnotes in Table III.

gave indene (IN) as the only detectable product in 75–80% isolated yield (based on formation of 2 mol of IN/mol of **1** used). On the other hand, P and DCNB were recovered in 85 and 90% yields, respectively. In the absence of either P or DCNB, no photoreaction occurred.

The formation of IN increased linearly with irradiation time up to ca. 8% conversion. Quantum yields for indene formation (ϕ_{IN}) were determined at less than 3% conversion (Table I). A plot of ϕ_{IN}^{-1} vs. the reciprocal of [**1**] is linear and independent of the intensity of the incident light at 313 nm (Figure 1). It was found that ϕ_{IN} depends on both concentration of P and dryness of solution, as shown in Table II and Figure 2.

Quenching by Cation Radical Quenchers. The redox-photosensitized cycloreversion of **1** was quenched by *p*-dimethoxybenzene (Q) (Table III). The Stern–Volmer plot was linear up to ca. 10^{-3} M Q (Figure 3). At higher concentrations of Q, however, the plot deviates from linearity (Figure 4). It was found that the end absorption of DCNB (0.1 M) shifted very slightly to longer wavelength in the presence of relatively high concentrations of Q, while the absorption of P was identical with that in the absence of Q. A CT complex is perhaps formed between Q and DCNB in the ground state. The deviation from linearity at higher concentrations of Q would arise from the absorption of the incident light at 313 nm by the CT complex. Even at the maximum concentration of Q used (2×10^{-2} M), however, the absorbance of the CT complex at 313 nm is only 0.1% that of P.

Table IV. Slopes in the Linear Region of Stern-Volmer Plots in the Quenching by Various Quenchers[a]

quencher	$E_{1/2}^{Ox}$, V	$10^3 K_{SV}$, M^{-1}
p-dimethoxybenzene	0.90	7.11
m-dimethoxybenzene	1.01	6.34
p-methylanisole	1.11	1.27
o-methylanisole	1.20	0.80
triethylamine	0.37	6.10

[a] Degassed dry acetonitrile solution; [1] = 0.01 M, [P] = 0.01 M, and [DCNB] = 0.1 M; at 313 nm.

Table V. Intercepts and Slopes of Linear Plots of ϕ_{IN}^{-1} vs. $[1]^{-1}$ for Various Aromatic Hydrocarbons (S)[a]

S	$E_{1/2}^{Ox}$(S), V	$10^{-3} \times$ (slope), M	intercept	ϕ_{IN}^{∞}
triphenylene (TR)	1.29	1.32	0.110	9.1
naphthalene (NT)	1.22	1.47	0.116	8.5
phenanthrene (P)	1.17	1.54	0.112	8.2
1,4-dimethylnaphthalene	1.10	171	2.00	0.50
1,2-dimethylnaphthalene	1.06	184	3.23	0.31
chrysene (CR)	1.05	90.0	1.41	0.71
1,3-dimethylnaphthalene	1.02	163	3.70	0.27
2,3-dimethylnaphthalene	0.99	203	3.76	0.27
pyrene (PR)	0.78	*b*	*b*	0.00[b]
anthracene (AN)	0.75	*b*	*b*	0.00[b]

[a] Degassed dry acetonitrile solution; [S] = 0.01 M and [DCNB] = 0.1 M; at 313 nm; see text. [b] Lack of ring cleavage.

Moreover, an identically curved Stern–Volmer plot was again obtained at 334 nm, where the absorbance of the CT complex is absent (Table II). It was confirmed that the fluorescence of P is not quenched even by 0.1 M Q. Thus, the curved plot clearly arises from the quenching of reaction intermediates by Q. With the other quenchers, linear Stern–Volmer plots were obtained at relatively low concentrations of the quenchers, where no CT absorption was observed. Table IV lists the slopes of the plots together with the oxidation potentials of the quenchers.

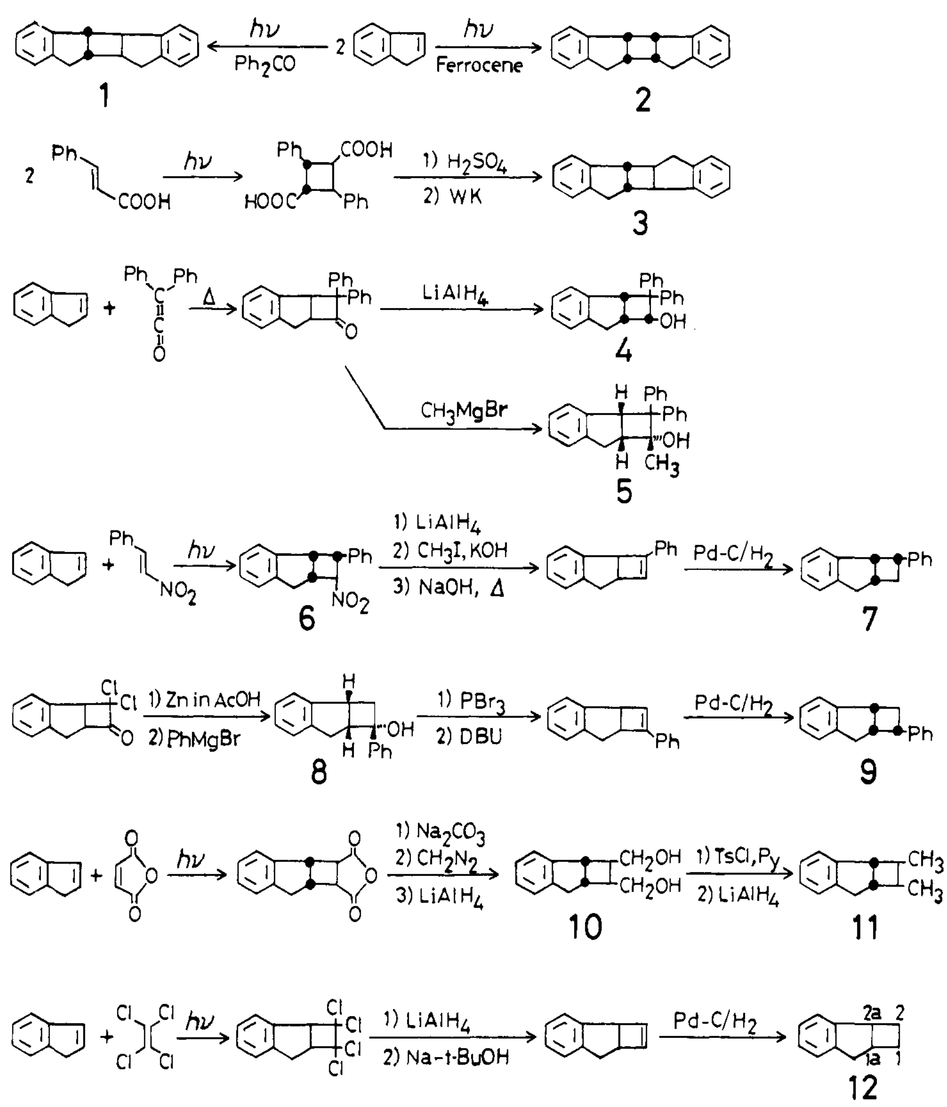
Redox-Photosensitized Cycloreversion of 1 with Other Aromatic Hydrocarbons. Photosensitized cycloreversion of **1** occurred with triphenylene (TR), naphthalene (NT), chrysene (CR), and dimethylnaphthalenes but not with pyrene (PR) and anthracene (AN). ϕ_{IN} was determined for TR, NT, CR, and the dimethylnaphthalenes; a plot of ϕ_{IN}^{-1} vs. $[1]^{-1}$ for each was linear. Table V lists the intercepts and slopes of the plots and ϕ_{IN}^{∞} together with the oxidation potentials of S.

Redox-Photosensitized Cycloreversion of Other Cyclobutane Compounds. Cyclobutanes **2**, **4**, **5**, and **7** (Scheme II) were the reactive compounds among those investigated. The cycloreversion of cis,syn dimer **2** occurred more efficiently than that of **1**, giving IN in 85% isolated yield. In the case of **7**, IN and styrene were formed in a 1:1 ratio; other products could not be detected. The photosensitized ring cleavage of **4** and **5** gave IN along with diphenylacetaldehyde and 1,1-diphenylacetone, respectively; the carbonyl compounds are evidently formed by the keto–enol rearrangement of the corresponding enols which are initially formed by ring cleavage. However, the formation of the carbonyl compounds was much less than that of IN, even at low conversions. It was confirmed that the carbonyl compounds are relatively stable upon irradiation in the presence of P and DCNB at 313 nm. Therefore, unreclaimed reactions appear to consume the enols; other product could not be detected by GLC. In contrast, the other cyclobutanes are entirely unreactive; irradiation for a long time resulted only in the complete recovery of the starting materials. The results are summarized in Table VI.

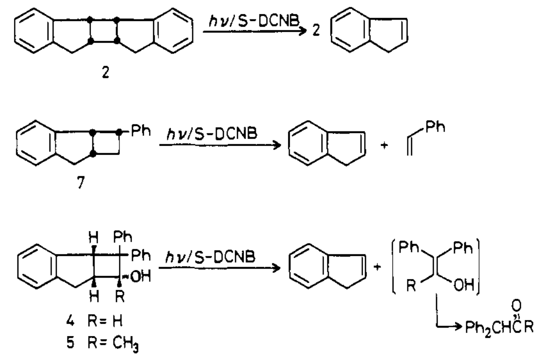
Discussion

Mechanism of Redox-Photosensitized Cycloreversion of 1. The fluorescence of each S was not appreciably quenched by cyclo-

Scheme I



Scheme II



butanes **1**–**12**. Moreover, cycloreversion of **1** was not sensitized by such typical triplet photosensitizers as benzophenone and acetophenone, whose triplet excitation energies are higher than those of S. Therefore, neither triplet excitation transfer nor singlet exciplex mechanisms can be accepted as the mechanism of the redox photosensitization. It was confirmed that no CT complex was formed between each cyclobutane and DCNB or S in the ground state, as shown by UV spectroscopic measurements.

As has been discussed in a previous paper,[8] electron transfer from the excited singlet state of S ($^1S^*$) to DCNB is responsible for the initiation process, giving the cation radical of S ($S^{+}\cdot$) and the anion radical of DCNB ($DCNB^{-}\cdot$). Since ϕ_{IN}^{∞} decreases with a decrease of the oxidation potential of S (Table III), $S^{+}\cdot$ is perhaps a reactive species for the cycloreversion. This is strongly supported by the observation that the cycloreversion of **1** is quenched by the compounds possessing low oxidation potentials.

Table VI. Redox-Photosensitized Ring Cleavage of 1–12 and Limiting Quantum Yields (ϕ_{IN}^{∞})[a]

cyclobutane	$E_{1/2}^{Ox}$, V	S^b TP	NT	P	CR
1	1.32	9.1	8.5	8.2	0.71
2	1.32	12.1	11.8	11.3	0.92
3	1.49	×	×	×	×
4	1.43	ND[c]	ND[c]	0.19	×
5	1.41	0.20	ND[c]	0.12	×
6	1.70	×	×	×	×
7	1.44	0.08	0.047	0.033	×
8	1.50	×	×	×	×
9	1.58	×	×	×	×
10	1.60	×	×	×	×
11	1.69	×	×	×	×
12	1.73	×	×	×	×

[a] Extrapolated values from linear plots of ϕ_{IN}^{-1} vs. reciprocals of concentration of the cyclobutanes; [S] = 0.01 M and [DCNB] = 0.1 M; at 313 nm. The cross mark indicates a lack of ring cleavage. [b] See abbreviations in Table V. [c] Ring cleavage occurred but the values were not determined.

It has been reported that some cyclobutane compounds undergo the ring-cleavage reaction via the cation radicals.[14-16] Therefore,

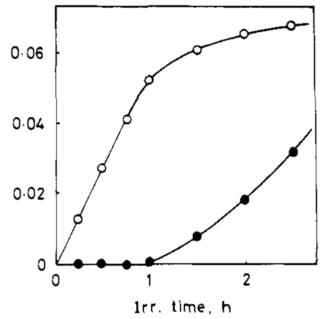


Figure 5. Formation of indene (○) and 2-methoxyindan (MI) (●) vs. irradiation time. Degassed 3:1 acetonitrile–methanol solutions; 313-nm irradiation; [**1**] = 0.05 M, [P] = 0.01 M, and [DCNB] = 0.1 M.

complete hole transfer from $S^{+\cdot}$ to **1** would occur to give the cation radical of **1**, which subsequently undergoes the cycloreversion, i.e., $S^{+\cdot} + \mathbf{1} \rightarrow S + \mathbf{1}^{+\cdot} \rightarrow S + IN + IN^{+\cdot}$. If this were the case, irradiation in the presence of methanol would yield 2-methoxyindan as an initial product, since the anti-Markovnikov photoaddition of methanol to phenyl-substituted olefins via the cation radicals is known.[5] In fact, we confirmed that 2-methoxyindan is formed upon irradiation of a 10:1 acetonitrile–methanol solution containing IN and 1-cyanonaphthalene.[20] However, when the redox-photosensitized cycloreversion was carried out in 3:1 acetonitrile–methanol, only IN was formed as the initial product at low conversion (Figure 5). On the other hand, 2-methoxyindan was formed only when IN was accumulated to a significant extent. This clearly demonstrates that 2-methoxyindan is a secondary product from the redox-photosensitized addition of methanol to initially formed IN.[8] Moreover, methanol adducts of **1** or related compounds could not be detected. The results require that the redox-photosensitized cycloreversion must occur by means of a mechanism which involves neither the cation radical of **1** nor IN. In this regard, it should be pointed out that the oxidation potential of P is considerably lower than that of **1**; complete hole transfer from $P^{+\cdot}$ to **1** is endothermic, thus being unlikely for the occurrence of the efficient (chain) cycloreversion.

The possible mechanistic pathways that interpret reasonably the results obtained are shown in Scheme III. A key mechanistic pathway is the catalytic cycloreversion of **1** by $S^{+\cdot}$ via π complex $(S\cdot\mathbf{1})^{+\cdot}$; this results in the formation of two neutral indene molecules and the recovery of $S^{+\cdot}$ without complete hole transfer. This mechanism is supported by the curved Stern–Volmer plot in Figure 4 that demonstrates the existence of two different cation radical species as reaction intermediates, i.e., $S^{+\cdot}$ and the π complex. The formation of the π complex is not surprising, since it has been reported that the cation radical of methylated benzenes forms π complexes with neutral molecules of other methylated benzenes in the vapor phase.[21] The π complex may collapse into S and/or other products as a chain-termination process. The formation of dimer cation radical $S_2^{+\cdot}$ should be taken into account as another chain-termination process, since ϕ_{IN} decreases with an increase of concentration of S; the dimer cation radical of pyrene is known to be formed.[22]

In the presence of Q, hole transfer from either $S^{+\cdot}$ or $(S\cdot\mathbf{1})^{+\cdot}$ to Q should be considered as the quenching processes, since the oxidation potential of Q is relatively low. The cation radical intermediates are also quenched by impurities involving water. However, this process appears to be of minor importance, since their concentration is probably very low. Charge neutralization between the cation radicals and $DCNB^{-\cdot}$ is not important, since ϕ_{IN} is independent of the light intensity. The complete quenching of the fluorescence of S by 0.1 M DCNB indicates that the unimolecular decay processes from $^1S^*$ can be neglected.

Scheme III

$$S \xrightarrow{h\nu} {}^1S^* \tag{1}$$

$${}^1S^* \xrightarrow{1/\tau} S \tag{2}$$

$${}^1S^* + DCNB \xrightarrow{\alpha} S^{+\cdot} + DCNB^{-\cdot} \tag{3}$$

$${}^1S^* + DCNB \xrightarrow{1-\alpha} S + DCNB \tag{4}$$

$$S^{+\cdot} + \mathbf{1} \xrightarrow{k_c} (S\cdot\mathbf{1})^{+\cdot} \equiv C^{+\cdot} \tag{5}$$

$$S^{+\cdot} + S \xrightarrow{k_s} S_2^{+\cdot} \tag{6}$$

$$C^{+\cdot} \xrightarrow{k_r^c} S^{+\cdot} + 2IN \tag{7}$$

$$C^{+\cdot} \xrightarrow{k_d^c} S \text{ and/or others} \tag{8}$$

$$C^{+\cdot} + S \xrightarrow{k_s^c} S_2^{+\cdot} + \mathbf{1} \tag{9}$$

$$S^{+\cdot} + Q \xrightarrow{k_q} S + Q^{+\cdot} \tag{10}$$

$$C^{+\cdot} + Q \xrightarrow{k_q^c} S + \mathbf{1} + Q^{+\cdot} \tag{11}$$

$$S^{+\cdot} + X \xrightarrow{k_x} S \text{ and/or others} \tag{12}$$

$$C^{+\cdot} + X \xrightarrow{k_x^c} S + \mathbf{1} \text{ and/or others} \tag{13}$$

$$S_2^{+\cdot} + Q \rightarrow 2S + Q^{+\cdot} \tag{14}$$

$$S_2^{+\cdot} + X \rightarrow 2S \text{ and/or others} \tag{15}$$

$$X = DCNB^{-\cdot},\ H_2O, \text{ and impurities}$$

Analysis of Kinetics. In the absence of Q, steady-state analysis gives eq 16 and 17, where α represents the limiting quantum yield

$$\frac{1}{\phi_{IN}} = \frac{1}{2\alpha}\left(\frac{k_s^c[S] + k_d^c}{k_r^c}\right)\left(1 + \frac{k_s[S]}{\beta k_c[\mathbf{1}]}\right) \tag{16}$$

$$\beta = \frac{k_s^c[S] + k_d^c}{k_r^c + k_s^c[S] + k_d^c}$$

$$[S] = 0.01\ M$$

$$\frac{1}{\phi_{IN}} = \left(\frac{1}{2\alpha}\right)\left(\frac{k_d^c}{k_r^c}\right)\left[1 + \left\{\frac{k_s^c}{k_d^c} + \frac{(k_r^c + k_d^c)k_s}{k_d^c k_c[\mathbf{1}]}\right\}[S]\right] \tag{17}$$

$$[\mathbf{1}] = 0.05\ M$$

for $S^{+\cdot}$ formation. In eq 16 it has been assumed that $(k_s^c[S] + k_d^c) \gg k_x^c[X]$ and $k_s[S] \gg k_x[X]$. In eq 17 $[S]^2$ has been neglected since a plot of ϕ_{IN}^{-1} vs. [P] is linear. From the intercepts and slopes in Figures 1 and 2, the rate ratios in eq 18–20 are obtained.

$$\alpha k_r^c/k_d^c = 4.72 \tag{18}$$

$$k_s/\beta k_c = 1.26 \tag{19}$$

$$k_d^c/k_s^c = 6.6 \times 10^{-2} \tag{20}$$

In the presence of Q, the Stern–Volmer equation can be represented by eq 21, where [S] = 0.01 M. In this equation it has

$$\frac{1}{\phi_{IN}^{Q}} = \frac{1}{\phi_{IN}} + \frac{k_q[Q]}{2\alpha k_r^c}\left(1 + \frac{k_r^c + k_d^c + k_s^c[S] + k_s[S]}{k_c[\mathbf{1}]} + \frac{k_q[Q]}{k_c[\mathbf{1}]}\right) \tag{21}$$

---

(20) M. Yasuda, C. Pac, and H. Sakurai, *Bull. Chem. Soc. Jpn.*, **53**, 502 (1980).

(21) M. Meot-Ner, E. P. Hunter, and F. H. Field, *J. Am. Chem. Soc.*, **100**, 5466 (1978).

(22) M. A. J. Rodgers, *Chem. Phys. Lett.*, **9**, 107 (1971); A. Kira, S. Arai, and M. Imamura, *J. Chem. Phys.*, **54**, 4890 (1971).

Table VII. Dependence of Quantum Yields ($\phi_{IN}{}^{Q}$) on Concentration of either **1** or *p*-Dimethoxybenzene (Q)[a]

	10^4[Q], M	10^2[**1**], M 1.3	1.8	3.0	5.0	10.0
	0.0	4.15	4.81	5.75	6.58	7.14
	1.5	1.00	1.35	2.43	2.77	7.55
	3.0	0.48	0.55	1.21	1.67	3.44
	4.5	0.38	0.41	0.76	1.21	2.43
	6.0	0.28	0.30	0.61	1.08	2.02
	8.0	0.20	0.26	0.43	0.81	1.96
	10.0	0.17	0.19	0.37	0.63	1.41
$10^{-3}K_{SV}$,[b] M^{-1}		5.76	4.81	2.54	1.36	0.53

[a] See footnotes in Table I. [b] Slopes of linear Stern–Volmer plots.

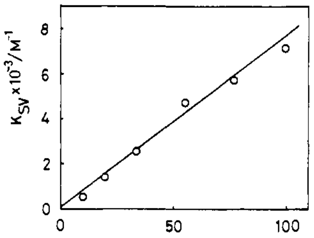


Figure 6. Least-squares plot of K_{SV} vs. $[1]^{-1}$. The slope and intercept are 72.8 and 24.53 M^{-1}, respectively.

been assumed that $k_q \simeq k_q{}^c$ (vide infra). The slope (K_{SV}) in the linear region of the plot of $(\phi_{IN}{}^{Q})^{-1}$ vs. [Q] should depend on the concentration of **1**, as is represented by eq 22.

$$K_{SV} = \frac{k_q}{2\alpha k_r{}^c}\left(1 + \frac{k_r{}^c + k_d{}^c + k_s{}^c[S] + k_s[S]}{k_c[1]}\right) \quad (22)$$

As in Figure 3, linear Stern–Volmer plots at several points of concentration of **1** were obtained; the slopes (K_{SV}) are listed in Table VII. The plot of K_{SV} vs. $[1]^{-1}$ is linear, as shown in Figure 6; the intercept and slope give the rate ratios in eq 23 and 24.

$$k_q/2\alpha k_r{}^c = 24.53 \quad (23)$$

$$(k_r{}^c + k_d{}^c + k_s{}^c[S] + k_s[S])/k_c = 2.97 \quad (24)$$

Hole transfer from the cation radical of P to Q probably occurs at a diffusion-controlled rate since this process is exothermic by 6.2 kcal/mol (0.27 eV). In regard to $k_q{}^c$, it should be noted that K_{SV} for triethylamine, which possesses a very low oxidation potential, is quite similar to that for Q. Therefore, it is reasonable to assume that $k_q \simeq k_q{}^c \simeq 10^{10}$ M^{-1} s^{-1}. On the basis of this assumption, $k_s{}^c$ and $k_d{}^c$ can be calculated by eq 18, 20, and 23 to be 6.6×10^8 M^{-1} s^{-1} and 4.3×10^7 s^{-1}, respectively. In the quenching by *o*- and *p*-methylanisoles, however, $k_q{}^c$ may not be equal to k_q and/or k_q may be less than the rate constant for a diffusion-controlled process.

If α is given, the other rate constants can also be calculated. We have estimated the value of α and the rate constants as follows: (1) presumption of an appropriate value for α; (2) $k_r{}^c$ from eq 18 and then k_c and k_s from eq 19 and 24; (3) quantum yields $(\phi_{IN}{}^{Q})_{calcd}$ from eq 21; (4) repeated computation of $(\phi_{IN}{}^{Q})_{calcd}$ with various values of α until they agree with the observed quantum yields. The best fit values were obtained when $\alpha = 0.2$ (Table III). This value seems to be reasonable, since it has been reported that α is 0.38 for the pyrene–DCNB–acetonitrile system.[23] Table VIII lists the calculated rate constants.

An interesting point of the results is that the π complex is very short-lived and collapses into two neutral indene molecules and $P^{+}\cdot$ within 1 ns, suggesting a low energy barrier for the cycloreversion of **1** via the π complex. On the other hand, the π-complex formation occurs at a rate 2 orders of magnitude less than a diffusion-controlled process, being perhaps only slightly exothermic or nearly isothermal. This seems to be reasonable since the oxidation potential of **1** is considerably higher than that of P.

Table VIII. Rate Constants in Redox-Photosensitized Cycloreversion of **1**[a]

process	symbol	value
formation of $(P\cdot 1)^{+}\cdot$	k_c	3.6×10^8 M^{-1} s^{-1}
formation of $P_2{}^{+}\cdot$ from $P^{+}\cdot$ and P	k_s	2.1×10^7 M^{-1} s^{-1}
formation of $P_2{}^{+}\cdot$ from $(P\cdot\mathbf{1})^{+}\cdot$ and P	$k_s{}^c$	6.6×10^8 M^{-1} s^{-1}
ring cleavage of 1 from $(P\cdot 1)^{+}\cdot$	$k_r{}^c$	1.0×10^9 s^{-1}
unimolecular decay of $(P\cdot\mathbf{1})^{+}\cdot$	$k_d{}^c$	4.3×10^7 s^{-1}
efficiency for formation of $P^{+}\cdot$	α	0.2
fraction of ring cleavage from $(P\cdot 1)^{+}\cdot$	$1 - \beta$	0.953[b]

[a] See text. [b] Value at [P] = 0.01 M.

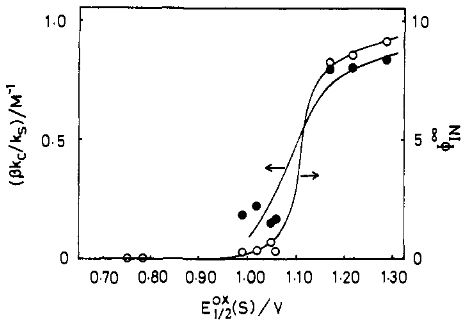


Figure 7. Plots of $\phi_{IN}{}^{\infty}$ and $\beta k_c/k_s$ vs. $E_{1/2}{}^{ox}(S)$ (see Table V).

Although k_s is very small compared with the reported rate constant for the formation of pyrene dimer cation radical in dichloromethane,[22] it should be noted that the reversible dissociation of $S_2{}^{+}\cdot$ was not taken into account in the calculation. If $S_2{}^{+}\cdot$ is reversibly formed, k_s should be replaced by $\gamma k_s'$, where $\gamma = k_d{}^s/(k_{-s} + k_d{}^s)$. The loss of the positive charge of $S_2{}^{+}\cdot$ would be caused by the reactions with $DCNB^{-}\cdot$, water, and other impurities. Therefore, $k_d{}^s$ might be very small compared with k_{-s}.

$$S^{+}\cdot + S \underset{k_{-s}}{\overset{k_s'}{\rightleftharpoons}} S_2{}^{+}\cdot \xrightarrow{k_d{}^s} 2S \text{ and/or others}$$

Dependency of ϕ_{IN} on Oxidation Potentials of S. Both $\phi_{IN}{}^{\infty}$ and $\beta k_c/k_s$ depend on the oxidation potentials of S ($E_{1/2}{}^{ox}(S)$), as shown in Figure 7; the plots sharply change in the vicinity of 1.1–1.15 V. The dependencies reflect all the changes of the rate constants involved. However, it is not unreasonable to assume that the dimer cation radicals of S are formed at similar rates since the structures of S are similar. Moreover, it is known that α does not significantly change for exciplex formation systems of similar electron donor–acceptor pairs where photochemical electron transfer is exothermic.[23] Therefore, it appears that the dependency of $\phi_{IN}{}^{\infty}$ on $E_{1/2}{}^{ox}(S)$ mainly reflects that of $k_r{}^c$. Since β decreases with an increase of $k_r{}^c$, the plot of $\beta k_c/k_s$ vs. $E_{1/2}{}^{ox}(S)$ indicates that k_c increases with an increase of $E_{1/2}{}^{ox}(S)$, suggesting that bonding of the π complex $(S\cdot\mathbf{1})^{+}\cdot$ might arise from charge resonance.

$$(S\cdot\mathbf{1})^{+}\cdot \equiv \{(S^{+}\cdot)\cdot\mathbf{1} \leftrightarrow S\cdot(\mathbf{1}^{+}\cdot)\}$$

If this is the case, the positive charge of the π complex will increasingly develop on the side of **1** as $E_{1/2}{}^{ox}(S)$ increases. Therefore, the dependency of $\phi_{IN}{}^{\infty}$ on $E_{1/2}{}^{ox}(S)$ implies that energy barriers for the cycloreversion of **1** decrease with increasing development of the positive charge on **1**. When $E_{1/2}{}^{ox}(S)$ is over about 1.15 V, the energy barriers would be low enough for the catalytic cycloreversion of **1** by $S^{+}\cdot$ to occur much faster than the other processes.

Structure–Reactivity Relationship in Redox-Photosensitized Ring Cleavage of Cyclobutanes. As has been discussed above, it can be expected that smaller differences of oxidation potential between

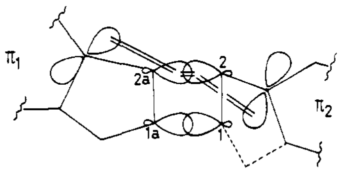
---

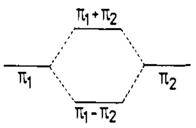
(23) T. Hino, H. Akazawa, H. Masuhara, and N. Mataga, *J. Phys. Chem.*, **80**, 33 (1976).

S and the cyclobutanes appear to be more favorable for ring cleavage. However, this is not always true in all cases. For example, even chrysene is effective for the cycloreversion of **1**, while ring cleavage of **3** did not occur by redox photosensitization when triphenylene was used; the difference of oxidation potential of the former pair is greater than that of the latter pair.

In this regard, the following facts are pointed out: (1) phenyl substitution at C_2 is required for the occurrence of redox-photosensitized ring cleavage of the cyclobutanes investigated; (2) the reactive cyclobutanes (e.g., **1** and **7**) have lower oxidation potentials than the unreactive cyclobutanes (e.g., **3** and **9**); (3) compound **6** having a phenyl group at C_2 but a nitro group at C_1 has a relatively high oxidation potential and is unreactive.

In order to interpret the lower oxidation potentials of the reactive cyclobutanes, we assume interactions between the two π-electron systems through the C_2–C_{2a} σ bond of the cyclobutane ring; a relatively strong through-bond interaction between the n orbitals of 1,4-diazabicyclo[2.2.2]octane (Dabco) has been demonstrated.[24] The two benzene rings of **1** and **2** are fixed and much more favorably located for the through-bond interaction than those of the other reactive cyclobutanes **4**, **5**, and **7**; the lowest oxidation potential of **1** and **2** can thus be reasonably understood.

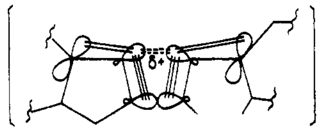




From the structures of the reactive cyclobutanes, therefore, it is suggested that the through-bond interaction is essential for the occurrence of redox-photosensitized cleavage of the cyclobutane ring. In the π complex of a reactive cyclobutane with $S^{+}\cdot$, a partial positive charge might develop on the C_2–C_{2a} bond because of the through-bond interaction, thus leading to weakening of this bond; the degree of bond weakening perhaps depends on either the difference of oxidation potential between S and the cyclobutane or the degree of the through-bond interaction.

Since the oxidation potential of **6** is much higher than that of **7**, the nitro group at C_1 may perturb the highest occupied molecular orbital of the two π-electron systems interacting through the C_2–C_{2a} bond; interactions between the C_1–C_{1a} and C_2–C_{2a} σ bonds might play significant roles in anodic one-electron oxidation of the cyclobutanes. This interpretation would be in line with the observation that the oxidation potentials of **3** and **9** are lower than those of the parent cyclobutane **12** and its methylated compound **11**.

Although it is not yet clear whether redox-photosensitized ring cleavage is concerted or stepwise, we believe that a discrete 1,4-diradical arising from initial cleavage of the C_2–C_{2a} bond is energetically unlikely.[25] Since the cycloreversion of **1** occurs very fast via the π complex with $P^{+}\cdot$, a concerted mechanism might, at least in part, participate in this reaction. A speculative mechanism can be delineated by assuming that the σ orbitals of the C_1–C_{1a} bond interact more and more with those of the C_2–C_{2a} bond as the latter bond is breaking during the lifetime of the π complex. We intend to investigate the stereochemistry in the redox-photosensitized cleavage of the cyclobutane ring and determine thermochemical parameters for thermolyses of the present compounds.



Finally, it should be noted that ring-strain energies and steric repulsion affect the efficiency of ring cleavage; the highly reactive nature of **1** and **2** appears to be caused, in part, by ring strain. Moreover, the cis configuration of **2** makes this compound more reactive. It can be reasonably interpreted in terms of steric repulsion that **4** is 6 times more efficiently cleaved than **7** by the redox photosensitization using phenanthrene, though their oxidation potentials are nearly identical.

Conclusion

The photogenerated cation radical of aromatic hydrocarbons can act as an efficient catalyst for ring cleavage of the cyclobutane compounds which possess structures capable of through-bond interactions. In the redox-photosensitized cycloreversion of **1**, the intermediacy of the π complex with the cation radical of phenanthrene (or other aromatic hydrocarbons) has been demonstrated and a concerted nature has been suggested from the value of k_r^c. Thus, redox photosensitization can provide another route for ring cleavage of cyclobutane compounds. For example, the redox-photosensitized monomerization of the cis,syn dimer of *N*,*N*′-dimethylthymine was found to occur by means of a chain-reaction mechanism while the cis,anti isomer is unreactive to redox photosensitization,[1] thus providing a possible model reaction for enzymatic photoreactivation of damaged DNA. The importance of through-bond interactions in this reaction is again emphasized since the oxidation potential of the cis,syn dimer is much lower than the cis,anti isomer.

Experimental Section

Materials. Spectral grade acetonitrile was distilled three times from phosphorus pentoxide and then twice from calcium hydride before use. Indene, *o*- and *p*-methylanisoles, and *m*-dimethoxybenzene were distilled from sodium in vacuo before use. Triethylamine was refluxed over and distilled from potassium hydroxide before use. *p*-Dimethoxybenzene was distilled from sodium in vacuo and then recrystallized from hexane–benzene. The dimethylnaphthalenes except the 2,3-isomer were purified by fractional distillation. The other aromatic hydrocarbons were recrystallized three times from methanol or ethanol–benzene mixtures and then sublimed. *p*-Dicyanobenzene was purified by recrystallization from benzene and sublimation. The following compounds were prepared by the cited methods: β-nitrostyrene,[26] tetraethylammonium tetrafluoroborate,[27] diphenylacetaldehyde.[28] 1,1-Diphenylacetone was prepared by chromic acid oxidation[29] of 1,1-diphenylpropan-2-ol which had been obtained from diphenylacetaldehyde and methylmagnesium iodide. All other chemicals and solvents were reagent grade and purified by fractional distillation and/or recrystallization.

Analytical Methods. Melting points were taken on a hot stage and are uncorrected. Column chromatography was on silica gel (70–230 mesh, Merck). Analytical gas–liquid chromatography (GLC) was performed on a Shimadzu GC-3BF dual-column instrument with flame ionization detectors. The 75 cm × 4 mm column used for quantitative analyses of indene, 2-methoxyindan, and styrene employed 10% Ucon Oil LB-550X on Neopak-1A, and *n*-tridecane was used as an internal standard. GLC analyses of the cyclobutanes, the aromatic hydrocarbons, *p*-dicyanobenzene, diphenylacetaldehyde, and 1,1-diphenylacetone were carried out with 75 cm × 4 mm columns packed with 5% SE-30 on Shimalite W, 5% Ucon Oil LB-550X on Shimalite W, and 10% PEG 20M on Shi-

---

(24) P. Bischof, J. A. Hashmal, E. Heilbronner, and V. Hornung, *Tetrahedron Lett.*, 4025 (1969); E. Heilbronner and K. A. Muszkat, *J. Am. Chem. Soc.*, **92**, 3818 (1970).

(25) (a) The activation energy for the thermal cleavage of *trans*-1,2-diphenylcyclobutane into styrene has been reported to be 35.6 kcal/mol and a partial participation of a concerted mechanism has been suggested.[25b] Since **1** is very stable even at 170 °C, the activation energy for the thermal cycloreversion of **1** is roughly estimated to be ~30 kcal/mol. If thermolyses of cyclobutane compounds occurred by way of 1,4-diradicals in a ~10 kcal/mol shallow minimum of the potential surface,[25c,d] activation energies for the cycloreversion of **1** via the 1,4-diradical should be over ~20 kcal/mol. (b) G. Jones, II, and V. L. Chow, *J. Org. Chem.*, **39**, 1447 (1974). (c) L. M. Stephenson and J. I. Brauman, *J. Am. Chem. Soc.*, **93**, 1988 (1971). (d) MO calculations predict a large flat region of a potential surface but no minima for intermediates: R. Hoffmann, S. Swaminathan, B. G. Odell, and R. Gleiter, *J. Am. Chem. Soc.*, **92**, 7091 (1970).

(26) D. E. Worrall, "Organic Syntheses", Collect. Vol. I, Wiley, New York, 1941, p 413.

(27) H. O. House, E. Feng, and N. P. Peet, *J. Org. Chem.*, **36**, 2731 (1971).

(28) D. J. Rief and H. O. House, "Organic Syntheses", Collect. Vol. IV, Wiley, New York, 1963, p 375.

(29) E. J. Eisenbraun, "Organic Syntheses", Collect. Vol. V, Wiley, New York, 1973, p 310.

malite W. Preparative GLC was performed with a Hitachi 023 instrument with thermal conductivity detectors, using a 2 m × 7 mm column of 10% Ucon Oil LB-550X on Neopak-1A.

Proton nuclear magnetic resonance (NMR) spectra were recorded at 100 MHz on a JEOL JNM-PS-100 spectrometer or at 60 MHz on a JEOL JNM-60 spectrometer. The solvent was carbon tetrachloride or chloroform-*d*. The chemical shifts are in δ, measured downfield from tetramethylsilane internal standard. Infrared (IR) spectra were obtained on a Shimadzu IR-400 spectrophotometer as Nujol mulls or solutions in carbon tetrachloride or chloroform. Ultraviolet spectra were obtained on a Hitachi 124 spectrophotometer. Fluorescence measurements were carried out on a Hitachi MPF-2A fluorometer. Mass spectra were obtained on a Hitachi RMU-6E instrument.

Elemental analyses were performed at the Elemental Analysis Center of The Institute of Scientific and Industrial Research, Osaka University.

Quantum Yields. All the volumetric flasks and pipettes used were dried in a desiccator in vacuo and the irradiation tubes (Pyrex, 8-mm i.d.) were heated under high vacuum before use. Aliquots (4 mL) of solutions of samples and 2-hexanone actinometer[30] were introduced into the tubes, degassed by 5 freeze–pump–thaw cycles to a reduced pressure $<5 \times 10^{-5}$ torr, and irradiated on a "merry-go-round" apparatus, in the center of which was an Eikosha PIH-300 high-pressure mercury lamp surrounded by a double-cylindrical Pyrex vessel filled with a filter solution. All of them were immersed in a water bath kept at 20 ± 1 °C. Potassium chromate solutions of different concentrations were used for isolation of the 313-nm light and change of the light intensity. In the quenching experiments at 334 nm, relative quantum yields were obtained from the equipment above and a hexane solution of naphthalene (0.1 M) as the light filter. The quantum yields in the absence and presence of 1×10^{-3} and 1×10^{-2} M *p*-dimethoxybenzene were determined by using a Shimadzu-Bausch & Lomb high-intensity monochromator and a potassium ferrioxalate actinometer.[31] In all the runs, conversions were kept below 3%, usually 0.5–1%. Each value was averaged for three runs.

Oxidation Potentials. The oxidation potentials were determined in acetonitrile by cyclic voltammetry. The cell consisted of two compartments and the reference electrode with an agar bridge was separated from the platinum anode and the cathode by a glass frit. A platinum circle (5-mm i.d.) sealed in glass (Beckman) was used as the working electrode, a platinum sheet (10 mm × 10 mm) was employed as the counterelectrode, an Ag/Ag^+ (0.1 M silver nitrate in acetonitrile) was used as the reference electrode, and 0.1 M tetraethylammonium tetrafluoroborate was the supporting electrolyte. A Hokuto Denko HB-107A voltage scanner, a Hokuto Denko HA-104 potentiostat, and a Yokogawa Type 3083 XY recorder were used. All the measurements were carried out at a constant scan speed (0.2 V/s) at 23 ± 0.1 °C under a nitrogen atmosphere. In most cases, voltammograms showed no cathodic peaks corresponding to reversible reduction of cation radicals. Therefore, half-peak potentials were employed as the half-wave oxidation potentials ($E_{1/2}^{\mathrm{Ox}}$). Experimental errors were confirmed to be less than 0.015 V.

***trans*,*syn*-Cyclobuta[*a*]diindene (1).** This compound was prepared by the benzophenone-sensitized dimerization of indene[32] and was recrystallized from methanol: mp 111–112 °C (lit.[32] mp 110–112 °C).

Anal. Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 92.91; H, 6.88.

***cis*,*syn*-Cyclobuta[*a*]diindene (2).** An acetonitrile solution of indene (10 g, 0.17 mol) and ferrocene (1 g, 5.4 mmol) placed in a Pyrex vessel was flushed by a nitrogen stream for 30 min and irradiated for 15 h with a high-pressure mercury lamp. After removal of half the solvent, the remainder was added into 300 mL of diethyl ether. The ether solution was washed with several portions of cold 0.1 M nitric acid and then with water and dried. Filtration and evaporation left a brownish oil, which was chromatographed on silica gel. Elution with hexane gave **2** (3.2 g, 32% yield) as colorless crystals: mp 60.5–62 °C (lit.[32] mp 61–63 °C).

Anal. Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 92.91; H, 6.80.

***trans*,*anti*-Cyclobuta[*a*]diindene (3).** To a solution prepared by dissolution of sodium (1.5 g, 65 mmol) in 70 mL of dry triethylene glycol were added 3 g of α-truxone[33] (12 mmol) and 6 mL of 85% hydrazine hydrate. The mixture was heated at about 200 °C for 20 h, cooled to room temperature, added into 200 mL of 0.1 M hydrochloric acid under ice cooling, and extracted with 100 mL of diethyl ether. The ether extract was washed with saturated sodium bicarbonate and brine, dried, and filtered. The ether was removed to give 0.76 g of colorless solids. Recrystallization from ethanol gave pure **3**: mp 141–142 °C (lit.[32] mp 142–144 °C).

Anal. Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 92.84; H, 6.79.

***endo*-1-Hydroxy-2,2-diphenyl-1,1a,2,2a-tetrahydro-7*H*-cyclobut[*a*]indene (4).** To lithium aluminum hydride (4.8 g, 128 mmol) in 100 mL of diethyl ether was added dropwise 2,2-diphenyl-1,1a,2,2a-tetrahydro-7*H*-cyclobut[*a*]inden-1-one[34] (5 g, 16 mmol) in 50 mL of diethyl ether under ice cooling and the mixture was stirred at ambient temperature for 10 h. After careful addition of saturated ammonium chloride, the ether solution was decanted, washed with 0.1 M hydrochloric acid, saturated sodium bicarbonate, and brine, dried, and filtered. Evaporation left an oil, which was triturated in hexane to give solids. Recrystallization from hexane–benzene gave pure **4** (3.0 g, 60% yield): mp 91–92 °C; IR 3590 cm^{-1} (OH); NMR δ 1.66 (s, 1 H), 2.90 (dd, J = 16.6, 9.4 Hz, 1 H), 3.30 (m, 1 H), 3.31 (dd, J = 16.6, 1.8 Hz, 1 H), 4.50 (dd, J = 7.8, 2.2 Hz, 1 H), 4.78 (dd, J = 7.4, 2.2 Hz, 1 H), 6.80–7.50 (m, 14 H); mass spectrum, *m*/*e* 312 (M^+).

Anal. Calcd for $C_{23}H_{20}O$: C, 88.42; H, 6.45. Found: C, 88.18; H, 6.18.

***endo*-1-Hydroxy-*exo*-1-methyl-2,2-diphenyl-1,1a,2,2a-tetrahydro-7*H*-cyclobut[*a*]indene (5).** To a solution of methylmagnesium iodide prepared from methyl iodide (8 g, 56 mmol) and magnesium shots (1.8 g, 74 mmol) in 100 mL of dry diethyl ether was added dropwise 2,2-diphenyl-1,1a,2,2a-tetrahydro-7*H*-cyclobut[*a*]inden-1-one (7.2 g, 23 mmol) in 50 mL of dry diethyl ether under ice cooling. After 3 h of stirring, the mixture was treated with saturated ammonium chloride. The ether solution was decanted, washed with 0.1 M hydrochloric acid, saturated sodium bicarbonate, and brine, dried, and filtered. Evaporation left white solids. Recrystallization from hexane–benzene gave pure **5** (7.0 g, 92% yield): mp 155–156 °C; IR 3590 cm^{-1} (OH); NMR δ 0.95 (s, 3 H), 1.64 (br s, 1 H), 2.96 (dd, J = 16.4, 7.6 Hz, 1 H), 3.23 (dd, J = 16.4, 1.6 Hz, 1 H), 3.29 (ddd, J = 7.6, 7.2, 1.6 Hz, 1 H), 4.72 (d, J = 7.2, 1 H), 6.80–7.60 (m, 14 H); mass spectrum, *m*/*e* 326 (M^+).

Anal. Calcd for $C_{24}H_{22}O$: C, 88.31; H, 6.79. Found: C, 88.08; H, 6.55.

***exo*-1-Nitro-*endo*-2-phenyl-1,1a,2,2a-tetrahydro-7*H*-cyclobut[*a*]indene (6).** A solution of indene (100 g, 0.86 mol) and β-nitrostyrene (40 g, 0.27 mol) in 200 mL of benzene was flushed with a nitrogen stream for 30 min and irradiated for 16 h with a high-pressure mercury lamp. After evaporation of the benzene, the residue was chromatographed on silica gel. Elution with 30% benzene in hexane gave yellow solids. Recrystallization from methanol gave pure **6** (55 g, 78% yield): mp 75–78 °C; IR 1540, 1370 cm^{-1}; NMR δ 3.20 (m, 2 H), 3.63 (m, 1 H), 4.03 (t, J = 8 Hz, 1 H), 6.35 (d, J = 15 Hz, one of the aromatic protons), 6.80–7.40 (m, 8 H); mass spectrum, *m*/*e* 265 (M^+).

Anal. Calcd for $C_{17}H_{15}NO_2$: C, 72.96; H, 5.70; N, 5.28. Found: C, 76.89; H, 5.48; N, 5.21.

***endo*-2-Phenyl-1,1a,2,2a-tetrahydro-7*H*-cyclobut[*a*]indene (7).** Reduction of **6** with lithium aluminum hydride gave the corresponding amine in 92% yield. This amine was converted into the methiodide with methyl iodide and sodium hydroxide.[35] A mixture of the methiodide (15 g, 37 mmol) and 15 mL of water placed in a stainless steel vessel was heated and then 50 g of sodium hydroxide in 40 mL of water was added with vigorous stirring. The temperature was raised to 200 °C while stirring was continued, and water was added from time to time to replace that lost by evaporation. During the reaction, yellow solids were distilled azeotropically together with water and collected. After the completion of the reaction, the residue was extracted with 300 mL of diethyl ether. The ether solution was combined with the yellow solids, washed with 0.1 M hydrochloric acid, saturated sodium bicarbonate, and brine, dried, and filtered. After evaporation of the ether, the residue was chromatographed on silica gel. Elution with 10% benzene in hexane gave colorless solids. Recrystallization from methanol gave 3.5 g of 2-phenyl-1a,2a-dihydro-7*H*-cyclobut[*a*]indene (44% yield): mp 105–106 °C; NMR δ 2.96 (m, 2 H), 3.52 (m, 1 H), 4.56 (m, 1 H), 6.28 (dd, J = 2.1, 1.9 Hz, 1 H), 6.93–7.46 (m, 9 H); mass spectrum, *m*/*e* 218 (M^+).

Anal. Calcd for $C_{17}H_{14}$: C, 93.54; H, 6.46. Found: C, 93.78; H, 6.47.

This olefin was hydrogenated over 5% palladium–carbon to afford **7** in 80% yield: mp 49–50 °C; NMR δ 2.06 (m, 1 H), 2.46 (m, 1 H), 3.05 (m, 3 H), 3.98 (m, 2 H), 6.03 (d, J = 15 Hz, one of the aromatic

---

(30) P. J. Wagner, *Tetrahedron Lett.*, 5795 (1968).

(31) C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, **235**, 518 (1956).

(32) W. Metzner and D. Wendisch, *Justus Liebigs Ann. Chem.*, **730**, 111 (1969).

(33) C. Lieberman and O. Bergami, *Ber. Dtsch. Chem. Ges.*, **22**, 784 (1889).

(34) N. Campbell and H. G. Heller, *J. Chem. Soc.*, 933 (1967).

(35) D. E. Applequist and J. D. Roberts, *J. Am. Chem. Soc.*, **78**, 4012 (1956).

protons), 6.60–7.23 (m, 8 H); mass spectrum, *m/e* 220 (M^+).

Anal. Calcd for $C_{17}H_{16}$: C, 92.68; H, 7.32. Found: C, 92.45; H, 7.18.

***endo*-1-Hydroxy-*exo*-1-phenyl-1,1a,2,2a-tetrahydro-7*H*-cyclobut[*a*]indene (8).** The cycloadduct of indene and dichloroketene[36] was reduced with activated zinc dust to afford 1,1a,2,2a-tetrahydro-7*H*-cyclobut[*a*]inden-1-one in 77% yield; mp 41–42 °C. The IR and NMR spectra were in accord with those reported.[36]

In a manner similar to that used in the preparation of **5**, the reaction of this ketone with phenylmagnesium bromide gave **8** in 93% yield: mp 61–63 °C; IR 3590 cm^{-1} (OH); NMR δ 1.62 (s, 1 H), 2.07 (ddd, J = 25.4, 7.8, 2.0 Hz, 1 H), 3.05 (m, 2 H), 3.51 (m, 3 H), 6.95–7.44 (m, 9 H); mass spectrum, *m/e* 236 (M^+).

Anal. Calcd for $C_{17}H_{16}O$: C, 86.41; H, 6.82. Found: C, 86.13; H, 6.88.

***endo*-1-Phenyl-1,1a,2,2a-tetrahydro-7*H*-cyclobut[*a*]indene (9).** Bromination of **8** with phosphorus tribromide gave the corresponding bromide as an oil in 88% yield: bp 105–110 °C (0.01 mmHg). A hexamethylphosphoric triamide solution (50 mL) of the bromide (12.7 g, 43 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (13 g, 86 mmol) was heated at 80 °C for 10 h under a nitrogen atmosphere, cooled to room temperature, and then added to 200 mL of diethyl ether. The ether solution was washed with 0.1 M hydrochloric acid, saturated sodium bicarbonate, and brine, dried, and filtered. After evaporation of the ether, fractional distillation of the residual oil gave a colorless oil: bp 103–104 °C (0.01 mmHg). This oil solidified and was recrystallized from methanol to give pure 1-phenyl-1a,2a-dihydro-7*H*-cyclobut[*a*]indene (5.8 g, 70% yield): mp 55–57 °C; NMR δ 3.06 (m, 2 H), 3.88 (m, 1 H), 4.22 (m, 1 H), 6.50 (s, 1 H), 6.80–7.31 (m, 9 H); mass spectrum, *m/e* 218 (M^+).

Anal. Calcd for $C_{17}H_{14}$: C, 93.54; H, 6.46. Found: C, 93.29; H, 6.25.

Catalytic hydrogenation of this olefin over 5% palladium–carbon gave **9** as a colorless oil in 82% yield: bp 81–82 °C (0.01 mmHg); NMR δ 2.25 (m, 1 H), 2.78 (m, 2 H), 2.98 (m, 1 H), 3.53 (m, 1 H), 3.88 (m, 2 H), 6.80–7.32 (m, 9 H); mass spectrum, *m/e* 220 (M^+).

Anal. Calcd for $C_{17}H_{16}$: C, 92.68; H, 7.32. Found: C, 92.39; H, 7.26.

***exo,cis*-1,2-Bis(hydroxymethyl)-1,1a,2,2a-tetrahydro-7*H*-cyclobut[*a*]indene (10).** The dimethyl ester of the photocycloadduct of indene and maleic anhydride[37] was reduced with lithium aluminum hydride to afford dialcohol **10** in 55% yield. This compound was recrystallized from hexane: mp 80–81 °C; IR 3580 cm^{-1} (OH); NMR δ 2.09 (s, 2 H), 2.80 (m, 2 H), 3.14 (m, 2 H), 3.63 (m, 2 H), 3.86 (s, 4 H), 7.06 (s, 4 H); mass spectrum, *m/e* 204 (M^+).

Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.20; H, 7.64.

***exo,cis*-1,2-Dimethyl-1,1a,2,2a-tetrahydro-7*H*-cyclobut[*a*]indene (11).** Dialcohol **10** was converted into the corresponding ditosylate in 62% yield by the published method.[38] This ditosylate was reduced with lithium aluminum hydride to afford **11** in 49% yield. This compound was purified by preparative GLC and fractional distillation: bp 58–60 °C (0.01 mmHg); NMR δ 0.98 (d, 3 H), 1.23 (d, 3 H), 2.40–4.12 (m, 6 H), 6.80–7.25 (m, 4 H); mass spectrum, *m/e* 172 (M^+).

Anal. Calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.90; H, 9.12.

1,1a,2,2a-Tetrahydro-7*H*-cyclobut[*a*]indene (12). To lithium aluminum hydride (3.9 g, 110 mmol) in 300 mL of dry diethyl ether was added dropwise the photocycloadduct of indene and tetrachloroethylene[39] (15 g, 53 mmol) in 200 mL of dry diethyl ether under ice cooling and the mixture was refluxed for 8 h. After careful addition of saturated ammonium chloride, the ether solution was decanted, washed with 0.1 M hydrochloric acid, saturated sodium bicarbonate, and brine, dried, and filtered. Evaporation left colorless solids. Recrystallization from methanol gave pure 1,2-dichloro-1a,2a-dihydro-7*H*-cyclobut[*a*]indene (9.5 g, 85% yield); mp 48–49 °C (lit.[39] mp 49–50 °C). The NMR spectrum was in good agreement with that reported.[40]

This dichloro olefin was dechlorinated by sodium in *tert*-butyl alcohol according to the published method[41] to give 1a,2a-dihydro-7*H*-cyclobut[*a*]indene in 40% yield. This compound was purified by preparative GLC and fractional distillation; bp 37–38 °C (0.1 mmHg). The NMR spectrum was in good agreement with that reported.[40]

The catalytic hydrogenation of this olefin over 5% palladium–carbon gave **12** in 80% yield. This compound was purified by preparative GLC and fractional distillation: bp 81–82 °C (18 mmHg); mass spectrum, *m/e* 144 (M^+). The NMR spectrum was in good agreement with that reported.[40]

Anal. Calcd for $C_{11}H_{12}$: C, 91.61; H, 8.39. Found: C, 91.29; H, 8.67.

Acknowledgments. This work was supported by Scientific Research Grant-in-Aid No. 447067 from the Ministry of Education. C.P. is grateful to the Kim Man Yu Science & Technology Foundation for financial support.

---

(36) L. Ghosez, R. Montaigne, A. Roussel, H. Vanlierde, and P. Mollet, *Tetrahedron*, **27**, 615 (1971).

(37) W. Metzner, H. Partale, and C. H. Krauch, *Chem. Ber.*, **100**, 3156 (1967).

(38) C. S. Marvel and V. S. Sekera, "Organic Syntheses", Collect. Vol. III, Wiley, New York, 1955, p 366.

(39) W. Metzner and W. Hartmann, *Chem. Ber.*, **101**, 4099 (1968).

(40) W. Wendisch and W. Metzner, *Chem. Ber.*, **101**, 4106 (1968).

(41) P. G. Gassman and J. L. Marshall, "Organic Syntheses", Collect. Vol. V, Wiley, New York, 1973, p 424.