Photochemistry of Cyclobutanes. I. Photolysis of Naphthalene *peri*-Fused Cyclobutanes in Rigid Media. Photocleavage from an Upper Triplet State

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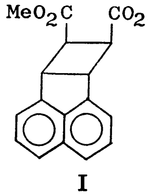
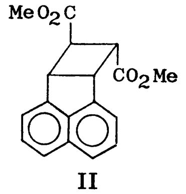
The photocleavage reaction of naphthalene *peri*-fused cyclobutanes (I—IV) in rigid media is found to proceed from one (or several) of the upper triplet states. Nearly planar cyclobutanes (I—III), which were photocleaved in fluid solutions to yield acenaphthylene and 1,2-ethylenedicarboxylic acid derivatives, afford 1,8-naphthalenediacrylic acid derivatives in addition to the above products by irradiation in rigid media. Twisted cyclobutane (IV), which is considerably stable to irradiation in fluid solutions, was also photocleaved in rigid media to give dimethyl 1,8-naphthalenediacrylate. An NMR study shows that the formation of these diacrylic acid derivatives from I—IV in rigid media is considerably stereospecific. The yield ratio of diacrylic acid derivatives to acenaphthylene formed in the photolysis of I—III is independent of the viscosity of the solvents, *i.e.*, of the matrix rigidity, but depends on other properties of the rigid solvents. A concerted mechanism is proposed for the photocleavage reaction of I—IV in rigid media in order to explain the photochemistry different from that in fluid solutions.

There are two possible modes for the photocleavage of four-membered rings of cyclobutane compounds. In the case of cyclobutanes formed from the photocycloaddition of two olefins, one mode of cleavage corresponds to the photoreverse reaction and another leads to the formation of new olefins, if the two modes are not equivalent. However, the photolysis of cyclobutane derivatives frequently shows cleavage-mode selectivity in spite of the energetic possibility of both cleavage modes. It is important to find the factors determining this selectivity. One of the factors must be the steric strain of the cyclobutane ring caused by the interaction of substituent groups. This is supported by the fact that highly-twisted strain-free cyclobutanes are remarkably stable to irradiation.

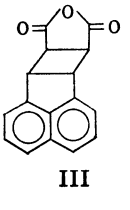
The present authors studied the photolysis of some naphthalene *peri*-fused cyclobutanes (I—IV) to elucidate the factors influencing the cleavage mode. In fluid solutions, the photocleavage of I—III having nearly planar cyclobutane rings takes place from S_1 and T_1, affording only one mode of cleavage products, acenaphthylene and 1,2-ethylenedicarboxylic acid derivatives, but twisted strain-free cyclobutane IV is not photocleaved. In contrast, the irradiation of I—III in rigid media results in two possible modes of cleavage, giving 1,8-naphthalenediacrylic acid derivatives (the valence isomers of I—III) in addition to the photoclevage products observed in fluid solutions. Moreover, IV, for which two photocleavage modes are equivalent, is also photolyzed in rigid media to yield a diacrylate.



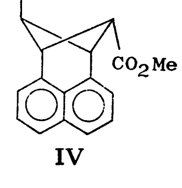
I



II



III



IV

In the present paper, the present authors report that the photocleavage reaction of I—IV in rigid glassy matrices proceeds from higher triplet state(s) by a concerted mechanism, and that this causes a photochemical reaction different from that in fluid solutions.

Experimental

Cyclobutanes I—IV were prepared by a method described elesewhere.[1] All the compounds were purified by repeated recrystallization and the purity was checked by GLC. Low-temperature photolysis was performed in EPA (5: 5: 2) prepared by mixing diethyl ether, isopentane and ethanol, in MP by mixing 3-methylpentane and isopentane, and in glycerol. The solvents except for glycerol were used after purification using alumina column chromatography. A spectrally-pure grade glycerol was used without further purification.

Electronic absorption spectra were obtained using a Shimadzu D-40R spectrometer, emission spectra using a Hitachi MPF-2 spectrometer, and NMR spectra using a Hitachi R-24A instrument.

Two different cell-Dewar arrangements (the cell was immersed in a Dewar containing a coolant) were used. One arrangement consisted of a small cylindrical quartz cell (with a 10-mm pathlength and a 10-mm diameter) and a quartz Dewar equipped with two large flat windows (parallel each other, 20 mm in diameter). This arrangement was used in order to achieve complete photochemical conversion of all sample in the cell. The completely converted samples were used to study the photochemical reaction of the photoproducts. The other arrangement consisted of a cubic quartz cell (with a 10-mm pathlength) and a quartz Dewar equipped with three flat windows (two are parallel and one is at right angles to the other two, 10 mm in diameter). This arrangement was used for following photochemical changes simultaneously using absorption and emission spectroscopy. Generally, liquid nitrogen was used as the coolant, and Dry Ice–ethanol or ice water–sodium chloride was used for glycerol solvent.

A 500-W high-pressure mercury arc lamp with quartz optics (Ushio-501C), a water heat filter (with a 10-mm pathlength), and Toshiba glass filters UV D25 and UV 29 (transparent between 270 and 400 nm) were used for ordinary irradiation. A neutral filter (50% transparency) was added to the lamp system for changing the light intensity. Simultaneous irradiation with two light beams was obtained using the following light sources: a 10-W low pressure mercury lamp with the Toshiba UV D25 filter (to cut out the 185 nm radiation) for excitation, and the 500-W mercury arc system with Toshiba glass filters VV 40 and UV 39 (transparent between 370 and 470 nm) for long-wavelength light irradiation.

The concentration of samples for photochemistry and spectroscopy was usually about 10^{-4} M. Almost all experiments were performed in an aerated system, since the photochemical reactions were confirmed to be unaffected by air after a comparison between aerated and degassed samples.

An immersion photoreactor consisting of a quartz reaction vessel (doughnut type with a 10-mm pathlength and a 250-ml volume), a quartz Dewar jacket, a quartz jacket for lamp cooling (using circulating water) and a 100-W high-pressure mercury arc lamp was used for the preparative work. The reactor was the most satisfactory one of the several reactors tested. Solutions of I—IV (50 mg in 500 ml EPA) were divided into two 250-ml portions and each was irradiated in the reactor. Irradiation and thawing was repeated to achieve as large a degree of conversion as possible. After the irradiation of each portion for a total of 3 h, the solutions were added and the solvent was evaporated off under reduced pressure. NMR spectra of the residue were obtained without further isolation and the formation of 1,8-naphthalenediacrylic acid derivatives were confirmed, but isolation of the products by preparative GLC was unsuccessful.

Results

Identification of the Products. The photochemical reaction of cyclobutanes I—IV in an EPA rigid glassy matrix at liquid nitrogen temperature was followed using UV spectroscopy; the cyclobutane bands gradually disappeared while the bands of the products grew at longer wavelengths. The starting and the fully-converted spectra of I are shown in Fig. 1, as an example of the spectral changes of the cylobutanes. The photochemical reactions of I—III in fluid solutions were cleavage into acenaphthylene and 1,2-ethylenedicarboxylic acid derivatives,[2] and IV was found to be rather stable to irradiation in fluid solutions.[3] The frozen-state spectrum of acenaphthylene obtained by the photolysis of I in an EPA solution at room temperature under otherwise similar conditions is also shown in Fig. 1. A comparison of the final spectra resulting from the photolysis of I in rigid and fluid states of EPA solutions (Fig. 1) suggests the formation of acenaphthylene and unidentified product(s) resulting in a broad band at about 340—350 nm in EPA at 77 K under the irradiation of I in an EPA matrix. The spectral changes of II and III were similar to that of I, and the final spectra were a superposition of the spectra of acenaphthylene and unidentified products. The irradiation of IV in the rigid matrix also caused spectral changes and gave product(s) having a broad band at about 340 nm, but no acenaphthylene was formed. The conversion efficiency of the highly-twisted cyclobutane, IV, was lower than that of the nearly planar cyclobutanes, I—III.

The unidentified products characteristic of the rigid-state photolysis of I—IV, P_I—P_{IV}, respectively, were identified to be 1,8-naphthalenediacrylic acid derivatives which were formed by the photocleavage of the cyclobutane rings of I—IV, on the basis of their photochemical behavior and absorption, fluorescence and NMR spectra.

Photochemical Behavior of P_I—P_{IV}: The products from the photolysis of I—IV in an EPA glassy matrix did not undergo any more photochemical reactions in the matrix due to selective irradiation. However, after the matrix was melted by warming to room temperature, P_I—P_{IV} reacted easily under the same irradiation to give products whose spectra closely resembled those of the starting cyclobutanes I—IV. Since the irradiation of these products from P_I—P_{IV} at room temperature no

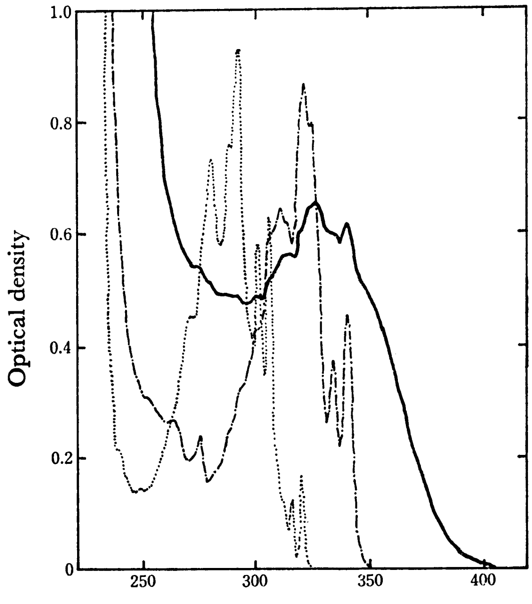


Fig. 1. Absorption spectrum of I in EPA at 77K (···); after irradiation at 77K (—); after irradiation at room temperature and frozen at 77K, *i.e.*, spectrum of produced acenaphthylene (-·-·-).

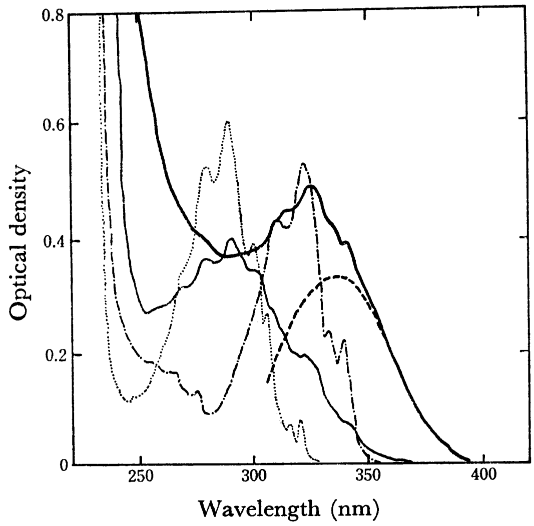
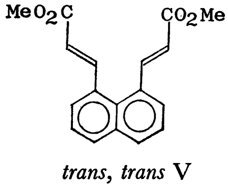


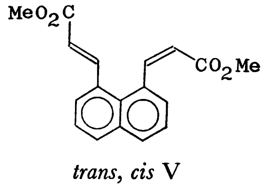
Fig. 2. Absorption spectrum of I in EPA at room temperature (···); after irradiation at 77K and warmed up to room temperature (—); after irradiation at wavelengths longer than 330 nm (—). The operations were sequential.
Absorption spectrum of acenaphthylene (see caption to Fig. 1) (-·-·-) and net absorption spectrum of P_I derived from the spectral separation (---).

longer gave acenaphthylene as did I—III,[4] most of them are considered to be twisted cyclobutanes like IV, if they are indeed cyclobutanes. Acenaphthylene coexisting with $\mathrm{P_I}$—$\mathrm{P_{III}}$ remained almost unchanged throughout these photochemical procedures. Thus, the net absorption spectra of $\mathrm{P_I}$—$\mathrm{P_{III}}$ could be respectively obtained as the differences between the superposed spectra and that of the remaining acenaphthylene. The spectral change of $\mathrm{P_I}$ and its net absorption spectrum obtained in these procedures are shown in Fig. 2. The net spectra of $\mathrm{P_I}$—$\mathrm{P_{III}}$ and the spectrum of $\mathrm{P_{IV}}$ resemble each other and their maximum peaks occur at about 330—340 nm in EPA solutions at room temperature.

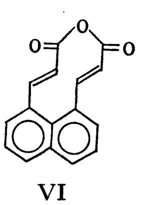
The net absorption spectra and the photochemical behavior of $\mathrm{P_I}$—$\mathrm{P_{IV}}$ agreed well with those of 1,8-naphthalenediacrylic acid derivatives, which was expected from our previous study of the photochemistry of dimethyl 1,8-naphthalenediacrylate (V).[1] The irradiation of V in fluid solutions gave predominantly intramolecular head-to-tail adducts (the main product is IV), while V is photochemically unreactive in rigid matrices. The photochemistry of 1,8-naphthalenediacrylic anhydride (VI) was not studied but was inferred to be almost the same as that of V except for the formation of larger amounts of head-to-head adducts like III due to the fixed structure of VI. This was consistent with the photochemical behavior observed with respect to $\mathrm{P_{III}}$.[4]



trans, *trans* V



trans, *cis* V



VI

Fluorescence Spectra of P_{I}—P_{IV}: Absorption and fluorescence spectral changes of I—IV due to irradiation in EPA at 77 K were observed simultaneously. The fluorescence was measured using 290, 340, or 365 nm radiation for excitation. The fluorescence of both the starting cyclobutanes and the products were observed using 290 nm light for excitation, while using 340 or 365 nm light, only product fluorescence was observed. Intense fluorescence bands due to the products from I—IV appeared and increased with irradiation time in parallel with the growth of the absorption bands of the products, while the intensity of the fluorescence of I—IV decreased at the same time. Since acenaphthylene does not fluoresce,[5] the observed fluorescence of the products was attributed to $\mathrm{P_I}$—$\mathrm{P_{IV}}$ even in the case of I—III. The excitation spectra of the fluorescence of the products from I—IV agreed well with the absorption spectra of $\mathrm{P_I}$—$\mathrm{P_{IV}}$, respectively.

The shape and the position of the fluorescence spectra of $\mathrm{P_I}$—$\mathrm{P_{IV}}$ agree well with those of V and probably VI, as is shown in Fig. 3. No phosphorescence of $\mathrm{P_I}$—$\mathrm{P_{IV}}$ was observed and the intensity of the fluorescence was lowered remarkably upon melting the matrix. This is in accord with the observation with respect to V (non-phosphorescent, with a fluorescence quantum yield in EPA of *ca.* 0.9 at 77 K and *ca.* 0.03 at room temperature).[1] These emission spectral observations also suggest that $\mathrm{P_I}$—$\mathrm{P_{IV}}$ are 1,8-naphthalenediacrylic acid derivatives.

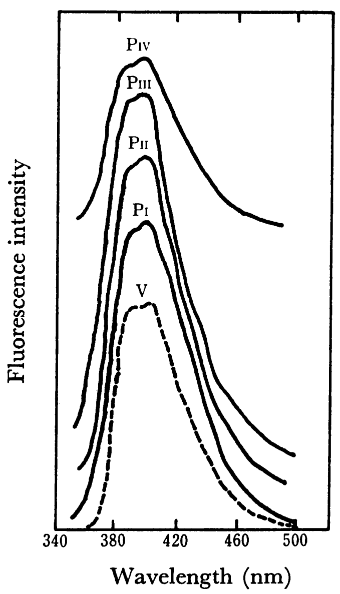


Fig. 3. Fluorescence spectra of $\mathrm{P_I}$—$\mathrm{P_{IV}}$ observed after 1 min-irradiation of I—IV in EPA at 77K respectively, and that of *trans*, *trans* V in EPA matrix (excited with 340 nm light).

NMR Spectra of P_{I}—P_{IV}: Preparatory work on the photolysis of I—IV in EPA at 77 K was performed in order to confirm the formation of the diacrylic acid derivatives. Since the isolation of $\mathrm{P_I}$—$\mathrm{P_{IV}}$ from the reaction mixtures by means of preparative GLC was unsuccessful because of the thermal high-reactivity of these substances, an attempt was made to detect them by means of proton NMR spectroscopy. The formation of the dialkenes could be confirmed clearly, since their NMR peaks (of vinyl and/or methyl protons) are not interrupted by the peaks of compounds coexisting with them.[6]

The NMR spectrum of $\mathrm{P_I}$ agreed with that of authentic *trans*, *trans* V, while those of $\mathrm{P_{II}}$ and $\mathrm{P_{IV}}$ were identical with each other and agreed with that of authentic *trans*, *cis* V.[7] The spectrum of $\mathrm{P_{III}}$ was

Table 1. NMR spectral data of $\mathrm{P_I}$—$\mathrm{P_{IV}}$

Compound	NMR ($CDCl_3$) δ ppm	Assignment
$\mathrm{P_I}$	3.80 (s, *trans* methyl H) 6.29, 8.37 (pair of d, J=15.6 Hz, *trans* vinyl H) 7.2—7.8 (m, aromatic H)	dimethyl *trans*, *trans*-1,8-naphthalenediacrylate, (*trans*, *trans* V)
$\mathrm{P_{II}}$, $\mathrm{P_{IV}}$	3.80 (s, *trans* methyl H) 3.59 (s, *cis* methyl H) 6.29, 8.37 (pair of d, J=15.6 Hz, *trans* vinyl H) 6.16 (d, J=12.6 Hz, *cis* vinyl H)[a] 7.2—7.8 (m, aromatic H)	dimethyl *trans*, *cis*-1,8-naphthalenediacrylate, (*trans*, *cis* V)
$\mathrm{P_{III}}$	6.16, 8.01 (pair of d, J=15.6 Hz, *trans* vinyl H) 7.2—7.8 (m, aromatic H)	*anti*-1,8-naphthalenediacrylic anhydride, (VI)

a) Another doublet peak is expected to be hidden in the peaks for aromatic protons.

considered to be reasonable for that of VI, although the authentic spectrum of this substance could not be obtained.[8] The observed NMR spectral data of P_I—P_{IV} and their assignments are shown in Table 1. The NMR study suggests that the formation of diacrylic acid derivatives from I—IV in rigid matrices is stereospecific to within the sensitivity of the NMR spectrometer.[6]

Product Yield. The yield of the photocleavage products upon the photolysis of I—IV in an EPA rigid matrix was estimated on the basis of the UV spectra resulting from irradiation to the point of complete conversion. In the case of I—III, the spectral separation of two olefinic products was effected by the photochemical procedures described above. The amount of the products was calculated from the intensity of their spectra using ε at λ_{max}: 4900 (340 nm) for acenaphthylene, 17400 (335 nm) for *trans, trans* V and VI, and 13000 (332 nm) for *trans, cis* V.[9] The quantum yields for the photocleavage of I—IV in rigid matrices were remarkably small and actually zero, since prolonged irradiation with monochromatic light (290 or 313 nm light from the 500 W Hg lamp) which is strong enough for reactions at room temperature scarcely caused any reaction in EPA at 77 K. Thus, the relative disappearance rates of the starting cyclobutanes for irradiation with strong filtered light were determined spectrally in order to compare their photochemical reactivity. The product yield and relative disappearance rate are summarized in Table 2. The total yield of the photocleavage products is much smaller than 100% with respect to all the cyclobutanes studied, and reactions other than photocleavage reach about 60% of the total reactions, as is shown in Table 2.

Table 2. Product yields in the photolysis of I—IV in EPA at 77 K

Compound	R[a]	Product yield (%)		
		Acenaphthylene	1,8-Naphthalenedialkene	Others
I	1.0	13	28	59
II	2.0	44	12	44
III	2.3	20	20	60
IV	0.5	—	43	57

a) Relative disappearance rate.

Fluorescence and Phosphorescence of I—IV. Remarkably intense fluorescence and fairly intense phosphorescence were observed for I—IV in rigid media. The fluorescence and phosphorescence spectra of I—IV in EPA solutions at 77 K were similar to those of naphthalene except that the former was located at a wavelength about 10 nm longer than the latter. The quantum yields for fluorescence and phosphorescence were determined using naphthalene as a standard ($\phi_f=0.55$, $\phi_p=0.10$ in EPA at 77 K).[10] Phosphorescence lifetimes were also measured by the usual method. The results, summarized in Table 3, show that the cyclobutanes have almost the same emission spectral characteristics as naphthalene, and possess considerably long phosphorescence lifetimes.

Contribution of Upper Triplet State(s). Photocleavage into 1,8-naphthalenedialkenes proceeds only in those instances in which solvents are changed into rigid glasses and the long-lived phosphorescence of the cyclobutanes is observed. This was confirmed using glycerol as a solvent at several reaction temperatures (0 to −80 °C) where the solvent was convertible from a cooled viscous fluid into a rigid glass. Thus, it is suggested that the actual substrates of the photochemical reaction in rigid media are the lowest triplets of the cyclobutanes and the reaction proceeds from upper triplet states which are populated when the metastable triplet absorbs another photon of sufficient energy. In order to verify this, two standard experiments were performed with respect to the cyclobutanes in EPA at 77 K.

Table 3. Quantum yields for fluorescence and phosphorescence, and the phosphorescence lifetime of I—IV in EPA at 77 K[a]

Compound	φ_f	φ_p	τ_p (s)
I	0.58	0.05	2.54
II	0.61	0.07	2.47
III	0.46	0.05	2.40
IV	0.13	0.10	2.54

a) φ_f, φ_p, and τ_p denote the quantum yields for fluorescence (excited with 290 nm light) and phosphorescence (excited with 313 nm light), and the phosphorescence lifetime derived from the decay at the 490 nm and 520 nm peaks, respectively. Naphthalene ($\varphi_f=0.55$, $\varphi_p=0.10$ in EPA at 77 K)[10] was used as a standard.

Table 4. Dependence of the primary rate of formation of photocleavage products on the light intensity

Rate (full intensity)/Rate (50% intensity)

Compound	Acenaphthylene	1,8-Naphthalenedialkene
I	4.0	3.9
II	3.8	3.9
III	4.0	4.0
IV	—	4.0

(1) The dependence of the primary rate of formation of the photocleavage products on the light intensity was determined. When the intensity of the incident light was decreased to one half using the neutral filter of 50% transparency, the rate was decreased to about a fourth with respect to the formation of both acenaphthylene and dialkenes. The ratio of the rate at full intensity to that at a one-half intensity is shown in Table 4. The fact that the rate is approximately proportional to the square of the light intensity suggests that almost all the photocleavage products are formed by a two-photon mechanism.

(2) The effect of simultaneous irradiation with strong long-wavelength light on the product forming rate was measured. The rate due to a weak source of 254 nm light increased seven- to eight-fold when the samples were irradiated simultaneously with intense light (370—470 nm) which itself had no effect on the cyclobutanes.[11] The effective wavelengths of the second beam

corresponded to those at which the intense bands of the triplet-triplet absorption spectra of naphthalene and alkylnaphthalenes are located.[12] In the case of I—III, the product ratio of acenaphthylene and 1,8-dialkenylnaphthalene was almost independent of irradiation with the long-wavelength light. These results also show that the photocleavage reaction of I—IV in rigid matrices proceeds from upper triplet state(s) formed by the subsequent absorption of two photons.

TABLE 5. SOLVENT EFFECT ON THE PHOTOCLEAVAGE OF I

Solvent	Viscosity (p)[13]	Cleavage ratio (A : N)[a]
EPA (5: 5: 2)[b]	$\approx 10^5$	31 : 69
Glycerol[c]	$\approx 10^{12}$	85 : 15
IP–3MP (97: 3)[b]	8.9×10^5	66 : 34
IP–3MP (50: 50)[b]	5.9×10^8	62 : 38
IP–3MP (0: 100)[b]	9.4×10^{11}	69 : 31

a) A=acenaphthylene, N=dimethyl 1,8-naphthalenediacrylate. b) At 77 K (liq. nitrogen). c) At 196 K (Dry Ice–ethanol).

Solvent Effect. In order to examine the effect of the solvents used as matrices on the cleavage mode of the cyclobutanes I—III, the photocleavage of I was studied in some rigid solvents. The yield ratio of the acenaphthylene and *trans, trans* V formed from I according to the two photocleavage modes is shown in Table 5. The ratios are nearly equal to within the experimental errors for the hydrocarbon solvents IP–3-MP, which have remarkably different viscosity but are otherwise similar in nature,[13] while the ratio varies for solvents of different nature. Thus, the ratio of the two modes of cleavage is found to be independent of solvent viscosity, *i.e.*, the rigidity of the matrix, but is found to depend on some other solvent characteristics.

Discussion

Reaction from the Upper Triplet State(s). The photocleavage reaction of I—IV in rigid matrices is found to proceed from the upper triplet state(s) formed by the subsequent absorption of two photons. Since the photoexciting moiety of the cyclobutane compounds is the naphthalene ring, the cleavage is expected to occur in one (or several) of the upper triplet states of the naphthalene chromophore. The triplet state energies (10^3 cm^{-1}) of naphthalene itself, and probably of I—IV, are as follows: $T_1=21.3$, $T_2=30.8$, $T_3=38.7$, $T_4=45.5$, $T_5=58.9$, and $T_6=63.7$.[14] The T_1-T_4 and T_1-T_6 absorption transitions have remarkably large extinction coefficients (33000 and 55000, respectively), but only the former transition is possible energetically under the present conditions. Furthermore, the energy of the T_1-T_4 transition is in accord with the second-photon energy which is effective in causing the reaction. Thus, the photocleavage reaction may be occuring in any of the states T_2-T_4 of the cyclobutanes.

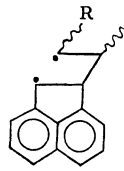
The contribution of the upper triplet state(s) has been reported by Kolc and Michl[15] for a photochemical study of the ring-opening of naphthalene-fused cyclobutenes into the pleiadene family in rigid matrices. Furthermore, it was found that the *cis* dimer of acenaphthylene is also photocleaved to acenaphthylene from the upper triplet state(s) in rigid matrices.[16] It seems to be noteworthy that the long-lived T_1 state of naphthalene chromophore acts as a second-photon receiver in all the reactions described above.

The photochemical reactions of I—III in fluid media take place from the S_1 and T_1 states rather efficiently at room temperature, whereas the reactions of I—IV in rigid matrices occur almost exclusively from the upper triplet state(s). This shows that the S_1 and T_1 states of I—III become unreactive in rigid matrices, although those of IV are inactive even in fluid solutions. In other words, thanks to the unreactivity of the S_1 and T_1 states and the long lifetime of the T_1 state, the reaction from the upper triplet becomes noticeable in rigid matrices. The difference of the reactivities in fluid and in rigid media suggests that the reaction from the S_1 and T_1 states requires some activation energy. The activation energy of I—III may be so small that the reaction can proceed in fluid solutions. Since the reaction from the S_1 and T_1 states is stopped in rigid matrices, the S_1 and T_1 states of I—III should dissipate most of their energy as emission (and as heat). In fact, the fluorescence yields for I—III in EPA matrices at 77 K are about two times larger than those at room temperature, although the yield of IV does not change so much.

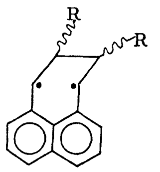
Side Reactions. In fluid media, reactions other than photocleavage are unimportant in I—III and IV is stable under the usual conditions, while in rigid media, side reactions become about 60% of the total photochemical reactions (Table 2). Therefore, most of the side reactions in rigid media seem to be related to the upper triplet states. However, photoionization and photosensitized solvent decomposition are excluded from the side reactions because these high-energy processes are energetically impossible in such low upper triplet states as T_2-T_4. Moreover, secondary photolysis of the primary olefinic products is also excluded, since the products are considerably stable to irradiation in rigid matrices. Hence, the side reactions are expected to be fragmentations of I—IV in upper triplet states except for the cleavage of the cyclobutane ring.

In view of the fact that absorption bands based on the naphthalene rings of I—IV disappear almost completely, but that no long-wavelength bands other than those due to the cleavage products appear, the destruction of the naphthalene rings seems to be involved in the side reactions, though the details are not known. In fact, naphthalene itself undergoes photolysis under similar conditions, and its spectrum is gradually changed to an ambiguous one having bands at shorter wavelengths.

Reaction Mechanism. The primary products in fluid solutions show that the photocleavage proceeds preferentially through biradical intermediates (VII).[2] Nonformation of naphthalenedialkenes demonstrates that biradicals (VIII), which are expected to lead, at least partly, to the dialkenes even in rigid media,[17] are energetically unfavorable intermediates.[18] If the reaction in the upper triplet states proceeds by a biradical mechanism, the predominant formation of acenaphthylene must hold for the photolysis in rigid glassy matrices. The occurence of two modes of cleavage in rigid matrices must be explained in terms of a change in the reaction mechanism. The difference in the photochemistries in fluid solutions and in rigid matrices is attributable to the difference in the reaction mechanism for the S_1 and T_1 states and that for the upper triplet states. Therefore, a concerted mechanism is proposed for the photocleavage reactions of I—III in rigid media.

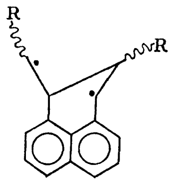


VII



VIII

R=CO_2Me or 2R=$(CO)_2O$



IX

R=CO_2Me

In contrast to I—III, IV is inactive in the S_1 and T_1 states. The cleavage of its strain-free cyclobutane ring may require much a higher energy than in the cases of I—III. For the upper triplet states, the energetic requirement is satisfied and the cleavage can proceed. It is also supposed that a concerted mechanisms for the reaction of IV in rigid media, without rationalization by the MO theory, from an analogy with naphthalene-fused cyclobutene compounds which are inert in the S_1 and T_1 states and reactive in upper triplet states.[15]

A concerted mechanism for the cleavage reactions for I—IV in rigid matrices is supported by the stereospecific formation of naphthalenedialkenes. If the formation is through the biradical VIII (in the case of I—III) or IX (in the case of IV), geometrical isomers of the diolefinic products must be observed except for the case of II, since the inversion of the cycloheptane ring of VIII and the cyclohexane ring of IX is possible even in rigid media. In fact, Pagni *et al.*[17] reported that biradicals of the IX type are highly flexible and ring inversion occurs easily in an ethanol matrix at liquid nitrogen temperature.

The ineffectiveness of matrix rigidity on the yield ratio of the two photocleavage products from I and probably from II and III (Table 5) also supports the concerted cleavage mechanism. If the reaction is nonconcerted, biradicals VII and VIII must be affected differently by solvent rigidity when they change their geometries at the product forming stage, and consequentely, the ratio must vary with matrix rigidity. The dependence of the yield ratio on the solvent may be explained in terms of a solvent-induced shift of the relative positions of the crossing points of the potential curves for the upper triplet cyclobutanes and of those for some excited states of the olefinic products.

Substituent and Structual Effects. A comparison of the photolysis of isomers I and II shows that II always gives a greater amount of acenaphthylene and has a higher reactivity than I (Table 2). In a glycerol matrix, II gives only acenaphthylene. This is obviously due to the higher ring strain of II caused by the interaction of the naphthalene ring with the substituent at its *cis* position. Kaupp[19] has reported in a study of the photocleavage of some phenyl-substituted cyclobutanes that the cleavage of the *cis*-disubstituted bond is particularly favored due to the relief of a large part of the steric strain in the cyclobutane ring. The relative reactivity (Table 2) shows that IV is less reactive than I—III even in reactions from the upper triplet states in spite of its higher phosphorescence yield.

Therefore, ring strain is an important factor for determining the cleavage mode and the reactivity even in reactions from the upper triplet states.

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References

1) K. Honda, A. Yabe, and H. Tanaka, *Bull. Chem. Soc. Jpn.*, **48**, 2062 (1975).

2) In the cases of I and II, small amounts of isomerization products (I→II, II→I) were found in the course of the photochemical reactions in fluid solutions, but the final products after complete irradiation were acenaphthylene, dimethyl maleate and dimethyl fumarate. The formation of the isomers of cyclobutane and ethylenedicarboxylate suggests that the photocleavage reactions of I, II, and probably III proceed by a biradical mechanism in fluid solutions.

3) Prolonged intense irradiation of IV in fluid solutions caused some reactions other than the cleavage of the cyclobutane ring.

4) In the case of products from P_{III}, a small amount of acenaphthylene was formed by irradiation. This suggests that a small amount of III was involved in the products from P_{III}.

5) R. Livingston and K. S. Wei, *J. Phys. Chem.*, **71**, 541 (1967); A. Bree, C. Y. Fan, and R. A. Kydd, *Spectrochim. Acta, Part A*, **25**, 1375 (1969). Although the fluorescence spectrum of acenaphthylene in hexane at 77 K determined by a photographic method has been reported (V. I. Mikhailenko and P. A. Teplyakov, *Opt. Spectrosk.*, **22**, 48 (1967); *Opt. Spectrosc.*, **22**, 24 (1967)), we could not detect the fluorescence.

6) In the cases of I—III, 1,2-ethylenedicarboxylic acid derivatives must be formed as one of photocleavage products, but they produced almost no NMR peaks. These derivatives may have been removed by a solvent during evaporation under reduced pressure. Thus, their stereochemistries (in the cases of I and II) are unknown.

7) The NMR spectrum of *trans, cis* V was measured without isolation in the course of the photoisomerization of *trans, trans* V.[1]

8) The synthesis of VI from 1,8-naphthalenediacrylic acid by the usual methods was unsuccessful.

9) The molar extinction coefficient of VI was assumed to be nearly equal to that of *trans, trans* V. The coefficient of *trans, cis* V was assumed to be three quarters of that of *trans. trans* V, since the value for a *cis* acrylic group has about one half of that for a *trans* group in the usual aromatic acrylic acid derivatives.

10) R. S. Becker, "Theory and Interpretation of Fluorescence and Phosphorescence," Wiley Interscience (1969), p. 118.

11) When an intense light source (*e.g.*, 500-W mercuty arc with UV 29 filter) was used for exciting a sample, the effect of the second light was negligibly small.

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13) W. G. Herkstroeter, "Creation and Detection of the Excited State," Vol. I, Part A, Marcel Dekker (1971), p. 43.

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15) J. Michl and J. Kolc, *J. Am. Chem. Soc.*, **92**, 4148 (1970); J. Kolc and J. Michl, *ibid.*, **95**, 7391 (1973).

16) Unpublished results; the *trans* dimer of acenaphthylene is decomposed into acenaphthylene exclusively from S_1 and/or T_1.

17) R. M. Pagni, C. R. Watson, Jr., J. E. Bloor, and J.R. Dodd, *J. Am. Chem. Soc.*, **96**, 4064 (1974); C. R. Watson, Jr., R. M. Pagni, J. R. Dodd, and J. E. Bloor, *ibid.*, **98**, 2551 (1976).

18) Other possible biradical intermediates for the dialkenes are less favorable than IX, since they are not stabilized by benzylic resonance and their formation requires scission of the C–C bond of the four-membered ring far from the naphthalene ring, the exciting chromophore.

19) G. Kaupp, *Angew. Chem. Int. Ed. Engl.*, **13**, 817 (1974).