BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48 (7), 2062—2067 (1975) [Vol. 48, No. 7

Photochemistry of *peri*-Substituted Naphthalenes. I. Photochemistry of Dimethyl 1,8-Naphthalenediacrylate

Koichi Honda, Akira Yabe, and Hideaki Tanaka

National Chemical Laboratory for Industry, 7th Division, 85 Shinshuku, Hiratsuka, Kanagawa 254

(Received October 29, 1974)

The photochemical reactions of dimethyl 1,8-naphthalene diacrylate (I) in solution are found to be *cis,trans* isomerization and concomitant intramolecular cycloaddition through a triplet state (E_T is *ca.* 40 kcal/mol). Cyclization reaction gives naphtho[1′,8′]bicyclo[3.1.1]hept-2-ene-6-*exo*,7-*endo*-dimethyl dicarboxylate (VI), its 6-*endo*, 7-*endo* substituted isomer (VII) and *cis-anti*-naphtho[1′,8′]bicyclo[3.2.0]hept-2-ene-6,7-dimethyl carboxylate (II) in a ratio of *ca.* 85: 10: 5. Predominant formation of crossed adducts is discussed, taking into consideration the ground-state conformations of (I). Biradical mechanism is proposed for the cyclization to explain the stereochemistry of the crossed products.

It is well-known that cinnamic acid derivatives photodimerize to yield stereospecific cyclobutane compounds in solid state, but isomerize to their geometrical isomers by irradiation in solution or in liquid state. The photochemical behavior differing according to state is attributable to the fixed distance and orientation between two olefin molecules in crystalline state. Schmidt[1] concluded in his topochemical studies that the photodimerization in crystalline state can take place only when the intermolecular distance between two olefin molecules is less than *ca.* 4 Å. Since the distance between 1 and 8 positions of naphthalene molecules is 2.57 Å, 1,8-naphthalene diacrylic acid derivatives are expected to undergo intramolecular photodimerization even in solution. As a part of photochemical studies of *peri*-substituted naphthalenes, we studied the photochemistry of *trans*, *trans*-dimethyl 1,8-naphthalenediacrylate (I) in solution.

Experimental

Spectral data of compounds I, II, III and VI are given in Table 1.

Preparation of I. Compound I was prepared by the Wittig condensation of naphthalaldehyde hydrate[2] with carbomethoxymethylene-triphenyl-phosphorane.[3] A solution of 5.0 g (25 mmol) of dialdehyde in 100 ml of benzene was heated at reflux temperature for 30 min. This hot benzene solution was then added dropwise to 200 ml of a refluxing benzene solution of 25 g (75 mmol) of the Wittig reagent over a period of 15 min. The solution was heated at reflux temperature for 5 hr with stirring in N_2 atmosphere and then filtered, the solvent being removed under reduced pressure. The residue was extracted with 300 ml of ether and the solvent of extract was evaporated off. The yellow residue enriched in I was chromatographed on a column of silica gel with ether to give, after recrystallization from ether, 2.8 g of pure product (I), mp 117—118 °C.

Preparation of II and III. Compound II was prepared from the photoproduct of maleic anhydride with acenaphthylene[4] by usual hydrolysis and esterification, mp 150—151 °C. Compound III was synthesized by base-catalysed epimerization of II. A solution of 0.5 g of II and 0.3 g of sodium methoxide in 5 ml dry methanol in a sealed tube was heated at 70 °C for 8 hr. Recrystallization of the product from methanol gave an equilibrated mixture of II and III in a 5: 95 ratio. Pure III was separated from the mixture by tlc (silica gel, elution

Table 1. Spectral data of I, II, III, and VI

Compd.	Mp (°C)	NMR ($CDCl_3$) δ ppm	IR (KBr) cm^{-1}	UV in cyclohexane nm (log ε)	Mass (M^+)
I	117—118	3.80 (s, 6 methyl H) 7.25 (pair of d, J=15.4 Hz, 4 *trans* vinyl H) 7.2—8.0 (m, 6 aromatic H)	2960, 1710, 1630, 1435, 1370, 1312, 1275, 1197, 1172, 1035, 980, 872, 820, 780	209(4.49), 240(4.30) 265(sh), 332(4.26)	296
II	150—151	3.27 (m, 2 *endo* H) 4.51 (m, 2 benzyl H) 3.77 (s, 6 *exo* methyl H) 7.2—7.7 (m, 6 aromatic H)	2960, 1740, 1440, 1365, 1350, 1265, 1226, 1187, 1160, 829, 796	229(4.91), 278(3.82) 289(3.89), 300(3.71) 306(3.56), 316(2.97) 320(2.99)	296
III	125—128	3.40 (m, 1 *endo* H) 4.30 (m, 2 benzyl H, 1 *exo* H) 3.77 (s, 3 *exo* methyl H) 3.51 (s, 3 *endo* methyl H) 7.2—7.7 (m, 6 aromatic H)	2960, 1730, 1315, 1234, 1185, 1195, 1150, 1020, 784	229(5.15), 279(3.83) 290(3.90), 300(3.72) 306(3.58), 317(2.97) 320(2.83)	296
VI	98—99	2.92 (s, 1 *endo* H) 4.11 (s, 2 benzyl H, 1 *exo* H) 3.79 (s, 3 *exo* methyl H) 3.14 (s, 3 *endo* methyl H) 7.2—7.7 (m, 6 aromatic H)	2970, 1725, 1435, 1358, 1288, 1435, 1212, 1179, 1170, 1018, 829, 798, 789	213(4.53), 229(4.59) 236(4.59), 277(3.89) 288(3.98), 299(3.80) 317(2.88), 321(2.64)	296

with chloroform), mp 125—128 °C.

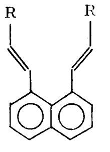
Photocyclization of I in a Preparative Scale. An immersion-well type photoreactor with a 100 W high pressure Hg arc lamp was used for the irradiation of I in a preparative scale. Ethanol solution of naphthalene was circulated as a filter solution to prevent light absorption by the cyclized products. The reaction temperature was maintained at 25 °C.

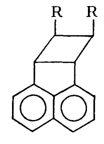
A solution of 400 mg of I in 1.1 *l* of cyclohexane (0.0013 M) was irradiated with the reactor with bubbling N_2 gas. The reaction was monitored by following the disappearance of the absorption peak at 332 nm in the UV spectrum of I, and the starting material was entirely consumed after 5 hr. The solvent was completely evaporated under reduced pressure, and the residual crystal was dissolved in ether and treated with activated charcoal. The recrystallization of the ether solution yielded 320 mg of VI, mp 98—99 °C.

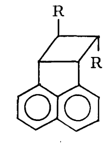
Photocyclization of I in an Analytical Scale. A solution of I (0.0013 M) in a quartz cubic (1 cm in length, 4 ml in volume) was irradiated at room temperature with use of a 500 W high pressure Hg arc lamp. Toshiba UV D25 and UV 35 filters were used for direct irradiation. Toshiba filters VY 42, VY 43, VY 48 and VY 49 were used for benzil, benzanthraquinone, erythrosine and rose bengal sensitization, respectively. The reaction was also monitored by the change of UV spectrum except for some sensitized experiments, the irradiation time required to reach the complete disappearance of I being used as a measure of the reaction rate. After the reaction was complete, the solvent was removed under reduced pressure and 0.5 ml of benzene was added. The concentrated benzene solution was used for product analysis. Quantitative analysis was performed by glc (Carbowax 20 M on Chromosorb W, 80—100 mesh, 2 m, 240 °C). In almost all experiments, only intramolecular cyclization products were obtained, but in the case of benzil sensitization and piperylene addition, some by-products from the sensitizer or the quencher were formed. In the dye sensitized experiments, the sensitizers themselves were slightly photo-bleached.

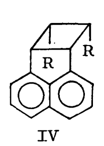
Results and Discussion

Photocyclization Reaction. We found that the direct and sensitized photochemical reaction of I in solution underwent *cis, trans* isomerization with concomitant cyclization and ultimately led exclusively to the formation of cyclized products. Glc analysis of the final products showed the formation of three intramolecular cyclized products, and no intermolecular adducts were formed. Six structures II—VII were considered for the cyclized products. The main product was identified to be VI by comparing its spectral data with those of II and III which were obtained from the photoadduct of maleic anhydride and acenaphthylene.[4] One of the two minor products was identified to be II by comparing its glc retention time with that of an authentic sample of II. The other minor product, the first eluent in glc, was presumed to be V or VII, since the crossed adducts (intramolecular head-to-tail adducts, V—VII) were expected to be eluted more rapidly than the straight adducts (intramolecular head-to-head adducts, II—IV). Photoproducts mixture obtained from the methanol solution, in which this minor product was involved in *ca.* 20% yield, gave almost the same NMR spectrum as that of pure VI, but the peak ratio of *exo*- and *endo*-carbomethoxy protons at δ 3.79 and 3.14 respectively (Table 1) was about 1: 1.4. The NMR spectrum suggested the inclusion of the crossed adduct having *endo*-carbomethoxy group except VI. Hence, the minor product unidentified was determined to be VII, which has two *endo*-carbomethoxy groups.

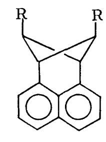

I

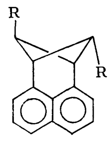

II


III


IV

R = CO_2Me


V


VI

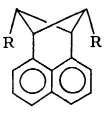

VII

TABLE 2. RESULTS OF PRODUCT ANALYSIS[a)]

Solvent	Condition	Yields of products (%) VII	VI	II
Cyclohexane	Degassed	9	86	5
	N_2 Saturated	11	81	8
	Aerated	10	75	15
	O_2 Saturated	8	77	16
	Benzil Sensitized	10	85	5
	Benzanthraquinone Sensitized	10	86	4
	Piperylene Added	9	84	7
Methanol	N_2 Saturated	21	76	3
	Erythrosine Sensitized	19	79	2
	Rose Bengal Sensitized	17	80	3
	Rose Bengal Added	21	75	4
n-Propyl Bromide	Aerated	16	79	4
	N_2 Saturated	14	84	2

a) Sensitized or quenching experiments were performed in degassed or N_2 saturated solutions.

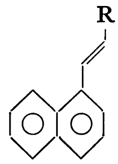
The results of the photochemical reaction in an analytical scale are summarized in Table 2. The product ratio in direct irradiation was almost the same as that of sensitized reaction. It is seen that benzil (the triplet energy, E_T=54 kcal/mol),[5] benz[*a*]anthraquinone (E_T=47 kcal/mol)[6] and erythrosine (E_T 42 kcal/mol)[7] are efficient sensitizers, while rose bengal (E_T=39 kcal/mol)[7] is a very inefficient one, acting rather as an effective quencher, whereas piperylene (E_T=47—49 kcal/mol)[8] shows no quenching action. The triplet energy of I was thus estimated to be *ca.* 40 kcal/mol, though the phosphorescence of I was not observed in the measurement in EPA solution at 77 K. In the presence of oxygen, II slightly increased and VI decreased complementarily, the reaction rate being suppressed at the same time. Decrease in the rate may be caused by triplet quenching since the fluorescence of I was scarcely quenched by oxygen. Dependence of product ratio on solvents was slightly seen. A larger amount of VII seemed to be produced in the more polar solvents. In addition, in *n*-propyl bromide solution, the reaction rate was greatly accelerated probably by an external heavy atom effect.

The results suggest that the cyclization reaction proceeds predominantly through the triplet state of I, although from the oxygen addition experiments, II is considered to be formed from the singlet state to some extent.

Our results for the cyclization of I, in addition to those of Meinwald and Young[9] for 1,8-divinylnaphthalene (R=H in I) and 1,8-distyrylnaphthalene (R=Ph in I) seem to suggest that the intramolecular photocyclization of naphthalene-1,8-diolefins generally leads to crossed adducts. Interestingly, the photochemical tendency of naphthalene-1,8-diolefins to give predominantly crossed adducts differs from the well-known property of 1,6-dienes but is similar to that of 1,5-dienes,[10] although the present diolefins are 1,6-dienes.

We did not detect V in the photochemical reaction of I, but Meinwald and Young[9] found the product corresponding to V to be one of the main products in the photocyclization of distyrylnaphthalene. Since the reactive conformation should be common to the two diolefins, the difference in stereoselectivity might be due to different excited states or different intermediates, although they have not discussed what kind of excited state contributes to the reaction of distyrylnaphthalene.

Quantum Yields of Geometrical Isomerization, Cyclization and Fluorescence. Since attempts to isolate the geometrical isomers of I (*cis*, *trans* isomer, I′; *cis*, *cis* isomer, I″) were unsuccessful, an accurate quantum yield for the isomerization could not be determined. However, as a measure of photoreactivity under various conditions, we estimated the quantum yields for isomerization and cyclization from the disappearance rate of I followed by the UV spectral changes. The absorption spectrum changed with irradiation time on exciting with 365 nm light as follows. At first, the peak at 332 nm rapidly decreased and the shoulder peak at 265 nm disappeared, the cycloadducts even at this stage being detected by glc. Decrease of the 332 nm peak then became slow with concomitant appearance of adduct peaks (Table 1), and finally I was completely converted into adducts by prolonged irradiation. The change of spectrum with irradiation time is shown in Fig. 1. The spectral behavior of I would be explained by considering that the rapid decrease in the first stage is due to the superposition of rapid isomerization and considerably slow cyclization of I, and the slow decrease in the second stage is due only to cyclization of the *pseudo*-photostationary mixture of I and I′ (and I″) formed at first. In fact, *trans*-methyl-1-naphthaleneacrylate (VIII), where only geometrical isomerization is possible, showed a spectral change similar to that of I in the first stage. Namely, on exciting with 350 nm light, the peak of VIII at 318 nm decreased rapidly with irradiation time and reached a photostationary state, as shown in Fig. 2.



R = CO_2Me

VIII

The plot of the optical density of I at λ_{max} (332 nm) against irradiation time (Fig. 3) showed two approximately linear parts corresponding to the two stages of

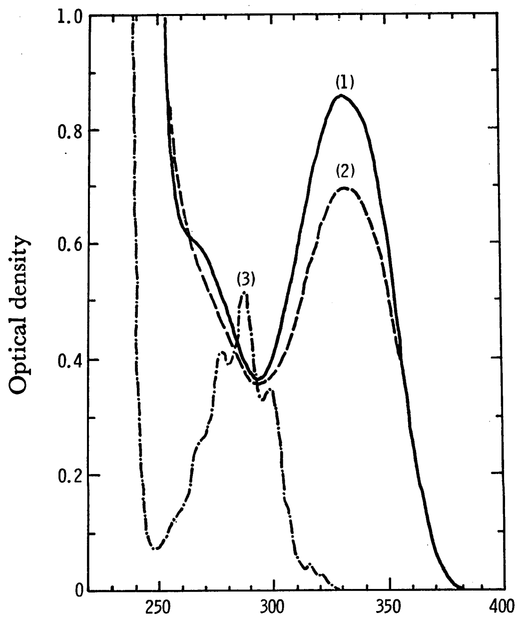


Fig. 1. UV absorption spectral change of (I) in cyclohexane solution with irradiation time on exciting 365 nm light.
(1); initial spectrum, (2); intermediate spectrum (*pseudo*-photostationary state between I and I′ (and I″), (3); final spectrum (intramolecular cycloadducts).

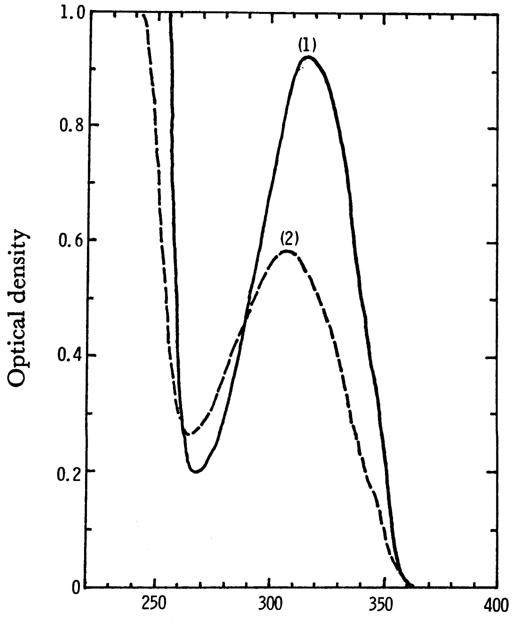


Fig. 2. UV absorption spectra change of VIII in cyclohexane solution with irradiation time on exciting 350 nm light.
(1); initial spectrum, (2); final spectrum (photostationary state between *trans*- and *cis*-isomer of VIII).

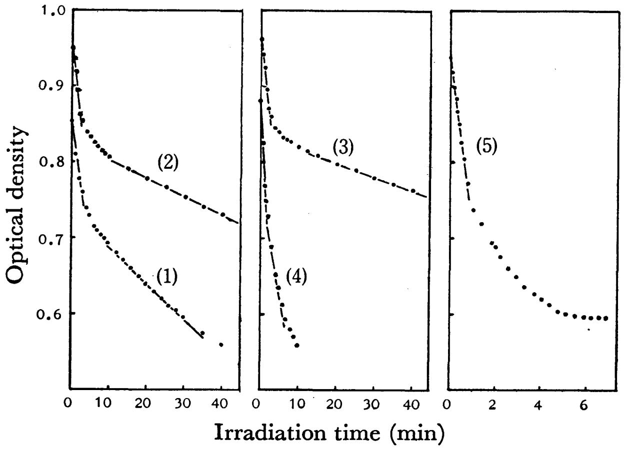


Fig. 3. The change of optical density of I and VIII at λ_{max} with irradiation time.
(1), (2), (3), and (4) denote respectively the conditions: degassed, N_2 saturated, O_2 saturated cyclohexane solution and N_2 saturated *n*-propyl bromide solution, in the change of (I) at 322 nm on exciting 365 nm light.
(5) denotes the change of VIII in N_2 saturated cyclohexane solution at 318 nm on exciting 350 nm light, when the intensity of the exciting light is normalized to that of 365 nm light.

the spectral change in small conversions. From the slope of the plot, we determined the quantum yields for isomerization and cyclization* without any corrections, since the absorptivity of I at 365 nm (exciting light) was almost constant in small conversions and the cyclized products did not absorb the exciting light. The results are given in Table 3 together with those of VIII. Both quantum yields for isomerization and cyclization decrease slightly with the addition of oxygen and increase remarkably on using *n*-propyl bromide as a heavy atom solvent. The quantum yield of fluorescence of I under various conditions is also summarized in Table 3. Anthracene was used as a fluorescence standard (the quantum yield is 0.30),[11] since the fluorescence peak of I is at about 410 nm. The yield of fluorescence in the heavy atom solvent is reduced to about one-half the yield in cyclohexane, although it is not affected by oxygen. The results on the quantum yield measurement also suggest that the photochemical reaction of I proceeds mainly through the triplet state of I.

Table 3. Quantum yields of reactions and fluorescence[a)]

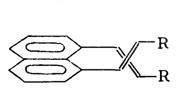
		φ_i	φ_c	φ_f
I/Cyclohexane	Degassed	4.6×10^{-2}	0.57×10^{-2}	—
	N_2 saturated	4.5×10^{-2}	0.28×10^{-2}	3.5×10^{-2}
	O_2 saturated	4.3×10^{-2}	0.20×10^{-2}	3.5×10^{-2}
VIII/Cyclohexane	N_2 saturated	28×10^{-2}	—	—
I/*n*-PrBr	N_2 saturated	5.9×10^{-2}	2.5×10^{-2}	1.9×10^{-2}

a) φ_i, φ_c and φ_f denote the quantum yields of isomerization, cyclization and fluorescence, respectively. Potassium ferrioxalate is used as a chemical actinometer.

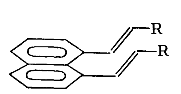
Photochemical reaction of a fairly concentrated solution of I (*ca.* 0.1 M $CDCl_3$ solution) was studied by following NMR spectral change with irradiation time (irradiated with 365 nm light). Rapid isomerization of I to I′ was confirmed by an appearance of NMR peaks based on *cis*-olefinic group (δ 6.16, doublet, J= 12.6 Hz, *cis*-vinyl H, another doublet peak is hidden in the peaks of aromatic protons; 3.59, methoxy H). Simultaneous appearance of peaks based on *trans*-vinyl protons (δ 6.24, 8.62, pair of doublet, J=15.4 Hz) differing from those of I (δ 6.29, 8.37, J=15.4 Hz) and lack of the peaks of intramolecular cyclization products on irradiating for a long time suggest that photochemical reaction of concentrated solution of I would be geometrical isomerization and intermolecular dimerization. Detailed analysis of dimerized products was not performed.

Since the predominant formation of VI is almost independent of irradiation time, namely independent of whether the *pseudo*-photostationary state between I and I′ (and I″) is attained or not, the main product from I′ is expected to be the same VI as that from I. The photocyclization of I and I′ greatly resembles that of 1,5-dienes. Scheffer and Wostradowski[12)] reported that acetone sensitized photochemical reaction of *trans, trans*- and *trans,cis*-isomers of dimethyl octa-2,6-diene-1,8-dioate, $(-CH_2-CH=CH-CO_2Me)_2$, leads to *cis, trans* isomerization with concomitant formation of the cyclized products corresponding to VI and VII in the same 65: 35 ratio.

Reaction Mechanism. The predominant formation of crossed adducts in photochemical reaction of naphthalene-1,8-diolefins irrespective of their substituents (H, Ph or CO_2Me) suggests that ground-state conformations contribute strongly to the course of cyclization. Examination of molecular models suggests that two ground-state conformers, I-A and I-S, are stable sterically, where two olefinic groups rotate to a considerable extent from naphthalene plane due to their steric inhibition.



I-A



I-S

R = CO_2Me

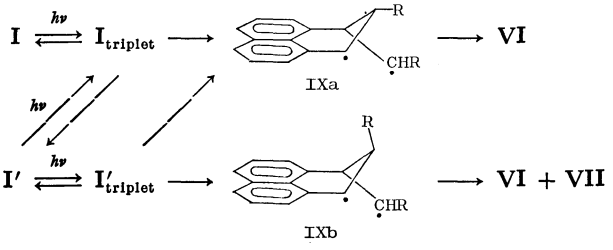
From *anti* conformer I-A, only crossed adducts formation would be possible, and both crossed and straight adducts could be produced from *syn* conformer I-S. However, I-S is less favorable than I-A due to larger nonbonding interactions between two olefinic groups. Hence, the contribution of I-S to the crossed adducts formation is considered to be less important.

From the observations that (1) stereochemistry of crossed products VI and VII cannot be explained by the concerted mechanism, (2) isomerization and cyclization take place concomitantly through the triplet state and (3) both geometrical isomers I and I′ yield the same main product VI, we propose the reaction mechanism for the formation of crossed adducts as

---

* Since the contribution of I″ is negligible, at least in small conversions, isomerization is that from I to I′, and cyclization is that of a *pseudo*-photostationary mixture of I and I′ (and I″).

follows, assuming intermediate 1,4-biradicals from *anti* conformers, I-A and I′-A.

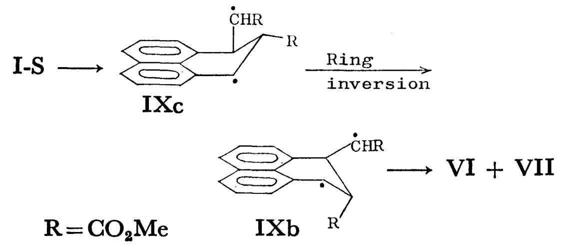


R = CO₂Me

The back reactions of the biradicals to the ground state or the triplet state of I or I′ are omitted to avoid complexity of the scheme.

Sole biradical IXa could be formed from I-A, but formation of two biradicals IXa and IXb would be possible from I′-A. Since the spin of the biradicals is expected still to be parallel, spin inversion is necessary for ring closure. The biradicals would be long-lived enough to change into the most stable conformation. For ring closure of biradical IXa, rapid rotation of the terminal carbomethoxy methine site into the satble conformation, where the interaction with an *equatrial* carbomethoxy group is minimized, would lead to preferential formation of main product VI. If the lifetime of the biradical is comparable to the rotational rate of terminal site, V and VI would be produced from the biradical. Cyclization of distyrylnaphthalene would be the case, if the reaction proceeds through the biradical corresponding to IXa. Biradical IXb would yield VI and minor product VII for ring closure.

Formation of VII from less-favored conformer I-S would be possible, if ring inversion of biradical IXc is considered as follows.



R = CO₂Me

However, considering the reduced importance of I-S and the formation of most products from *pseudo*-photostationary mixture of I and I′ (and I″), most of minor product VII would be formed from I′ through the biradical IXb. Although details are not available since neither I′ nor I″ is isolated, the observed solvent effect (increase of VII in polar solvents) could be interpreted, if the portion of I′ in the *pseudo*-stationary mixture increases in polar solvents.

Formation of straight adduct II would be related to less-favored conformer I-S. In fact, this is supported by the predominant formation of straight adducts in the photochemical reaction of the compound fixed to *syn* conformer, 1,7-(1′,8′-naphthalene)-1,6-heptadienes ($RR=(-CH_2-)_3$ in I and I″). However, a biradical mechanism would be unreasonable for the formation of II, since straight adducts other than II are not detected. Two possible biradicals, IXd and IXe, from the conformer I-S are expected to give at least two straight adducts for ring closure with nearly equivalent probability.[14]

IXd IXe

R = CO₂Me

If the observed oxygen effect (increase of II in the presence of oxygen) is considered, a concerted mechanism from singlet state would be more reasonable than a biradical one for the formation of another minor product II, although the formation of a small amount of II by triplet sensitization cannot be explained in a satisfactory manner.

Increase in cyclization efficiency by *n*-propyl bromide is much greater than that in isomerization efficiency (Table 3), even if experimental errors are considered. This suggests that the intermediate biradicals formed from the triplet state of I must be again affected by the heavy atom solvent, since the enhancement of triplet yield by heavy atom effect should increase the quantum yields of cyclization and isomerization at the same ratio. The additional heavy atom effect should cause an acceleration of spin-inversion rate of biradicals, resulting in an increase in the rate of their ring-closure to cyclized products.

Irradiation in Rigid Matrix and in Solid State. Prolonged irradiation of I in EPA rigid glassy solution at 77 K did not bring about any UV spectral changes. The unreactivity would be attributed to the reduced triplet-yield of I, since the fluorescence yield increases remarkably under these conditions (φ_f=*ca.* 0.5).

When I is irradiated in a crystalline state, the IR absorption peaks based on the olefinic groups of I disappear completely but the amount of cyclization products is negligible. Although further detailed analysis of the products was not performed, polymeric substances could be produced.

The authors are grateful to Prof. Makoto Takahasi, the University of Tokyo, for his valuable discussions, and to Mr. Kazuo Sato for his assistance in experiments.

References

1) G. M. J. Schmidt, *J. Chem. Soc.*, **1964**, 2014.

2) F. W. Lichtenthaler and A. El-Scherbiney, *Chem. Ber.*, **101**, 1799 (1968).

3) O. Isler, H. Gutmann, M. Montavon, R. Rüegg, G. Ryser, and P. Zeller, *Helv. Chim. Acta*, **40**, 1242 (1957).

4) W. Hartmann and H. G. Heine, *Angew. Chem. Int. Ed. Engl.*, **10**, 272 (1971), J. E. Shields, D. Gavrilovic, J. Kopecky, W. Hartmann, and H. G. Heine, *J. Org. Chem.*, **39**, 515 (1974).

5) N. J. Turro, "Molecular Photochemistry," Benjamin, New York (1967), p. 132.

6) The triplet energy was estimated from the phosphorescence spectrum.

7) K. Gollnick, "Advances in Photochemistry," **6**, p. 14, John Wiley & Sons, Inc. (1968).

8) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

9) J. Meinwald and J. W. Young, *J. Amer. Chem. Soc.*, **93**,

725 (1971).

10) J. J. Bloomfield and D. C. Owsley, *Tetrahedron Lett.*, **21**, 1795 (1973) and references cited therein.

11) J. B. Birks, "Photophysics of Aromatic Molecules," Wiley Interscience, (1970), p. 251.

12) J. R. Scheffer and R. A. Wostradowski, *Chem. Commun.*, **1971**, 144 and *J. Org. Chem.*, **37**, 4317 (1972).

13) S. F. Nelsen and J. P. Gillespie, *J. Amer. Chem. Soc.*, **95**, 2940 (1973).

14) R. M. Pagni and C. R. Watson, Jr., *ibid.*, **96**, 2291 (1974); R. M. Pagni, C. R. Watson, Jr., J. E. Bloor, and J. R. Dodd, *ibid.*, **96**, 4064 (1974).