

INTRAMOLECULAR ALKENE CYCLOADDITION VIA EXCITED DONOR-ACCEPTOR COMPLEXES

GUILFORD JONES II, WILLIAM G. BECKER and SHEAU-HWA CHIANG

Department of Chemistry, Boston University, 685 Commonwealth Avenue, Boston, MA 02215 (U.S.A.)

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Summary

The intramolecular photoaddition of 1,4,4a,5,8,8a-hexahydro-1,4,5,8-*endo,endo*-dimethanonaphthalene to provide a cage isomer is reported. The internal addition of non-conjugated alkene moieties is induced on quenching the fluorescence of electron acceptors or by irradiation of ground state charge transfer (CT) complexes of the diene. Quantum efficiencies for rearrangement are generally high and even exceed 1.0 for irradiation in a polar solvent, indicative of a chain mechanism involving radical ions. A novel dependence of quantum yield on the excitation wavelength for irradiation of CT complexes was observed and is ascribed to dissociation of the Franck-Condon CT state. The triplet sensitized isomerization which proceeds with unit quantum efficiency is also reported. The rearrangement of the electron donor diene is compared with the well-known isomerization of norbornadiene.

1. Introduction

The photochemical cycloaddition of alkenes has been identified for some time as the principal means of obtaining cyclobutane ring systems [1]. The methods for photocyclodimerization vary widely and include direct and triplet sensitized reactions [2] and electron transfer processes involving radical ion intermediates [1, 3]. The latter ionic mechanisms are of particular interest in view of their quantum chain characteristics and the potential for efficient olefin polymerization [4].

Intramolecular variations of alkene photocycloaddition are best known in terms of the synthesis of novel polycyclic ring systems [2, 5]. Other strategies involve the deployment of such reactions for photochemical energy storage [6], an example of which is the rearrangement of norbornadiene to quadricyclene ($1 \rightarrow 2$) [7 - 9] (Fig. 1). We have for some time had an interest in developing new methods of sensitization for reactions of this type [10]. Our attention has been most recently focused on electron donor-

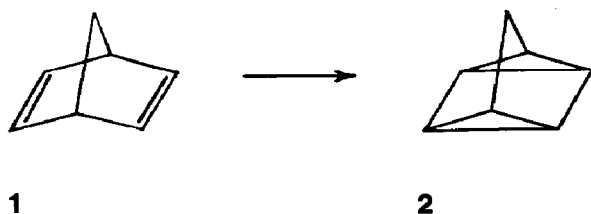


Fig. 1.

acceptor complexes of isomerization substrates capable of photochemically induced ring opening or ring closure [11 - 14].

An interesting relative of norbornadiene (1) is 1,4,4a,5,8,8a-hexahydro-1,4,5,8-*endo,endo*-dimethanonaphthalene (3). Through-space and through-bond interactions of alkene moieties are pronounced for this hydrocarbon, resulting in an especially low ionization potential ($IP_v = 8.1$ eV) [15]. Thus diene 3 is an attractive candidate for photochemical reactions requiring participation as an electron donor. Of the 1-2 pair, the cage isomer is the more capable donor (for 2, $IP_v = 8.3$ eV [16]) so that interaction with electron acceptor sensitizing agents brings about only 2 \rightarrow 1 rearrangement [9, 13].

We report here the first detailed study of the photochemistry of 3 (the photochemistry of isodrin, the chlorinated derivative from which 3 was prepared, has been reported elsewhere [17]) and note the following interesting features: (1) generally high efficiencies for 3 \rightarrow 4 isomerization (Fig. 2) using acceptor sensitizers under a variety of irradiation conditions in both polar and non-polar media; (2) a quantum chain reaction for rearrangement in a polar solvent; (3) photolysis involving irradiation of ground state (charge transfer (CT)) complexes of 3, for which an unusual wavelength dependence of quantum yield is important.

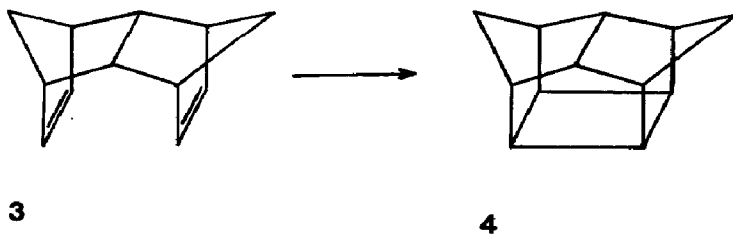


Fig. 2.

2. Results and discussion

2.1. Isomerization via fluorescence quenching

The fluorescence of the electron acceptor sensitizers, 9,10-dicyanoanthracene (DCA), 1-cyanonaphthalene (CN) and 1,2,4,5-tetracyanobenzene (TCNB), was quenched by the addition of moderate concentrations of 3.

TABLE 1

Fluorescence quenching data and quantum yields of isomerization sensitized by acceptor fluorophores^a

Acceptor	Solvent	$k_q\tau^b$ (M ⁻¹)	k_q ($\times 10^{-9}$ M ⁻¹ s ⁻¹)	i/s^c (M ⁻¹)	ϕ
DCA (0.0001 M)	Cyclohexane	86.1	2.1	67.8	(0.14) ^d
CN (0.004 M)	Cyclohexane	55.6	5.7	48.5	(1.08) ^d
CN (0.057 M)	Acetonitrile	81.7	9.2		8.4 ^e
TCNB (0.057 M)	Acetonitrile	185	13		3.0 ^e

^a For runs in cyclohexane the quantum yields were obtained from parallel irradiation in a Rayonet chamber reactor with RUL 300 (CN) and RUL 3500 (DCA) lamps; in other runs a monochromator apparatus (313 nm) was used.

^b Slopes of Stern–Volmer plots for fluorescence quenching by 3.

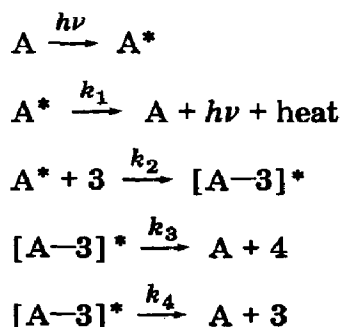
^c Intercept-to-slope ratios from double reciprocal quantum yield–concentration plots.

^d Limiting quantum efficiencies.

^e Quantum efficiency at about 90% quenching of sensitizer fluorescence.

Stern–Volmer plots yielded values for $k_q\tau$ (Table 1) and, using lifetimes for the sensitizers from the literature [18], values for the bimolecular quenching constants k_q were obtained. Under no conditions was the emission from an exciplex of acceptors and 3 observed.

Irradiation of the fluorophores in the presence of 3 resulted in efficient isomerization to 4 (more than 90% chemical yield). For DCA- and CN-sensitized photolysis in cyclohexane solution, the concentration dependence of quantum yields was determined. Linear plots of $1/\phi$ versus $1/[3]$ were obtained, consistent with a mechanism involving sensitizer singlets as the activating species [11]. A minimum number of steps for such a mechanism is shown in the following scheme:



The double reciprocal relationship

$$\frac{1}{\phi} = \frac{1}{P} + \frac{Pk_1}{k_2[3]} \quad (1)$$

where $P = k_3/(k_3 + k_4)$ results in an identity of the intercept-to-slope ratios ($i/s = k_2/k_1$) with the Stern–Volmer quenching constants $k_q\tau$ (note the agreement in Table 1).

The quenching of CN and TCNB fluorescence in acetonitrile resulted in quantum efficiencies for isomerization well in excess of unity. A concentration dependence more complex than that given above was expected based on the probability of a radical ion chain reaction [19] (*vide infra*).

2.2. Isomerization on irradiation of charge transfer complexes

Solutions of 3 and the electron acceptors fumaronitrile (FUM) and diethyl-1,2-dicyanofumarate (DDF) ($E_{1/2}(\text{red})$ is -1.29 V (SCE) for FUM [20] and -0.32 V (SCE) for DDF [21], both in acetonitrile solutions) displayed new absorption bands (Table 2) which depended on the strength of the acceptor and which were assigned to relatively weak ($K_{CT} \leq 0.1 \text{ M}^{-1}$) bimolecular CT complexes [22] (saturation criteria [23] necessary to determine reliable formation constants and extinction coefficients of absorbance could not be met). Irradiation of the CT bands using a monochromator-light pipe-quantum counter apparatus [24] resulted again in clean conversion to 4. Quantum yields varied greatly according to the polarity of the solvent and the irradiation wavelength (Table 2).

TABLE 2

Quantum yields for 3 \rightarrow 4 isomerization via charge transfer complexes^a

Acceptor	Solvent	CT absorption λ_{max} (nm)	Excitation wavelength ^b (nm)	ϕ
FUM	Acetonitrile	290	313	0.30
FUM	Acetonitrile	290	334	0.13
FUM	Dichloromethane	310	313	0.054
DDF	Dichloromethane	424	436	0.026
DDF	Acetonitrile	390	366	6.2
DDF	Acetonitrile	390	405	0.10

^a Nitrogen-purged solutions (25 °C): [3] = 0.055 M, [FUM] = 0.6 M, [DDF] = 0.20 M.

^b Monochromator-quantum counter apparatus [24].

2.3. Isomerization with triplet sensitizers

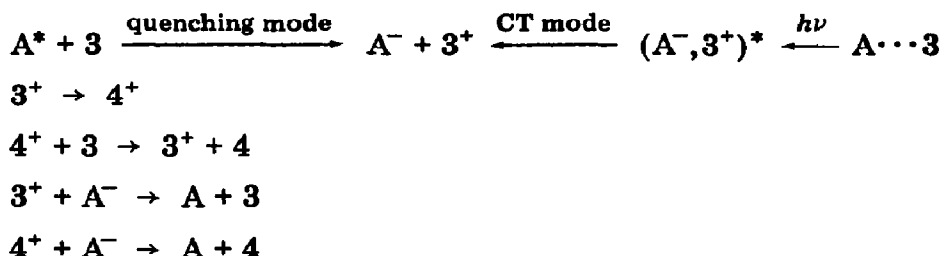
For comparison with the results for electron acceptor sensitizers, a series of classical triplet energy transfer agents was examined. Nitrogen-purged samples of 3 (0.10 M in benzene) were employed for parallel irradiation in a Rayonet reactor (RUL 3000 lamps, Pyrex tubes). Acetone (80), benzophenone (69), Michler's ketone (65), phenanthrene (61) and naphthalene (61) were about equally effective in driving the reaction 3 \rightarrow 4, whereas chrysene (57), biacetyl (56) and benzil (53) were relatively ineffective (the numbers in brackets are the triplet energies in kilocalories per mole taken from ref. 25). The absolute quantum efficiency of isomerization using benzophenone as the sensitizer was determined using the monochromator apparatus ($\phi = 1.00 \pm 0.05$; 4% conversion at 366 nm and 25 °C).

3. Discussion

The isomerization $3 \rightarrow 4$ is highly favorable under a variety of photochemical conditions. The strong interaction of π moieties for **3** is dramatized by the results using triplet sensitizers which indicate a triplet energy for **3** ($E_T \approx 58 \text{ kcal mol}^{-1}$) well below that estimated for **1** ($E_T = 69 \text{ kcal mol}^{-1}$ [26]). Unlike the behavior of **1**, however, efficient rearrangement of **3** is also observed on interaction with electron acceptors (the isomerization of copper(I) complexes of **1** is well known [8]).

Four different characteristics for donor-acceptor sensitization are readily distinguished by the quantum yield data. For singlet quenching in cyclohexane where electron transfer to an acceptor sensitizer is least likely, efficiencies are high but do not exceed 1.0 ($\pm 10\%$) at their limiting values. However, yields are dependent on properties of the sensitizer (DCA or CN), consistent with a mechanism involving exciplexes (*i.e.* $[A-3]^*$) which induce ring closure through polarization of **3** [13]. Thus, withdrawal of electron density from the highest occupied molecular orbital of **3** [15] through collision with the sensitizer results in an increase in transannular bond order and passage along a reaction coordinate to **4**.

For isomerization via fluorescence quenching in acetonitrile, a quantum chain process is dominant. The reaction is analogous to the chain reaction which is important for vinyl carbazoles and similar systems which cyclodimerize in the presence of acceptors [1]. A mechanism involving formation and propagation of radical cations [27][†] is shown in the scheme



which is analogous to the sequence of steps proposed for the ring opening of hexamethyl(Dewar benzene) on fluorescence quenching in a polar solvent [19]. The intervention of discrete radical cations for **3** and **4** is supported by chemically induced dynamic nuclear polarization results for the 1-2 system [28]. Furthermore the net reaction for propagation steps $3 \rightarrow 4$ is apparently exothermic since the isomerization can be carried out with acid catalysis [29].

[†]The structures of the radical cations of **3** and **4** are not yet known. Presumably, the former do not display a transannular bond between π moieties, whereas one single bond has been completed for 4^+ . Ring-closed radical cations have been proposed for vinyl-carbazole adducts where groups which readily accommodate radical and cationic sites are appended [27].

The differences in behavior for the CT systems are striking. In a less-polar solvent (dichloromethane, $\epsilon = 8.9$) the quantum yield of rearrangement is diminishingly small. This result can be accounted for if the excited CT state (unlike the exciplex) is a true contact ion pair [30]. If dissociation of the ion pair is prohibited in a medium of low polarity, rapid decay involving only back electron transfer is dominant [12]. Separation of ions and propagation of radical ion chains is probable for CT excitation in a polar solvent (acetonitrile, $\epsilon = 38.8$) [31]. The novel feature of this mechanism is the wavelength dependence which has been observed for other CT-induced isomerizations (hexamethyl(Dewar benzene) [12] and quadricyclene [13] ring opening). This dependence has been associated with excitation to higher vibrational levels within the CT band and extension of the intermolecular ionic bond stretch. This vibration permits passage from the initial contact ion pair to a solvent-separated species which is allowed to rearrange in competition with recombination and diffusion into bulk solution (for recent discussions of the distinction between contact and solvent-separated ion pairs for photochemical donor-acceptor systems see ref. 31). This wavelength effect may indeed be important for the initiation step in "charge transfer photopolymerization" [4].

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References

- 1 L. J. Kricka and A. Ledwith, *Synthesis*, (1974) 539.
- 2 W. L. Dilling, *Chem. Rev.*, 66 (1966) 373.
- 3 A. Yamamoto, M. Irie, Y. Yamamoto and K. Hayashi, *J. Chem. Soc., Perkin Trans. II*, (1979) 1517.
S. Farid and S. E. Shealer, *J. Chem. Soc., Chem. Commun.*, (1973) 77.
- 4 Y. Shirota, T. Tomikawa, T. Nogami, K. Tada, N. Yamamoto, H. Tsubomura and H. Mikawa, *Bull. Chem. Soc. Jpn.*, 47 (1974) 2099, and references cited therein.
- 5 P. E. Eaton, *Acc. Chem. Res.*, 1 (1968) 50.
- 6 H.-D. Scharf, H. Fleischauer, H. Leismann, I. Ressler, W. Schleker and R. Weitz, *Angew. Chem. Int. Edn. Engl.*, 18 (1979) 652.
G. Jones II, in R. R. Hautala, R. B. King and C. Kutal (eds.), *Solar Energy: Chemical Conversion and Storage*, Humana, Boston, MA, 1979.
G. Jones II, T. E. Reinhardt and W. R. Bergmark, *Sol. Energy*, 20 (1978) 241.
- 7 R. R. Hautala, R. B. King and C. Kutal, in R. R. Hautala, R. B. King and C. Kutal (eds.), *Solar Energy: Chemical Conversion and Storage*, Humana, Boston, MA, 1979.
- 8 D. P. Schwendiman and C. Kutal, *J. Am. Chem. Soc.*, 99 (1977) 5677.

- 9 A. J. G. Barwise, A. A. Gorman, R. L. Leyland, P. G. Smith and M. A. J. Rogers, *J. Am. Chem. Soc.*, **100** (1978) 1814.
- 10 G. Jones II, S.-H. Chiang and P. T. Xuan, *J. Photochem.*, **10** (1979) 1.
- 11 G. Jones II and S.-H. Chiang, *Tetrahedron*, **37** (1981) 3397.
- 12 G. Jones II and W. G. Becker, *J. Am. Chem. Soc.*, **103** (1981) 4630.
- 13 G. Jones II, S.-H. Chiang, W. G. Becker and D. P. Greenberg, *J. Chem. Soc., Chem. Commun.*, (1980) 681.
- 14 G. Jones II and W. G. Becker, *Chem. Phys. Lett.*, **85** (1982) 271.
- 15 H.-D. Marin and R. Schwesinger, *Chem. Ber.*, **107** (1974) 3143.
- 16 H.-D. Martin, C. Heller, E. Haselbach and Z. Lanyjova, *Helv. Chim. Acta*, **57** (1974) 465.
- 17 R. C. Cookson and E. Crundwell, *Chem. Ind.*, (1958) 1004.
J. K. Stille and D. R. Witherell, *J. Am. Chem. Soc.*, **86** (1964) 2188.
- 18 D. R. Arnold and A. J. Maroulis, *J. Am. Chem. Soc.*, **98** (1976) 5931.
W. R. Ware, J. D. Holmes and D. A. Arnold, *J. Am. Chem. Soc.*, **96** (1974) 7861.
G. Jones II and W. G. Becker, unpublished results, 1981.
- 19 T. R. Evans, R. W. Wake and M. M. Sifrain, *Tetrahedron Lett.*, (1973) 701.
- 20 P. C. Wong and D. R. Arnold, *Can. J. Chem.*, **57** (1979) 1037.
- 21 G. Jones II and W. G. Becker, submitted for publication.
- 22 R. Foster, *Organic Charge-transfer Complexes*, Academic Press, New York, 1969.
- 23 D. A. Deranleau, *J. Am. Chem. Soc.*, **91** (1969) 4044, 4050.
- 24 W. R. Bergmark, G. Jones II, T. E. Reinhardt and A. M. Halpern, *J. Am. Chem. Soc.*, **100** (1978) 6665.
- 25 S. L. Murov, *Handbook of Photochemistry*, Dekker, New York, 1973.
- 26 R. R. Hautala, J. Little and E. M. Sweet, *Sol. Energy*, **19** (1977) 503.
- 27 A. Ledwith, *Acc. Chem. Res.*, **5** (1972) 133.
- 28 H. D. Roth, M. L. M. Schilling and G. Jones II, *J. Am. Chem. Soc.*, **103** (1981) 1246.
- 29 P. Bruck, D. Thompson and S. Winstein, *Chem. Ind.*, (1960) 590.
- 30 S. Fukuzumi and J. K. Kochi, *J. Org. Chem.*, **46** (1981) 4116, and references cited therein.
- 31 H. Mauhara and N. Mataga, *Acc. Chem. Res.*, **14** (1981) 312.
J. D. Simon and K. S. Peters, *J. Am. Chem. Soc.*, **103** (1981) 6403.