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light source, and the progress of the reaction was followed by NMR. In no case did the presence of trap influence the rate of benzene formation. Photolysis of 1,2-dihydrophthalic anhydride (10 mg in 100 μL of THF) was conducted in the same fashion and found to produce benzene considerably faster than the decomposition of **24**. The addition of O_2 to the photolysis reactions of **24** produced little or no effect, while the use of benzene as the solvent considerably inhibited the rate of decomposition. Irradiation of **24** in an ESR cavity afforded no radical signal.

Synthesis of 1-Methyl-1-(trimethylsilyl)sila-α-pyran (35). (A) (*Z*)-1-(2-Heptamethyltrisilanyl)-4-methoxybut-1-yn-3-ene (33). Compound **33** was prepared in an identical fashion as for **3** except that (2-chloro)-heptamethyltrisilane was employed in the coupling: 67%; pb 89 °C (0.3 mm); NMR ($DCCl_3$) δ 0.06 (s, 18 H), 0.12 (s, 3 H), 3.65 (s, 3 H), 4.34 (d, 1 H, J = 8 Hz), 6.05 (d, 1 H, J = 8 Hz); IR (neat) 2975, 2130, 1630, 1245 cm^{-1}; mass spectrum, *m/e* (% relative intensity) 270 (9), 255 (15), 167 (17), 141 (24), 73 (100); calcd for $C_{12}H_{26}Si_3O$ *m/e* 270.12916, measured *m/e* 270.12928.

(B) (*Z,Z*)-4-Methoxy-1-(2-heptamethyltrisilanyl)-1,3-butadiene (34). Diene **34** was prepared by DIBAL reduction of **33** in an identical manner with that employed in the synthesis of **4**: 48%, bp 73 °C (0.1 mm); NMR ($DCCl_3$) δ 0.13 (s, 9 H), 0.22 (s, 3 H), 3.61 (s, 3 H), 5.01 (d of d of d, 1 H, J = 12, 6, and <1 Hz), 5.26 (d of t, J = 13 and 1 Hz), 5.79 (d of t, 1 H, J = 6, 1, and <1 Hz), 7.01 (d of d of d, 1 H); IR (neat) 2800, 1640, 1250, 1115 cm^{-1}; mass spectrum, *m/e* (% relative intensity) 272 (0.9), 257 (2), 169 (16), 131 (25), 89 (30), 73 (100); calcd for $C_{12}H_{28}OSi_3$ *m/e* 272.14481, measured *m/e* 272.14570.

(C) 1-Methyl-1-(trimethylsilyl)sila-α-pyran (35). The procedure used was identical with that described for the pyrolysis of **4**. Thus, pyrolysis of **34** afforded two major products, tetramethylsilane (GC/MS identification only) and **35**, which was isolated by preparative GC (12 ft, 15% OV101 on Chromosorb W): 46%; NMR (CCl_4) δ 0.09 (s, 9 H), 0.30 (s, 3 H), 4.89 (d of t, 1 H, J = 7, 7, and 1 Hz), 5.32 (d of t, 1 H, J = 15, 1, and 1 Hz), 6.50 (m, 2 H); IR (neat), 3050, 2960, 1610, 1255 cm^{-1}; mass spectrum, *m/e* (% relative intensity) 184 (15), 169 (58), 143 (71), 111 (89), 73 (100); calcd for $C_8H_{16}Si_2O$ *m/e* 184.07698, measured *m/e* 184.07363.

Reaction of 35 and Perfluoro-2-butyne in the Presence of Triethylsilane or 2,2,5,5-Tetramethyl-2,5-disila-1-oxacyclopentane (36). A solution of **35** (60 mg, GC prep) and Me_3SiH (1 mL) in an NMR tube was degassed (freeze–thaw) and a large excess of perfluoro-2-butyne was distilled into the tube. After sealing under vacuum, the tube was heated at 60–70 °C for 10 h. Analysis by GC/MS revealed only **12** as a major product and no evidence for 1,1,1-triethyl-2-methyl-2-trimethylsiloxydisilane, the product expected from insertion of **32** into the Si–H bond of Et_3SiH. When the reaction was run identically, but with **36** replacing Et_3SiH, a clean reaction mixture containing **12** (87%) and cyclic trisiloxane **37** (63%), which was identified by NMR and MS spectral comparison with literature data, was obtained. When each of the above reactions was performed by dropping mixtures of **35** and Et_3SiH or **36** through a vertical, quartz chip packed tube heated at 440–480 °C with perfluoro-2-butyne as the carrier gas (40 mL/min), virtually identical results were obtained although the yield of **37** dropped to 40% and with Et_3SiH an isomer corresponding to trapping of silanone **31** by starting **35** was detected by GC/MS.

Reaction of 35 and Maleic Anhydride. A solution of **35** (0.61 g, 0.0033 mol) and freshly sublimed maleic anhydride (0.30 g, 0.0030 mol) in 15 mL of benzene was stirred at 70 °C for 12 h. After removal of the benzene, adduct **38** was isolated and purified by recrystallization from hexane/Et_2O to afford 0.31 g (33%) as a mixture of syn and anti isomers: NMR (D_6C_6) δ [−0.05 (s, SiMe), 0.01 (s, $SiMe_3$), 0.09 (s, SiMe), 0.10 (s, $SiMe_3$), total 12 H], 2.65 (m, 3 H), 4.82 (m, 1 H), 5.90 (m, 2 H); IR (KBr) 3040, 2960, 1860, 1780, 1250 cm^{-1}; mass spectrum, *m/e* (% relative intensity) 209 (2), 133 (31), 117 (31), 78 (41), 73 (100); calcd for $C_{12}H_{18}O_4Si_2$ *m/e* 282.07431, measured *m/e* 282.07412.

Photolysis of 38 in the Presence of Et_3SiH or $Me_2Si(OMe)_2$. Adduct **38** (15 mg) was dissolved in ca. 200 μL of Et_3SiH or dimethyldimethoxysilane in a quartz NMR tube, degassed with argon, septum sealed, and irradiated for 2 h. GC/MS and NMR analysis indicated no evidence for disilane **40**, the expected trapping product from silylene **32**. In $Me_2Si(OMe)_2$ solution the photolysis of **38** afforded benzene (54%) and disiloxane **39** (29%): NMR ($DCCl_3$) δ 3.61 (s, 2 OCH_3), 0.22 (overlapped SiMe's, 18 H); IR (neat) 2960, 1255, 1060, 1010 cm^{-1}; mass spectrum, *m/e* (% relative intensity) 237 (19), 179 (100), 149 (82), 133 (65), 73 (72); calcd for $C_7H_{21}O_3Si_3$ ($M^+ - CH_3$) *m/e* 237.07986, measured *m/e* 237.08000.

Thermolysis of 38 in $Me_2Si(OMe)_2$. A solution of **38** (55 mg) in 1.0 mL $Me_2Si(OMe)_2$ in an NMR tube was degassed (freeze–thaw) and sealed under vacuum. After heating for 8 h at 150 °C the tube was opened and the contents analyzed. The three major products were identified by NMR and GC/MS comparison with authentic samples: 1,2-dihydrophthalic anhydride (54%), phthalic anhydride (16%), and **39** (39%).

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Registry No. 3, 70606-53-0; **4**, 70606-54-1; **5**, 67078-75-5; **9**, 84521-16-4; **12**, 433-95-4; **13**, 5526-16-9; **16**, 18187-24-1; **17**, 18269-67-5; **18**, 84521-17-5; **19**, 70624-44-1; **20**, 84521-18-6; **21**, 2943-62-6; **22**, 18297-87-5; **24**, 84521-19-7; **25**, 84521-20-0; **26**, 35941-47-0; **27**, 84521-21-1; **33**, 84521-22-2; **34**, 84521-23-3; **35**, 84521-24-4; **36**, 7418-20-4; **38**, 84521-25-5; **39**, 84521-26-6; $ClSiMe_2SiMe_3$, 1560-28-7; $F_3CC{\equiv}CCF_3$, 692-50-2; $Me_2Si(OMe)_2$, 1112-39-6; Me_3SiCl, 75-77-4; $MeO_2CC{\equiv}CCO_2Me$, 762-42-5; $Ph_2Si(OMe)_2$, 6843-66-9; Et_3SiH, 617-86-7; *cis*-4-methoxybut-1-yn-3-ene, 3685-19-6; *o*-bromobenzyl methyl ether, 52711-30-5; triethyl orthoacetate, 78-39-7; maleic anhydride, 108-31-6; 3,5-dimethyl-1,2-dihydrophthalic anhydride, 84521-27-7; 2-chloroheptamethyltrisilane, 754-38-1.

Variations in Mechanism for Photoinduced Valence Isomerization of an Electron-Donor Nonconjugated Diene

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Abstract: Photoisomerization of 1,4,4a,5,8,8a-hexahydro-1,4,5,8-*endo,endo*-dimethanonaphthalene (**3**) has been studied in detail. Rearrangement to the cage photoisomer **4** occurs on direct irradiation or with triplet sensitizers with quantum efficiency as high as 1.0. Irradiation in the presence of electron acceptors whose fluorescence is quenched by **3** also results in cage formation. Quantum yields approach 1.0 for donor–acceptor sensitization in a nonpolar solvent. For this reaction, a mechanism is proposed that involves excitation transfer within an exciplex of sensitizer and **3** and partitioning of locally excited **3** at a biradicaloid geometry. Quantum efficiencies exceed unity for rearrangement sensitized by electron acceptors in polar media. A chain mechanism is proposed that involves radical-cation intermediates obtained through electron transfer from **3**. Irradiation of ground-state (charge-transfer) complexes of **3** and fumaronitrile or diethyl 1,2-dicyanofumarate also results in valence isomerization with quantum yields that are dependent on solvent polarity and excitation wavelength. The options available for photosensitization of **3** and a related diene, norbornadiene, are discussed.

Photochemically induced internal cycloaddition (valence isomerization) of nonconjugated dienes has been the focus of considerable attention for some years.[1] The utility of preparing novel polycyclic compounds possessing significant cumulative ring strain

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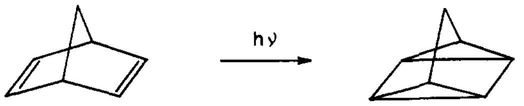
by means that would be difficult to duplicate in nonphotochemical processes was appreciated in the earliest work.[2] The synthesis of cubane derivatives offers a classic example of deployment of internal photoaddition in the synthesis of novel small-ring systems.[1,3] Alternatively, photochemical energy storage has been the objective of a number of studies of valence isomerization.[4,5] Conversion of norbornadiene[6] and its derivatives[7] to valence isomers (e.g., **1** → **2**) is the best known energy-storing molecular arrangement, although a number of other reactions have been suggested.[5,8] A variety of mechanisms of sensitization (broadly defined) have been applicable to valence isomerizations of the norbornadiene type, including direct photolysis,[7b,8b,9] triplet sensitization,[7a,10] complexation with metal ions,[11] and electron-donor–acceptor (EDA) interaction.[12]



1 **2**

A significant body of theoretical and experimental study has been devoted to the consequences of proximal (e.g., "face-to-face") arrangement of double bonds. The importance of through-space and through-bond overlap of orbitals in determining the symmetry of high-lying occupied molecular orbitals has been a common concern for theorists.[13] The experimental work on ground-state reactions has revealed influences of proximal double-bond interaction on reaction rate and the distribution of products (e.g., "cross" vs. "parallel" internal addition).[14] Correlations of photochemical reactivity have been less frequent. Although variations in structure that are permitted within the norbornadiene family appear to be quite large,[9,15] other polycyclic systems undergo internal photoaddition with efficiencies that reflect subtle differences in the separation and homoconjugation of π moieties.[16] Osawa and his co-workers[17] have provided a survey of isomerizations for which the distance and angular displacement of double bonds and the strain energy that is onset with ring closure were assessed. For these comparisons, chemical yields but not quantum efficiency data were available.

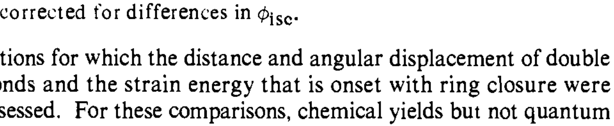
Table I. Relative Quantum Efficiencies for Valence Isomerization of **3** Induced by Triplet Sensitizers[a]

sensitizer (M)	triplet energy,[b] kcal/mol	ϕ_{isc}[c]	ϕ_{isom}[d]
acetone (1.0)	80	~1.0	0.84
benzophenone (0.10)	69	1.0	1.0
Michler's ketone (0.10)	65	1.0	1.02
phenanthrene (0.10)	62	0.85	0.97
naphthalene (0.11)	61	0.80	0.96
chrysene (0.05)	57	0.85	0.09
biacetyl (1.0)	56	~1.0	0.19
benzil (0.10)	53	0.92	0.23

[a] Irradiation in parallel in chamber reactor at 280–330 nm; nitrogen-purged benzene solutions, 35 °C. [b] Reference 28. [c] Quantum efficiency for intersystem crossing of sensitizer (ref 28). [d] Quantum yields relative to benzophenone, uncorrected for differences in ϕ_{isc}.

The endo,endo isomer of 1,4,4a,5,8,8a-hexahydro-1,4,5,8-dimethanonaphthalene (**3**) provides an especially interesting example of strong through-space interaction, similar to that found in norbornadiene (**1**). Additional through-bond coupling results in a particularly high-lying HOMO in **3** (vertical ionization potential = 8.1 eV).[18] If the stabilization of radical cations by transannular interaction in this series is assumed to be a fair indicator of excited-state reactivity, then **3** should be at least as successful in valence isomerization as **1** (IP = 8.6 eV).[19] In addition, the IP data show that **3** should be a relatively good electron donor and offer opportunities for sensitization through formation of donor–acceptor excited complexes. Photoisomerization induced by EDA interaction for the **1**,**2** pair is more favorable for the "back reaction", **2** → **1**,[20] since the saturated isomer, quadricyclene, is especially strained and is the better electron donor.[21] A similar reactivity is not expected for **4**.[22]

Despite the novel electronic properties of **3**, its photochemistry has not been reported.[23] The hexachloro derivative (a well-known pesticide, isodrin) has been investigated, including demonstration of the isomerization analogous to **3** → **4**.[24] Diene **3** is in fact the parent of another series of structures in which the relative energy content of photoproducts is dependent on losses of delocalization energy in fused rings and for which valence photoisomerization is known (e.g., **5** → **6**).[25] Our efforts involving **3** have been part of a detailed investigation of photosensitization mechanisms ap-



3 **4**

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(1) Dilling, W. L. *Chem. Rev.* **1966**, *66*, 373.

(2) Dauben, W. G.; Cargill, R. L. *Tetrahedron* **1961**, *15*, 197.

(3) Eaton, P. E. *Acc. Chem. Res.* **1968**, *1*, 50.

(4) Scharf, H.-D.; Fleischauer, J.; Leismann, H.; Ressler, I.; Schleker, W.; Weitz, R. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 652.

(5) Jones, G., II; Reinhardt, T. E.; Bergmark, W. R. *Sol. Energy* **1978**, *20*, 241.

(6) Hautala, R. R.; King, R. B.; Kutal, C. In "Solar Energy: Chemical Conversion and Storage"; Hautala, R. R., King, R. B., Kutal, C. Eds.; Humana: Clifton, NJ, 1979.

(7) (a) Jones, G., II; Xuan, P. T.; Chiang, S.-H., ref 6. (b) Maruyama, K.; Terada, K.; Yamamoto, Y. *J. Org. Chem.* **1981**, *46*, 5294.

(8) (a) Sasse, W. In "Solar Power and Fuels"; Bolton, J. R., Ed.; Academic Press: New York, 1975. (b) Mukai, T.; Yamashita, Y. *Tetrahedron Lett.* **1978**, 357. (c) Hamada, T.; Iijima, H.; Yamamoto, T.; Numao, N.; Hirao, K.; Yonemitsu, O. *J. Chem. Soc., Chem. Commun.* **1980**, 696. (d) Demuth, M.; Amrein, W.; Bender, C. O.; Braslavsky, S. E.; Burger, U.; George, M. V.; Lemmer, D.; Schaffner, K. *Tetrahedron* **1981**, *37*, 3245.

(9) Kaupp, G.; Prinzbach, H.; *Helv. Chim. Acta* **1969**, *52*, 956.

(10) (a) Hautala, R. R.; Little, J.; Sweet, E. M. *Sol. Energy* **1977**, *19*, 503. (b) Cristol, S. J.; Kaufman, R. L. *J. Photochem.* **1980**, *12*, 207. (c) Barwise, A. J. G.; Gorman, A. A.; Leyland, R. L.; Smith, P. G.; Rodgers, M. A. J. *J. Am. Chem. Soc.* **1978**, *100*, 1814.

(11) (a) Schwendiman, D. P.; Kutal, C. *J. Am. Chem. Soc.* **1977**, *99*, 5677. (b) Kutal, C.; Schwendiman, D. P.; Grutsch, P. *Sol. Energy* **1977**, *19*, 651. (c) See also: Ever, J. Th. M.; Mackor, A. *Tetrahedron Lett.* **1978**, 2321 and references cited therein.

(12) Jones, G., II; Chiang, S.-H.; Xuan, P. T. *J. Photochem.* **1979**, *10*, 1.

(13) (a) Hoffman, R. *Acc. Chem. Res.* **1971**, *4*, 1. (b) Goldstein, M. J.; Natowsky, S.; Heilbronner, E.; Hornung, V. *Helv. Chim. Acta* **1973**, *56*, 294.

(14) Osawa, E.; Aigami, K.; Inamoto, Y. *Tetrahedron* **1978**, *34*, 509.

(15) Sauter, H.; Horster, H.-G.; Prinzhach, H. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 991.

(16) (a) Sedelmeir, G.; Prinzbach, H.; Martin, H.-D. *Chimia* **1979**, *33*, 329. (b) Prinzbach, W.; Sedelmeier, G.; Martin, H.-D. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 103.

(17) Osawa, E.; Aigami, K.; Inamoto, Y. *J. Org. Chem.* **1977**, *42*, 2621.

(18) Martin, H.-D.; Schwesinger, R. *Chem. Ber.* **1974**, *107*, 3143.

(19) Heilbronner, E.; Martin, H.-D. *Helv. Chim. Acta* **1972**, *55*, 1490.

(20) (a) Roth, H. D.; Schilling, M. L. M.; Jones, G., II *J. Am. Chem. Soc.* **1981**, *103*, 1246. (b) Jones, G., II; Chiang, S.-H.; Becker, W. G.; Greenberg, D. P. *J. Chem. Soc., Chem. Commun.* **1980**, 681 and references cited therein. (c) Jones, G., II; Chiang, S.-H.; Becker, W. G.; Welch, J. A. *J. Phys. Chem.* **1982**, *26*, 2805.

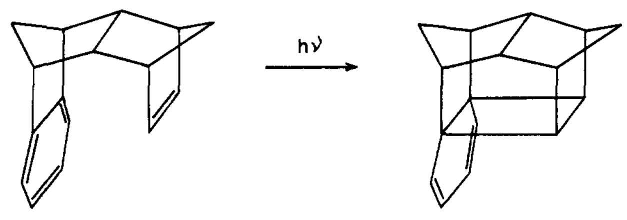
(21) The oxidation potentials for **1** and **2** are respectively 1.56 and 0.91 V vs. SCE (acetonitrile): Gassman, P. G.; Yamaguchi, R.; Koser, G. F. *J. Org. Chem.* **1978**, *43*, 4392.

(22) With other saturated fused-ring systems serving as models for **4**, the IP_v is estimated to be >9.0 eV: Martin, H.-D.; Kagabu, S.; Schwesinger, R. *Chem. Ber.* **1974**, *107*, 3130.

(23) For a preliminary account, see: Jones, G., II; Becker, W. G.; Chiang, S.-H. *J. Photochem.* **1982**, *19*, 245.

(24) (a) Cookson, R. C.; Crundwell, E. *Chem. Ind.* (*London*) **1958**, 1004. (b) Plimmer, J. R. *Pestic. Chem., Proc. Int. IUPAC Congr. Pestic. Chem., 2nd*, **1971**, *6*.

(25) Prinzbach, H.; Sedelmeir, G.; Kruger, C.; Goddard, R.; Martin, H.-D.; Gleiter, R. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 171.



5

6

propriate for valence isomerization with special attention paid to EDA interaction (including electron-transfer sensitization).[12,20,26] In this paper, four distinct pathways for photoisomerization are revealed for **3** → **4**[23] involving direct photolysis, triplet energy transfer, the quenching of singlet sensitizers, and irradiation of ground-state complexes of **3** and electron acceptors. The discussion will focus on the dependences of quantum yield on a variety of factors and on the intermediacy of exciplexes and radical-ions in sensitized isomerization.

Results

Isomerization on Direct Photolysis and with Triplet Sensitizers. The absorption spectrum of GLC-purified **3** displays a relatively intense end absorption with a perceptible shoulder at 218 nm (ϵ 13 000) and ϵ_{254} = 2000 (C_6H_{12}). Photolysis of a cyclohexane solution 0.016 M in **3** at 254 nm resulted in conversion to **4** with $\phi \cong 0.5$.[27] Irradiation of samples of **3** in the presence of triplet sensitizers also resulted in valence isomerization, with relative yields dependent on the sensitizer triplet energy as shown in Table I. A concentration of **3** (0.10 M) was employed which insured that for those sensitizers having sufficient energy for exothermic energy transfer, triplet quenching would be complete ($k_q \sim 10^{10}$ M^{-1} s^{-1}; sensitizer triplet lifetime is assumed $>10^{-8}$ s for nitrogen-purged samples). Since the quenching of singlets of hydrocarbon sensitizers (Table I) could possibly have led to rearrangement (vide infra), a check for fluorescence quenching was made; no quenching of emission was found at relevant concentrations of **3**.

An absolute quantum efficiency for triplet-sensitized isomerization was measured for benzophenone and **3** by using the monochromator/light-pipe apparatus: $\phi = 1.00 \pm 0.05$, 0.10 M **3** in benzene, ~5% conversion, 366 nm, 25 °C. For comparison, the quantum yield of isomerization of **1** (0.10 M in benzene) sensitized by benzophenone is 0.54, with values for various concentrations of diene that extrapolate to ~1.0 for infinite [**1**].[10c] Notably, for sensitization of **3**, quantum yields fall for sensitizers having triplet energies below ~60 kcal/mol, whereas the critical energy level for norbornadiene (**1**) is approximately 70 kcal/mol.[10]

Isomerization via Fluorescence Quenching. Addition of **3** to solutions of DCA, CN, and TCNB (excitation at 423, 313, and 313 nm, respectively) resulted in quenching of the fluorescence of the electron-acceptor sensitizers. Stern–Volmer plots of relative intensity of emission vs. [**3**] gave $k_q\tau$ values (Table II). With use of literature values for sensitizer lifetime,[29] quenching constants (k_q) were calculated. Under no conditions was the emission from an exciplex of acceptors and **3** observed.

Table II. Fluorescence Quenching Data and Quantum Yields of Isomerization Sensitized by Acceptor Fluorophores[a]

acceptor (M)	solvent	$k_q\tau$,[b] M^{-1}	$k_q \times 10^{-9}$, M^{-1} s^{-1}	i/s,[c] M^{-1}	ϕ
9,10-dicyanoanthracene (DCA) (0.0001)	C_6H_{12}	86.1	2.1	67.8	(0.14)[d]
1-cyanonaphthalene (CN) (0.004)	C_6H_{12}	55.6	5.7	48.5	(1.08)[d]
1-cyanonaphthalene (CN) (0.057)	CH_3CN	81.7	9.2		8.4[e]
1,2,4,5-tetracyanobenzene (TCNB) (0.057)	CH_3CN	185	13		3.0[e]

[a] For runs in C_6H_{12}, quantum yields from parallel irradiation in Rayonet chamber reactor with RUL 3000 (CN) and RUL 3500 (DCA) lamps; other runs using monochromator apparatus (313 nm). [b] Slopes of Stern–Volmer plots for fluorescence quenching by **3**. [c] Intercept/slope ratios from double-reciprocal quantum yield–concentration plots. [d] Limiting quantum efficiencies. [e] Quantum efficiency at ~90% quenching of sensitizer fluorescence.

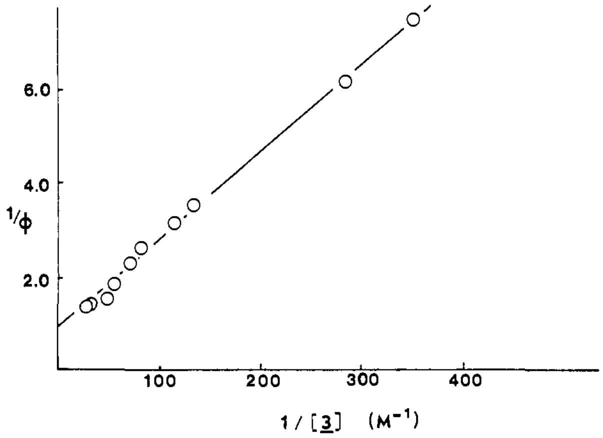


Figure 1. Concentration dependence of quantum efficiency for isomerization **3** → **4** sensitized by 1-cyanonaphthalene in cyclohexane.

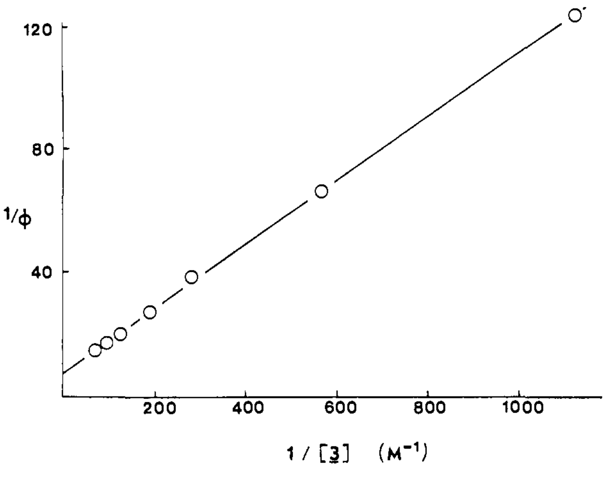


Figure 2. Concentration dependence of quantum efficiency for isomerization **3** → **4** sensitized by 9,10-dicyanoanthracene in cyclohexane.

On irradiation of **3** in the presence of acceptor sensitizers, under conditions where all incident light was absorbed by the fluorophore, isomerization to **4** was observed. For DCA and CN photolysis

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(26) (a) Jones, G., II; Becker, W. G. *J. Am. Chem. Soc.*, following paper in this issue. (b) Jones, G., II; Becker, W. G., submitted for publication. (c) Jones, G., II; Chiang, S.-H. *Tetrahedron* **1981**, *37*, 3397. (d) Jones, G., II; Becker, W. G. *J. Am. Chem. Soc.* **1981**, *103*, 4630. (e) Jones, G., II; Becker, W. G. *Chem. Phys. Lett.* **1982**, *85*, 271.

(27) Although the data for the appearance of **4** were reproducible (+15%), we are nevertheless cautious in reporting this value, realizing that most trace impurities could competitively absorb at 254 nm, a wavelength at the tail of end absorption of **3** (i.e., the value 0.5 may well be a lower limit for the quantum efficiency).

(28) Murov, S. L. "Handbook of Photochemistry"; Marcell Dekker: New York, 1973.

(29) (a) Ware, W. R.; Holmes, J. D.; Arnold, D. A. *J. Am. Chem. Soc.* **1974**, *96*, 7861. (b) Arnold, D. R.; Maroulis, A. J. *Ibid.* **1976**, *98*, 5931. (c) A value of 13 ns for the singlet lifetime of TCNB in acetonitrile was calculated by using a diffusion-controlled quencher, hexamethyl(Dewar benzene),[26c] for inhibition of TCNB fluorescence ($k_q\tau$ = 211 M^{-1}) and a value of $k_q = 1.6 \times 10^{10}$ M^{-1} s^{-1}, an average rate constant obtained by quenching the fluorescence of several cyanoaromatic sensitizers with known lifetime: Becker, W. G. Ph.D. Dissertation, Boston University, 1982.

(30) For CN sensitization, a small component of triplet-sensitized rearrangement at low [**3**] cannot be excluded (14% of CN singlets are quenched at 0.003 M **3**). From phosphorescence spectra, a CN triplet energy of 57 kcal/mol (near the triplet energy for **3**) can be estimated: see ref 26c and 29b.

Table III. Reduction Potentials for Electron Acceptors and Absorption Data for Charge-Transfer Complexes of Acceptors and **3**

electron acceptors	$E_{1/2}$ (red)[a]	$\lambda_{\max}{}^{\mathrm{CT}}$,[b] nm	$\nu_{\max}{}^{\mathrm{CT}} \times 10^{-3}$, cm^{-1}
5, R = H (FUM)	−1.29	310	32.3
5, R = CO_2Et (DDF)	−0.32	424	23.6
5, R = CF_3		428	23.4
6 (CHL)	0.02	450	22.2
5, R = CN (TCNE)	0.24	568	17.6

[a] Half-wave reduction potentials (V vs. SCE, acetonitrile, ref 33). [b] Absorption maxima for complexes in CH_2Cl_2.

in cyclohexane solution, the concentration dependence of quantum yields was determined as shown in Figures 1 and 2. The data are consistent with the participation of acceptor singlets (but not triplets) in the sensitization process. A simple mechanism employing a single exciplex intermediate (Scheme I) provides sufficient rationale for the observed concentration dependence.

Scheme I

$$\begin{array}{ll} \mathrm{A} \xrightarrow{h\nu} \mathrm{A}^* & \\ \mathrm{A}^* \rightarrow \mathrm{A} + h\nu + \text{heat} & (k_1) \\ \mathrm{A}^* + \mathbf{3} \rightarrow [\mathrm{A}\text{--}\mathbf{3}]^* & (k_2) \\ [\mathrm{A}\text{--}\mathbf{3}]^* \rightarrow \mathrm{A} + \mathbf{3} & (k_3) \\ [\mathrm{A}\text{--}\mathbf{3}]^* \rightarrow \mathrm{A} + \mathbf{4} & (k_4) \end{array}$$

Steady-state analysis leads to the linear double-reciprocal relationship between quantum yield and [**3**] shown in the following equation, where $P = k_4/(k_3 + k_4)$:

$$\frac{1}{\phi} = \frac{1}{P} + \frac{Pk_1}{k_2[\mathbf{3}]}$$

According to this analysis, the intercept/slope ratio (i/s) for quantum efficiency plots (k_2/k_1) should equal $k_q\tau$ values for fluorescence quenching. The data of Table II shows a satisfactory match of these parameters.

Quantum yields exceeding unity were observed for **3** → **4** isomerization resulting from fluorescence quenching in acetonitrile (Table II). This finding is consistent with the imposition of a radical-ion chain mechanism for ring closure (Scheme II), analogous to the ring opening of hexamethyl(Dewar benzene) in polar media[26a,d] (vide infra). Electrochemical experiments showed that on oxidation of **3** at 2.0 V vs. SCE in acetonitrile, isomerization to **4** could be observed (see Experimental Section).

Isomerization on Irradiation of Charge-Transfer (CT) Complexes. Solutions of **3** and several strong electron acceptors displayed new absorption bands, which were assigned to bimolecular CT complexes as shown in Figure 3 (additional data, Table III). The shift in absorption to the red was dependent on the strength of the acceptor (Table III). In fact, a plot of transition energies for CT band maxima vs. acceptor reduction potentials provided a satisfactory correlation ($r = 0.985$) of these parameters (slope = −1.1 eV V^{-1}). For this limited set of data, the correlation suggests that electronic factors rather than steric factors[31] (for the acceptors chosen) largely determine the relative energies of ground and excited CT species. A similar monotonic dependence on electron-donor–acceptor properties has been determined for complexes of other nonconjugated dienes including **1** and tetracyanoethylene (TCNE).[32]

Scheme II

$$\begin{array}{ll} \mathrm{A}^* + \mathbf{3} \longrightarrow \mathrm{A}^- + \mathbf{3}^+ & \text{electron transfer} \\ \left.\begin{array}{l} \mathbf{3}^+ \longrightarrow \mathbf{4}^+ \\ \mathbf{4}^+ + \mathbf{3} \longrightarrow \mathbf{4} + \mathbf{3}^+ \end{array}\right\} & \text{chain propagation} \\ \left.\begin{array}{l} \mathrm{A}^- + \mathbf{3}^+ \longrightarrow \mathrm{A} + \mathbf{3} \\ \mathrm{A}^- + \mathbf{3}^+ \longrightarrow \mathrm{A} + \mathbf{4} \end{array}\right\} & \text{chain termination} \end{array}$$

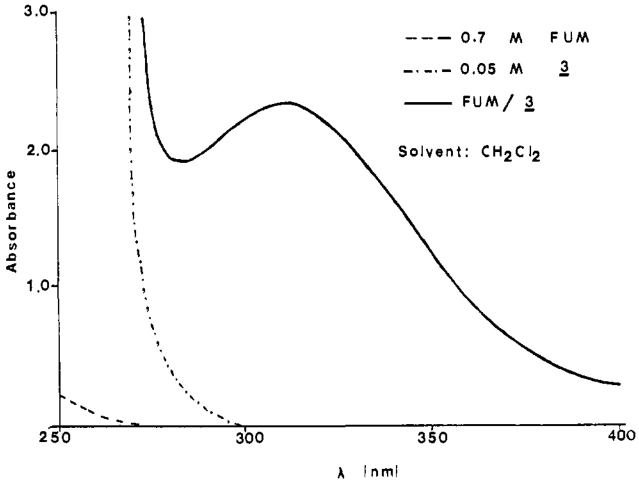
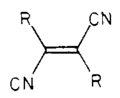


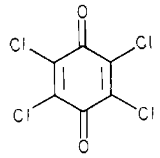
Figure 3. Absorption spectra of fumaronitrile (FUM) and **3** alone and taken together at the same concentrations.

Thermal bleaching of the complexes of **3** with TCNE and CHL was observed so photochemical studies were limited to the FUM and DDF systems, that were stable at room temperature. These complexes proved to be weak, however, so that even for relatively high concentrations of excess donor or acceptor, the "saturation" criteria recommended by Deranleau[34] could not be met, and formation constants and extinction coefficients were not obtained (estimated $K < 0.5$ M^{-1} from Benesi–Hildebrand plots[35,36]).

Irradiation of CT complexes of **3** under a variety of conditions led to clean valence isomerization to **4** with chemical yields in excess of 90% (material balance by GLC). Quantum efficiency data are presented in Table III. A search for geometrical isomerization of FUM was conducted, but for irradiation in acetonitrile, no maleonitrile was observed ($\phi < 0.01$).



5, R = H (FUM)
5, R = CO_2Et (DDF)
5, R = CF_3
5, R = CN



6 (CHL)

Discussion

Our study shows that although photoisomerization of **3** is generally efficient, considerable variation in quantum yield is

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(31) Fukuzumi, S.; Kochi, J. K. *J. Phys. Chem.* **1981**, *85*, 648; *Ibid.* **1980**, *84*, 608, 617.

(32) Haselbach, E.; Rossi, M. *Helv. Chim. Acta* **1976**, *59*, 2635.

(33) Reduction potentials for acceptors: (a) FUM: Wong, P. C.; Arnold, D. R. *Can. J. Chem.* **1980**, *58*, 918. (b) DDF: ref 25a; CHL: Patai, S., Ed., "The Chemistry of Quinonoid Compounds", Wiley: New York, 1974; Part 1, Chapter 9. (c) TCNE: Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259. (d) DCA: Chandross, E. A.; Ferguson, J. *J. Chem.* **1970**, *8*, 259. (e) CN: ref 29b. (f) TCNB: Zweig, A.; Lehnsen, J. G.; Hodgson, W. G.; Jura, W. H. *J. Am. Chem. Soc.* **1963**, *85*, 3937.

(34) Deranleau, D. A. *J. Am. Chem. Soc.* **1969**, *91*, 4044, 4050.

(35) Foster, R. "Organic Charge-Transfer Complexes"; Academic Press: New York, 1969.

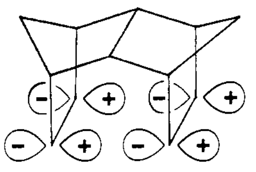
(36) Plots of $[A]_0/A$ vs. $1/[D]_0$ were linear for limited portions of the saturation curve[34] with intercepts near zero, suggesting that the weak complexes of **3** are "contact" rather than intrinsic CT complexes. Haselbach and Rossi[32] reported blue shifts of absorption maxima for the TCNE complexes of dienes in low-temperature glasses and attributed the spectral change to a contribution made by contact complexes (although pointing out that the alteration in absorption could have been due to restrictive forces of the matrix). If complexes of **3** have a single geometry or a limited range of similar geometries, the relative locations of donor and acceptor cannot be assigned as yet, although an "endo" geometry for complexes of **1** was proposed,[32] on the basis of the absence of steric effects for the 7,7-dimethyl derivative.

possible according to the mode of excitation. Direct photolysis of triplet-sensitized isomerization proceeds efficiently with yields comparable to or greater than values for **1**.[37] These results are not unexpected due to the favorable interaction of π moieties (2.94-Å separation)[17] that is revealed in the low ionization energy[18] and relatively strong absorption in the near UV displayed by **3**.

The quenching of fluorescence of electron-acceptor aromatic sensitizers is robust in polar solvent (near the diffusion-controlled limit). This result is routinely found for donor–acceptor quenching under circumstances in which electron transfer is exothermic.[33c] The important parameters for DCA, CN, and TCNB fluorophores show in Table V reveal that this condition is met (compare E_∞ and $E_{ox} - E_{red}$ values). The rate of donor–acceptor quenching is typically reduced from the maximum value in a nonpolar solvent, as was found for DCA and CN in cyclohexane.

The quantum yield results (Table II and the concentration profiles, Figures 1 and 2) show that the isomerization, **3** → **4**, induced by acceptor fluorophores is primarily a singlet-sensitized process.[30] In contrast, singlet quenching is unimportant for aromatic sensitizers that are weaker acceptors ($E_{1/2}$ (red) < −2.0 V vs. SCE), and ring closure is brought about (in benzene) by triplet energy transfer (Table I).

Rearrangement via Exciplexes in Nonpolar Solvent. A Mechanism for Exciplex Isomerization Involving Excitation Transfer at Critical Reaction Geometries. Beyond this division of reactivity, the singlet-sensitized rearrangement must be examined in terms of the influence of the solvent medium. For nonpolar media, the quenching act may be viewed as a collisional encounter in which acceptor sensitizer and donor **3** are mutually polarized. This close encounter permits withdrawal of electron density from the donor with a particular influence on electrons populating the HOMO of **3**[20b] (depicted in part[18] with structure **7**). Thus, electron-donor–acceptor interaction results in an increase in transannular bond order and progress along the reaction coordinate for ring closure.[12,41]



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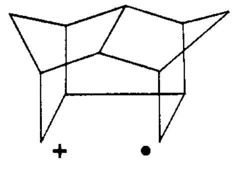

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Attention now turns to the point at which nonradiative decay from an excited surface that includes sensitizer and **3** returns molecules to the ground state with appropriate changes in geometry and electronic configuration. Several models come to mind, including the proposals of Murov and Hammond concerning the sensitized rearrangement of quadricyclene (**2** → **1**)[42] and the geometrical isomerization of *trans,cis*-1,3-cyclooctadiene.[43] Their mechanism focuses on the conversion of electronic energy (excitation energy of the sensitizer) into vibrational energy localized

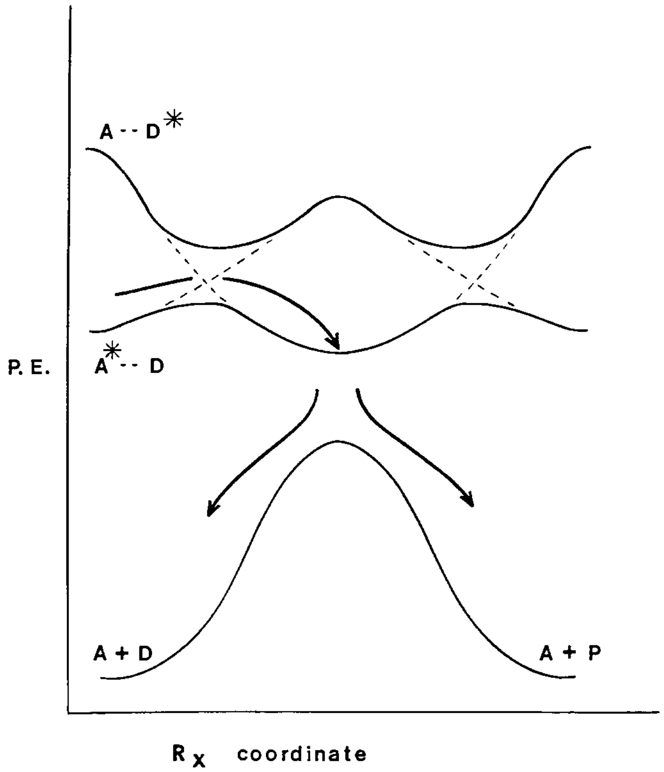
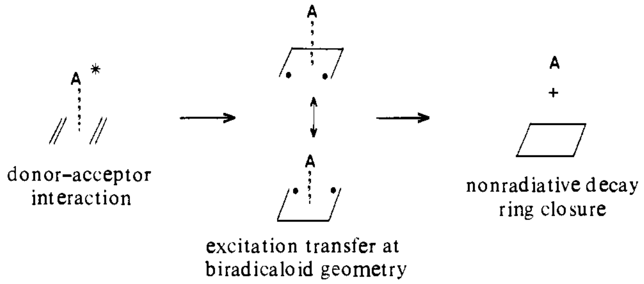


Figure 4. Potential energy surfaces for rearrangement of an electron donor D to product P through interaction with an electron-acceptor sensitizer A (nonpolar medium). The diagram does not dipict the coordinate for approach and separation of donor and acceptor.

Scheme III



in the isomerizable quencher, with emphasis on the requirement to surmount the barrier for thermal isomerization of the quencher in the ground state. Solomon, Steel, and Weller[44] made the alternative proposal that the **2** → **1** rearrangement progresses by distortion within a quench-complex ion pair with partitioning to **2** and **1** through back electron transfer.

Since other modes of sensitization for **3** → **4**, which are more likely to involve ionic dissociation, have been studied with different results (vide infra), we favor a different working hypothesis for the nonclassical singlet-sensitization mechanism for nonpolar media. According to this model, donor–acceptor quenching results in a polar but nonionic exciplex, within which exchange of excitation energy between donor and acceptor is possible. The evolution of excited complexes involving an isomerizable donor and a product P is shown simply as follows:

$$A^* + D \rightarrow [A^*\text{--}D] \rightarrow [A\text{--}D^*] \rightarrow A + P$$

The timing of excitation transfer is critical, since reaction is launched at a point at which the excitation energies of sensitizer and quencher (with no low-lying excited state) are widely separated. However, the potential energy curves representing locally excited configurations for sensitizer and quencher are destined

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[37] The isomerization of **1** under direct photolysis conditions is believed to be inefficient although some uncertainty remains. Roquitte[38] reports a low yield of toluene (ϕ = 0.042) and no **2** on irradiation in ether solution (results similar for the gas phase). The original report[2] on the isomerization of **1** indicates a 66% chemical yield of **2** and no accompanying toluene. The difference in singlet and triplet reactivity for **1** is understood in terms of biradicaloids that partition in favor of **1** for the singlet surface and in favor of **2** for triplet decay.[39]

[38] Roquitte, B. C. *J. Phys. Chem.* **1965**, *69*, 2475.

[39] Turro, N. J.; Cherry, W. R.; Mirbach, M. F.; Mirbach, M. J. *J. Am. Chem. Soc.* **1977**, *99*, 7399.

[40] Miller, L. L.; Nordbloom, G. D.; Mayeda, E. A. *J. Org. Chem.* **1972**, *37*, 916.

[41] For a quantitative theory of excited-state bond orders (the ΔP matrix) and predictions of the course of photochemical reactions, see: Zimmerman, H. E.; Gurenbaum, W. T.; Klun, R. T.; Steinmetz, M. G.; Welter, T. R. *J. Chem. Soc., Chem. Commun.* **1978**, 228.

[42] Murov, S. L.; Hammond, G. S. *J. Phys. Chem.* **1978**, *72*, 3797.

[43] Murov, S. L.; Yum, L.; Giering, L. P. *J. Am. Chem. Soc.* **1973**, *95*, 4329.

[44] Solomon, B. S.; Steel, C.; Weller, A. *J. Chem. Soc., Chem. Commun.* **1979**, 927.

to approach each other and attempt to cross (Figure 4) as the energy of D* dissipates to the conventional pericyclic minimum (biradical geometry)[45] for isomerization. Simultaneously, the local configuration involving A* follows the change in energy for D (largely parallel with changes in the ground-state surface). This mixing of local configurations leads to avoided crossings of potential surfaces and a completion of excitation energy transfer at the reaction midpoint, where decay to the ground surface (partitioning and loss of A) is facilitated.[45] The progress of reaction is presented in terms of structural changes shown in Scheme III.

The relative importance of dative or charge-transfer configurations and contributions of locally excited states to the structure of an electron-donor–acceptor excited complex (EC) is represented by the following linear combination:

$$\psi_{EC} = c_1\psi(D^+,A^-) + c_2\psi(D^-,A^+) + c_3\psi(D^*,A) + c_4\psi(D,A^*)$$

The influences of medium and component structure (donor, D, and acceptor, A) on the geometry, polarity, spectral properties, lifetime, and reactivity of excited complexes have received considerable recent attention.[46] We interpret the behavior of **3**, in quenching the fluorescence of CN and DCA in hydrocarbon solvent, as representing an important subset of the total range of donor–acceptor interaction, for which charge separation in the excited complex is modest and the medium contributes little to the stability of a polar species. Recent calculations,[47] and flash photolysis studies that reveal the absorption properties of excited complexes,[46] support the notion that charge transfer need not be the dominant structural feature for exciplexes in nonpolar media. The sensitization mechanism of Scheme III and Figure 4 is therefore a manifestation of heavy weighting for locally excited configurations (sizable c_3 and c_4) and the sharing of excited-state identity between sensitizer and isomerizable donor as reaction proceeds. The yield of isomerization for quenching in nonpolar solvent contrasts sharply with the results for systems in which it is likely that the excited species is prepared as an ion pair (e.g., CT excitation, heavy weighting, c_1; vide infra).

An important feature that is likely to control the efficiency of isomerization by the excitation transfer mechanism has to do with the energy separation of local excited states (A–A* vs. D–D*). A larger state separation would appear to require a larger barrier at the point of first avoided crossing (Figure 4), an inhibition for reaction A*–D, and the intervention of competing modes of exciplex decay. The data for rearrangement of **3** are qualitatively consistent with this prediction in that CN-induced isomerization proceeds with an efficiency near unity (limiting quantum yield in cyclohexane, Table II).[48] The barrier for excitation transfer is not so readily crossed for the sensitizer having a reduced excitation energy (DCA). This difference could have been ascribed to covalent interaction with the anthracene sensitizer,[49] but no disappearance of either sensitizer is observed. A more subtle alternative for decay involving exciplex intersystem crossing[50] might also be involved. A triplet exciplex could deposit excitation energy in the local triplet of the sensitizer, although to accommodate the data, this feature would be highly discriminating. Triplet decay would exclusively populate triplet **3** (E_T = 58 ± 2 kcal/mol from data, Table I) over triplet CN (of comparable energy[30]) as well as favor DCA excitation ($E_T \sim$ 40 kcal/mol) at the expense of **3**.

Table IV. Quantum Yields for **3** → **4** Isomerization via Charge-Transfer Complexes[a]

acceptor	solvent	CT absorption λ_{max}, nm	excitation wavelength,[b] nm	ϕ
fumaronitrile (FUM)	CH_3CN	290	313	0.30
	CH_3CN	290	334	0.13
	CH_2Cl_2	310	313	0.054
diethyl 1,2-dicyano-fumarate (DDF)	CH_2Cl_2	424	436	0.026
	CH_3CN	390	366	6.2
	CH_3CN	390	405	0.10

[a] Nitrogen-purged solutions, [**3**] = 0.055 M, [FUM] = 0.6 M, [DDF] = 0.20 M, 25 °C. [b] Monochromator/quantum counter apparatus.

The proposed mechanism of excitation transfer and biradicaloid partitioning (Figure 4) should be of general value, although the supporting data are as yet meager. The trend of quantum yields for sensitized **2** → **1** rearrangement[20b,42] shows a modest dependence on excitation energy of the acceptor sensitizer (lower efficiency for a less robust sensitizer[20b]). In addition, the partitioning of a singlet biradicaloid for the **1**,**2** energy surface appears to favor **1**,[37,39] as required for efficient rearrangement via exciplexes.[48] The dependence on excitation energy (e.g., CN vs. DCA) is absent for ring opening of hexamethyl(Dewar benzene).[26c] However, in this case, one might anticipate a less discriminating, "early", mixing of configurations due to the highly skewed nature of Dewar benzene surfaces (very large heat of reaction).[51]

Isomerization Involving Radical Ions. The unusually high values for quantum yield of isomerization of **3** on sensitization in acetonitrile (Table II) suggest a different course for rearrangement in polar media. The radical-ion mechanism of Scheme II was first proposed[52] to rationalize the quantum chain characteristics of sensitized isomerization of hexamethyl(Dewar benzene). The success of electrooxidation in driving the **3** → **4** rearrangement shows that radical cations can indeed be involved. Oxidized **3** must be capable of rearrangement to an isomeric radical cation (e.g., structure **8**), which is in turn capable of propagating the chain via electron exchange with neutral **3**. A requirement for isomeric radical cations has also been found in a photo-CIDNP study of the norbornadiene/quadricyclene rearrangement system (**1**/**2**)[20a] and is supported by MINDO/3 calculations,[53] which show a low barrier for rearrangement **2**$^+$ → **1**$^+$. In addition, the net result of chain propagation steps (the conversion **3** → **4**) appears to be exothermic since the ground-state isomerization can be catalyzed, including reaction of **3** with acid[54] or under oxymercuration conditions.[55]

A principal distinction among these valence isomerizations via radical cations involves the favored direction of rearrangement. Ring opening is observed for **2**[20] and for hexamethyl(Dewar benzene),[52] whereas ring closure is feasible for **3**. A common feature is the exothermicity of the net reaction of neutrals (**2** → **1**, **3** → **4**). One can estimate from heat of formation and ionization potential data that ring closure for species **1**$^{+\cdot}$ and **3**$^{+\cdot}$ is endo-

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(45) (a) Michl, J. *Photochem. Photobiol.* **1977**, *25*, 141; *Top. Curr. Chem.* **1974**, *46*, 1 and references cited therein. (b) The approach of locally excited surfaces is analogous to excited-ground-state surface separations, which respond dramatically to selected changes in local bond orders: Zimmerman, H. E.; Steinmentz, M. G. *J. Chem. Soc., Chem. Commun.* **1978**, 230.

(46) Mataga, N.; Ottolenghi, M. In "Molecular Association"; Foster, R., Ed.; Academic Press: New York, 1979; Vol. 2.

(47) (a) Eaton, D. F.; Pensak, J. *J. Phys. Chem.* **1981**, *85*, 2760. (b) Tavares, M. A. F. *J. Chem. Phys.* **1980**, *72*, 43.

(48) The high limiting yield of CN-sensitized rearrangement suggests that the exciplex partitioning match the decay that is important for direct photolysis (the reactivity of **3***) and that the latter indeed displays ϕ = 1.0.[27] Alternatively, the exciplex ensemble might avoid an unproductive decay inherent in unperturbed **3*** or the exciplex might assume a partition ratio slightly different from **3*** favoring **4** (i.e., the products of exciplex–biradicaloid partitioning will not necessarily be those of vertical excitation of the donor).

(49) Sakaki, T.; Kanematsu, K.; Audo, I.; Yamashita, O. *J. Am. Chem. Soc.* **1977**, *99*, 871.

(50) For reviews in which the intersystem crossing of exciplexes is discussed, see ref 46 and: (a) Mattes, S. L.; Farid, S. *Acc. Chem. Res.* **1982**, *15*, 80. (b) Lewis, F. D. *Ibid.* **1979**, *12*, 152. (c) Mataga, N.; Ottolenghi, M. In "Molecular Association"; Foster, R., Ed.; Academic Press: New York, 1979; Vol. 2.

(51) Michl, J. *Photochem. Photobiol.* **1977**, *25*, 141.

(52) Evans, T. R.; Wake, R. W.; Sifain, M. M. *Tetrahedron Lett.* **1973**, 701.

(53) Haselbach, E.; Bally, T.; Lanyiova, Z.; Baertschi, P. *Helv. Chim. Acta* **1979**, *62*, 583.

(54) Bruck, P.; Thompson, D.; Winstein, S. *Chem. Ind.* (*London*) **1960**, 590.

(55) Howe, R. K.; Winstein, S. *J. Org. Chem.* **1973**, *38*, 2797.

Table V. Acceptor Excitation and Ion-Pair Energies

acceptor	E_{00}[a]	E_{red}[b]	$E_{ox} - E_{red}$[c]
DCA	71	−0.82	54
CN	89	−1.8	76
TCNB	87	−0.66	50
FUM		−1.29	65
DDF		−0.32	42

[a] Singlet energies (kcal/mol) estimated from absorption and emission spectra for DCA, CN, and TCNB. [b] Polarographic half-wave potentials for reduction in acetonitrile (V vs. SCE) (ref 33). [c] Ion-pair energies (potentials converted to kcal/mol) estimated from acceptor reduction potentials and a value for the oxidation potential for **3**, E_{ox} = 1.5 V vs. SCE, by using the relationship $E_{ox} = 0.92\text{IP} - 5.9$ (ref 40) and IP (**3**) = 8.1 eV (ref 18).

thermic. However, only in the case of **3** is the diene ring-closure process propelled by a sufficiently exothermic cation-exchange propagation step (Scheme II).[56]

To include now all modes of sensitization for **3** that involve an interaction with electron acceptors, we provide the following summary of quantum yield results. (1) For fluorescence quenching in polar media, a quantum chain reaction ($\phi > 1$) is observed. (2) For quenching in nonpolar medium, yields are high but not exceeding unity. (3) For irradiation of a ground-state complex in nonpolar solvent, quantum efficiency for rearrangement is low. (4) For CT excitation in polar solvents, the quantum yield is variable but dependent on excitation wavelength. We emphasize that most of these features have now been observed for isomerization of **2** and hexamethyl(Dewar benzene) as well as rearrangement of **3**.[20b,c,26]

The mechanism for rearrangement on fluorescence quenching in a nonpolar solvent has been discussed above in terms of collisional encounter of donor and acceptor and the dynamics of polar exciplexes capable of excitation transfer between components. The rationale for quenching in polar media and for irradiation of CT complexes, which is presented elsewhere in detail,[20c,26] includes the following elements. The collision mechanism is bypassed for quenching in sufficiently polar solvent (e.g., CH_3CN) due to facile electron transfer, yielding directly a solvent-separated ion-pair intermediate. This species may dissociate to participate in the formation of radical-ion chains or recombine with no net reaction.[58] This "short circuit" decay via electron transfer is particularly pronounced for the excited charge-transfer complex that appears as a contact ion pair[46,59] on excitation. Unproductive decay is prohibitive for excited CT complexes except for rearrangement in polar media in which contact ion pairs are likely to evolve into solvent-separated species and free ions (note chain component for strongest acceptor, DDF entry, Table IV). The wavelength effect for CT irradiation in polar media is associated with Franck–Condon excited species that dissociate via extension of the intermolecular ionic bond stretch.[26]

In summary, internal photoaddition of **3** is robust under a variety of conditions. Unlike the isomerization **1** → **2**, which is efficient only through interaction with a metal[11] or as a triplet-sensitized process, rearrangement of **3** proceeds by involvement with conventional electron acceptors. The quenching of acceptor sensitizers may involve exciplexes of sufficient lifetime to allow orbital perturbation, molecular distortion, and excitation transfer that result in ring closure. In polar media, a chain reaction of radical cations of **3** is important. Exceptionally high quantum yields are possible for this mechanism, particularly for the mode of sensitization involving fluorescence quenching. Excitation of CT complexes of **3** that absorb at long wavelengths also brings about isomerization, with quantum yields that are dependent on excitation frequency.

The mechanism of ring closure of **3** involving radical cations is also of interest in providing an intramolecular example of ionic cyclodimerization.[60] Addition involving radical ions is indeed important in the photodimerization and photopolymerization of alkenes, exemplified by the well-known reaction of *N*-vinylcarbazole in the presence of electron acceptors.[61]

Experimental Section

Diene **3** (mp 80–82 °C) was prepared from isodrin following literature procedures.[62] Quantum yield measurements were carried out with **3**, which was purified by preparative GLC (1 cm × 1 m column of 15% OV-225 on Anakrom 78/80, column temperature 130 °C). The structure of diene **3** was verified by comparison of IR and NMR spectra and elemental analysis results with data previously reported.[63]

The valence isomer **4** was prepared by irradiation of 2 g (0.013 mol) of **3** in 10 mL of acetone (sensitizer) for 4 h. The nitrogen-purged solution was contained in a stoppered tube that was held in proximity to a quartz immersion well containing a 450-W medium-pressure Hg lamp. After irradiation, acetone was removed by evaporation in vacuo to give a clear oil (~2 g). Preparative GLC (1 cm × 1 m column of 15% FFAP on 70/80 Chromosorb W, column temperature 100 °C) yielded white crystals of the cage compound: mp 157–158 °C; IR ($CDCl_3$)[64] 2950, 2875, 1310, 1295, 1185 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.5–2.0 (m, 4 H), 2.2–2.7 (m, 10 H). Anal. Found, C, 90.99, H, 8.90. Theoretical, C, 91.08; H, 8.92%.

The electron-acceptor fluorophores and complexing agents were obtained and purified as previously described.[26a,c] The triplet sensitizers (Table I) were recrystallized three times from appropriate solvents (usually ethanol). Biacetyl was distilled at atmospheric pressure, and acetophenone was purified by vacuum distillation. The acetonitrile was MCB Omnisolve quality (distilled in glass), which was dried by distillation first from calcium hydride and then from P_2O_5. Dichloromethane was used as received (Aldrich Gold Label spectroquality). Benzene and cyclohexane were purified by washing with sulfuric acid and distillation from calcium hydride.

Equipment and procedures utilized for determination of quantum yields are described for photolysis using monochromator/quantum-counter equipment[26a] or for parallel irradiation using a Rayonet chamber reactor and turntable apparatus.[26c] Temperatures at which photolysis was carried out were 25 °C (monochromator system) and 32 ± 2 °C (chamber reactor). Isomerization **3** → **4** was followed by GLC (digital integration of peaks) using a Varian Model 1400 instrument and a 0.3 cm × 2 m column packed with 12% FFAP on Chromosorb W (100/120) and operated at 95 °C. Retention times were 2.1 (tridecane internal standard), 3.5 (**4**), and 4.4 (**3**) min. Peak areas were corrected for detector response.

The electrolysis of a 0.05 M acetonitrile solution of **3** was carried out on a Bioanalytical Systems potentiostat equipped with a glassy-carbon working electrode, a Pt auxiliary electrode, and 0.1 M tetraethylammonium perchlorate as supporting electrolyte. The potential was

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(56) The endothermicity of ring closure is apparent in that the adiabatic IP for diene (e.g., ~8.3 eV for **1**) is less than the sum of values of IP_a for the cage isomer (~7.8 eV for **2**) and the heat of the forward reaction (ΔH_{12} = 1.0 eV).[57] A similar thermochemical cycle is not complete for **3**,**4**, but it appears that IP_a (**4**) ≥ 8.8 eV[22] and $\Delta H_{34} < -0.1$ eV (thermal reaction is catalyzed),[54,55] whereas IP_a (**3**) ≃ 7.8 eV.[18]

(57) Rogers, D. W.; Choi, L. S.; Girellini, R. S.; Holmes, T. J.; Allinger, N. L. *J. Phys. Chem.* **1980**, *84*, 1810.

(58) The primary yield of ions for fluorescence quenching by **3** and the extent of chain propagation in CH_3CN cannot be determined from our data. However, if the results for **2** → **1** rearrangement along with flash photolysis data[20c] are a guide, the ion yield on singlet quenching is quite low (implicating a moderate chain length for **3**). Another mechanism of interest[20a] involves radical ion-pair recombination to give triplet **3**, followed by rearrangement.[20a] Although this mechanism is energetically feasible for the pairs, CN-3 and FUM-3 (Table V) and cannot be excluded as a contributor to isomerization in acetonitrile, it would not be a part of the chain sequence for CN sensitization. For a discussion of the radical-ion/triplet mechanism for norbornadiene ring closure, see: Jones, G., II; Schwarz, W.; Malba, V. *J. Phys. Chem.* **1982**, *86*, 2286.

(59) Davis, K. M. C. In "Molecular Association"; Foster, R., Ed.; Academic Press: New York, 1975; Vol. 1.

(60) (a) Kricka, L. J.; Ledwith, A. *Synthesis* **1974**, 539. (b) Mattes, S. L.; Farid, S. *Acc. Chem. Res.* **1982**, *15*, 80.

(61) (a) Tomikawa, T.; Nogami, T.; Tada, K.; Yamamoto, N.; Tsubomura, H.; Mikawa, H. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 2099. (b) Ledwith, A. *Acc. Chem. Res.* **1972**, *5*, 133. (c) Yamamoto, M.; Asanuma, T.; Nishijima, Y. *J. Chem. Soc., Chem. Commun.* **1975**, 53.

(62) (a) Soloway, S. B.; Damiana, A. M.; Sims, J. W.; Bluestone, H.; Lidov, R. E. *J. Am. Chem. Soc.* **1970**, *82*, 5377. (b) Lap, B.; Paddon-Row, M. N. *J. Org. Chem.* **1979**, *44*, 4979.

(63) (a) Stille, J. K.; Witherell, D. R. *J. Am. Chem. Soc.* **1964**, *86*, 2188. (b) Marchand, A. P.; Rose, J. E. *Ibid.* **1968**, *90*, 3724.

(64) deVries, L.; Winstein, S. *J. Am. Chem. Soc.* **1960**, *82*, 8363.

stepped out to +2.0 V vs. SCE and held for a period of 45–60 min. Solutions were analyzed by GLC vs. internal standard. Conversions of 30–40% to the cage isomer **4** were observed.

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Registry No. 3, 1076-13-7; **4**, 704-02-9; **3·5** (R = H), 84415-05-4; **3·5** (R = CO_2Et), 84415-06-5; **3·5** (R = CF_3), 84415-07-6; **3·6**, 84415-08-7; **3·5** (R = CN), 84471-47-6.

Photoisomerization of Charge-Transfer Complexes of Hexamethyl(Dewar benzene). Contrasting Paths for Rearrangement Involving Adiabatic Reaction and Ionic Photodissociation

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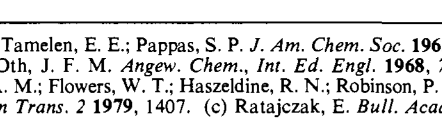
Abstract: The charge-transfer (CT) complexes of hexamethyl(Dewar benzene) (HMDB) with electron acceptors, fumaronitrile, diethyl 1,2-dicyanofumarate, and 1,2,4,5-tetracyanobenzene, have been characterized and compared to similar complexes of hexamethylbenzene (HMB). Irradiation of HMDB CT bands in the 313–435-nm region under a variety of conditions leads to HMDB → HMB isomerization. The quantum yield of rearrangement in a nonpolar solvent is low (e.g., 0.06), although the relative yield of adiabatic isomerization, monitored by emission from excited complexes of HMB, is high (0.72). Quantum efficiencies for isomerization of complexes in polar media generally exceed unity, consistent with a radical-ion chain mechanism for ring opening. The quantum chain reaction depends on the polarity of the solvent, the reduction potential of the acceptor, the extent of conversion, and the wavelength of irradiation. The wavelength effect is associated with excitation to upper vibrational levels of a CT band with enhancement of ionic photodissociation. Comparison of the quantum yield results for excited CT complexes with the findings for rearrangement of HMDB via exciplexes reveals generally different patterns of reactivity.

Dewar benzene and its derivatives have been the focus of extensive investigation since the first synthesis of the parent compound by van Tamelen and Pappas in 1963.[1] The kinetics,[2] thermochemistry,[3] and mechanistic detail[4] for the highly exothermic ring opening to benzene valence isomers have been studied. The reactivity of Dewar benzenes with electrophilic agents has been investigated,[5] with particular attention to hexamethyl(Dewar benzene) (HMDB), the most readily accessible of the simple derivatives.[6] This structure claims the longest known C–C bond (C_1–C_4) (1.63 Å),[7] and it liberates 60 kcal/mol on isomerization to its valence isomer **2**.[2a,3c] Reaction of HMDB with acids,[8] cycloaddition reagents,[9] other conventional electrophiles,[10] and metals[11] has been widely studied. A number of theoretical investigations of Dewar benzenes have been carried out,[12] including the mapping of the potential surfaces for ring opening to the aromatic isomer.[13] Photoelectron spectra have been employed in the assignment of molecular orbital energy levels for several Dewar benzene derivatives; the data predict a relatively high reactivity for HMDB as an electron donor (vertical ionization potential = 7.8 eV).[14]



HMDB **HMB**

Dewar benzenes were initially of photochemical interest as precursors to prismanes.[15] More recently, attention has turned to the large exothermicity of ring opening and its consequences in terms of thermal generation of electronically excited molecules.

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(1) Van Tamelen, E. E.; Pappas, S. P. *J. Am. Chem. Soc.* **1963**, *85*, 3297.

(2) (a) Oth, J. F. M. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 646. (b) Dabbagh, A. M.; Flowers, W. T.; Haszeldine, R. N.; Robinson, P. J. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1407. (c) Ratajczak, E. *Bull. Acad. Pol. Sci., Ser. Sci. Chim.* **1973**, *21*, 691. (d) Munduich, R.; Plieninger, H. *Tetrahedron* **1976**, *32*, 2335.

(3) (a) Greenberg, A.; Liebman, J. *Tetrahedron* **1979**, *35*, 2623. (b) Grimme, W.; Heinze, U. *Chem. Ber.* **1978**, *111*, 2563. (c) Adam, W.; Chang, J. C., *Int. J. Chem. Kinet.* **1969**, *1*, 487.

(4) Goldstein, M. J.; Leight, R. S. *J. Am. Chem. Soc.* **1977**, *99*, 8112.

(5) Van Tamelen, E. E.; Carty, D. *J. Am. Chem. Soc.* **1971**, *93*, 6102.

(6) Schafer, W. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 669.

(7) Cardillo, M. J.; Bauer, S. H. *J. Am. Chem. Soc.* **1970**, *92*, 2399.

(8) (a) Hogeveen, H.; Kwant, P. W. *Acc. Chem. Res.* **1975**, *8*, 413. (b) Hogeveen, H.; Kwant, P. W.; Schuddle, E. P.; Wade, P. A. *J. Am. Chem. Soc.* **1974**, *96*, 7518. Dunbar, R. C.; Fu, E. W.; Olah, G. A. *Ibid.* **1977**, *99*, 7502.

(9) (a) Paquette, L. A.; Haluska, R. J.; Short, M. R.; Read, L. K.; Clardy, J. *J. Am. Chem. Soc.* **1972**, *94*, 529. (b) Bruentrup, G.; Christl, M. *Tetrahedron Lett.* **1973**, 3369. (c) Iwamura, H.; Tanabe, Y.; Kobayashi, H. *Ibid.* **1976**, 1987.

(10) Paquette, L. A.; Lang, S. A., Jr.; Short, M. R. *Tetrahedron Lett.* **1972**, 3141.

(11) Taylor, S. H.; Maitlis, P. M. *J. Am. Chem. Soc.* **1978**, *100*, 4700.

(12) Newton, M. D.; Schulman, J. M.; Manus, M. M. *J. Am. Chem. Soc.* **1974**, *96*, 17 and references cited therein.

(13) (a) Dewar, M. J. S.; Kirschner, S.; Kollmar, H. W. *J. Am. Chem. Soc.* **1974**, *96*, 7579. (b) Tsuda, M.; Oikawa, S.; Kimura, K. *Int. J. Quantum Chem.* **1980**, *18*, 157.

(14) Bieri, G.; Heilbronner, E.; Kobayashi, T.; Schmelzer, A.; Goldstein, M. J.; Leight, R. S.; Lipton, M. S. *Helv. Chim. Acta* **1976**, *59*, 2657.

(15) (a) Schafer, W.; Criegee, R.; Askani, R.; Gruner, G. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 78. (b) Bryce-Smith, D.; Gilbert, A. *Tetrahedron* **1976**, *32*, 1309. (c) See also: Harman, P. J.; Kent, J. E.; O'Dwyer, M. F.; Griffith, D. W. T.; *J. Phys. Chem.* **1981**, *85*, 2731.

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