(d), 55.1 (q), 49.4 (d), 34.5 (d), 15.2 (q); mass spectrum, *m/e* 240 (0.5), 148 ($M^+/2$, 100).

(1α,2β,3α,4α)-1,2-Bis(4-methoxyphenyl)-3,4-dimethylcyclobutane (2). Dimer **2** was prepared by the method of Bauld and co-workers.[3] To a solution containing tris(4-bromophenyl)aminium hexachloroantimonate ($(4\text{-BrC}_6H_4)_3NSbCl_6$, 1 g, 1.22 mmol) in dichloromethane (100 ml), anethole (cis/trans = 90/10, 5.1 g, 34.5 mmol) was added at 0 °C under nitrogen. After 15 min the reaction was quenched by MeONa/MeOH (250 ml). GC analysis showed the reaction mixture was predominantly a ca. 1:1 mixture of dimers **2** and **4**. The dimers could not be separated from one another by preparative GC or column chromatography; however, the NMR spectrum of **2** could be assigned by subtraction of the signals from an authentic sample of dimer **4**.[13] ^{13}C NMR data for dimer **4** and the diphenyl analogue of **2** are reported below. **2**: ^{13}C NMR ($CDCl_3$) δ 157.8 (s), 136.0 (s), 129.0 (d), 128.7 (d), 113.7 (d), 113.5 (d), 55.0 (q), 48.0 (d), 27.5 (d), 34.5 (d), 14.3 (q), 10.8 (q); mass spectrum, *m/e* 240 (2.6), 148 ($M^+/2$, 100).

(1α,2β,3α,4β)-1,2-Bis(4-methoxyphenyl)-3,4-dimethylcyclobutane (4):[13] ^{13}C NMR ($CDCl_3$) δ 158.0 (s), 135.8 (s), 127.7 (d), 113.7 (d), 55.0 (q), 52.6 (d), 43.3 (d), 18.9 (q).

(1α,2β,3α,4α)-1,2-Dimethyl-3,4-diphenylcyclobutane:[3] ^{13}C NMR ($CDCl_3$) δ 48.4 (d), 46.4 (d), 37.6 (d), 34.6 (d), 14.4 (q), 10.8 (q).

(1α,2α,3α,4β)-1,2-Bis(4-methoxyphenyl)-3,4-dimethylcyclobutane (3). Dimer **3** was obtained from the direct irradiation of 1 g of anethole (6.7 mmol, cis/trans = 85/15) in acetonitrile (100 ml) with a Hanovia 450-W high-pressure mercury lamp for 24 h under nitrogen atmosphere. Flash chromatography (silica gel/benzene) yielded a mixture of dimers **3**, **2**, and **1** in a ratio of 70:17:13 as established by GC analysis. The presence of dimers **1** and **2** did not interfere with the NMR assignment of dimer **3**: ^{13}C NMR ($CDCl_3$) δ 157.3 (s), 157.2 (s), 133.8 (s), 131.3 (d), 127.8 (d), 113.4 (d), 112.8 (d), 54.8 (q), 54.7 (q), 47.5 (d), 47.1 (d), 41.8 (d), 39.5 (d), 20.4 (q), 14.6 (q); mass spectrum, *m/e* 240 (2.6), 148 ($M^+/2$, 100).

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Registry No. 1, 19043-23-3; **2**, 84107-48-2; **3**, 117467-12-6; **4**, 84107-47-1; t-A, 4180-23-8; c-A, 25679-28-1.

Electron Transfer Induced Photoisomerization, Dimerization, and Oxygenation of *trans*- and *cis*-Anethole. The Role of Monomer and Dimer Cation Radicals

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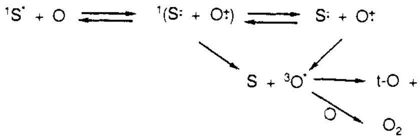
Evanston, Illinois 60208. *Received June 9, 1988*

Abstract: Irradiation of *trans*- or *cis*-anethole in the presence of electron acceptors results in cis,trans isomerization, cyclodimerization, and (in the presence of oxygen) oxidative cleavage. The initial step in each of these reactions is photoinduced electron transfer to yield a singlet radical ion pair. Anethole cation radicals are the initial reactive intermediates formed in each reaction. Isomerization occurs via reverse electron transfer to generate triplet anethole which decays to a mixture of cis and trans isomers. Dimerization occurs via the [2 + 1] cycloaddition of a cation radical and a neutral which proceeds with retention of olefin configuration to yield a mixture of syn and anti head-to-head dimers. The syn/anti dimer ratio is sensitive to reaction conditions because of the lower stability of the syn vs anti dimer cation radical. Reaction of the monomer cation radical with O_2^- or O_2 results in formation of *p*-anisaldehyde. It is unlikely that an acyclic 1,4-cation radical is the precursor of any of the observed products.

The cation radicals of electron-rich olefins can be readily generated by photoinduced electron transfer to a suitable acceptor.[1] Among the most extensively investigated reactions which occur via olefin cation radical intermediates are the cis,trans isomerization of internal olefins and the dimerization of terminal olefins.[1a] Both isomerization[2] and dimerization[3] can occur via triplet mechanisms in which photoinduced electron transfer from the olefin (O) to a singlet acceptor (*S[1]) generates a singlet radical ion pair which can undergo reverse electron transfer to yield the locally excited olefin triplet (Scheme I). The resulting isomerization and dimerization processes are analogous to those obtained via conventional triplet sensitization.

Of greater current mechanistic interest are isomerization and dimerization processes with quantum yields greater than 1.0 in which the cation radical is the reactive intermediate in a chain process. The mechanism outlined in Scheme II was originally proposed by Ledwith[4] to account for the triplet chloranil sensitized reaction of *N*-vinylcarbazole to yield the head-to-head trans dimer and has subsequently been invoked to account for the [2 + 2] cyclodimerization of numerous enamines,[4] vinyl ethers,[5] styrenes,[6] and acetylenes.[7] We recently proposed a cation radical chain mechanism for the one-way isomerization of *cis*-stilbene.[8] The proposed mechanism requires unimolecular cis → trans cation radical isomerization, a process which we have subsequently found

Scheme I



Scheme II

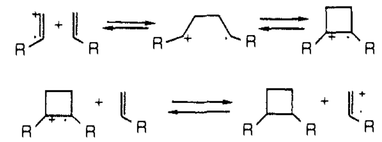


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Table I. Quenching of 9-Cyanoanthracene Fluorescence by Anetholes

isomer	solvent	$k_q\tau$, M^{-1} [a]	$10^{-10}k_q$, M^{-1} s^{-1}
trans	C_6H_6	94	0.68
	CH_3CN	248	1.4
cis	C_6H_6	36	0.26
	CH_3CN	215	1.3

[a] Slope of linear Stern–Volmer plot for quenching of CA fluorescence intensity. [b] Calculated with literature lifetimes. See text.

Table II. Excitation Energies and Redox Potentials

molecule	E^*, eV[a]	E_{red}, V[b]	E_{ox}, V[c]
9-cyanoanthracene (CA)	2.96	−0.98	
9,10-dicyanoanthracene (DCA)	2.88	−0.43	
1,4-dicyanobenzene (DCNB)	4.2	−1.13	
trans-anethole (t-A)			1.75
cis-anethole (c-A)			1.83
biphenyl (BP)			2.40
phenanthrene (P)			2.12
triphenylene (T)			2.24
1,2,4-trimethoxybenzene (TMB)			1.51

[a] Singlet energy from absorption and fluorescence spectra. [b] Half-wave potential for reversible reduction in acetonitrile solution vs Ag/AgI. [c] Peak potential for irreversible oxidation in acetonitrile solution vs Ag/AgI.

does not occur at room temperature in solution.[9] Exploration of alternative mechanisms led us to consider the reversible formation (with stereomutation) of a 1,4-cation radical intermediate analogous to that proposed in cation radical dimerization (Scheme II).

While the occurrence of both isomerization and dimerization via a common 1,4-cation radical intermediate presents an economy of mechanism, there are no available examples of concurrent isomerization and dimerization of internal olefin cation radicals generated via photoinduced electron transfer. In fact, dimerization of an internal olefin has been reported only in the case of *trans*-*N*-propenylcarbazole.[4b] Unfortunately, its cis isomer fails to undergo either isomerization or dimerization, plausibly due to steric inhibition of delocalization in the cis cation radical. We selected *trans*- and *cis*-anethole [1-(4-methoxyphenyl)propene] as candidates for investigation of concurrent cation radical isomerization and dimerization on the basis of previous reports of (a) their isomerization via photoinduced electron transfer[10] and (b) their dimerization via nonphotochemical one-electron oxidation using tris(*p*-bromophenyl)aminium hexachloroantimonate.[11] The results of our investigation are reported herein.

Results

Fluorescence Quenching and Electrochemical Data. Both *trans*-anethole (t-A) and *cis*-anethole (c-A) are efficient quenchers of the fluorescence of 9-cyanoanthracene (CA). Values of $k_q\tau$ obtained from linear Stern–Volmer plots of data for 10^{-3} M CA and (1.0–5.0) × 10^{-3} M anethole in benzene and acetonitrile solutions are reported in Table I along with k_q values calculated with literature lifetimes for methylcyclohexane (13.8 ns[12]) and acetonitrile (17.2 ns[13]) solutions. The resulting k_q values are close to the calculated rates of diffusion in benzene and acetonitrile solution (1.5 and 2.7 × 10^{10} M^{-1} s^{-1}, respectively).[14] No exciplex emission is observed to accompany CA fluorescence quenching by c-A or t-A in either solvent. Exciplex fluorescence has been observed from t-A and singlet cyanophenanthrenes in benzene solution.[15]

Table III. Electron Transfer Sensitized Reactions of *trans*-Anethole

entry	sens[a]	cosens[b]	solvent	[t-A], M	% conv	% yield[c]		
						c-A	**1**	**2**
1	none		CH_3CN	0.05	28	47	25	0
2	DCNB		CH_3CN	0.05	22	16	1.5	5.2
3	DCN	BP	CH_3CN	0.05	23	13	1.3	5.1
4	DCNB	T	CH_3CN	0.05	27	14	1.0	8.8
5	DCNB	P	CH_3CN	0.05	29	14	0.9	7.2
6	DCNB	P	CH_3CN	0.005	28	100	0	tr
7	DCNB	P	CH_3CN	0.50	15	0	5.9	6.4
8	DCNB	P	C_6H_6	0.05	23	93	1.4	tr
9	CA		CH_3CN	0.05	33	12	0.8	33.0
10	CA		CH_2Cl_2	0.05	13	9	1.8	3.9
11	DCA		CH_3CN	0.05	19	0	2.2	12.9

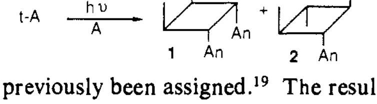
[a] Results for deoxygenated solutions of 0.05 M t-A irradiated for 7 h with 0.1 M DCNB (313 nm) or 10^{-3} M CA or DCA (365 nm). See Table II for abbreviations. [b] Cosensitizer concentration = 0.1 M. See Table II for abbreviations. [c] Yields based on consumed t-A.

The oxidation potentials of t-A and c-A measured in acetonitrile solution containing 0.1 M Et_4NBF_4 vs Ag/AgI are reported in Table II as peak potentials for irreversible oxidation. The value for t-A is in good agreement with a previously reported value (E_{ox} = 1.28 V vs SCE[16]) when corrected for the difference in reference electrodes (−0.36 V). Also reported in Table II are the electronic excitation energies and reduction potentials of several electron acceptors and several aromatic hydrocarbons used as cosensitizers or quenchers in this investigation. Free energies for photoinitiated electron transfer in acetonitrile solution can be calculated from the data in Table II by using Weller's equation (eq 1).[17] For

$$\Delta G_{et} = E_D^{ox} - E_A^{red} - E_s - 0.06 \text{ eV} \qquad (1)$$

example, electron-transfer quenching of CA by t-A is calculated to be exothermic by 0.31 eV. Since CA is the weakest of the excited-state electron acceptors investigated, exothermic and diffusion-controlled electron-transfer quenching is expected to occur for t-A and c-A with all of the acceptors in Table II.

Electron Transfer Sensitized Isomerization and Dimerization of *trans*-Anethole. Direct (313 nm, unsensitized) irradiation of 0.05 M t-A in acetonitrile solution results in the formation of c-A and the syn head-to-head dimer **1** as the only detectable products at moderate conversions of t-A.[18,19] In contrast, irradiation of t-A with several electron acceptors, A (with and without cosensitizers), results in the formation of c-A and mixtures of **1** and the anti head-to-head dimer **2** (eq 2). The structures of **1** and



(2)

2 have previously been assigned.[19] The results of fixed-duration

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Table IV. Electron Transfer Sensitized Reactions of *cis*-Anethole

entry	sens[a]	cosens[b]	solvent	[c-A_0], M	% conv	% yield[c] t-A	2	3	4	5
1	none		CH_3CN	0.05	12	20	0	17	14	0
2	DCNB		CH_3CN	0.05	21	25	1.2	0.4	3.5	2.1
3	DCNB	BP	CH_3CN	0.05	25	25	2.1	0.4	5.2	3.5
4	DCNB	T	CH_3CN	0.05	27	21	2.0	0.3	*d*	3.0
5	DCNB	P	CH_3CN	0.05	24	33	2.4	0.4	5.6	2.8
6	DCNB	P	CH_3CN	0.005	31	49	3.5	0	6.4	2.0
7	DCNB	P	CH_3CN	0.50	25	78	2.1	0.7	3.6	0.6
8	DCNB	P	C_6H_6	0.05	15	54	0	0.3	0.1	0
9	CA		CH_3CN	0.05	27	1	1.2	0.2	3.3	1.7
10	DCA		CH_3CN	0.05	21	0	0.6	*d*	1.6	0.8

[a-c] See footnotes to Table III. [d] Not detected due to interfering GC peaks.

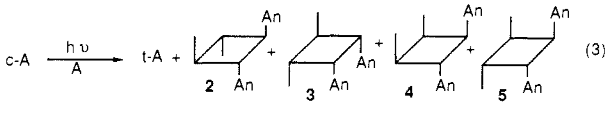
irradiations under various conditions are summarized in Table III. Yields of c-A, **1**, and **2** are based on consumed t-A. The low mass balance in most of these reactions is presumed to result from t-A polymerization; however, the insoluble residues from these reactions have not been characterized.

The use of DCNB aromatic hydrocarbon cosensitization to effect the cis,trans isomerization of the anetholes and other electron-rich alkenes was reported by Majima et al.[10] In agreement with their report, DCNB/phenanthrene cosensitization of 0.005 M t-A is found to result predominantly in isomerization, with excellent mass balance (Table III, entry 6). Cosensitization results in slightly higher conversions than is obtained with DCNB alone (Table III, entries 2–5). At 0.05 M t-A, isomerization and dimerization are roughly competitive, while dimerization predominates at 0.5 M t-A (Table III, entries 5 and 7). The accompanying decrease in mass balance suggests that dimerization and polymerization are competing, concentration-dependent reactions. The ratio of dimers **2**/**1** decreases with increasing t-A concentration. In the nonpolar solvent benzene, isomerization is the predominant reaction even at 0.05 M t-A (Table III, entry 8).

Photodimerization of t-A can also be effected by using the singlet acceptors 9-cyanoanthracene (CA) and 9,10-dicyanoanthracene (DCA) with 365-nm irradiation. The yield of dimers is higher than with DCNB, as is the dimer ratio **2**/**1**. The yield of c-A is lower for CA vs DCNB sensitization and is too low to be detected with DCA. The efficiency of the CA-sensitized reaction is lower in dichloromethane vs acetonitrile solution. Conventional triplet (energy transfer) sensitizers effect the trans,cis isomerization of the anetholes but not their dimerization.[18,19]

The absorption of 313-nm irradiation by t-A, DCNB, and the cosensitizers renders the measurement of quantum yields problematical. Quantum yields for the CA-sensitized reactions of 0.05 M t-A have been measured at low (<5%) conversion with 365-nm irradiation. The values obtained are $\Phi_i = 0.0036$, $\Phi_1 = 0.0033$, and $\Phi_2 = 0.026$. The ratio $(\Phi_1 + \Phi_2)/\Phi_i$ is similar to that in the higher conversion experiments (Table III); however, the ratio Φ_2/Φ_1 is lower. Evidently, the Φ_2/Φ_1 ratio increases with increasing conversion as well as increasing t-A concentration and increasing solvent polarity.

Electron Transfer Sensitized Isomerization and Dimerization of *cis*-Anethole. Direct (313 nm, unsensitized) irradiation of 0.05 M c-A in acetonitrile solution results in the formation of t-A and the nonsymmetric dimers **3** and **4**.[19] In contrast, irradiation with several electron acceptors results in the formation of t-A and dimers **2–5** (eq 3). The structures of dimers **3** and **4** have previously been assigned,[19] while that of the symmetrical anti head-to-head dimer **5** was confirmed by independent synthesis (see the Experimental Section).



(3)

The results of fixed-duration irradiation of c-A under the same conditions employed for t-A are summarized in Table IV. The results are qualitatively similar to those for t-A but are more complex due to the formation of four dimers. As is the case with t-A, isomerization is the major process for DCNB sensitized (and cosensitized) reactions in acetonitrile solution and predominates in benzene solution. Sensitization with CA or DCA results in dimerization but little or no isomerization.

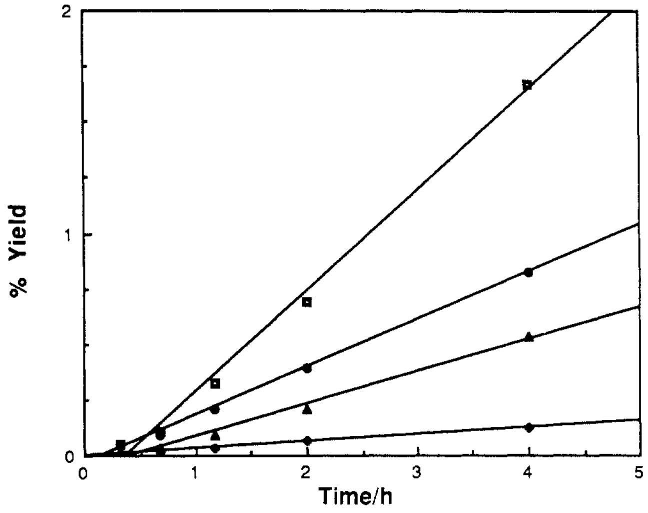


Figure 1. Formation of dimers **2** (▲), **3** (◆), **4** (□), and **5** (●) upon DCNB/P-sensitized irradiation of *cis*-anethole.

The dimer ratios obtained from c-A are highly dependent upon reaction conditions; however, **4** is the major dimer under the conditions given in Table IV. The yields of dimers **2–5** at short reaction times under the conditions outlined in Table IV, entry 5, are shown in Figure 1. The concentration of t-A increases linearly from 0.5% at 0 h to 4.4% at 4 h. For reaction times under 1 h, **5** is the major dimer, whereas at longer irradiation times **4** becomes the major dimer. Non-zero intercepts are observed in the linear plots for dimers **2** and **4**, but not for dimer **5**.

Quenching of Dimerization by 1,2,4-Trimethoxybenzene. Low concentrations of 1,2,4-trimethoxybenzene (TMB) have been employed to quench reactions which occur via cage-escaped cation radicals that are of higher oxidation potential than TMB (Table II).[20] Quantum yields for the CA-sensitized dimerization of t-A in the presence of (0.5–2.0) × 10^{-5} M TMB are given in Table V. While the formation of dimers **1** and **2** is quenched by TMB, the extent of quenching is substantially larger for dimer **2** than for dimer **1**.

Effect of Oxygen. Irradiation of t-A or c-A in acetonitrile solution (with or without electron-transfer sensitizers) in the presence of oxygen (8 × 10^{-3} M[21]) results in more rapid consumption of the initial isomer, partial quenching of isomerization and dimerization, and formation of oxygenated products (eq 4).

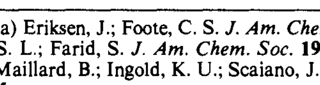


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Table V. Quantum Yields for 9-Cyanoanthracene-Sensitized Dimerization of *trans*-Anethole in the Absence and Presence of Trimethoxybenzene[a]

10^5TMB, M	Φ_1	Φ_2	10^5TMB, M	Φ_1	Φ_2
0	0.0033	0.026 ± 0.001	1.25	0.0030	0.011
0.5	0.0033	0.022	1.5	0.0027	0.010
0.75	0.0030	0.016	2.0	0.0023	0.0071
1.0	0.0033	0.017			

[a] Values for 365-nm irradiation of deoxygenated acetonitrile solutions of 10^{-3} M CA and 0.05 M t-A.

Table VI. Effect of Oxygen on the Electron Transfer Sensitized Reactions of the Anetholes[a]

anethole	sens	O_2	% conv	% yield AnCHO	isomer	**1** or **4**	**2** or **5**
trans	DCNB	–	22		16	1.5	5.2
trans	DCNB	+	56	18	8	0.3	2.9
trans	CA	–	33		12	0.8	33.0
trans	CA	+	100	20		tr	2.8
trans	DCA	–	19			2.2	12.9
trans	DCA	+	34	27		0.8	5.6
cis	DCNB	–	21		25	3.5	2.1
cis	DCNB	+	28	12	10	1.0	0.8
cis	CA	–	27		1	3.3	1.7
cis	CA	+	100	23		0.2	0.3
cis	DCA	–	21			1.6	0.8
cis	DCA	+	34	8		0.8	0.2

[a] Reaction conditions are the same as in Tables III and IV.

Table VII. Electron Transfer Sensitized Cycloreversion of Anethole Dimers

dimer	E_{ox}, V[a]	O_2	% conv[b]	t-A % yield
1	1.75	–	11	45
		+	15	49
2	1.85	–	2.6	55
		+	8.0	*c*
5	2.04	–	4.4	*c*
		+	12	*c*

[a] See Table II, note *c*. [b] Results for irradiation of 0.01 M dimer and 10^{-3} M CA in acetonitrile solution for 1 h. [c] Yield of t-A not determined.

Product formation was monitored by GC and ^{13}C NMR. The major oxygenated product is *p*-anisaldehyde and the minor product is tentatively identified as the epoxide of t-A,[22] on the basis of ^{13}C NMR analysis of the oxygenation product mixtures. No additional products were detected. These products are also formed in the autoxidation of t-A.[23] Results obtained for fixed-duration irradiation of t-A and c-A with several acceptors in the absence and presence of oxygen are summarized in Table VI. The minor dimers (**2** and **3**) obtained from the reactions of c-A are omitted from the table for the sake of brevity.

Cycloreversion of Anethole Dimers. The electron transfer sensitized cycloreversion of dimer **1** has previously been reported by Pac.[24] We have investigated the CA-sensitized reactions of dimers **1**, **2**, and **5** (0.01 M) in acetonitrile solution in the absence and presence of oxygen. Results obtained for fixed-duration 365-nm irradiation are summarized in Table VII along with the dimer oxidation potentials. The major product from these reactions is t-A; however, the mass balance is low (ca. 50%), suggesting the occurrence of competing reactions leading to polymeric products. Only trace amounts of anisaldehyde were obtained from the reaction of **1** in the presence of oxygen, and the yield of t-A is increased, as previously reported.[24] The cycloreversion of **1** is more efficient than that of **2** or **3**; this difference being more noticeable in the absence of oxygen than in its presence.

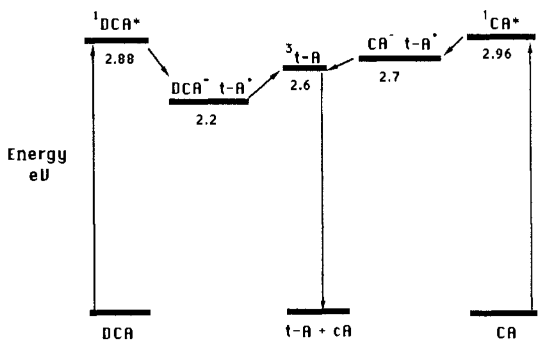

Figure 2. Energy-level diagram for the locally excited states of cyanoanthracene (CA) and dicyanoanthracene (DCA) and their singlet radical ion pairs with *trans*-anethole (t-A) and the t-A triplet state.

Discussion

Isomerization Mechanism. As discussed in the introduction, two mechanisms have been described for electron transfer induced olefin isomerization. In the first of these (Scheme I), the initially formed radical ion pair undergoes intersystem crossing followed by reverse electron transfer to yield a locally excited olefin triplet which decays to a mixture of cis and trans olefins. Since reverse electron transfer can occur either in the initially formed radical ion pair or upon reencounter of free-radical ions, isomerization can occur in nonpolar as well as in polar solvents, as long as the initial electron transfer is exothermic and the locally excited triplet is of lower energy than the radical ion pair.[2] In contrast, isomerization via a cage-escaped cation radical intermediate requires a highly polar solvent in order for cage escape to occur. A second difference between triplet and cation radical mechanisms is the isomerization of both cis and trans isomers via the triplet but of only the cis isomer via the cation radical.

The electron transfer sensitized isomerization of t-A to give a 1:1 mixture of t-A and c-A was briefly noted by Majima et al. at the end of their paper describing the isomerization of 1-phenoxypropene.[10] The use of both an electron acceptor (DCNB) and a donor (phenanthrene, etc.) was found necessary to effect the photoisomerization of 1-phenoxypropene. Isomerization was proposed to occur via a π-complex of the donor cation radical with the phenoxypropene or alternatively, by electron-hole transfer to form the phenoxypropene cation radical.[1a] A mechanism for cation radical isomerization was not proposed; however, triplet mechanisms were excluded on the basis of the absence of quenching by 1.0 M isoprene.[10]

In agreement with the results of Majima et al.,[10] we find that DCNB/P cosensitization of 0.005 M t-A or c-A results in efficient isomerization and little or no dimerization (Tables III and IV). Our data are also consistent with the previously reported photoequilibrium ratio of t-A/c-A ~ 1.0. Unlike the isomerization of 1-phenoxypropene which requires a co-sensitizer and a polar solvent, the DCNB-sensitized isomerization of t-A or c-A occurs with comparable efficiency in the absence or presence of cosensitizers and in nonpolar or polar solvents (Tables III and IV). These results are compatible with isomerization via triplet t-A or c-A formed upon reverse electron transfer (Scheme I) rather than cation radical isomerization. The small enhancement in isomerization and dimerization yields in the presence of cosensitizers indicates that the yield of t-A cation radical obtained by direct electron transfer to singlet DCNB is comparable to that obtained by photoinduced electron transfer from singlet P to DCNB followed by exothermic secondary electron transfer from t-A to $P^{\cdot+}$.

Further evidence for a triplet isomerization mechanism is provided by the results obtained with the singlet electron acceptors CA and DCA (Tables III and IV). CA-sensitized isomerization of t-A is observed to occur in both acetonitrile and dichloromethane solution, but little or no isomerization of t-A is observed with DCA or of c-A with either CA or DCA. Since dimerization and oxygenation (Table VI) occur under these conditions, we conclude that *formation of free t-A of c-A radicals is not a sufficient*

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[22] Marples, B. A.; Saint, C. G. *Synth. Commun.* **1982**, *12*, 545.

[23] Iwamuro, H.; Kanehiro, M.; Matsubare, Y. *Yakazaku* **1982**, *31*, 222; *Chem. Abstr.* **1982**, *97*, 23367*s*.

[24] Pac, C. *Pure Appl. Chem.* **1986**, *58*, 1249.

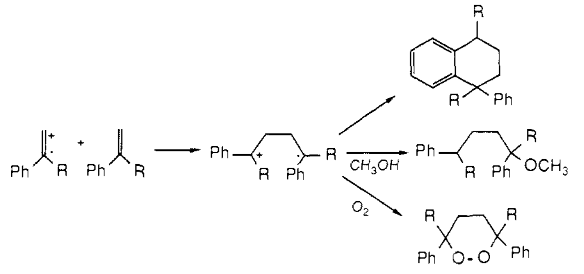
condition for isomerization. The sensitization of t-A isomerization by CA or DCNB but not by DCA can be rationalized with the energy-level diagram shown in Figure 2. The energies of singlet CA and DCA and the radical ion pair energies ($-E_D^{ox} + E_A^{red}$) are taken from Table II and the triplet energy of t-A (2.6 eV) is assumed to be similar to that for *trans*-1-phenylpropene.[25] The triplet of t-A is seen to lie below the CA/t-A ion pair energy, but above the DCA/t-A ion pair energy. The triplet energy of c-A (assumed to be similar to that for *cis*-1-phenylpropene, 3.0 eV[25]) lies above the ion pair energies for the ion pairs of c-A with both CA and DCA. Thus isomerization only occurs when the radical ion pair is of higher energy than the anethole triplet.

The failure of 1 M isoprene to quench the electron transfer sensitized isomerization of 1-phenoxypropene or t-A was previously cited as evidence against a triplet isomerization mechanism.[10] Styrene derivatives, including anethole, are known to prefer twisted, 1,2-biradical vs planar structures.[26] While the anethole twisted triplet lifetime is moderatly long (τ = 30 ns), quenching does not reduce the quantum yield of isomerization.[26] Thus isoprene would not be expected to reduce the efficiency of isomerization via the triplet mechanism of Scheme I. The efficiency of electron transfer sensitized isomerization is reduced by oxygen (Table VI). Presumably, the oxidation of free anethole cation radicals (vide infra) competes with homogeneous cation radical–anion radical recombination to yield triplet anethole.

While electron transfer sensitized isomerization of the anetholes using cyano aromatic singlet acceptors results in reversible cis,trans isomerization, irradiation of the anetholes and other styrene derivatives in the presence of CdS powder results in one-way cis → trans isomerization, yielding photostationary states similar to those for iodide atom catalyzed free-radical isomerization.[27] A triplet mechanism has been logically ruled out on the basis of the nonreactivity of the trans isomer. Oxidation of the adsorbed cis isomer by a light-generated surface hole, followed by cation radical cis → trans isomerization, has been proposed as the mechanism of aryl olefin isomerization.[27] While we previously suggested that cis → trans isomerization of stilbene cation radicals might occur at room temperature,[8a] more recent evidence effectively rules out this possibility for *cis*-stilbene as well as for c-A.[9] A photochemically generated surface sulfur radical has been suggested as the active catalyst for CdS photoinduced cis → trans isomerization of simple alkenes[28] and may also be involved in the isomerization of aryl olefins.

Dimerization and Cycloreversion Mechanism. A triplet mechanism for electron transfer induced dimerization of anethole (Scheme I) can be readily excluded on the basis of our results and the previously observed failure of triplet sensitization to effect dimerization.[18,19] Whereas isomerization of t-A and c-A occurs more efficiently in nonpolar vs polar solvent, the converse is true for dimerization (Tables III and IV). A cation radical mechanism for dimerization (Scheme II) is consistent with the solvent dependence and other available data. The ratio of dimerization/isomerization increases with increasing anethole concentration in accord with the anticipated competition between cation radical addition to neutral anethole (Scheme II) and homogeneous reencounter with the anion radical (Scheme I). Quenching of dimerization by 1,2,4-trimethoxybenzene (Table V) presumably results from electron-hole transfer to generate the more stable cation radical (Table I). Reaction of the cation radical with oxygen (Table VI) inhibits both dimerization and isomerization and results in the formation of anisaldehyde.

Scheme III



Scheme IV

$$\text{t-A} + \text{Ar}_3\text{N}^{+\cdot} \rightleftharpoons \text{t-A}^{+\cdot} + \text{Ar}_3\text{N}$$

$$\text{t-A}^{+\cdot} + \text{t-A} \longrightarrow \text{Dimer}^{+\cdot}$$

$$\text{Dimer}^{+\cdot} + \text{t-A} \longrightarrow \text{Dimer} + \text{t-A}^{+\cdot}$$

According to Ledwith's[4] mechanism for cation radical dimerization (Scheme II), nonsynchronous bond formation results in the formation of an acyclic 1,4-cation radical which is in equilibrium with a cyclobutane cation radical. Evidence for the formation of acyclic 1,4-cation radical intermediates from terminal aryl olefins includes the formation of dihydronaphthalene dimers,[6c] trapping with nucleophiles,[7,29] and trapping with oxygen[6c,30] (Scheme III). An acyclic 1,4-cation radical is also the presumed intermediate in the electron transfer induced cis → trans isomerization of 1,2-diphenoxycyclobutane as well as the dimerization of phenyl vinyl ether.[5]

While the above experimental evidence is supportive of a trappable acyclic 1,4-cation radical intermediate, recent theoretical analysis of the cation radical dimerization of ethene by Bauld et al.[11,31] led to the proposal of a quasiconcerted [$\pi^2{}_s + \pi^1{}_s$] reaction to yield a cyclobutane cation radical with a long (one-electron) bond, the second intermediate in the Ledwith mechanism (Scheme II). A long-bond intermediate might also undergo the reactions attributed to the acyclic intermediate (Scheme III). Experimental evidence for the quasi-concerted cation radical dimerization was provided by a stereochemical analysis of the tris(*p*-bromophenyl)aminium hexachloroantimonate catalyzed (nonphotochemical) dimerization of t-A and c-A.[11] Cation radical dimerization of t-A is reported to yield a ca. 1:1 mixture of dimer **1** and **2** at −35 °C and predominantly **2** at 0 °C. Dimer **1** was found to undergo cycloreversion under the reaction conditions. Reaction of c-A yielded t-A and a mixture of dimers **2**, **4**, and **5**, with an induction period being observed for the formation of dimer **2**. A cation radical chain mechanism (Scheme IV) with a chain length of ca. 20 was proposed for t-A dimerization. Activation parameters for the overall reaction are $\Delta H^{\ddagger} = 2.1$ kcal and $\Delta S^{\ddagger} = 29$ eu and the estimated activation enthalpy for the cycloaddition step is $\Delta H_{\text{add}} = 0.8$ kcal.[32]

The stereochemical consequences of electron transfer induced dimerization of t-A and c-A are qualitatively similar to those obtained for the aminium salt catalyzed reaction by Bauld and Pabon.[11] Both reactions convert t-A to mixtures of dimers **1** and **2**, with the dimer ratio dependent upon reaction conditions. Dimer **2** is favored by higher temperature in the aminium salt catalyzed reaction, in accord with its anticipated greater thermodynamic stability. The formation of dimer **1** but not dimer **4** or c-A upon aminium salt or photochemical (using DCA sensitization) oxidation of t-A effectively rules out the existence of an acyclic 1,4-cation radical intermediate of sufficient lifetime to allow stereomutation.

In the photoinduced reactions of t-A, dimer **2** is favored by low t-A concentration and by the more delocalized cyanoanthracene acceptors, CA and DCA (Table III). The dimer ratio **2**/**1** is also dependent upon the concentration of the electron-hole scavenger 1,2,4-trimethoxybenzene, TMB (Table V). Quenching of the

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(26) Caldwell, R. A.; Cao, C. V. *J. Am. Chem. Soc.* **1982**, *104*, 6174.

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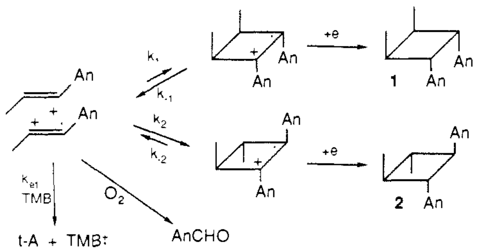
Scheme V



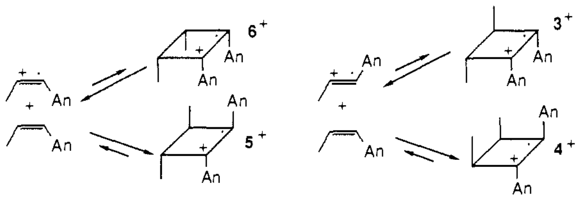
formation of dimer **2** is much more efficient than quenching that of dimer **1**, resulting in a decrease in the **2**/**1** ratio with increasing TMB concentration. Reduction in the **2**/**1** ratio bears superficial analogy with reduction in the trans/cis dimer ratio from phenyl vinyl ether (PVE) observed by Mattes et al.[5b] They proposed that a common acyclic 1,4-cation radical forms the cis cyclobutane cation radical reversibly and the trans cyclobutane cation radical irreversibly. Reduction of the cis cation radical by either PVE or TMB results in a decrease in the trans/cis ratio.

While our stereochemical results are incompatible with a common acyclic 1,4-cation radical intermediate in the formation of dimers **1** and **2**, they are compatible with the mechanism outlined in Scheme V in which the cyclobutane cation radical $\mathbf{1}^{\cdot+}$ is formed more reversibly than $\mathbf{2}^{\cdot+}$. Evidence for the greater stability of $\mathbf{2}^{\cdot+}$ vs $\mathbf{1}^{\cdot+}$ is provided by the relative yields of electron transfer induced cycloreversion of dimers **1** and **2** (Table VII). According to Scheme V, cycloreversion of $\mathbf{1}^{\cdot+}$ and $\mathbf{2}^{\cdot+}$ competes with their reduction to the neutral dimers. Possible reductants include an acceptor anion radical, neutral t-A, or added TMB. Reduction of $\mathbf{1}^{\cdot+}$ by t-A is exergonic by 0.1 eV, whereas reduction of $\mathbf{2}^{\cdot+}$ by t-A is isoergonic. Thus the lower **2**/**1** ratio at higher t-A concentration (Table III) may reflect the more rapid reduction of $\mathbf{1}^{\cdot+}$.[33] Added TMB can reduce t-$A^{\cdot+}$, resulting in a decrease in the yield of $\mathbf{1}^{\cdot+}$ and $\mathbf{2}^{\cdot+}$. It can also reduce $\mathbf{1}^{\cdot+}$ or $\mathbf{2}^{\cdot+}$, resulting in an increase in the yield of dimers. In the case of the relatively stable cyclobutane cation radical intermediate $\mathbf{2}^{\cdot+}$, reduction of $\mathbf{2}^{\cdot+}$ by TMB is unimportant compared to the decreased yield of $\mathbf{2}^{\cdot+}$ upon reduction of t-$A^{\cdot+}$ by TMB. In contrast, reduction of the relatively unstable intermediate $\mathbf{1}^{\cdot+}$ by TMB may largely compensate for the decreased yield of $\mathbf{1}^{\cdot+}$. Hence formation of dimer **2** is quenched to a greater extent than is formation of dimer **1** by added TMB.

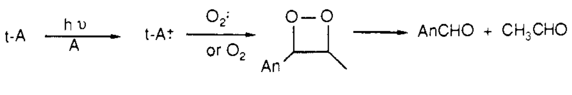
In the limit of high t-A concentration or TMB concentration, the ratio of dimers **2**/**1** is near unity, indicating that the rate constants for formation of $\mathbf{1}^{\cdot+}$ and $\mathbf{2}^{\cdot+}$ are similar (Scheme V, $k_1 \sim k_2$). The lack of selectivity in both the photoinitiated and aminium salt initiated [2 + 1] dimerization[11] of t-A stands in marked contrast to the highly selective formation of dimer **1** in the singlet-state [2 + 2] dimerization of t-A.[18,19] Singlet dimerization is believed to occur via a sandwich-type excimer in which π-orbital overlap is maximized in a geometry leading to the syn head-to-head dimer **1**. Quite obviously a single oriented π-complex cannot be the precursor of both $\mathbf{1}^{\cdot+}$ and $\mathbf{2}^{\cdot+}$ in cation radical [2 + 1] dimerization.

Analysis of the stereochemistry of electron transfer induced dimerization of c-A is complicated by the formation of four dimers with ratios which depend upon the conversion (Figure 1) and reaction conditions (Table IV). The major product at low conversions is dimer **5**, which plausibly is formed by a quasi-concerted anti [2 + 1] reaction of c-$A^{\cdot+}$ with c-A to form $\mathbf{5}^{\cdot+}$, which is moderately stable under the conditions of electron-transfer sensitization (Table VII). Syn dimerization would yield a particularly unstable all cis-substituted cyclobutane cation radical, $\mathbf{6}^{\cdot+}$. We presume that our failure to observe a sixth dimer even as a trace product by capillary GC reflects the instability of $\mathbf{6}^{\cdot+}$. Dimers **3** and **4** are plausiblly formed via the syn and anti addition, respectively, of t-$A^{\cdot+}$ and c-A. Exergonic electron exchange between c-$A^{\cdot+}$ and the low concentration t-A impurity (0.5%) can lead to the formation of t-$A^{\cdot+}$ even at very low conversions.[33] The selective formation of the anti vs syn dimer (**4** vs **3**) upon reaction of t-$A^{\cdot+}$ with c-A is analogous to the selective formation of the anti dimer **2** upon cation radical dimerization of t-A and of dimer **5** from c-A. The concentration of t-A increases in the early stages of the reaction, leading to upward curvature in the plots of the yields of **4** and the major t-A dimer **2** vs irradiation time (Figure 1).

Scheme VI



Scheme VII



Our proposed mechanisms for the reactions of c-$A^{\cdot+}$ with c-A and t-$A^{\cdot+}$ with c-A are summarized in Scheme VI. As in the cation radical dimerization of t-A (Scheme V), both syn and anti dimer cation radicals are formed; however, the greater stability of the anti dimer cation radicals under the reaction conditions results in highly selective formation of **5** vs **6** and moderately selective formation of **3** vs **4**. Stepwise cycloreversion of the dimer cation radicals **3**–**6** might provide a mechanism for isomerization of c-A to t-A. However, the low yield of t-A obtained with CA (Table IV), which also sensitizes the cycloreversion of **5**, eliminates cyclobutane decomposition as a major source of isomerization under the reaction conditions outlined in Table IV.

A rough estimate of the rate constant for addition to t-$A^{\cdot+}$ and t-A to form **2** can be obtained from the TMB quenching data and the assumption that TMB will quench t-$A^{\cdot+}$ with a rate constant near the rate of diffusion in acetonitrile solution (2×10^{10} M^{-1} s^{-1}). Since ca. 10^{-5} M TMB is sufficient to quench about half of the formation of **2** from 0.05 M t-A, the rate constant for addition is $k_2 \sim 2 \times 10^6$ M^{-1} s^{-1}. This value is distinctively lower than previously reported values for the terminal olefins 1,1-diphenylethylene (1×10^{10} M^{-1} s^{-1} [6c]) and phenyl vinyl ether (6×10^8 M^{-1} s^{-1} [5c]), but it is comparable to the value for the internal olefin 1,1-dimethylindene (1×10^6 M^{-1} s^{-1} [5c])). Evidently, cation radicals, like free radicals, add more rapidly to terminal vs internal olefins. The estimated value of k_2 is consistent with the low activation enthalpy estimated by Bauld et al.[32]

Photooxygenation Mechanism. The photooxygenation of aryl olefins has been extensively investigated by Foote and co-workers.[20a,34] They have proposed that oxidative cleavage occurs via the reaction of the olefin cation radical with the superoxide ion (generated by secondary electron transfer from the acceptor anion radical to O_2) to yield an unstable dioxetane, which decomposes to yield two carbonyl-containing products. This mechanism, applied to the reaction of t-A, is outlined in Scheme VII. An alternative mechanism (Scheme III) has been proposed by Gollnick and Schnatterer[30,35] and by Mattes and Farid[6c] to account for the formation of stable 1,2-dioxanes from 1,1-diaryl olefins.

We have monitored the electron transfer induced photooxygenation of t-A both by capillary GC and by ^{13}C NMR and can detect no products other than *p*-anisaldehyde and a small amount of the epoxide of t-A. The failure to detect a 1,2-dioxane product is consistent with our conclusion that neither electron transfer induced isomerization nor dimerization involves a long-

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(33) A rate constant of 2×10^9 M^{-1} s^{-1} has recently been reported for a slightly exergonic electron transfer from a cis aryl olefin cation radical to its trans isomer. Ebbesen, T. W.; Akaba, R.; Tokumaru, K.; Washio, M.; Tagawa, S.; Tabata, Y. *J. Am. Chem. Soc.* **1988**, *110*, 2147.

(34) (a) Manring, L. E.; Kramer, M. K.; Foote, C. S. *Tetrahedron Lett.* **1984**, *25*, 2523. (b) Manring, L. E.; Eriksen, J.; Foote, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 4275. (c) Foote, C. S. *Tetrahedron* **1985**, *41*, 2221.

(35) Gollnick, K.; Schnatterer, A. *Photochem. Photobiol.* **1986**, *43*, 365.

lived acyclic 1,4-cation radical intermediate. Evidently oxygenation of t-A occurs via reaction of the monomer cation radical (Scheme VII). The increased conversion of t-A (and c-A) in the presence of oxygen indicates that reverse electron transfer from S$^{\bullet-}$ to t-A$^{\bullet+}$ (or c-A$^{\bullet+}$) is responsible, at least in part, for the low quantum yields for CA-sensitized isomerization and dimerization (Table V). Tsuchiya et al.[36] have recently reported that the second-order decay of the *trans*-stilbene cation radical is more rapid with CA$^{\bullet-}$ ($5.\times 10^9$ M^{-1} s^{-1}) than with O$_2^-$ (1.9×10^9 M^{-1} s^{-1}).[37] Thus both a longer cation radical lifetime and reactions with O$_2^-$ or O$_2$ may contribute to the higher conversions of the anetholes observed in the presence of oxygen. Oxygen reduces the yield of dimers, indicating that reaction of t-A$^{\bullet+}$ with 0.05 M t-A and with O$_2^-$ (ca. 5×10^{-8} M under steady state irradiation) or O$_2$ (8×10^{-3} M) are roughly competitive processes.

The presence of O$_2$ also enhances the yield of CA-sensitized cycloreversion of dimers **1**, **2**, and **5** (Table VII) as previously reported by Pac[24] for dimer **1**. According to Pac, cycloreversion of **1** is completely quenched by 10^{-3} M TMB, indicating that cycloreversion of **1**$^{\bullet+}$ is a relatively slow process. Thus, in the absence of O$_2$, reverse electron transfer from CA$^{\bullet-}$ to **1**$^{\bullet+}$ can compete with cycloreversion. Slower reaction of **1**$^{\bullet+}$ with O$_2^-$ vs CA$^{\bullet-}$ can account for the increased yield of cycloreversion in the presence of oxygen. While cycloreversion leads to the formation of t-A$^{\bullet+}$ and t-A, *p*-anisaldehyde or other oxygenation products are not formed in appreciable yield in the presence of oxygen. Thus neither **1**$^{\bullet+}$ nor t-A$^{\bullet+}$ undergoes efficient oxygenation. Evidently, thermoneutral or slightly exothermic[24] electron transfer from **1** to t-A$^{\bullet+}$ is more rapid than the reaction of t-A$^{\bullet+}$ with O$_2^-$ or O$_2$.

Concluding Remarks. Photoinduced one-electron oxidation of t-A and c-A results in trans,cis isomerization, cyclodimerization, and oxidative cleavage. Isomerization is found to occur via reverse electron transfer to generate triplet t-A or c-A, which isomerize via a common twisted 1,2-biradical intermediate (Scheme I). Dimerization is found to occur via quasi-concerted [2 + 1] cycloaddition to form a mixture of syn and anti head-to-head dimers with retention of olefin configuration (Schemes V and VI). The syn dimer cation radicals are less stable than their anti isomers, thus accounting for the variation in syn/anti isomer ratios with reaction conditions. Oxidative cleavage to yield *p*-anisaldehyde is found to occur upon reaction of the monomer cation radical with O$_2^-$ or O$_2$ (Scheme VII).

Our results serve to conclusively eliminate an acyclic 1,4-cation radical as an intermediate in the isomerization, dimerization, and oxygenation reactions of t-A and c-A. The absence of an acyclic 1,4-cation radical can account for our failure to detect [2 + 4] dimers or 1,2-dioxanes in the presence of oxygen. The formation of these products from terminal aryl olefins requires either an acyclic 1,4-cation radical intermediate (Scheme III) or trapping of a long bonded intermediate in some cases but not others. Reconciliation of these apparently conflicting results can be provided by considering the relative stabilities of the acyclic and cyclic forms of the dimer cation radicals. Bauld et al.[31] concluded on the basis of MNDO calculations that the cyclic dimer of the ethylene cation radical is ca. 5 kcal/mol more stable than the acyclic dimer. In the case of 1,1-diaryl olefins, nonbonded repulsions would be expected to destabilize the cyclic vs acyclic form of the dimer cation radical. Nonbonded repulsion also accounts for the more rapid cycloreversion of *cis*- vs *trans*-1,2-diarylcyclobutane cation radicals.[24] In the case of the anethole cation radical dimers, delocalization of the electron hole onto the anisyl group may increase the bond order of the one-electron cyclobutane σ bond and hence stabilize the cyclic vs acyclic form of the dimer cation radical. An example of nearly isoergic cyclic and acyclic dimer cation radicals may be provided by phenyl vinyl ether, for which cis,trans isomerization of the neutral cyclobutane dimers occurs upon photooxidation.[5] Hence we would caution that generalizations about the structure of cyclobutane cation radicals should not be drawn from a single experimental result or calculation.

Experimental Section

General Methods. ^{13}C NMR spectra were recorded on a JEOL FX-270 spectrometer with TMS as an internal standard. Ultraviolet and visible absorption spectra were measured with a Hewlett-Packard 8452A diode-array spectrophotometer. Mass spectra were determined with a Hewlett Packard 5985 GC/MS system using an ionizing voltage of 70 eV. Fluorescence spectra were recorded on a Perkin-Elmer MPF-44A spectrophotometer. The light source was a 450-W Hanovia medium-pressure mercury lamp enclosed in a water-cooled Pyrex glass well. A potassium chromate solution filter was used to isolate the 313-nm line, and Corning glass filters 7-54 and 0-52 were used to isolate the 365-nm line. Analytical-style irradiations and quantum yield measurements were conducted under dry N$_2$ in 13-mm-o.d. Pyrex tubes on a merry-go-round apparatus in a temperature-controlled water bath. Irradiated mixtures were analyzed on a Varian 3700 gas chromatograph equipped with a 10 m × 0.53 mm glass column packed with polyethylene glycol for analysis of *p*-anisaldehyde, c-A, and t-A and on a Hewlett-Packard 5890 gas chromatograph equipped with a 10 m × 0.53 mm glass column packed with polydimethylsiloxane for analysis of c-A, t-A, and dimers **1–5**. Both chromatographs are equipped with flame-ionization detectors. Light intensities were determined with *trans*-stilbene[38] (313 mm) or Aberchrome 540[39] (313 or 365 nm) actinometers.

Materials. Solvents were all spectra grade. Acetonitrile (Aldrich) was distilled from calcium hydride prior to use. *trans*-Anethole (Aldrich) was distilled prior to use and contained <0.7% *cis*-anethole as established by GC analysis. *cis*-Anethole was prepared via Micheler's ketone sensitized isomerization of *trans*-anethole by using the method of Futamura et al.[40] Spinning band distillation yielded *cis*-anethole containing 0.5% *trans*-anethole. The synthesis and spectroscopic properties of dimers **1–4** are described in the accompanying paper. It should be noted that numbering of the dimers is not the same in both papers.

(1α,2β,2β,4α)-1,2-Bis(4-methoxyphenyl)-3,4-dimethylcyclobutane (5). Irradiation of 4,4′-dimethoxystilbene (Aldrich) with *trans*-2-butene in benzene solution failed to yield adducts; however irradiation of dimethoxystilbene (8.3 mmol) with methyl crotonate (0.2 mol) in 0.2 L benzene under nitrogen with a Pyrex-filtered 4.50-W high-pressure mercury arc afforded methyl *trans*-3-*cis*-4-bis(4-methoxyphenyl)-*trans*-2-methyl-1-cyclobutanecarboxylate. Precedent for the preferential formation of the syn cycloadduct is provided by the reaction of *trans*-stilbene with methyl crotonate.[41] The cyclobutanecarboxylate was reduced by an excess of LiAlH$_4$ in diethyl ether to give 1-(hydroxymethyl)-*trans*-3,*cis*-4-bis(4-methoxyphenyl)-*trans*-2-methylcyclobutane. This alcohol was converted to its tosylate, which was then reduced by an excess of LiAlH$_4$ in diethyl ether to give the dimer **5** in 75% yield based on the amount of dimethoxystilbene remaining: mp 61–62 °C; ^{13}C NMR (CDCl$_3$) δ 157.9 (s), 133.4 (s), 128.6 (d), 113.6 (d), 54.8 (q), 42.0 (d), 38.1 (d); mass spectrum, *m/e* 240 (7.1%), 148 (M$^+$/2, 100%).

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Registry No. 5, 84107-49-3; t-A, 4180-23-8; t-A$^{\bullet+}$, 117467-10-4; c-A, 25679-28-1; c-A$^{\bullet+}$, 117467-11-5; CA, 1210-12-4; DCA, 1217-45-4; DCNB, 623-26-7; BP, 92-52-4; P, 85-01-8; T, 217-59-4; TMB, 135-77-3; AnCHO, 123-11-5; An$\overline{\mathrm{CHCH(CH_3)O}}$, 51410-46-9; O$_2^-$, 106-77-4; O$_2$, 7782-44-7; 4,4′-dimethoxystilbene, 4705-34-4; *trans*-2-butene, 624-64-6; methyl crotonate, 18707-60-3; methyl *trans*-3,*cis*-4-bis(4-methoxyphenyl)-*trans*-2-methyl-1-cyclobutanecarboxylate, 117371-28-5; 1-(hydroxymethyl)-*trans*-3,*cis*-4-bis(4-methoxyphenyl)-*trans*-2-methylcyclobutane, 117371-29-6; 1-[(tosyloxy)methyl]-*trans*-3,*cis*-4-bis(4-methoxyphenyl)-*trans*-2-methylcyclobutane, 117371-30-9.

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