Photochemical Cycloaddition of Singlet and Triplet Diphenylvinylene Carbonate with Vinyl Ethers

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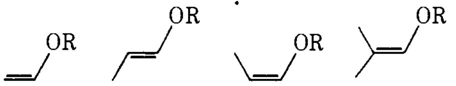
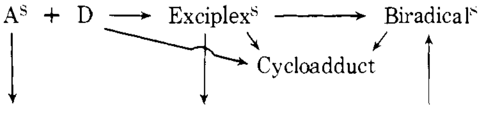
Abstract: The singlet and triplet excited states of diphenylvinylene carbonate (V) react with vinyl ethers to produce 2 + 2 cycloadducts. Weak exciplex emission is observed when the fluorescence of V is quenched by high concentrations of 2-methyl-1-methoxypropene. Rate constants for fluorescence quenching and limiting quantum yields for singlet cycloaddition increase with decreasing vinyl ether ionization potential, in accord with an exciplex mechanism for cycloaddition. The solvent dependence of the cycloaddition quantum yields is indicative of a moderately polar exciplex. Singlet addition to the isomeric 1-methoxypropenes is stereospecific, whereas triplet addition proceeds with substantial loss of stereochemistry. Comparison of solvent effects and adduct stereochemistry for the singlet and triplet addition reactions suggests that a triplet exciplex is the precursor of a triplet biradical intermediate.

Vinyl ethers have been widely employed as substrates in thermal[2-8] and photochemical[9-14] electrophilic 1,2-cycloaddition reactions. The following series of methyl-substituted vinyl ethers can provide information about the relative importance of steric and electronic effects on chemical reactivity and the stereo- and regioselectivity of the cycloaddition process. Interest in electronic effects on cycloaddition rections has been stimulated by the development of frontier molecular orbital models for reactivity, according to which the energies (ionization potentials and electron affinities) and shapes of the highest occupied and lowest unoccupied molecular orbitals determine chemical reactivity.[15] Investigations of photochemical cycloaddition mechanisms are complicated by the possibility of reaction from singlet and/or triplet states.[11] Furthermore, evidence continues to accumulate that excited state π complexes or exciplexes are intermediates in many, if not all, photochemical cycloaddition reactions.[11,14,16-21] Since exciplexes can form cycloadducts via either concerted or stepwise (biradical or zwitterionic) bonding, the complete photochemical cycloaddition process can follow any of the numerous pathways outlined in Scheme I,[22] where S and T indicate singlet and triplet states, respectively. We report here our quantitative study of the 2 + 2 cycloaddition reactions of singlet and triplet diphenylvinylene carbonate (V) with several vinyl ethers. The results serve to illuminate several facets of the cycloaddition process.

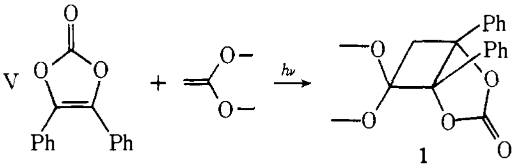


Scheme I. Pathways for Photochemical Cycloaddition

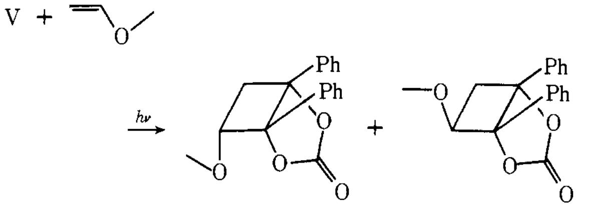


Results

Preparative Photochemistry. Direct or Michler's ketone sensitized irradiation of a benzene solution of V containing excess ketene dimethyl acetal results in the efficient formation of a single cycloadduct (eq 1). Direct or sensitized irradiation of V in the presence of excess methyl vinyl ether, ethyl vinyl ether, 2-methyl-1-methoxypropene, or 2,3-dihydropyran leads to the formation of two isomeric cycloadducts (eq 2-5).

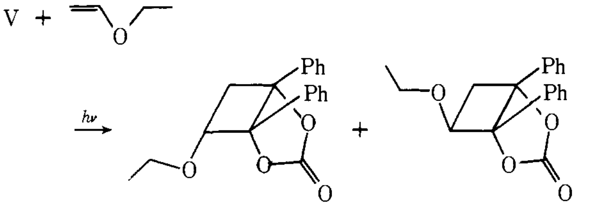


1 (1)



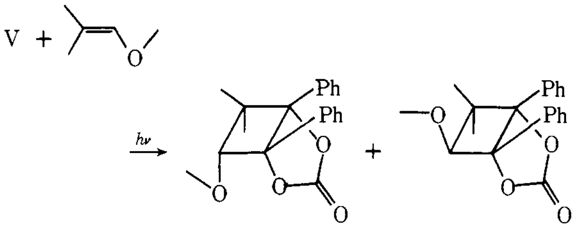
(2)

	2	3
direct	53%	47%
sensitized	57%	43%



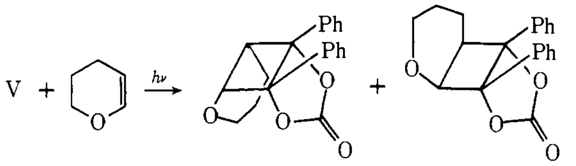
(3)

	4	5
direct	75%	25%
sensitized	60%	40%



(4)

	6	7
direct	75%	25%
sensitized	53%	47%

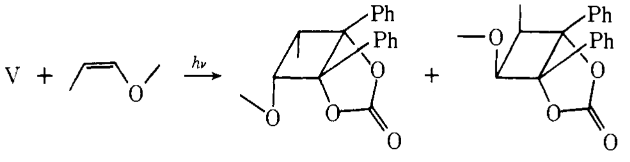


(5)

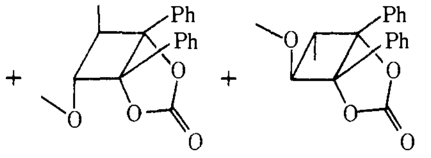
	8	9
direct	75%	25%
sensitized	70%	30%

Structures for the isolated cycloadducts were readily assignable on the basis of their NMR and IR spectra (see Experimental Section). Product compositions were determined by VPC analysis and were independent of the extent of conversion of V to cycloadducts. No products other than the cycloadducts could be detected by VPC or NMR analysis of the crude photolysis mixtures, except in the case of the sensitized irradiation of V with dihydropyran for which additional products (~40% of total) were detected by VPC but not characterized.

Direct irradiation of V with excess *cis*-1-methoxypropene results in the formation of two cycloadducts (eq 6) which differ in VPC retention time and spectral properties from the two adducts obtained with *trans*-1-methoxypropene (eq 7). As little as 1% of adduct **13** could have been detected by VPC analysis of the direct photolysis products from *cis*-1-methxypropene. Analysis of the unreacted vinyl ethers by VPC showed that no isomerization occurs during the direct photolysis. Sensitized photolysis of V with either *cis*- or *trans*-1-methoxypropene results in the formation of the three cycloadducts **10, 12,** and **13,** albeit in different ratios. Adduct **11** was not detected by VPC analysis of either of the photolysis mixtures. The vinyl ethers are isomerized during the course of the sensitized photolysis. Thus these product ratios are dependent on the extent of conversion and initial vinyl ether concentration. The product ratios given in eq 6 and 7 were determined by VPC analysis at low conversions of V and vinyl ether (<10%). Direct and sensitized photolysis of V with *cis*-1,2-dimethoxyethylene also resulted in the formation of isomeric cycloadducts, which had identical VPC retention times. No attempt was made at their isolation and characterization.

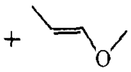


	10	11
direct	54%	46%
sensitized	34%	0



(6)

	12	13
direct	0	0
sensitized	24%	42%

V +  $\xrightarrow{h\nu}$ 10 + 11 + 12 + 13 (7)

	10	11	12	13
direct	0	0	70%	30%
sensitized	6%	0	85%	9%

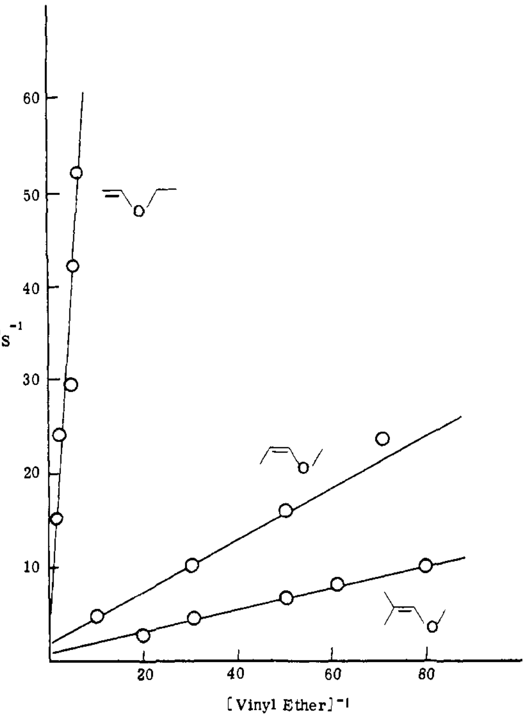
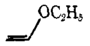
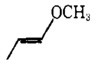
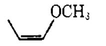
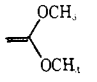
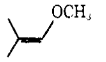
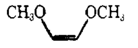


Figure 1. Variation in quantum yield for singlet cycloadduct formation with vinyl ether concentration.

Table I. Quantum Yields and Kinetics for Singlet Reaction in Benzene Solution

Vinyl ether	Φ_S[a]	$k_S\tau_S$,[b] M^{-1}	$k_S\tau_S$,[c] M^{-1}	$k_S \times 10^{-9}$,[d] $M^{-1}\,s^{-1}$
	0.20	0.064	0.10	0.20
			0.28	0.56
	0.58	0.60	0.75	1.5
			1.1	2.2
	1.0	0.98	2.9	5.8
			5.8	12

[a] Limiting cycloaddition quantum yield obtained from intercepts shown in Figure 1, limits of error ± 20%. [b] Obtained from intercept/slope ratios in Figure 1, limits of error ±50%. [c] Slopes of fluorescence quenching plots. Correlation coefficients 0.98 or better, limits of error ±10%. [d] Calculated from fluorescence quenching data and τ (0.5 × 10^{-9} s).

Singlet Reactions. Quantitative Studies. Quantum yields for cycloadduct formation were determined as a function of vinyl ether concentration for degassed benzene solutions of V (0.015 M) at 23 °C using 313 nm irradiation. The variation in total cycloadduct quantum yield with vinyl ether concentration is shown in Figure 1 for several vinyl ethers. These plots display some curvature, yet give reasonably good least-squares fits to the linear equation:

$$\Phi_A^{-1} = \Phi_S^{-1}(1 + (k_S\tau_S[E]^{-1})) \qquad (8)$$

where Φ_S is the quantum yield at infinite vinyl ether concentration and $k_S\tau_S$ is the Stern-Volmer constant obtained from the intercept/slope ratios. Values of Φ_S and $k_S\tau_S$ are given in Table I. The quantum yield for addition of V with 0.5 M 2-methyl-1-methoxypropene (Φ = 0.30 ± 0.03) is independent of the concentration of V (2.8 × 10^{-3} to 2.9 × 10^{-2} M). The quantum yield for addition of V to 0.1 M 2-methyl-1-methoxypropene is highly solvent dependent, decreasing from 0.093 in benzene to <10^{-3} in acetonitrile (Table II).

The fluorescence of V[23] can be quenched by vinyl ethers. When the fluorescence of V is quenched by high concentrations (>2 M) of 2-methyl-1-methoxypropene, a slight broadening of the residual emission is observed. This increased emission at longer wavelengths is attributed to a V-vinyl ether exciplex. Attempts to enhance the exciplex emission by variation of the solvent were unsuccessful. Stern-Volmer plots for fluorescence quenching of V by vinyl ethers in benzene solution show dis-

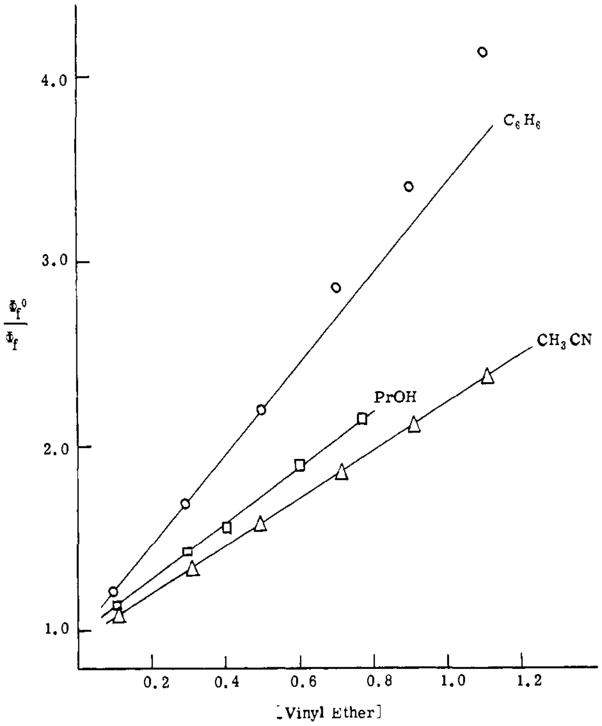


Figure 2. Stern-Volmer plots for fluorescence quenching by 2-methyl-1-methoxypropene in benzene (○), *n*-propyl alcohol (□), and acetonitrile (△).

tinct upward curvature (Figure 2). Imposition of the linear form of the Stern-Volmer equation (eq 9) upon the data, again yields reasonable least-squares fits (Table I). The agreement between $k_S\tau_S$ values obtained by fluorescence quenching (eq 9) and reciprocal quantum yield (eq 8) plots is only fair (Table I).

$$\Phi_f^0/\Phi_f = 1 + k_S\tau_S[E] \qquad (9)$$

The effect of solvent on fluorescence quenching was also investigated. Stern-Volmer plots in solvents of moderate and high polarity are linear (Figure 2). Values of $k_S\tau_S$ obtained from least-squares analyses are given in Table II. The lifetime of V is approximately four times longer in benzene (~0.5 ± 0.2 ns) than in the other solvents (0.15 ± 0.1 ns) as judged by the solvent dependence of the fluorescence quantum yield.[21] Values of k_S calculated from the $k_S\tau_S$ and lifetime data are given in Table II and approximate the rates of diffusion in these solvents. The reason for the longer lifetime in benzene solution is unclear, but may be due to complex formation with solvent.

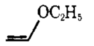
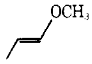
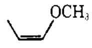
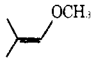
Triplet Reactions. Quantitative Studies. The choice of sensitizer for quantitative studies was complicated by rapid chemical reaction of the vinyl ethers with benzophenone,[12c] benzil, and phenanthrene. Michler's ketone proved suitable since it neither reacts with vinyl ethers nor sensitizes the isomerization of the 1-methoxypropenes. The variation in triplet cycloaddition quantum yield with vinyl ether concentrations for degassed benzene solutions of Michler's ketone (1.2 × 10^{-4} M) and V (1.0 × 10^{-2} M) irradiated at 365 nm is shown in Figure 3 for several vinyl ethers. Values of the limiting quantum yield for triplet sensitized cycloaddition (Φ_T) obtained from the intercept and $k_T\tau_T$ obtained from the intercept/slope ratios in Figure 3 are summarized in Table III. The quantum yields for 2-methyl-1-methoxypropene are too low to allow valid estimation of $k_T\tau_T$. The quantum yield for Michler's ketone sensitized addition of V to 0.2 M ethyl vinyl ether (0.031 ± 0.003) is independent of the concentration of V from 5 × 10^{-3} to 2 × 10^{-2} M. Thus triplet quenching of Michler's ketone by 1 × 10^{-2} M V must be completely efficient.

Table II. Solvent Effects on Singlet Kinetics and Singlet and Triplet Cycloaddition Quantum Yields

Solvent	ϵ^a	$k_S\tau$,[b] M^{-1}	$k_S \times 10^{-9}$,[c] $M^{-1} s^{-1}$	Φ_S[d]	Φ_T[e]
Benzene	2.27	2.9	5.8	0.093	0.014
Diethyl ether	4.23	1.6	10		
Ethyl acetate	6.02			0.0047	0.0034
Dimethoxyethane	7.2	1.4	9.2		
tert-Butyl alcohol	12.5	1.4	9.2	0.012	0.0088
n-Propyl alcohol	20.3	1.4	9.2	0.0055	0.0055
Acetonitrile	38.8	1.3	8.4	<0.001	0.0018

[a] Solvent bulk dielectric constant. [b] Slope of Stern–Volmer plot for fluorescence quenching by 2-methyl-1-methoxypropene, limits of error ±10%. [c] Rate constant for singlet quenching assuming τ = 0.5 ns in benzene and τ = 0.15 ns in other solvents. [d] Quantum yield determined in 0.1 M 2-methyl-1-methoxypropene, limits of error ±20%. [e] Quantum yield determined in 0.1 M *cis*-1-methoxypropene, limits of error ±20%.

Table III. Quantum Yields and Kinetics for Triplet Reaction in Benzene Solution

Vinyl ether	Φ_T[a]	$k_T\tau_T$, M^{-1}[b]
 OC_2H_5	0.35	1.2
 OCH_3	0.16	0.51
 OCH_3	0.18	0.85
 OCH_3	<0.01	
 CH_3O OCH_3	0.068	8.6

[a] Limiting cycloaddition quantum yields obtained from intercepts shown in Figure 3, limits of error ±40%. [b] Obtained from intercept/slope ratios in Figure 3, limits of error ±50%.

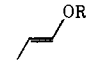
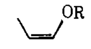
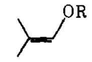
The quantum yield for isomerization of *cis*-1-methoxypropene during the Michler's ketone sensitized addition of 1.0 × 10^{-2} M V and 0.2 M vinyl ether was determined by VPC analysis of unreacted vinyl ether as a function of conversion of V. The quantum yield at low conversions (<20%) is 7.5 ± 0.9 × 10^{-3}. Correction of this value for incomplete quenching of triplet V by 0.2 M vinyl ether (Figure 3) gives a limiting quantum yield for vinyl ether isomerization of 0.052 ± 0.006.

The quantum yield for Michler's ketone sensitized addition of V with 0.1 M *cis*-methoxypropene was determined in several solvents. The results are summarized in Table II.

Discussion

Singlet Cycloaddition. The absence of intersystem crossing for diphenylvinylene carbonate (V)[21] simplifies analysis of the singlet and triplet reactions with vinyl ethers. Direct photolysis of V in the presence of vinyl ethers or dienes[21a,24] results in exclusively singlet state cycloaddition. The singlet cycloaddition is preceded by formation of an exciplex intermediate (Scheme I). The V-vinyl ether exciplexes do not fluoresce as strongly as the V-diene exciplexes.[21] Thus a detailed investigation of V-vinyl ether exciplex fluorescence proved impossible. Additional evidence for an exciplex intermediate is provided by the correlation between fluorescence quenching rate constants (Table I) and the electron-donating ability of the vinyl ether. Exciplexes are known to be stabilized by full or partial electron transfer and correlations between fluores-

Table IV. Relative Reactivities of Vinyl Ethers

	V* singlet	V* triplet	Acetone singlet[12c]	Acetone triplet[12c]	Zinc carbenoid[5]	Diphenyl ketene[4c]	TCNE[3]
	1.0	1.0	1.0	1.0	1.0	1.0	1.0
	2.8	0.4	14	4.7	5.5	2.4	2.9
	7.5	0.7	13	17	8.3	0.03	2.2
	29		31	63		3×10^{-5}	0.7
	58	7.0	116				0.09

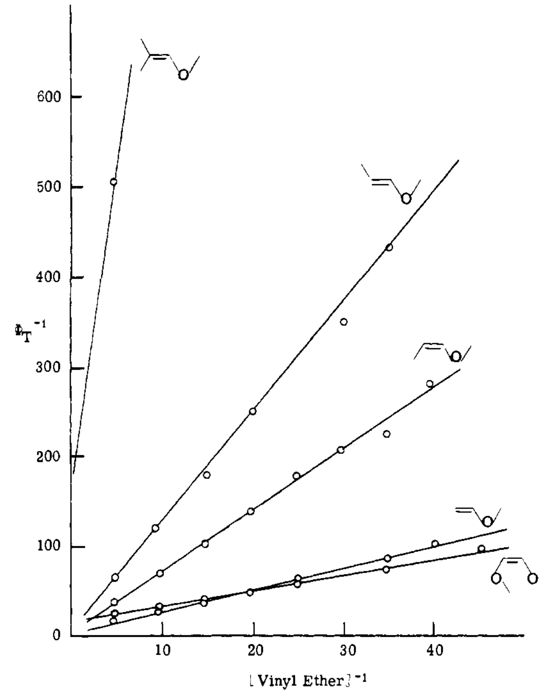


Figure 3. Variation in quantum yield for triplet cycloadduct formation with vinyl ether concentration.

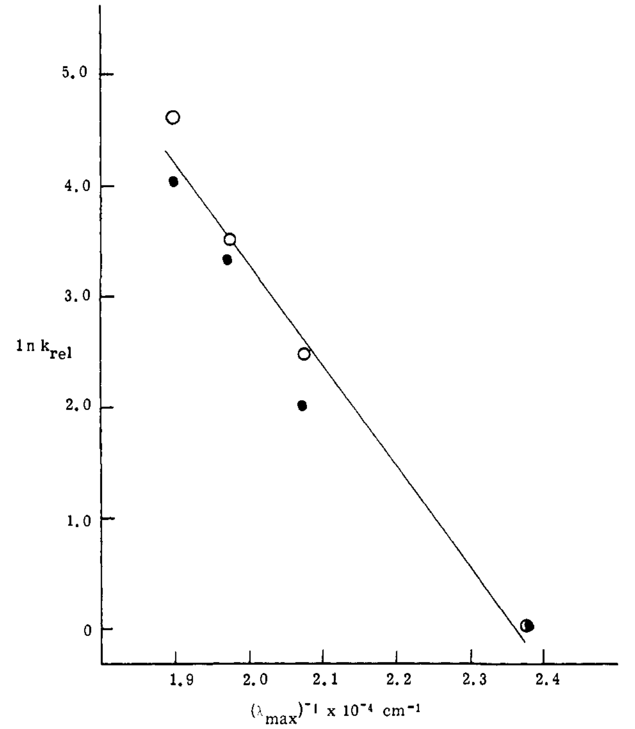


Figure 4. Correlation of diphenylvinylene carbonate (●) and acetone (○) fluorescence quenching rate constants with vinyl ether–tetracyanoethylene charge transfer absorption maxima.

cence quenching rate constants and quencher electron-donating (or accepting) ability have been frequently observed.[12,25,26] The electron-donor ability of the various vinyl ethers can be compared using either the absorption maxima of the vinyl ether–tetracyanoethylene charge transfer complexes[3] or the vinyl ether ionization potentials.[12c] The correlation of charge transfer maxima and the fluoresence quenching data in Table I are shown in Figure 4 along with the data of Schore and Turro[12c] for quenching of acetone fluorescence by vinyl ethers (Table IV). The singlet states of acetone and V show remarkably similar reactivity toward quenching by vinyl ethers.

Cycloadduct formation from a singlet exciplex can be either a concerted or stepwise process (Scheme I). Since cycloaddition of singlet V with the isomeric 1-methoxypropenes (eq 6, 7) occurs with complete retention of vinyl ether stereochemistry, the reaction is most likely concerted.[21a] In general, singlet state photochemical cycloaddition reactions which are symmetry allowed ($_\pi 2_s + {}_\pi 2_s$ or $_\pi 4_s + {}_\pi 4_s$) are highly stereospecific,[14,21a,27] whereas those which are symmetry forbidden ($_\pi 4_s + {}_\pi 2_s$) proceed via biradical intermediates.[28] An important exception to this generalization is the Paterno-Buchi reaction of singlet acetone with vinyl ethers which occurs with only partial retention of stereochemistry.[11] Simultaneous overlap of both the half-filled n,π^* orbitals of acetone with the vinyl ether π orbital is geometrically prohibited.

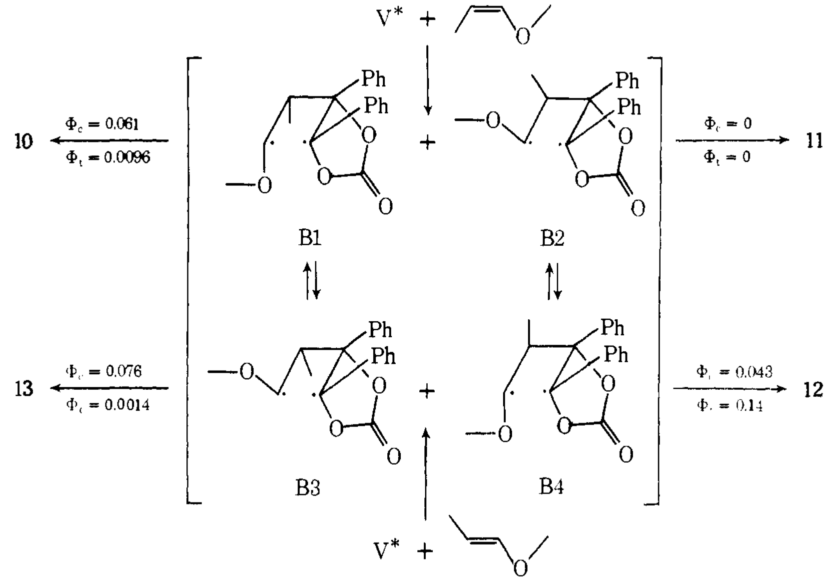
The limiting quantum yields for singlet cycloadduct formation (Table I) are less than unity and decrease with decreasing vinyl ether substitution. One possible explanation of the quantum inefficiency is that a short-lived biradical intermediate is formed which can either cyclize or decay to ground-state reactants. However, since biradical cyclization is subject to steric hindrance (vide infra), the variation in limiting quantum yield with vinyl ether structure is contrary to expectations for a biradical mechanism. An alternative explanation for limiting quantum yields less than unity is nonradiative decay of the singlet exciplex intermediate to ground-state V and nonisomerized vinyl ether. This process has been termed "energy wastage" by Hammond.[29]

The complete mechanism for concerted singlet cycloaddition via an exciplex intermediate (X) is given in Scheme II, where

Scheme II. Singlet Cycloaddition Mechanism

$$\begin{tikzcd}
 & V^* + E \arrow[dl, "k_d"'] \arrow[d, "k_f"] \arrow[r, shift left, "k_e"] & X \arrow[l, shift left, "k_{-e}"] \arrow[r, "k_a"] \arrow[d, "k_{ed}"] & \text{adduct} \\
V & V + h\nu & V + E &
\end{tikzcd}$$

Scheme III. Biradical Intermediates in the Triplet Cycloaddition Reaction with *cis*-(Φ_c) and *trans*-1-Methoxypropene-(Φ_t)



exciplex fluorescence has been neglected due to its low quantum yield. This mechanism results in the following equations for variation in adduct quantum yield (eq 10) and fluorescence quantum yield (eq 11) with vinyl ether concentration. The values of k_S (Table I) have the complex kinetic form given in eq 12.

$$\frac{1}{\Phi_A} = \frac{k_a + k_{ed}}{k_a} + \frac{k_{-e} + k_a + k_{ed}}{\tau k_a k_e[E]} \qquad (10)$$

$$\frac{\Phi_f^0}{\Phi_f} = 1 + \frac{k_e(k_a + k_{ed})\tau[E]}{(k_{-e} + k_a + k_{ed})} \qquad (11)$$

$$k_S = \frac{k_e(k_a + k_{ed})}{(k_{-e} + k_a + k_{ed})} \qquad (12)$$

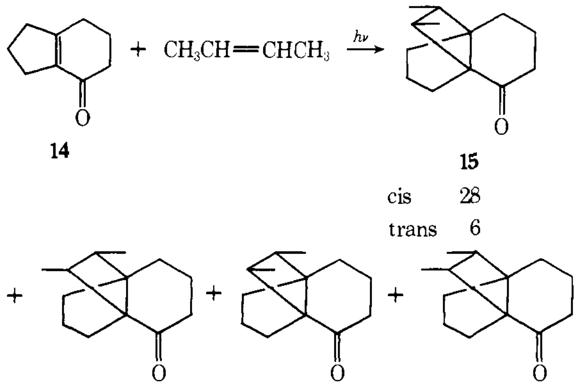
Numerous papers on exciplex formation make the implicit assumption that exciplex formation is irreversible ($k_{ed} + k_a \gg k_{-e}$), in which case $k_S = k_e$. The few investigations of the temperature dependence of k_S indicate that this assumption is incorrect.[26,30,31] Thus the variation of k_S with vinyl ether electron donor ability (Figure 4) may reflect an increase in k_{-e} with decreasing exciplex stability rather than a decrease in k_e.[31] In the absence of a detailed kinetic analysis such as that performed by Ware[31] for α-cyanonaphthalene-olefin exciplexes, no significance should be attributed to the slopes of plots such as those shown in Figure 4.[12,25g]

The limiting quantum yields for singlet cycloaddition (Table I) are determined by the ratio of rate constants $k_a/(k_a + k_{ed})$ (eq 10). Thus the ratio k_a/k_{ed} must increase with vinyl ether substitution and electron-donor ability. The apparent absence of a steric effect on singlet cycloaddition has also been observed for the addition of singlet V to conjugated dienes.[21a] The highly exothermic addition of the zinc carbenoid, obtained from diethyl zinc and methylene iodide, to vinyl ethers also shows no evidence for steric rate retardation (Table IV).[5] In contrast, the symmetry-allowed $_\pi 2_s + _\pi 2_a$ cycloaddition of diphenyl ketene with vinyl ethers is subject to steric hindrance, particularly with cis-disubstituted vinyl ethers (Table IV).[4c] A cursory inspection of the photochemical literature indicates that symmetry-allowed singlet cycloaddition reactions are not subject to steric hindrance, unlike thermal cycloaddition reactions such as the Diels-Alder reaction. We believe that *the absence of steric effects results from transition states which resemble the loosely bound singlet exciplexes rather than the sterically congested products.*

Solvent polarity has little effect on the rate constants for fluorescence quenching (k_S) of V by 2-methyl-1-methoxypropene (Table II). The high values of k_S make diffusion-controlled exciplex formation in all solvents appear likely. The higher value of $k_S\tau_S$ in benzene vs. more polar solvents is due entirely to the longer lifetime of singlet V in the aromatic solvent.[21c] The quantum yield for cycloadduct formation is solvent sensitive, being distinctly higher in benzene and lower in acetonitrile than in solvents of intermediate polarity. Analogous behavior has been observed for singlet V-diene exciplexes.[21b] The virtual absence of product formation in acetonitrile can be attributed to rapid formation of solvated radical ions either from the exciplex and/or upon encounter of singlet V and ground-state vinyl ether.[21b] The decrease in Φ_S in going from benzene to ethyl acetate may be due to a greater degree of solvent stabilization for the polar exciplex than the nonpolar transition state for cycloaddition. The effect of solvent on adduct quantum yield and the lifetime of singlet V readily explain the curvature of Stern-Volmer plots obtained in benzene solution (Figures 1, 2). Since high concentrations of vinyl ether are necessary to quench singlet V, the bulk solvent polarity will increase with increased vinyl ether concentration resulting in a decrease in τ_S and Φ_S (Table II).

Triplet Cycloaddition. In contrast to the stereospecific addition of singlet V to the isomeric 1-methoxypropenes, triplet sensitized addition proceeds with substantial loss of vinyl ether stereochemistry (eq 6, 7). A triplet biradical intermediate mechanism (Scheme III) similar to that proposed by Turro and Wriede[11] for the addition of triplet acetone to the isomeric 1-methoxybutenes can explain the nonstereospecificity of the triplet cycloaddition. Initial bonding is assumed to occur at the β carbon, yielding the oxygen-stabilized biradical intermediates B1-B4. The different isomer ratios from *cis*- and *trans*-1-methoxypropene result from preferential initial bonding to give more B1 than B2 from the *cis*-vinyl ether and more B4 than B3 from the *trans*-vinyl ether. The same preferred cis relationship of carbonate and alkoxy groups is observed in all the singlet cycloaddition reactions (eq 1-7). Rotational interconversion of the biradicals B1 $\rightleftarrows$ B3 and B2 $\rightarrow$ B4 must be more rapid than cyclization in view of the similar product ratios **10**/**13** and **11**/**12** obtained from the isomeric vinyl ethers. Collapse of the biradical intermediates B3 and B4 to give ground-state V and *trans*-vinyl ether can account for the observed isomerization of *cis*-vinyl ether ($\Phi = 0.052$) during the triplet sensitized reactions. Neither the triplet sensitizer, Michler's ketone, nor singlet V can effect the vinyl ether isomerization.

The stereoselective cyclization of the biradical intermediates in Scheme III (**10**/**13** = 0.8, **11**/**12** < 0.1) attests to the importance of steric effects on biradical cyclization.[21a,32] The absence of adduct **11** in the triplet sensitized addition reactions is analogous to the absence of adduct **18** in the cycloaddition of the triplet state of enone **14** with *cis*- and *trans*-2-butene (eq 13).[33] The variation in the quantum yields for triplet sensitized cycloaddition of V with vinyl ether (Table III) is also consistent with a steric effect on biradical cyclization.



(13)

	14	**15**	**16**	**17**	**18**
cis		28	65	4	0
trans		6	86	7	0

A simple biradical mechanism for triplet sensitized cycloaddition is shown in Scheme IV and the resulting relationship between Φ^{-1} and $[E]^{-1}$ in eq 14. There are several shortcomings of this mechanism. First, the total limiting quantum yield for cycloaddition (0.18) and vinyl ether isomerization (0.052) in the reaction of triplet V with *cis*-1-methoxypropene (Scheme III) is only 0.23. If biradical formation is completely efficient, biradicals B1 and B2 must collapse to ground-state V and unisomerized vinyl ether (Φ = 0.77) much faster than they undergo cyclization or bond rotation. The ratio of biradical collapse/cyclization (k_{bd}/k_a = 13) calculated for biradicals B1 and B2 is substantially larger than that observed for biradicals B3 and B4 (k_{bd}/k_a = 0.4). Dervan and Uyehara[34] have recently reported an "extra component of stereospecific cleavage of retained stereochemistry" in the thermolysis of tetrahydropyridazines at 439 °C. The triplet biradical mechanism (Scheme IV) appears to require an unreasonably large component of stereospecific cleavage of B1 and B2 to ground-state V and *cis*-vinyl ether. Thus some other energy wastage pathway seems necessary in the quenching of triplet V by vinyl ethers. Additional shortcomings of the simple triplet biradical mechanism are its failure to account for the effect of solvent on the quantum yields[35] for addition of triplet V with *cis*-1-methoxypropene (Table II) and the variation in triplet reactivity with vinyl ether structure (Table III). According to eq 14, the intercept/slope ratios from Figure 3 provide values of $k_b\tau_T$. Radical additions to olefins are known to be sterically sensitive[36] in accord with the observed reactivities of ethyl vinyl ether > 1-methoxypropene > 2-methyl-1-methoxypropene. However, the two cis-disubstituted ethylenes *cis*-1-methoxypropene and *cis*-1,2-dimethoxypropene differ in reactivity by a factor of 10.

Scheme IV. Biradical Mechanism for Triplet Cycloaddition

$$\begin{tikzcd}
V^3 + E \arrow[r, "k_b"] \arrow[d, "k_d = \tau_{T^{-1}}"] & B \arrow[r, "k_a"] \arrow[d, "k_{bd}"] & \text{adducts} \\
V & V + E &
\end{tikzcd}$$

$$\Phi_T{}^{-1} = \frac{k_a + k_{bd}}{k_a} + \frac{k_a + k_{bd}}{k_a k_b \tau_T[E]} \qquad (14)$$

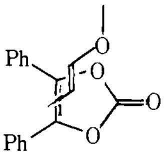
The shortcomings of the simple triplet biradical mechanism can be overcome by postulating a triplet exciplex intermediate[19,20,29,37] as precursor of the triplet biradical (Scheme V). Assuming irreversible biradical formation from a reversibly formed triplet exciplex, the relationship between Φ^{-1} and $[E]^{-1}$ is given by eq 15 and the intercept/slope ratio by eq 16. Decay of the triplet exciplex to ground-state V and nonisomerized vinyl ether (k_{ed}) provides the energy wastage[29] pathway needed to explain the low triplet quantum yields. Comparison of solvent effects (Table II) and adduct stereochemistry (eq 1-7, Scheme III) on the singlet and triplet cycloaddition provides the strongest evidence for a triplet exciplex intermediate. The triplet reaction shows less solvent sensitivity than the singlet reaction; however, the trends are clearly the same. The preferred orientation of V and vinyl ether prior to bonding are also the same (e.g., **19** > **20**) for the concerted singlet and nonconcerted triplet reactions. Scheme V can also accommodate the observed variation in triplet reactivity with vinyl ether structure. The ratio k_e/k_{-e} for formation of a loosely bound triplet exciplex should increase with vinyl ether electron-donating ability and be independent of steric effects. However, the rate constant for biradical formation, k_b, may be sterically sensitive,[36] unlike the rate constant for concerted cycloaddition.

Scheme V. Triplet Exciplex Mechanism

$$\begin{tikzcd}
V^3 + E \arrow[r, shift left, "k_e"] \arrow[d, "k_d = \tau_{T^{-1}}"] & X^3 \arrow[l, shift left, "k_{-e}"] \arrow[r, "k_b"] \arrow[d, "k_{ed}"] & B \arrow[r, "k_a"] \arrow[dl, "k_{bd}"] & \text{adduct} \\
V & V + E & &
\end{tikzcd}$$

$$\Phi_T{}^{-1} = \frac{(k_a + k_{bd})(k_b + k_{ed})}{k_b k_a} + \frac{(k_a + k_{bd})(k_b + k_{-e} + k_{ed})}{k_a k_b \tau_T[E]} \qquad (15)$$

$$k_T = \frac{k_e(k_b + k_{ed})}{(k_b + k_{-e} + k_{ed})} \qquad (16)$$



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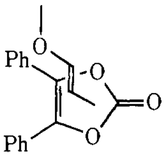
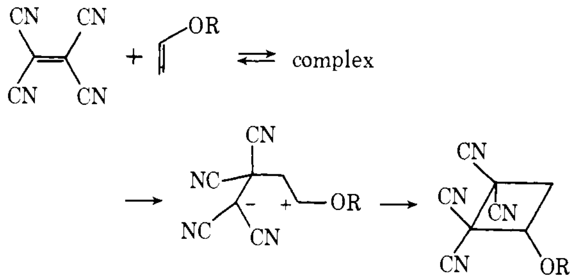


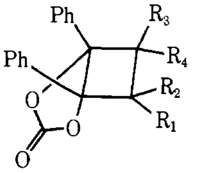
20

The triplet exciplex mechanism (Scheme V) is similar to the mechanism shown in eq 17 for cycloaddition of tetracyanoethylene with vinyl ethers[3,38] except that a zwitterion rather than a biradical is formed in the latter reaction. Vinyl ether reactivities are qualitatively similar for the two reactions except in the case of 1,2-dimethoxyethylene (Table IV). It is interesting to note that the rates of reaction of triplet acetone and benzophenone with vinyl ethers show no evidence for steric hindrance (Table IV).[12] The limiting quantum yields for addition of triplet acetone to the isomeric 1-methoxybutenes are quite small (Φ < 0.1). If the dominant mode of exciplex deactivation is nonradiative decay rather than biradical formation (Scheme V, $k_{ed} > k_b$), then steric effects on k_b would have little effect on the observed values of k_T (eq 16).



(17)

Table V. ^{1}H NMR Data for Cycloadducts[a,b]



Adduct	R_1	R_2	R_3	R_4	Phenyl	$J_{\alpha,\beta}$, Hz	$J_{\beta,\gamma}$, Hz	$J_{\alpha,\gamma}$, Hz
1	OCH_3 3.41 (s)	OCH_3 3.07 (s)	H[c] 3.08–3.14	H[c]	7.20 (s)			
2	OCH_3 3.33 (s)	H (α) 4.50 (q)	H (β) 2.74 (m)	H (γ) 3.38 (m)		5.0	14:7	8.1
3	H (α) 4.40 (q)	OCH_3 2.97 (s)	H (β) 3.02 (m)	H (γ) 3.24 (m)	7.12 (m)	8.2	14.0	8.2
4	$OCH_2{}^aCH_3{}^b$ a = ~3.34 (q)[d] b = 1.18 (t)	H (α) 4.49 (q)	H (β) ~3.0 (m)	H (γ) ~3.0 (m)	7.06 (s) 7.08 (s)	8.1	15.0	5.0
5	H (α) 4.38 (q)	$OCH_2{}^aCH_3{}^b$ a = ~3.05 (q)[d] b = 0.80 (t)	H (β) ~3.05 (m)	H (γ) ~3.05 (m)	7.05 (m)	8.0		8.0
6	OCH_3 3.55 (s)	H 4.45 (s)	CH_3 0.95 (s)	CH_3 1.32 (s)	7.20 (m)			
7	H 4.20 (s)	OCH_3 3.38 (s)	CH_3 1.05 (s)	CH_3 1.45 (s)	7.28 (m)			
8	OCH_2–	H (α) 4.17 (d)	H (β) 3.10 (m)[d]	CH_2CH_2– ~2.0 (m)	7.10 (m)	6.6		
9	H (α) 4.17 (d)	OCH_2–	CH_2CH_2– ~1.2 (m)	H (β) 3.0 (m)[d]	7.19 (m)	5.8		
10	OCH_3 3.47 (s)	H (α) 4.38 (d)	H (β) 3.60 (m)	CH_3 (γ) 1.30 (d)	7.15 (m)	7.9	7.0	
11	H (α) 4.50 (d)	OCH_3 3.33 (s)	CH_3 (β) 0.96 (d)	H (γ) 3.35 (m)	7.20 (m)	7.8	7.4	
12	OCH_3 3.43 (s)	H (α) 4.41 (d)	CH_3 (β) 0.90 (d)	H (γ) 3.05 (m)	6.95 (m)	7.4	7.4	
13	H (α) 3.89 (d)	OCH_3 2.95 (s)	H (β) 3.75 (m)	CH_3 (γ) 1.40 (m)	7.01 (m)	8.0	6.5	

[a] δ Values in dilute $CDCl_3$, Me_4Si internal standard. [b] s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. [c] Both proton resonances were under the OCH_3 peak. [d] Approximate value determined by decoupling the adjacent protons.

Experimental Section

General Procedures. Preparative photolyses were carried out using a 450-W Hanovia medium-pressure mercury lamp. Samples were contained in a Pyrex annulus or test tube under nitrogen atmosphere. In cases where monochromatic light was used, the 313-nm mercury line was isolated using a potassium chromate solution filter and the 365-nm mercury line using Corning glass filters 7-54 and 0-52 in combination. Irradiated solutions were monitored by GC with a Hewlett-Packard 5750 dual-flame gas chromatograph using a 6 ft × ⅛ in. column containing 5% SF-96 on Chromosorb G. In all cases, irradiation was continued until all the initial V was consumed. Vinyl ether isomerization was monitored using a 20 ft × ⅛ in. column containing 5% Apiezon L on Chromosorb G. Infrared spectra were recorded on a Beckman IR 5 spectrophotometer, NMR spectra on a Perkin-Elmer R20B 60 MHz spectrometer, emission spectra on a Perkin-Elmer MPF-2A spectrophotometer, and ultraviolet absorption spectra on a GCA/McPherson EU-700 spectrophotometer.

Diphenylvinylene carbonate was prepared by the method of Lewis and Hirsch.[21a] Ethyl vinyl ether and 2,3-dihydropyran were obtained from Chemical Samples and distilled prior to use. Methyl vinyl ether was obtained from Matheson. Ketene dimethyl acetal was prepared by the method of Corey et al.[9,39] The 1-methoxypropenes were synthesized from their corresponding acetals using the method of Effenberger et al.[40] *cis*- and *trans*-1-methoxypropene were separated by preparative GC using a 20 ft × ⅜ in. column containing 5% Apiezon L on Chromosorb G. One separation was sufficient for preparative work. Rechromatography yielded ethers of >99.5% isomeric purity which were distilled from lithium aluminum hydride prior to use in quantitative studies. 1,2-Dimethoxyethylene was prepared by the method of McElvain and Stammer.[41] Solvents were spectroquality or were purified by standard techniques.[42]

Direct photolysis quantum yields were determined for degassed benzene solutions of V (0.015 M) containing various concentrations of vinyl ether. Samples were contained in sealed 15-mm o.d. Pyrex test tubes and irradiated on a merry-go-round apparatus immersed in a thermostated water bath (20 ± 2 °C) using monochromatic 313-nm light. Samples were analyzed for product formation after 1-15% conversion using a GC column calibrated with pure samples of the cycloadducts vs. eicosane internal standard. Light intensities were determined by benzophenone-benzhydrol actiometry.[43] Triplet quantum yields were determined for degassed solutions of V (0.010 M) containing Michler's ketone (0.0012 M) and varying amounts of vinyl ether. Monochromatic 365-nm light from a Hanovia 200-W mercury lamp was used to selectively excite the Michler's ketone.

The NMR data for the cycloadducts are compiled in Table V.

***r*-1,*c*-2-Diphenyl-3,3-dimethoxycyclobutane-1,2-diol Carbonate (1).**[44] A solution of V (475 mg, 1.99 mmol) and ketene dimethyl acetal (3 ml) in 25 ml of benzene was irradiated through Pyrex (Hanovia 450-W medium-pressure mercury lamp) for 18 h. Removal of the solvent and vinyl ether under reduced pressure gave yellow crystals (382 mg, 59%): mp 136-137 °C (CH_3OH); IR (KBr) 5.55 μm.

Anal. Calcd for $C_{19}H_{18}O_5$: C, 69.93; H, 5.56. Found: 70.75; H, 5.53.

***r*-1,*c*-2-Diphenyl-*t*-3-methoxycyclobutane-1,2-diol Carbonate (2) and *r*-1,*c*-2-Diphenyl-*c*-3-methoxycyclobutane-1,2-diol Carbonate (3).** A solution of V (1.057 g, 4.44 mmol) and methyl vinyl ether (28 ml) in 30 ml of acetonitrile sealed in an annulus with a serum cap was irradiated for 11.5 h at 15 °C. GC analysis indicated the formation of two products (ratio 47:53). The solvent was removed and the residue chromatographed on 60 g of silica gel (ether-hexane). **2** was obtained as colorless prisms (0.326 g, 28%): mp 69-72 °C (EtOH); IR (KBr) 5.55 μm.

Anal. Calcd for $C_{18}H_{16}O_4$: C, 72.96; H, 5.44. Found: C, 73.14; H, 5.62.

3 was subjected to two bulb-to-bulb distillations to give a light yellow oil (0.669 g, 51%): IR (neat) 5.52 μm. The lanthanide-induced shifts of **2** and **3** are given in Table VI.

***r*-1,*c*-2-Diphenyl-*t*-3-ethoxycyclobutane-1,2-diol Carbonate (4) and *r*-1,*c*-2-Diphenyl-*c*-3-ethoxycyclobutane-1,2-diol Carbonate (5).**

Table VI. Lanthanide-Induced Shift (LIS) Values for Adduct Protons[a]

$Eu(fod)_3$ equivalent		Major isomer			Minor isomer		
		2			**3**		
		H_X (R_2)	OCH_3		$H_X(R_1)$	OCH_3	
0.00		270	200		264	180	
0.30		296	226		311	194	
0.60		325	248		361	210	
	Δ	55	48		95	30	
			4			**5**	
		$H_X(R_2)$	OCH_3–	CH_3	$H_X(R_1)$	OCH_3–	CH_3
0.00		272	208[b]	73	271	188[b]	52
0.20		293		87	303		58
0.40		309	254[b]	98	335	205[b]	63
	Δ	37	46	25	45	17	11

[a] Chemical shifts (Hz) from Me_4Si for solutions containing 30 mg of adduct in 0.30 ml of $CDCl_3$. [b] Value obtained by decoupling the adjacent protons.

A solution of V (500 mg, 2.10 mmol) in 40 ml of ethyl vinyl ether was photolyzed for 6 h. GC analysis indicated the formation of two products (ratio 40:60). The solvent was evaporated and the residue crystallized from methanol to give **4** (293 mg, 43%): mp 107.5–109.5 °C.

Anal. Calcd for $C_{19}H_{18}OR$: C, 73.53; H, 5.85. Found: C, 73.67; H, 6.05.

The filtrate was concentrated and the residue subjected to two bulb-to-bulb distillations to give **5** as a light yellow oil (250 mg, 37%): IR (neat) 5.52 μm. The lanthanide-induced shifts of **4** and **5** are given in Table VI.

***r*-1,*c*-2-Diphenyl-3,3-dimethyl-*t*-4-methoxycyclobutane-1,2-diol Carbonate (6) and *r*-1,*c*-2-Diphenyl-3,3-dimethyl-*c*-4-methoxycyclobutane-1,2-diol Carbonate (7).** A solution of V (500 mg, 2.10 mmol) and 2-methyl-1-methoxypropene (3 ml) in 25 ml of benzene was irradiated for 50 h. GC analysis indicated the formation of two products (ratio 70:30). The solvent was removed and the residue chromatographed on 50 g of silica gel (ether–hexane). **6** was obtained as white crystals (283 mg, 42%): mp 91–92 °C (CH_3OH); IR (KBr) 5.54 μm.

Anal. Calcd for $C_{20}H_{20}O_4$: C, 74.04; H, 6.23. Found: C, 75.53; H, 6.78.

7 was obtained as white crystals (93 mg, 14%): mp 128–129 °C (CH_3OH); IR (KBr) 5.51 μm.

Anal. Calcd for $C_{20}H_{20}O_4$: C, 74.04; H, 6.73. Found: C, 74.29; H, 6.22.

***r*-1-H-*c*-7,*c*-8-Diphenyl-*c*-2-oxabicyclo[4.2.0]octane-7,8-diol Carbonate (8) and *r*-1-H-*t*-7,*t*-8-Diphenyl-*c*-2-oxabicyclo[4.2.0]-octane-7,8-diol Carbonate (9).** A solution of V (500 mg, 2.10 mmol) and 2,3-dihydropyran (14 ml) in 14 ml of benzene was irradiated for 36 h. GC analysis indicated the formation of two products (ratio 25:75). The solvent was removed and the residue crystallized from carbon tetrachloride to give **8** as a white powder (340 mg, 50%): mp 156–159 °C; IR (KBr) 5.50 μm. The filtrate was concentrated and chromatographed on silica gel (hexane) to give **9** as a yellow oil (50 mg, 7%).

***r*-1,*c*-2-Diphenyl-*t*-3-methoxy-*t*-4-methylcyclobutane-1,2-diol Carbonate (10) and *r*-1,*c*-2-Diphenyl-*c*-3-methoxy-*c*-4-methylcyclobutane-1,2-diol Carbonate (11).** A solution of V (1.0 g, 4.20 mmol) and *cis*-1-methoxypropene (2 ml) in 5 ml of benzene was irradiated for 34 h. GC analysis indicated the formation of three products (4:51:45).[45] The solvent was removed and the residue chromatographed on 50 g of silica gel (ether–hexane) to give **11** as a colorless oil (321 mg, 25%): IR (neat) 5.54 μm. **10** was obtained as an oil and crystallized from methanol (397 mg, 31%): mp 86–87 °C; IR (KBr) 5.56 μm.

Anal. Calcd for $C_{19}H_{18}O_4$: C, 73.53; H, 5.84. Found: C, 73.85; H, 5.94.

***r*-1,*c*-2-Diphenyl-*t*-3-methoxy-*c*-4-methylcyclobutane-1,2-diol Carbonate (12) and *r*-1,*c*-2-Diphenyl-*c*-3-methoxy-*t*-4-methylcyclobutane-1,2-diol Carbonate (13).** A solution of V (200 mg, 0.85 mmol) and *trans*-1-methoxypropene (0.40 ml) in 5 ml of benzene was irradiated for 37 h. GC analysis indicated the formation of three products (ratio 24:8:68).[45] The solvent was removed and the residue chromatographed on 21 g of silica gel to give **12** and **13** as yellow oils. **12** was subjected to two bulb-to-bulb distillations to give a pale-yellow oil (198 mg, 73%): IR (neat) 5.54 μm. **13** was subjected to two bulb-to-bulb distillations to give a pale-yellow oil (113 mg, 42%):[46] IR (neat) 5.54 μm.

Addition of 1,2-Dimethoxyethylene. A solution of V (4.4 mg) and vinyl ether (50 μl) in 2 ml of benzene was irradiated for 6.5 h. GC analysis showed a single product peak. The reaction mixture was analyzed on a Hewlett-Packard 5930A GC-Mass Spectrometer. No parent ion was observed for the cycloadducts: *m/e* 88, 118, 145, 251, 260.

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Cyclophanes. 8.[1] [2.2](1,4)Tropylioparacyclophane Tetrafluoroborate. Synthesis and Charge-Transfer Interaction[‡]

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Abstract: The synthesis of [2.2](1,4)tropylioparacyclophane tetrafluoroborate (**1**) is described. It is prepared from [2.2]paracyclophane (**4**) in six steps in 27% overall yield. Reduction of **4** with Na/NH_3 affords the tetrahydro derivative tricyclo[8.2.2.2^{4,7}]-hexadeca-1(12),4,7(15),10(13)-tetraene (**5**). Treatment of **5** with KO-*t*-Bu/$CHBr_3$ at 0 °C gives a 4:1 mixture of mono- and dicarbene adducts 11,11-dibromotetracyclo[8.3.2.2^{4,7}.0^{10,12}]heptadeca-1(14),4,7(17)-triene (**6a**) and 11,11,14,14-tetrabromopentacyclo[8.3.3.2.0^{4,15}.0^{10,12}]octadeca-1(17),6-diene (**6b**), respectively. Monocarbene adduct **6a** is treated with DDQ and the resulting 11,11-dibromotetracyclo[8.3.2.2^{4,7}.0^{10,12}]heptadeca-1(14),4,6,16-tetraene (**7**), dehydrobrominated with pyridine to give 11-bromotricyclo[8.3.2.2^{4,7}]heptadeca-1(14),4,6,10(15),11,16-hexaene (**8**). Bromide **8** is reduced with *tert*-butyllithium giving tricyclo[8.3.2.2^{4,7}]heptadeca-1(14),4,6,10(15),11,16-hexaene (**9**). Treatment of **9** with trityl fluoroborate affords the title compound, **1**. Characterization and spectral comparisons of the above compounds are described. Cyclophane **1** exhibits a broad band at 323 nm in its electronic spectrum indicative of an intramolecular charge-transfer interaction between the neutral and charged aromatic rings.

Charge-transfer complexes have been observed and studied in a wide variety of chemical and biological systems.[2] Interest in these complexes stems from the fact that many molecular interactions are potentially charge transfer in nature. Examples of how complexes have been used to better understand interacting molecular systems can be found in the theory of activated complexes of chemical reactions[3] and the binding of substrate molecules to enzyme sites in biochemical reactions.[4] Most recently, charge-transfer complexes have been the focus of purely applied research in which their semi-, photoconductive and other electrical properties are being tested.[5] Due to the above and the ever growing interest in charge-transfer complexes and charge-transfer interaction, it is important to continuously refine the qualitative and quantitative descriptions that define charge-transfer interaction.

Several groups have investigated model chemical systems for the study of intramolecular charge-transfer interaction. Some have connected donor and acceptor with saturated hydrocarbon chains[6] while others have incorporated the interacting groups within an inflexible framework.[7] Along with other investigators, we recognized that the cyclophane macrocycle offers a unique model system for the study of charge-transfer complexation. Some advantages which the cyclophane macrocycle offers are the following: (a) the effective distance between the interacting groups can be changed synthetically by the variation of the number of atoms in the chains bridging the donor–acceptor pair; (b) for the [*m.n*] cyclophane, where *m* and *n* are not greater than four, the structural features of the cyclophane macrocycle forces a nearly parallel orientation of the interacting groups; (c) it is possible to incorporate a large number of donor–acceptor pairs into the cyclophane structure by practical synthetic methods.

We have been interested in the potential interaction that a fully charged moiety would have on a second neutral or charged group in a rigid framework.[1] Examples of three systems which are of interest to us for charge-transfer and conductance studies are **1**, **2**, and **3** (see Figure 1). This paper describes our work on the synthesis of the first member of this series [2.2](1,4)tropylioparacyclophane tetrafluoroborate (**1**) and on the charge-transfer interaction that is present in this molecule.

Synthesis. Scheme I shows the synthetic sequence used to obtain cyclophane **1**. Birch reduction of [2.2]paracyclophane by the method of Marshall and Folsom[8a] affords the tetrahydro derivative **5** in 96% yield. When **5** is treated with bromoform and potassium *tert*-butoxide in benzene:*tert*-butyl alcohol solution at 0 °C, starting material **5** and a mixture of the mono- and dicarbene adducts **6a** and **6b**[9] are obtained in yields of 46, 42, and 10%, respectively, after chromatography on silica gel. Monocarbene adduct **6a** is then treated with dichlorodicyanobenzoquinone (DDQ) at room temperature in benzene and is quantitatively converted to dibromide **7**. Dehydrobromination of **7** in refluxing pyridine affords bromide **8** in 81%

[‡] Dedicated to Professor Robert Burns Woodward on the occasion of his 60th birthday.