Photochemical Cycloaddition of Singlet and Triplet Diphenylvinylene Carbonate with Conjugated Dienes

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Abstract: The singlet and triplet excited states of diphenylvinylene carbonate (V) react with conjugated dienes to produce 2 + 2 cycloadducts. The singlet reaction occurs with retention of diene stereochemistry via a singlet exciplex intermediate. Singlet cycloaddition is only moderately regioselective and stereoselective, indicative of a loosely bound exciplex intermediate. The triplet cycloaddition occurs with substantial loss of diene stereochemistry and high regioselectivity. The high triplet regioselectivity is a consequence of selective collapse of the more substituted biradical rather than selective bonding to the less substituted diene terminus. The regioselectivity of initial bonding is the same for the singlet and triplet reactions.

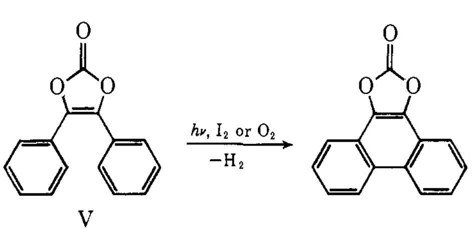
The hypothesis of an oriented π complex or exciplex intermediate in photochemical cycloaddition reactions was originally advanced by Corey[2] to rationalize the regioselectivity of triplet enone-olefin cycloaddition reactions.[3] Singlet[4-6] and triplet[7,8] exciplexes have subsequently been postulated as intermediates in a large number of photochemical cycloaddition reactions. In most cases evidence for exciplexes has been indirect and based on inferences derived from kinetic or product studies. The absence of observable exciplex fluorescence in cycloaddition reactions led some investigators to question the existence of exciplex intermediates.[9] Recently there have been several reports of concurrent exciplex fluorescence and cycloaddition[4-6] and conclusive demonstration of the intermediacy of singlet exciplexes in several ${}_{\pi}2_s + {}_{\pi}2_s$ photocycloaddition reactions.[4] It is also evident from several recent studies that the orientation and efficiency of photochemical cycloaddition can be determined by the nature of the exciplex.[4a,5]

We have observed that diphenylvinylene carbonate (V) undergoes efficient ${}_{\pi}2_s + {}_{\pi}2_s$ photochemical cycloaddition with conjugated dienes[10] and enol ethers[11] from both its singlet and triplet excited states. The reactions with conjugated dienes provide a wealth of stereochemical information about both the singlet and triplet reactions. Direct spectroscopic evidence for an exciplex intermediate in the singlet cycloaddition has been obtained and will be presented in detail in a subsequent publication.[12] Evidence for a triplet exciplex as the precursor of a 1,4-biradical intermediate can be inferred from the regioselectivity of the triplet cycloaddition reaction.

Results

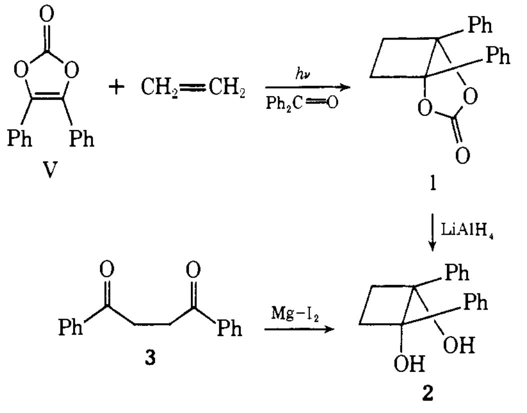
Excited State Properties. The uv absorption spectrum of V consists of a broad, structureless band with λ_{max} 295 nm (ϵ 1.37 $\times 10^4$, C_6H_6). The fluorescence spectrum of V in benzene solution displays a single maximum at 378 nm. Comparison of the corrected fluorescence spectrum with that of quinine sulfate[13] provides a value for the fluorescence quantum yield of 0.13 ± 0.02 at 20 °C in benzene solution. The singlet lifetime of V is 0.5 ± 0.2 ns, as determined by single photon counting using deconvolution by the method of moments.[14] The quantum yield for intersystem crossing of the lowest excited singlet state of V is <0.01, based upon comparison of the direct and triplet sensitized quantum yields for adduct formation with 1-hexene (vide infra). No emission other than short-lived fluorescence is observed for V at room temperature or 77 K. The 77 K phosphorescence of benzophenone in a methylcyclohexane glass is quenched by V, but no new emission is observed. The room temperature phosphorescence of benzophenone, biacetyl, and benzil can be quenched by V. The rate constant for quenching of benzil triplet by V (2.6×10^8 M^{-1} s^{-1}) is similar to that reported by Sandros[15] for biacetyl quenching of benzil (2.7×10^8 M^{-1} s^{-1}). Thus the triplet energy of V is probably similar to that of biacetyl (56 kcal/mol).[15]

Preparative Photochemistry. Irradiation of benzene solutions of V in the presence of iodine or oxygen leads to the formation of phenanthrene carbonate as the major product (eq 1).[16] In the absence of oxygen, V undergoes very slow conversion to benzil and several unidentified products.[16a] Addition of excess alkene (ethylene, 1-hexene, 2-butene, or 2,3-dimethyl-2-butene) does not result in the formation of new products or enhanced destruction of V.[17] No products were observed upon triplet sensitized photolysis of V using several different sensitizers, including benzophenone, Michler's ketone, and benzil. Sensitized photolysis in the presence of excess ethylene or terminal alkenes resulted in cycloadduct formation (eq 2); however, no adducts were observed with more highly substituted alkenes. The product of V with ethylene is assigned structure **1** on the basis of ir and NMR spectral data (see Experimental Section) and its conversion to *cis*-1,2-diphenyl-1,2-cyclobutanediol (**2**) upon reduction with lithium aluminum hydride. Diol **2** was identical with the product of 1,4-diphenyl-1,4-butanedione (**3**) pinacolization.[18] Sensitized cycloaddition of V with 1-propene or 1-hexene results in the formation of two adducts in approximately 3:1 ratio (eq 3). The

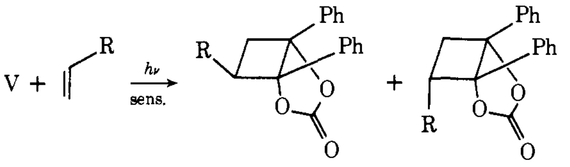


V

(1)



(2)

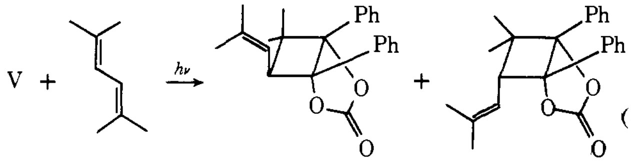


(3)

R = CH$_3$ **4**, 70% **5**, 30%
R = n-C$_4$H$_9$ **6**, 75% **7**, 25%

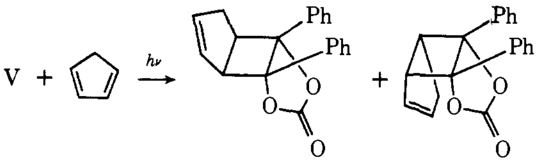
basis for stereochemical assignments is discussed at the conclusion of this section.

In contrast to the behavior of V with alkenes, direct photolysis in the presence of conjugated dienes results in rapid and quantitative adduct formation. Direct photolysis with symmetrically substituted dienes leads to the formation of two adducts (eq 4-7). The adducts of V with 2,5-dimethyl-2,4-hexadiene and cyclopentadiene were isolated and characterized. The two adducts of V with *trans,trans*-2,4-hexadiene were not isolated, but differ in VPC retention time from the pair of adducts obtained with *cis,cis*-2,4-hexadiene. Recovered diene shows no isomerization even at high conversions of V to cycloadducts. Benzil-sensitized irradiation of V in the presence of 2,5-dimethyl-2,4-hexadiene does not result in adduct formation. Sensitized irradiation of V with cyclopentadiene yields the two adducts obtained upon direct photolysis; however, the product ratio is substantially altered. Neither direct nor sensitized addition with cyclopentadiene afforded 2 + 4 adducts, as judged by the absence of norbornene-type protons in the NMR spectra of the photolysis mixtures. Benzil sensitized irradiation of V with *trans,trans*-2,4-hexadiene gives predominantly the products of direct photolysis albeit in altered ratio, along with 4% of a product identical in VPC retention time with a minor product of the direct photolysis of V with *cis,trans*-2,4-hexadiene. In contrast, sensitized irradiation of V with *cis,cis*-hexadiene gives only 10% of the two direct photolysis products and 90% of two products identical in VPC retention time with the major and one minor product of the direct photolysis of V with *cis,trans*-2,4-hexadiene. The product ratios for sensitized photolysis in eq 6 and 7 are determined by VPC at low conversions of V (<10%). Product ratios change at higher conversions, and recovered diene is increasingly isomerized.



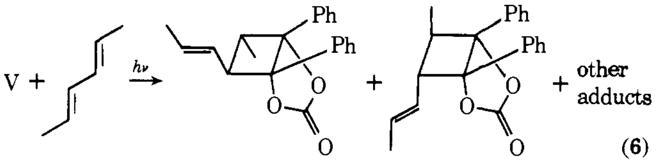
(4)

direct **8**, 71% **9**, 29%



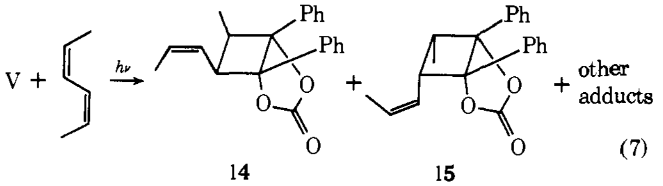
(5)

	10	11
direct	80%	20%
sensitized	10%	90%



(6)

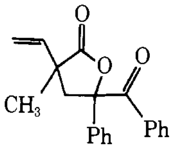
	12	13	
direct	72%	28%	0%
sensitized	10%	68%	4%



(7)

	14	15	
direct	67%	33%	0%
sensitized	4%	6%	90%

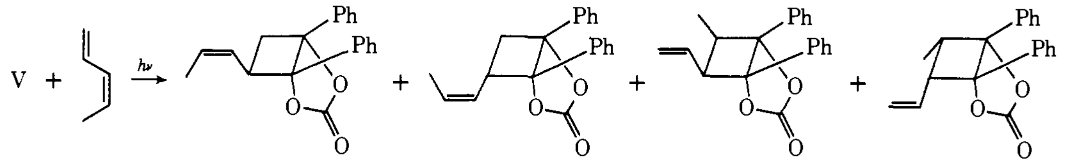
Direct photolysis of V with nonsymmetric dienes leads to formation of four isomeric 2 + 2 adducts. The three major adducts from *cis*-1,3-pentadiene were isolated and the structures of all four adducts assigned on the basis of ir and NMR spectra of isolated adducts or adduct mixtures (eq 8). Addition to the monosubstituted double bond accounts for 68% of the adduct mixture. Addition to the disubstituted double bond is stereospecific, within the limits of NMR and VPC detection. Similar results are obtained with *trans*-1,3-pentadiene (eq 9). Sensitized photolysis of V with either *cis*- or *trans*-1,3-pentadiene results in ~95% addition to the monosubstituted double bond. The minor products are assumed to be adducts of the disubstituted double bond, but were not isolated or characterized. The two major adducts obtained upon direct or sensitized addition of V with 4-methyl-1,3-pentadiene were isolated and characterized as adducts of the monosubstituted diene double bond (eq 10). The two minor products are assumed to be adducts of the trisubstituted double bond. Similar product ratios were obtained for direct and sensitized addition of V with isoprene (eq 11). The two major products were isolated and characterized as adducts of the disubstituted diene double bond. Direct photolysis of V and isoprene using monochromatic light (313 nm) resulted in the formation of an additional primary product (24% of the product mixture), not observed under other photolysis conditions. Spectral data for this product differ markedly from that for the 2 + 2 cycloadducts and are consistent with the γ-benzoyl-γ-butyrolactone structure **30**.



30

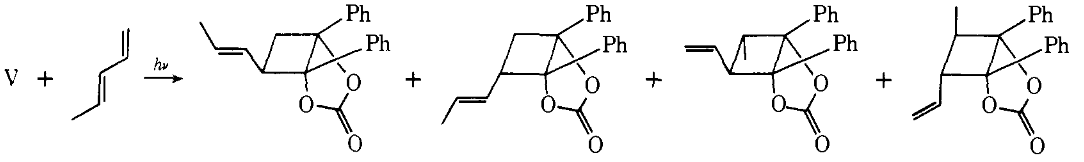
Stereochemical Assignments. The regioselectivity of cycloadducts with nonsymmetric dienes is readily assigned on the basis of the ^{1}H NMR spectra of the vinyl protons in conjunction with spin decoupling. Assignment of cyclobutane stereochemistry is complicated by the equivocal nature of cis and trans vicinal coupling constants in substituted cyclobutanes.[19] The primary basis for stereochemical assignments is the known shielding effect of a β-*cis*-phenyl group on protons[20] or methyl groups.[21] Assignments were both internally consistent (for a single adduct) and externally consistent (e.g., all major adducts from the direct photolysis reactions have *cis*-phenyl-vinyl stereochemistry). In several cases stereochemical assignments were corroborated by use of the lanthanide shift reagent Eu(fod)$_3$.[22] It is assumed that the shift reagent coordinates with the carbonate group, resulting in larger shifts for cyclobutane substituents cis to carbonate.

Singlet Cycloaddition. Quantitative Studies. Quantum yields for cycloadduct formation were determined for degassed benzene solutions of V (4.4×10^{3} M) at 25 °C using 313-nm irradiation. The variation in total adduct quantum yield with diene concentration is shown in Figure 1 for several dienes. These linear plots are of the form given in the following equation:



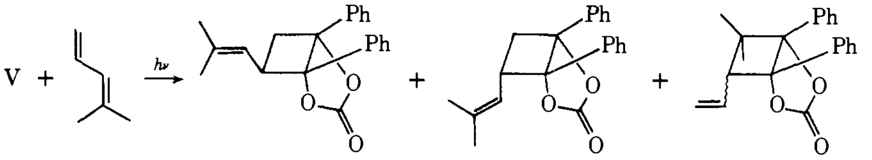
(8)

	16	17	18	19
direct	34%	34%	20%	12%
sensitized	48%	48%		



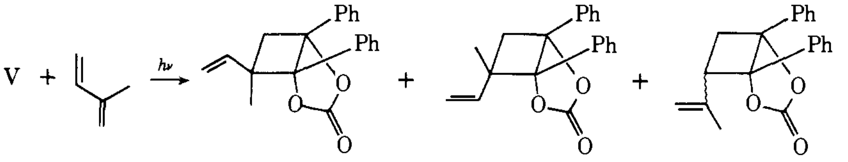
(9)

	20	21	22	23
direct	54%	20%	15%	11%
sensitized	55%	42%		



(10)

	24	25	26
direct	41%	35%	24%
sensitized	49%	51%	



(11)

	27	28	29
direct	43%	34%	23%
sensitized	43%	35%	22%

$$\Phi_a^{-1} = \Phi_s^{-1}(1 + (k_q\tau[D])^{-1}) \qquad (12)$$

where Φ_s is the quantum yield at infinite diene concentration and $k_q\tau$ is the usual Stern–Volmer constant obtained from the intercept/slope ratio. Values of Φ_s and $k_q\tau$ are given in Table I. For nonsymmetric dienes, the quantum yield for addition to each double bond is included. Values of $k_q\tau$ can also be obtained by quenching the fluorescence of **1** by dienes, a far less tedious procedure than quantum yield measurements. The two methods provide values which are in good agreement. Measurement of the product quantum yield at a single concentration and $k_q\tau$ from fluorescence quenching permits calculation of Φ_s. Quantum yield data for several dienes obtained by this method is included in Table I.

Triplet Cycloaddition. Quantitative Studies. Conjugated dienes are known to be efficient quenchers of benzophenone and other triplet sensitizers with triplet energies >60 kcal/mol.[23] Competitive quenching of the sensitizer by diene can be avoided by using benzil as the triplet sensitizer (53 kcal/mol[15]) and appropriate choice of the concentrations of V and diene. Quenching of the room temperature phosphorescence of benzil in degassed benzene provides the Stern–Volmer quenching constants, $k_q\tau$, given in Table II. The rate constants for triplet quenching can be calculated from $k_q\tau$ values and the measured lifetime of benzil (58 μs, lit.[15] 70 μs). Benzil fluorescence was unaffected by V or the dienes at the concentrations employed. The variation in triplet cycloaddition quantum yield with diene concentration for solutions 0.04 M in benzil and 0.05 M in V irradiated at 365 nm are shown in Figure 2 for several dienes. The diene concentrations employed insure that competitive quenching of benzil by diene is negligible. Values of $k_t\tau_t$ obtained from the ratio of slope to intercept and extrapolated values of Φ_t are summarized in Table III. No sensitized adduct formation was observed for 2,5-dimethyl-2,4-hexadiene.

Quantum yields for isomerization of recovered diene were determined for the benzil-sensitized addition of V (0.055 M) with *cis,cis*-2,4-hexadiene (0.055 M). The concentration of *cis,trans*- and *trans,trans*-2,4-hexadiene increases with photolysis time as shown in Figure 3. There is an induction period for formation of *trans,trans*-2,4-hexadiene, indicative of its formation from *cis,trans*-2,4-hexadiene. Extrapolation of the quantum yield for *cis,trans*-2,4-hexadiene formation to zero conversion gives a value of 0.53 ± 0.05. Since 0.055 M *cis,cis*-hexadiene quenches only 65% of the excited states of triplet V (Table III), the corrected quantum yield for diene isomerization is 0.81 ± 0.1.

Discussion

The photochemical conversion of diphenylvinylene carbonate (V) to phenanthrene carbonate is analogous to the reactions of *cis*-stilbene[23] and 1,2-diphenylcyclopentene.[24,25] In its spectroscopic properties V resembles *trans*-stilbene (Table IV),[26] rather than *cis*-stilbene which does not fluoresce at room temperature. Incorporation of the *cis*-[27] or *trans*-stilbene[28] chromophore into a rigid ring system is known to increase the fluorescence quantum yield by inhibiting the major pathway for nonradiative decay, twisting about the central double bond.[23] Unlike V and 1,2-diphenylcyclobutene,

Table I. Quantum Yields and Kinetics for Singlet Reactions

Diene	Φ_S[a]	$\Phi_{1,2}$[b]	$\Phi_{3,4}$[c]	$k_q\tau$,[d] M^{-1}	$k_q\tau$,[e] M^{-1}
2,5-Dimethyl-2,4-hexadiene	0.93			3.5	3.5
1,3-Cyclohexadiene					1.9
trans,trans-2,4-Hexadiene	0.86			1.8	1.7
4-Methyl-1,3-pentadiene	0.81[f]	0.59	0.22		1.7
trans-1,3-Pentadiene	0.83	0.61	0.22	0.65	0.68
cis-1,3-Pentadiene	0.83[f]	0.56	0.27		0.72
Cyclopentadiene					0.55
Isoprene	0.53[f]	0.41	0.12		0.30

[a] Obtained from intercept of plots shown in Figure 1, except as noted. Limits of error ±10%. [b] Quantum yield for addition to the C(1)C(2) diene double bond. [c] Quantum yield for addition to the C(3)C(4) diene double bond. [d] Stern–Volmer constant obtained from the intercept/slope ratio from Figure 1. Limits of error ±20%. [e] Slopes of fluorescence quenching plots (±10%). [f] Estimated values from the quantum yield in 2.0 M diene and $k_q\tau$ values from fluorescence quenching.

Table II. Quenching of Benzil Room Temperature Phosphorescence by V and Conjugated Dienes[a]

Quencher	$10^2 k_q\tau$, M^{-1}	$10^8 k_q$, $M^{-1}\ s^{-1}$
V	150	2.6
2,5-Dimethyl-2,4-hexadiene	30	0.52
1,3-Cyclohexadiene	160	2.8
trans,trans-2,4-Hexadiene	6.1	0.11
cis,cis-2,4-Hexadiene	17	0.29
4-Methyl-1,3-pentadiene	7.3	0.13
trans-1,3-Pentadiene	1.2	0.021
cis-1,3-Pentadiene	1.9	0.032
Cyclopentadiene	0.77	0.013
Isoprene	0.60	0.010

[a] Degassed solutions of 0.009 M benzil in benzene, τ = 58 μs.

Table III. Quantum Yields and Kinetics for Triplet Reactions

Diene	Φ_t[a]	$\Phi_{1,2}$[b]	$\Phi_{3,4}$[c]	$k_q\tau$, M^{-1}[d]
trans,trans-2,4-Hexadiene	0.18			79
cis,cis-2,4-Hexadiene	0.13			270
4-Methyl-1,3-pentadiene	0.63	0.63	<0.01	315
trans-1,3-Pentadiene	0.63	0.60	0.03	115
cis-1,3-Pentadiene	0.57	0.54	0.03	205
Cyclopentadiene	0.40			24
Isoprene	0.70	0.53	0.17	60
1-Hexene	0.15			0.3

[a] Obtained from intercept of plots shown in Figure 2. Limits of error ±20%. [b] See Table I, footnote *b*. [c] See Table I, footnote *c*. [d] Stern–Volmer constant obtained from the intercept/slope ratio from Figure 2. Limits of error ±40%.

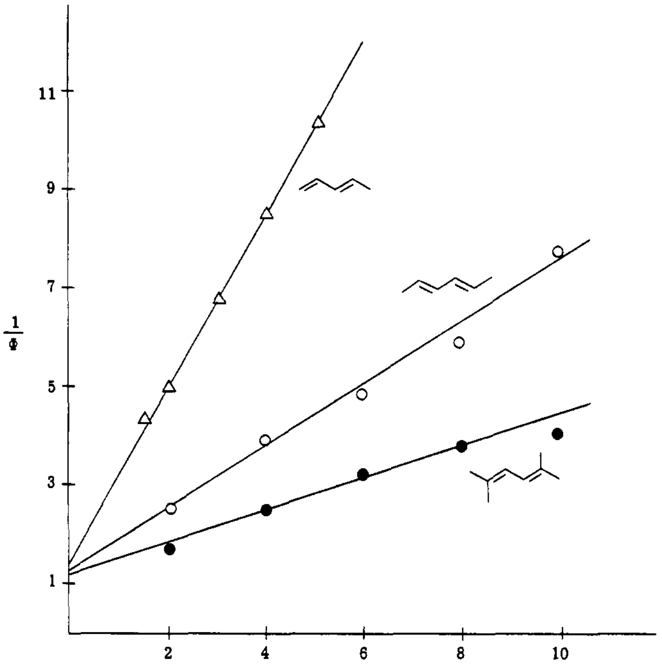


Figure 1. Variation in quantum yield for singlet cycloadduct formation with diene concentration.

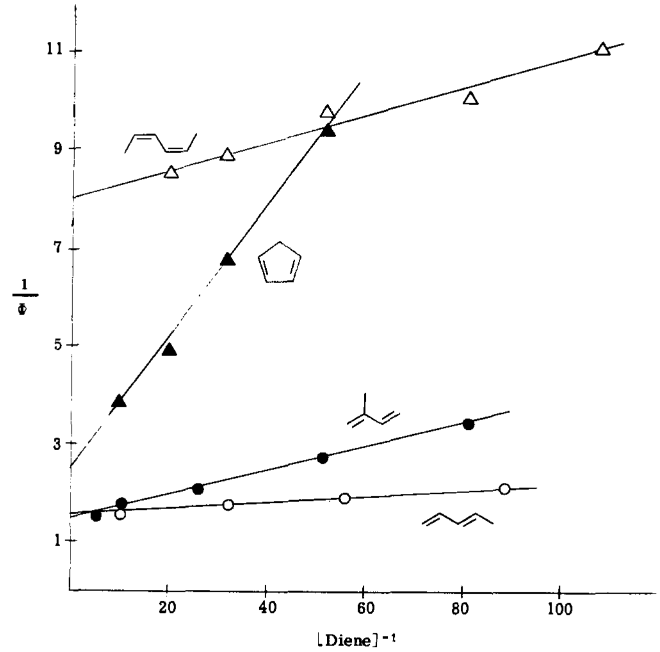


Figure 2. Variation in quantum yield for triplet cycloadduct formation with diene concentration.

1,2-diphenylcyclopentene does not fluoresce detectably at room temperature, but rather undergoes very efficient dihydrophenanthrene formation (Φ = 0.58 at −70 °C).[27] Apparently the electrocyclic reaction is far more facile for the cyclopentene than for the cyclobutene or cyclic carbonate. The triplet lifetimes of 1,2-diphenylcycloalkenes are not a simple function of ring size, as is the case for the 1-phenylcycloalkenes.[29]

Singlet 2 + 2 cycloaddition reactions have previously been reported for *trans*-stilbene[19] and 1,2-diphenylcyclobutene[30] with conjugated dienes. The failure of singlet *cis*-stilbene and triplet *cis*- and *trans*-stilbene to react with dienes[19] and electron-rich alkenes[31] has been attributed to very rapid twisting about the central double bond. The twisted singlet and triplet states fail to undergo cycloaddition in spite of having substantially longer lifetimes[32,33] than the planar excited singlet state. The present report provides the first instance of singlet and triplet 2 + 2 cycloaddition with conjugated dienes.[34] Incorporation of the stilbene chromophore into a small ring apparently increases the lifetime of both the planar singlet (Table IV) and triplet states. The absence of intersystem crossing following direct excitation of V greatly simplifies the analysis of the singlet and triplet products and reaction mechanisms.

The abundance of stereochemical information available for the singlet and triplet cycloaddition reactions of V with conjugated dienes aids in establishing the reaction mechanisms. The triplet reaction displays stereochemical features expected for product formation via a long-lived 1,4-biradical intermediate. The adducts are formed with substantial loss of diene stereochemistry (eq 6, 7), and, in the case of *cis,cis*-2,4-hexadiene, recovered diene is substantially isomerized (Figure 3).

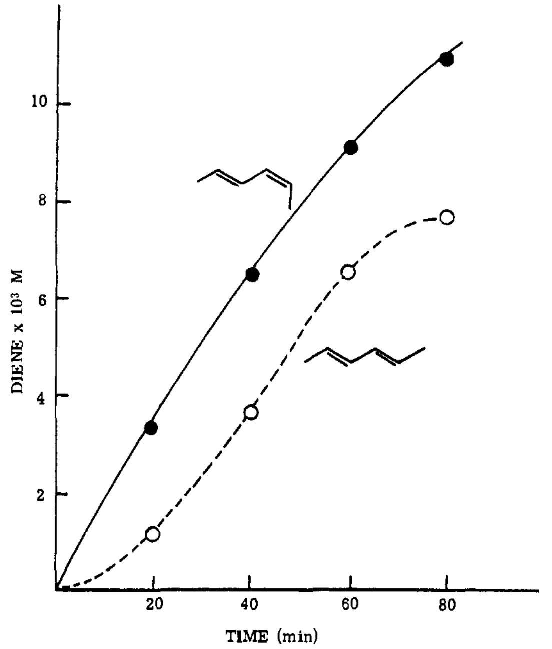


Figure 3. Isomerization of *cis,cis*-2,4-hexadiene during the benzil-sensitized addition with diphenylvinylene carbonate.

Table IV. Photophysical Properties of Stilbene Singlet States

	Φ_f	τ_S, ns	τ_R, ns
trans-Stilbene	0.08[a]	1.5	19
1,2-Diphenylcyclobutene	1.0[b]	4[c]	4
Diphenylvinylene carbonate	0.13	0.5[c]	4
1,2-Diphenylcyclopentene	<0.001[d]		

[a] Values from ref 26. [b] Values from ref 27. [c] Measured by single photon counting. [d] Value from ref 24.

In all the triplet cycloadditions, the major products have the minimum number of *cis*-1,2-dialkyl or alkyl–phenyl interactions and thus are the thermodynamically more stable adducts.[19] Finally, the regioselectivity of triplet cycloaddition with several nonsymmetric dienes (Table III) closely resembles that for a number of singlet and triplet 1,2-cycloaddition reactions known to occur via biradical intermediates.[35]

The cycloaddition reactions of singlet V with conjugated dienes display the stereochemical features normally associated with a concerted cycloaddition. Diene stereochemistry is retained both in the cycloadducts (eq 6-9) and the recovered dienes. If a singlet biradical is involved, it must cyclize or collapse to ground state reactants faster than rotations about single bonds ($k_{rot} \ll k_{cyc}$). The ratio k_{cyc}/k_{rot} is highly variable for singlet 1,4- and 1,3-biradicals.[36-38] The only claim of completely stereospecific singlet 1,4-biradical reactions is for the type II reactions of alkanones;[39] however, complete breaking of the γ C–H bond in the singlet reaction has been questioned.[40] The regioselectivity of singlet cycloaddition with the 1,3-pentadienes (Table I) is much lower than that for triplet cycloaddition (Table III). We recently reported that cycloaddition of singlet *trans*-stilbene occurs preferentially at the more substituted diene double bond,[41] a result in accord with the principle of maximum frontier orbital overlap for a concerted cycloaddition reaction.[42] The preferred formation of the thermodynamically less stable adducts with *cis*-1,2-phenyl–vinyl stereochemistry in the singlet cycloaddition reactions of V and *trans*-stilbene[19] is also consistent with frontier orbital theory for a concerted cycloaddition with secondary π orbital overlap[43] between the phenyl and vinyl groups lowering the energy of the transition state leading to the less stable product.

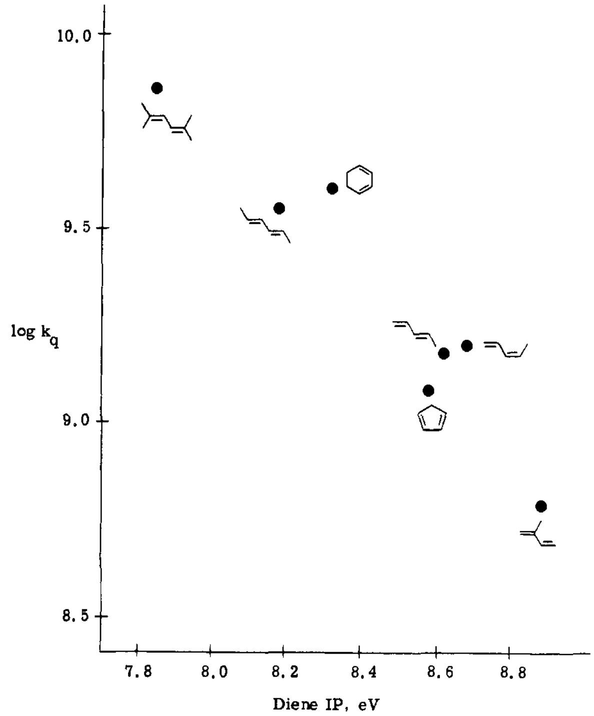


Figure 4. Correlation of fluorescence quenching rate constants with diene vertical ionization potential.

Turning from stereochemical to kinetic evidence, both the Stern–Volmer constants for fluorescence quenching of V by dienes and the extrapolated singlet quantum yields for adduct formation decrease with decreasing diene substitution (Table I). Quantum yields less than unity require an intermediate capable of decaying to ground state V and diene, yet a biradical intermediate is not consistent with the stereochemical evidence. The fluorescence quenching data give a moderately good semi-log correlation with diene ionization potential (Figure 4). Similar correlations for fluorescence quenching of aromatic hydrocarbons,[44] alkanones,[45] and azoalkanes[46] by dienes have been attributed to exciplex formation. Yang[5,47] has recently reported the observation of exciplex emission from several substituted anthracenes in the presence of dienes. Chapman[31] had previously shown that the Stern–Volmer constant for interaction of electron-rich alkenes with singlet *trans*-stilbene has a negative temperature dependence, providing circumstantial evidence for an exciplex intermediate. Weak but distinct exciplex emission can be observed when the fluorescence singlet V is quenched by dienes in benzene solution.[12] Furthermore, the Stern–Volmer constant for fluorescence quenching of V by *trans*-1,3-pentadiene shows zero temperature dependence, indicative of a reversibly formed exciplex intermediate.[48]

The mechanism for formation of cycloadducts via a singlet exciplex is given in Scheme I, where E is the exciplex and A the cycloadducts. Expressions for the variation in adduct quantum yield (eq 13, $\tau^{-1} = k_d + k_f$) and fluorescence quantum yield

Scheme I. Singlet Cycloaddition via an Exciplex Intermediate

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

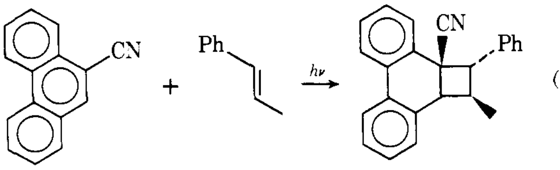
(eq 14) with diene concentration have been derived by Chapman and Lura.[31a] Equation 13 is of the same form as eq 12

$$\frac{1}{\Phi_a} = \frac{k_a + k_{ed}}{k_a} + \frac{k_{-e} + k_a + k_{ed}}{\tau k_a k_e[\mathrm{D}]} \tag{13}$$

$$\frac{\Phi_f{}^0}{\Phi_f} = 1 + \frac{k_e(k_a + k_{ed})\tau[\mathrm{D}]}{(k_{-e} + k_a + k_{ed})} \tag{14}$$

and provides kinetic expressions for Φ_s [$k_a/(k_a + k_{ed})$] and k_q [intercept/slope = $k_e(k_a + k_{ed})/(k_a + k_{ed} + k_{-e})$]. The intercept/slope ratio from eq 13 provides the same kinetic expression as the slope from eq 14. The results in Table I show the excellent agreement between the $k_q\tau$ data obtained from product quantum yields and fluorescence quenching.

Quantum yields for singlet adduct formation (Table I) decrease with increasing diene ionization potential (Figure 4). This decrease could reflect either a decrease in k_a or an increase in k_{ed} (eq 13). Exciplex stability increases with decreasing diene ionization potential;[12,44] thus the *most stable exciplex forms cycloadducts most efficiently*.[4a,49] This conclusion illustrates the parallelism between charge transfer stabilization of an exciplex and bond interchange in a cycloaddition reaction, first emphasized by Fukui.[42a] Since the same frontier orbital interactions which stabilize the cycloaddition transition state stabilize the exciplex, the stereochemical consequences of adduct formation via an exciplex should be similar to those for a concerted cycloaddition. A particularly nice example of the operation of maximum frontier orbital overlap in singlet exciplex cycloaddition reactions is the exclusive formation of adduct (**31**) from singlet 9-cyanophenanthrene and β-methylstyrene (eq 15).[4a] The decrease in fluorescence quenching rate constant with increasing diene ionization potential (Figure 4) could reflect either a decrease in k_e or an increase in the reversibility of exciplex formation (eq 14). The conventional assumption of decreasing k_e[44] has recently been shown to be incorrect in several cases.[48,50] The weaker exciplexes formed with high ionization potential dienes form cycloadduct less readily, but dissociate more readily.



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The mechanism for triplet cycloaddition via an irreversibly formed triplet biradical intermediate (B) is given in Scheme II. According to this mechanism, the intercept of a plot of $\Phi_a{}^{-1}$ vs. $[\mathrm{D}]^{-1}$ (Figure 3) provides the efficiency of product formation from the biradical intermediate ($k_a/(k_a + k_{bd})$) and the intercept/slope ratio provides a value of $k_b\tau$ (eq 16).

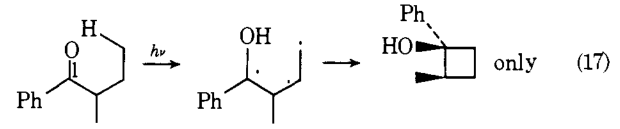
Scheme II. Triplet Cycloaddition via a Biradical Intermediate

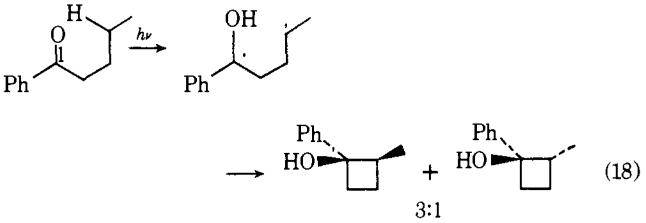
$$\begin{tikzcd}
\mathrm{V}^* + \mathrm{D} \arrow[r, "k_b"] \arrow[d, "k_d = 1/\tau"] & \mathrm{B} \arrow[r, "k_a"] \arrow[d, "k_{bd}"] & \mathrm{A} \\
\mathrm{V} & \mathrm{V} + \mathrm{D} &
\end{tikzcd}$$

$$\frac{1}{\Phi_a} = \frac{k_a + k_{bd}}{k_a}\left(1 + \frac{1}{k_b\tau[\mathrm{D}]}\right) \tag{16}$$

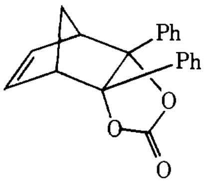
Comparison of the singlet and triplet quantum yields (Tables I and II) shows similar values for addition to terminal double bonds, but greatly diminished triplet quantum yields for addition to 1,2-disubstituted double bonds. No triplet addition is observed with the trisubstituted double bonds of 4-methyl-1,3-pentadiene or 2,5-dimethyl-2,4-hexadiene. Similarly, triplet addition is observed for terminal alkenes but not for 1,2-disubstituted alkenes.

The behavior of the 1,4-biradical intermediates formed from triplet V and *cis,cis*-2,4-hexadiene is summarized in Scheme III. Diene isomerization must result from collapse of a biradical intermediate rather than energy transfer from triplet V or the triplet sensitizer, benzil. Triplet sensitization of *cis,cis*-2,4-hexadiene leads to direct formation of *trans,-trans*-2,4-hexadiene as well as *cis,trans*-2,4-hexadiene,[51] whereas we observe no formation of *trans,trans*-2,4-hexadiene in the early stages of the reaction of triplet V with *cis,cis*-2,4-hexadiene (Figure 3).[52] It appears that biradical formation from triplet V and *cis,cis*-2,4-hexadiene occurs with unit efficiency, since cycloadducts and isomerized diene account for 94% of the excited triplets. Assuming that the residual inefficiency is due to biradical collapse to nonisomerized diene (k_{ed}), biradical collapse is moderately stereoselective ($k_{td}/k_{cd} \sim 13$). Biradical cyclization displays similar stereoselectivity with respect to the C(3),C(4) bond (Scheme III), both for *cis,cis*-2,4-hexadiene adducts ($k_{ta}/k_{ca} \sim 9$) and for *trans,trans*-2,4-hexadiene adducts ($k_{ta}/k_{ca} \sim 16$). The stereoselectivity of C(1),C(4) bond formation in the biradical is low for addition to terminal double bonds (eq 8-11) and moderate for addition to more highly substituted double bonds (eq 4-7). These observations are analogous to previous results for the 1,4-biradicals formed upon photochemical γ-hydrogen abstraction in α-methylbutyrophenone (eq 17) and valerophenone (eq 18).[53]





Since the C(1),C(4) bond is only partially formed in the transition state for biradical cyclization, incipient steric repulsion between substituents at the radical centers is smaller than that between substituents at adjacent bonded carbons.[53] In this connection it is interesting to note the absence of 4 + 2 adducts from triplet V and cyclopentadiene (eq 5). The two possible 4 + 2 adducts (**32**, **33**) both have cis endo substituents.



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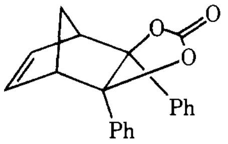

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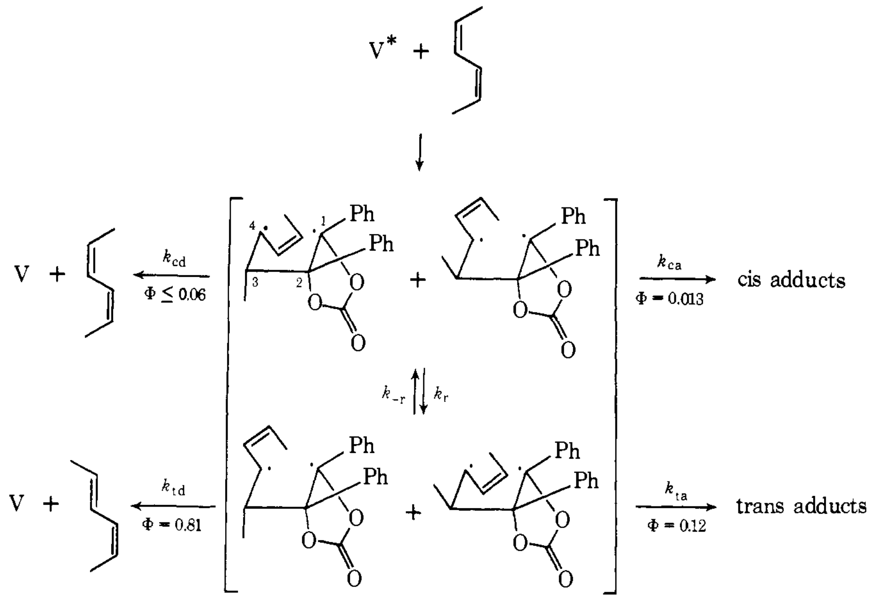
Kramer and Bartlett's[54] investigation of the addition of triplet cyclopentadiene to the isomeric 2-butenes indicates that biradical closure to cis endo substituted norbornenes is sterically unfavorable.

Addition of triplet V to the 1,3-pentadienes is highly regioselective (eq 8-10). It is commonly assumed that regioselective 1,2 cycloaddition to the pentadienes results from selective bonding to the less substituted diene terminus, leading to the formation of the more stable bifunctional intermediate.[35] We find that the regioselectivity of triplet V is instead the result of selective collapse of the more substituted biradical intermediate. The behavior of the biradical intermediate formed

Scheme III. Triplet Biradical Behavior



upon addition of triplet V to *cis,cis*-2,4-hexadiene (Scheme III) can be used as a model for the biradical formed upon addition to the disubstituted double bond of *cis*-1,3-pentadiene. If only 13% of these biradicals form cycloadduct, then the observed quantum yield for adduct formation (0.03) indicates that the quantum yield for biradical formation is approximately 0.23. This value is within the experimental error of the quantum yield for singlet cycloaddition to the disubstituted double bond (0.27). Similar analysis for triplet addition to the disubstituted double bond of *trans*-1,3-pentadiene provides a quantum yield of 0.17 for formation of the more substituted biradical, in reasonable agreement with the singlet quantum yield (0.22). Thus, *the regioselectivity of initial bonding is the same for singlet and triplet V.*[55] Steric destabilization of the transition state for cycloaddition[53,56] is apparently responsible for selective collapse of the more substituted biradical intermediate to ground state V and diene as well as stereoselective biradical cyclization. The addition of triplet V with isoprene proceeds with high quantum yield and with regioselectivity similar to that for singlet addition. Since both isoprene double bonds are terminal, little or no selectivity of biradical collapse would be expected. We suspect that some previous reports of highly regioselective biradical addition to dienes[35] may also reflect selective collapse of the more substituted biradical. The extent of biradical collapse to isomerized diene is apparently highly dependent upon the attacking species and reaction temperature.[57]

Values of $k_q\tau$ for reaction of dienes with triplet V (Table III) increase with decreasing ionization potential; however, the correlation is inferior to that obtained for fluorescence quenching (Figure 4). The absence of a pronounced steric effect on the triplet reaction is in accord with the observation of similar singlet and triplet regioselectivity of initial bonding. This suggests the possibility that the triplet cycloaddition, like singlet cycloaddition, is preceded by formation of an exciplex. Triplet exciplex intermediates in cycloaddition reactions have not been observed spectroscopically; however, convincing kinetic evidence for their existence has recently been presented by Caldwell[7] and Farid.[8] Triplet cycloaddition via a reversibly formed exciplex (Scheme IV) yields the complex expression shown in eq 19 for the dependence of adduct quantum yield upon diene concentration.

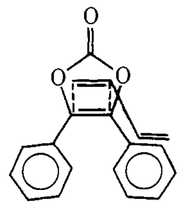
$$\frac{1}{\Phi_a} = \frac{(k_a + k_{bd})(k_b + k_{ed})}{k_a k_b} + \frac{(k_a + k_{bd})(k_b + k_{-e} + k_{ed})}{k_a k_b k_e [D]\tau} \qquad (19)$$

Scheme IV. Triplet Cycloaddition via Exciplex and Biradical Intermediates

$$\begin{tikzcd}
V^{T} + D \arrow[r, shift left, "k_e"] \arrow[d, "k_d = \tau^{-1}"] & E \arrow[l, shift left, "k_{-e}"] \arrow[r, "k_b"] \arrow[d, "k_{ed}"] & B \arrow[r, "k_a"] \arrow[d, "k_{bd}"] & A \\
V & V + D & V + D &
\end{tikzcd}$$

For addition to mono- or disubstituted double bonds, the extrapolated quantum yields for biradical formation are high ($k_b > k_{ed}$). Thus the intercept reduces to the same form as in eq 16. The intercept/slope ratio remains a complex kinetic expression as long as reversible exciplex formation is considered a possibility.

In summary, the cycloaddition of singlet V with conjugated dienes occurs via a reversibly formed singlet exciplex intermediate. The cycloadducts are formed with complete retention of diene stereochemistry, indicative of synchronous bond formation. The low regioselectivity of singlet cycloaddition indicates that there cannot be a single lowest energy exciplex geometry leading to adducts, as appears to be the case in other exciplex cycloaddition reactions.[4a] It is possible that a single sandwich type exciplex leads to all four adducts observed for nonsymmetric dienes (eq 8-11). Alternatively, several exciplex energy minima may be responsible for the different adducts, minima with secondary π orbital overlap being somewhat more stable (**34** vs. **35**). We favor the latter interpretation since it explains both the moderately stereoselective formation of the thermodynamically less stable adducts and the increase in singlet quantum yield with exciplex stability. Evidence for an exciplex intermediate in the addition of triplet V with conjugated dienes is tenuous at present, resting primarily upon the similar regioselectivity of singlet and triplet bonding.



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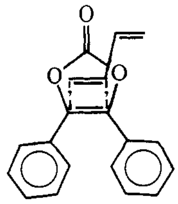

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Experimental Section

General Procedures. Preparative photolyses were carried out using a 450-W Hanovia medium-pressure mercury lamp in a Pyrex immersion well. Samples were contained in either a Pyrex annulus or test tubes under an argon 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. Dienes were obtained from Chemical Samples or Aldrich and distilled prior to use. Irradiated solutions were monitored by GC with a Hewlett-Packard 5750 dual flame gas chromatograph using a 5 ft × ⅛ in. column containing 5% SF 96 on Chromosorb G. In most cases, irradiation was continued until all the initial diphenylvinylene carbonate was consumed. Diene isomerization was monitored using a 10 ft × ⅛ in. column containing 25% dimethylsulfolane on Chromosorb P. Infrared spectra were recorded on a Beckman IR 5 spectrophotometer, NMR spectra on a Perkin-Elmer R20B 60 MHz, Bruker 90 MHz, or Varian HR-220 spectrometer,[58] emission spectra on a Perkin-Elmer MPF-2A spectrophotometer, and ultraviolet absorption spectra on a Cary 14 spectrophotometer.

Direct photolysis quantum yields were determined for degassed benzene solutions of V (4.4×10^{-3} M) containing various concentrations of diene. Samples were contained in sealed 13-mm o.d. Pyrex tubes and irradiated on a merry-go-round apparatus immersed in a thermostated water bath (23 ± 1 °C) using monochromatic 313-nm light. The benzene solvent was spectrograde, twice distilled from phosphorus pentoxide. Samples were analyzed for product formation after 3–10% conversion using a GC column calibrated with pure samples of the cycloadducts vs. eicosane internal standard. Light intensities were determined using benzophenone–benzhydrol actinometry.[59] Triplet quantum yields were determined for degassed solutions of V (0.05 M) containing benzil (0.04 M) and varying amounts of diene. Monochromatic 365-nm light from a Hanovia 200-W mercury lamp was used to selectively excite benzil. The room temperature phosphorescence of degassed benzene solutions of benzil (0.009 M) was quenched by added V or dienes. The total emission spectrum was corrected for the contribution of unquenched fluorescence. The phosphorescence lifetime of benzil was measured using the signal averaging apparatus previously described.[60]

Diphenylvinylene Carbonate V. Diphenylethylene carbonate was prepared by the method of Overberger and Drucker.[61] Reaction of hydrobenzoin (40.9 g, 0.19 mol) and diethyl carbonate (34.0 g, 0.29 mol) in the presence of sodium methoxide yielded 32.6 g of product (71%) upon recrystallization from 95% ethanol: mp 123–126 °C (lit.[61] 126.5–128 °C). Diphenylethylene carbonate was converted to diphenylvinylene carbonate via bromination–dehydrobromination. To a stirred refluxing solution of diphenylethylene carbonate (24.0 g, 0.1 mol) in ethanol-free chloroform (200 ml) irradiated with a GE 150-W reflector flood lamp was added a solution of bromine (16 g, 0.1 mol) in carbon tetrachloride over a period of 1.5 h. Illumination was discontinued 10 min after addition was complete, and the solvent was removed yielding a greenish residue. Two recrystallizations from methanol gave colorless plates (15.4 g, 81%): mp 77.5–79.0 °C (lit.[16a] 71–73 °C).

Sensitized Addition of Ethylene. A solution of V (0.30 g, 1.25 mmol) and benzophenone (0.29 g) in benzene was saturated with ethylene and irradiated through Pyrex (Hanovia 450-W medium-pressure mercury lamp) while ethylene was continuously bubbled through the solution. After 34 h GC analysis indicated approximately 50% unreacted V and a single adduct of slightly longer GC retention time. The reaction mixture was separated on 12 g of silica gel (hexane–benzene). Adduct **1** was obtained as a white solid (0.1 g, 31%): mp 113–119 °C; ir ($CHCl_3$) 5.55 μ; NMR ($CDCl_3$) δ 2.83 (m, 4 H), 7.09 (s, 10 H).

Treatment of carbonate 1 with lithium aluminum hydride in benzene–ether gave 1,2-diphenyl-1,2-cyclobutanediol (**2**) as a white solid: mp 155.5–157.0 °C (from chloroform). This material was identical with a sample prepared by the method of Griffin and Hager:[18] mp 158–159 °C (lit.[18] 148–150 °C). Ir dilution studies show a strong bound OH (3535 cm^{-1}) for 0.09 M **2**. The AA′BB′ spectrum of **2** resembles that of *cis*- rather than *trans*-1,2-dibromo-1,2-dicarbomethoxycyclobutane.[62]

Sensitized Addition of Propene. A solution of V (0.36 g, 1.5 mmol) and Michler's ketone (0.001 g) in 20 ml of benzene was saturated with propene at 10 °C, sealed with a serum cap, and irradiated for 12 h. GC analysis indicated 65% conversion of V and formation of two products (30:70 ratio). The solution was filtered through alumina to remove Michler's ketone, the solvent removed, and the residue crystallized from hexane to yield a mixture of **4** and **5** (0.14 g, 33%): mp 135–145 °C. Fractional crystallization from carbon tetrachloride gave the major isomer **4** as white needles (0.094 g, 22%): mp 158–162 °C. The filtrate was chromatographed on 16 g of silica gel (10% benzene–hexane) to yield the minor isomer **5**. The NMR spectra of **4** and **5** and lanthanide-induced shifts of the methyl and methine protons are given in Table V.

Sensitized Addition of 1-Hexene. A solution of V (0.5 g, 2.1 mmol), 1-hexene (14 ml), and Michler's ketone (0.005 g) in benzene (14 ml) was irradiated for 12 h. GC analysis indicated the formation of two products (ratio 25:75). Filtration through alumina, removal of the solvent, and bulb-to-bulb distillation, followed by crystallization from hexane gave a mixture of **6** and **7** (0.49 g, 73%): mp 90–95 °C. Fractional crystallization from hexane gave the major adduct **6** as colorless needles: mp 93–95 °C; ir (KBr) 5.55 μ. The filtrate contained a mixture of **6** and **7** enriched in **7**. Attempts at further purification of **7** by a number of chromatographic techniques were unsuccessful. The NMR spectra of **6** and **7** are included in Table V.

Addition of 2,5-Dimethyl-2,4-hexadiene. Direct irradiation of V (3.1 g, 13.1 mmol) and 2,5-dimethyl-2,4-hexadiene (2.3 g, 20.7 mmol) in 80 ml of benzene for 16.5 h resulted in quantitative conversion of V and formation of a single product peak (GC analysis). Removal of the solvent and a single crystallization from hexane gave 4.36 g (96%) of crystalline material. Fractional crystallization from hexane gave the major isomer (**8**) as colorless hexagonal prisms: mp 126–128 °C; ir (KBr) 5.55 μ. Anal. Calcd for $C_{23}H_{14}O_3$: C, 79.28; H, 6.94. Found: C, 79.40; H, 7.15. NMR analysis of the crude photolysis mixture indicated the formation of two products (ratio 71:29 by NMR). The minor product **9** was not isolated; however, its structure was apparent from the NMR spectrum of the mixture by subtracting the spectrum of **8**. The NMR spectra of **8** and **9** and the lanthanide-induced shifts of the vinyl and methine protons are included in Table V.

Sensitized irradiation of a solution of V (0.1 g, 0.4 mmol), diene (1 ml), and Michler's ketone (0.3 mg) in benzene (6 ml) for 48 h gave a product mixture identical with that obtained upon direct photolysis as judged by GC and NMR. Benzil-sensitized photolysis using monochromatic 365-nm light did not result in detectable product formation.

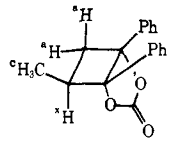
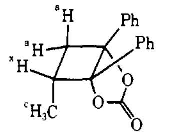
Addition of Cyclopentadiene. Direct irradiation of V (0.25 g, 1.04 mmol) and cyclopentadiene (1.4 g, 21 mmol) in benzene (18 ml) for 7 h resulted in complete conversion of V. GC analysis indicates the formation of two products (80:20 ratio). Filtration through alumina and removal of the solvent yielded a yellow oil. Attempts to separate the mixture of **10** and **11** by fractional crystallization or chromatography on silica gel were unsuccessful. The NMR spectrum of the major isomer **10** was assigned from the spectrum of the mixture (see Table V).

Sensitized irradiation of V (0.11 g, 0.45 mmol), cyclopentadiene (0.13 g, 1.7 mmol), and benzil (0.076 g, 0.32 mmol) in benzene (10 ml) with monochromatic 365-nm light resulted in complete conversion of V after 9 h. GC analysis indicated the formation of two products (10:90 ratio) with identical retention time with the products of direct photolysis. Filtration through alumina, removal of solvent, and crystallization from methanol yielded the major product **11**: mp 120–122 °C; NMR, see Table V.

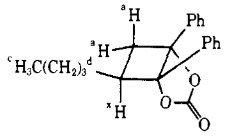
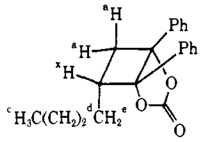
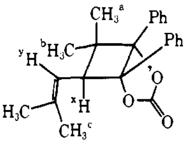
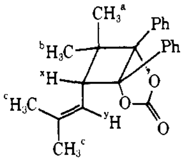
Addition of *trans,trans*-2,4-Hexadiene. Direct irradiation of V (0.1 g, 0.42 mmol) and diene (0.38 g, 4.5 mmol) in benzene (6 ml) for 12 h resulted in conversion to two products (GC ratio 72:28). The NMR spectrum of the photolysis mixture shows two sets of methyl doublets at δ 0.76, 1.47 (tentatively assigned to adduct **12**) and 1.12, 1.36 (assigned to adduct 13). Photolysis of an identical solution containing Michler's ketone (0.3 mg) using 365-nm monochromatic light resulted in the formation of four products (GC ratio 36:55:6:3). GC coinjection showed the major products of the sensitized photolysis coincide in retention time with the direct photolysis products.

Addition of *cis,cis*-2,4-Hexadiene. Direct photolysis of V (0.1 g) and diene (0.38 g) in benzene (6 ml) for 12 h results in formation of two products (GC ratio 67:33). The NMR spectrum of the photolysis mixture showed two sets of methyl doublets at δ 0.70, 1.55 (assigned to adduct **14**) and 1.17, 1.64 (assigned to adduct **15**). Neither the GC retention times nor the NMR chemical shifts correspond to those of the *trans,trans*-2,4-hexadiene adducts. Sensitized photolysis (0.3 mg Michler's ketone) results in the formation of four products (GC ratio

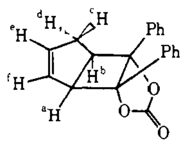
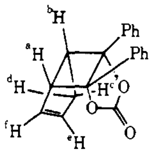
Table V. NMR Spectra of Cycloadducts

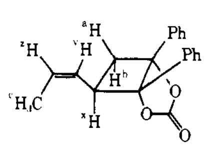
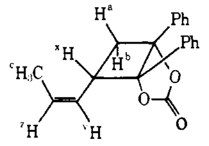
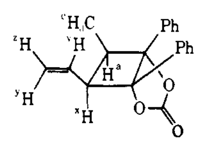
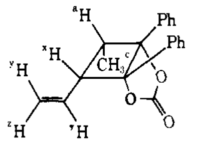
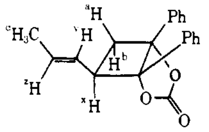
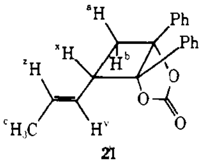
		δ, ppm	*J*, Hz
 **4**	c	0.81 d	$J_{xc} = 6.3$
	a	2.3–3.2 m	
	x	3.13 m	
		7.10 m	
 **5**	c	1.32 d	$J_{xc} = 6.5$
	a	2.3–3.3 m	
	x	3.22 m	
		7.10 m	

Eu(fod)$_3$ equivalence	LIS, minor isomer, **5** ring proton	LIS, minor isomer, **5** CH$_3$	LIS, major isomer, **4** ring proton	LIS, major isomer, **4** CH$_3$
0.00	193	79	188	50
0.19		98		54
0.39	224	111	214	60
	31	32	26	10

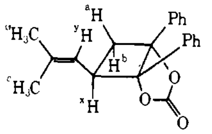
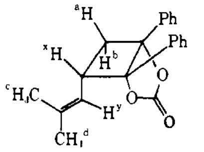
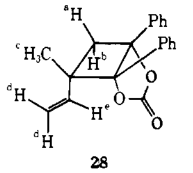
		δ, ppm	*J*, Hz
 **6**	c	0.60 t	$J = 7.0$
	d	1.0–1.3 m	
	a	2.5–3.0 m	
	x	2.8 m	
 **7**	c	0.87 t	$J = 7.0$
	d	1.15–1.40 m	
	e	1.65–1.90 m	
	a	2.3–3.2 m	
	x	3.1 m	
 **8**	a	1.02 s	
	b	1.43 s	
	c	1.63 br s	
	x	3.52 d	$J_{xy} = 7.5$
	y	4.90 d	$J_{xy} = 7.5$
		7.10 m	
 **9**	a	0.77 s	
	b	1.20 s	
	c	1.82 br s	
	x	3.70 d	$J = 9.0$
	y	5.68 d	$J = 9.0$
		7.10 m	

Eu(fod)$_3$ equivalence	LIS, minor isomer, **9** vinyl H^y	LIS, minor isomer, **9** ring H	LIS, major isomer, **8** vinyl H^y	LIS, major isomer, **8** ring H
0.00	337 Hz	225 Hz	292 Hz	216 Hz
0.15	345	230	296	224
0.21	366	245	309	258
0.39	382	258	317	288
	45 Hz	33 Hz	25 Hz	72 Hz

		δ, ppm	*J*, Hz
 **10**	a	4.06 m	
	b	3.49 t	8.0
	c	2.31 d	8.0
	d	2.73 d	8.0
	e,f	5.8 m	
 **11**	a,b	2.8 m	
	c	3.75 m	7.5, 2.0
	d	3.92 m	
	e	6.1 m	
	f	5.8 m	

		δ, ppm	*J*, Hz
 **16**	c	1.50 br d	$J_{cz} = 5.0$, $J_{cv} = 0.6$
	a,b	3.00 m	
	x	3.85 m	
	v,z	5.20 m	
		7.02 m	
 **17**	c	1.40 br d	$J_{cz} = 5.4$, $J_{cv} =$ ca. 0.6
	a,b	3.00 m	
	x	3.80 m	
	z,v	5.58 m	
		7.05 m	
 **18**	c	0.70 d	$J_{ac} = 7.3$
	a	3.29 m	
	x	3.77 t	$J_{vx} = J_{av} = 9.8$
		5.05 m	
	y,z	5.28 m	
	v	5.70 m	
		7.10 s	
 **19**	c	1.15 d	$J_{ac} = 7.0$
	a	3.30	
	x	3.75	
	y,z	5.10 m	
		5.32 m	
	v	5.87 m	
		7.02 s	
		7.06 s	
 **20**	c	1.48 br d	$J_{ab} = 5.6$, $J_{ac} = \sim 0.61$
	a,b	~2.8 m	
	x	3.52 m	
	v	4.98 q	$J = 15.2$, $J = 5.2$
	z	5.45 m	
		7.10 m	
 **21**		1.65 br d	$J_{ab} = 4.0$, $J_{ac} = \sim 0.6$
		2.95 m	
		3.65 m	
		5.69 m	
		7.10 m	

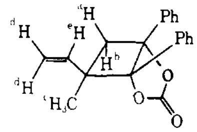
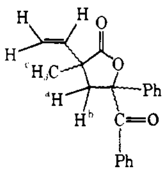
Eu(fod)$_3$ equivalence	LIS, 20 1.48 ppm doublet	LIS, 21 1.65 ppm doublet
0.00	89 Hz	.99 Hz
0.20	95	107
0.42	104	119
	15 Hz	20 Hz

		δ, ppm	*J*, Hz
 **24**		1.43 br s	
	a,b	~2.92	$J_{ab} = 13.5$
	x	3.87 m	
	y	4.85 br d	$J_{yx} = 7.2$, $J_{yc} =$ ca. 1.1
		7.05 m	
 **25**	c,d	1.58 br s	
		1.72 br s	
	a,b	~2.8 m	
	x	3.8 m	
	y	5.4 br d	$J_{xy} = 8.0$, $J_{y,cd} = 1.3$
		6.97 s	
		7.07 s	
 **28**	c	0.92 s	
	a	2.78 d	$J_{ab} = 14.8$
	b	3.28 d	
	d	5.20–5.60 m	
	e	5.95–6.40 m	
		7.20 m	

41:50:3:5). GC coinjection showed the retention times of the two minor products of the sensitized photolysis coincide with those of the products of direct photolysis.

Addition of *cis*-1,3-Pentadiene. Direct irradiation of V (0.5 g) and *cis*-1,3-pentadiene (2.1 g) in benzene (30 ml) for 12 h resulted in the formation of three product peaks by GC analysis (ratio 68:12:20). The

Table V (*Continued*)

	δ, ppm	*J*, Hz
 **27**	c 1.44 s a 2.60 d b 3.40 d e,d 4.75–5.70 m 7.10 m	J_{ab} = 14.2
Eu(fod)$_3$ equivalence	LIS, **27** ring methyl	LIS, **28** ring methyl
0.00	93	56
0.29	118	70
0.59	144	78
	51 Hz	22 Hz
 **30**	c 1.20 s a,b 2.05 d 3.65 d 7.0–7.5 m 7.65–8.0 m	J_{ab} = 13.1

solution was filtered through alumina, the solvent removed, and the residue purified by bulb-to-bulb distillation. Chromatography on 24% silver nitrate–silica gel using hexane solvent gave, in order of elution, pure samples of **18** (the product with longest GC retention time), **19** (the product of intermediate retention time), and **16** (the product of shortest retention time). Products 18 and **19** were obtained as yellow oils and characterized by NMR. Product **16** was crystallized from hexane: mp 108–111 °C; ir (KBr) 5.60 μ. A fourth isomer (**17**) could not be isolated from the direct photolysis mixture. However, NMR analysis of the product mixture prior to chromatography indicated the presence of a second adduct to the terminal double bond formed in nearly the same yield as **16** (NMR integration). This product **17** was isolated from the sensitized photolysis (vide infra) and found to have the same GC retention time as **16**. The NMR spectral assignments for **16–19** are included in Table V. Assignments were supported by spin decoupling experiments. Sensitized photolysis (Michler's ketone) of V and *cis*-1,3-pentadiene results in the formation of two product peaks (GC ratio 4:96). The major peak has the same GC retention time as the major peak of the direct photolysis mixture; however, the minor peak does not coincide in retention time to any of the products of direct photolysis. NMR analysis of the photolysis mixture after filtration through alumina and removal of solvent showed the formation of **16** and 17 in equal amounts.

***trans*-1,3-Pentadiene Addition.** Direct irradiation of V (1.0 g, 4.2 mmol) and *trans*-1,3-pentadiene (2.8 g, 41 mmol) in benzene (25 ml) for 12 h resulted in complete conversion of V. GC analysis showed three product peaks (ratio 15:11:74). NMR analysis of the product mixture showed four methyl doublets at δ 0.74, 1.37, 1.48, and 1.65 (ratio by GC and NMR 15:11:54:20). Apparently the major GC product peak is due to the two major products. Crystallization of the reaction mixture gave 0.39 g (30%) of colorless trigonal prisms: mp 72.5–74.0 °C. The crystalline material corresponds to the major GC product peak; however, NMR analysis showed it to be a 1:1 mixture of **20** and **21**. Chromatography of the photolysis mixture on 24% silver nitrate–silica gel provided a pure sample of **20**. The NMR spectra of **20** and **21** (obtained by subtracting the spectrum of **20** from that of the crystalline mixture of **20** and **21**) along with the lanthanide-induced shifts of the methyl doublets are included in Table V. Further elution of the silver nitrate–silica gel column provided a mixture of **22** and **23** as a yellow oil free from the major isomers. The NMR spectrum of this mixture showed two doublets (1.37 ppm, J = 6.0 assigned to **27** and 0.74 ppm, J = 6.5 assigned to **28**). Sensitized photolysis (Michler's ketone) of V and *trans*-1,3-pentadiene results in the formation of two product peaks (GC ratio 4:96). The retention time of the major peak and the NMR of the photolysis mixture are identical with the mixture of **20** and **21** obtained in the direct photolysis (ratio 55:42 by NMR). The GC retention time of the minor product does not coincide with those of **22** or **23**. Crystallization of the sensitized photolysis mixture from methanol gives the same 1:1 mixture of **25** and **26** obtained from the direct photolysis: mp 72–74 °C.

4-Methyl-1,3-pentadiene Addition. Direct irradiation of V (1.0 g, 4.2 mmol) and 4-methyl-1,3-pentadiene (3.5 g, 42 mmol) in diethyl ether (40 ml) for 9 h resulted in the formation of four products (GC ratio 10:41:35:12). Filtration through alumina and crystallization from hexane gave a mixture of the two major products. Fractional crystallization of this mixture from methanol gave the major product **24** in >90% purity by GC: mp 122–123 °C. The second major isomer (**25**) was isolated by preparative TLC (Quanta-PQ1 F-1000, benzene elution). The NMR spectra of **24** and **25** are included in Table V. No attempt was made to characterize the minor products, which are assumed to be the isomeric adducts of the trisubstituted double bond (**26**). Sensitized irradiation (Michler's ketone) gave only two adducts (GC ratio 49:51). The NMR spectrum and GC retention times of the triplet adduct mixture correspond to those of the major products **24** and **25** obtained from the direct photolysis.

Isoprene Addition. Direct irradiation of V (0.54 g, 2.3 mmol) and isoprene (1.4 g, 20 mmol) in benzene (40 ml) for 7.5 h resulted in the complete conversion of V to four products (GC ratio 43:9:14:34). Removal of solvent and crystallization from methanol afforded the product of longest GC retention time (**28**) (0.19 g, 27%): mp 138–143 °C; ir (KBr) 5.56 μ. The filtrate was sufficiently enriched in the major isomer **27** to allow assignment of its NMR spectrum. Isolation of the two minor products (**29**) was not attempted. Direct irradiation using monochromatic 313-nm light resulted in the formation of a fifth product **30** of shorter GC retention time than the adducts obtained using polychromatic light (GC ratio 24:33:7:10:26). Unlike the other diene adducts (**8–29**) which are stable under the photolysis conditions (λ >300 nm), **30** disappears when irradiated at 313 nm or through Pyrex. A pure sample of **30** was obtained as the first component of the photolysis mixture eluted from 13% silver nitrate–silica gel with hexane: ir (film) 5.60, 5.95 μ; uv (CH_3CN) λ_{max} 322 (ε 288). The NMR spectra of **27**, **28**, and **30** are included in Table V. Sensitized photolysis (Michler's ketone) of V with isoprene gave a mixture of four adducts virtually identical with that obtained in the direct photolysis (GC and NMR analysis). Product **30** is unstable to the conditions of sensitized photolysis.

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Stereomutation of 1-Hydroxyallyl Cations. Thermal and Photochemical Isomerizations of Protonated Enones[1]

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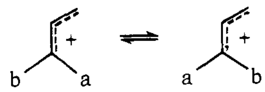
Abstract: Protonated *trans*-crotonaldehyde (**2**), *trans*-crotonic acid (**4**), *trans*-tiglaldehyde (**6**), *trans*-pent-3-en-2-one (**8**), and *trans*-3-methylpent-3-en-2-one (**10**), prepared by protonation of the analogous enones or acid in FSO_3H, isomerized to give the corresponding cis isomers **11**, **12**, **13**, **14**, and **15**, respectively, when irradiated at low temperatures. A photostationary state was set up between the cis and trans isomers of these hydroxyallyl cations, which in the case of the **2**/**11** and **4**/**12** systems, could be approached by starting with either the cis or trans forms. The cis isomers were all thermally unstable and quantitatively reverted to the corresponding trans isomers on heating. The rate constants for these stereomutations have been obtained in FSO_3H and FSO_3H/SbF_5 (4:1) media at +50 °C. In particular it was found that the rate constants for the isomerization of **11** → **2** and **13** → **6** were decreased by a factor of 10^2 on the addition of SbF_5 to FSO_3H, while a comparable change in medium for the isomerizations of **14** → **8** and **15** → **10** enhanced their rates of isomerization by a small amount. No deuterium incorporation could be detected when these photochemical or thermal isomerizations were carried out in FSO_3D or FSO_3D/SbF_5 (4:1). It is suggested that in FSO_3H the thermal isomerizations of **11** and **13** take place by a mechanism involving addition of a nucleophile to C(3) of the allyl cations, rotation and subsequent reionization. However, it would appear that the thermal stereomutation of **12**, **14**, and **15** in both FSO_3H and FSO_3H/SbF_5 and the stereomutation of **11** and **13** in FSO_3H/SbF_5 all proceed by formation and subsequent ring opening of a protonated oxete. Possible reasons for the operation of these two pathways and the implications of this work to the parent allyl cations are discussed.

Allyl cations were one of the first classes of carbonium ions to be characterized as long-lived entities, and it is not surprising, therefore, that many studies of their properties have been reported.[2] While the initial thrust of these reports has been largely directed toward their characterization, more recently there has been considerable experimental[3-8] and theoretical[9-11] interest in the stereomutation of allyl cations (eq 1).



(1)

These cis/trans isomerization reactions, which have been studied very largely with alkyl-substituted cations, typically take place with fairly low activation energies ($\Delta F^{\ddagger} \sim$ 12-25 kcal/mol). Some four different mechanisms have been con-