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REGIOSELECTIVE 2 + 2 CYCLOADDITION OF SINGLET AND TRIPLET DIPHENYLVINYLENE CARBONATE WITH CONJUGATED DIENES

Frederick D. Lewis*[1] and Richard H. Hirsch[2]

Department of Chemistry, Northwestern University,
Evanston, Illinois 60201

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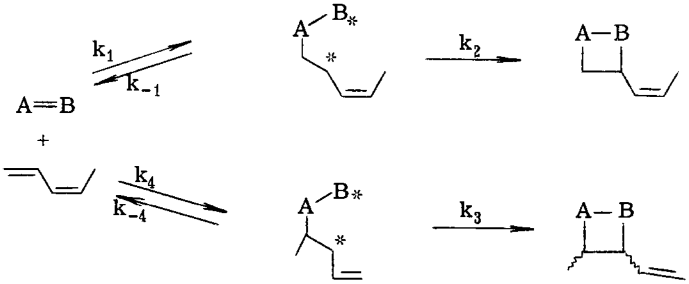
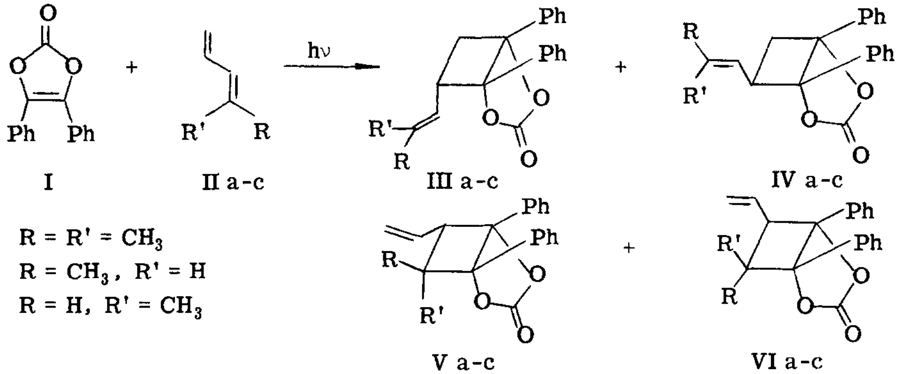
Conjugated dienes undergo thermal 1, 2 cycloaddition reactions with such diverse reagents as haloethylenes,[3] tetracyanoethylene,[3b] ketenes,[4] carbenes,[5] and 1, 3-dipolar[6] species. All of these reagents add preferentially (>90%) to the mono-substituted double bond of the isomeric-1, 3-pentadienes. It is generally assumed that the observed regioselectivity results from preferred bonding to the less substituted terminus (Scheme I, $k_1 > k_4$), leading to the formation of the more stable biradical or dipolar intermediate.[3-6] Regioselective addition

Scheme I



could also result from selective collapse of the more substituted intermediate ($k_{-4}/k_3 > k_{-1}/k_2$); however, this alternative appears to have been ignored in discussions of thermal cycloaddition regioselectivity. We wish to present evidence that the regioselectivity of photochemical 2 + 2 cycloaddition of triplet diphenylvinylene carbonate (I) is due to selective collapse of the more substituted biradical intermediate.

Both direct irradiation (313 nm) and triplet sensitized irradiation (benzophenone, Michler's ketone, or benzil, 365 nm) of I in the presence of dienes result in formation of mixtures 2 + 2 cycloadducts. Direct photolysis involves only the singlet state of I. An upper limit for the intersystem crossing quantum yield of 10^{-2} is provided by comparison of the quantum yields for direct and triplet sensitized addition to 1-hexene ($<10^{-3}$ vs. 0.15).[7] Two stereoisomers result from singlet addition to either double bond of a non-symmetric diene, addition to the disubstituted double bond being stereospecific (eq 1).[8] Singlet addition to dienes IIa-c is only moderately regioselective (68-76% terminal addition); however, triplet sensitized addition is highly regioselective ($\geq$95% terminal addition). The low yield of adducts to the disubstituted double bonds of dienes IIb, c prevents determination of triplet adduct stereochemistry. Triplet addition to the isomeric 2, 4-hexadienes proceeds with substantial loss of stereochemistry (vide infra).



I   IIa-c   IIIa-c   IVa-c   Va-c   VIa-c   (1)

a: $R = R' = CH_3$
b: $R = CH_3$, $R' = H$
c: $R = H$, $R' = CH_3$

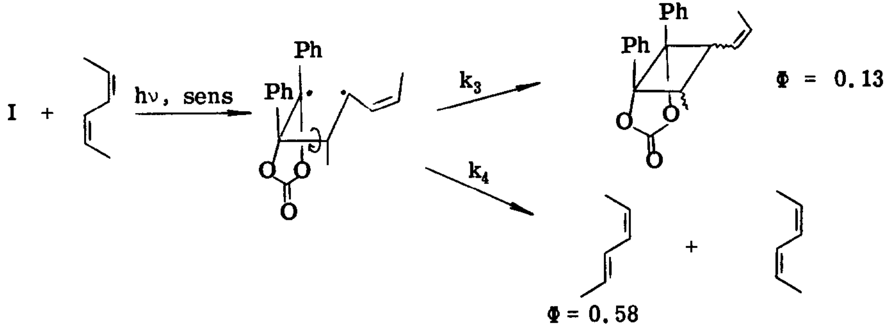
Quantum yields for cycloadduct formation increase with increasing diene concentration. Values given in Table I are obtained from the intercepts of linear plots of Φ^{-1} vs $[\text{diene}]^{-1}$. The high total quantum yields and stereospecificity of the singlet addition are indicative of either a concerted $[_{\pi}2_s + {}_{\pi}2_s]$ cycloaddition or a short-lived singlet biradical mechanism. The quantum yields for triplet addition decrease with increasing diene substitution. No triplet addition is observed for the trisubstituted double bonds of IIa or 2, 5-dimethyl-2, 4-hexadiene. The reaction of triplet I with cis, cis-2, 4-hexadiene proceeds with substantial isomerization of recovered diene (Φ = 0.58) as well as non-stereospecific cycloadduct formation. These observations are consistent with the formation of a triplet 1, 4-biradical intermediate[3] with

Table I. Quantum Yields for Cycloadduct Formation

Diene	Singlet[a]		Triplet[b]	
	Φ_{III+IV}	Φ_{V+VI}	Φ_{III+IV}	Φ_{V+VI}
4-methyl-1,3-pentadiene (IIa)	0.69	0.22	0.63	<0.01
trans-1,3-pentadiene (IIb)	0.61	0.22	0.60	0.03
cis-1,3-pentadiene (IIc)	0.56	0.27	0.53	0.03
trans,*trans*-2,4-hexadiene	0.91[c]		0.18[c]	
cis,*cis*-2,4-hexadiene	0.91[c]		0.13[c]	
2,5-dimethyl-2,4-hexadiene	1.0[c]		<0.01[c]	

[a] Singlet quantum yield for 4 x 10^{-3} M I in degassed benzene solution extrapolated to infinite diene concentration, error limits ±10%. [b] Reaction conditions ensured that triplet sensitizer (0.04 M benzil) was completely quenched by I (0.05 M) without competitive quenching by diene. Quantum yields are extrapolated to infinite diene concentration and corrected for benzil intersystem crossing efficiency (0.92), error limits ±10%. [c] Total adduct quantum yield.

sufficient lifetime to undergo rotation about the 2,3-bond prior to cyclization or collapse to diene and ground state I (eq 2). The high quantum yield for diene isomerization establishes that biradical collapse rather than inefficient biradical formation is responsible for the low adduct quantum yield.



(2)

The behavior of the biradical intermediate formed upon addition of triplet I to *cis*,*cis*-2,4-hexadiene (eq 2) can be used as a model for the biradical formed upon addition to the disubstituted double bond of *cis*-1,3-pentadiene (Scheme I). 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 we conclude that the initial bond formation between either singlet or triplet I and conjugated dienes is only moderately regioselective. Highly regioselective triplet cycloaddition is the result of selective collapse of the more substituted biradical intermediate. It should be noted that the triplet and thermally generated[3] biradical intermediates revert to isomerized addend; whereas the products of direct photolysis are formed stereospecifically and without addend isomerization.

Diphenylvinylene carbonate is similar to other cis-stilbene derivatives in its ability to form 9,10-phenanthrene carbonate in the presence of oxygen[7] and in its gross spectroscopic properties.[9,10] However, it is unusual in its ability to undergo cycloaddition from both the singlet and triplet excited state. trans-Stilbene undergoes 2 + 2 cycloaddition with dienes exclusively from the singlet state and both singlet and triplet cis-stilbene fail to undergo cycloaddition reactions.[11] Apparently, decay of the excited states by twisting about the π bond is sufficiently retarded by the cyclic carbonate structure of I to allow cycloaddition to compete effectively.[12] In support of this conclusion, we find that 1,2-diphenylcyclobutene[13] undergoes both singlet and triplet 2 + 2 cycloaddition with certain electron-rich alkenes.[14]

References and Notes

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8. Structural assignments for the cycloadducts will be discussed in a full paper.
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