

Photocycloaddition of Acetone to 1,2-Dicyanoethylene¹J. C. Dalton,² P. A. Wriede,³ and N. J. Turro⁴Contribution from the Chemistry Department,
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Abstract: The photocycloaddition of acetone to *trans*-1,2-dicyanoethylene (*t*-DCE) and *cis*-1,2-dicyanoethylene (*c*-DCE) to yield oxetanes **1** and **2**, respectively, has been studied in detail. The photocycloaddition, although inefficient, is stereospecific. Kinetic analysis reveals that the reaction occurs by attack of singlet acetone on the ground-state olefin. At low DCE concentrations, acetone triplet-sensitized *cis*-*trans* isomerization of DCE also occurs. The stereospecificity of oxetane formation can be rationalized in terms of simple MO models of the n, π^* excited state of alkyl ketones. Possible factors causing the inefficiency of the photocycloaddition reaction are discussed.

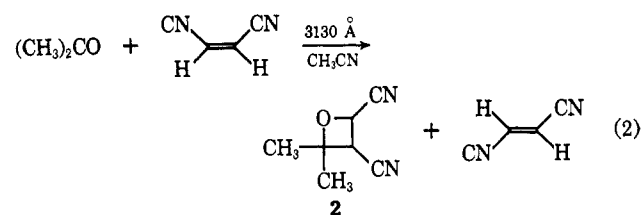
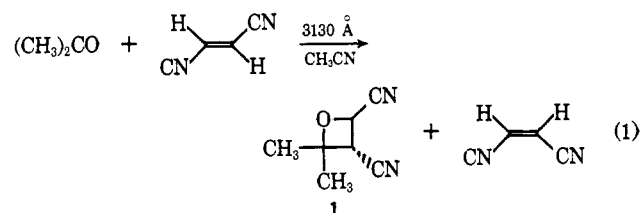
The bimolecular photocycloaddition of ketones to olefins yielding oxetanes (the Paterno-Buchi reaction⁵) has been the subject of much recent study.⁶ Although a few cases are known for which ketone singlets initiate attack on the ethylene,⁷ in general, ketone triplets are thought to be the chemically active species in the Paterno-Buchi reaction.^{6,8} For the case of electron-rich olefins (alkenes and alkoxyethylenes) the mechanism is usually considered to involve electrophilic attack by the oxygen atom of the n, π^* triplet state of the ketone on the olefin to preferentially generate the more stable biradical intermediate.^{6,8} The evidence which implicates this mechanism is (a) ketones which exhibit phosphorescence from n, π^* triplets and undergo efficient photoreduction in 2-propanol through n, π^* triplets also photoadd efficiently to olefins, while ketones which phosphoresce from a π, π^* lowest triplet and are photostable in 2-propanol photoadd much less efficiently to olefins;^{8a,e} (b) the photocycloaddition is retarded by triplet quenchers^{8a,b,e} and when the triplet energy of the olefin is below that of the ketone;^{8a} (c) the stereochemistry of the major oxetane adduct with asymmetric olefins is predicted from Markovnikov addition (which generally also results in formation of the most stable biradical intermediate);⁶ and (d) the *cis,trans* stereochemistry of the oxetanes is generally scrambled and essentially the same mixture of

isomeric oxetanes is formed starting with either *cis*- or *trans*-olefin.⁶

These results are consonant with simple models for the n, π^* excited state which predict that the half-vacant n orbital on the carbonyl excited state should be electrophilic in nature.⁹ The simple MO model for the n, π^* state predicts, in addition, nucleophilic electron-rich (three-electron) π systems above and below the plane of the carbonyl group. We wish to report here our studies of the stereospecific photocycloaddition reaction of acetone with *trans* (*t*-) and *cis* (*c*-) 1,2-dicyanoethylene (DCE) which appears to involve nucleophilic attack on the electron-deficient olefin by the n, π^* singlet state of acetone.¹⁰

Results

Mechanism. Irradiation of acetonitrile solutions of acetone *c*-DCE or *t*-DCE leads both to formation of oxetanes and geometrical isomerization of the olefin as shown in eq 1 and 2. The photocycloaddition reactions are stereospecific since starting with pure *t*-DCE



only **1** is initially formed and starting with pure *c*-DCE only **2** is initially formed. The isomeric oxetanes appear only after some of the starting olefin has been isomerized.

The following evidence indicates that formation of **1** and **2** results from attack of singlet acetone on *t*-DCE and *c*-DCE, respectively, while *cis*-*trans* isomerization occurs exclusively *via* acetone triplet sensitization:

(9) (a) M. Kasha in "Light and Life," W. D. McElroy and B. Glass, Ed., Johns Hopkins University, Baltimore, Maryland, 1961, p 31; (b) H. E. Zimmerman, *Advan. Photochem.*, **1**, 183 (1963).

(10) For preliminary communications of this work see ref 7a,b.

(1) (a) Molecular Photochemistry. Part XXIV. Part XXIII, N. J. Turro and D. M. McDaniel, *Mol. Photochem.*, in press. (b) The authors wish to thank the Air Force Office of Scientific Research (Grants No. AFOSR-1000-66 and 1381-68) for their generous support of this work. The support of the National Science Foundation is also gratefully acknowledged (Grant No. NSF-GP-4280).

(2) National Institutes of Health Predoctoral Fellow, 1966-1969.

(3) National Institutes of Health Trainee, 1965-1966.

(4) Alfred P. Sloan Fellow.

(5) E. Paterno and G. Chieffi, *Gazz. Chim. Ital.*, **39**, 341 (1909); G. Buchi, C. G. Inman, and E. S. Lipinsky, *J. Amer. Chem. Soc.*, **76**, 4327 (1954).

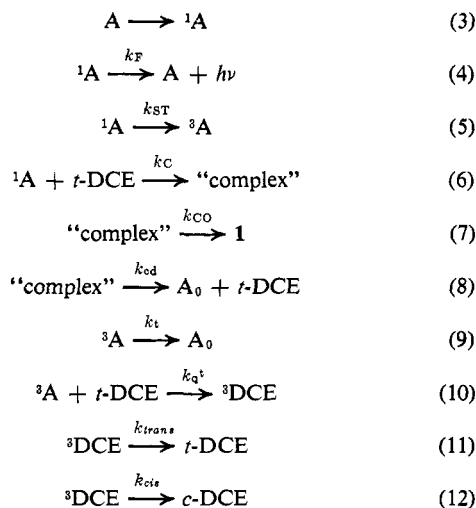
(6) Recent reviews: (a) D. R. Arnold, *Advan. Photochem.*, **6**, 301 (1968); (b) L. L. Muller and J. Hamer, "1,2-Cycloaddition Reactions," Interscience Publishers, New York, N. Y., 1967, p 111.

(7) (a) N. J. Turro, P. A. Wriede, and J. C. Dalton, *J. Amer. Chem. Soc.*, **90**, 3274 (1968); (b) N. J. Turro, P. A. Wriede, J. C. Dalton, D. Arnold, and A. Glick, *ibid.*, **89**, 3950 (1967); (c) L. A. Singer, G. A. Davis, and V. P. Muralidharan, *ibid.*, **91**, 897 (1969); (d) N. C. Yang and R. L. Loesch, *Tetrahedron Lett.*, 2571 (1968); (e) N. C. Yang, *Photochem. Photobiol.*, **7**, 767 (1968).

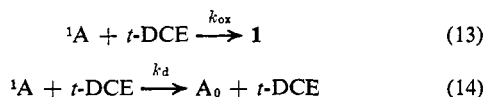
(8) (a) D. R. Arnold, R. H. Hinman, and A. H. Glick, *Tetrahedron Lett.*, 1425 (1964); (b) N. C. Yang, R. Loesch, and D. Mitchell, *J. Amer. Chem. Soc.*, **89**, 5465 (1967); (c) J. S. Bradshaw, *J. Org. Chem.*, **31**, 237 (1966); (d) R. Srinivasan and K. A. Hill, *J. Amer. Chem. Soc.*, **88**, 3765 (1966); (e) N. C. Yang, M. Nussim, M. J. Jorgenson, and S. Murov, *Tetrahedron Lett.*, 3657 (1964).

(a) the fluorescence of acetone is quenched by the addition of *t*-DCE or *c*-DCE; (b) the formation of **1** and **2** is only slightly affected by the addition of sufficient 1,3-pentadiene (1 *M*) to quench 80% of the *cis-trans* isomerization of DCE; and (c) *cis-trans* isomerization, but not oxetane formation, is quenched at high concentrations of DCE. The quantum yield for oxetane formation is much lower than unity even at very high DCE concentrations, implying that the reaction of acetone singlets with DCE is inefficient. However, quenching of acetone singlets is efficient. These observations are consistent with the mechanisms suggested in Schemes I and II. The observed inefficiency in formation of **1**

Scheme I



Scheme II



can be accounted for either by formation of an intermediate, C (eq 6), which can collapse to **1** (eq 7) or to acetone and *t*-DCE (eq 8), or by competition between oxetane formation (eq 13) and quenching which reforms acetone and the starting DCE isomer (eq 14). Thus, we may consider the trial mechanisms of Scheme I and Scheme II, where eq 7–9 are replaced by eq 13 and 14.

Kinetics. Quenching of Acetone Fluorescence by *t*-DCE. Addition of *t*-DCE to acetonitrile solutions of acetone quenches the broad acetone fluorescence. A Stern–Volmer treatment of the fluorescence quenching using eq 15 yields a slope of $6.7 \pm 0.2 \text{ M}^{-1}$.

$$\frac{F^0}{F} = 1 + \frac{k_q^s[t\text{-DCE}]}{k_{ST} + k_F} \quad (15)$$

F^0 = acetone fluorescence intensity in absence of *t*-DCE
 F = acetone fluorescence intensity in presence of *t*-DCE

$$k_q^s = \begin{cases} k_C & \text{Scheme I} \\ k_{ox} + k_d & \text{Scheme II} \end{cases}$$

The fluorescence of many other alkyl ketones is also quenched by *t*-DCE.¹¹ Concentrations of *t*-DCE, however, up to >0.1 *M* do not measurably quench the fluorescence of 0.03 *M* biacetyl in aerated benzene.

(11) J. C. Dalton and D. M. Pond, unpublished results.

Kinetics of the Acetone *t*-DCE Photocycloaddition. A Stern–Volmer analysis of formation of **1** as a function of *t*-DCE concentration assuming Scheme I results in eq 16

$$\frac{1}{\Phi_1} = \frac{k_{CO} + k_{cd}}{k_{CO}} \left\{ 1 + \frac{k_F + k_{ST}}{k_C[t\text{-DCE}]} \right\} \quad (16)$$

Φ_1 = quantum yield for formation of **1**

If, on the other hand, Scheme II obtains, eq 17 is appropriate. After rearranging eq 17 we can write a more general expression (eq 18).

$$\frac{1}{\Phi_1} = \frac{k_{ox} + k_d}{k_{ox}} + \frac{k_F + k_{ST}}{k_{ox}} \frac{1}{[t\text{-DCE}]} \quad (17)$$

$$\frac{1}{\Phi_1} = a \left\{ 1 + \frac{k_F + k_{ST}}{k_q^s} \frac{1}{[t\text{-DCE}]} \right\} \quad (18)$$

$$a = \begin{cases} (k_{CO} + k_{cd})/k_{CO} & \text{Scheme I} \\ (k_{ox} + k_d)/k_{ox} & \text{Scheme II} \end{cases}$$

k_q^s as defined for eq 15

Table I summarizes the data on Φ_1 as a function of *t*-DCE concentration.

Table I. Quantum Yields for the Formation of **1** and *c*-DCE as a Function of the *t*-DCE Concentration^{a,b}

[<i>t</i> -DCE], <i>M</i>	Φ_1	Φ_1^{-1}	$\Phi_{c\text{-DCE}}$	$\Phi_{c\text{-DCE}}^{-1}$
Run No. 1				
0.104	0.026	38.5	0.078	12.8
0.202	0.038	26.3	0.065	15.4
0.303	0.047	21.2	0.056	17.9
0.40	0.051	19.6	0.050	20.0
0.50	0.054	18.5	0.042	23.8
Run No. 2				
0.037	0.012	83.5	0.083	12.0
0.059	0.018	55.5	0.090	11.1
0.086	0.023	43.5	0.092	10.9
0.100	0.026	38.5	0.088	11.4
0.210	0.038	26.3	0.070	14.3
0.322	0.046	21.8	0.063	15.9
0.403	0.052	19.2	0.059	17.0
0.53	0.053	18.9	0.047	21.2
Limiting ^c value	0.076	13.2		
Slope ^c = 2.6				

^a Aerated solution, 5 *M* acetone in acetonitrile. ^b Quantum yields determined by cyclopentanone actinometer, with an error in the light intensity measurement of $\pm 50\%$. ^c From least-squares calculations.

The behavior predicted by eq 18 is observed experimentally as shown in Figure 1 and a slope of 2.6 and extrapolated intercept of 13.2 are obtained. An analogous analysis using *c*-DCE yields a slope of 1.16 and an extrapolated intercept of 11.6.

Kinetics of the Photosensitized Isomerization of DCE. From the reaction schemes the following Stern–Volmer relationship for the acetone triplet-sensitized isomerization of *t*-DCE can be derived (eq 19). Φ_{ST} , the quantum

$$\frac{1}{\Phi_{cis}} = \frac{1}{\Phi_{ST}} \left\{ \frac{k_{trans} + k_{cis}}{k_{cis}} \right\} \left\{ 1 + \frac{k_t}{k_q^s[t\text{-DCE}]} \right\} \quad (19)$$

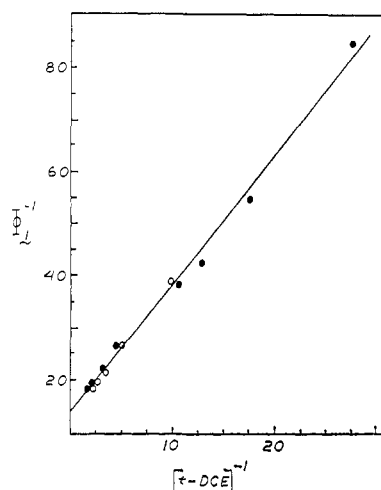


Figure 1. The effect of *t*-DCE concentration on Φ_1 : O, run no. 1; ●, run no. 2.

Φ_{cis} = quantum yield for photosensitized *t*-DCE \rightarrow *c*-

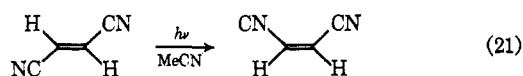
$$\Phi_{ST} = \frac{k_{ST}}{k_F + k_{ST} + k_q^s[t-DCE]} \quad (20)$$

$$k_q^s = \begin{cases} k_C & \text{Scheme I} \\ k_{ox} + k_d & \text{Scheme II} \end{cases}$$

DCE yield for intersystem crossing of acetone singlets in the presence of *t*-DCE will be nearly unity at low *t*-DCE concentrations ($k_{ST} \gg k_q^s[t-DCE] + k_F$). Under these conditions a plot of Φ_{cis}^{-1} vs. $[t-DCE]^{-1}$ should be nearly linear. However, as we approach high *t*-DCE concentrations ($k_q^s[t-DCE] > k_{ST}$), Φ_{ST} will approach zero and $1/\Phi_{cis}$ should increase rapidly. Figure 2 demonstrates that this type of behavior is found for the acetone-sensitized isomerization of *t*-DCE. A similar result was observed for the dependence of $1/\Phi_{trans}$ on $[c-DCE]$. Plots of Φ_1/Φ_{cis} vs. $[t-DCE]$ and Φ_2/Φ_{trans} vs. $[c-DCE]$ both yield straight lines with positive slope further demonstrating that just the isomerization is quenched at high olefin concentration.

Additional data on the photosensitized isomerization of *t*-DCE were obtained by comparing the rates at which *t*-DCE and 1,3-pentadiene quench the photoreduction of benzophenone by benzhydrol. Using a standard Stern-Volmer treatment and published data on the photoreduction,¹² a value of $1.2 \times 10^9 M^{-1} \text{sec}^{-1}$ was determined for the rate constant for quenching of benzophenone triplets by *t*-DCE. An identical value was found for 1,3-pentadiene, which is known to quench benzophenone triplets at the diffusion-controlled rate. This implies that *t*-DCE quenches benzophenone triplets ($E_T = 69 \text{ kcal/mol}$) at the diffusion-controlled rate.

Direct Isomerization of *t*-DCE and Photostability of 1. Acetonitrile solutions of *t*-DCE were found to undergo isomerization to *c*-DCE when irradiated with the full spectrum from a medium pressure mercury lamp (eq 21). The *trans*-oxetane, **1**, however, was found to be



(12) (a) W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Amer. Chem. Soc.*, **83**, 2789 (1961); (b) R. P. Foss, Ph.D. Thesis, California Institute of Technology, Pasadena, Calif., 1963.

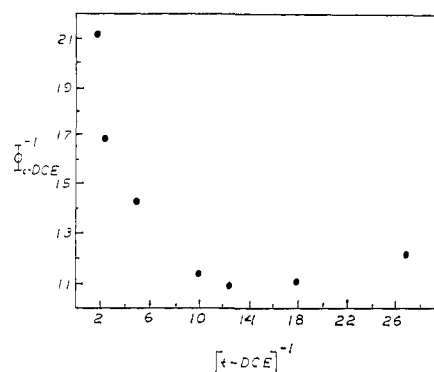
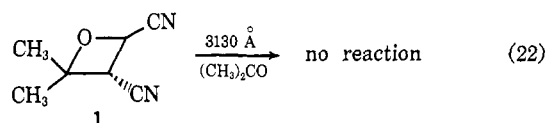


Figure 2. The effect of *t*-DCE concentration on Φ_{cis} .

stable under the kinetic photolysis conditions (eq 22).



Photoreaction of Other Ketones with *t*-DCE. In addition to acetone, we have observed photocycloaddition of *t*-DCE to 2-pentanone, 2-hexanone, cyclopentanone, and cyclohexanone.¹³ We have also irradiated *t*-DCE with cyclobutanone, biacetyl, 2-acetonaphthone, 9-fluorenone, benzophenone, xanthone, decafluorobenzophenone, 2-cyclohexenone, and 5-hexen-2-one. No oxetane formation was observed with any of these ketones, although irradiation always led to some isomerization of the *t*-DCE. When *t*-DCE was irradiated with 3-methyl-3-penten-2-one, however, neither oxetane formation nor isomerization of the *t*-DCE was observed.

Acetone Fluorescence Lifetime. The lifetime (τ_s) of the broad acetone fluorescence which maximizes at around 405 nm was measured using a single photon-counting apparatus. The lifetimes determined for three different concentrations of acetone in acetonitrile are given in Table II. *t*-DCE was observed to quench the lifetime as well as the intensity of the acetone fluorescence.

Table II. Acetone Fluorescence Lifetimes in Acetonitrile

Concn, M	τ_s , nsec
0.03	1.9 ± 0.5
1.0	2.1 ± 0.5
Neat	2.1 ± 0.5

Concentration Dependence of Acetone Fluorescence. Testa and O'Sullivan¹⁴ have recently reported that at very low concentrations the usual broad acetone fluorescence ($\lambda_{\text{max}} \sim 405 \text{ nm}$) is replaced by a sharper, shorter wavelength emission ($\lambda_{\text{max}}^{\text{hexane}} \sim 345 \text{ nm}$), which they consider to be monomer emission from an acetone excited singlet. The broad, longer wavelength emission, observed at higher acetone concentrations, is attributed to emission from acetone excimers. We have been unable to reproduce these results working in a similar concentration range in *n*-hexane. At concentra-

(13) N. J. Turro and P. A. Wriede, *J. Org. Chem.*, **34**, 3562 (1969).

(14) M. O'Sullivan and A. C. Testa, *J. Amer. Chem. Soc.*, **90**, 6245 (1968); this report has subsequently been retracted by Professor Testa, private communication.

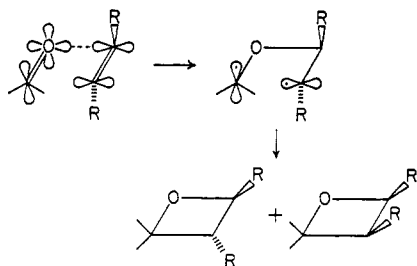


Figure 3. Attack of electrophilic n orbital of acetone singlet n, π^* excited state on olefin double bond leading to nonstereospecific oxetanes.

tions well below $2.7 \times 10^{-3} M$, where Testa reported the band at 345 nm to be >8 times as intense as the band at 405 nm, we can still observe the 405-nm emission but see no other emission bands at wavelengths greater than 320 nm.

Discussion

Stereospecificity of Singlet Cycloaddition. It is clear that the addition of singlet acetone to either *t*-DCE or *c*-DCE occurs with high retention of the stereochemistry of the olefin. This stereospecificity cannot be explained by the usually proposed mechanism for photocycloadditions of ketones to olefins which involves initial attack on the olefin by the half-vacant electrophilic n orbital of the carbonyl excited singlet state.^{6a} This type of attack would be expected to occur preferentially in the plane of the carbonyl to yield initially a 1,4 biradical in which the two orbitals which will subsequently form the 1,4 bond are more or less orthogonal to each other (see Figure 3).¹⁵ Regardless of spin multiplicity, bond rotation will almost certainly occur in this biradical before closure is possible; thus, oxetane formation cannot be concerted and stereospecificity is unexpected. This has been verified in several cases. Arnold and Glick^{6a,10} observed total loss of stereochemistry in the addition of benzophenone triplets to *trans*- and *cis*-2-butene. Also Turro and Wriede¹⁶ found that acetone triplets add to *cis*- and *trans*-1-methoxy-1-butene with total loss of initial olefin stereochemistry in the oxetane product while acetone singlets add to these olefins with only partial loss of stereochemistry. Thus, the observed stereospecificity of the photocycloaddition of acetone singlets to *t*- and *c*-DCE is inconsistent with initial attack of the half-vacant electrophilic oxygen n orbital on the electron-deficient olefin π system. Therefore a different mechanism must be postulated in order to explain the stereospecific photocycloaddition of acetone to *t*- and *c*-DCE. (A new mechanism is entirely reasonable since the electrophilic oxygen n orbital would not be expected to attack an olefin as electron deficient as *t*- or *c*-DCE.)

The acetone n, π^* excited state has another reactive site, in addition to the half-vacant electrophilic n orbital, which has seldom been considered as a factor in the bimolecular photochemistry of carbonyl compounds. Molecular orbital considerations predict the presence of an electron rich π system above and below the plane of the carbonyl group in the n, π^* excited state of ketones. This (three-electron) system should

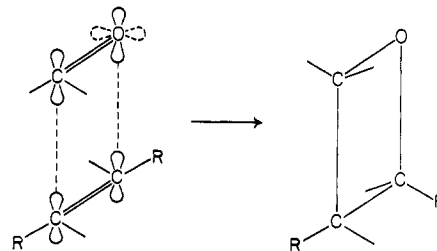


Figure 4. Concerted or "quasi-concerted" attack of nucleophilic π system of acetone singlet n, π^* excited state on olefin double bond yielding stereospecific oxetane.

be nucleophilic and would be expected to readily attack electron-poor double bonds. Attack of this nucleophilic system on the electron-deficient π system of *t*- or *c*-DCE can account for the observed formation of stereospecific products (see Figure 4).

Thus, we propose that the cycloaddition of acetone to DCE occurs *via* a concerted or "quasi-concerted" attack of the nucleophilic π system of the singlet n, π^* state of acetone on the π system of ground-state *c*- or *t*-DCE (Figure 4). In accord with Salem's definitions,¹⁷ a concerted attack is one in which both oxetane bonds close at the same time and at the same rate, while a "quasi-concerted" attack is one in which both oxetane bonds are formed at the same time but at different rates, thereby forming an asymmetric transition state. This "quasi-concerted" attack is probable in this system since no symmetry exists in the reaction system as a whole and the (theoretically expected) higher electronic density at the carbon lobe of the π^* orbital makes this end more nucleophilic and thus more likely to add first.

If one bond is formed initially, note that no bond rotation in the biradical is required for formation of the second bond, since the structure of the proposed transition state is very similar to that of the products. The two orbitals which will form the second bond are parallel for the case of nucleophilic attack. Whatever the precise mechanism may be, the observed stereospecificity of the photocycloaddition demands that bond formation in the transition state be fast relative to bond rotation.¹⁸

Our observation that acetone adds to DCE *via* the singlet state provides a possible explanation for the lack of reactivity toward cycloaddition shown by several aromatic ketones, since these compounds have singlet state lifetimes on the order of 10^{-10} sec, too short for efficient bimolecular reactions to occur. However, the observation that biacetyl does not undergo cycloaddition suggests that a short singlet-state lifetime is not the only factor involved in the lack of reactivity shown by some ketones. This α -diketone has both a lowest n, π^* singlet and triplet and undergoes most of the typical ketone photoreactions such as hydrogen abstraction and electrophilic addition.¹⁹ Biacetyl also has a singlet-state lifetime similar to that of acetone and measurably ($\phi_f \sim 0.002$) fluoresces at room temperature.¹⁹

Attempts to quench the fluorescence of biacetyl with *t*-DCE demonstrated that the olefin had absolutely no

(15) P. D. Bartlett, *Science*, **159**, 833 (1968).

(16) (a) N. J. Turro and P. A. Wriede, *J. Amer. Chem. Soc.*, **92**, 320 (1970); (b) N. J. Turro and P. A. Wriede, *ibid.*, **90**, 6863 (1968).

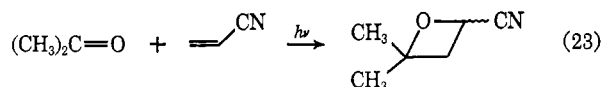
(17) L. Salem, *ibid.*, **90**, 553 (1968).

(18) R. Gompper, *Angew. Chem. Intern. Ed. Engl.*, **8**, 312 (1969).

(19) N. J. Turro and R. Engel, *J. Amer. Chem. Soc.*, **90**, 2989 (1968).

effect on the emission. The observed long-wavelength absorption of biacetyl is due to a splitting of both the π and π^* energy levels; however, the energy of the n orbital is not expected to be greatly affected by conjugation. It is thus possible that in the n, π^* transition an electron is promoted to a π^* orbital which is delocalized over two carbonyls, thereby diminishing the nucleophilicity of the isolated carbonyl group. No cycloaddition was observed with α, β -unsaturated ketones in which delocalization of the π^* electron can also occur. More surprising is the lack of photocycloaddition of the γ, δ -unsaturated ketone, 5-hexen-2-one to *t*-DCE.

Barltrop²⁰ has recently reported that the photocycloaddition of acetone to acrylonitrile, methacrylonitrile, and crotonitrile yields only the oxetanes with the cyano group in the 3 position (eq 23). No oxetane with the cyano group in the 4 position was observed.



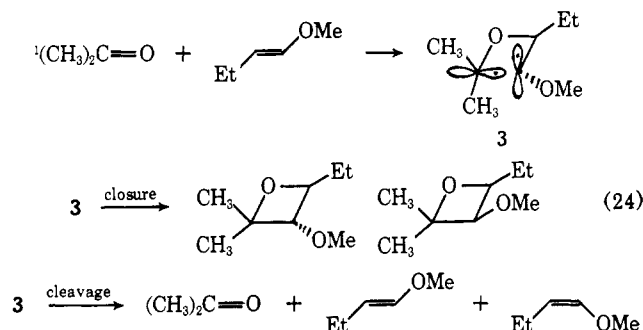
This is consistent with addition of the higher electron-density carbon lobe of the π^* orbital to the most electron-deficient end of the acrylonitrile double bond. Attack of the electrophilic oxygen n orbital to yield the most stable biradical would have led to formation of the 4-cyanooxetane.

It is unlikely that the "triene" character of DCE plays any special role in the photocycloaddition to acetone, in light of the reports of addition of acetone to acrylonitrile, crotonitrile, and methacrylonitrile.²⁰

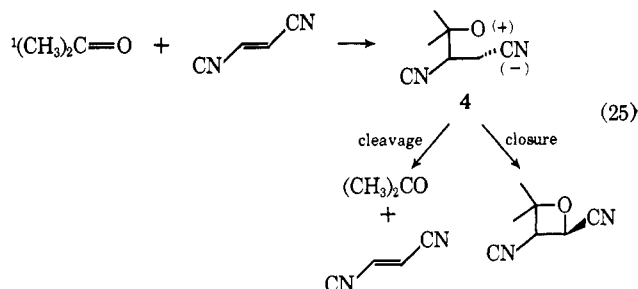
Inefficiency in Cycloaddition. The observed inefficiency in the cycloaddition of acetone singlets to *t*- and *c*-DCE cannot be due to secondary photolysis, as **1** was found to be stable under the conditions of the photolysis. As noted, Schemes I and II present different ways of accounting for this inefficiency. Since we cannot at present distinguish between these two possibilities, both will be considered in some detail.

Scheme I proposes that oxetane formation and deactivation both occur from a common intermediate, **C**, which is formed by reaction of singlet acetone with *t*- or *c*-DCE. Three possibilities for this intermediate are a 1,4-biradical or bipolar species, a π - or charge-transfer complex and a "hot" oxetane.²¹ In several instances, inefficiency in the photocycloaddition of alkyl and aryl ketones to electron-rich olefins has been shown to result from competition in the 1,4-biradical intermediate between closure to an oxetane and cleavage to generate ground-state ketone and olefin.²² In the cases where stereochemistry was pertinent, cleavage of the biradical resulted in isomerization of the electron-rich olefin. Although most of the examples involved reaction of ketone triplets with electron-rich olefins, the reaction of singlet acetone with *t*- and *c*-1-methoxy-1-butene led to partial loss of stereochemistry in the oxetanes formed and some isomerization of the olefin double bond (eq 24).¹⁶ This demonstrates that the

biradicals formed by attack of singlet alkyl ketones, at least on electron-rich olefins, can also undergo cleavage in competition with closure. The inefficiency in the



photocycloaddition of acetone singlets to *t*- and *c*-DCE could also be due to intervention of a 1,4-biradical (or bipolar) intermediate **4** which can either cleave or close to an oxetane (eq 25). Since no isomerization of DCE results from reaction with singlet acetone, if the intermediacy of **4** is to explain the inefficiency, cleavage or closure must occur before bond rotation.



Another possibility for **C**, the intermediate in Scheme I, is a complex that partitions between oxetane formation and dissociation to ground-state acetone and DCE. This could be a π - or charge-transfer complex between the electron-poor DCE olefin system and the nucleophilic π system of the acetone $^1n, \pi^*$ excited state. Electron-deficient olefins, such as *t*- or *c*-DCE are known to form π complexes with nucleophilic reagents.²³ These π complexes partition between dissociation and formation of a σ complex which subsequently goes on to product. Similarly, a π complex between singlet acetone and *t*- or *c*-DCE, which has a lower energy of activation for dissociation to ground-state acetone and DCE than for formation of oxetane could then explain the observed inefficiency. Olefin stereochemistry would be expected to be retained in a π complex. Such a π complex should rigorously be considered an "exciplex" since no ground-state complex seems to form between acetone and *t*-DCE.^{24, 25}

The intermediate **C** could also be a vibrationally excited "hot" oxetane which cleaves to acetone and DCE unless it is rapidly deactivated. A "hot" oxetane intermediate can be invoked to explain the methyl group exchange observed by Pomerantz²¹ in the photolysis of perdeuterioacetone and tetramethylethylene (eq 26). Since we observe no isomerization of *c*- or *t*-DCE from reaction with acetone singlets, the cleavage of "hot" oxetane would have to be a concerted or

(20) J. A. Barltrop and H. A. J. Carless, *Tetrahedron Lett.*, 3901 (1968).

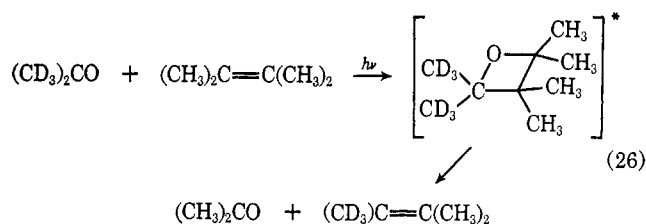
(21) S. M. Jaspar, M. Pomerantz, and E. W. Abrahamson, *Chem. Phys. Lett.*, **2**, 137 (1968).

(22) (a) Toki and H. Sakurai, *Bull. Chem. Soc. Jap.*, **40**, 2885 (1967); (b) N. C. Yang, J. I. Cohen, and A. Shani, *J. Amer. Chem. Soc.*, **90**, 3264 (1968); ref 7e; (c) J. Saltiel, D. R. Neuberger, and M. Wrighton, *J. Amer. Chem. Soc.*, **91**, 3658 (1969); (d) ref 16.

(23) A. N. Nesmeyanov, M. I. Rybinskaya, and L. V. Rybin, *Russ. Chem. Rev.*, **36**, 453 (1967).

(24) T. Förster, *Angew. Chem. Intern. Ed. Engl.*, **8**, 333 (1969).

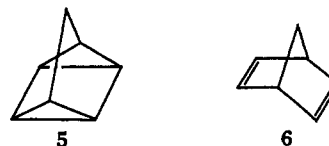
(25) No new uv absorption is found in solutions of acetone and DCE.



“quasi-concerted” process in which there was no loss of stereochemistry.

In Scheme II, acetone singlets undergo two competitive reactions with *t*-DCE. One reaction (eq 13) is the cycloaddition yielding **1** while the other (eq 14) results in deactivation of the excited acetone singlet with no resulting photochemistry. Several possibilities exist for the mechanism of the deactivation process. The first excited singlet state of either isomer of DCE is at least 20–30 kcal/mol above the singlet state of acetone (based on their absorption spectra) so that vertical singlet-energy transfer from acetone to DCE is unlikely. Nonvertical energy transfer to a twisted DCE molecule is conceivable,²⁶ but would *not* be expected to occur at the near diffusion-controlled rate (*vide infra*) at which *t*- and *c*-DCE are observed to quench acetone singlets. The strongest argument, however, against any energy-transfer process is that *t*-DCE undergoes isomerization to *c*-DCE when directly irradiated. Thus, any process which generates free-excited singlets of *t*-DCE would be expected to result in isomerization of the olefin. Since the reaction of singlet acetone with *t*-DCE leads to no isomerization of the olefin we must assume that the first excited singlet state of *t*-DCE is not generated, ruling out electronic energy transfer from acetone to *t*-DCE.

The possibility remains that an excited complex (exciplex) could be formed between singlet acetone and *c*- or *t*-DCE leading to deactivation of the excited acetone with no photochemistry resulting. Recently a number of reports dealing with the quenching of aromatic hydrocarbon-excited singlets by compounds having no low lying singlet states have been published. Hammond, *et al.*, have observed that dienes such as piperylene and 1,3-cyclohexadiene efficiently quench naphthalene and 1-methylnaphthalene fluorescence with little or no chemical reaction observed.²⁷ However, they have also found that when quadricyclene (**5**) quenches naphthalene singlets,²⁸ it undergoes sensitized isomerization to bicycloheptadiene (**6**) with a quantum yield of 0.50. Also, the quenching of naphthalene singlets by optically active aryl alkyl sulfoxides²⁹ and 1,2-diphenylcyclopropanes²⁸ results in racemization and *cis-trans* isomerization, respectively. In all these cases the proposed mechanism for singlet quenching is the intermediate formation of an exciplex between singlet naphthalene and the quencher. The electronic energy of the naphthalene is converted into vibrational energy in the exciplex which then may or may not give rise to “hot” ground-state chemistry in the quencher. In all the cases where chemistry resulted from naph-



thalene quenching, the quencher reactions observed have low ground-state activation energies (<45 kcal/mol). Clearly, this should be a necessary requirement for quencher chemistry to result from exciplex quenching. However, since the usual activation energies for the *cis-trans* isomerization of olefins lie in the 35–46 kcal range, and yet no isomerization of piperylene was observed from naphthalene-singlet quenching, a low activation energy must not be a sufficient condition for quencher chemistry to result from exciplex quenching. Thus the fact that quenching of acetone singlets led to no *cis-trans* isomerization of DCE is not sufficient to rule out an exciplex mechanism in which electronic energy is converted into vibrational energy in the exciplex.

In addition to an exciplex in which acetone electronic energy is converted into vibrational energy, other complexes between acetone singlets and *c*- or *t*-DCE resulting in deactivation could be possible. Singer and Davis have suggested the formation of a singlet-state complex of nonspecified type between fluorenone and a ketenimine to explain the observed quenching of fluorenone singlets.^{7c} This singlet complex leads to both deactivation and adduct formation. Also the same type of nucleophilic acetone singlet electron-deficient DCE π complex that was suggested as a possible common intermediate for both oxetane formation and deactivation, could result in just deactivation with the cycloaddition occurring by a separate mechanism.

In conclusion, in the absence of data to the contrary, it seems reasonable and conceptually most economical to assume that the deactivation of acetone singlets by DCE is related to the mechanism for cycloaddition. Most probably this involves initial formation of a π complex, possibly with some charge-transfer character, which partitions between oxetane formation and cleavage to ground-state acetone and DCE.³⁰

Triplet-Sensitized *c* \rightleftharpoons *t* Isomerization. The acetone-sensitized *c* \rightleftharpoons *t* isomerization of DCE clearly involves interaction of acetone triplet states with ground-state olefin molecules. This interaction, which we have shown to occur at the diffusion-controlled rate, is most probably exothermic energy transfer³¹ from triplet acetone to the olefin, generating a triplet DCE molecule which can decay to either *t*- or *c*-DCE. Although spin and energetic considerations prohibit concerted triplet-state nucleophilic cycloaddition of acetone to DCE, nonconcerted formation of oxetane should be possible. We could not detect oxetane formation *via* the triplet state, however, presumably because the diffusion-controlled electronic energy transfer predominated. The rate for the necessarily nonconcerted triplet addition would be expected to be less than that of the singlet reaction and our results (*vide infra*) indicate that the

(26) L. M. Stephenson and G. S. Hammond, *Angew. Chem. Intern. Ed. Engl.*, **8**, 261 (1969).

(27) (a) L. M. Stephenson and G. S. Hammond, *Pure Appl. Chem.*, **16**, 125 (1968); (b) L. M. Stephenson, D. G. Whitten, G. F. Vesley, and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 3665 (1966).

(28) S. L. Murov, R. S. Cole, and G. S. Hammond, *ibid.*, **90**, 2957 (1968).

(29) R. S. Cooke and G. S. Hammond, *ibid.*, **90**, 2958 (1968).

(30) Professor W. C. Herndon (Texas Tech) has informed us that the addition of acetone to DCE is predicted to be concerted by perturbational MO calculations. It is not obvious how to apply the Woodward-Hoffmann rules to a reaction involving a n, π^* state and a ground state.

(31) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Amer. Chem. Soc.*, **86**, 3197 (1964).

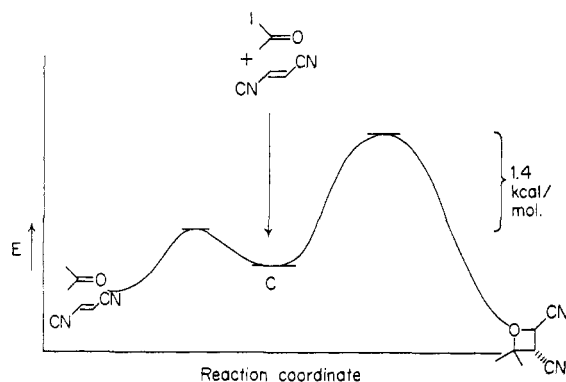


Figure 5. Energy profile of Scheme I for the reaction $(\text{CH}_3)_2\text{CO} + t\text{-DCE} \xrightarrow{h\nu} 1$.

singlet addition rate is already less than diffusion controlled. Triplet-state nucleophilic cycloaddition would therefore not be expected to compete efficiently with triplet energy transfer.

Alternatively, the triplet acetone could add to the DCE to form a biradical which undergoes rotation causing loss of stereochemistry and subsequently cleaves yielding ground-state acetone and *t*- or *c*-DCE.^{32,22b,c} This mechanism could also explain the sensitized isomerization although it would require postulation that the rate of addition of triplet acetone to DCE to form the biradical is diffusion controlled and that the rate of cleavage of the biradical is much larger than the rate of closure to oxetane.

Kinetics of Photocycloaddition. From the slope and intercept of the Stern-Volmer analysis for oxetane formation with *t*-DCE (Figure 1)

$$\frac{\text{intercept}}{\text{slope}} = \frac{k_q^s}{k_F + k_{ST}} = 5.1$$

Since $(k_F + k_{ST})^{-1}$ is equal to τ_s , the measured acetone singlet lifetime in the absence of *t*-DCE: $k_q^s \tau_s = 5.1$. This is close to the value of $k_q^s \tau_s$ of 6.7 obtained by a Stern-Volmer treatment of the quenching of acetone fluorescence by *t*-DCE.³³ By monitoring the decay of the broad acetone fluorescence beyond 4000 Å, we have determined a value of 2.0 ± 0.5 nsec for τ_s of nonde-gassed neat acetone. This is in excellent agreement with the value of 2.0 nsec, obtained by Wilkinson and Dubois from quenching studies.³⁴ Using this value of τ_s , and a k_q^s value of 5.1, the calculated rate constant for quenching of singlet acetone by *t*-DCE (k_q^s) is $2.5 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$. Similarly, the rate constant for quenching of singlet acetone by *c*-DCE is found to be $5.0 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$. These rate constants are within an order of magnitude of the diffusion-controlled rate constant in acetonitrile.

The close agreement of $k_q \tau_s$ values from fluorescence quenching and oxetane formation data, coupled with our detection of only the 405-nm acetone emission at low concentration in *n*-hexane and the observation that the lifetime of the 405-nm acetone fluorescence is quenched by *t*-DCE, lead us to conclude that both the

cycloaddition to DCE and the 405-nm fluorescence are coming from a monomeric acetone singlet.

From the intercept, *a*, of the $1/\Phi_1$ vs. $1/[t\text{-DCE}]$ plot, the inefficiency of the photocycloaddition can be determined. From Figure 1 we obtain $a = 13.2$ implying that either (see eq 18) $(k_{CO} + k_{cd})/k_{CO} = 13.2$ (Scheme I) or $(k_{ox} + k_d)/k_{ox} = 13.2$ (Scheme II). For the photocycloaddition of *c*-DCE to singlet acetone it is found that

$$11.6 = \begin{cases} (k_{CO} + k_{cd})/k_{CO} & \text{(Scheme I)} \\ (k_{ox} + k_d)/k_{ox} & \text{(Scheme II)} \end{cases}$$

If we attribute the inefficiency of the photocycloaddition of singlet acetone to *t*-DCE to partitioning of an intermediate complex between oxetane formation and dissociation to ground-state acetone and *t*-DCE (Scheme I) we can construct the energy profile shown (Figure 5). The intercept, *a*, from Figure 1 yields a value of 1.4 kcal/mol for the difference in activation energy for dissociation and oxetane formation from the intermediate complex.

It is interesting that *c*-DCE appears to quench acetone singlets twice as fast as the *trans*-olefin, yet the efficiency of going from complex to oxetane is about the same as that of the *trans*. A possible explanation for these results is that the greater polarity of the *c*-DCE increases the rate of complex formation, but that once the complex is formed it behaves similarly to that formed with the *trans*-olefin. However, it should be noted that the difference between k_q^s for *c*-DCE and *t*-DCE is close to the experimental error.

Very little is known about the relative rates of excited-state or ground-state cycloaddition to *cis*- or *trans*-olefins, making it impossible to determine if the results that were obtained with acetone and the DCE isomers are part of a general trend. Martin, *et al.*,³⁵ have observed that dimethyl ketene reacts with an excess mixture of *cis*- and *trans*-1-ethoxy-1-butene to form only a *cis*-cyclobutanone. Since addition of the ketene is entirely to the *cis*-olefin isomer, the reactivity of the *cis*-olefin toward cycloaddition is much greater than that of the *trans*. The reaction of dimethyl ketene is a good analog to the acetone-DCE reaction in the respect that both form stereospecific products and therefore seem to be concerted in nature.

Experimental Section³⁶

General Procedure for Irradiations, Analyses, and Quantum Yield Determinations. The mechanistic studies of the acetone-1,2-DCE photoreactions, including quantum yield determinations and concentration and quenching studies were carried out as described elsewhere^{16a} at 313 nm using the "merry-go-round" apparatus.³⁷ Solutions of acetone in acetonitrile with varying amounts of *t*- or *c*-DCE were prepared and irradiated nonde-gassed. Solutions of acetone and olefin were routinely photolyzed to low conversions (3–10% of product, based on olefin) to minimize (a) the extent of conversion to the other olefin isomer and (b) the effect of low-yield side reactions leading to colored solutions.

The samples were analyzed by vapor phase chromatography and concentrations of products of the 0.001–0.005 *M* range were easily detected. The chromatographic conditions under which the

(32) N. J. Turro, *Photochem. Photobiol.*, **9**, 555 (1969).

(33) A similar value has been obtained for the quenching of 2-hexanone singlets by biacetyl: N. C. Yang and S. P. Elliott, *J. Amer. Chem. Soc.*, **90**, 4194 (1968).

(34) F. Wilkinson and J. T. Dubois, *J. Chem. Phys.*, **39**, 377 (1963).

(35) J. C. Martin, V. W. Goodlett, and R. D. Burpitt, *J. Org. Chem.*, **30**, 4309 (1965).

(36) Analyses of new compounds and all other synthetic details of the photocycloaddition of acetone to DCE are reported elsewhere.⁴

(37) F. G. Moses, R. S. H. Liu, and B. M. Monroe, *Mol. Photochem.*, **1**, 245 (1969).

various analyses were performed varied little between runs and are outlined below.

The acetone-DCE photoreactions were analyzed on either a 10 ft 20% Carbowax 20M (Chromosorb P) column at 210° or on a 10 ft 50:50 mixture of 20% SE-30-20% Carbowax 20M (Chromosorb P) column at 190°. The pure carbowax column gave excellent separation of the *trans*-oxetane 1 and *c*-DCE; however, the high temperature (210°) often led to an unstable base line and poor analyses. The mixed column was slightly less effective in separating 1 and *c*-DCE, but the lower temperatures possible with this column lessened the chance of base-line instability. Typical retention times at 190° and 25 ml/min He flow were 2 min for *t*-DCE, 3½ min for 1, 4½ min for *c*-DCE, and 15½ min for 2.

Peak areas were obtained by multiplying the height of the peak times the width at half-height. This method was found to be as reliable as the use of the Disc integrator on the recorder and was in general much easier to use.

Absolute yields of products were obtained in the following manner. A standard solution of *cis*- and *trans*-DCE and the *trans*- or *cis*-oxetanes was analyzed and relative response factors (*t*-DCE = 1) were obtained. The samples were then analyzed and using the response factors, relative areas of *t*-DCE, *c*-DCE, and oxetanes were obtained. The yield of each product was computed as the ratio of product area to total area of product and *cis*- and *trans*-DCE. Knowing the initial concentration of *t*-DCE (or *c*-DCE) the quantum yield of product could be calculated by eq 27

$$\Phi = \frac{[\text{prod}]V(6.023 \times 10^{23})}{It} \quad (27)$$

where V = volume of sample, I = light intensity in quanta/second, t = time of irradiation in seconds, and $[\text{prod}] = [\text{DCE}] \times \% \text{ yield of product}$.

Actinometry. The light intensity of the "merry-go-round" lamp was measured using the photochemical conversion of cyclopentanone to 4-pentenal as the actinometer.³⁸ The quantum yield of this reaction at 3130 Å has been reported to be 0.37.³⁸ The actinometer solution used was neat cyclopentanone (nondegassed), which was irradiated under the same conditions as the acetone-DCE samples. Srinivasan³⁹ has reported that the unsaturated aldehyde formed in the photolysis of cyclohexanone acts as an internal quencher, and therefore prevents the buildup of substantial quantities of aldehyde. Care was therefore taken that the cyclopentanone photolyses were not carried out past 0.5% conversion.

Analyses for 4-pentenal were carried out on a 10 × 1/8 in. 20% Carbowax 20M column at 90–100°. One-microliter injections of the actinometer solution were made and compared to 1-μl injections of a 0.074 *M* solution of 4-pentenal in cyclohexane. The average area of the aldehyde peak was calculated in both cases by the height × the width at half-height, and the molarity of aldehyde in the actinometer solution was calculated as (area of aldehyde in actinometer/area of aldehyde in standard) × 0.074 *M*. The light intensity is obtained from eq 28 where $\phi = 0.37$, $t =$

$$I = \frac{[\text{aldehyde}](V)(6.023 \times 10^{23})}{\phi t} \quad (28)$$

time of irradiation in seconds, and V = volume of sample. The intensities measured by this method ranged between 9×10^{16} and 3×10^{16} quanta/sec.

Quenching of Acetone-*t*-DCE Photoreaction by *trans*-1,3-Pentadiene. Aerated solutions of acetone (5 *M*) and *t*-DCE (0.1 *M*) with and without 1 *M* *trans*-1,3-pentadiene were irradiated on the "merry-go-round" using the 313-nm filter solution. Analysis of oxetane formation and olefin isomerization as described earlier yielded values of 1.09 for Φ_1^0/Φ_1 and 4.45 or Φ_{cis}^0/Φ_{cis} , where the superscript zero refers to the quantum yield in the absence of *trans*-1,3-pentadiene. The small amount of oxetane quenching observed is not real but rather is due to competitive absorption by, apparently, a complex formed between the *t*-DCE and *trans*-1,3-pentadiene. Thus Φ_1^0/Φ_1 for solutions without and with 1 *M* *trans*-1,3-pentadiene decreases with decreasing *t*-DCE concentration reaching a limiting value of 1.0 at low *t*-DCE concentrations. Φ_{cis}^0/Φ_{cis} increases with decreasing *t*-DCE concentration for solu-

tions with and without 1 *M* *trans*-1,3-pentadiene as would be expected for a reaction involving acetone triplets.

Quenching of Benzophenone Photoreduction by *t*-DCE and *trans*-1,3-Pentadiene. Benzene solutions of benzophenone (0.05 *M*) and benzhydrol (0.10 *M*) containing varying amounts of *t*-DCE or *trans*-1,3-pentadiene in constricted 10-mm Pyrex test tubes were degassed by subjecting the samples to 4 freeze-degas-thaw cycles at 5 μ of pressure and sealed. The samples were then irradiated in the "merry-go-round" irradiation apparatus with the 313-nm filter solution. The extent of photoreduction was determined by monitoring the uv absorbance of benzophenone at 3450 Å after samples had been opened and diluted 10:1 in benzene. Using the slope (~300) of the Stern-Volmer plot (eq 29) and the published values¹² of 0.33 for k_d/k_t and 1×10^8 for k_d , we obtain a value for k_q of 1.2×10^9 l. mol⁻¹ sec⁻¹. The Stern-Volmer plot for quenching of the benzophenone photoreduction by *trans*-1,3-pentadiene also had a slope of approximately 300. $\phi_r^0, \phi_r =$ quantum yields for

$$\phi_r^0/\phi_r = 1 + \frac{k_q[t\text{-DCE}]}{k_t[\text{BH}_2]} + k_d \quad (29)$$

photoreduction of benzophenone in the absence and presence of *t*-DCE, respectively; k_q = bimolecular rate constant for quenching of benzophenone triplets by *t*-DCE; k_d = unimolecular rate constant for decay of benzophenone triplets; k_t = bimolecular rate constant for hydrogen abstraction from benzhydrol (BH₂) by benzophenone triplet.

Isomerization of *t*-DCE. About 0.5 ml of a 2.1 *M* *t*-DCE in MeCN solution was irradiated in a Pyrex nmr tube strapped to Vycor well equipped with a Hanovia 450-W medium pressure mercury lamp. After about 3 hr of irradiation the solution contained 32% *c*-DCE and 68% *t*-DCE.

Photolysis of 1 in Acetone. A dilute solution of adduct 1 in acetone was irradiated for 4 hr through Pyrex. Nmr of the photolyzed solution revealed no change in the composition of the solution. No *t*-DCE, *c*-DCE, or other decomposition products were formed after 4 hr of irradiation.

Reaction of Various Ketones with *t*-DCE. Concentrated solutions of *t*-DCE and the ketone were irradiated through Pyrex in acetonitrile, methylene chloride, or neat ketone. Oxetane formation and isomerization of the *t*-DCE were analyzed for by nmr after irradiation times (6–20 hr) sufficient for cycloaddition to be observed with dialkyl ketones.

Fluorescence Quenching. Acetone solutions, 0.048 *M* and 0.77 *M*, were prepared in Matheson Coleman and Bell Chromatography acetonitrile. It was found necessary to test the acetonitrile for fluorescence prior to use as some lots exhibited rather strong emission in the 4000-Å region. A known volume of the acetone solutions was pipetted into a quartz fluorescence cell and the fluorescence observed in an Aminco spectrophotofluorimeter using an excitation wavelength of 313 nm. The spectra were recorded on a Beckman linear log potentiometric recorder using the 10-mV range. Aliquots of *t*-DCE were added to the solution while monitoring the decrease in fluorescence intensity at the broad maximum around 405 nm. The optical density of the acetone solutions at 313 nm, measured on a Cary 14 ultraviolet spectrophotometer, did not change with added *t*-DCE.

The fluorescence ($\lambda_{\text{max}} \sim 470$ nm) of 0.03 *M* biacetyl in aerated benzene solutions containing concentrations of *t*-DCE up to >0.1 *M* was monitored using the Aminco spectrophotofluorimeter ($\lambda_{\text{excitation}} 420$ nm). No quenching of the intensity of the fluorescence was observed.

Concentration Dependence of Acetone Fluorescence. Acetone solutions (0.00035–0.022 *M*) in newly opened Baker spectrograde *n*-hexane were prepared by dilution. The fluorescence spectra of these solutions were taken using an Aminco spectrophotofluorimeter with a Bausch and Lomb 200-W high pressure mercury lamp with high intensity grating monochromator as the excitation source. The standard Xenon lamp in the Aminco was removed and the output from the Bausch and Lomb lamp and monochromator directed through the Aminco lamp housing into the excitation monochromator. This set-up results in both a more intense and a more monochromatic excitation beam in the vicinity of the mercury emission lines. The solutions were excited at 285 nm and the spectra recorded with a Beckman linear-log potentiometric recorder using the 10-mV range. All solutions were mixed and stored in glass volumetric flasks as the use of vials with plastic caps was found to lead to an emission at 330 nm in *n*-hexane and acetonitrile.

Fluorescence Lifetimes. The fluorescence decay times (τ_a) of neat acetone and 0.03 and 1 *M* solutions of acetone in Matheson

(38) P. Dunion and C. N. Trumbore, *J. Amer. Chem. Soc.*, **87**, 4211 (1965).

(39) S. Cremer and R. Srinivasan, *ibid.*, **86**, 4197 (1964).

Coleman and Bell Chromatoquality acetonitrile were measured using the single photon counting technique.⁴⁰ Excitation was by an N₂ spark lamp filtered through a Corning 7-54 glass filter, while a Jarrel-Ash 0.25-m monochromator was used to isolate the acetone

(40) For a discussion of this technique see J. B. Birks and I. H. Munro, *Progr. Reaction Kinetics*, **4**, 239 (1967).

fluorescence. Details of the single photon-counting apparatus used are given elsewhere.⁴¹

Acknowledgment. The authors wish to thank Dr. Louis Brus and Terrence Tao for making the acetone fluorescence lifetime determinations.

(41) T. Tao, *Biopolymers*, in press.

Electronic vs. Steric Effects in the Addition of Iodine Isocyanate to Olefins¹

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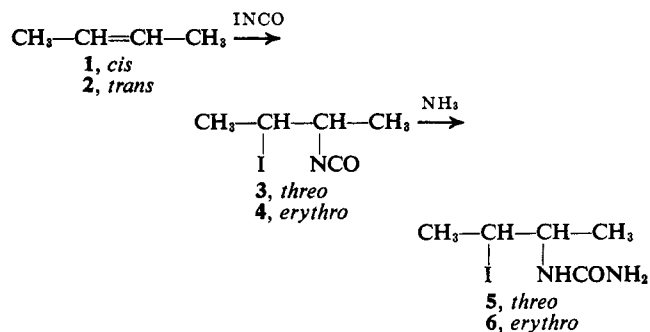
Contribution from the Department of Chemistry, University of Colorado, Boulder, Colorado. Received July 22, 1969

Abstract: The reaction of INCO with a number of olefins has been studied with a view toward elucidating electronic and steric influences in the addition. The stereospecific addition of INCO to *cis*- and *trans*-2-butene and β -deuteriostyrene is consistent with the intermediacy of a three-membered iodonium ion. A definite dependency on steric factors is evidenced by the *I-r*-Bu regioselectivity in the INCO addition to *t*-butylethylene. The structure proof in these systems was facilitated by our finding that hydrogenolysis of the iodo function in iodo carbamates is possible. Except in diaxial iodo carbamates for which zinc treatment leads to olefin by elimination, this method serves for the introduction of a carbamate function starting with olefins. Although no methyl migration or neighboring hydroxyl participation was observed during INCO addition, examples of skeleton rearrangement have been found.

The addition of the pseudohalogens iodine isocyanate (INCO) and iodine azide to unsaturated systems has been extensively studied in our laboratory in recent years.^{2,3} The reactions of INCO have proved of preparative value leading to the stereospecific synthesis of *trans*-N-(2-iodoalkyl) carbamates,³ aziridines,⁴ oxazolidones,³ *cis*- and *trans*-2-amino alcohols,³ 1,2-diamines,⁵ and azepines.⁶ It has been demonstrated that these additions in cyclic olefins generally occur in a stereospecific manner and that the two functional groups are introduced *trans* to each other and diaxially in fused cyclohexanes. These results have been explained by the formation of a three-membered ring iodonium ion intermediate which was opened from the backside by isocyanate (or azide) ion.

Stereoselectivity in INCO Additions

Consistent with these interpretations are our current findings that the open chain *cis*- and *trans*-2-butenes give cleanly and in almost quantitative yield *threo*- and *erythro*-iodo isocyanate adducts, respectively. This was apparent from the distinctive ir and nmr spectra of iodo isocyanates 3 and 4.



The major difference in the nmr spectra of these diastereomers is the relative shielding of the proton geminal to isocyanate in 3 relative to 4. This average shielding is attributable to the anisotropic effect of the iodine atom in preferred conformation 3a (I *anti* to H) vs. 4a (I *gauche* to H). *erythro* isomer 4 is assigned the *gauche* conformation 4a rather than an *anti* conformation as previously described,^{1c} because of the low H-H coupling ($J = 3.5$ Hz) characteristic of *gauche* protons. The isocyanates 3 and 4 were converted with ammonia to solid urea derivatives 5 and 6.

It has been shown that addition of INCO to disubstituted terminal olefins proceeds in an I-H regioselective⁷ manner leading to tertiary isocyanates.³ While monoalkyl olefins, such as 1-hexene, lead to a mixture of regioisomeric adducts, unsymmetrical arenes give exclusively the *NCO-phenyl* regioselective adduct, suggesting involvement of a benzyl carbonium ion 8. If such an ion were free to rotate (8a \rightleftharpoons 8b) *trans* addition would not be observed. To test this possibility and to

(1) (a) Stereochemistry. XLV. For paper XLIV see A. Hassner and F. Boerwinkle, *Tetrahedron Lett.*, 3309 (1969); (b) presented in part before the Gordon Research Conference on Organic Reactions and Processes, New Hampton, N. H., July 1965; (c) a preliminary report of part of this study has appeared in *Tetrahedron Lett.*, 1125 (1964).

(2) F. W. Fowler, A. Hassner, and L. A. Levy, *J. Amer. Chem. Soc.*, **89**, 2077 (1967).

(3) A. Hassner, M. E. Lorber, and C. Heathcock, *J. Org. Chem.*, **32**, 540 (1967), and references cited.

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