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Structure–Reactivity Correlations for the Quenching of Acetone Fluorescence by Enol Ethers and by Conjugated Unsaturated Nitriles[1]

Sir:

It has been recently reported that the methods of correlations of photochemical reactivities with system atic structural variation should provide one of the most promising means of establishing, in the field of organic photochemistry, truly reliable generalizations and predictive capabilities.[2] We report here such a study for the quenching of alkanone fluorescence by a series of enol ethers (Tables I and II) and conjugated, unsaturated nitriles (Tables III and IV).

Table I. Photocycloaddition of Acetone to Enol Ethers

Enol ether[a]	Regio-specificity[b]	Stereo-specificity
$CH_2{=}CHOC_2H_5$[e]	3:1	
$CH_2{=}C(OC_2H_5)$[e]	7:3	
cis-$C_2H_5CH{=}CHOCH_3$[d,f]	3:2	4.5:1[c]
trans-$C_2H_5CH{=}CHOCH_3$[d,f]	3:2	2.7:1[c]
cis-$C_2H_5OCH{=}CHOC_2H_5$[d,g]		*h*

[a] Chemical yields of oxetanes are greater than 60%. [b] Ratio of 3-alkoxyoxetane to 2-alkoxyoxetane in product mixture. Regiospecificity is essentially insensitive to the presence of 1,3-pentadiene, a triplet trap. [c] Limiting ratio of oxetane with retained stereochemistry to oxetane with inverted stereochemistry, obtained in the presence of 1,3-pentadiene or at high olefin concentrations. Ratio approaches 1:1 at low enol ether concentrations in the absence of 1,3-pentadiene. [d] Cis–trans isomerization of the enol ether also occurs. [e] S. H. Schroeter and C. M. Orlando, *J. Org. Chem.*, **34**, 1181 (1969). [f] N. J. Turro and P. A. Wriede, *J. Amer. Chem. Soc.*, **92**, 320 (1970). [g] M. Niemczyk, unpublished results, Columbia University. [h] Mixture of stereoisomers is obtained.

Table II. Relative Quenching Rates of Alkanone Fluorescence by Enol Ethers[a]

Alkanone	*cis*-$C_2H_5OCH{=}CHOC_2H_5$	$CH_2{=}C(OC_2H_5)_2$	$C_2H_5OCH{=}CH_2$
$(CH_3)_2CO$	1.0[b]	0.42	0.032
Adamantanone	1.0[c]	0.13	0.007

[a] Acetonitrile solutions. Error limits ±20%. [b] The absolute rate constant for fluorescence quenching is $2.0 \times 10^9\ M^{-1}\ sec^{-1}$. [c] The absolute rate constant for fluorescence quenching is $1.1 \times 10^9\ M^{-1}\ sec^{-1}$.

The products formed from the interactions of acetone singlets with enol ethers (Table I) and conjugated, unsaturated nitriles (Table III) suggest different mechanisms for the quenching interaction. For instance, neither the 1,2-dicyanoethylenes[3a] nor the crotononitriles[3b] are cis–trans isomerized by alkanone singlets, but alkanone singlets do sensitize the cis–trans isomerization of 1,2-disubstituted enol ethers.[4] Further evidence for a mechanistic dichotomy resides in the striking contrast between the strongly stereospecific

Table III. Photocycloaddition of Acetone to α,β-Unsaturated Nitriles

Nitrile	Regio-specificity	Stereo-specificity
$CH_2{=}CHCN$[b,e]	*a*	
$CH_2{=}C(CH_3)CN$[b,e]	*a*	
cis-$NCCH{=}CHCN$[c,f]		>99:1[d]
trans-$NCCH{=}CHCN$[c,f]		>99:1[d]
cis-$CH_3CH{=}CHCN$[c,e]	*a*	>98:2[d]
trans-$CH_3CH{=}CHCN$[c,e]	*a*	>98:2[d]

[a] Oxetane product is entirely the 2-cyano isomer. No 3-cyanooxetane is observed. [b] Cis and trans head-to-head dimers are also formed. [c] Cis–trans isomerization of the olefin also occurs. [d] Oxetanes retain stereochemistry of starting olefin. The other stereoisomer is not formed at low conversions. [e] J. A. Barltrop and H. A. J. Carless, *Tetrahedron Lett.*, 3901 (1968). [f] J. C. Dalton, P. A. Wriede, and N. J. Turro, *J. Amer. Chem. Soc.*, **92**, 1318 (1970).

Table IV. Relative Quenching Rates of Alkanone Fluorescence by α,β-Unsaturated Nitriles[a]

Alkanone	*trans*-$NCCH{=}CHCN$	$CH_2{=}CHCN$	$CH_2{=}C(CH_3)CN$	$CH_3CH{=}CHCN$
$(CH_3)_2CO$	1.0[b]	0.046	0.020	<0.01
Adamantanone	1.0[c]	0.020	0.011	0.001

[a] Acetonitrile solution. Error limits ±20%. [b] The absolute quenching rate constant is $2.5 \times 10^9\ M^{-1}\ sec^{-1}$. [c] The absolute quenching rate constant is $5.0 \times 10^9\ M^{-1}\ sec^{-1}$.

and regioselective addition[3] of acetone singlets to unsaturated nitriles compared to the (at best) partially stereospecific and modestly regiospecific addition of acetone singlets to enol ethers.[4] A study of the effect of alkanone structure on the rate constants for alkanone fluorescence quenching by 1,2-dicyanoethylene (DCE) and 1,2-diethoxyethylene (DEE) has defined the preferred quenching path by DEE as the area of space near the "edges" of the excited carbonyl oxygen, while the preferred quenching path by DCE is the area above or below the faces of the excited carbonyl function.[5]

Quenching rates given in Tables II and IV strongly corroborate the nucleophilic nature of the excited singlet alkanone reagent when it attacks DCE (and other unsaturated nitriles) and the electrophilic nature of the excited singlet alkanone reagent when it attacks DEE (or other enol ethers). Furthermore, calculations[6] of the energy of the lowest unoccupied orbital (LUO) of *trans*-1,2-dicyanoethylene suggest that the dinitrile, while a nonpolar reagent relative to acrylonitrile, gains its greater reactivity from its lower energy LUO, which presumably is responsible for the major mode of quenching interaction. On the other hand, both *trans*- and *cis*-1,2-diethoxyethylenes possess *higher* energies highest occupied orbital (HOO) than either ethyl vinyl ether or 1,1-diethoxyethylene (Table V).[6]

Consideration of all of the available data suggests to us that the original mechanism[7] suggested for addition of acetone singlets to DCE (exciplex formation, followed by decomposition of the exciplex to (a) ground-

(1) (a) Molecular Photochemistry. XLV. Paper XLIV: N. J. Turro and D. R. Morton, *J. Amer. Chem. Soc.*, **93**, 2569 (1971). (b) The authors gratefully acknowledge the generous support of the Air Force Office of Scientific Research (Grants AFOSR-1381 and 1848).

(2) G. S. Hammond, *Advan. Photochem.*, **7**, 373 (1969).

(3) (a) J. C. Dalton, P. A. Wriede, and N. J. Turro, *J. Amer. Chem. Soc.*, **92**, 1318 (1970); (b) J. A. Barltrop and H. A. J. Carless, *Tetrahedron Lett.*, 3901 (1968); H. A. J. Carless, Ph.D. Dissertation, Oxford University, 1970.

(4) N. J. Turro and P. A. Wriede, *J. Amer. Chem. Soc.*, **92**, 320 (1970).

(5) N. J. Turro, J. C. Dalton, G. Farrington, M. Niemczyk, and D. M. Pond, *ibid.*, **92**, 6978 (1970).

(6) Method: J. D. Roberts, "Notes on M. O. Calculations," W. A. Benjamin, New York, N. Y., 1962, Chapters 2 and 3. Parameters: B. Pullman and A. Pullman, *Rev. Mod. Phys.*, **32**, 428 (1960).

(7) N. J. Turro, P. A. Wriede, and J. C. Dalton, *J. Amer. Chem. Soc.*, **90**, 3274 (1968).

Table V. Comparison of HOO Energy Levels and Fluorescence Quenching Constants

	ROCH=CHOR	CH_2=C(OR)$_2$	CH_2=CHOR
E_{HOO}[a]	$\alpha + 0.47\beta$	$\alpha + 0.58\beta$	$\alpha + 0.73\beta$
k_q[b]	2.5×10^9	1.1×10^9	$<5 \times 10^8$

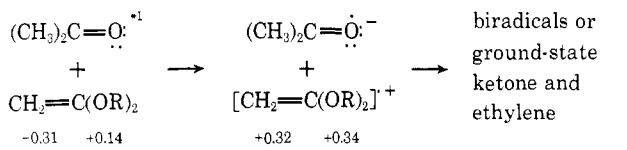
[a] Energy of highest occupied orbital. [b] Rate constant for quenching of acetone fluorescence, M^{-1} sec^{-1}.

state acetone and ethylene or (b) oxetane) is strongly corroborated by the new data reported here. However, details of the mechanism suggested for addition of acetone singlets to enol ethers[4,8] (direct addition of acetone singlets to the enol ether to form a biradical intermediate) should be modified in light of the results reported here and in other recent reports.[9-12] Thus, direct formation of a biradical intermediate from singlet acetone and an enol ether is not consonant with the relative reactivities reported in Table II, since on this basis, 1,1-diethoxyethene would be expected to be considerably more reactive than DEE. Furthermore, in order to explain the poor regiospecificity of oxetane formation from enol ethers, either preferred dissociation (relative to oxetane formation) of the "best" biradical or some other factor must be brought into consideration.

Caldwell[9-11] has suggested that a precursor to the biradical preceding oxetane formation from benzophenone triplets and ethylenes may explain certain isotope effects. Similar conclusions were reached from consideration of the reactivities of quenching of butyrophenone triplets by a series of ethylenes.[12] Our results are consistent with a similar attitude toward the reaction of alkanone singlets with enol ethers. Thus, a biradical intermediate is attractive in order to explain the loss of stereochemistry in oxetane formation and concurrent cis–trans isomerization when alkanone singlets interact with ethylenes.

The evidence presented here strongly supports a major charge-transfer interaction contribution to the transition state for quenching of alkanone singlets by enol ethers. Furthermore, the same features, if operating in a product (or biradical) producing step sequential to the quenching step, suggest a possible source of the poor regiospecificity of oxetane formation. Scheme I indicates that although the ground states of

Scheme I. Comparison of Charge Distributions at the Ethylenic Carbons for the Ground-State and Radical Cation of a 1,1-Dialkoxyethylene



enol ethers (*e.g.*, 1,1-dialkoxyethylenes) are strongly polarized so that C-2 has considerable negative charge characteristics, the radical cation possesses surprisingly comparable positive charge characteristics at both ethylenic carbons. Thus, collapse of the radical cation–radical anion pair to biradicals might well be nonselective and may not reflect biradical stability. A "free" charged radical pair need not exist, but only the transition state for partitioning to biradicals need "feel" the coulombic influences suggested by the charge densities given in Scheme I. It should be noted, however, that lack of regiospecificity can also be explained by (1) reversibility arguments (*i.e.*, addition to the 2-carbon atom of CH_2=C(OCH$_3$)$_2$ may be favored over addition to the 1-carbon, but the former addition may be more reversible[13] than the latter addition) and (2) "hot" or indiscriminant intermediates.

In summary, although (1) the rates of alkanone fluorescence quenching by unsaturated nitriles parallel LUO energies and (2) the rates of alkanone fluorescence quenching by enol ethers parallel HOO energies, the regiospecificities of products which result from these interactions are determined by other mechanistic factors. In the case of unsaturated nitriles, stereospecific and regiospecific collapse of a singlet exciplex seems likely, while for enol ethers initial attack of alkanone singlets on the π cloud, rather than a specific carbon, seems likely. The latter process is then followed by product formation from a transition state (or intermediates) possessing strong charge-transfer characteristics.

(8) N. J. Turro and P. A. Wriede, *J. Amer. Chem. Soc.*, **90**, 6863 (1968).
(9) R. A. Caldwell, *ibid.*, **92**, 1439 (1970).
(10) R. A. Caldwell and S. P. James, *ibid.*, **91**, 5184 (1969).
(11) R. A. Caldwell and G. W. Sovocool, *ibid.*, **90**, 7138 (1968).
(12) I. H. Kochevar and P. J. Wagner, *ibid.*, **92**, 5742 (1970).
(13) In other words, collapse of a radical cation–radical anion pair might lead preferentially to the most stable biradical, which then also collapses preferentially. The low total quantum yields of oxetanes (~0.1) under the conditions reported here allow entertainment of such a proposal.
(14) National Institutes of Health Predoctoral Fellow, 1970–present.

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Reduction of Disulfide Bonds in Peptides and Proteins by Dithiothreitol in Liquid Ammonia[1,2]

Sir:

Disulfide bonds in peptides and proteins were completely and rapidly reduced by dithiothreitol (DTT)[3] in liquid ammonia[4] without apparent side reactions.[5] The resulting thiol groups were selectively alkylated by alkyl chlorides added to the liquid ammonia solutions.[6,7] Essentially homogeneous *S*-alkylated derivatives were isolated after evaporation of the ammonia

(1) Supported by Public Health Service Research Grants C-6516 from the National Cancer Institute and FR-05526 from the Division of Research Facilities and Resources, National Institutes of Health.
(2) Abbreviation: DTT, dithiothreitol.
(3) W. W. Cleland, *Biochemistry*, **3**, 480 (1964).
(4) In aqueous solution high concentrations of denaturants are often necessary to assure full disulfide reduction [J. L. Bailey, "Techniques in Protein Chemistry," Elsevier, New York, N. Y., 1967, pp 115–124; T. A. Bewley and C. H. Li, *Int. J. Protein Res.*, **1**, 117 (1969)].
(5) Reduction of disulfide bonds by sodium in liquid ammonia [V. du Vigneaud, L. F. Audrieth, and H. S. Loring, *J. Amer. Chem. Soc.*, **52**, 4500 (1930)] can give peptide bond cleavage [K. Hofmann and H. Yajima, *ibid.*, **83**, 2289 (1961); M. Wilcheck, S. Sarid, and A. Patchornik, *Biochim. Biophys. Acta*, **104**, 616 (1965); W. F. Benisek and R. D. Cole, *Biochem. Biophys. Res. Commun.*, **20**, 655 (1965); W. F. Benisek, M. A. Raftery, and R. D. Cole, *Biochemistry*, **6**, 3780 (1967)].
(6) V. du Vigneaud, L. F. Audrieth, and H. S. Loring, *J. Amer. Chem. Soc.*, **52**, 4500 (1930).
(7) M. D. Armstrong and J. D. Lewis, *J. Org. Chem.*, **16**, 749 (1951).