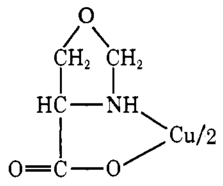

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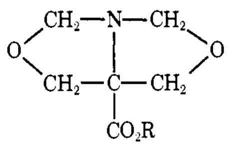

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cell constants obtained (from the setting angles of 12 high-angle reflections on a Picker diffractometer) with monochromatic Cu $K\alpha$ radiation (λ_1 1.5405 Å) are a = 18.559 (1), b = 10.142 (1), and c = 7.345 (1) Å and β = 101.60 (1)°. The measured density is 1.86 g/cm^3 (by flotation). The formula $C_{12}H_{16}CuN_2O_8$ (mol wt = 379.8 g-atoms) corresponds to the asymmetric unit, and for $Z = 4$ the calculated density is 1.863 g/cm^3. A total of 2035 diffractometer data with $I > 3\sigma(I)$ were collected. Absorption corrections (μ(Cu $K\alpha$) = 28.00 cm^{-1}) were not applied. Structure analysis by the heavy-atom method established the molecular formula, and full-matrix, least-squares refinement converged with a R factor on F of 0.041.

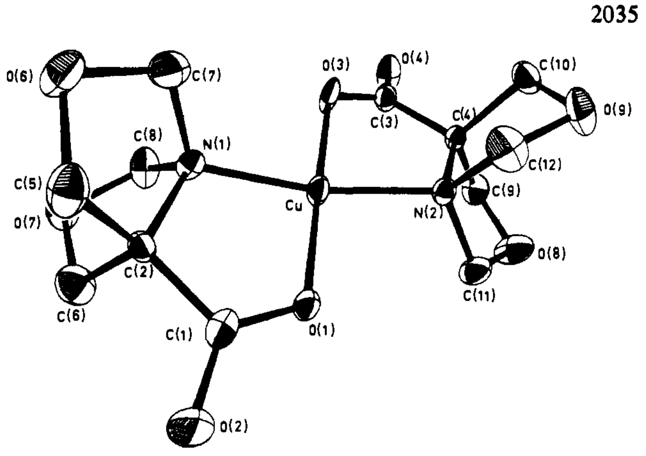

Figure 1. The molecular structure of bis(dioxazolecarboxylate)-copper(II). The copper is five coordinate in the crystal. Atoms are shown as 50% probability ellipsoids and methylene hydrogens are omitted for clarity.

The chelate molecules (Figure 1) are linked into chains in the crystal by a glide-related O(4) atom to Cu interaction of length 2.35 (1) Å. This interaction results in a square-pyramidal coordination of the copper ion. While the O(1)-Cu-O(3) atoms are linear (angle, 177.5°) the N(1)-Cu-N(2) atoms are bent (161.6°) so that the highly substituted nitrogen atoms are moved away from the fifth coordination site. This bending must have a steric origin and some close interchelate contacts exist in the chain. Thus the glide-related O(3) atom associated with the fifth ligand (O(4′)) imposes a close contact with a C(8) hydrogen atom. The C(8)···O(3′) distance is 3.28 Å and this repulsive contact leads to an opening of the Cu-N(1)-C(8) angle (117.0 (5)°) compared to the other chemically equivalent angles (av 113.0 (10)°). Steric effect considerations also explain why the copper is only five coordinate and not six as in many other bis(amino acid) complexes.[9,14] Five coordination however need not arise solely for this reason; *cis*-Cu((*S*)-α-alanine)$_2$ for instance is similarly five coordinate[14] and six coordination is not sterically blocked. The averaged molecular geometry (Table I) agrees well with that for copper-α-amino acid complexes.[14] All four oxazolidine rings are closely similar and adopt envelope conformation with the oxygen as the envelope tip.

Table I. Averaged Molecular Geometry[a]

Bond	Distance, Å	Atoms	Angle, deg
Cu-O(3)	1.925 (7)	O(3)-Cu-N(2)	85.5 (10)
Cu-N(2)	2.025 (2)	Cu-N(2)-C(4)	107.1 (10)
O(3)-C(3)	1.267 (3)	N(2)-C(4)-C(3)	110.9 (20)
O(4)-C(3)	1.236 (1)	C(4)-C(3)-O(3)	117.8 (10)
C(3)-C(4)	1.527 (4)	C(4)-C(3)-O(4)	116.9 (10)
N(2)-C(4)	1.515 (4)	Cu-O(3)-C(3)	114.5 (20)
N(2)-C(12)	1.492 (4)	O(3)-C(3)-O(4)	125.4 (10)
C(4)-C(10)	1.536 (10)	C(4)-N(2)-C(12)	104.1 (5)
C(10)-O(9)	1.416 (4)	C(10)-O(9)-C(12)	104.4 (10)
		C(10)-C(4)-N(2)	103.3 (5)
		N(2)-C(12)-O(9)	106.4 (5)
		C(4)-C(10)-O(9)	104.4 (5)

[a] Atom numbers refer to one chelate, but the values are averages for both chelates. Standard deviations in the mean values are given in parentheses.

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Photochemical Generation of Electronically Excited Organic Products in Adiabatic Pericyclic Photoreactions. An Unexpected Propensity toward Spin Inversion in a Retrocycloaddition and in a Valence Isomerization[1]

Sir:

Careful scrutiny of the photochemical literature reveals[2,3] that the overwhelming majority of organic photochemical reactions leads directly from an initial electronically excited state to a product in its ground state (eq 1). The intuitively acceptable conversion of an *electronically excited state of a reactant into an electronically excited product molecule* (eq 2) is exceedingly rare for molecules possessing a high number of vibrational modes.[4] The best known examples of these electronically excited product-forming reactions are photoinduced acid-base reactions[5] and excimer (or

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(14) H. C. Freeman, *Advan. Protein Chem.*, 257 (1967).

(1) The authors wish to thank the Air Force Office of Scientific Research (Grant AFOSR-70-1848), the National Science Foundation (Grant GP-26602X), and the National Institutes of Health (Grant GM-19173) for their generous support of this work. Molecular Photochemistry. LXIV. Paper LXIII: N. J. Turro and P. Lechtken *Pure Appl. Chem.*, **33**, 363 (1973). Paper LXII: N. J. Turro and P. Lechtken, *J. Amer. Chem. Soc.*, **95**, 264 (1973).

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

(3) (a) R. C. Dougherty, *J. Amer. Chem. Soc.*, **93**, 7187 (1971), and references therein; (b) Th. Förster, *Pure Appl. Chem.*, **24**, 443 (1970).

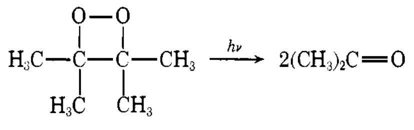
(4) A. Weller, *Progr. React. Kinet.*, **1**, 187 (1961).

(5) Th. Förster, *Angew. Chem., Int. Ed. Engl.*, **8**, 333 (1969).

exciplex) formation,[6] neither of which involves substantial electronic or nuclear reorganization of the reactants, and both of which are fast, reversible reactions (which complicates quantitative analysis and observation of the processes). Hammond[2] has pointed out the analogy between photochemical reactions and radiationless transitions, but our present understanding of the details controlling the rates of either of these processes is woefully imperfect. We report here a study of a direct photochemical fragmentation of tetramethyl-1,2-dioxetane (**1**) and a direct photochemical valence isomerization of naphthvalene (**2**). These systems were found to reveal (a) two striking exceptions to the rule that electronically excited reactants do not efficiently lead to electronically excited products; (b) a totally unexpected proclivity for multiplicity change in reactions conforming to eq 2; (c) a wavelength dependence of singlet and triplet yields of products; (d) application of a technique which allows one to limit the lifetime of a conceivable intermediate to less than 10^{-10} sec.

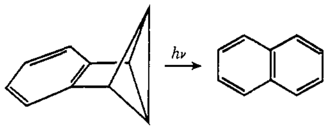
$$R^* \longrightarrow P \qquad (1)$$

$$R^* \longrightarrow P^* \qquad (2)$$



$$H_3C-\overset{O-O}{\underset{H_3C}{C}}-\underset{CH_3}{C}-CH_3 \xrightarrow{h\nu} 2(CH_3)_2C{=}O \qquad (3)$$

1



(4)

2

Our experimental results with the dioxetane are listed in Table I. The results may be summarized as follows:

Table I. Production of Electronically Excited Acetone in the Direct and Photochemical Decomposition of Tetramethyl-1,2-dioxetane

Condition	$(CH_3)_2CO$ (S_1), %	$(CH_3)_2CO$ (T_1), %	Comment
Direct, 366 nm	10	43	*a*
Direct, 320 nm	25		*b*
Direct, 297 nm	30		*b*
Direct, 240 nm	35		*b*

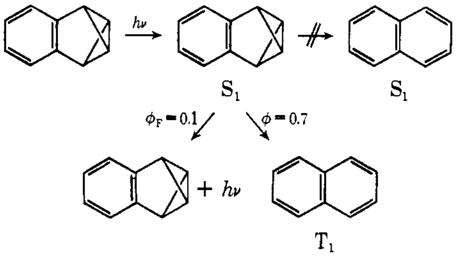
[a] At 6° in benzene solution by the method of P. Lechtken and N. J. Turro, *J. Amer. Chem. Soc.*, **94**, 2886 (1972). The exciting light is absorbed solely by the dioxetane. [b] Determined by comparison of dioxetane luminescence (pure acetone fluorescence) to that of equally absorbing acetone solutions.

(a) direct excitation (366 nm) of **1** in cyclohexane[7] at room temperature results in disappearance of dioxetane with a quantum efficiency of 1.0; (b) the yields of electronically excited acetone produced from 366-nm excitation of **1** are 10% singlet acetone and 40% triplet acetone; (c) the yield of excited acetone singlet increases with increasing excitation wavelength; (d) analysis of the rise time[8] of acetone fluorescence from excitation of **1**[9] requires that no intermediate of lifetime greater than 10^{-10} sec can intervene between initially excited **1** and production of acetone singlet states.

The salient features of these data are the remarkably efficient production of the electronically excited product molecules from direct excitation of **1**. Of great interest also is the propensity of excited **1** to yield *acetone triplets selectively* upon direct irradiation at 366 nm. Examination of the luminescence spectrum of **1** at 77°K shows essentially pure acetone *phosphorescence*.

Strikingly, a study of the excitation of **2**[10] at 77°K revealed an efficient, selective production of naphthalene triplets! The latter was established by noting that excitation of **2** results in *naphthalene phosphorescence but not in naphthalene fluorescence*. Our analysis of the data is summarized in Scheme I. The absolute phosphorescence yield of **2** is essentially the same as that of naphthalene when it is excited under direct irradiation. Thus, the efficiency of reaction 4 must be about 70%, the intersystem crossing yield of naphthalene.[10–12]

Scheme I. Photochemistry of Naphthvalene at 77°K in a Methylcyclohexane Glass



We feel that this work may provide implications of interest to spectroscopists interested in radiationless transitions, photochemists involved in searching for adiabatic excited state reactions, and theoretical chemists concerned with calculations of chemical reactivity. Furthermore, it can be seen that acetone photochemistry can be affected by relatively long-wavelength light (>400 nm). Since acetone is a very popular photosensitizer, its use can now be extended (*via* excitation of the dioxetane) to systems in which the quencher absorbs all of the light which would normally be needed to excite the acetone!

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(6) J. Menter and Th. Förster, *Photochem. Photobiol.*, **15**, 289 (1972). This paper on the photodissociation of di-9-methylanthracene may represent the most substantial example of a severe nuclear change in which an electronically excited product is produced. The measured efficiency of excited product formation, however, was less than 0.1%.

(7) The uv of **1** shows a maximum at about 280 nm (ϵ ~24). We assign this interesting transition to a $\pi_{OO}^* \rightarrow \pi_{OO}^*$ excitation. It is interesting to note that **1** is *yellow*, owing to a long tail in its absorption. That this yellow color belongs to **1**, and not an impurity, is convincingly supported by the observation that excitation of **1** at wavelengths greater than 420 nm results in acetone fluorescence!

(8) In this single photon counting experiment, the fluorescence rise time for acetone fluorescence from excited **1** was found to be identical with that of the rise time for directly excited acetone fluorescence within an experimental error of 0.1 nsec. For a description of the theory and applications of the single photon counting technique, see W. Ware in "Creation and Detection of the Excited State," A. A. Lamola, Ed., Marcel Dekker, New York, N. Y., 1971.

(9) The dioxetane **1** was prepared by the method of R. Kopecky, *Can. J. Chem.*, 47, 709 (1965).

(10) The quantum yield for intersystem crossing of naphthalene, originally reported as 0.40, has now been revised to a value of 0.7–0.8: A. R. Horrocks and F. Wilkinson, *Proc. Royal Soc., Ser. A*, 306, 257 (1968); C. A. Parker and T. A. Joyce, *Trans. Faraday Soc.*, **62**, 2785 (1966).

(11) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965). The value for the triplet yield of naphthalene was complicated by singlet quenching in this case: L. Stephenson, Ph.D. Dissertation, California Institute of Technology, Pasadena, Calif., 1967.

(12) Apparently about 20% of the absorbed photons are not accounted for by either naphthvalene fluorescence or by conversion to naphthalene triplets. It is possible that this inefficiency is an artifact of experimental accuracy or it may reflect a real deactivation path, yet undetected, *i.e.*, internal conversion of naphthvalene singlets or radiationless conversion of **2** directly into naphthalene.

In summary, two unusual examples of formation of electronically excited products from electronically excited precursors are reported. Each reaction is characterized by an unexpected propensity to form triplet rather than singlet products.[13]

(13) After submission of this manuscript, Professor Josef Michl, Department of Chemistry, University of Utah, informed us that he has made MO calculations which suggest that photochemical valence isomerizations of the naphthvalene to naphthalene type should be adiabatic. We are very grateful to Professor Michl for preprints of his work on this subject. We also wish to thank Professor Lionel Salem, University of Orsay, for some stimulating discussions concerning adiabatic excited state reactions.

(14) NATO Postdoctoral Fellow, 1971–1972.

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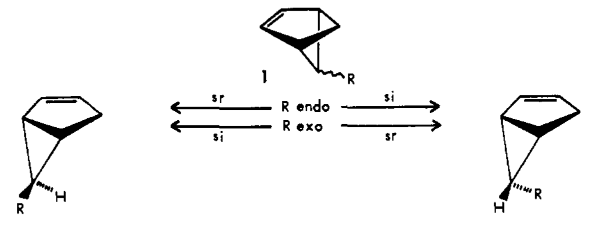
Forbidden 1,3-Sigmatropic Rearrangements[1]

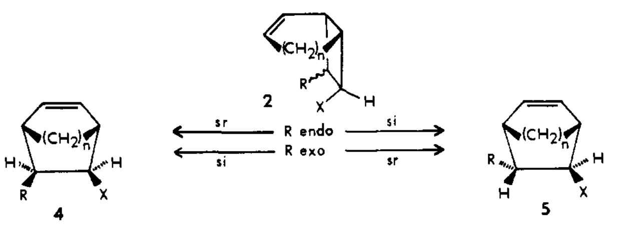
Sir:

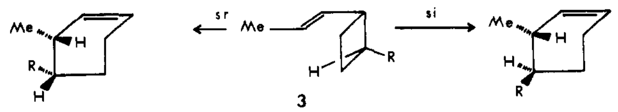
To conserve orbital symmetry, a thermal suprafacial 1,3-sigmatropic rearrangement of carbon must occur with inversion of configuration of the migrating group.[2-5] It has been assumed that when some extrasymmetric factor (for example, a steric blockade of inversion[4b]) forces retention, a nonconcerted diradical mechanism prevails. However, recent theoretical speculations[6] suggest that subjacent orbital effects may stabilize the "forbidden" concerted transition state relative to the nonconcerted one and thereby permit violations of the conservation rule.

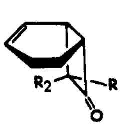
The present paper reports four new rearrangements in the bicyclo[4.2.0]octene series (**2**, $n = 2$), which exemplify a type of reactant structure intermediate between those with a freely rotating allylic migration framework (*e.g.*, **3**) and those in which a rigid ring system sharply restricts the conformational possibilities (*e.g.*, **2**, $n = 1$, and **1**). The pattern of stereospecificities now observed in the series **1**, **2**, and **3** suggests the occurrence of forbidden concerted reactions under subjacent orbital control.

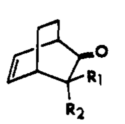
Alcohols **2** (R = *endo*-Me, X = OH, $n = 2$), **2** (R = *exo*-Me, X = OH, $n = 2$), **4**, and **5** (R = Me, X = OH) are obtained from the corresponding ketones **6**, **7**, **8**, and **9**, the *endo*-methyl[4.2.0]ketone **6** being the major cycloadduct from the 1,3-cyclohexadiene–methyl ketene reaction.[7-10] Lanthanide-induced nuclear magnetic resonance shifts (LIS), supported by spin decoupling experiments and infrared measurements, establish the stereochemical relationships of hydroxyl to methyl and hydroxyl to olefin in the alcohols and hence in the reactants (**2**, R = *endo*- or *exo*-Me, X = OAc or $OSiMe_3$, $n = 2$) and products (**4** and **5**, R = Me, X = OAc or $OSiMe_3$, $n = 2$).[11,12]











6, $R_1 = H$; $R_2 = Me$ **8**, $R_1 = H$; $R_2 = Me$
7, $R_1 = Me$; $R_2 = H$ **9**, $R_1 = Me$; $R_2 = H$

The rates of gas-phase pyrolysis of the reactants are not affected by added glass surface. Table I shows the ratios of rates of formation of products by the forbidden suprafacial-retention (sr) and allowed suprafacial-inversion (si) pathways[13] as determined by kinetic analysis[14] and/or by extrapolation of the product ratio to zero time. The allowed si reaction predominates in the "unblocked" series, but in the "blocked" series, especially in **2** ($n = 1$ or 2), the endo substituent interferes with the somersault required for this process, and rearrangement occurs with a large contribution from the forbidden sr pathway.

A conventional interpretation of the sr component as a nonconcerted diradical reaction is difficult to support on kinetic or stereochemical grounds. For example, the rate of rearrangement with inversion (k_{inv})

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(1) The support of this work by the National Science Foundation (GP-33909X) and by the National Institute of General Medical Sciences (GM-16962) is gratefully acknowledged.

(2) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 395 (1965).

(3) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970.

(4) (a) J. A. Berson and G. L. Nelson, *J. Amer. Chem. Soc.*, **89**, 5303 (1967), (b) *ibid.*, 92, 1096 (1970).

(5) (a) J. A. Berson, *Accounts Chem. Res.*, **1**, 152 (1968); (b) Abstracts, American Chemical Society 22nd National Organic Chemistry Symposium, Ann Arbor, Mich., June 13–17, 1971, p 28; (c) G. L. Nelson, Ph.D. Dissertation, University of Wisconsin, 1969.

(6) (a) J. A. Berson and L. Salem, *J. Amer. Chem. Soc.*, **94**, 8917 (1972); (b) J. A. Berson, *Accounts Chem. Res.* **5**, 406 (1972).

(7) The stereochemistry **6** is strongly suggested by many analogies.[8-10]

(8) W. T. Brady and R. Roe, Jr., *J. Amer. Chem. Soc.*, 92, 4618 (1970).

(9) M. Rey, S. Roberts, A. Dieffenbacher, and A. S. Dreiding, *Helv. Chim. Acta*, **53**, 417 (1970).

(10) W. T. Brady and B. M. Holifield, *Tetrahedron Lett.*, 5511 (1966); *Tetrahedron*, **23**, 4251 (1967).

(11) R. W. Holder, Ph.D. Dissertation, Yale University, 1972.

(12) The assignments in the cases of **4** and **5** ($n = 2$, R = Me, X = OH) are confirmed by a fit of the LIS data to structural parameters: M. R. Willcott, R. E. Davis, and R. W. Holder, *J. Amer. Chem. Soc.*, submitted for publication.

(13) Antarafacial reaction is precluded by the structure of the reactants in **1** and **2** ($n = 1$ or 2).

(14) Since an epimerization interconverting the *endo*-methyl and *exo*-methyl isomers **2** (R = *endo*- or *exo*-Me, X = $OSiMe_3$, $n = 2$) competes with the sigmatropic rearrangement, the data are fitted to the kinetic scheme by a numerical integration procedure using a program and subroutine for the Runge-Kutta method kindly supplied by Professor Martin Saunders and Mr. Peter Dervan.[15]

(15) See J. A. Berson and P. B. Dervan, *J. Amer. Chem. Soc.*, **95**, 267, 269 (1973); P. B. Dervan, Ph.D. Dissertation, Yale University, 1972.