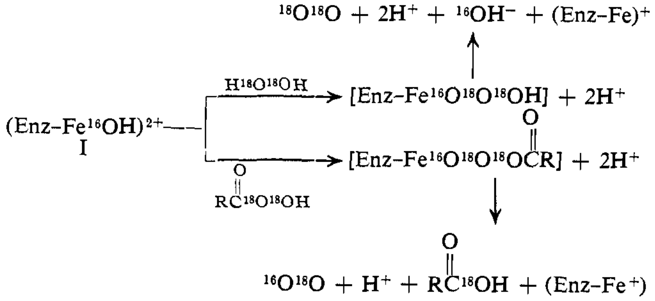
model studies,[12,13] suggest that the two-electron oxidation leading to I involves oxidation of iron(III) to iron(IV) and the porphyrin ring system to a π cation radical. The combination of these elements presents a nearly complete structure for the active center of I of the peroxidases and catalases.

In accord with previous results[18] with catalase we find that the CPO–H_2O_2 reaction proceeds by a nonscrambling mechanism.[23] This is compatible with the spectral evidence for the identity of I formed from H_2O_2 and *m*-CPB, if an additional mechanism, here illustrated schematically, is operative for the oxidation of H_2O_2 by I.



Acknowledgment. This research was supported by National Science Foundation Research Grants GB 30758X (L. P. H.) and GP 30491X (J. C. M.) and an instrumentation grant for the purchase of an isotope ratio mass spectrometer.

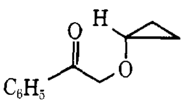
(23) L. P. Hager and coworkers, unpublished results.

Lowell P. Hager,* Dennis L. Doubek, Robert M. Silverstein
J. Howard Hargis, J. C. Martin
Departments of Biochemistry and Chemistry
Roger Adams Laboratory, University of Illinois
Urbana, Illinois 61801
Received March 8, 1972

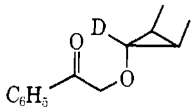
Photochemistry of α-Cyclopropoxyacetophenones. An Unexpected Internally Sensitized Cis–Trans Isomerization[1]

Sir:

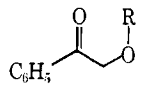
The Norrish type II reactions of butyrophenone and related aryl ketones represent one of the most thoroughly studied and best understood classes of photoreactions.[2] We have undertaken a program to explore the synthetic prospects for these reactions.[3] For example, it seemed possible that suitably substituted α-cyclopropoxyacetophenones might provide a useful route to substituted cyclopropanones, a family of relatively inaccessible but interesting molecules.[4] Indeed, irradiation of benzene solutions of Ia with 313-nm light produces acetophenone and cyclopropanone,[5,6] albeit in low yield, in addition to cyclization product IIIa. However, under identical conditions of excitation, Id (cis-exo) did not produce detectable amounts of dimethylcyclopropanone or significant quantities of acetophenone. The principal reactions of Id (cis-exo) were found to be cyclization and isomerization of the cyclopropane ring (Scheme I) to give, respectively, IIIb and Ib (trans).[7] The occurrence of isomerization products represented a rather unexpected and novel course of reaction and demanded closer mechanistic scrutiny. Our study produced evidence that the standard mechanisms for type II processes[2] are inadequate for proper understanding of the data.



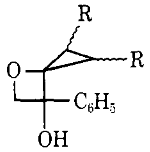
Ia



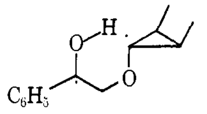
Ie



IIa, R = CH_3
IIb, R = CD_3



IIIa, R = H
IIIb, R = CH_3



IV

Scheme I

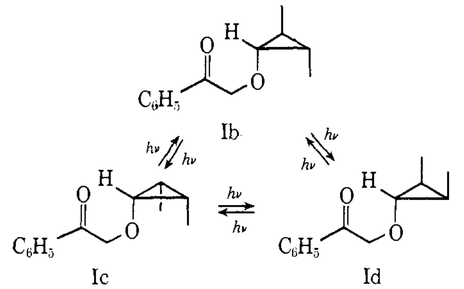


Table I. Quantum Yield and Kinetic Data[f]

Compd	$k_q\tau$	$\tau^{-1\,a}$ ($\times 10^{-8}$)	Φ
Ia	21	2.4	0.077,[b] 0.018[c]
Ib	2.3	22	0.0060,[b] 0.0030[d]
Ic	0.65	77	0.023,[b] 0.0011,[d] 0.0067[e]
Id	4.4	11	0.015,[b] 0.0043[e]
Ie	10.7	4.7	0.025,[b] 0.0078[e]
IIa	1.6	31	0.99,[b] 0.42[c]
IIb	8.9	5.6	

[a] Assuming $k_q = 5 \times 10^9\ M^{-1}\ sec^{-1}$ in benzene at 25°. [b] Disappearance of ketone. [c] Type II cleavage. [d] Appearance of Id (cis-exo). [e] Appearance of Ib (trans). [f] Plots of product formation *vs.* time were linear out to 15% conversion. Stern–Volmer quenching was confined to this range.

Table I summarizes quantum yield and kinetic data for the photoreactions of Ia–e in benzene. The ketones IIa–b are included for comparison. The salient features of the data are (1) the tremendous drop in reaction efficiency as one proceeds from IIa to Ia (a factor of 13) and then from Ia to Id (a factor of 5); (2) the increase in $1/\tau$ between Ia and Id (cis-exo); (3) the sizable effect of γ deuteration on $1/\tau$ and Φ for Id

---

(1) Molecular Photochemistry. LV. Paper LIV, R. R, Hautala and N. J. Turro *Tetrahedron Lett.*, 1229 (1972); paper LIII, N. J. Turro *Pure. Appl. Chem.*, 27, 697 (1972); paper LII, N. J. Turro and P. Lechtken, *J. Amer. Chem. Soc.*, **94**, 2886 (1972).

(2) P. J. Wagner, *Accounts Chem. Res.*, **4**, 168 (1971).

(3) N. J. Turro, R. B. Gagosian, and J. C. Dalton, *J. Amer. Chem. Soc.*, **92**, 4752 (1970).

(4) N. J. Turro, *Accounts Chem. Res.*, **2**, 25 (1969).

(5) F. L. Lewis, *Mol. Photochem.*, **2**, 259 (1970).

(6) We have repeated Lewis' work as a control and have obtained independent agreement with his reported quantum yields and quenching constants within his experimental error. Formation of cyclopropanone was monitored by ir and nmr upon partial photolysis of Ia at −60° in methylene chloride solution.

(7) Upon extended irradiation, the photolysis mixture consists of 70% isomeric oxetanols and 5% acetophenone. No detectable olefinic products were formed.

(cis-exo); and (4) although the mass balance for product formation is good to moderate, the remarkably low efficiency of net chemical transformation.

Consider the last point first. One notes that the decrease in reaction efficiency may be explained in terms of the standard mechanism for aryl alkyl ketones if (1) reversible transfer hydrogen in the biradical IV is exceedingly efficient relative to closure and cleavage,[8] or (2) a new deactivation is possible for Id (and to a lesser extent Ia) which effectively degrades electronic excitation of triplets before γ hydrogen abstraction can occur.

With regard to methyl substitution in the ring, the faster rate of deactivation of Id (cis-exo) and Ic (cis-endo) *vs.* Ia suggests that the methyl groups are playing an important electronic rather than steric role in the deactivation process. On the other hand, the substantial deuterium isotope effect on $1/\tau$ for Ie (d-cis-exo) *vs.* Id (cis-exo) suggests that *degradation of electronic excitation is coupled to the electronic influence of the methyl groups via the γ-CH bond!* One can thus view the deactivation as occurring *via* coupling of the electronically excited carbonyl group to the C_2–C_3 cyclopropane bond *via* a γ-CH stretching motion.[9] This motion, of course, implies a strong coupling between the γ-CH stretching vibration and the C_2–C_3 ring stretching vibration; *i.e.*, energy degradation involves specific conversion of electronic energy into vibrational energy associated with a normal mode of the γ-HC_2C_3 unit. Significantly, we have observed that 1,1-dimethoxycyclopropane quenches acetophenone phosphorescence at a rate comparable to simple aliphatic ethers; thus, cyclopropyl ethers, *per se*, do not appear to possess special deactivation paths for standard n,π^* triplets.

In summary, we report that the introduction of remote methyl groups into α-cyclopropoxyacetophenone produces a surprising increase in the rate of chemically nonproductive radiationless decay to ground-state parent ketone. The low reaction efficiencies, compared to model compounds, point to the operation of a novel mechanism for radiationless deactivation not previously encountered in type II photoreactions.[10] The observation of a deuterium isotope effect on triplet ketone lifetime and isomerization efficiency strongly implicates the γ-H in both the novel radiationless deactivation and ring isomerization. We suggest that the fast rates of radiationless decay may result from electronic vibrational coupling in which the stretching of the C_2–C_3 bond,[11] induced by excited ketone γ-H interaction, serves as an energy sink.

Acknowledgment. The authors wish to thank Professor Frederick D. Lewis for a preprint of his work on α-cyclopropoxyacetophenone and for productive and stimulating discussions. The authors also thank the referees for making several valuable comments on the original manuscript. They also acknowledge the Air Force Office of Scientific Research for its generous support of this work (Grant No. AFOSR-70-1848D).

Thomas R. Darling, Nicholas J. Turro*
Department of Chemistry, Columbia University
New York, New York 10027

Received October 7, 1971

---

[8] For this situation to be the case, nearly 99% of the biradicals derived from Id, compared to only about 1% of the biradicals derived from IIa, would be required to reabstract the hydroxyl hydrogen without prior transformation.

[9] B. H. Al-Sader and R. J. Crawford, *Can. J. Chem.*, **46**, 3301 (1968).

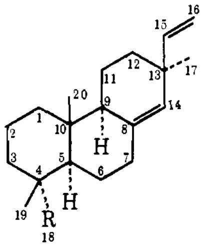
[10] Any alternative deactivation, such as charge transfer or reversible carbonyl addition to the ring, which accounts for the ring isomerization and the large inefficiency must contribute the entire deuterium dependence in $1/\tau$.

[11] The ring cleavage of conjugated cyclopropyl ketones is a well-established photochemical process. For leading references see: D. N. Marsh, J. N. Pitts, Jr., K. Schaffner, and A. Truinman, *J. Amer. Chem. Soc.*, **93**, 333 (1971); H. E. Zimmerman, S. S. Hixon, and E. F. McBride, *ibid.*, **92**, 2000 (1970); and W. H. Dauben, L. Schutte, and R. E. Wolf, *J. Org. Chem.*, **34**, 1849 (1969).

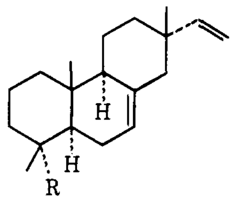
Carbon-13 Nuclear Magnetic Resonance Spectroscopy of Naturally Occurring Substances. X. Pimaradienes[1]

Sir:

In continuation of our ^{13}C nmr study of organic natural products the first systematic analysis of diterpenic compounds was undertaken. The following chemical-shift data for the pimaradienic substances **1–4** were utilized for the determination of the otherwise difficultly assignable ring C conformation of the $\Delta^{8(9)}$-pimaradienes (**4**) as well as for the elucidation of the biosynthesis of the virescenosides, fungal isopimaradienic glycosides.[2]

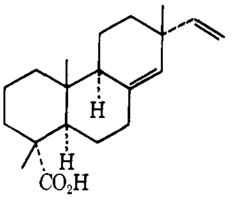


1

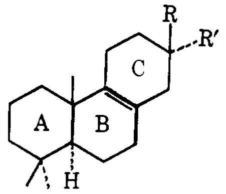


2

a, R = Me
b, R = CH_2OH
c, R = CO_2H



3



4a, R = C_2H_3; R′ = Me
b, R = Me; R′ = C_2H_3

Application of chemical-shift theory[3] to the noise decoupled and off-resonance decoupled spectra[1] of the nine compounds and inspection of cmr spectra of pimarol (**1b**) in the presence of the paramagnetic shift agent,[4] Pr(dpm)$_3$, yielded the data collated in Table I.

---

[1] For the preceding paper see E. Wenkert, D. W. Cochran, F. M. Schell, R. A. Archer, and K. Matsumoto, *Experientia*, **28**, 250 (1972).

[2] J. Polonsky, Z. Baskevitch, N. Cagnoli-Bellavita, P. Ceccherelli, B. L. Buckwalter, and E. Wenkert, *J. Amer. Chem. Soc.*, **94**, 4369 (1972).

[3] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon Press, New York, N. Y., 1966; D. K. Dalling and D. M. Grant, *J. Amer. Chem. Soc.*, **89**, 6612 (1967); H. J. Reich, M. Jautelat, M. T. Messe, F. J. Weigert, and J. D. Roberts, *ibid.*, **91**, 7445 (1969); D. W. Cochran, Ph.D. Dissertation, Indiana University, 1971.

[4] *Cf.* M. Christl, H. J. Reich, and J. D. Roberts, *J. Amer. Chem. Soc.*, **93**, 3463 (1971); J. Briggs, F. A. Hart, G. P. Moss, and E. W. Randall, *Chem. Commun.*, 364 (1971); O. A. Gansow, M. R. Willcott,