ppm at 13.8 MHz) with an intensity ratio of ca. 4:1. The poor resolution vitiated accurate, simultaneous determination of the individual relaxation times. Addition of small quantities of Eu(fod)$_3$ to the extent of $\rho = 0.01$ (ρ being the molar ratio of lanthanide reagent to acetone-d_6) resulted in complete separation of the two resonances ($\Delta\nu = 0.4$ ppm) and allowed simultaneous determination of the individual relaxation times. The relaxation times determined in this manner were found to agree, within experimental error (±10%), with those determined on separate chloroform solutions of the individual components not containing the shift reagent. Subsequent additions of Eu(fod)$_3$ up to and including $\rho = 0.02$ ($\Delta\nu = 0.8$ ppm) led to the same result. *At* $\rho > 0.02$ *significant shortening of the relaxations times of the components was observed.*

To quantify the effect of Eu(fod)$_3$ on the relaxation time of acetone-d_6 and to probe the nature of the interactions contributing to this effect, the relaxation time of acetone-d_6 in a chloroform solution of acetone-d_6 (0.81 *M*) and CDCl$_3$ (1.0 *M*) (for internal referencing) containing varying amounts of Eu(fod)$_3$, and in separate experiments the diamagnetic La(fod)$_3$,[4] was determined (six samples of each reagent in the range $0.0 \leq \rho \leq 0.14$). At least five separate T_1 measurements were performed on each sample. In this range of ρ the chemical shift of the acetone resonance with respect to internal CDCl$_3$ is linearly correlated with the concentration of Eu(fod)$_3$ (slope of the best least-squares line = 10.2 ppm per unit ρ). Similarly, $1/T_1$ is linearly correlated with respect to ρ. In the case of Eu(fod)$_3$ the slope is 7.03×10^{-1} sec^{-1} per unit ρ (correlation coefficient 0.934) and the intercept ($\rho = 0.0$) is 0.223 sec^{-1}; for La(fod)$_3$ the slope is 6.64×10^{-1} sec^{-1} per unit ρ (correlation coefficient 0.927) and the intercept ($\rho = 0.0$) is 0.223 sec^{-1}.

These findings suggest that the pseudocontact paramagnetic interaction effect (ca. 6%), if experimentally significant, is at best very small in the entire range of ρ studied. Thus, the relaxation of acetone-d_6 in the presence of the lanthanide shift reagent is still primarily dominated by the quadrupolar relaxation mechanism, suggesting that the molecular reorientation time of the acetone molecule is significantly affected by complexation with the bulkier shift reagent molecule. For small ρ (<0.02), however, even this effect is practically negligible. It should be possible, therefore, to employ shift reagents in small quantities for small or strongly complexed molecules, and probably in even greater amounts for large or weakly complexed molecules, to separate overlapping resonances to allow quantitative determination of ^{2}H relaxation times.

Utilization of specifically labeled ^{2}H compounds, in conjunction with shift reagents, should markedly enhance the ability to measure ^{2}H relaxation times; we are currently testing these possibilities on a variety of systems (bicyclics, steroids, acyclics, and aromatics).

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(3) The dominant mode of ^{1}H and ^{13}C relaxation is generally dipolar, necessitating degassing of solutions. In the presence of paramagnetic shift reagents or impurities, e.g., oxygen, T_1 is generally shortened (see, for example, A. F. Cockerill, G. L. O. Davies, R. C. Harden, and D. M. Rackham, *Chem. Rev.*, **73**, 553 (1973), and references cited therein).
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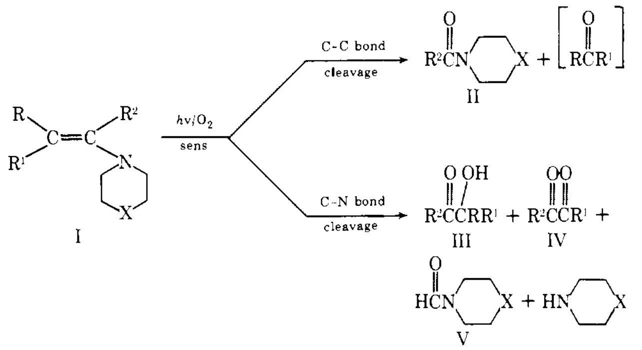
Singlet Oxygen Reaction. IV. Photooxygenation of Enamines Involving a Two-Step Cleavage of a 1,2-Dioxetane Intermediate[1]

Sir:

Recently, we described the first example of the formation of an α-diketone and an α-hydroxy ketone in the decomposition of 1,2-dioxetane as a possible intermediate in oxygenation of electron rich sulfides.[2,3] The formation of these α-diketones and α-hydroxy ketones was established to involve the two-step biradical cleavage of the intermediate of 1,2-dioxetane. In attempt to find more examples of this two-step biradical process in the decomposition of 1,2-dioxetane intermediate, we examined the photooxygenation of α-alkyl substituted enamine I (R^2 = alkyl), since the relative bond strength of the carbon-nitrogen and carbon-carbon bonds is probably sufficient to make the scission of the carbon-nitrogen bond comparative to that of the carbon-carbon bond.[4] The pioneering work of Foote and Lin have shown that the carbon-carbon double bond of enamine I (R^2 = H) was cleaved to give a ketone or aldehyde and an amide in quantitative yield,[5] and these products appear to originate from decomposition of a 1,2-dioxetane intermediate,[6-9] but by no means requires that the cleavage of 1,2-dioxetane be concerted.[10]

Photooxygenation of Ia in pyridine, at room temperature, sensitized by hemaporphyrin with visible light, proceeded rapidly and ceased abruptly after uptake of approximately 1.2 equiv of oxygen. Both sensitizer and light were found to be essential under the reaction time. Evaporation followed by GLPC gave methyl phenyl diketone (IVa) (30%), 2-hydroxyethyl phenyl ketone (IIIa) (13%), *N*-benzoylmorpholine (IIa) (18%), *N*-formylmorpholine (Va) (10%), and a trace of morpholine; unidentified nonvolatile compounds are also produced.[11] Enamine Ib gave 2-hydroxyisopropyl phenyl ketone (IIIb) (22%), *N*-benzoylmorpholine (IIb) (49%), and a trace of methyl phenyl diketone (IVb). Products were characterized by spectroscopic and gas chromatographic comparison with authentic materials. Addition of 0.1 *M* 2,6-di-*tert*-butylphenol, a good free radical inhibitor, produced no effect either on O$_2$ uptake rate or on product yield in photooxygenation of Ia or Ib. Under the same conditions, enamines Ic, Id, and Ie gave 2-hydroxy ketone, III, and *N*-formyl derivatives V in 10 and 20% yields, respectively, together with the formation of carbon-carbon bond cleavage products II in 20-35% yields.[12] Enamine If gave a trace of 2-hydroxy ketone, III, and produced the carbon-carbon bond cleavage product as a major product (75%).



a, R = H; R^1 = Me; R^2 = Ph; X = O
b, R = R^1 = Me; R^2 = Ph; X = O
c, R = R^1 = Me; R^2 = Ph; X = CH_2
d, R = H; R^1 = Me; R^2 = Et; X = O
e, R = H; R^1 = Me; R^2 = Et; X = CH_2
f, R = R^1 = Me; R^2 = *i*-Pr; X = O

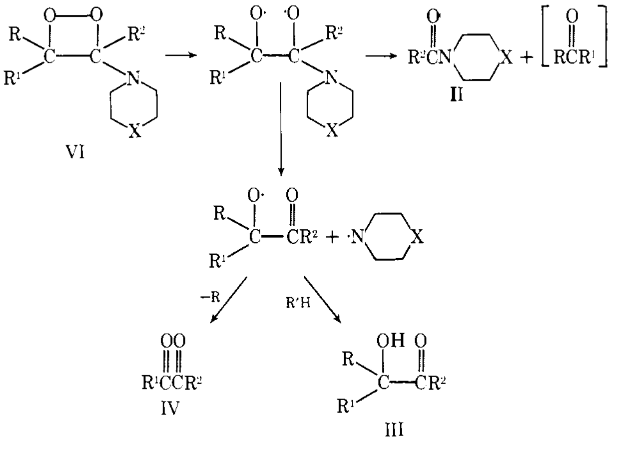
An overall view of these results summarized in Table I shows that the structural features leading to C-N bond

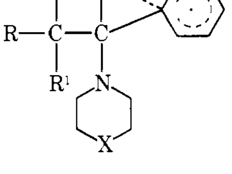
Table I. Substituent Effects for the Cleavage of C–N and C–C Bonds in Oxygenation of Enamines I (at 20°)

Substituent				Relative yield, %	
R	R^1	R^2	X	C–C cleavage	C–N cleavage
Me	Me	H	O	100	0
Et	Et	H	O	100	0
H	Me	Et	O	69	31
H	Me	Et	CH$_2$	78	22
Me	Me	*i*-Pr	O	95	5
H	Ph	CH$_2$Ph	O	95	5
Me	Me	Ph	O	68	32
Me	Me	Ph	CH$_2$	49	51
H	Me	Ph	O	29	71

cleavage can be classified into two categories: (1) a hydrogen atom on the β-carbon and (2) a phenyl group on the α-carbon. Another example of the first case has been observed quite recently by Wasserman and Terao[13] when *N*-(1-cycloalkenyl)morpholines were photooxygenated, and the authors postulate for the mechanism of C–N cleavage, a β-elimination from the intermediate dioxetane induced by the presence of base. Formation of the C–N cleavage products observed in the reaction of Id and Ie might be explained by the same mechanism, since the photooxygenations in the present work were carried out in basic solvent (pyridine).

However, β-elimination mechanism could not be applied to the C–N cleavage in the photooxygenation of enamines of the second category, especially Ib and Ic which bear no hydrogen atom on their β-carbon. This C–N cleavage can be best explained in terms of a biradical mechanism, in which the O–O bond is completely broken followed by C–N bond cleavage to give a nitrogen center radical and a keto alkoxy radical. The keto alkoxy radical either abstracts a hydrogen to give III or undergoes unimolecular fragmentation by scission of the C–C bond or H-atom abstraction by another radical to give IV. 1,2-Dioxetane can collapse through two modes: (1) a concerted fission of O–O and C–C bonds forming two carbonyl group[7] and (2) two-step homolysis involving a biradical process.[10] The phenyl substituent would assist homolysis of a O–O bond by participating as seen in the decomposition of benzoyl peroxide,[14] and the biradical thus formed could undergo cleavage of C–C and C–N bonds competitively.





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(4) Cleavage of the C–C bond of a biradical produced through homolysis of an O–O bond of 1,2-dioxetane is so highly exothermic that one of two carbonyl compounds produced may be in the excited state.[7] Thus, the net exothermicity of the C–C bond fission may be small. Now, about 10 kcal/mol difference in average bond energy between C–C and C–N bonds may be apparently sufficient to make the C–N bond fission competitive with the C–C bond fission process.

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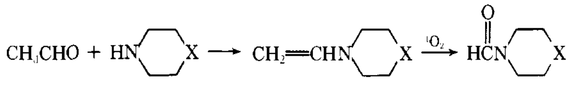
(11) Under the reaction conditions, an acetaldehyde formed in C–C bond cleavage reacts with morpholine to give enamine, which reacts with singlet oxygen to give *N*-formylmorpholine (V). Intermediate enamine is unstable under the reaction conditions.



(12) The enamines Ic–Id were not stable under the reaction conditions, and unidentified non-volatile compounds are also formed. However, the products II, III, and V are only formed in the presence of sensitizer, light, and oxygen.

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Suggested Method for Multiple Comparisons of Treatment Means

Sir:

Often chemical data consists of *nk* observations; as shown in Table I for each of *n* "blocks" (molecules, etc.) there is one "observation" (experimental or theoretical result) for each of *k* "treatments" (method of calculation, etc.). The basic task is to test the hypothesis that there are no treatment differences, and, if the hypothesis is rejected, multiple comparisons of the treatments are required.

Due to major developments in the past few decades, nonparametric statistics may be employed to perform this basic task. These methods offer the following advantages: (1) they forgo the assumption that the populations under consideration are normal, (2) they are often easier to apply than normal theory counterparts, and (3) they have a high efficiency when the populations are not normal and are only slightly less efficient for normal populations than the normal theory counterparts.[1] In cases of data subject to systematic error these advantages are compelling.

In statistics the basic task as cited above is a two way analysis of variance with multiple comparisons, and the objective of this paper is to point out the utility of doing this analysis nonparametrically using the Friedman S-test and Friedman rank sums.[2]

In Table I the observations within a given block are not independent, but are associated in some way. The Friedman *S* statistic tests the null hypothesis