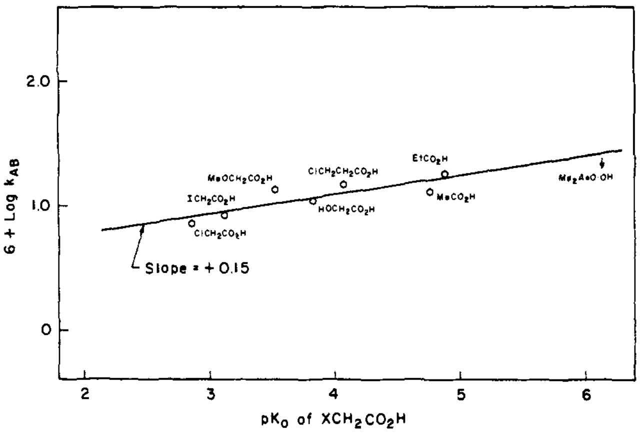

**Figure 1.** Bronsted plot of the third-order rate constants for catalysis of acetone enolization by acid-base pairs at 25°, ionic strength 2.0 ($KNO_3$). Initial rates were measured by iodination with buffer concentrations of 0-2 *M* as described previously;[6] control experiments showed no major specific salt or solvent effects.

close to 0.2,[7] the same as is found for many carbonyl addition reactions,[8] and the value of $\beta_B$ is 0.88,[2] it was predicted that the value of $\beta_{AB}$ for the third-order term would be 0.88-0.2 or approximately 0.68.

In fact, the magnitude of the third-order term is almost independent of the p$K$ of the acid-base pair used, with a value of $\beta_{AB} = 0.15$ (Figure 1). The third-order term could be detected for all carboxylic acids of p$K \geq 2.8$ but not for cacodylic acid, for which an upper limit is shown in the figure. The small Bronsted slope means that when the p$K$ of the acid-base pair is increased the increase in the effectiveness of the catalyzing base is largely cancelled by a decrease in the effectiveness of the catalyzing acid. The dependence on the base strength of B must lie between $\beta_B = 0.88$ (no protonation of the carbonyl oxygen) and $\beta_B = 0.45$[9] (complete protonation of the carbonyl oxygen). The dependence on the strength of the catalyzing acid must therefore be relatively large ($\alpha_A \sim 0.5$) for the third-order term to account for the observed $\beta_{AB}$ of 0.15.[10]

The C-H isotope effect for the third-order term was determined from the rates of enolization of $CH_3COCH_3$ and $CD_3COCD_3$ with AcOH and $AcO^-$ as catalysts. The observed rate constant ratio of 5.8 gives a normal primary isotope effect (uncorrected for secondary effects of adjacent C-H groups) similar to values previously reported for acid and base catalyzed enolization[4a,11] and indicates considerable C-H (or C-D) bond cleavage in the transition state. The solvent deuterium isotope effect for the third-order term was found to be $k_{H_2O}/k_{D_2O} = 2.0$ for both $CH_3COCH_3$ and $CD_3COCD_3$. In contrast, the solvent deuterium isotope effect is only 1.0-1.25 for $k_B$ and 1.1-1.5 for $k_A$;[4b,11,12] the latter value corresponds to a value of $k_{H_2O}/k_{D_2O} = 0.9$-1.2 for proton abstraction by acetate from protonated acetone, after correction for isotope effects on the dissociation constants of HOAc and $CH_3COHCH_3^+$.[13] The larger value for the $k_{AB}$ term shows that there is a significant loss of H-O zero-point energy in the transition state.

The catalytic constants for trimethylamine *N*-oxide (p$K_a$ = 4.95, $k_A = 20 \times 10^{-6}\ M^{-1}\ \text{min}^{-1}$, $k_B = 50 \times 10^{-6}\ M^{-1}\ \text{min}^{-1}$, $k_{AB} = 140 \times 10^{-6}\ M^{-2}\ \text{min}^{-1}$) are significantly larger, especially the third-order term, than those for acetic acid (p$K_a$ = 4.68, $k_A = 4.8 \times 10^{-6}\ M^{-1}\ \text{min}^{-1}$, $k_B = 12.5 \times 10^{-6}\ M^{-1}\ \text{min}^{-1}$, $k_{AB} = 12.6 \times 10^{-6}\ M^{-2}\ \text{min}^{-1}$). This shows that special structural features of carboxylic acids or their conjugate bases are not required for any of these catalytic terms.

These results, particularly the value of $\alpha_A = 0.5$ and the solvent isotope effect $k_{H_2O}/k_{D_2O} = 2.0$ for the third-order term, establish that the mechanism of bifunctional catalysis of the enolization of acetone is different from the mechanism of either the second-order base-catalyzed or acid-catalyzed reactions, with a significant movement of the proton from the catalyzing acid toward the carbonyl oxygen atom in the transition state. Although we do not yet wish to exclude other mechanisms, the data appear to be consistent with the hypothesis that the two proton transfers in the third-order reaction are truly concerted.

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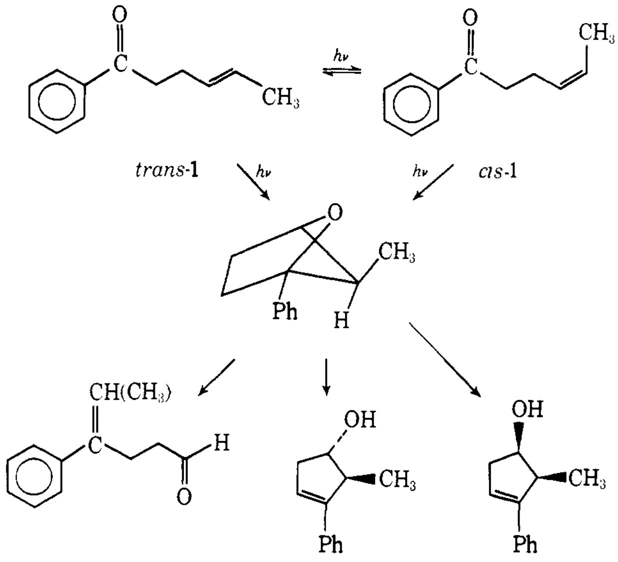
## Intramolecular Charge Transfer Quenching in Excited β-Vinyl Phenyl Ketones[1]

*Sir:*

There is now general agreement that, when triplet energy transfer is endothermic, olefins interact with excited ketones by a charge transfer process which probably yields an exciplex intermediate.[2,3] The complexes collapse to oxetane products in variable and often low quantum yields. Synthetically interesting bicyclic oxetanes are known to be formed upon irradiation of various unsaturated ketones.[4-7] Such intramolecular excited state interactions are gaining increased attention,[5,8] but there is very little quantitative information available which indicates how rapidly, in bifunctional compounds, intramolecular interactions compete with normal decay reactions of individual chromophores. We have now obtained this information for two γ,δ-unsaturated phenyl ketones by (1) monitoring the cis-trans photoisomerization of 1-phenyl-4-hexene-1-one, **1**, and (2) monitoring the type II photoelimination of 1-phenyl-2-ethyl-4-pentene-1-one, **2**. In both cases the β-vinyl group quenches ≥99% of

Scheme I



the triplet excitation initially on the benzoyl group. This intramolecular quenching yields bicyclic oxetanes very inefficiently (1-2%).

The uv absorption spectra of **1** and **2** are nearly superimposable upon that of a typical phenyl alkyl ketone such as valerophenone; therefore, there is no evidence for any significant ground state interaction between the benzoyl group and the double bond.[9] Irradiation of 0.02 *M* hexane solutions of either *cis*- or *trans*-**1**[10] causes rapid interconversion of the two isomers and slow formation of three products, all of which presumably arise from an intermediate bicyclo[2.1.1]oxetane.[4-6,11]

Quantum efficiencies[12] were determined at 313 nm: $\Phi_{c\to t} = 0.32 \pm 0.03$; $\Phi_{t\to c} = 0.095 \pm 0.008$; $\Phi_{-\text{ketone}} = 0.021$. The photostationary state is 82% trans.

The intramolecular nature of the isomerization is evidenced by the inability of 0.12 *M trans*-2-hexene to quench it and by the lack of **1**-sensitized photoisomerization of 0.02 *M* 2-hexene. 1,3-Pentadiene, a known efficient quencher of triplet phenyl ketones,[15] does quench the isomerizations of the two isomers with low efficiency. Initial slopes of Stern-Volmer plots are 0.9 $M^{-1}$ in hexane at room temperature.[16]

Irradiation of degassed benzene solutions of **2**[20] produced six products as shown in Scheme II.[11] Quantum yields[22] of each product at 313 nm are indicated in parentheses.

Scheme II

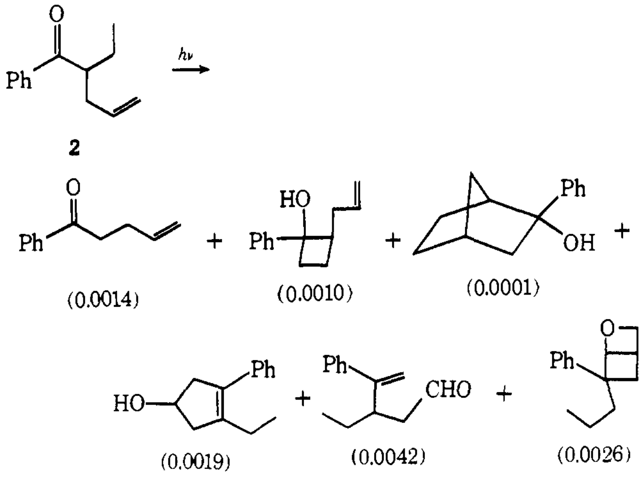


Table I. Some Rate Constants for Quenching of the Triplet Benzoyl Group by Double Bonds

| Intramolecular | | Intermolecular | |
|---|---|---|---|
| Compound | $k_{ct}$, $10^9$ sec$^{-1}$ $^a$ | Olefin | $k_{ct}$, $10^7$ $M^{-1}$ sec$^{-1}$ $^b$ |
| *cis*-1 | 15.0 | *cis*-2-Pentene | 5.0 |
| *trans*-1 | 15.0 | *trans*-2-Pentene | 2.0 |
| 2 | 0.8 | 1-Pentene | 0.8 |

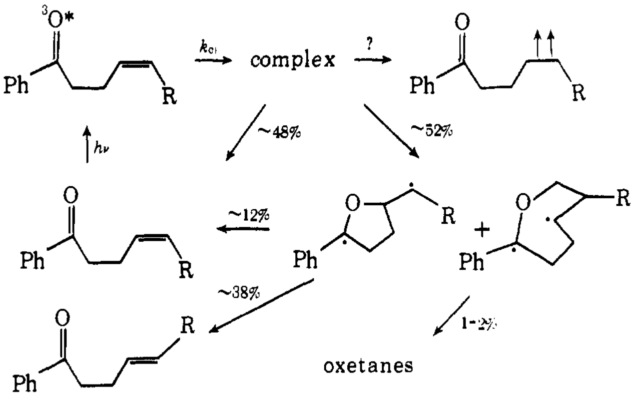
$^a$ $k_{ct} = 1/\tau$, calculated from the measured $k_q\tau$ values with $k_q = 5 \times 10^9\ M^{-1}$ sec$^{-1}$ in benzene and $1.3 \times 10^{10}\ M^{-1}$ sec$^{-1}$ in hexane.[17] $^b$ From ref 2.

The first two products are the expected type II products,[23] in comparable yields as expected for α-alkyl ketones.[24] The formation of the norbornanol has been reported separately.[25] The cyclopentenol and the aldehyde are again expected rearrangement products of the relatively unstable bicyclo[2.1.1]oxetane. All six products from **2** are quenched equally by 1,3-pentadiene; the resulting linear Stern-Volmer plot has a slope of 6 ± 0.5 $M^{-1}$ in benzene at 25°C. The total quantum yield for type II products from **2** is less than 1% the value reported for α-methylbutyrophenone.[24] (The diradicals from these two ketones might be expected to partition themselves comparably.) This decrease in type II quantum yield is matched by a 100-fold increase in the rate of triplet decay compared to that of butyrophenone.[25]

In both ketones **1** and **2**, triplet decay is dominated by intramolecular quenching by the double bond. In **2** the competing hydrogen abstraction is only $^1/_{100}$ as rapid; in **1** the only competitive decay would be slow self-quenching.[26] These rate constants for intramolecular CT quenching are compared in Table I to the 100-700-fold lower values reported for bimolecular quenching.[2] It is important to note that these intramolecular reactions, although quite rapid, are not so rapid as to be rotationally controlled,[27] as may well be the case[28] for ω-styryl ketones[8f] and for ω-dialkylamino ketones.[8p] In the latter cases, the analogous bimolecular quenching reactions are close to diffusion-controlled. For olefin quenching, bimolecular rate constants are far below diffusion-controlled values. Moreover, the disubstituted double bond remains more reactive than the terminal double bond in the intramolecular quenching and neither quenches the triplet ketone as rapidly as does a β-styryl group.[8f] It is therefore very unlikely that any significant unquenchable triplet reaction proceeds from conformations in which the β-double bond happens to be within interaction distance of the carbonyl in the ground state.

Alkenes quench both singlet and triplet n,π* ketones at comparable rates.[2,29] If the rate of intersystem crossing in these phenyl ketones is close to the 5 × $10^{10}$ sec$^{-1}$ reported for benzophenone,[30] no measurable singlet quenching would be expected in **2** but some 30% might be anticipated for **1**. In fact, the ability of **2** to photosensitize the geometric

Scheme III



isomerization of 1,3-pentadiene[14] indicates an intersystem crossing yield within experimental error of unity. However, singlet **1** apparently is partially quenched by its double bond, since the intercept of a sensitization plot[31] is significantly above unity (1.15).

Finally, these results provide a fairly clear picture of the competing reactions of the excited CT complex. Scheme III is suggested by our measured triplet, oxetane, and isomerization yields and by the observation that the photostationary trans/cis ratio from **1** is characteristic of that from chemical (Schenck) isomerization.[32] The conclusion that half the complex decays to ground state reactant is based on the assumption that reversion of both diradicals to ground state would yield geometric isomerization of the double bond. As usual in triplet state photochemistry, product quantum yields reveal very little about excited state rate constants when one or more metastable photoproducts can revert to ground state reactant.

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(10) Details of their preparation will be presented in the full paper.

(11) Since the products do not possess unexpected structures, details of their characterization will be delayed to our full papers.

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## Indole–Singlet Oxygen Reactions. A Novel Rearrangement of the Peroxidic Intermediates to 2,3-Dihydro-1,4-benzoxazines[1]

*Sir:*

Although extensive studies of the reaction of indoles, including tryptophan,[2] with molecular oxygen have been made,[2,3] there are very few reports on the nature of the peroxidic intermediates involved in the reactions, with the exception of 3-hydroperoxyindolenines.[2g,3] We report here results of the reaction of 3-substituted indoles with singlet oxygen, in which we show that (i) the peroxidic intermediates are efficiently intercepted by the functional groups of the side chain to yield 3-hydroperoxyindolines, and that (ii) the hydroperoxidic products readily undergo a new type of rearrangement to give 2,3-dihydro-1,4-benzoxazines in the presence of catalytic amounts of acid. Thus the results provide a new method for the oxidative transformation of indoles into 1,4-benzoxazine systems.

Rose bengal-sensitized photooxygenation[4] of *N*-methyltryptophol (**1**) (2 m*M*) in methanol at room temperature gave a normal $C_2$–$C_3$ ring cleavage product, **2**[5] (90%), which is generally considered to be formed through dioxetane **3**.[6,7] However, when the same photooxygenation of **1** (2 m*M*) was carried out at −70° until 1 molar equiv of oxygen was absorbed and the reaction mixture was stripped of solvents under vacuum at 0°, 3-hydroperoxyindoline (**4**) was obtained in 95% yield; dioxetane **3** was not detected.[8] The structure of **4** was assigned on the basis of the following spectral data and chemical reactions: uv (EtOH) 249 (log $\epsilon$ 3.84), 298 nm (log $\epsilon$ 3.20); ir (Nujol) 3400 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 2.12–2.43 (m, 2 H, $CH_2$), 2.87 (s, 3 H, NMe), 3.30–4.12 (m, 2 H, $CH_2O$), 5.13 (s, 1 H, NCHO), 5.47 (s, 1 H, OOH, exchangeable), 6.33–7.29 (m, 4 H, aromatic H); mass spectrum (*m/e*, 70 eV) 207 ($M^+$, 5%), 191 ($M^+ - O$, 6%), 189 ($M^+ - H_2O$, 9%), 174 ($M^+ - OOH$, 6%), 173 ($M^+ - H_2O_2$, 10%), 142 (100%). Dimethyl sulfide reduction of **4** in methanol gave **5**[5] (90%) (mp 63–64°; uv (EtOH) 249 (log $\epsilon$ 3.82), 306 nm (log $\epsilon$ 3.16); ir (Nujol) 3290 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 2.20 (s, 1 H, OH), 2.25–2.50 (m, 2 H, $CH_2$), 2.90 (s, 3 H, NMe), 3.38–4.13 (m, 2 H, $CH_2O$), 5.15 (s, 1 H, NCHO), 6.35–7.33 (m, 4 H, aromatic H); mass spectrum (*m/e*) 191 ($M^+$)) which was identical with the sample prepared by the oxidation of **1** with *m*-chloroperbenzoic acid in methylene chloride (48%). Treatment of the hydroperoxide **4** with methanol containing catalytic amounts of HCl at room temperature gave 2,3-dihydro-1,4-benzoxazine (**6**)[5,9] (75%): a pale yellow oil, bp 64–65° (1 mmHg); uv (EtOH) 243 (log $\epsilon$ 3.77), 288 nm (log $\epsilon$ 3.23); ir (Nujol) 1120, 1050 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 2.20–