

ticular we have examined the $n_N \rightarrow 3s$ transitions of ammonia and some alkylated amines and the $N \rightarrow V$ and $N \rightarrow R$ transitions of ethylene and some of its alkylated derivatives using He, Ne, Ar, N_2 and CF_4 as perturbing gases.

- 1 M. B. Robin, *Higher Excited States of Polyatomic Molecules*, Vol. I, Academic Press, New York, 1974.

C5

Excited Electronic States of α -, β -, and γ -Dicarbonyls

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The lower-energy $^1\Gamma_{n\pi^*}$ states of dicarbonyls will be discussed on the basis of optical absorption, photoelectron spectroscopic and theoretical results. Examples of molecules which exhibit multiple $^1\Gamma_{n\pi^*}$ excited states will be presented. Vacuum ultraviolet spectra of mono- and dicarbonyls will be presented and analysed, particular emphasis accruing to the utility of one- and two-chromophore models for the dicarbonyl Rydberg states.

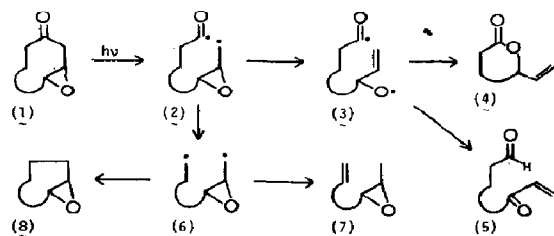
E6

The Photochemistry of β , γ -Epoxy Cyclic Ketones

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A general scheme is proposed to summarize the photochemistry of β , γ -epoxy cyclic ketones. Irradiation of a β , γ -epoxy cyclic ketone (1) initially leads to Norrish Type I bond cleavage and the formation of an apparent diradical species 2 which undergoes subsequent epoxide ring opening to give the acylalkoxy diradical 3. Unless specific sub-



stituent and/or skeletal constraints are present, product formation proceeds from 3 by competitive ring closure to give lactone 4 and hydrogen transfer to provide aldehyde 5. If the formation of either 4 or 5 is prevented, then the other product predominates. If the formation of both 4 and 5 is precluded, then decarbonylation occurs to give diradical 6 which undergoes disproportionation to provide 7 and/or ring closure to afford 8. Each of these possible contingencies has been examined experimentally.

E7

Reactivity of Carbonyl $^1n, \pi^*$ States Toward Alkyl Amines

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We have investigated the bimolecular reactivity of $^1n, \pi^*$ states of eleven acyclic, cyclic and bicyclic alkyl ketones and five acyclic aldehydes toward the electron donors, diethylamine (DEA) and triethylamine (TEA), by monitoring amine quenching of carbonyl fluorescence. Observed bimolecular rate constants for quenching, k_q , are obtained from Stern-Volmer treatments of fluorescence quenching as a function of amine concentrations and the measured carbonyl fluorescence lifetime, τ_f . The effects of carbonyl and amine structure, as well as the nature of the solvent, on the observed k_q values are determined. We will note several key observations. (1) The k_q values for the ketones are found to be very sensitive to α -methyl substitution. For example, k_q for TEA quenching of acetone $^1n, \pi^*$ states is $2.7 \times 10^9 M^{-1} s^{-1}$, while k_q for TEA quenching of $^1n, \pi^*$ states of di-*tert*-butyl ketone is $< 4 \times 10^6 M^{-1} s^{-1}$. (2) DEA, although it has a higher oxidation (or ionization) potential than TEA, is consistently a somewhat better quencher of carbonyl excited singlets in hexane than TEA. (3) The observed k_q values are only minimally effected by solvent changes. (4) Acetone $^1n, \pi^*$ states are determined to be about an order of magnitude more reactive toward amine quenching than acetone $^3n, \pi^*$ states. (5) Alkanal $^1n, \pi^*$ states are found to be 5 - 10 times more reactive toward TEA quenching than alkanones $^1n, \pi^*$ states.

Overall, our results indicate that quenching of carbonyl $^1n,\pi^*$ states by alkyl amines occurs in an initially formed encounter complex, in competition with diffusion apart of the encounter complex. Steric effects suggest that the quenching requires a specific orientation of the carbonyl compound and the amine in the encounter complex. Quenching appears to occur by interaction of the electrophilic half-vacant oxygen n orbital of the n,π^* excited state and the lone pair electrons on the amine to form a charge-transfer complex [2]. Calculations of the free-energy change for formation of charge-transfer complexes between carbonyl S_1 states and alkyl amines indicate that complex formation is sufficiently exothermic that amine oxidation potential and solvent polarity would be expected to have little effect on the observed k_q values [3]. The observation that acetone $^1n,\pi^*$ states are more reactive than acetone $^3n,\pi^*$ states toward amine quenching, is consistent with the lower free energy change asso-

ciated with formation of the charge-transfer complex from the higher energy $^1n,\pi^*$ state. The greater reactivity of alkanal than alkanone n,π^* singlets toward TEA quenching is attributed to steric effects.

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- 1 R. W. Yip, R. O. Loutfy, Y. L. Chow and L. K. Magzinski, *Can. J. Chem.*, 50 (1972) 3426.
- 2 See, for example, S. G. Cohen, A. Parola and G. H. Parsons, Jr., *Chem. Rev.*, 43 (1973) 141.
- 3 For related calculations, see (a) R. O. Loutfy and R. O. Loutfy, *Can. J. Chem.*, 50 (1972) 4052; (b) J. B. Guttenplan and S. G. Cohen, *J. Amer. Chem. Soc.*, 94 (1972) 4040; (c) J. G. Guttenplan and S. G. Cohen, *Tetrahedron Letts.*, (1972) 2163.

E8

On the Chemistry of Cyclic Ketones Containing Photochemically Generated Twisted Double Bonds

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When ketones 1 - 4, which have nearly identical chromophores and similar structures, are irradiated in an inert solvent, the resulting products have grossly different structures, or there may be no net reaction, as shown:

