

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 $\alpha$ -, $\beta$ -, and $\gamma$ -Dicarbonyls

P. BRINT and S. P. McGLYNN

*Department of Chemistry, The Louisiana State University, Baton Rouge, La. 70803 (U.S.A.)*

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.

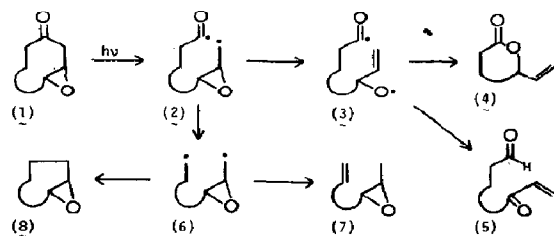
### E6

#### The Photochemistry of $\beta$ , $\gamma$ -Epoxy Cyclic Ketones

R. K. MURRAY, Jr., T. K. MORGAN, Jr., J. A. S. POLLEY, C. A. ANDRUSKIEWICZ, Jr., and D. L. GOFF

*Department of Chemistry, University of Delaware, Newark, Del. (U.S.A.)*

A general scheme is proposed to summarize the photochemistry of  $\beta$ ,  $\gamma$ -epoxy cyclic ketones. Irradiation of a  $\beta$ ,  $\gamma$ -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

J. C. DALTON, J. J. SNYDER and M. C. GEIGER

*Department of Chemistry, University of Rochester, Rochester, N. Y. 14627 (U.S.A.)*

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,  $\tau_f$ . 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  $\alpha$ -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.