

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.

This research has been supported by the Merck Foundation, the Research Corporation and the Petroleum Research Fund, administered by the American Chemical Society.

- 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.

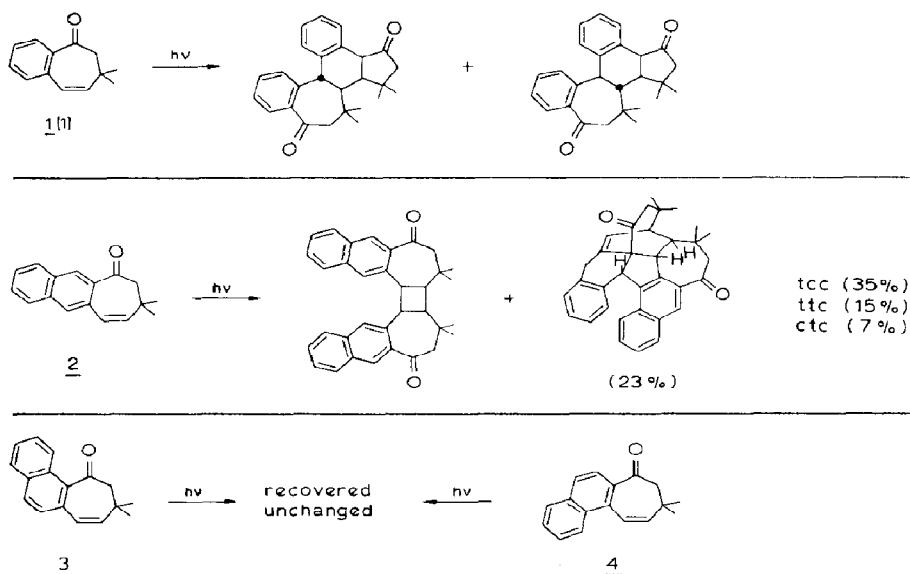
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On the Chemistry of Cyclic Ketones Containing Photochemically Generated Twisted Double Bonds

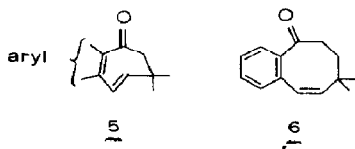
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When ketones 1 - 4, which have nearly identical chromophores and similar structures, are irradiated in an inert solvent, the resulting products have grossly different structures, or there may be no net reaction, as shown:



Nevertheless, the primary photochemical process in all cases appears to be identical. These reactions proceed via a trans cycloheptadienone **5** or an excited state with a similarly twisted geometry. This conclusion is supported by the results of trapping experiments and of product studies on the eight-membered ring analog, **6**.



The dimerization mechanisms will be discussed. The wide structural variation of the dimers is a consequence of subtle reactivity differences in the reactive species and in the substrates with which they react. These results will be compared with previous studies on strained seven [2] and eight-membered [3] rings. [4]

We thank the National Institutes of Health for a grant (GM-15997) in support of this research.

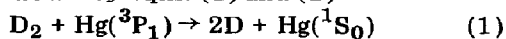
- 1 H. Hart, T. Miyashi, D. N. Buchanan and S. Sasson, *J. Am. Chem. Soc.*, **96** (1974) 4857.
- 2 E. J. Corey, M. Tada, R. LeMahieu and L. Libit, *J. Am. Chem. Soc.*, **87** (1965) 2051; P. E. Eaton and K. Lin, *ibid.*, **87** (1965) 2052; H. Nozaki, M. Kurita and R. Noyori, *Tetrahedron Lett.*, (1968) 2025; H. Nozaki, and M. Kurita, *ibid.*, (1968) 3635.
- 3 P. E. Eaton and K. Lin, *J. Am. Chem. Soc.*, **86** (1964) 2087; J. K. Crandall and R. P. Haseltine, *ibid.*, **90** (1968) 625; R. Noyori, A. Watanabe and M. Kato, *Tetrahedron Lett.*, (1968) 5443; T. S. Cantrell and J. S. Salomon, *J. Am. Chem. Soc.*, **92** (1970) 4656; R. Noyori, H. Inoue and M. Kato, *ibid.*, **92** (1970) 6699; G. L. Lange and E. Neidert, *Tetrahedron Lett.*, (1971) 4215 and (1972) 1349; J. K. Crandall, C. F. Mayer, J. P. Arrington and R. J. Watkins, *J. Org. Chem.*, **39** (1974) 248.
- 4 For reviews, see P. E. Eaton, *Accounts Chem. Res.*, **1** (1968) 50; O. L. Chapman and D. S. Weiss, *Organic Photochemistry*, Marcel Dekker, Inc., New York, **3** (1973) 215.

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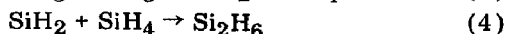
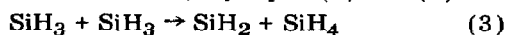
Mercury Photosensitized Reactions of Silyl Radicals

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Deuterium atoms, formed by mercury photosensitization in a flow system coupled to a mass spectrometer, react with monosilane to form silyl radicals and hydrogen-d₁ as shown by eqns. (1) and (2)



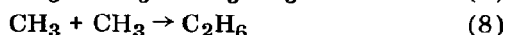
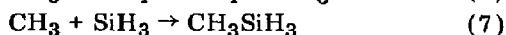
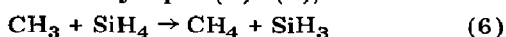
With only deuterium and monosilane present in the flow system, the silyl radicals react with each other to form disilane, which is the only significant product observed. When mixtures of monosilane-d₀ and monosilane-d₄ are subjected to D-atom attack via eqn. (2), isotopically labelled disilane is produced. Detailed mass spectrometric studies of the dependence of this isotopic distribution on ionizing electron energy show the virtual absence of Si₂D₃H₃ and thus confirm recent reports [1, 2] that disilane is formed from silyl radicals solely by eqns. (3) and (4).



In the presence of methyl chloride the rapid abstraction of chlorine atoms by silyl radicals (5) competes effectively with eqn. (3) so that monochlorosilane is formed simultaneously with disilane. Under the conditions of our experiments



methane, methylsilane and ethane are observed in comparable amounts. This suggests that the methyl radicals formed in (5) are consumed by eqns. (6) - (8), viz.



The relative rates of formation of disilane and chlorosilane are such that, with the assumption that k_3 is equal to the specific collision rate of SiH₃ radicals, a value of $k_6 \sim 2 \times 10^{-16} \text{ cm}^3/\text{s}$ is obtained. This rather large rate constant at 300 °K is consistent with the fact that the Si-Cl bond is much stronger than the C-Cl bond.