

PHOTOCHEMISTRY OF 6-SUBSTITUTED 2-METHYL-
2-ALKOXYCARBONYLCYCLOHEXANONES

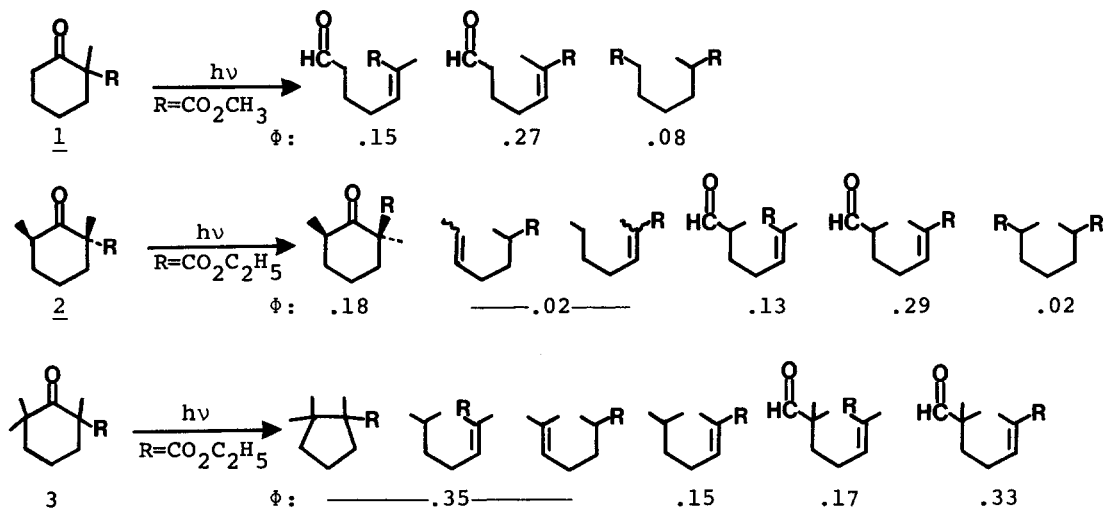
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Ketone photochemistry,¹ the Norrish type I reaction of cyclic ketones in particular, has received considerable mechanistic attention² and some synthetic application.³ The primary photoproduct of this reaction, an acyl alkyl biradical, can and often does cascade to a multitude of products the variety apparently being determined mainly by structural features in the biradical. Therefore, a knowledge of these features is obviously of considerable relevance in terms of biradical chemistry as well as for the rational design of synthetic applications of ketone photochemistry. Recently, some of the effects of molecular structure on the disproportionation reactions resulting in alkenals and ketenes,² and the oxycarbene producing ring closure,⁴ have been elucidated. Our interest is in the decarbonylation reaction, and although it has been known for some time that radical stabilizing substituents facilitate photochemical α -cleavage^{1,2} as well as acyl radical decarbonylation,⁵ studies were often carried out on molecules in which processes other than decarbonylation were structurally suppressed. We wish to report our results on the photochemistry of three 2-methyl-2-alkoxycarbonylcyclohexanones in which the competition between decarbonylation, disproportionation and reclosure of the acyl alkyl biradical intermediate has been quantitatively determined as a function of structure.

Irradiation of compounds 1-3 in cyclohexane-methanol(ethanol) resulted in the products shown with the indicated quantum yields.⁶ The reactions of 1 and 2 were quenched with trans-1,3-pentadiene resulting in nonlinear Stern-Volmer behavior and the formation of new, unidentified, products. However, by taking the Stern-Volmer slopes from the linear, low quencher concentration portion of the plots,⁷ we estimate that $\tau^{-1} = 6 \times 10^9 \text{ sec}^{-1}$ for both 1 and 2.⁸ Assuming that the rate of α -cleavage is influenced only by the α -substituents and that this determines the triplet lifetime ($\tau^{-1} = 1.1 \times 10^7 \text{ sec}^{-1}$ for cyclohexanone,⁹ $\tau^{-1} = 2.6 \times 10^8 \text{ sec}^{-1}$ for 2-methylcyclohexanone,⁹ and $\tau^{-1} = 1.8 \times 10^9 \text{ sec}^{-1}$ for 2,2-dimethylcyclohexanone¹⁰), we predict that about 100%, 96% and 77% of the cleavage should occur at the α -carbon bearing the alkoxy carbonyl substituent in 1, 2 and 3, respectively. The increased rate of cleavage occasioned by the



alkoxycarbonyl group, 1 cleaves 3.3 times faster than 2,2-dimethylcyclohexanone, is reasonable and indicates that this substituent is slightly better than methyl at stabilizing an adjacent radical.¹¹ The extent to which cleavage actually occurs on the opposite side of the carbonyl is difficult to ascertain with certainty since both acyl alkyl biradical intermediates would necessarily give rise to the same reclosure and decarbonylation products. However, a surprising observation is that disproportionation products resulting from the alternative α -cleavage mode are not observed even from 3 where a significant fraction of the excited states must fragment in this manner.

The quantitative information we have obtained permits us to analyze the observed chemistry in terms of the behavior of the α -cleavage produced acyl alkyl biradicals which undergo three competing processes: recombination, disproportionation and decarbonylation. Cleavage in compounds 1 and 2 occurs almost exclusively at the alkoxy carbonyl substituted carbon (call this cleavage mode-A) to produce biradicals which have reclosure probabilities of 0.50 and 0.54, respectively, the latter producing 2 and its epimer¹² in a 2:1 ratio. In addition, disproportionation occurs with probabilities of 0.50 and 0.44 and decarbonylation is only a minor contributor to the photochemistry of 2. The behavioral similarities between the biradicals from 1 and 2 are reasonable since the extra methyl group in 2 should have relatively little effect on the transition states for reclosure and disproportionation and although the acyl radical from 2 should decarbonylate with a lower activation energy than that from 1, the activation energies and A factors for disproportionation vs. decarbonylation are such that at room temperature little of the latter process is expected.¹⁴

The contrast between the photochemistry of 1 and 2 vs. 3 is remarkable. Based upon the rates of cleavage in 1 and 2, we expect significant (23%) cleavage at the carbon bearing the dimethyl substituents (cleavage mode-B) yet the products which would result from disproportionation of this biradical are not observed. Since the total quantum yield for product formation from 3 is unity, we must conclude that this acyl radical undergoes decarbonylation with a probability of 1.00.¹⁵ This unusual behavior is underscored by the observation that the biradical produced by mode-A cleavage undergoes disproportionation and decarbonylation in a ratio of 65:35, a result which is in line with the reported photochemistry of 2,2,6,6-tetramethylcyclohexanone.¹⁶ The dramatic differences in behavior of these two acyl alkyl biradicals could be due to two factors: an increase in the steric requirements for disproportionation of the mode-B intermediates and/or a decrease in the activation energy for decarbonylation of this species. Examination of the six-membered ring transition states for disproportionation indicates that they should not have significantly different steric requirements, and it is known that the steric influence of a methoxycarbonyl substituent on a cyclohexane ring is less than that of methyl.¹⁷ On the other hand, the alkoxycarbonyl substituent stabilizes an adjacent radical better than methyl,¹¹ and we believe that this is the major determining factor in the chemistry of these biradicals. If this is so, and the A factors are assumed equivalent, we estimate 3.0 kcal/mol as the approximate difference in activation energies for decarbonylation of the mode-A vs. the mode-B acyl radicals.

In summary, by quantitatively studying the photochemistry of compounds 1, 2 and 3, we have been able to assess the effect of radical stability, stabilization by alkoxycarbonyl vs. methyl, on the α -cleavage reaction and on the subsequent reactions of the acyl alkyl biradical. Our results show that the slightly greater stabilization afforded a radical center by the alkoxycarbonyl substituent will not only substantially increase the rate of α -cleavage but will in some cases also dramatically shift the delicate balance which exists between recombination, disproportionation and decarbonylation of the acyl alkyl biradical intermediate in favor of the latter process.

References

- (a) J. C. Dalton and N. J. Turro, Ann. Rev. Phys. Chem., 21, 499 (1970); (b) O. L. Chapman and D. S. Weiss, Org. Photochem., 3, 197 (1973); (c) R. Srinivasan, Adv. in Photochem., 1, 83 (1963).
- (a) N. J. Turro, J. C. Dalton, K. Dawes, G. Farrington, R. Hautola, D. Morton, M. Niemczyk and N. Shore, Acc. Chem. Res., 5, 92 (1972); (b) W. C. Agosta and S. Wolff, J. Am. Chem. Soc., 98, 4182 (1976), ibid., 99, 3355 (1977); (c) N. C. Yang and R. H.-K. Chen, J. Am. Chem. Soc., 93, 530 (1971); (d) J. D. Coyle, J. Chem. Soc. (B), 1736 (1971);

- (e) W. B. Hammond and T. S. Yeung, Tetrahedron Lett., 1169 (1975); (f) J. C. Dalton, K. Dawes, N. J. Turro, D. S. Weiss, J. A. Barltrop and J. D. Coyle, J. Am. Chem. Soc., 93, 7213 (1971).
3. (a) J. P. Morizur, G. Bidan and J. Kossanyi, Tetrahedron Lett., 4167 (1975); (b) A. P. Krapcho and F. J. Waller, J. Org. Chem., 37, 1079 (1972).
 4. P. Yates, J. Photochem., 5, 91 (1976).
 5. (a) G. Quinkert, K. Opitz, W. W. Wiersdorff and J. Weinlich, Tetrahedron Lett., 1863 (1963); (b) J. E. Starr and R. H. Eastman, J. Org. Chem., 31, 1393 (1966).
 6. Solutions of 0.02-0.05 M were irradiated with a Hanovia 450-W mercury lamp through a filter solution of basic potassium chromate (transmission maximum 313 nm). Quantum yields were determined relative to 2-methylcyclohexanone^{2f} at less than 6% conversion to products. Product ratios were determined by gas chromatography (5% Carbowax 20M) and are not corrected for detector response because for those compounds checked corrections of 5% or less were indicated. Products were isolated by preparative gas chromatography and the structures assigned on the basis of, and are entirely consistent with, nmr, ir, and mass spectroscopic properties.
 7. At 1.2 M diene in cyclohexane, the Stern-Volmer slopes for quenching of the major enal from 1 and 2 were 1.1 and 1.0, respectively, and both plots had correlation coefficients of 0.94. k_q in cyclohexane was taken to be $6.6 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$.
 8. The fluorescence quantum yields (0.0037, 0.0050 and 0.011 for 1, 2 and 3) indicate that these reactions most likely occur from the triplet state.
 9. D. S. Weiss, N. J. Turro and J. C. Dalton, Mol. Photochem., 2, 91 (1970).
 10. P. J. Wagner and R. W. Spoerke, J. Am. Chem. Soc., 91, 4437 (1969).
 11. E. N. Cain and R. K. Solly, J. Am. Chem. Soc., 95, 4791 (1973), estimate a 1 kcal/mol stabilization difference.
 12. These compounds were differentiated on the basis of the 2-methyl substituent chemical shifts of δ 1.28 and 1.45 for 2 and its epimer, respectively.¹³
 13. S. J. Branca and A. J. Smith, III, J. Org. Chem., 42, 1026 (1977).
 14. The effect of temperature on the photochemistry of these compounds has been determined and the results used to formulate a more detailed mechanistic picture which will be presented elsewhere.
 15. It is possible that the low yield decarbonylation products from 2 are also the result of mode-B α -cleavage.
 16. R. Eastman and J. Beard, Tetrahedron Lett., 3029 (1970).
 17. F. R. Jensen, C. H. Bushweller and B. H. Beck, J. Am. Chem. Soc., 91, 344 (1969).