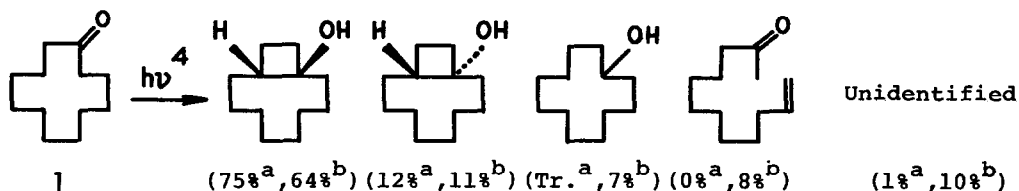


PHOTOCHEMISTRY OF 2-METHYLCYCLODODECANONE.

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(Received in USA 20 December 1976; received in UK for publication 28 January 1977)

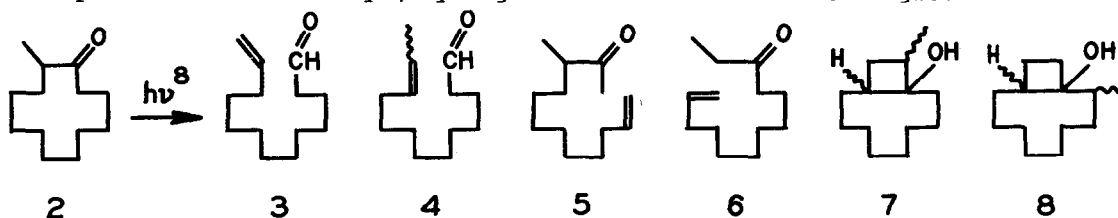
The photochemistry of medium ring-cycloalkanones typified by cyclododecanone (1) is dominated by γ -hydrogen abstraction as the primary photochemical process for both the $^1(n,\pi^*)$ and $^3(n,\pi^*)$ excited states, and products resulting from closure, disproportionation and cleavage of the resulting biradical are found.¹ Discrepancies in the reported products and product ratios may reflect subtle differences in reaction conditions and their effects on the mobile conformational equilibria of this ketone.^{2,3}



Noticeably absent in these photolyses are products resulting from α -cleavage as the primary photochemical event. This reaction dominates the photochemistry of small ring cycloalkanones⁵ and has been extensively studied with respect to both the primary process⁶ and factors influencing the behavior of the acyl alkyl biradical intermediate.⁷ In general, it has been found that for cyclopentanones and cyclohexanones, the $^3(n,\pi^*)$ state is more reactive than the $^1(n,\pi^*)$ state toward α -cleavage,⁶ and the acyl alkyl biradical intermediate is sufficiently long-lived to make conformational equilibration of prime importance in product formation.⁷ Where both α -cleavage and γ -hydrogen abstraction are available primary processes, it is possible to predict the relative importance of each by comparison of the rates of these processes in appropriate model

compounds for the excited state under consideration.^{5,6b} Analysis of cyclo-dodecanone photochemistry in this manner predicts only γ -hydrogen abstraction from $^1(n,\pi^*)$ but about 4% α -cleavage in $^3(n,\pi^*)$. Thus, as predicted, the photochemistry of this compound is dominated by γ -hydrogen abstraction. However, this analysis neglects subsequent reactions of biradical intermediates and therefore will not necessarily reflect quantum yield ratios, so the lack of α -cleavage products may be due to efficient reclosure of the biradical intermediate rather than the absence of the primary process.

To determine the importance of structural factors in the photochemical behavior of medium ring cyclic ketones, we have examined the photochemistry of 2-methylcyclo-dodecanone (2) under a variety of reaction conditions. An analysis of the type described above predicts that 2 should show 40% α -cleavage from the triplet state and mainly γ -hydrogen abstraction from the singlet.

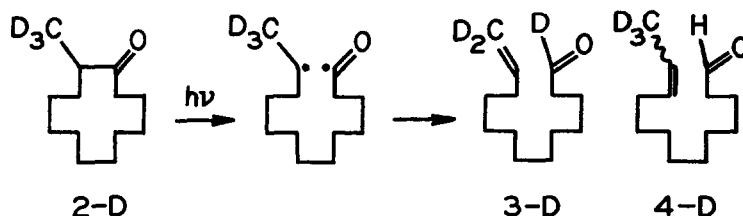


The photochemistry of 2 is as predicted and products derived from both α -cleavage and γ -hydrogen abstraction are isolated.⁸ The alkenals (3, 4, $\phi = .19^9$), alkenones (5, 6) and cyclobutanols (7, 8) were isolated and spectroscopically analyzed as mixtures. Gas chromatographic product ratios after 5 hours irradiation ($\sim 25\%$ conversion) were as follows: benzene, 85% (3+4), 5% (5+6), 10% (7+8); cyclohexane, 77% (3+4), 6% (5+6), $<17\%$ (7+8).^{10a,b} Careful analysis of the vinyl region in the 100 MHz nmr spectrum of (3+4) allowed determination of $89 \pm 1\%$ 3 and $11 \pm 1\%$ 4 (mainly trans) for this mixture. With longer irradiation times photodecarbonylation products of the aldehydes were observed.

Since γ -hydrogen abstraction is usually a singlet and triplet state process while α -cleavage involves mainly the latter, it was of interest to determine the excited state(s) responsible for the photochemistry of 2. Production of alkenal (3, 4) was quenched by trans-1,3-pentadiene giving a linear Stern-Volmer plot, $k_q \tau = 30$, indicating that mainly the triplet state is involved in this process,¹¹ and that the rate constant for α -cleavage in 2 is quite similar to that of 2-methylcyclohexanone.^{6b} On the other hand, formation of 5 and 6 did not appear to be quenched to the same extent. Because of the low yields of these products, quantitative analysis was difficult but our observations are consistent with singlet state involvement in γ -hydrogen abstraction.

The production of 3 was unexpected since disproportionation of the acyl-alkyl biradical intermediates from small ring cycloalkanones usually produces alkenals of the type 4.^{5,6,7} To be certain of our structure assignments, 2-trideuteromethylcyclo-dodecanone (2-D) was synthesized and irradiated under the

same conditions as 2. The expected labeling results are shown below. Since terminal alkene formation involves deuterium abstraction while the alternative is hydrogen abstraction, the two processes are readily distinguished.



Careful analysis of the 100 MHz nmr spectrum of the deuterium labeled alkenal mixture¹² confirmed the structure assignments and indicated a product ratio of (75±2%) 3-D to (25±2%) 4-D. Assuming that the differences in the product ratios of the alkenal fraction from 2 and 2-D are due mainly to a deuterium isotope effect in disproportionation of 2 to 3, an isotope effect $k_{\text{H}}/k_{\text{D}} = 1.19 \pm 0.04$ is obtained. This value is unexceptional and consistent with other recently reported values for the disproportionation of biradicals produced by photochemical α -cleavage.¹³

In conclusion, 2-methylcyclohexanone, unlike the non-methylated ketone, undergoes both α -cleavage and γ -hydrogen abstraction primary processes. The former, occurring from the triplet state with a rate constant similar to that of 2-methylcyclohexanone, accounts for most of the isolated product. Disproportionation of the acyl alkyl biradical intermediate occurs with preferential abstraction from the methyl rather than the methylene group, with a small deuterium isotope effect. Possible reasons for this preference and the photochemistry of smaller ring 2-methylcycloalkanes will be discussed in a subsequent paper.

Acknowledgment. We wish to thank the University of Michigan for financial support.

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8. 0.02 M solutions were purged with nitrogen and irradiated through Pyrex with a 450W Hanovia high pressure mercury lamp. Product isolation was accomplished by preparative gas chromatography and product ratios determined by integration (uncorrected for response factors) except where otherwise indicated. Structures were assigned on the basis of and are entirely consistent with observed nmr, ir and mass spectroscopic properties.
9. Quantum yield in benzene (.05 M) relative to 2-methylcyclohexanone. ^{6b}
10. (a) When irradiated in benzene with methanol no new products were observed indicating the absence of ketene formation;^{5,6,7} (b) The quantum yield of (3+4) and the relative amount of (5+6) determined by gas chromatography at low conversions is not influenced by solvent: benzene, cyclohexane, t-butanol and benzene with 20% methanol. However, in acetonitrile the yield of (5+6) is cut in half with (3+4) remaining as in the other solvents.
11. A maximum of 5% singlet participation is possible.
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