

REINVESTIGATION OF THE PHOTODECOMPOSITION OF 3-DIAZO-4-HEPTANONE

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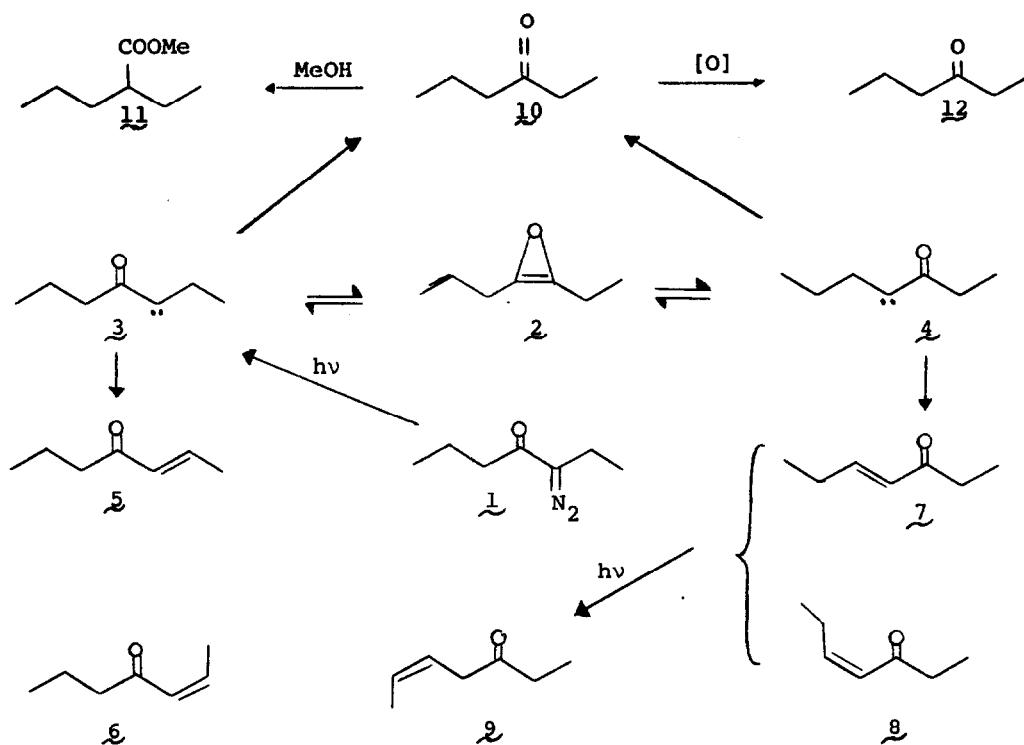
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(Received in USA 12 April 1977; received in UK for publication 17 May 1977)

Oxirenes have long been of theoretical and synthetic interest.² This interest has intensified in recent years, since oxirene may be considered a potential 4π anti-aromatic system.³ Despite several early incorrect claims, an oxirene has never been isolated or even detected directly.⁴ Nevertheless, oxirenes have been postulated as intermediates in various transformations, most notably in the thermal and photochemical decompositions of α -diazo ketones and in the peracid oxidations of acetylenes.² Compelling evidence for the intermediacy of oxirenes has been provided by photochemical decomposition of isotopically labelled α -diazo ketones⁵ and by thermal and photochemical decomposition of unsymmetrically substituted α -diazo ketones.⁶ Theoretical calculations have suggested that oxirenes may exist as stable intermediates;⁷ however, more recent calculations have contradicted this conclusion.⁸

Our interest in oxirenes led us to the use of dissimilar alkyl substituents as a chemical probe for the intermediacy of oxirenes in various reactions. Thus we were prompted to reinvestigate the photodecomposition of 3-diazo-4-heptanone (1), as reported initially by Matlin and Sammes.⁶ From the beginning, we found considerable discrepancies between our observations and those of Matlin and Sammes, and we wish to report our findings here. The results of our irradiations of diazo ketone 1 at 300 nm in pentane and ether solutions are summarized below and in the table.⁹

Since the formation of 3-enones 7, 8, and 9 involves oxygen migration and equilibration between oxocarbenes 3 and 4, the intervention of an intermediate or transition state such as oxirene 2 is clearly implicated by these results. A pseudo-symmetrically substituted oxirene such as 2 is expected to partition itself equally between the two different oxocarbenes, ultimately to produce equal amounts of the 3- and 4-enones. From our results, a comparison of the amount of 3-enone products formed to the total enone product indicates a minimum of 85-88% oxirene involvement in the formation of these enone products.

Photodecomposition of 3-Diazo-4-Heptanone^a

Solvent	Percentage Yields ^b							Total	% Oxirene 2 ^d
	5	6	7	8	9	11	12		
Pentane	13	16	11	11	1	-	13	65	88
Pentane ^c (MeOH)	14	17	12	10	1	27	-	81	85
Ether	13	17	11	11	1	-	13	66	87
Ether ^c (MeOH)	13	16	11	11	1	28	-	80	88

^aIrradiations were performed using either Rayonet RPR-100 or RMR-400 photochemical reactors equipped with RPR-3000 Å lamps. The diazo ketone solutions (ca. 0.03 M) were contained in Pyrex vessels and were degassed by bubbling through nitrogen.

^bReported yields were obtained from calibrated vpc measurements.

^cApproximately 10% (v/v) of methanol was added after the irradiation was completed.

$$\text{d} \text{ \% Oxirene} = 2 \left[\frac{7+8+9}{5+6+7+8+9} \right]$$

Irradiations were carried out until all of the diazo ketone was consumed, as indicated by disappearance of the diazo absorption at ca. 2100 cm^{-1} in the ir spectrum. In all cases, disappearance of this absorption was accompanied by simultaneous appearance of an absorption at ca. 2050 cm^{-1} , which is assigned to the Wolff rearrangement product, ketene 10. The identity of 10 was established by conversion with methanol to methyl ester 11, which was identical in all respects with an authentic sample prepared by reaction of diazomethane with α -ethylvaleric acid.¹⁰ Alternatively, ketene 10 was adventitiously oxidized during workup to 3-hexanone (14). Identical results in all respects were obtained whether the irradiations of 1 were carried out through Pyrex using 2537 Å, 3000 Å, or medium pressure mercury lamp sources.

Control experiments verified that no interconversion occurs between 3-heptenones and 4-heptenones under the conditions of the irradiations. Further, enone 9 was demonstrated to arise from photodeconjugation of enones 7 and 8, although this secondary reaction may be minimized by carrying out the photolyses only until diazo ketone 1 has been completely decomposed. In addition, it was found that prolonged irradiation does result in decomposition of ketene 10, together with the other photo-products, however slowly, to yield a much more complex product mixture in much diminished total yield.

The foregoing results are in sharp contrast to those reported by Matlin and Sammes.⁶ These authors report relatively low yields (ca. 30% total) of very complex product mixtures. Moreover, they report only very small amounts of products such as ketone 12 derived directly from ketene 10; even when the photodecomposition of 1 was carried out in aqueous dioxane, they report only small amounts of acid product. We believe that the previously reported complex product mixtures arise from secondary photolysis of ketene 10¹¹ and the initially formed heptenone products. As such, these products do not represent the products obtained directly from the oxirene-oxocarbene equilibrium [3 \rightleftharpoons 2 \rightleftharpoons 4]. In short, because of the interception of ketene 10, we believe that the results reported herein more accurately represent the oxirene-oxocarbene equilibrium and the extent to which oxirene 2 is an intermediate in the photodecomposition of 3-diazo-4-heptanone (1). The present report has demonstrated that this photodecomposition proceeds smoothly and in high yield. Moreover, it has shown that oxirene intermediacy in the reaction is even more significant than originally reported. It appears fortuitous that both the present findings and those of Matlin and Sammes obtained proportionately the same amounts of 3-heptenones, and, therefore, the same degree of oxirene involvement.

The present results have verified that the method of Matlin and Sammes employing dissimilar alkyl substituents is a very useful and simple test for the intermediacy of oxirenes. We intend to utilize this labelling technique further to investigate the involvement of oxirenes in other reactions in which they have been proposed as intermediates.

Acknowledgements. This work was supported in part by a Cottrell College Science Grant from Research Corporation. Additional support was provided by the Chemistry Departments of Bucknell University and the University of Colorado. We are also grateful to Dr. Shelby A. Sherrod and Mr. Kenneth Kolonko for assistance with the analytical problems and to Ms. Sarah Updike for preparing a sample of 3-diazo-4-heptanone.

References and Notes

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