On the Oxocarbene – Oxirene Equlibrium

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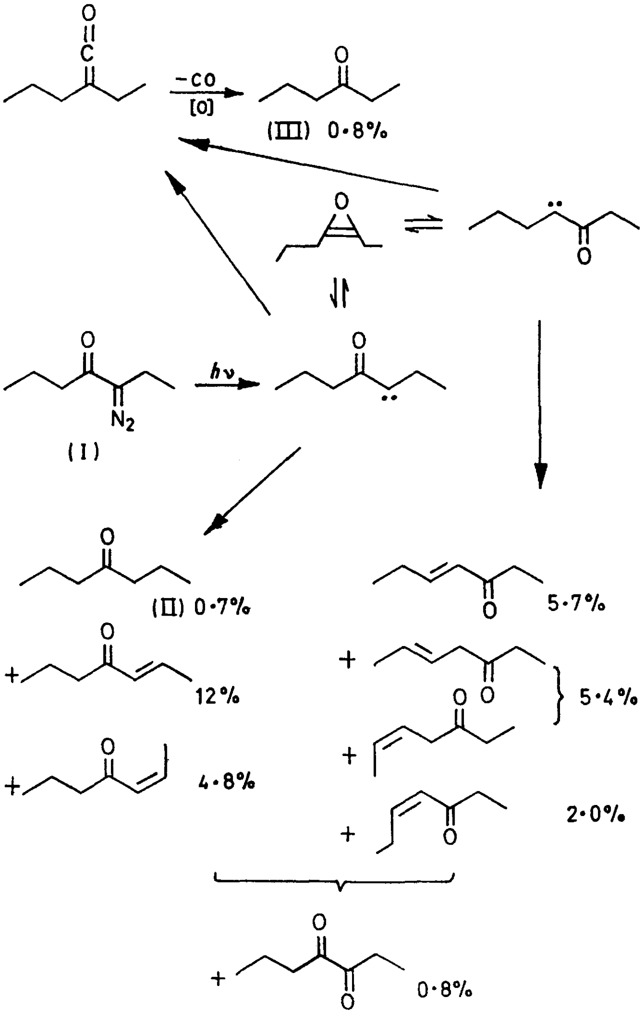
Summary A simple chemical test for the participation of oxirenes in the decomposition of certain α-diazoketones has been devised; results are reported for 3-diazoheptan-4-one.

Evidence for the formation of oxirenes in the photochemical decomposition of α-diazoketones has recently been presented by Strausz and his co-workers,[1] who used a ^{13}C-tracer technique, analysing for the mixture of labelled and unlabelled carbon monoxide formed. Oxirene formation has also been postulated to occur in the peracid oxidation of alkynes.[2]

We have devised a simple chemical test for the participation of oxirenes in the decomposition of α-diazoketones. The method is based on the known alternative fate of oxocarbenes which bear adjacent methylene groups, *viz.* hydrogen migration leading to an αβ-unsaturated ketone.[3] If the oxocarbene intermediate can equilibrate with an oxirene, suitable substitution of the starting diazoketone would lead to two isomeric αβ-unsaturated ketones. *E.g.* photolysis of 0·025M 3-diazoheptan-4-one (I)[4] in anhydrous ether, using a 450 W medium-pressure mercury lamp (Pyrex filter) gave the results shown (Scheme).† Products were, in the first instance, analysed by combined g.l.c.–mass spectrometry. The unsaturated ketones formed were also characterised by comparison with authentic samples, as were heptan-4-one (II) and hexan-3-one (III).‡

The absolute yield of the unsaturated ketones was 30% of which 43% had the oxygen substituent rearranged into the 3-position. Assuming a true equilibrium between the isomeric oxocarbenes, *via* participation of an oxirene, this implies 86% involvement of ethylpropyloxirene in the formation of the unsaturated ketones. Intermolecular oxygen transfer was ruled out by dilution studies, which gave similar product ratios. Thus, oxygen migration must proceed *via* transient participation of an unstable oxirene species, a result consistent with that of Strausz *et al.*[1] and in contrast to that of earlier workers.[5] We have also observed similar rearrangements in the photolysis



Scheme

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† The βγ-unsaturated ketones arise by further photochemical reaction of the initial αβ-unsaturated isomers. G.l.c.–mass spectral analysis showed no hept-1-en-4-one, which is known to be particularly unstable with respect to its conjugated form (M.E.E. Blaise, *Bull. Soc. chim. France*, 1905, **33**, 39).

‡ The photochemical reactions were carried out under oxygen-free nitrogen; hexan-3-one arises by the rapid autoxidation of ethyl propyl keten during work-up (see H. Staudinger, K. Dyckerhoff, H. W. Klever, and K. Ruzicka, *Ber.*, 1925, **58**, 1079).

of 1-diazo-3-phenylpropan-2-one and 1-diazoheptan-2-one.

Decomposition of the diazoketone (I) has also been carried out under a variety of conditions. No hepten-3-ones were observed when the photolysis was carried out in the presence of benzophenone under conditions in which the benzophenone was absorbing >95% of the light. This suggests that oxirene participation only occurs from a singlet carbene species.[6] Thermal decomposition of (I) in refluxing cyclohexane gave a reaction mixture very similar in content to that from the unsensitized photolysis. However, under these conditions, only 17·5% of the unsaturated ketone fraction had the rearranged (hepten-3-one) structure. A series of thermal decompositions of the neat diazoketone showed an increasing amount of oxirene participation with temperature (32·5% hepten-3-ones at 225 °C). The lower energy decomposition thus by-passes oxirene formation and this can be explained by operation of an alternative pathway involving a concerted hydrogen shift with nitrogen loss, yielding only (unrearranged) hepten-4-one.§

In the presence of metal catalysts, *e.g.* with silver oxide in either aqueous dioxan or anhydrous ether,[3] or with copper oxide in refluxing cyclohexane,[7] no evidence for oxirene participation could be found.

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§ As pointed out by a referee, the change in mechanism with temperature may merely reflect a higher activation energy for oxirene formation from the initial ketocarbene. A method for the possible differentiation of these alternatives is under study.

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[6] *Cf.* D. E. Thornton, R. K. Gosavi, and O. P. Strausz, *J. Amer. Chem. Soc.*, 1970, **92**, 1768.

[7] C. Grundman, *Annalen*, 1923, **536**, 29; for recent references see W. F. Erman and L. C. Stone, *J. Amer. Chem. Soc.*, 1971, **93**, 2821; and J. E. McMurry and T. E. Glass, *Tetrahedron Letters*, 1971, 2575.