

## PHOTOLYSIS OF $\alpha$ -BENZALDOXIME: HYDROXYL FREE-RADICAL INTERMEDIACY IN THE PHOTO-BECKMANN REARRANGEMENT

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### Summary

The photolysis of  $\alpha$ -benzaloxime in isopropanol, ethanol, methanol, cyclohexane and acetic acid gave, in addition to benzamide and benzaldehyde, products indicative of attack by  $\text{HO}^\cdot$  on the solvent molecules. Acetone, acetaldehyde, formaldehyde, cyclohexene and *p*-hydroxybenzaldehyde respectively are obtained. A mechanism is proposed involving homolysis of the N—O bond in the excited oxime molecule as the primary photochemical step.

### 1. Introduction

In 1963, Amin and De Mayo [1] examined the products of irradiation of  $\alpha$ -benzaloxime and reported the formation of benzamide. The highest yield obtained was reported when acetic acid was used as the solvent. In cyclohexane, methanol and dioxane the yield drops markedly (to a value of 6% - 12%). With no evidence other than reference to the report of Splitter and Calvin [2] on nitrene photoisomerization, an oxazirane intermediate was invoked. In a subsequent study, De Mayo and coworkers [3] observed the retention of  $^{18}\text{O}$  in the benzamide produced when  $^{18}\text{O}$ -labelled  $\alpha$ -benzaloxime was irradiated with an equimolar amount of unlabelled *p*-tolualdoxime in acetic acid. This result established the intramolecularity of the oxygen transfer and that the photo-Beckmann rearrangement resembles the normal Beckmann rearrangement only in so far as the products are concerned. However, the question as to whether an oxazirane intermediate is involved in the rearrangement to benzamide remained unanswered, particularly since phenyloxazirane itself is not known to rearrange thermally to benzamide. In the same year Oine and Mukai [4] examined the photolysis of 1,1-dimethyl-2-naphthalenone oxime. Although the stable oxazirane was successfully trapped by reaction with an added Schiff base, these researchers doubted that an oxazirane is a required intermediate in the photoisomerization to amides. Again, further irradiation or heating did not result in an increased production of the rearranged carboamide.

In this paper the photolysis products of  $\alpha$ -benzaldoxime are re-examined in various solvents to assess the primary photochemical step in the photoisomerization of benzaldoxime to benzamide.

## 2. Results

The photolysis of pure  $\alpha$ -benzaldoxime in isopropanol, ethanol, methanol, glacial acetic acid and cyclohexane was carried out by irradiating a 0.5 vol.% solution with a high pressure mercury arc (Philips HPK; 125 W) inserted inside a quartz tube immersed in the reaction system. The temperature was kept at 20 °C, and the extent of the reaction was monitored in terms of the oxime concentration by recording the UV spectrum of aliquots withdrawn. Experiments were run to about 50% conversion to minimize photodegradation of the primary photoproducts. After the irradiation had been discontinued, the bulk of the solution was smoothly distilled with precautions taken to avoid possible loss of volatile products. The residue was fractionated by column chromatography. Alumina was used throughout. The identification and purity of the products were determined using thin layer chromatography (TLC), IR and nuclear magnetic resonance (NMR) techniques. Solid derivatives of the carbonyl compounds were prepared whenever convenient.

Our results are summarized in Table 1. Benzamide, benzaldehyde and acetone are the chief products obtained in isopropanol. The formation of

TABLE 1  
Photolysis of  $\alpha$ -benzaldoxime

<i>Solvent</i>	<i>Products<sup>a</sup></i>	<i>Yield</i>	<i>Conversion<sup>b</sup> (%)</i>
Isopropanol	Benzamide	32.6%	46.7
	Benzaldehyde	67.4%	
	Acetone	60.9%	
Ethanol	Benzamide	28.6%	49.5
	Benzaldehyde	71.4%	
	Acetaldehyde	ND	
Methanol	Benzamide	26.2%	41.9
	Benzaldehyde	73.8%	
	Formaldehyde	ND	
Cyclohexane	Benzamide	22.1%	45.0
	Benzaldehyde	77.9%	
	Cyclohexene	72.4%	
Acetic acid	Benzamide	36.0%	60.0
	Benzaldehyde	25.0%	
	<i>p</i> -Hydroxybenzaldehyde	38.6%	

ND, not determined.

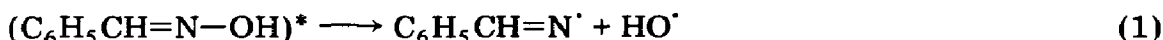
<sup>a</sup>The yields are based on the amount of oxime consumed.

<sup>b</sup>The percentage conversion was determined by NMR.

acetone is striking since this can only result from oxidation of the solvent. Similarly, in ethanol and methanol, acetaldehyde and formaldehyde are trapped by distillation into a solution containing 2,4-dinitrophenylhydrazine. The identification of the hydrazones was confirmed by their melting points and TLC. In cyclohexane, cyclohexene was characterized as the dibromide. In addition, NMR of the irradiated  $\alpha$ -benzaldoxime in cyclohexane gave a singlet at  $\delta = 5.5$  ppm, which is typical for cyclohexene olefinic protons. Interestingly, in acetic acid, *p*-hydroxybenzaldehyde is isolated. It was characterized using IR, NMR and by its melting point and by the melting point of its 2,4-dinitrophenylhydrazone derivative. A quantitative analysis was obtained by NMR for experiments in which the oxime was photolysed in the NMR tubes inserted in the cooling bath around the irradiation source.

### 3. Discussion

The number of dark reactions that the excited oxime molecule undergoes, *e.g.* *syn-anti* isomerization [5], Beckmann-type rearrangements [6], formation of nitriles [7], is indeed remarkable. However, a unified mechanism that can successfully account for the above pathways remains lacking. The results in Table 1 additionally indicate that oxidation of the solvent molecules also occurs. The formation of *p*-hydroxybenzaldehyde in the photolysis of  $\alpha$ -benzaldoxime in acetic acid as well as the initiation of methyl methacrylate polymerization by excited oxime molecules suggest that a free-radical mechanism operates and that homolysis of the N—O bond is conceivably the primary photochemical step producing a hydroxyl free-radical HO $\cdot$ :



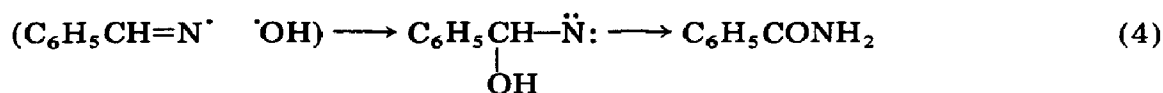
The highly reactive HO $\cdot$  that escapes the radical pair thus attacks the solvent molecules (RH) [8]:



The imine radical in step (1) can also abstract a hydrogen atom from the solvent, forming an imine that on hydrolysis produces benzaldehyde [9]. Steps (2) and (3) account for our results in Table 1.

Although the flash photolytic studies by Horne and Norrish [10] on formaldoxime and acetaldoxime and the results obtained by Sakuragi and coworkers [11] on *O*-acyl oximes of aromatic ketones which undergo homolytic N—O bond cleavage on excitation to their triplet states lend support to step (1) as the primary photochemical step, the competing production of benzamide in the photolysis of benzaldoxime raises the interesting question of the role of HO $\cdot$  in effecting the rearrangement. At this point, we can plausibly assume that the rearrangement results from a fast

addition of the HO<sup>•</sup> radical to the double bond of the imine radical, which is produced as a radical pair with OH<sup>•</sup> within the solvent cage, thus generating an electron-deficient nitrogen sextet:



Hydride migration leads to the photo-Beckmann product whereas intramolecular cyclization forms the suspected oxazirane [3]. In this formulation an oxazirane intermediate is not a prerequisite for the photo-Beckmann rearrangement to amides, but its formation is not negated either since mounting evidence for its production has been accumulated [12]. The above steps (2) - (4) are competing pathways and, if the mechanism presented is accurate, the relative yields of stable products ought to depend on the relative reactivity of the HO<sup>•</sup> radical towards the solvent molecules (out-of-cage reactions) compared with that of addition of OH<sup>•</sup> to the double bond of the imine radical (inside cage reactions). Thus, as a test of the above mechanism the yield of benzaldehyde is taken as a measure of the extent of the reactions taking place outside the cage and the yield of benzamide is assumed to give the extent of the reactions occurring within the solvent cage. If the mechanism is correct, then the ratio of the yields should be solvent dependent. In isopropanol, this ratio is 2.0 whereas in acetic acid it drops to 0.30 (*p*-hydroxybenzaldehyde, a product of intramolecular rearrangement, is added to the benzamide yield in the calculation). When it is taken into account that HO<sup>•</sup> abstracts hydrogen from isopropanol with a rate constant  $K = 2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  but that it abstracts hydrogen from acetic acid with a rate constant two orders of magnitude less ( $K = 3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ) [13, 14], our results appear to support the implicit assumptions that the collapse of the radical pair produced in step (1) leads to the variety of products observed in the photolysis of oximes and that the HO<sup>•</sup> radical is the species which is important in effecting the photo-Beckmann rearrangement. Furthermore, the mechanism outlined above accommodates the ring contraction products observed by Sato and Obase [15] in the photolysis of camphor oxime, since an imine radical undergoing  $\beta$  scission affords via disproportionation the five-membered ring products obtained. The ring expansion products of naphthalenone oxime observed by Oine and Mukai [4] support our assertion that a nitrogen sextet is involved at some stage in the reaction.

We are at present extending our treatment to other aromatic oximes to delineate more convincingly the intermediacy of nitrenes in the photo-Beckmann rearrangement.

#### 4. Experimental details

Quantitative analysis of the photoproducts was performed by NMR using the olefinic proton of benzaldoxime at  $\delta = 8.1$  ppm, to measure the

percentage conversion, and the aldehyde proton of benzaldehyde at  $\delta = 9.8$  ppm. Combined gas-liquid chromatography analysis for benzamide was carried out using a 5 ft  $\times$  1/8 in Ucon-50HB-5100 column.

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