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DYE SENSITIZED PHOTOOXYGENATION OF SUBSTITUTE OXIME CARBAMATES[1]

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ABSTRACT: Solvolytic cleavage of oxime carbamates can be achieved by dye sensitized photooxygenation. A study with substituted oxime carbamates has revealed an unusual chemoselectivity of singlet oxygen towards carbon-nitrogen single bonds in preference over carbon-nitrogen double bonds in such compounds.

Recent tragedy involving methyl isocyanate[2] has warranted fresh investigations into the chemistry of carbamate insecticides with special emphasis on their hydrolytic cleavage and photoreactions.[3,4] In connection with this and our attempts to prepare oxazabicyclobutanes[5] from azirines, we decided to investigate the dye sensitized photooxygenation of oxime carbamates. The choice of photooxygenation to achieve epoxidation was prompted by recent studies on the subject and reports of successful isolation of epoxides in such reactions.[6-9] In this communication we present our preliminary results on dye sensitized photooxygenation of oxime carbamates containing both C=N and C-N in the same molecule.

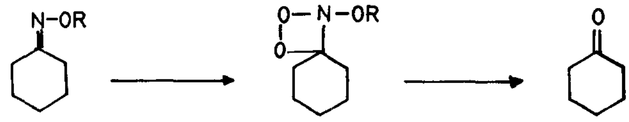
We find that the oxime esters 3-5 are cleaved by singlet oxygen produced during dye sensitization of triplet oxygen in methanol solutions to methyl carbamates and our results indicate an unusual chemoselectivity of singlet oxygen towards carbon-nitrogen single bonds. The study demonstrates the efficacy of dye sensitized photooxygenation for cleavage of oxime esters under conditions where strong acids and bases are to be avoided.

In a typical experiment, the oxime esters 3-5 or oxime ethers, 1-2 (100mg) were dissolved in 200 ml of an appropriate solvent (methanol or a mixture of methylene chloride-methanol, 90:10 v/v) in a two necked flask equipped with an oxygen/air inlet and a water condenser attached to a trap to collect volatile products. A catalytic amount of sensitizer, Rose Bengal (10^{-5}M) was added and the solution was irradiated with three 75 watt tungsten filament lamps while air was continuously passed through the solution. The progress of the reaction was monitored by thin layer chromatography on neutral alumina. When about 70% of the reaction was complete, the solvent was removed by evaporation and the residue extracted with ethyl acetate, chloroform and benzene respectively. A small amount of the Rose Bengal sensitizer which came along with the extractives was removed by adsorption over silica gel and filtration through charcoal[10] and the extractions were subjected to column chromatography. The products were identified by spectroscopic methods, comparison of their literature physical data and co-chromatography with authentic samples. The product distribution of the dye-sensitized photooxygenation of substituted oxime carbamates is given in Table I.

The participation of singlet oxygen was confirmed by repeating the reaction in the absence of the sensitizer, or of light, and in the presence of well known singlet oxygen quenchers, DABCO and 1, 3-diphenylisobenzofuran[10], in which case no reaction took place. The rates of photooxygenation for approximately the first 10% of reaction were found to be enhanced one to two fold when the reaction was performed in methylene chloride containing about 4% of methanol rather than 100% methanol. The reaction rates were enhanced in deuterated acetone and only marginally altered by addition of the free radical quencher, 2, 6-di-tertbutylphenol. These facts are also in consonance with singlet oxygen mediated reactions.[11]

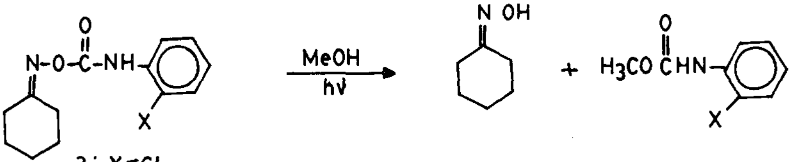
The results of the above dye-sensitized photooxygenations can be explained by the pathways A-C. Path A was ruled out because in the absence of sensitizer or oxygen no reaction of 3-5 was observed even when irradiation proceeded for 150 hr. While the only predominant product isolated in addition to methyl carbamates was the cyclohexanone oxime, mechanism B would predict the formation of cyclohexanone as one of the major products of photooxygenation as a result of decomposition of the initially formed dioxetane (6), and this leaves path C as a likely possibility.[12] This was supported by the fact that the chloro derivative (3) reacted slower than the methoxy compount (4) to yield the carbamate ester, and may be ascribed to the increased nucleophilicity of the adjacent nitrogen to react with electrophilic singlet oxygen as depicted. Intermediate 7 may result directly from 3-5 with $^1O_2$ or via an ene reaction of the enol form of 3-5. The conversion of 7 to 8 probably proceeds well because of the good leaving group characteristics of the oxime anion. Intermediates 7 or 8 might also decompose to an isocyanate which would react with methanol. Obviously path B is operative, through as a much slower reaction, for substracts 1 and 2. Further work to study the mechanism is in progress.[12]

This constitutes the first report of the sensitized photooxygenation of oxime carbamates and also the first example of this type of chemoselective reaction of singlet oxygen for the C-N rather than the C=N bond which is unusual and appears different from observed reactions of singlet oxygen with enamines and related compounds.[4] Since the reaction does not require any acid or base catalysis, it can be employed for achieving solvolytic cleavage of oxime esters where acids and bases cannot be employed.



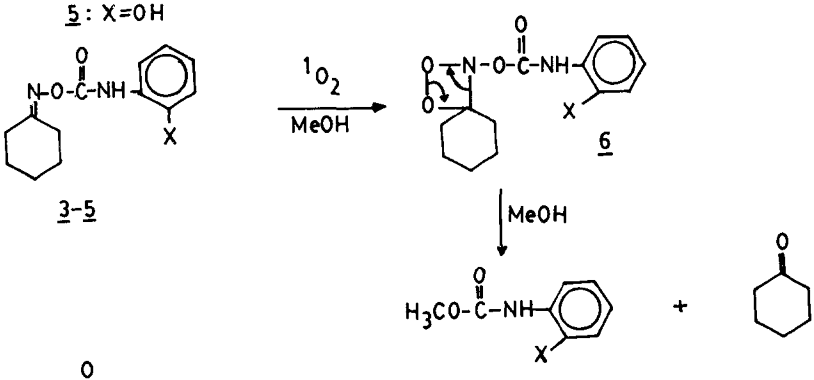
1: R=H
2: R=CH_3

(A)
attack at C=O



3: X=Cl
4: X=OMe
5: X=OH

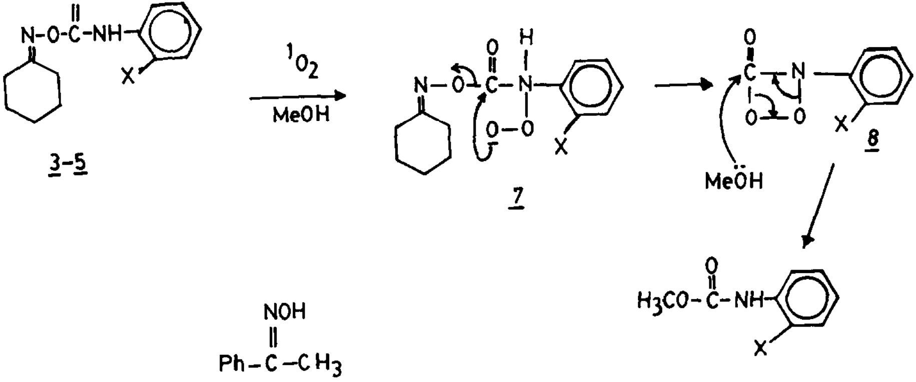
(B)
attack at C=N



3-5

6

(C)
attack at N



3-5

7

8

$$Ph-\overset{\overset{\displaystyle NOH}{\|}}{C}-CH_3$$

9

Table I

Products of Dye-Sensitized Photooxygenation of Oxime Carbamate Derivatives 1-9

Substrate	Time for Photo-oxygenation(hr)	Products[a](% yield)	Solvent
1	115	Cyclohexanone[b,c](10)	MeOH-CH_2Cl_2
2	91	Cyclohexanone[b](13)	MeOH-CH_2Cl_2
3	93	Cyclohexanone oxime(11) Methyl N-(o-chlorophenyl)-carbamate(7)	MeOH
4	68	Cyclohexanone oxime(9) and Methyl N-(o-methoxyphenyl)-carbamate(44)	MeOH
5	72	Cyclohexanone oxime(10) and Methyl N-(o-hydroxyphenyl)-carbamate(46)	MeOH-CH_2Cl_2
9	83	Acetophenone[b](5)	

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a) Yields were not optimized, refer to products without purification, and are based on substrates.

b) Unreacted starting material was also recovered.

c) No cyclohexanone formation could be noticed until 93 hr of reaction.

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12. An alternative pathway involving the information of an unlikely oxime-N-hydroperoxide could be discounted on the basis of earlier observations on reactions of C=N compounds with singlet oxygen[4] and a negative KI/AcOH test which rules out the involvement of distinct hydroperoxides. This conclusion was also supported by the observation that the reactions of 1 and 2 were extremely sluggish, which in that event should have given cyclohexanone in good yields. Though the mechanism is not firmly established and radical oxidation cannot be ruled out, we have determined that cyclohexanone withstands the photolytic reactions conditions and is most likely, not just formed and consumed in the reaction.

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