Full Length Research Paper

Photolysis of 4-oxazoline-2-one derivative in diverse solvent environments

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The photolysis of 4,5-diphenyl-3-(4-methylphenyl)-4-oxazolin-2-one in benzene or cyclohexane in the presence of singlet oxygen using UV light affords benzil, N-4-methylphenyl benzamide and N,N-dibenzoyl-4-methyl aniline. When the same reaction is carried out in protic solvents, the formation of benzil, N-4-methylphenyl benzamide, N,N-dibenzoyl-4-methyl aniline and benzoic acid is observed. The characterization uses spectral data and comparison (undepressed mixed melting point and identical IR spectra) with authentic samples. This study derives an interesting route for photooxidative fragmentation of oxazoline-2-one ring systems. The proposed mechanism involves the dioxetane derivative which after fragmentation yields radicals to afford aforementioned products.

Key words: Irradiation, column, chromatographic separation, evaporation, solvents.

INTRODUCTION

The oxazoline ring system has assumed marked significance due to their wide application (Frump, 1971). The synthetic utility of 2-oxazolines has been reviewed for aromatic systems in which they go for direct o-lithiation of benzene molecule (Reuman and Meyers, 1985). The reaction of dianions from ketomonoimines with ethyl chloroformate gives substituted 4-oxazoline-2-ones (Mehrotra et al., 1985). The thermal rearrangement of isoxazoline-3-one to 4-oxazoline-2-one has also been observed (Gagneux and Goschke, 1966). Because of the wide application of such compounds, it would be interesting and extremely significant to study the photochemistry of such systems. The photosensitized oxidation of 3,4,5-triphenyl-4-oxazoline-2-one affording a mixture of benzoic acid, benzanilide and ortho- and para-benzamide benzophenone has been reported (Tsugea et al., 1976). A similar photodecarbonylation of a cyclic carbonate of 1,2-diketone derivative has also been reported (Stahlke et al., 1972). The reactions of singlet oxygen with organic substances are very sensitive to the experimental environment (Chen et al., 1990). As such, the present study attempts to explore the effect of several protic and aprotic solvent systems.

This study uses singlet oxygen and aims to explore the effects of protic and aprotic solvents on photooxidative cleavage of 4-oxazolin-2-one ring system. In order to provide further insight in the mechanistic details of the fragmentation pattern of substituted 4-oxazoline ring systems, different protic and aprotic solvent combinations were used. In this study, photooxidative cleavage of 4,5-diphenyl-3-(4-methylphenyl)-4-oxazolin-2-one in protic and aprotic solvents has been discussed. The reaction route explored in this study demonstrates an interesting photochemistry.

MATERIALS AND METHODS

Instrumentation

Chemicals and reagents were purchased from Aldrich Chemical Co. and used without further purification. Melting points were determined in capillaries on melting point apparatus and are uncorrected. The NMR spectra in CDCl₃ were recorded on Varian A-60D and VN 1009 (S-60T) spectrophotometer with TMS as an internal standard. The IR spectra were measured on a Perkin Elmer 720 spectrophotometer and UV spectra on a Beckman DB-G spectrophotometer. Photochemical experiments were carried out using Hanovia type A, 450 W medium pressure mercury immersion lamp as light source.

Preparation of 2-Imino-1,2-diphenylethanone

The starting 2-imino-1,2-diphenylethanone was obtained by heating
an equimolar mixture of benzil and 4-methylphenylamine at 150°C for 2 to 3 h following the reported method and purified by fractional crystallization from ethanol (75 to 78%) (Padwa, 1965).

Preparation of 4,5-diphenyl-3-(4-methylphenyl)-4-oxazoline-2-one (1)

The starting material (1) was prepared by the reaction of dianions from a suitable 2-imino-1,2-diphenylethane with ethyl chloroformate and purified by using a reported method by Mehrotra et al. (1985). UV (Ethanol): 294 (ε1.89 × 104) nm; νmax (Nujol): 1600 cm⁻¹ (C = O); δH (CDCl₃): 7.42 (m, 14H, aromatic protons); 2.33 (s, 3H, methyl); νmax (Nujol): 1600 cm⁻¹ (C = G) and 1750 cm⁻¹ (C = O).

General procedure for irradiation

A dilute solution containing 0.5 g of oxazoline (1) in 300 mL of benzene (thiophene free) or cyclohexane or a mixture of benzene and protic (methanol, ethanol or isopropanol) solvent was irradiated with UV light from a 450W Hanovia lamp for 9.5 h while oxygen was continuously bubbled into the solution to ensure proper mixing as well. The course of the reaction was monitored by UV and TLC until the spot corresponding to the starting material disappeared.

Irradiation of 4,5-diphenyl-3-(4-methylphenyl)-4-oxazoline-2-one (1) in benzene

A dilute solution containing 0.5 g of (1) in 300 mL of benzene was used as the solvent. The starting material (1) in 300 mL of benzene was irradiated for 9.5 h following the general procedure as described earlier. Three such runs were combined. The solvent was removed under reduced pressure and the residue was triturated with ethanol to give 0.2 g (13.8%) of a solid, mp 142 to 44°C, identified as N,N-dibenzoyl-4-methylaniline on the basis of spectral data as described earlier. Three such runs were combined. The solvent was removed under reduced pressure. The residue was triturated with ethanol to give 0.28 g (19.5%) of solid, mp 142 to 44°C, identified as N,N-dibenzoyl-4-methylaniline; mp 157°C; δH (CDCl₃): 7.50 (m, 9H, arom); 3.4 (bs, H, NH, D₂O exchangeable) and 2.3 (s, 3H, CH₃); νmax (Nujol): 3300 cm⁻¹ (NH), 1620 cm⁻¹ (CO). Evaporation of the solvent from the fractions 31 to 36 under reduced pressure gave a viscous liquid which, however, could not be identified.

Irradiation of 4,5-diphenyl-3-(4-methylphenyl)-4-oxazoline-2-one (1) in cyclohexane in presence of oxygen

A dilute solution containing 0.5 g of (1) in 300 mL of cyclohexane was irradiated for 9.5 h following the general procedure as described earlier. Three such runs were combined. The solvent was removed under reduced pressure and the residue was triturated with ethanol to give 0.29 g (20%) of solid, identified as N,N-dibenzyol-4-methylaniline as described earlier. The mother liquor was concentrated and chromatographed on a column of silica gel (30 g, 12 × 2.2 cm) as described earlier. Two products were obtained which were identified as benzil 0.19 g (19.7%) and N-4-methylphenyl benzamide, 0.12 g (12.4%) as described earlier when benzene was used as the solvent.

Irradiation of 4,5-diphenyl-3-(4-methylphenyl)-4-oxazoline-2-one (1) in (1:1) methanol-benzene mixture in the presence of oxygen

A dilute solution containing 0.5 g of (1) in 300 mL of methanol-benzene mixture was irradiated for 9.5 h according to the general procedure. Three such runs were combined. The solvent was removed under reduced pressure. The residue was triturated with ethanol to give 0.2 g (13.8%) of a solid, mp 142 to 44°C, identified as N,N-dibenzyol-4-methylaniline on the basis of spectral data as described earlier. The mother liquor was concentrated and chromatographed on a column of silica gel (30 g, 12 × 2.2 cm) and the results are given in Table 2.

Evaporation of the solvent from the fractions 11 to 15 afforded a solid 0.08 g (8.3%), mp and mixed mp 95°C. The IR spectrum was superimposable to that of an authentic sample of benzil.

Evaporation of the solvent from the fractions 16 to 20 under reduced pressure gave a solid 0.06 g (10.7%), mp and mixed mp 121°C. The IR spectrum was superimposable to that of an authentic sample of benzoic acid. Evaporation of the solvent from fractions 21

Table 1. Results of chromatographic separation of irradiated sample in benzene.

<table>
<thead>
<tr>
<th>Fraction (50 ml)</th>
<th>Eluent</th>
<th>Product type</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 - 10</td>
<td>n-hexane</td>
<td>No product</td>
<td>No yield</td>
</tr>
<tr>
<td>11 - 18</td>
<td>n-hexane</td>
<td>Solid</td>
<td>0.18 g</td>
</tr>
<tr>
<td>19 - 30</td>
<td>n-hexane-benzene (1:1)</td>
<td>Solid</td>
<td>0.11 g</td>
</tr>
<tr>
<td>31 - 36</td>
<td>Benzene</td>
<td>Viscous liquid</td>
<td>No yield</td>
</tr>
</tbody>
</table>

Table 2. Results of chromatographic separation of irradiated sample in methanol-benzene mixture.

<table>
<thead>
<tr>
<th>Fraction (50 ml)</th>
<th>Eluent</th>
<th>Product type</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 - 10</td>
<td>Pet. Ether (petroleum ether)</td>
<td>No product</td>
<td>No yield</td>
</tr>
<tr>
<td>11 - 15</td>
<td>Pet. ether</td>
<td>Solid</td>
<td>0.08 g</td>
</tr>
<tr>
<td>16 - 20</td>
<td>Pet. ether-benzene(4:1)</td>
<td>Solid</td>
<td>0.06 g</td>
</tr>
<tr>
<td>21 - 30</td>
<td>Pet. ether benzene(1:1)</td>
<td>Solid</td>
<td>0.16 g</td>
</tr>
<tr>
<td>31 - 40</td>
<td>Benzene</td>
<td>Viscous liquid</td>
<td>No yield</td>
</tr>
</tbody>
</table>
Scheme 1. The reaction route for the formation of products.

RESULTS AND DISCUSSION

The starting material, 4,5-diphenyl-3-(4-methylphenyl)-4-oxazoline-2-one (1) was prepared using previously reported method by Mehrotra et al. (1985). Irradiation of a dilute solution of (1) in benzene in the presence of oxygen with UV light afforded benzil (6), N-4-methylphenyl benzamide (8) and N,N-dibenzoyl-4-methylaniline (5). Benzil was characterized by comparison (undepressed mixed melting point and superimposable identical IR spectrum) with authentic sample which was procured from Aldrich Chemical Company. N-4-methylphenyl benzamide was characterized by spectral data and comparison (undepressed mixed melting point) with authentic samples. The authentic sample of N-4-methylphenyl benzamide was prepared from the reaction of benzoyl chloride and p-toluidine in the presence of potassium hydroxide (Furniss et al., 1989). N,N-dibenzoyl-4-methylaniline has been characterized on the basis of spectral data. The reaction route for the formation of products by photooxidative fragmentation of (1) can be depicted in Scheme 1.

The addition of singlet oxygen to (1) gives the dioxetane derivative (2). The dioxetane derivative (2)
after fragmentation and simultaneous loss of carbon dioxide could give rise to benzyol radical (3) and N-4-methylphenyl benzamide radical (4). The benzyol radical (3) dimerizes to yield benzil (6), and the amide radical (4) abstracts hydrogen to give N-4-methylphenylbenzamide (8). The radical (3) and (4) combine to result in N, N-dibenzoyl-4-methylaniline (5).

Irradiation of a dilute solution of (1) in protic solvents in the presence of singlet oxygen with UV light gave four products which were identified as benzil, benzoic acid (7), N-4-methylphenyl benzamide and N, N-dibenzoyl-4-methylaniline. The product benzil and benzoic acid were characterized by comparison (undepressed mixed melting point and identical IR spectra) with authentic samples. As reported earlier, the products (5) and (8) have been characterized on the basis of its spectral data. The reaction route for the formation of products by the fragmentation of (1) in protic solvents seems to be similar to Scheme 1. The additional product, benzoic acid may arise from the benzyol radical (3).

The oxygenation of similar systems gave a mixture of benzoic acid, benzamide and ortho- and para-benzamide benzophenone (Tsugae et al., 1976). It has been observed that the reaction route involves a dioxetane derivative which is proposed on the basis of IR spectrum of photolysis mixture during the reaction. The IR spectrum exhibits a weak band at 880 cm⁻¹ which gives a strong support for the presence of dioxetane which, however, could not be isolated (Bellamy, 1958). A similar photodecarbonylation of a cyclic carbonate to 1,2-diketone derivative has been reported (Stahlke et al., 1972). In this study, N-4-methylphenyl benzamide (8) is obtained by hydrogen abstracion by radical (4). It was also found that the yield of (8) increases substantially in protic solvents as compared to that in aprotic solvents which offers a strong support for the proposed mechanism in Scheme 1.

**Conclusion**

The photolysis of substituted 4-oxazoline-2-ones in aprotic solvents in oxygen atmosphere yields a 1,2-diketone, N-substituted benzamide and N, N-dibenzoyl derivative. The similar photolysis in protic solvents affords benzoic acid in addition to the aforementioned three products. The reaction route involves a dioxetane intermediate which subsequently cleaves into radicals to lead to the final products.

**ACKNOWLEDGEMENTS**

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**REFERENCES**


