Note

Laser versus lamp photolysis: A comparative account of the photolysis of papavarine by laser and UV lamp

Shivraj Singh Chawada, M M Bokadia, Shubha Jain*
School of Studies in Chemistry Vikram University, Ujjain 456 010, India
Received 18 April 2000; accepted (revised) 20 February 2001

Papavarine, when irradiated by N₂ laser and UV lamp separately, gives different products. The time required is less and yields obtained are high under laser irradiation.

In continuation of our studies on the comparative photolysis under UV lamp and N₂ laser, here we report an account of comparative study with papavarine. We have earlier reported a comparative account of photolysis of nicotinic acid and carbazole under N₂ laser and UV lamp [1, 2].

Results and Discussion

Papavarine 1 when irradiated by UV light, gave 2 (Scheme I) after 30 hr, whereas when irradiated under N₂ laser, it gave five products 2–6 (Scheme II) after 8.5 hr. The major product 2 obtained by laser irradiation is found to be the same as that obtained by UV irradiation by co-TLC. It is formed by the insertion of –CH₂ group in the heterocyclic ring of papavarine resulting in ring expansion or it may be a rearrangement involving a benzylic radical (Scheme III) upon irradiation. Its structure has been confirmed by spectral and elemental analyses. Its IR spectrum shows a broad band at 3400 (N–H stretch) (absent in the IR spectrum of papavarine) and 1630 cm⁻¹ (N–H bending) along with other bands. The ¹H NMR spectrum gives signals at δ 3.6, 3.7, 3.8 and 3.9 (s, –OCH₃ protons), 6.4 (s, NH proton) 8.2 and 8.25 (H₆ and H₇), 7.3 and 7.35 (H₁ and H₂) and 6.7 (H₃) (Figure 1). Its ¹³C spectrum gives signals at δ 50–55 (four bands, –OCH₃ carbon atom), 125–138 (C₁, C₄–₁₃ and C₁₆), 158.6–160.2 (four bands C₂, C₃, C₁₄ and C₁₅) (Figure 1). The mass spectrum gives M⁺ peak at m/z 339 which is also the base peak, corresponding to the molecular weight of the product. A M+1 peak at m/z 340 and M+2 peak at m/z 341 indicate the presence of nitrogen and oxygen respectively. Other peaks are found at m/z 338 (M–H), 324 (M–CH₃) 308 (M–OCH₃) etc.

![Diagram](image-url)

Scheme I

Scheme II

1 Retd. Prof. & Head, School of Studies in Chemistry, Vikram University, Ujjain 456 010
Product 3, in its IR spectrum shows absorptions at 3000 (arom. C–H stretch), 2870 cm⁻¹ (aliph. C–H stretch) etc. The ¹H NMR spectrum shows signals at δ 3.7, 3.8 (s, O–CH₃ protons), 2.2 (s, –CH₃ protons) and 7.5–8.5 (m, arom. protons). Its ¹³C NMR spectrum shows signals at δ 25 (–CH₃ carbon), 60 (–OCH₃ carbon), 125.5, 126.1 (C₇ and C₈), 127.4, 128.2 (C₆ and C₅), 138, 140 (C₄ and C₃) and 159.1 and 160 (C₂ and C₃) (Figure 2). Its mass spectrum gives M⁺ peak at m/z 203. Other important peaks are at m/z 188 (M–CH₃), 172 (M–OCH₃), 157 (188–OCH₃) etc.

Product 4, 4-methylveratrole, in its IR spectrum, gives absorptions at 3030 (arom. C–H stretch), 2850 cm⁻¹ (aliph. C–H stretch) etc. Its ¹H NMR gives absorptions at δ 3.8, 3.9 (s, O–CH₃ protons), 2.5 (s, –CH₃ protons) and 8.0–8.2 (arom. protons). Its ¹³C NMR spectrum gives signals at δ 30 (–CH₃ carbon), 124.8 (C₃), 125.6 (C₄), 127 (C₅), 127.8 (C₆) and 156.8 and 157.4 (C₁ and C₂). Its mass spectrum shows M⁺ peak at m/z 152. Other important peaks are at m/z 137 (M–CH₃), 121 (M–OCH₃), 122 (M–CH₂O) etc.

Product 5, veratrole has been identified by comparing its b.p. with the literature value (lit. b.p. 207°C) and co-TLC with the authentic sample.

Product 6, in its IR spectrum shows important absorptions at 3000 (arom., CH stretch), 2960 (aliph. CH stretch) and 1660 cm⁻¹ (C=NS stretch) along with other bands. Its ¹H NMR gives signals at δ 3.75 at 3.8 (s, –OCH₃ protons), 6.9 (H₂), 7.2, 7.3 (H₁ and H₁₂), 8.15 and 8.2 (H₅ and H₆). Its ¹³C spectrum shows signals at δ 121.2, 123.1 (C₁ and C₂), 124.8, 125.5 (C₄ and C₅), 127.2 (C₆), 138.1, 139.0 (C₇ and C₈) and 159.1 (C₂ and C₃) (Figure 3).

Conclusion

The results show that the time required for the completion of the reaction is much less under laser compared to UV light and at the same time, under UV irradiation, the molecule undergoes simple rearrangements, whereas under laser it gets cleaved. This is because the laser radiations are much more coherent, collimated, directional and energetic compared to simple UV radiations. Similar results have been reported by Butcher et al., Ramaiah et al. and Hamanoue et al. by the comparison of products upon laser and lamp or steady state photolysis.

Experimental Section

Papavine (1g) was dissolved in dried and distilled ethanol (100mL). Benzophenone was added as sensitiser. The reaction mixture was then irradiated by 125 W medium pressure mercury vapour lamp and a laser (λ 337.1 nm, τ 7 x 10⁻⁹ sec., pps 20 Hz, peak power ~ 150 kw), separately. The progress of the reaction was followed by TLC.
Table 1 — M.p’s, yields and elemental analysis data of products 2-6

<table>
<thead>
<tr>
<th>Product</th>
<th>m.p. (°C)</th>
<th>Yield (g)</th>
<th>Found (Calcd.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>UV Laser</td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>2</td>
<td>230-32</td>
<td>0.37</td>
<td>0.45</td>
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<td></td>
<td></td>
<td>(70.79)</td>
<td>6.3</td>
</tr>
<tr>
<td>3</td>
<td>115</td>
<td>0.20</td>
<td>0.15</td>
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<tr>
<td></td>
<td></td>
<td>(70.93)</td>
<td>6.01</td>
</tr>
<tr>
<td>4</td>
<td>24</td>
<td>0.15</td>
<td>0.15</td>
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<tr>
<td></td>
<td></td>
<td>(71.05)</td>
<td>7.89</td>
</tr>
<tr>
<td>5</td>
<td>200 (b.p.)</td>
<td>0.08</td>
<td>0.09</td>
</tr>
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<td></td>
<td></td>
<td>(5.66)</td>
<td>5.66</td>
</tr>
<tr>
<td>6</td>
<td>110-11</td>
<td>0.09</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(5.66)</td>
<td>5.86</td>
</tr>
</tbody>
</table>

reaction was monitored by TLC. The products were separated by preparative TLC using benzene-methanol (9:1 v/v) solvent system and recrystallized from alcohol. The m.p’s, yields and elemental analyses data are given in Table 1. M.p’s have been recorded on electrically operated melting point apparatus and are uncorrected. The IR spectra have been recorded in KBr and NMR spectra have been recorded at 90 MHz in deuterated methanol.

Acknowledgement
The authors are thankful to Dr A.G. Bhujale, Head, Laser Division, Centre for Advanced Technology, Indore for providing laser facilities and to the Head, RSIC, CDRI, Lucknow for providing the spectral and elemental analyses data.

References