A novel oxidative reaction of 2-nitro-1-phenylpropane with sodium nitrite. A new approach to prepare 1-oximino-1-phenylacetones

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Received 17 August 2003; revised 8 September 2003; accepted 8 September 2003

Abstract—A useful method for preparation of 1-oximino-1-phenylacetones via a novel oxidative reaction of 2-nitro-1-phenylpropanes with sodium nitrite was reported. © 2003 Elsevier Ltd. All rights reserved.

Keywords: 2-nitro-1-phenylpropanes; nitrite; oxidation; 1-oximino-1-phenylacetones.

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Table 1. The yields of 1-oximino-1-phenylacetones from 2-nitro-1-phenylpropanes

<table>
<thead>
<tr>
<th>Entries</th>
<th>R Products</th>
<th>Yield (%)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>p-OCH₃</td>
<td>1a</td>
</tr>
<tr>
<td>3b</td>
<td>3,4-OCH₂O-</td>
<td>1b</td>
</tr>
<tr>
<td>3c</td>
<td>p-Cl</td>
<td>1c</td>
</tr>
<tr>
<td>3d</td>
<td>p-NO₂</td>
<td>1d</td>
</tr>
</tbody>
</table>

* The yield was not optimized.

Table 1. The yields of 1-oximino-1-phenylacetones from 2-nitro-1-phenylpropanes

Ing the ¹H NMR data of the product with literatures,⁵ we confirmed the product structure was 1. To further verify the configuration of this compound, we treated this compound with irradiation in chloroform, the conversion of E-isomer to Z-isomer was observed,⁶ which was in agreement with the reported literature.⁶ Therefore, we confirmed that the product was E-isomer (Scheme 2). NOE experiment results also supported this conclusion.

Meanwhile, a by-product, p-methoxybenzonitrile, was separated from the filtrate. It may arise from Beckmann rearrangement of Z-isomer.⁷

Other secondary nitro compounds were also tested under this condition,⁸ the results were listed in Table 1 (Scheme 3).

In conclusion, we have described one novel and convenient method to prepare 1-oximino-1-phenylacetones from 2-nitro-1-phenylpropanes.

Acknowledgements

Financial supports from the New Drug Foundation of Shanghai Institute of Pharmaceutical Industry are gratefully acknowledged.

References

8. General procedure for 1a–1d from 3a–3d (1a from 3a): acetic acid was added to a solution of 3a (0.56 g, 2.88 mmol) and NaN₂O (0.20 g, 2.89 mmol) in DMSO solution (2.5 ml) under stirring. This resulting mixture was stirred for 1.5 h at 35°C, cooled to room temperature, poured into ice-water 100 ml with vigorous stirring, a white precipitate was formed, which was collected by filtration to afford 1a (0.42 g, 74.0%; m/z (LR-EI) 193; mp: 150–152°C,⁵ ¹H NMR δ (DMSO, ppm) 12.40 (s, 1H, -OH), 7.24 (dd, J₁ = 2.7, J₂ = 11.6, 1H, Ar-H), 7.24 (d, J = 4.8, 1H, Ar-H), 6.94 (dd, J₁ = 2.7, J₂ = 11.8, 1H, Ar-H), 6.94 (d, J = 4.8, 1H, Ar-H), 3.77 (s, 3H, -OCH₃), 2.43 (s, 3H, CH₃). After irradiation under 254 nm for 48 h, ¹H NMR δ (DMSO, ppm) 12.45 (s, 0.82H, -OH), 11.60 (s, 0.18H, -OH), 7.36 (d, J = 9.0, 0.36H, Ar-H), 7.19 (d, J = 9.0, 1.54H, Ar-H), 6.95 (d, J = 9.0, 0.36H, Ar-H), 6.92 (d, J = 9.0, 1.54H, Ar-H), 3.83 (s, 1.08H), 3.74 (s, 1.92H), 2.39 (s, 1.08H), 2.38 (s, 1.92H); ¹³C NMR δ (DMSO, ppm) 196.8 (-C=O), 159.6 (C=N), 154.9, 131.2, 121.5, 113.1 (Ar-C), 55.3 (OCH₃), 26.3 (CH₃); IR (KBr, γ cm⁻¹): 2500–3500 (br, -OH), 1710 (s, -C=O), 1620 (m, -C=N).