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Tetrahedron Letters 44 (2003) 8061–8062

TETRAHEDRON LETTERS

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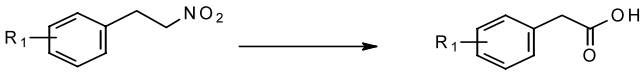
Received 17 August 2003; revised 8 September 2003; accepted 8 September 2003

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.

Aliphatic nitro compounds are important intermediates for organic synthesis.[1] However, the transformations of aliphatic nitro compounds to other functionalities are very limited. The conversions to aldehydes or ketones by the Nef reaction[2] and the reduction to amines[3] are the most common transformation of nitroalkanes. Although there are some reports concerned about the oxidation of primary nitro compounds,[4] to our knowledge, there is no corresponding report about the oxidation of the secondary nitro compounds except the Nef reaction. Here we would like to report for the first time that the secondary nitro compounds such as 2-nitro-phenylpropanes could be oxidized into α-oximinoketones with sodium nitrite under very mild conditions.

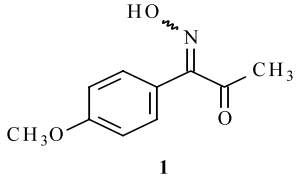


Scheme 1.

Matt et al. reported that primary nitro compounds reacted with sodium nitrite and acetic acid in DMSO to give the corresponding carboxylic acid (Scheme 1).[4a]

When secondary nitro compound 2-nitro-1-(4-methoxylphenyl) propane was treated with sodium nitrite under the conditions Matt reported,[4a] unexpectedly and interestingly, we found the product was neither the corresponding carboxylic acid which may arise from the mechanism Matt proposed[4a] or the corresponding ketone compound which may arise from the Nef reaction.

According to the spectrum of ^{1}H NMR and ^{13}C NMR, Mass spectrum, IR, the product might be **1** or **2** (Scheme 2), which were known compounds.[5] Compar-



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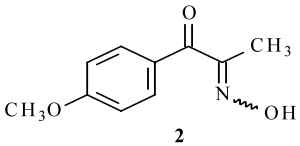

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Scheme 2.

Keywords: 2-nitro-1-phenylpropanes; nitrite; oxidation; 1-oximino-1-phenylacetones.
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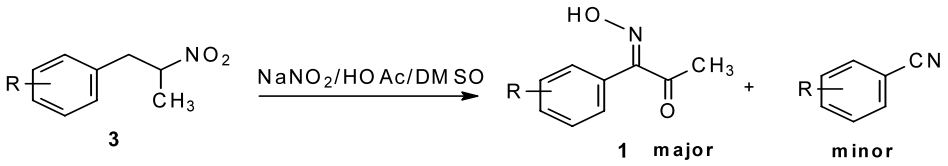
doi:10.1016/j.tetlet.2003.09.054



Scheme 3.

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

Entries	R	Products	Yield (%)*
3a	*p*-OCH_3	**1a**	74
3b	3,4-OCH_2O-	**1b**	85
3c	*p*-Cl	**1c**	82
3d	*p*-NO_2	**1d**	85

* The yield was not optimized.

ing the ^{1}H 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,[8] 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*-methoxylbenzonitrile, 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.

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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 $NaNO_2$ (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] ^{1}H NMR δ (DMSO, ppm) 12.40 (s, 1H, -OH), 7.24 (dd, $J_1=2.7$, $J_2=11.6$, 1H, Ar-H), 7.24 (d, $J=4.8$, 1H, Ar-H), 6.94 (dd, $J_1=2.7$, $J_2=11.8$, 1H, Ar-H), 6.94 (d, $J=4.8$, 1H, Ar-H), 3.77 (s, 3H, -OCH_3), 2.43 (s, 3H, CH_3). After irradiation under 254 nm for 48 h, ^{1}H 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); ^{13}C NMR δ (DMSO, ppm) 196.8 (-C=O), 159.6 (C=N), 154.9, 131.2, 121.5, 113.1 (Ar-C), 55.3 (OCH_3), 26.3 (CH_3); IR (KBr, γ cm^{-1}): 2500–3500 (br, -OH), 1710 (s, -C=O), 1620 (m, -C=N).