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# DMSO/NaNO<sub>2</sub>/49% HBr: A Novel and Powerful Oxidant for the Direct Conversion of Primary Benzylamines to Benzoic Acids

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## DMSO/NaNO<sub>2</sub>/49% HBr: A Novel and Powerful Oxidant for the Direct Conversion of Primary Benzylamines to Benzoic Acids

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**Abstract:** A mixture of DMSO, NaNO<sub>2</sub>, and 49% HBr is found to oxidize primary benzyl amines to benzoic acids at  $100^{\circ}$ C.

Keywords: Benzoic acid, benzyl amine, DMSO, HBr, NaNO2

#### INTRODUCTION

Recently, we have developed a method to convert primary benzyl amines into the corresponding benzyl ester derivatives.<sup>[1]</sup> The transformations of primary benzylamines into variety of derivatives include oximes using methyltrioxorhenium (MTO)-catalyzed oxidation,<sup>[2]</sup> imines using Fremy's salts,<sup>[3]</sup> nitriles using tetrabutylammonium peroxydisulfate catalyzed by nickel,<sup>[4]</sup> and halides by pyrolysis of the respective pyrylium, quinolium, or pyridinium salts.<sup>[5–10]</sup> In continuation of our ongoing work, we report for the first time an efficient oxidation of primary benzylamines to benzoic acids using DMSO/ NaNO<sub>2</sub>/49% HBr at 100°C (Scheme 1).

A mixture of benzylamine, inorganic acid, and DMSO was heated to  $100^{\circ}$ C for 32 h to obtain benzylammoniumbromide salt, which gave the starting material upon neutralization. We then carried out the diazotisation of benzylamine by using aq. NaNO<sub>2</sub> at  $0-10^{\circ}$ C in DMSO and under

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Scheme 1. Oxidation of benzylamines to benzoic acids.

an acidic medium at room temperature. This produced benzyloxydimethylsulfoxide salt intermediate. However, the reaction mixture was heated to  $100^{\circ}$ C for 30 min, we obtained benzoic acid (92%) but not benzaldehyde. This was further characterized by <sup>1</sup>H NMR, IR, and melting points. To optimize the conditions to select a suitable inorganic acid, conc. HCl, conc. H<sub>2</sub>SO<sub>4</sub>, and 49% HBr were utilized. Aq. HBr (49%) was the better acid to produce benzoic acid in 92% yield.

The mechanism proposed for this transformation is given in Scheme 2.

To substantiate the mechanism, benzaldehyde was subjected to same oxidation condition to yield benzoic acid as expected (Scheme 3).

A noteworthy feature of the reaction is that electron-accepting groups (entries 4-7, Table 1) and electron-releasing groups (entries 2 and 3, Table 1) on the aromatic ring do not contribute significantly to the rate of the reaction.

In conclusion, we have developed a novel and efficient oxidizing agent,  $DMSO/NaNO_2/49\%$  HBr, to convert primary benzylamines into benzoic acids.

#### **EXPERIMENTAL**

TLC was performed on precoated aluminum plates with Merck silica gel 60 F-254 as the adsorbent. The developed plates were air dried and irradiated with UV light. GC analysis was performed on a Shimadzu GC-MS QP 5050A instrument. IR spectra were recorded on a Nicolet 400D FT-IR spectrometer. <sup>1</sup>H NMR spectra were recorded on Bruker 400-MHz spectrometer as CDCl<sub>3</sub> solutions with TMS as internal standard.



Scheme 2. Plausible mechanism for oxidation of primary benzylamine to benzoic acid.

#### DMSO/NaNO<sub>2</sub>/49% HBr



Scheme 3. Oxidation of benzaldehyde to benzoic acid.

Entry	Substrate	Product	Time (h)	Yield $(\%)^a$
1	Benzylamine	Benzoic acid	1.0	92
2	4-Methoxybenzylamine	4-Methoxybenzoic acid	1.5	78
3	4-Hydroxybenzylamine	4-Hydroxybenzoic acid	1.5	82
4	4-Chlorobenzylamine	4-Chlorobenzoic acid	2.0	80
5	3-Chlorobenzylamine	3-Chlorobenzoic acid	2.5	82
6	3-Nitrobenzylamine	3-Nitrobenzoic acid	2.0	80
7	4-Nitrobenzylamine	4-Nitrobenzoic acid	2.5	86

Table 1. Oxidation of benzylamines into benzoic acids

<sup>*a*</sup>Isolated yields. All products are known and characterized by comparing mp, and IR spectral analysis with authentic samples.

# General Procedure for the Conversion of Benzylamine into Benzoic Acid

An aqueous solution of NaNO<sub>2</sub> (2.54 g, 37.38 mmol) was added to an ice-cold solution of benzylamine (2.0 g, 18.69 mmol), DMSO (10 mL), and 49% HBr (3.5 mL, 21 mmol) over a period of 15 min. The reaction mixture was allowed to attain room temperature and then heated to  $100^{\circ}$ C for 30 min. Water (10 mL) and brine (10 mL) were added and extracted into ether (4 × 10 mL). The ethereal solution was washed with brine (3 × 10 mL) and made alkaline with 10% NaHCO<sub>3</sub> solution, and the ether layer separated. Upon neutralizing the aqueous layer with 15% HCl, a precipitate of benzoic acid (2.09 g, 92%, mp 122°C, lit. mp 123°C) was obtained.

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