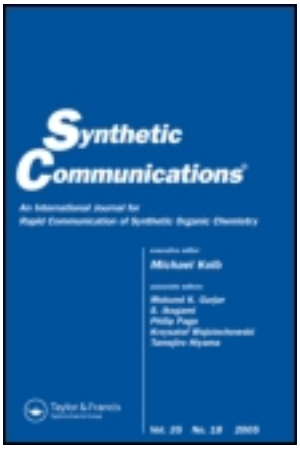

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Transformation of Primary Benzyl Amines to Benzyl Esters

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Abstract: Primary benzyl amines, upon treatment with aq. $NaNO_2$ and appropriate organic acids at 0–5°C, give their respective benzyl esters.

Keywords: Benzyl amines, benzyl esters, carboxylic acids, $NaNO_2$

INTRODUCTION

The transformation of benzyl amines into different functional groups is very important in synthetic organic chemistry. A number of reactions have been reported using secondary and tertiary benzyl amines to get a variety of organic compounds. However, there are only a few transformations of primary benzyl amines, which involve conversion of primary benzyl amines into oximes by the methyltrioxorhenium (MTO)-catalyzed oxidation with H_2O_2[1] into imines using Fremy's salt[2] and into nitriles using tetrabutylammonium peroxydisulfate catalyzed by nickel.[3] Katritzky and coworkers have demonstrated the indirect conversion of primary benzyl amines into respective halides, such as benzyl fluorides,[4,5] benzyl chlorides,[6] benzyl bromides,[7,8] and benzyl iodides[9] via pyrolysis of respective pyrylium, quinolium, or pyridinium salts.

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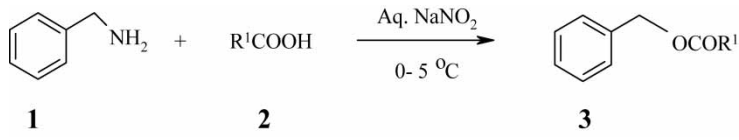

Scheme 1. Transformation of benzyl amines into benzyl esters.

In this communication, we report the conversion of primary benzyl amines into benzyl esters by aqueous $NaNO_2$/carboxylic acids as shown in Scheme 1.

Benzyl amine (**1**), aq. $NaNO_2$, and acetic acid initially at 0–5°C and then at room temperature gave benzyl acetate (Table 1, entry 1), which was identical to reported product.[10] Benzyl alcohol was also isolated from the reaction mixture. To minimize hydrolysis of benzyl acetate, many reaction conditions were tried. The optimal condition was the use of 2 equiv. of water, 3 equiv. of acid, and 2 equiv. of $NaNO_2$ (in minimum water) for 1 equiv of amine. Some representative primary benzyl amines with different acids have been conveniently converted into corresponding benzyl ester derivatives (Table 1). The use of CH_3CN for some solid carboxylic acids was necessary for efficient transformation.

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 Nicolet 400D FT-IR spectrometer. The ^1H NMR spectra were recorded on Bruker 400-MHz spectrometer as $CDCl_3$ solutions with TMS as internal standard.

General Procedure for the Conversion of Benzyl Amines to Benzyl Esters

An ice-cold solution of $NaNO_2$ (1.26 g, 18.6 mmol, in a minimum amount of water) was added in a dropwise manner over a period of 15 min to a mixture of benzyl amine (1 g, 9.3 mmol) in water (0.24 mL, 18.6 mmol) and acetic acid (3.39 mL, 27.9 mmol) at 0–5°C. After the addition, the reaction mixture was allowed to attain room temperature, neutralized with sat. $NaHCO_3$, and extracted with ether. The ether layer was washed with brine, dried over anhyd. Na_2SO_4, filtered, and concentrated. The crude mixture was

Table 1. Conversion of benzyl amines into benzyl esters

Entry	Substrate (**1**)	Acid (**2**) (R^1)	Product (**3**)	Time (min)	Yield (%)[a] (**3**)
1	Benzylamine	CH_3	Benzylacetate	20	80
2	Benzylamine	CH_2CH_3	Benzylpropionate	20	82
3	Benzylamine	Ar	Benzylbenzoate	25	85[b]
4	Benzylamine	$(CH_2)_2CH_3$	Benzylbutyrate	25	88
5	Benzylamine	CH_2Cl	benzylchloroacetate	20	85[b]
6	Benzylamine	$PhCH_3$	benzylphenylacetate	25	90[b]
7	Benzylamine	4-NO_2Ph	benzyl-4-nitrobenzoate	30	60[b,c]
8	4-Methoxybenzylamine	CH_3	4-Methoxybenzylacetate	20	75
9	4-Nitrobenzylamine	CH_3	4-Nitrobenzylacetate	22	78
10	2-Nitrobenzylamine	CH_3	2-Nitrobenzylacetate	25	80
11	3-Nitrobenzylamine	CH_3	3-Nitrobenzylacetate	25	84
12	3-Chlorobenzylamine	CH_3	3-Chlorobenzylacetate	25	84
13	2-Hydroxybenzylamine	CH_3	2-Hydroxybenzylacetate	22	78
14	2-Phenylethylamine	CH_3	2-Phenylethylacetate	25	65[c]

[a]Isolated yields.
[b]CH_3CN used as cosolvent.
[c]35% of alcohol recovered.

chromatographed on silica gel using EtOAc–pet. ether (1 : 9) as eluent to get benzyl acetate (1.12 g; 80%).

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