Pergamon

Tetrahedron Letters 43 (2002) 9715–9716

TETRAHEDRON
LETTERS

3,4,5-Trifluorobenzeneboronic acid: a mild and versatile catalyst for the one-pot synthesis of acyl azides from carboxylic acids

R. H. Tale* and K. M. Patil

Organic Chemistry Research Laboratory, School of Chemical Sciences, S.R.T.M. University, Nanded-6, Maharashtra, India

Received 22 July 2002; revised 24 September 2002; accepted 4 October 2002

Abstract—Acyloxyboron intermediates generated from carboxylic acids and 3,4,5-trifluorobenzeneboronic acid react with sodium azide to furnish the corresponding acyl azides in moderate to good yields. © 2002 Elsevier Science Ltd. All rights reserved.

There are several routes to acyl azides.[1–5] In most of these reactions, a carboxylic acid is converted into a more reactive intermediate, e.g. an acyl chloride, which is then allowed to react with an azide ion in either water or a water miscible organic solvent. However, these methods suffer from the limitation that acyl chlorides or other reactive acid derivatives are not always available. For practical reasons it is preferable to form reactive intermediates in situ.

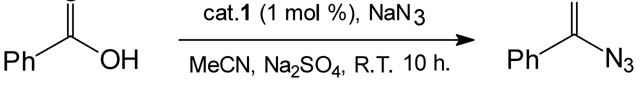
There have been some reports in the literature on the preparation of acyl azides directly from carboxylic acids. These include the use of acid activators such as ethyl chloroformate,[6] $SOCl_2$–DMF,[7] diphenylphosphoryl azide (DPPA)[8] and NCS–PPh_3.[9]

Attempts have also been made to prepare acyl azides directly from aldehydes by using special types of reagents such as chromic anhydride-trimethylsilyl azide[10] and triazidochlorosilane–manganese dioxide.[11] Very recently acyl azides have been prepared from carboxylic acids using triphosgene[12] and cyanuric chloride[13] as acid activators. Although these methods provide good yields of acyl azides, they involve the use of hazardous reagents.
The chemistry of boronic acids continues to be a growth area in synthetic methodology. Many organoboron compounds,[14] are air sensitive, tend to be easily hydrolyzed and in some cases are pyrophoric. Boronic acids, $RB(OH)_2$, in contrast, are usually crystalline solids, stable to air and moisture. Such evidence as exists indicates that they are of relatively low toxicity [benzeneboronic acid:[15] LD_{50}, oral-rat = 740 mg/kg] and environmental impact. Yamamoto has found that a boronic acid with electron withdrawing substituents, in particular 3,4,5-trifluorobenzeneboronic acid **1** can be an effective catalyst for amidation and esterification of carboxylic acids.[16] To our knowledge, however there are no reports in the literature on the boronic acid-catalyzed azidation of carboxylic acids.

In view of the great utility of acyl azides as synthetic intermediates in organic chemistry,[17] it is worthwhile to explore the generality and scope of boronic acid **1** as a catalyst for the azidation of carboxylic acids. In the present paper we wish to describe an extremely simple but powerful procedure for the one-pot synthesis of acyl azides from carboxylic acids using **1** and sodium azide which proceeds via acyloxyboron intermediates (Scheme 1).

The reaction is thought to involve a six-membered cyclic intermediate (Scheme 2).

Various structurally diverse carboxylic acids have been successfully converted into their corresponding acyl azides using catalytic amounts of **1** in the presence of sodium azide in moderate to good yields (Table 1). Mild reaction conditions, simplicity, ease of workup and the low toxicity and environmental impact of boronic acids[15] in contrast to the hazardous reagents

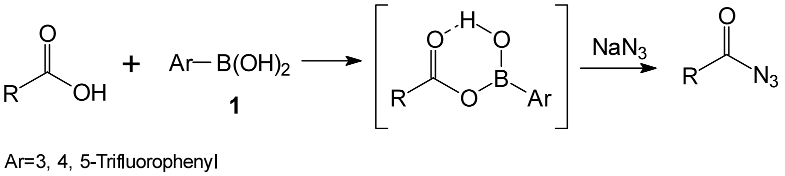


Scheme 1.

Keywords: carboxylic acid; 3,4,5-trifluorobenzeneboronic acid; acyl azide.

* Corresponding author. Fax: +91-2462-29245; e-mail: rkht2002@yahoo.com

PII: S0040-4039(02)02256-6



Scheme 2.

Table 1. Synthesis of acyl azides catalyzed by boronic acid **1**

Entry	Carboxylic acid	Acyl azide	Yield[a,b] (%)
1	Benzoic acid	Benzoyl azide	85
2	Cinnamic acid	Cinnamyl azide	83
3	2-Chlorobenzoic acid	2-Chlorobenzoyl azide	92
4	4-Chlorobenzoic acid	4-Chlorobenzoyl azide	94
5	4-Hydroxybenzoic acid	4-Hydroxybenzoyl azide	96
6	Hexanoic acid	Hexanoyl azide	92
7	Decanoic acid	Decanoyl azide	90
8	4-Iodobenzoic acid	4-Iodobenzoyl azide	95
9	4-Methoxybenzoic acid	4-Methoxybenzoyl azide	95
10	4-Nitrobenzoic acid	4-Nitrobenzoyl azide	71
11	Phenylacetic acid	Phenylacetyl azide	83
12	Phenoxyacetic acid	Phenoxyacetyl azide	83
13	3,5-Dinitrobenzoic acid	3,5-Dinitrobenzoyl azide	66

[a] Yields refer to the pure isolated product.

[b] The products were characterized by their physical constants, spectroscopic data (IR, ^{1}H NMR) and elemental microanalyses.

reported in the literature[12,13] are some of the noteworthy features of this method.

In conclusion, we have developed a mild, simple, general and environmentally benign protocol for the one-pot synthesis of acyl azides from carboxylic acids.

General procedure:

To a solution of the carboxylic acid (2 mmol) and sodium azide (10 mmol) in dry acetonitrile (20 ml) was added Na_2SO_4 (1 g) and boronic acid **1** (1 mol%) and the mixture was stirred at room temperature for 10 h. After completion of the reaction (TLC), the mixture was filtered, washed with aqueous $NaHCO_3$ and extracted with chloroform (3×10 ml). After drying over anhydrous Na_2SO_4, the solvent was evaporated to give the product. The product was purified by column chromatography (ethyl acetate:petroleum ether, 1:9).

Acknowledgements

The authors are grateful to Sudhir Dapurkar (Research Scholar, I.I.T., Mumbai) for the gift of boronic acid **1**.

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