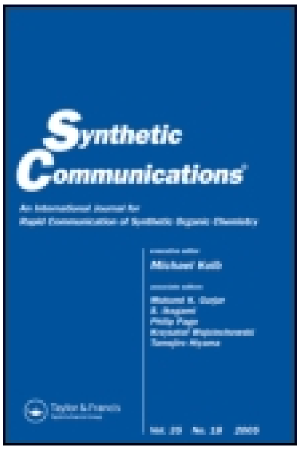

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Facile Preparation of Benzylic Iodides Under Solvent-Free Conditions Using Microwave Irradiation

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To cite this article: Jong Chan Lee , Jin Young Park & Eun Sang Yoo (2004): Facile Preparation of Benzylic Iodides Under Solvent-Free Conditions Using Microwave Irradiation, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 34:11, 2095-2099

To link to this article: http://dx.doi.org/10.1081/SCC-120037924

SYNTHETIC COMMUNICATIONS®
Vol. 34, No. 11, pp. 2095–2099, 2004

Facile Preparation of Benzylic Iodides Under Solvent-Free Conditions Using Microwave Irradiation

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ABSTRACT

Benzylic alcohols are rapidly converted to the corresponding benzylic iodides using combination of *p*-toluenesulfonic acid (PTSA) and potassium iodide under solvent-free microwave irradiation conditions.

Key Words: Benzylic alcohols; Iodides; Microwave; *p*-Toluenesulfonic acid.

INTRODUCTION

Benzylic iodides have recently attracted increasing attention as versatile intermediate in organic synthesis.[1,2] Conversion of benzylic alcohols into

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DOI: 10.1081/SCC-120037924
0039-7911 (Print); 1532-2432 (Online)

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benzylic iodides can be achieved using a number of reagent systems which include methanesulfonic acid/NaI,[3] KI/boron trifluoride diethyl etherate,[4] and cerium(III) chloride/NaI.[5] However, these methods usually suffered from one or more drawbacks such as use of excess organic solvents, employment of toxic reagents, or long reaction times.

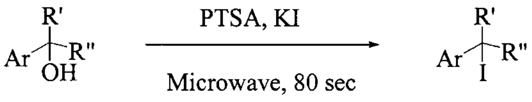
In continuation of our investigations on microwave promoted reactions under solvent-free conditions, we now report a facile and efficient method for synthesis of various benzylic iodides utilizing the reaction of benzylic alcohols with potassium iodide in the presence of *p*-toluenesulfonic acid (PTSA) under microwave irradiation (Sch. 1). Treatment of benzylic alcohols with KI (2.0 equiv.) and PTSA (1.5 equiv.) under microwave irradiation readily provided benzylic iodides in high yields for 80 sec.

A variety of benzylic alcohols were converted into the corresponding benzylic iodides as presented in Table 1. It is noteworthy to mention that this method is generally applicable to the iodination of secondary and tertiary benzylic alcohols (entries **5**, **9**, and **10**) as well as primary benzylic alcohols, which feature is hardly expected from the already existing methods. The reactions are presumably occurred by initial PTSA induced protonation of hydroxyl oxygen of benzylic alcohols followed by nucleophilic substitution by iodide ion. The analogous mechanism has been suggested in the reaction of benzhydrol with carboxylic acids in the presence of PTSA.[6]

In summary, we have developed a facile and rapid protocol for the conversion of benzylic alcohols into benzylic iodides using solvent-free microwave irradiation conditions. We believe this novel method can be served as a useful alternative to the existing methods.

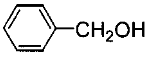
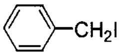
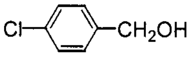
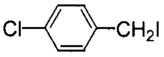
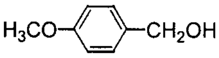
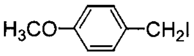
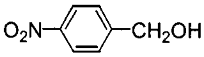
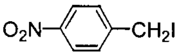
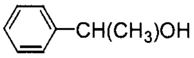
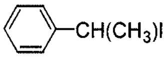
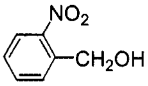
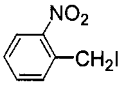
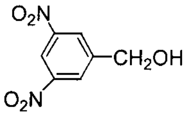
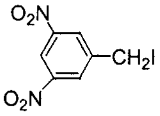
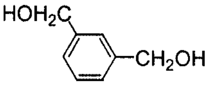
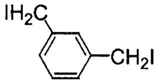
EXPERIMENTAL

All reactions were performed in a commercial domestic microwave oven (Samsung RE-21C). ^{1}H NMR spectra were obtained on Varian Gemini 2000—a 300 MHz spectrometer. Mass spectra were recorded with a Micromass Autospec system.



Scheme 1.

Table 1. Conversion of benzylic alcohols to benzylic iodides.

Entry	Substrate	Product	Yield (%)[a]
1		 **(1a)**	92
2		 **(2a)**	93
3		 **(3a)**	93
4		 **(4a)**	85
5		 **(5a)**	90
6		 **(6a)**	82
7		 **(7a)**	71
8		 **(8a)**	83
9	$(Ph)_2CHOH$	$(Ph)_2CHI$ **(9a)**	82
10	$(Ph)_3COH$	$(Ph)_3CI$ **(10a)**	74

[a] Isolated yield.

General Procedure

A mixture of benzylic alcohol (1.0 mmol), PTSA (0.285 g, 1.5 mmol), and potassium iodide (0.332 g, 2.0 mmol) was placed in a 50 mL of glass tube. The reaction mixture was inserted in an alumina bath inside a domestic microwave oven and irradiated (850 W) four times for a period of 20 sec with 10 sec intervals. On completion of the reaction, the product was extracted with dichloromethane and washed with water. The organic layer was separated and dried over $MgSO_4$. After evaporation of solvent, the product was purified by flash column chromatography on silica gel using dichloromethane as eluent to give pure benzylic iodide.

Benzyl iodide (1a). M.p.: 23–24°C (lit.[7] 23°C). ^1H NMR ($CDCl_3$) δ: 4.42 (s, 2H), 7.24–7.35 (m, 5H); MS m/z: 218 (M^+).

p-Chlorobenzyl iodide (2a). M.p.: 61–62°C (lit.[8] 62–63°C). ^{1}H NMR ($CDCl_3$) δ: 4.40 (s, 2H), 7.22–7.32 (m, 4H); MS m/z: 252 (M^+).

p-Methoxybenzyl iodide (3a). M.p.: 31–32°C (lit.[9] 32.5–32.8°C). ^{1}H NMR ($CDCl_3$) δ: 3.73 (s, 3H), 4.42 (s, 2H), 6.76–7.28 (m, 4H); MS m/z: 248 (M^+).

p-Nitrobenzyl iodide (4a). M.p.: 125–126°C (lit.[7] 125–127°C). ^{1}H NMR ($CDCl_3$) δ: 4.48 (s, 2H), 7.51–8.17 (m, 4H); MS m/z: 263 (M^+).

1-(1-Iodoethyl)benzene (5a). B.p.: 121°C/5 Torr (lit.[10] 70–80°C/2 Torr). ^{1}H NMR ($CDCl_3$) δ: 2.19 (d, 3H), 5.38 (q, 1H), 7.21–7.44 (m, 5H); MS m/z: 232 (M^+).

o-Nitrobenzyl iodide (6a). M.p.: 74–75°C (lit.[8] 73–75°C). ^{1}H NMR ($CDCl_3$) δ: 4.78 (s, 2H), 7.44–8.04 (m, 4H); MS m/z: 263 (M^+).

3,5-Dinitrobenzyl iodide (7a). M.p.: 90–92°C (lit.[11] 92–93°C). ^{1}H NMR ($CDCl_3$) δ: 4.57 (s, 2H), 8.55 (s, 2H), 8.93 (s, 1H); MS m/z: 308 (M^+).

α,α'-Diiodo-m-xylene (8a). M.p.: 105–106°C (lit.[12] 106°C). ^{1}H NMR ($CDCl_3$) δ: 4.39 (s, 4H), 7.20–7.37 (m, 4H); MS m/z: 358 (M^+).

Diphenyliodomethane (9a). M.p.: 70–71°C (lit.[7] 72°C). ^{1}H NMR ($CDCl_3$) δ: 5.53 (s, 1H), 7.09–7.27 (m, 10H); MS m/z: 294 (M^+).

Triphenylmethyl iodide (10a). M.p.: 132–133°C (lit.[13] 132–133°C). ^{1}H NMR ($CDCl_3$) δ: 7.22–7.32 (m, 15H); MS m/z: 370 (M^+).

ACKNOWLEDGMENT

This work was supported by the research grant of Chung-Ang University.

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Received in Poland December 12, 2003

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