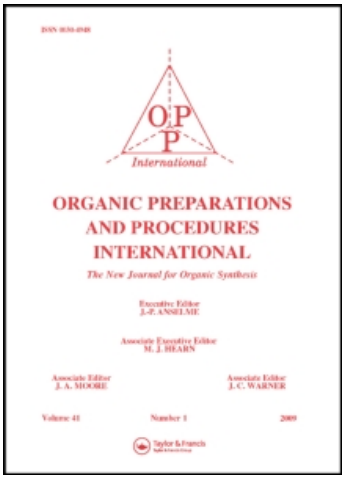

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Iodination of Alcohols using Triphenylphosphine/Iodine in Ionic Liquid under Solvent-Free Conditions

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Iodination of Alcohols using Triphenylphosphine/Iodine in Ionic Liquid under Solvent-Free Conditions

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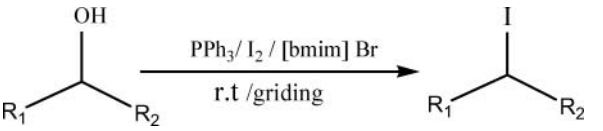
Ionic liquids (IL) have frequently been used as green solvents in place of conventional organic solvents [1–5] and may be superior owning to their extremely low vapor pressure, excellent thermal stability, reusability, and ability to dissolve many organic and inorganic substrates.[6]

We now report an efficient and mild procedure for the conversion of alcohols to the corresponding iodides with triphenylphosphine and iodine as previously reported,[7] but in the presence of 1-butyl-3-methylimidazolium bromide [bmim][Br] without using microwave under solvent-free conditions (*Scheme 1*). To optimize the reaction conditions,



Scheme 1

the conversion of benzyl alcohol to the benzyl iodide was studied by mixing benzyl alcohol (10 mmol, 1 mL), triphenylphosphine (10.0 mmol, 2.6 g), and iodine (10 mmol, 2.5 g) in a mortar. The mixture was ground with a pestle in the presence and absence of 1-butyl-3-methylimidazolium bromide [bmim][Br]. In the absence of the ionic liquid, the reaction was slower (10 min, 55% yield) than in the presence of ionic liquid (0.2 gr, 1 mmol) (2 min, 80% yield).

To study the generality of this method, a wide range of alcohols including primary, secondary, cyclic and benzylic alcohols were studied (Table 1). The procedure was scaled up to 100 mmol of benzyl alcohol without affecting yield; however, the reaction time had to be increased to 5 min.

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Table 1
Conversion of Alcohols to the Corresponding Iodides using Ph_3P/I_2/[bmim]Br[a]

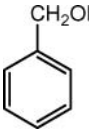
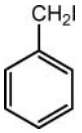
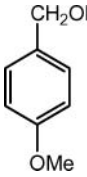
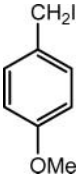
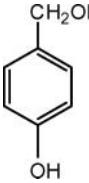
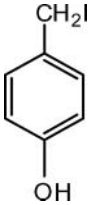
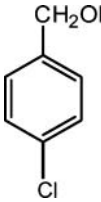
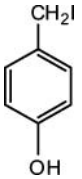
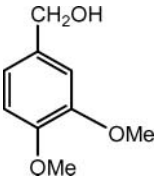
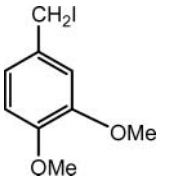
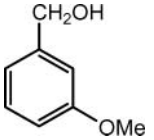
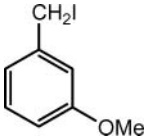
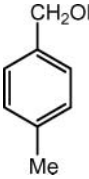
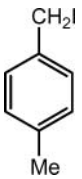
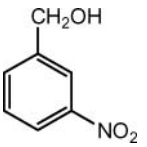
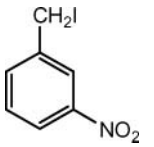
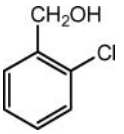
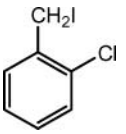
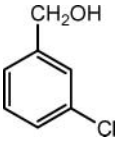
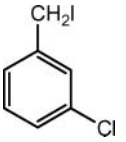
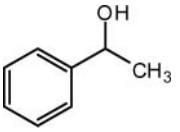
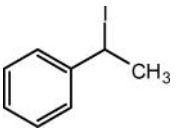
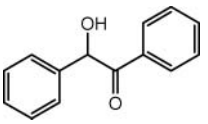
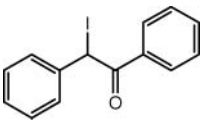
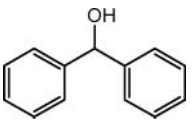
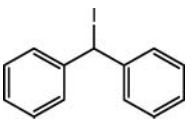
Entry	Substrate	Product	Time (min)	Yield (%)	mp. or bp.(mmHg) (°C) Found	Reported
1			2	80	21–23	24–25[8]
2			2	95	25–27	27[9]
3			2	85	108–110	108–110[10]
4			2	85	58–60	58–60[10]
5			2	90	41–43	40–42[10]
6			2	85	40–42	40[11]
7			2	85	46–47	47–48[12]
8			2	70	82–83	83.5–85.5[12]

Table 1
Conversion of Alcohols to the Corresponding Iodides using Ph_3P/I_2/[bmim]Br[a] *(Continued)*

Entry	Substrate	Product	Time (min)	Yield (%)	mp. or bp.(mmHg) (°C) Found	Reported
9			2	80	26–28	26–27[13]
10			2	75	162–164 (30)	141 (22)[13]
11			2	80	65–66	64–65[14]
12			2	30	92–93	90–92[10]
13			2	70	69–70	69–70[10]
14	$CH_3CH_2CH_2OH$	$CH_3CH_2CH_2I$	6	81	103 (760)	102.5 (760)[15]
15	$CH_3(CH_2)_2CH_2OH$	$CH_3(CH_2)_2CH_2I$	8	91	127 (760)	130.2 (760)[15]
16	$CH_3(CH_2)_4CH_2OH$	$CH_3(CH_2)_4CH_2I$	8	91	83–85 (36)	76.5 (23)[15]
17	$CH_3(CH_2)_6CH_2OH$	$CH_3(CH_2)_6CH_2I$	8	91	91–93 (15)	65.2–72 (23)[16]
17	*iso*-$C_5H_{11}OH$	*iso*-C_5H_{11}-I	4	78	143–144	145–147[16]
18	*c*-$C_6H_{11}OH$	*c*-C_6H_{11}-I	5	80	57–58 (360)	59–60 (360)[16]
19	*c*-C_5H_9OH	*c*-C_5H_9-I	5	75	160–162 (760)	160–164 (760)[17]
18	$C_6H_4(CH_2)_3OH$	$C_6H_4(CH_2)_3$-I	6	82	128–130 (10)	71.5–73 (0.25)[18]

[a] The products were characterized from their spectra (IR, ^{1}H NMR, and MS) and comparison with authentic samples.[8–18]

Experimental Section

All yields refer to isolated products after purification. The alkyl iodides were characterized by comparison of their spectral (IR, ^{1}H-NMR, combustion analysis, TLC, and GC) and physical data (melting and boiling points) with those of authentic samples. ^{1}H-NMR spectra were recorded at 300 MHz in $CDCl_3$ relative to TMS as an internal standard. ^{13}C-NMR spectra were recorded at 75 MHz in $CDCl_3$ relative to TMS as an internal standard. All of the reactions were carried out in a hood with strong ventilation. The ionic liquid used

may be prepared according to the literature procedure [19] and is also commercially available from Aldrich.

Iodination of Alcohol. General Procedure

In a mortar, a mixture of the alcohol (10 mmol), I_2 (10 mmol, 2.5 g), triphenylphosphine (10 mmol, 2.6 g), and 1-butyl-3-methylimidazolium bromide (0.2 g, 1 mmol, 10 mol%) was ground with a pestle for the time specified in Table 1. The progress of the reaction was monitored by TLC (n-hexane:EtOAc, 3:1) or GC. After disappearance of the alcohol (TLC), the reaction mixture was diluted with ether (25 ml) and filtered to remove solids. The organic layer was washed with an aqueous solution of $Na_2S_2O_3$ (10%, 10 ml), then H_2O (2 $\times$ 10 ml). The organic layer was dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure and the residue was purified by short column chromatography (n-hexane:EtOAc, 3:1). This procedure was scaled up to 100 mmol of benzyl alcohol (10.8 g) to give benzyl iodide in 80% yield in 5 min. The ionic liquid was not recoverable in this procedure.

Acknowledgments

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