Bull. Chem. Soc. Ethiop. **2014**, 28(2), 305-308. ISSN 1011-3924
Printed in Ethiopia
DOI: http://dx.doi.org/10.4314/bcse.v28i2.15

SHORT COMMUNICATION

EFFICIENT AND DIRECT IODINATION OF ALKYL BENZENES USING POLYMER/HIO_4 AND I_2 UNDER MILD CONDITION

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(Received September 7, 2013; revised December 27, 2013)

ABSTRACT. An efficient and rapid method has been found for the iodination of aromatic compounds using iodine and polymer-supported periodic acid (PSPIA) as an oxidant under mild aprotic conditions. The reagent after the completion of the reaction was easily removed by filtration and was regenerated for further use. This method has some advantages such as: mild reaction conditions, straight forward procedure, inexpensive method, high yields and one-pot conversion.

KEY WORDS: Iodine, Polymer-supported periodic acid, Oxidant, Iodination

INTRODUCTION

Iodobenzene derivatives are valuable compounds in organic synthesis, medicine, and biochemistry [1]. Iodine is an elemental halogen that has less reactive than the other halides in electrophilic substitution reactions, therefore iodination of arenes by use of iodine is hard [2]. In many methods some reagents like Lewis acids or an oxidizing agent may be needed to activate the iodine for introducing into the ring [3-6]. The wide range of methods reported until now revealed the lack of an efficient and general enough procedure, but the reaction by iodine or iodide in the presence of oxidants or Lewis acids is common and revealed some efficiency and selectivity [7-10].

To continuation our previous works on the preparation and application of polymer-supported reagents in iodination reactions and organic synthesis [11-17] we report here a practical and efficient aromatic iodination. A combination of iodine and polymer-supported periodic acid has been found to be an excellent reagent for the efficient iodination of aromatic compounds. These reactions are carried out at 40 °C using CH_3CN as the solvent.

EXPERIMENTAL

Materials and instrumentation. Chemicals were obtained from Merck and Fluka chemical companies. All compounds were known and identified by comparison of their physical and spectroscopic data with those of authentic samples. Melting points were determined in open capillary tubes with a Buchi 510 apparatus. Mass spectra were recorded on Micro Mass UKLTD spectra. NMR spectra were recorded on a Bruker DPX 400 MHz instrument. Poly(1,4-phenylene-2,5-pyridinedicarboxyamide) was prepared according to literature [15].

Typical procedure. To a solution of 1,2-dimethylbenzene (0.106 g, 1 mmol) in acetonitrile (10 mL), iodine (1 mmol. 0.126 g) and polymer-supported periodic acid (0.6 g, 1.05 mmol) were added and the mixture was stirred for 1 hour at 40 °C. The reaction progress was monitored by thin layer chromatography (TLC) using a mixture of ethyl acetate and n-hexane (1: 9 v/v) as

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solvent. After completion of the reaction, the mixture was cooled to room temperature and filtered. The excess of iodine was removed from the filtrate by drop wise addition of sodium bisulfite solution (1 M). The organic layers were separated, dried over magnesium sulfate, filtered, and the solvent was removed by evaporation. The residue was purified by column chromatography on silica gel using n-hexane and ethyl acetate. The related product was obtained with 95% isolated yield, b.p.: 235 °C (lit. [18] b.p.: 234 °C).

4-Iodotoluene. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.47 (s, 3H), 7.54 (dd, J = 7.6 Hz, 2H), 7.18 (dd, J = 7.6 Hz); ^{13}C NMR (400 MHz, CDCl3) δ: 21.3, 92.1, 134.6, 136.7,1 36.3 ppm; mass (m/z): 218 (M^+), 127, 91 (100%), 65, 51.

1-Iodo-3,4-dimethylbenzene. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.39 (s, 3H), 2.48 (s, 3H), 6.83 (d, J = 7.2 Hz, 1H), 7.04 (dd, J = 7.2 Hz and 3.1 Hz, 1 H), 7.65 (d, J = 2.3 Hz, 1H) ppm; ^{13}C NMR (400 MHz, $CDCl_3$) δ: 20.4, 21.5, 93.2, 132.3, 135.2, 136.1, 138.2, 139.8 ppm, mass (m/z): 232 (M^+ 97%).

RESULTS AND DISCUSSION

It is noteworthy that polymer-supported periodic acid is a mild oxidizing reagent compared to unsupported periodic acid ion. It is also a cheaper oxidizing reagent and can be prepared easier comparable with the other oxidizing agent. Furthermore, using polymer-supported oxidant provides the possibility of the running the reaction to completion in the presence of more than one equivalent ratio of the reagent to the substrate without serious changes in the reaction products. We first supported periodic acid on the poly(1,4-phenylene-2,5-pyridinedicarboxy-amide) by stirring them in water at room temperature for 48 h. Then unsupported periodate was removed by filtering and washing with H_2O. Polymeric reagent was obtained and dried to afford PSPIA (Figure 1) [15].

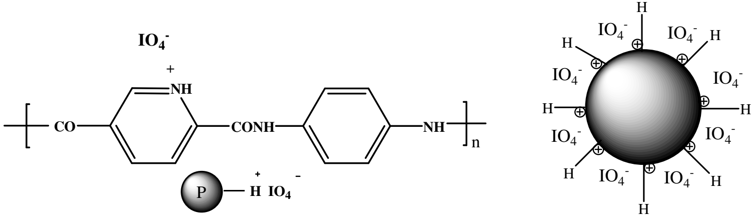


Figure 1. The structure of polymer-supported periodic acid.

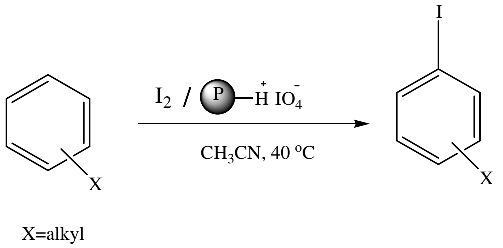
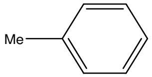
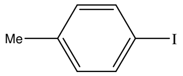
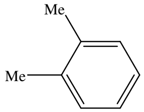
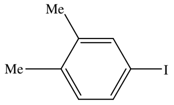
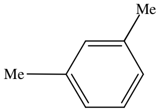
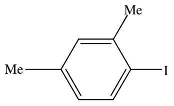
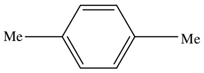
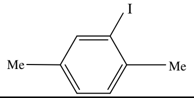
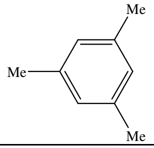
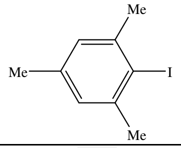
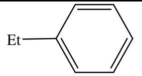
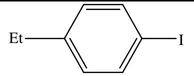
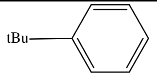
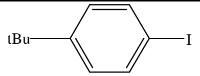
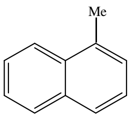
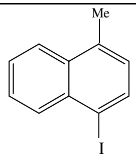
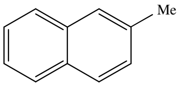
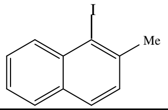


Figure 2. The direct iodination of alkylbenzenes.

By having weight of the polymeric reagent, we found that each gram of the reagent contains 1.75 mmol HIO_4. Thus, we used 0.60 g of the polymeric reagent and iodine (1 mmol) for the iodination of aromatic compound (1 mmol). We have studied direct iodination of arenes using iodine and polymer-supported periodic acid under mild condition in CH_3CN as an aprotic solvent (Figure 2). A set of alkyl substituted benzenes were subjected to this iodination process and monoiodination was achieved in each case with excellent yield of iodo product. The results are summarized in Table 1.

Table 1. The iodination of alkylbenzenes with PSPIA/I_2 in the presence of acetonitrile at 40 °C.

Entry	Substrate	Product	Time (min)	Yield [a] (%)	Mp/Bp(°C) Found. Rep. [18]
1			90	80	32 33
2			60	95	235 234
3			75	85	111 110
4			60	95	114 112
5			60	85	29 30
6			90	90	112 112
7			75	83	256 258 [19]
8			90	85	286 -
9			120	80	281 -

a: The ratio of alkylbenzenes (mmol), acetonitrile (mL), PSPIA (g) and I_2 (mmol) was 1:10:0.6:1.

The crude iodinated products that were obtained by this method were purified by column chromatography over silica gel and authenticated by TLC. Finally the iodo products were characterized by mass, ^1H NMR and ^{13}C NMR spectral studies.

CONCLUSION

In conclusion, this method is general, simple and efficient for iodination of alkylbenzenes. In addition, simple workup, short reaction time and excellent yields are the other advantages of the method, which makes it a useful addition to the available methodologies.

ACKNOWLEDGEMENT

We gratefully acknowledge the financial support from the Research Council of Damghan University, Iran.

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