Iodination of Alkylbenzenes using Benzyltriphenylphosphonium Dichromate / I₂ System

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Abstract: An efficient and rapid method have been found using benzyltriphenylphosphonium dichromate (PhCH₂PPh₃)₂Cr₂O₇ as an oxidant along with molecular iodine for the iodination of aromatic compounds. Iodination of a wide variety of alkyl benzenes were done under dichloromethane solvent system and high yields of iodo products were obtained

Keywords: Aromatic iodination, Benzyltriphenylphosphonium dichromate, Alkyl benzenes.

Introduction

The aromatic iodination reactions are important electrophilic substitution reactions and the resultant iodoarenes have been widely used in organic synthesis due to their ability to undergo metal catalyzed cross-coupling reactions¹. Iodoarenes are in many ways similar to bromo and chloro arenes in chemical properties except of their ability to form stable polyvalent iodine derivatives, which are versatile reagents in organic synthesis². Aromatic iodides are widely used in the production of organic photoreceptors that are used in electrophotography, organic electroluminescent device, dyestuffs and agricultural chemicals. Polyiodinated phenols have been used as imaging agents in noninvasive medical diagnostic techniques³. Since iodine is the least reactive one among the halogens, iodination of aromatic compounds simply by diiodine is not possible. Hence aromatic iodination reactions were done by using iodonium ion donating reagents such as iodine monochloride⁴, NaI-chloramine-T⁵ and *N*-iodosuccinimide⁶ or by oxidative iodination method using oxidants along with molecular iodine. Some of the oxidants reported⁷ are Pb(OAc)₄, sodium nitrate⁸, trimethyl orthoformate⁹, oxon¹⁰, silver(I)sulfate¹¹, KMnO₄¹² and peracetic acid¹³, KClO₃¹⁴, KBrO₃¹⁵ and NaIO₃¹⁶. As a part of on going synthetic project, an efficient and rapid method have been found using benzyltriphenylphosphonium dichromate (PhCH₂PPh₃)₂Cr₂O₇ as an oxidant along with molecular iodine for the iodination of alkyl benzenes were done in dichloromethane solvent system.

Experimental

TLC (Thin layer chromatography) was performed on silica gel-G coated aluminium plate (Merck 60, F-254) using hexane as eluent. The chromatogram was developed under a mixture of 1% vaniline and 5% ethanolic H_2SO_4 as reagent. Melting points were obtained on a Thomas-Hoover apparatus in open capillary tubes and are uncorrected. ^1H NMR and ^{13}C NMR spectra were acquired on JEOL 270 and 400 MHz and Varian Gemini 300 MHz Spectrophotometers. Mass spectra were recorded on a GC-Mass Spec Finnigan MAT 8230MS instrument.

Preparation of benzyltriphenylphosphonium dichromate

Benzyltriphenylphosphonium dichromate can be prepared easily by mixing an aqueous solution of benzyltriphenylphosphonium chloride with chromium(VI)oxide in HCl at room temperature¹⁷. It is a stable orange coloured powder which can be stored for a month and has the solubility in dichloromethane.

Typical iodination procedure

o-Xylene (1.06 g, 10 mmol) was added to a stirred solution of the benzyltriphenylphosphonium dichromate (1 mmol, 0.92 g) and iodine (5 mmol, 0.63 g) in 40 mL dichloromethane. The mixture was heated at reflux until TLC showed complete disappearance of starting material which required 1-2 h depending on the reactivity of the substrate. The reaction mixture was cooled to room temperature and then poured into vigorously stirred aq. Na_2SO_3 solutions (5 g Na_2SO_3 in 50 mL of water). The organic layers were separated, dried over anhydrous Na_2SO_4 , filtered, and the removal of solvent was worked up by evaporation. The residue was purified by column chromatography on silica gel using hexane as eluent to afford 1-iodo-3,4-dimethylbenzene (2.20 g, 95%), b.p. 234°C (lit. $231 - 233^\circ\text{C}$).

MS (m/e) : 232 ($[\text{M}^+]$ 97%). **^1H NMR** (CDCl_3): δ 2.24 (s, 3H), 2.38 (s, 3H), 6.73 (d, $J = 8.4$ Hz, 1H), 7.02 (dd, $J = 8.4$ Hz and 2.3 Hz, 1H), 7.61 (d, $J = 2.3$ Hz, 1H). **^{13}C NMR** (CDCl_3): δ 22.4, 23.5, 97.4, 131.3, 134.2, 135.1, 137.2, 138.8.

Results and Discussion

Initially, iodination of *o*-xylene was carried out with a mixture of benzyltriphenylphosphonium dichromate and iodine in dichloromethane according to the following stoichiometry under reflux condition (Eq.1).

The crude iodinated product obtained by this method were purified by column chromatography over silica gel and authenticated by TLC. Finally the iodo product was established by mass, ^1H NMR and ^{13}C NMR spectral studies. It was observed that *o*-xylene gave excellent yields of 1-iodo-3,4-dimethylbenzene.

Further 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. The possible reactions can be explained as follows. The oxidant above said is able to convert molecular iodine into more reactive electrophilic I^+ species. This *in situ* formed iodonium ion may lead to the iodination of aromatic compounds.

Table 1. Iodination of alkyl benzenes with benzyltriphenylphosphonium dichromate and iodine.

Substrate	^a Product	M.p (lit), °C	^b Yield, %
Toluene	4-Iodotoluene	33(32-35)	92
<i>m</i> -Xylene	1-Iodo-2,4-dimethylbenzene	b.p.110(112)	94
<i>o</i> -Xylene	1-Iodo-3,4-dimethylbenzene	b.p.234(233)	95
<i>p</i> -Xylene	2-Iodo-1,4-dimethylbenzene	b.p.112(113)	85
Mesitylene	2-Iodo-1,3,5-trimethylbenzene	30(31)	93
Ethylbenzene	4-Ethyliodobenzene	b.p.112(113)	86

^a Products were characterised by m.p or b.p, Mass, ¹H NMR and ¹³C NMR.

^b Isolated yield.

Conclusion

An inexpensive oxidant benzyltriphenylphosphonium dichromate can easily be prepared in laboratory at room temperature and can be used in the oxidative iodination process. This methodology is rapid, inexpensive and superior to previously reported methods in terms of yield and purity of products.

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