

Mild and Efficient Iodination of Aromatic Compounds with Trichloroisocyanuric Acid/I₂/Wet SiO₂ System

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Iodoarenes can be obtained using trichloroisocyanuric acid/I₂/wet SiO₂ system at room temperature with high yield in CH₂Cl₂.

Key Words: Iodination, trichloroisocyanuric acid, aromatic compound, wet SiO₂.

Introduction

Aromatic halogenated compounds have been used for over a century as important chemicals or intermediates in organic synthesis.¹ Iodoarenes are valuable intermediates in the synthesis of a wide variety of organic compounds via reactions involving C-C bond formation by transition metals.² They have many applications in pharmacology, medicine, and biochemistry.³ Since iodine is the least reactive halogen towards the electrophilic substitution, direct iodination of aromatic compounds with iodine is difficult.⁴ A large diversity of methods for synthesis of aromatic iodides have been reported.^{1,3,4} Some of the reported procedures need harsh conditions such as HNO₃/H₂SO₄,⁵ HIO₃ or HIO₄/H₂SO₄,⁶ KMnO₄/H₂SO₄,⁷ CrO₃ in acidic solution with I₂,⁸ vanadium salts/CF₃SO₃H at 100 °C,⁹ Pb(OAc)₄/HOAc.¹⁰ NIS/CF₃SO₃H has also been reported for direct iodination of highly deactivated aromatics.^{3b} The other reported protocols are: I₂/HgX₂,¹¹ ICl/Ag₂SO₄/H₂SO₄,¹² NIS/CF₃CO₂H,¹³ I₂/Ag₂SO₄,¹⁴ I₂/F-TEDA-BF₄,¹⁵ NIS/CH₃CN^{16a}, and (CH₃)₄NI₂.^{16b}

Our goal, in undertaking this line of work, was to overcome the limitations and drawbacks of the reported methods, which mentioned above, and also, to develop a high-yielding one-pot synthesis of iodoarenes using a novel combination of reagents.

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In addition, any reduction in the amount of liquid acids needed and/or any simplification in handling procedures would be highly convenient in terms of risk reduction, economic advantage, and environment protection.¹⁷ On the other hand, there is intense current research and general interest in heterogeneous systems because of the perceived opportunities that such systems present for basic research and because of the unquestioned importance they have in industry and in development technologies.¹⁸ Recently, Zolfigol^{19,20} and co-workers reported the mononitration and dinitration of phenols using trichloroisocyanuric acid/ NaNO_2 /wet SiO_2 . Trichloroisocyanuric acid,²¹ which is used primarily as a disinfectant, has found little application in organic chemistry so far.²² Therefore, we were interested in using this reagent for the iodination of aromatic compounds when used in conjunction with I_2 and wet SiO_2 in CH_2Cl_2 .

Experimental

The products were purified by column chromatography and the purity determinations of the products were accomplished by GLC on a Shimadzu model GC-10A instrument or by TLC on silica-gel polygram STL G/UV 254 plates. FT-IR spectra were recorded on a Perkin Elmer RXI spectrometer. NMR Spectra were recorded on a Bruker Avance DPX 250 MHz instrument. All products were identified by their comparisons with authentic samples.

Iodination of Anisole with Trichloroisocyanuric acid/ I_2 /wet SiO_2 : A Typical Procedure

A mixture of anisole (0.108 g, 1 mmol), trichloroisocyanuric acid (0.196 g, 1 mmol), wet SiO_2 (50% w/w, 1 g) and iodine (0.254 g, 1 mmol) was stirred at room temperature in CH_2Cl_2 . The progress of the reaction was monitored by TLC; *p*-iodo anisole was obtained immediately. The reaction mixture was filtered and washed with 5% aqueous sodium thiosulfate solution (2×10 mL). The resulting mixture was dried over anhydrous MgSO_4 and then applied on a silica-gel column (using *n*-hexane as eluent) to afford *p*-iodoanisole in 98% yield, m.p. 50-52 °C, (Lit^{23a} m.p. 50-53 °C).

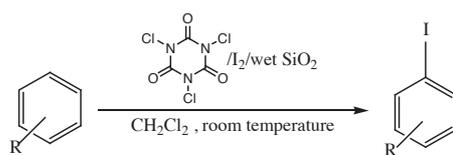
Results and Discussion

We wish to report a simple method for the effective monoiodination of aromatic compounds by using trichloroisocyanuric acid, as a cheap commercially available reagent, iodine, and wet SiO_2 under mild and heterogeneous conditions.

Initially, the test reaction was carried out on anisole with trichloroisocyanuric acid/ I_2 /wet SiO_2 in CH_2Cl_2 ; *p*-iodo anisole was obtained immediately in 98% yield.

Different aromatic compounds were also subjected to iodination in the presence of trichloroisocyanuric acid, I_2 , and wet SiO_2 (50% w/w) in dichloromethane (Scheme 1).

The iodination reactions were performed under mild and completely heterogeneous conditions at room temperature with moderate to good yields (Table 1).



Scheme 1

Table 1. Iodination of Aromatic Compounds Using Trichloroisocyanuric acid/I₂/Wet SiO₂ in CH₂Cl₂ at Room Temperature.

Entry	Substrate	Product ^a	Time (h)	Yield %
1			immediately	98
2			immediately	95
3			immediately	97
4			immediately	96
5			immediately	96
6			immediately	98
7			immediately	88

Table 1. Continued.

Entry	Substrate	Product ^a	Time (h)	Yield %
8			1.5	90
9			4.5	93
10			4.5	85
11			4.5	88
12			5.5	90
13			6	93
14			6	85

^aThe product was identified by the comparison of its physical constants and IR and NMR spectral data with those of an authentic sample (ref. 23).

As expected, all the substrates undergo iodination reactions and delivered monoiodo products in good to excellent yields.

We think that the presence of wet SiO₂ acts as a heterogeneous effective surface area for in situ generation of iodonium ion, efficiently making work-up easy. Trichloroisocyanuric acid as a commercially available reagent (slightly soluble in CH₂Cl₂) was used for the in situ generation of HOCl in the presence of wet SiO₂.²⁴ It was converted to cyanuric acid as a highly polar compound, which is completely insoluble in CH₂Cl₂, and was adsorbed by silica gel. However, highly iodo compounds were obtained by simple filtration and subsequent evaporation of the solvent.

In conclusion, we have provided a simple method for the direct, regioselective iodination of benzene, naphthalene, and other aromatic compounds using molecular iodine in the presence of trichloroisocyanuric acid and wet SiO₂ system. Moreover, cheapness and availability of reagents, easy and clean work-up, and good yields make this method attractive for organic chemists.

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