JNS 4 (2014) 309-315

Journal of
NANOSTRUCTURES

JNS NANOSTRUCTURES
JNS.kashanu.ac.ir

Solvent-Free Synthesis of Aryl Iodides Using Nano SiO_2/HIO_4 as a Reusable Acid Catalyst

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Article history:
Received 27/7/2014
Accepted 7/8/2014
Published online 1/9/2014

Keywords:
Sandmeyer reaction
Nano silica periodic acid
Solvent-free conditions
Grinding
Aril iodides

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Abstract

An efficient and environmentally benign method for the synthesis of aryl iodides have been developed by diazotization of aromatic amines with $NaNO_2$ and nanosilica periodic acid (nano-SPIA) as a green catalyst via grinding followed by a sandmeyer iodination by KI under solvent-free conditions at room temperature. The ensuing aryl diazonium salts supported on nano-SPIA were sufficiently stable to be kept at room temperature in the dry state. This method is a novel, efficient, eco-friendly route for solvent-free synthesis of aryl iodides.

1. Introduction

The Sandmeyer reaction can be used to synthesize arylhalides from aryl diazonium salts [1-3]. An aromatic (or heterocyclic) amine quickly reacts with $NaNO_2/HCl$ to form an aryl diazonium salt, which decomposes in the presence of copper (I) halide, to form the desired aryl halide [4,5]. The reaction is a radical-nucleophilic aromatic substitution. Nitrite esters are also useful reagents in a modification of the diazotizing reaction [6]. For the synthesis of aryl iodides diiodomethane is used [7,8] whereas bromoform is the desired solvent for the synthesis of aryl bromides [9]. Recently, a one-step method for the iodination of aromatic derivatives was reported using HI/KNO_2 in DMSO or $KI/NaNO_2$/p-TsOH in CH_3CN [10]. A recent publication also reports the synthesis of aryl halides using various arenediazonium salts [11]. Diazonium salts are versatile compounds in organic chemistry. However, their poor thermal stability limits the application of these derivatives. Usually these compounds are synthesized around 10 °C and to avoid their decomposition they are handled below 0 °C [12]. To the best of our knowledge, there are a few reports for room temperature diazotizing of aromatic amines and also preparation of stable diazonium salts at room temperature by using supported reagents under solvent-free conditions [13-15]. As a part of our ongoing research program for exploring the bifunctional catalytic properties, we herein describe a new process for diazotization and Sandmeyer reactions using nanosilica periodic acid as a catalyst toward the synthesis of aryl iodides under solvent-free conditions at room temperature by grinding.

2. Experimental procedure

2.1. Material

Chemicals were obtained from Merck and Fluka chemical companies. All products were known and are identified by comparison of their physical and spectroscopic data with those of authentic samples.

2.2. Apparatus

IR spectra were recorded as KBr pellets on a Perkin-Elmer 781 spectrophotometer and a Magna 550 Nicolet FT-IR spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX-400 Avance spectrometer with tetramethyl silane (TMS) as internal reference. The Scanning Electron Microscopy (SEM) of nano particles determined with VEGA/TESCAN scanning electron microscope. The transmission electron microscopy (TEM) was recorded by Philips CM10-HT100KV. The X-ray diffraction (XRD) patterns of materials were recorded by employing a Philips Xpert MP diffractometer equipped with a Cu Kα anode (λ = 1.54 Å) in the 2θ range from 5 to 80°. Melting points obtained with a Yanagimoto micro melting point apparatus are uncorrected. The purity determination of the substrates and reaction monitoring were accomplished by TLC on silica-gel polygram SILG/UV 254 plates (from Merck company).

2.3. Preparation of nano silica periodic acid

10 mL 70% aqueous solution of HIO_4 was added to 1 g of nanosilicagel and stirred for 30 minutes. After filtration from unreacted periodic acid, it was heated at 50°C for 1 h under vacuum to afford nano-SPIA as a free flowing powder.

2.4. Typical Procedure

A mixture of 4-bromo aniline (1 mmol, 0.172g), nano-SPIA (0.050g) and sodium nitrite (1.2 mmol, 0.083 g) were ground in a mortar for 10 minutes to obtain a homogeneous mixture (Table 1). Then, a few drops of water were gradually added to this mixture and it was ground for 10 minutes until the gas evolution completely finished. KI (1 mmol, 0.143g) was added to the stable diazonium salt and grinding continued for 10 minutes. The reaction progress was monitored by thin layer chromatography (TLC) using a mixture of ethyl acetate and n-hexane (1:9 v/v) as solvent. Further purification of the product was performed by column chromatography using n-hexane and ethyl acetate. The aryl iodide was obtained in 80 % yield, mp 91°C, (mp [17]92°C).

2.7. The spectral data of some representative products

Iodobenzene:

IR [ῡ (cm^{-1}) (KBr)]: 3000, 1575, 1465 ,1420, 1088, 1060, 742, 690. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.11 (2H, m), 7.56 (2H, m), 7.25 (1H, m). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm) 135.86, 131.24, 128.39, 97.57.

***p*-Bromo Iodobenzene:**

IR [ῡ (cm^{-1}) (KBr)]: 3012, 1470, 1375, 1006, 821. 45. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.45 (2H, d), 7.31 (2H, d). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm):145.62, 131.54, 125.21, 96. S

***p*-Iodotoluene:**

IR [ῡ (cm^{-1}) (KBr)]: 3028, 1478, 1050, 1012, 815. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.35 (2H, d), 7.86 (2H, d), 2.35 (3H, S). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm):136.25, 136.82, 128.21, 93.2, 23.54.

***p*- Iodo nitrobenzene:**

IR [ῡ (cm^{-1}) (KBr)]: 3010, 1665, 1532, 1520, 1350,1055, 1009, 805. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.65 (2H, d), 7.73 (2H, d).

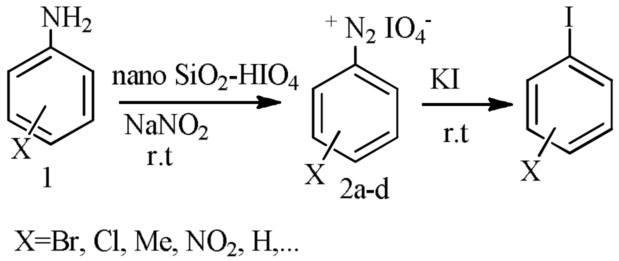
^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm):148.25, 132.51, 128.96, 98.75

***o*-Chloro Iodobenzene:**

IR [ῡ (cm^{-1}) (KBr)]: 3110, 1580, 1450,1431, 76. 91. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 77.72 (1H, m), 77.24 (1H, m), 77.01 (1H, m), 6.89 (1H, m). ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm):152, 146, 125, 120,

3. Results and discussion

In continuation of our previous researches on the synthesis and application of solid acid catalysts and supported reagents in organic syntheses [16], we describe the facile and modified synthesis of aryl iodides in the presence of nano-SPIA. In this work, a stable diazonium salt was formed under solvent-free conditions at room temperature (Scheme 1).



Scheme.1. One-pot conversion of aromatic amines to the corresponding aryl iodides under solvent-free conditions

We have prepared nano-SPIA by reacting nanosilicagel with a 70% HIO_4 solution. According to the SEM and TEM images and XRD pattern, the particle size of nano-SPIA is 35 nm (Fig.1).

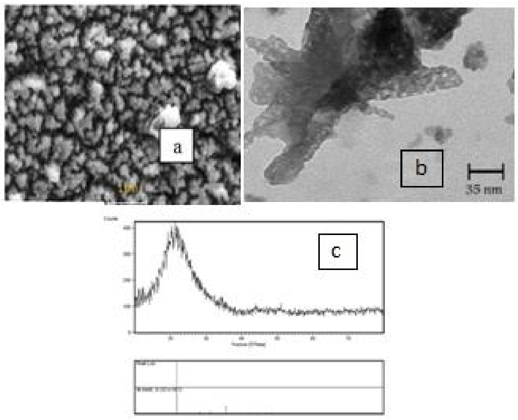


Fig.1. The SEM (a), TEM (b) images and XRD (c) pattern of nano-SPIA

By treatment of 4-bromo aniline (1 mmol) and sodium nitrite (1.2 mmol) in the presence of various amounts of nano-SPIA, we have obtained the corresponding diazonium salt in the excellent yield using 0.050 g of nano-SPIA (table 1, entry 4). After preparation of diazonium salt, KI (1mmol) was added to it and stirring for 10 minutes. The whole process of diazotization was performed in 30 minutes. The crude product was extracted with dichloromethane. Then the solvent was evaporated by rotary evaporator at reduced pressure and the crude product was purified by flash column chromatography. By this procedure, aryl iodides were obtained with 75-91% isolated yield (Table 2).

Table 1. Preparation of 4-bromophenyl diazoniumperiodate in the presence of various amounts of nano-SPIA[a]

Ent.	**Time (min)**	**Catalyst (g)**	**Yield (%)**
1	45	0.030	45
2	40	0.040	60
3	35	0.045	75
4	30	0.050	96
5	30	0.060	96

[a] 4-bromo Aniline (1 mmol) and sodium nitrite (1.2 mmol) was used.

Table. 2. Conversion of various aromatic amines to the corresponding aryl iodides under solvent-free conditions at room temperature

Entry	**Substrate**	**Product**	**Yield (%)**	**M.P.**	
				Found	**Reported.**[17]
1	aniline	Iodobenzene	75	186	188
2	2-chloro aniline	*o*-Chloro Iodobenzene	78	236	234
3	4-chloro aniline	*p*-Chloro Iodobenzene	85	59	57
4	4-cbromo aniline	*p*-Bromo Iodobenzene	80	91	92
5	2-nitro aniline	*o*-Iodo nitrobenzene	90	52	54
6	3-nitro aniline	*m*- Iodo nitrobenzene	85	40	38
7	4-nitro aniline	*p*- Iodo nitrobenzene	91	173	174
8	2-methyl aniline	*o*-Iodotoluene	70	210	211
9	4-methyl aniline	*p*-Iodotoluene	73	34	37
10	4-methoxy aniline	*p*- Iodoanisole	67	58	53

[a]The ratio of amines (mmol), $NaNO_2$ (mmol), KI (mmol) and nano-SPIA (g) is 1:1.2:1:0.05

The reusability of nano-SPIA was checked for several times without no important decrease in catalytic activity (Figure 2).

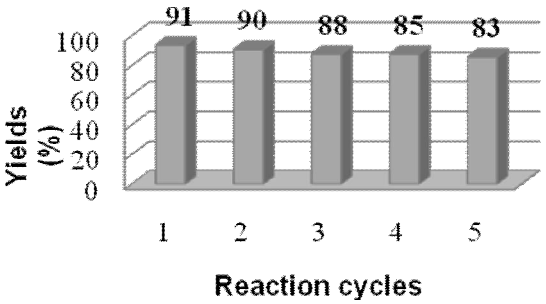
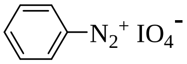
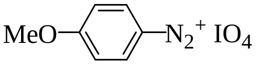
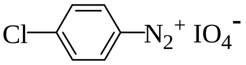
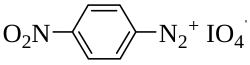


Fig. 2. Reusability of catalyst in the presence of 4-nitro Iodobenzene

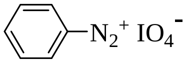
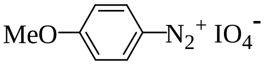
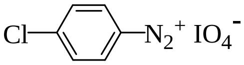
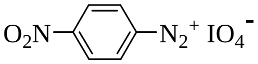
For determining the stability of the diazonium salts, some aryl diazonium nano-silicaperiodates were stored in a desicator at room temperature. After the specified times, 2-naphthol was added to each salt and the reaction mixture was ground at room temperature for 10 minutes. The products were extracted and the yield of azo dyes compared with the product provided with the corresponding fresh diazonium salts (Table 3). As shown in table 3, aryldiazonium nano-silica periodate with electron-withdrawing groups on aromatic ring, are more stable than those with electron donating groups because of the instability of the resulting aryl cation. Also, we have compared the stability of diazonium silica periodates *versus* diazonium nano-silica periodates and found that the diazonium silica periodates have less stability (Table 4).

Table 3. The stability study of some aryl diazonium nano silica periodate at room temperature [a]

Diazonium salt	Prduct	Yield (%) after						
		30 min	1 day	2 days	3 days	4 days	5 days	6 days
	2a	91	88	85	80	75	52	35
	2b	90	85	80	76	61	50	30
	2c	93	90	86	81	77	70	65
	2d	96	93	90	85	79	73	69

[a] The yields refer to the isolated pure products after adding 2-naphthol into their corresponding diazonium salts within the specified time

Table 4. The stability study of some aryl diazonium silica periodate at room temperature

Diazonium salt	Prduct	Yield (%) after						
		30 min	**1 day**	**2 days**	**3 days**	**4 days**	**5 days**	**6 days**
	2a	85	73	50	43	25	20	-
	2b	80	75	43	32	22	-	-
	2c	83	78	74	70	48	37	24
	2d	89	80	73	69	51	30	25

[a] The yields refer to the isolated pure products after adding 2-naphthol into their corresponding diazonium salts within the specified times

4. Conclusion

Various aromatic amines including electron-withdrawing and electron-donating groups were rapidly and efficiently converted to the corresponding aryl iodides under solvent-free conditions at room temperature. Especially nano silica periodic acid proved to be a suitable catalyst affording the highest stability of diazonium salts and yields. In order to evaluate the effect of the catalyst particle size on the catalytic activity, one reason for this behavior may be related to the number of available active sites which in turn increases the catalytic activity. The solvent free conditions employed in the present method, which make it environmental eco friendly and make it useful for industrial applications. This method is a novel, efficient and environmentally benign route for solvent-free synthesis of aryl iodides. Furthermore, it has other advantages such as mildness, short reaction times, low cost, ease of handling and simple experimental procedure.

Acknowledgment

The authors are grateful to University of Kashan for supporting this work by Grant No (159189/9).

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