

Direct One Pot Synthesis of Iodoarenes from Aromatic Amine Using TCT-Wet.Sio2 as an Effective Heterogeneous Catalyst

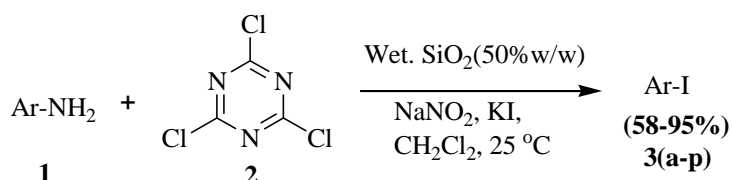
Somnath S. Gholap

Post graduate Department and Research Centre, Padmashri Vikhe Patil College, Pravaranagar (Loni Kd.), Rahata, Ahmednagar, India

ABSTRACT

The present article described the one pot direct synthesis of structurally diverse aryl iodides from primary aromatic amines in aprotic media. 1,3,5-Trichlorotriazine (TCT)-Wet. SiO₂ (50 % W/W) was found to be an effective heterogeneous catalyst for in situ generation of diazonium salt followed by iodination with potassium iodide. The methodology presented here was worked well for the variety of aromatic amines possessing electron donating as well as electron withdrawing substituents on aromatic ring at room temperature. The corresponding aryl iodides are obtained in good to excellent yield.

Keywords: Trichlorotriazine, diazonium salt, HCl



Keywords: Aromatic amine, diazotisation, 1,3,5-Trichlorotriazine, iodoarenes, heterogeneous catalyst.

I. INTRODUCTION

Aryl iodides are well known for their versatile synthetic utility as precursor for the synthesis of diverse biologically active compounds.¹ Moreover, iodo compounds are valuable as diagnostic aids and versatile synthetic intermediate for the synthesis of antimicrobial agents as well as in immunoassay studies along with in magnetic imaging study.² They have been radically fictionalized through C-N and C-C bond formation of diarenes, ethylenic or acetylenic condensation using transition metal catalyst bonds.³ The direct iodination of aromatic compounds with molecular iodine was found to be difficult due to its low reactivity. Hence, more powerful iodinating species is required for direct iodination.⁴

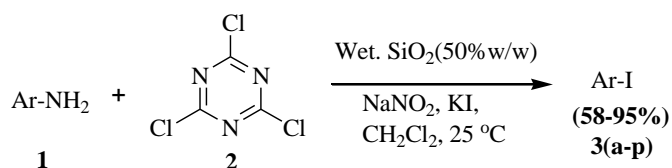
In recent years, direct iodination is extensively developed using various catalytic systems.⁵ However, the direct iodination method involves use of hazardous or toxic reagents, high reaction temperature for long reaction time with low product yields. In these methods

large amount of aromatic compounds were needed and reactions had conducted under strongly acidic conditions. It has been observed that in order to carry out the direct iodination reaction under milder condition, catalytic activation of an iodinating agents with Lewis acids⁶ or adding various oxidizing agents such as iodic acid, periodic acid, peracetic acid or silver (I) salts and recently reported periodinanes.⁷ In addition, P. R. Singh et al in 1972 have described the efficient method for the synthesis of para substituted iodobenzenes by nucleophilic aromatic substitution with KI in various reaction atmosphere such as nitrogen and oxygen. The iodoproucts obtained shows lower yield as 28-45% at 0 °C.⁸

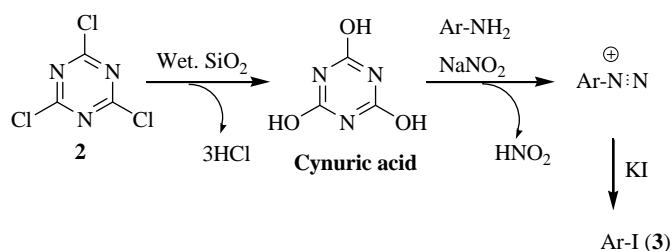
One of the commonly used methods for preparation of aryl iodides from primary amine is the Sandmeyer's reaction.⁹ The method discovered by Sandmeyer has advantages over direct iodination. In addition, this method was superior for the selective introduction of iodine at specified position on aromatic ring.¹⁰ However, the method discovered by Sandmeyer involved two step

process of diazotization-iodination by in situ generated nitrous acid from sodium nitrite and strong acid such as HCl or H₂SO₄ at 0 °C temperature followed by the reaction of KI in presence of transition metal catalyst such as Cu(I) iodide.¹¹

Apart from these traditional methods, there are some recent reports for the synthesis of title compound by modified Sandmeyer's reaction using HI/KNO₂ in DMSO,¹² Wet.CSA/NaNO₂/KI,¹³ Resin NO₂⁻, p-TsOH, H₂O,¹⁴ KI/NaNO₂/PTSA in MeCN,¹⁵ NaNO₂/sulfonated-resin/KI in H₂O,¹⁶ PTSA/NaNO₂/KI in water-paste form.¹⁷ Some of these reported methods were associated with different disadvantages such as long reaction time, low product yield, tedious reaction work-up and multistep reaction strategy. To overcome these problems we have developed new and efficient silica catalytic system. Herein, we have reported TCT-wet. SiO₂/NaNO₂/KI in CH₂Cl₂ catalyzed synthesis of aryl iodides from primary aromatic amines at 25 °C. (Scheme 1). The method presented here involves reduction in release of waste during workup procedures. It has been found that the said catalyst works well during the course of reaction.



Scheme 1. Synthesis of aryl iodides under heterogeneous conditions.



Scheme 2. Plausible mechanism for the synthesis of aryl iodides(3).

II. METHODS AND MATERIAL

All chemicals are of analytical grade. The melting points were determined on the open capillary tube and are

uncorrected. The IR spectra were recorded on Bomem FT-IR MB-104 Spectrophotometer. ¹H NMR were recorded on Bruker AC-300 MHz in CDCl₃ using TMS as an internal standard. Products were all known compounds and were identified by comparison of their physical and spectral data with those of reported in literature.

A General procedure for the synthesis of aryl iodides.

To a mixture of primary amine (5 mmol) and wet.SiO₂ (0.25 g, 50% w/w) in CH₂Cl₂ 10ml), KI (7 mmol) was added. The reaction mixture was stirred magnetically for specified time at room temperature. After reaction (as indicated by TLC), the reaction mixture was filtered. The solvent was removed under reduced pressure to afford the desired aryl iodide products with good to excellent yield. All the synthesized compounds are known compounds and confirmed by their spectroscopic data along with their physical constants.

III. RESULTS AND DISCUSSION

In continuation to our ongoing research on the development of novel methods using green techniques,¹⁸ herein we have reported the direct method for the synthesis of aryl iodides from primary aromatic amines.

During the course of our study, we have conducted the optimization of reaction by employing aniline (5 mmol), cynuric chloride (5 mmol), NaNO₂ and KI in water(10 mL) at room temperature. It has been observed that when reaction directly in water medium showed the formation of iodobenzene (**3a**) in low yield (37%). However, when same reaction was conducted in presence of wet silica (50%w/w) and aprotic medium such as dichloromethane (5 mL), the corresponding iodobenzene (**3a**) product is obtained in 95% yield (Table 1). Hence, further reactions for the formation of aryl iodides were conducted in heterogeneous medium. Various aromatic amines possessing electron donating as well as electron withdrawing groups are subjected to the formation of aryl iodides. The results obtained were summarized in Table 1. Moreover, aliphatic amines such as n-octyl amine reacts slowly to afford octyliodide in 58% yield (entry **3n**). All the synthesized compounds are known compounds and confirmed by their spectroscopic data along with their physical constants.

A plausible mechanism for the formation of aryl iodide via diazotization of primary amine (**1**) was depicted in Scheme 2. From the literature survey it was clear that cynuric chloride (**2**) reacts with water to form cynuric acid and HCl.^{19, 20} In situ generated HCl and cynuric acid may assist the diazotization by the formation of nitrous acid from sodium nitrite (Scheme 2).

IV. CONCLUSION

In conclusion, we have developed a new direct method for the synthesis of aryl iodides from aromatic amines using heterogeneous catalytic system in aprotic medium. 1,3,5-Trichlorotriazine (TCT)-Wet. SiO₂ (50 % W/W) was found to be an effective heterogeneous catalyst for in situ generation of diazonium salt followed by iodination with potassium iodide. The methodology presented here was worked well for the variety of aromatic amines possessing electron donating as well as electron withdrawing substituents on aromatic ring at room temperature. The corresponding aryl iodides are obtained in good to excellent yield.

Table 1. synthesis of aryl iodides from aromatic amines (**3**) in heterogeneous medium

Ent ry	Ar-NH ₂	Aryl iodide	Compo und No	Time(min.)	Yield (%)
1.	C ₆ H ₅ NH ₂	C ₆ H ₅ I	3a	30	95
2.	2-NO ₂ C ₆ H ₄ NH ₂	2-NO ₂ C ₆ H ₄ I	3b	45	89
3.	3-NO ₂ C ₆ H ₄ NH ₂	3-NO ₂ C ₆ H ₄ I	3c	40	95
4.	4-NO ₂ C ₆ H ₄ NH ₂	4-NO ₂ C ₆ H ₄ I	3d	40	92
5.	4-MeOC ₆ H ₄ NH ₂	4-MeOC ₆ H ₄ I	3e	30	73
6.	4-MeC ₆ H ₄ NH ₂	4-MeC ₆ H ₄ I	3f	30	70
7.	4-IC ₆ H ₄ NH ₂	4-IC ₆ H ₄ I	3g	30	79

8.	4-NH ₂ C ₆ H ₄ NH ₂	4-NH ₂ C ₆ H ₄ I	3h	30	74
9.	4-COOHC ₆ H ₄ NH ₂	4-COOHC ₆ H ₄ I	3i	30	86
10.	2-COOHC ₆ H ₄ NH ₂	2-COOHC ₆ H ₄ I	3j	40	90
11.	2,6-Di,MeC ₆ H ₃ NH ₂	2,6-Di,MeC ₆ H ₃ I	3k	50	84
12.	2,4,6-Tri-NO ₂ C ₆ H ₂ NH ₂	2,4,6-Tri-NO ₂ C ₆ H ₂ I	3l	30	92
13.	2,4-Di-NO ₂ C ₆ H ₃ NH ₂	2,4-Di-NO ₂ C ₆ H ₃ I	3m	30	87
14.	CH ₃ (CH ₂) ₇ NH ₂	CH ₃ (CH ₂) ₇ I	3n	30	58
15.	2-MeC ₆ H ₄ NH ₂	2-MeC ₆ H ₄ I	3p	30	61

[a] The yields refer to the pure isolated products. ^b All products were characterized by IR and ¹HNMR and compared with authentic samples

V. ACKNOWLEDGEMENTS

The authors are thankful to Dr. Dighe, P. M. Principal, Padmashri Vikhe Patil College of Art's, Science and Commerce, Pravaranagar (MS) for providing laboratory facilities and Dr. J. N. Nigal for constant encouragement.

VI. REFERENCES

- [1]. a) P.E. Fanta, Synlett., 1974, 9; b) M. Nilsson, Tetrahedron Lett., 1966, 679; c) H.O. House, W.L. Resress, G.M. Whiteside, J. Org. Chem., 1966, 31, 3128; d) H. Suzuki, H. Abe, A. Osuka, Chem. Lett., 1980, 1363.
- [2]. a) W.A. Volkert, T.J. Hofmann, Chem. Rev., 1999, 99, 2269; b) S.B. Yu, A.D. Watson, Chem. Rev., 1999, 99, 2353.
- [3]. For review see E.B. Merkushev, Synthesis, 1988, 923.

- [4]. T. Mukaiyama, H. Kitagawa, J.-I. Matsuo, *Tetrahedron Lett.*, 2000, 41, 9383-9386.
- [5]. F. Radner, *J. Org. Chem.*, 1988, 53, 3548.
- [6]. a) T. Sugita, M. Idei, Y. Ishibashi, Y. Takegami, *Chem. Lett.* 1982, 1481; b) S. Umemura, A. Onoe, M. Okano, *Bull. Chem. Soc. Jpn.*, 1974, 47, 147.
- [7]. a) H.O. Wirth, O. Konigslén, W. Kern, *Liebigs Ann. Chem.*, 1960, 634, 84; b) S. Ahmad, et al *Tetrahedron*, 1976, 32, 503; c) Y. Ogata, K. Nakajima, *Tetrahedron*, 1964, 20, 43; d) J. Janssen, C.V. Wilson, *Org. Synth.*, 1963, 547; e) L. Keefer, L. Andrews, *J. Am. Chem. Soc.* 1956, 78, 5623.
- [8]. Singh, R. P. and Kumar, R. *Tetrahedron Lett.* 1972, 7, 1972.
- [9]. (a) S. Patal In *The Chemistry of Diazonium and Diazogroups*, Ed; Wiley: NewYork, 1978; b) T.I Godovikova, O.A. Rakitin, L.I. Khmel'nitskii, *Russ. Chem. Rev.* 1983, 52, 440.
- [10]. E.A. Krasnokutskaya et al *Synthesis*, 2007, 1, 81-84.
- [11]. C. Galli, *Chem. Rev.*, 1988, 88, 765.
- [12]. W.Baik, W. Laun, H. J. Lee, C. H. Yoon, B. H. Kim, *Can. J. Chem.* 2005, 83, 213.
- [13]. F. Nemati, A. Elhampour, *Scientia Iranica* 2012, 19(6), 1594-1596.
- [14]. M. E. Trusova, E.A. Krasnokutskaya, P. S. Postnikov, Y. Choi, K.-W. Chi, V.D. Filimonov, *Synthesis*, 2011, 13, 2154-2158 ().
- [15]. E.A. Krasnokutskaya, N.I. Semenischeva, V.D. Filimonov, P. Knochel, *Synthesis*, 2007, 1, 81-84.
- [16]. V. D. Filimonov, N. I. Semenischeva, E. A. Krasnokutskaya, A. N. Tretyakov, H.Y. Hwang, K.-W. Chi, *Synthesis*, 2008, 2, 185-187.
- [17]. D. A. Gorlushko, V. D. Filimonov, E. A. Krasnokutskaya, N. I. Semenischeva, B. S. Go, H.Y. Hwang, E. H. Cha, K.-Wh. Chi, *Tetrahedron Lett.*, 2008, 49, 1080-1082.
- [18]. a) S. S.Gholap, S. R. Ugale, *ChemistrySelect*, 2017, 2(24), 7445-7449; b) S. S.Gholap, S. R.Ugale, *Chem. Pap.* 2017. Doi:10.1007/s11696-017-0237-1; c) S. S.Gholap, N. Gunjal, *Arabian. J. Chem.* 2017, 10, S2750-S2753; d) S. S.Gholap, Y. R. Sadaphal, *Sensors and Actuators B.* 2017, 253, 173-179; e) S. S. Gholap, *Eur. J. Med. Chem.* 2016, 110, 13-31; f) S. S. Gholap, Gunjal, N. *Iranian J. Catal.* 2016, 8, 147-152; g) S. S.Gholap, V. D. Dhakane, U. P. Deshmukh, H. V. Chavan, B. P. Bandgar, *C R Chim* 2014, 17, 431-436; h) S. S. Gholap, U. P. Deshmukh, *Iranian J. Catal.* 2013, 3, 171-176; i) S. S. Gholap, V. D. Dhakane, Sandeep S. Gholap, *Jordan J. Chem.* 2012, 7(3), 279-285; j) S. S. Gholap, V. D. Dhakane, S. N. Shelke, M. S. Tambe, *Bull. Catal. Soc. India* 2012, 11, 50; k) S. S. Gholap, *Heterocycl Lett.* 2012, 2(3), 461; l) S. S. Gholap, C. H. Gill, G. R. Pandhare, *Indian J. Heterocycl. Chem.* 2009, 18, 279.
- [19]. M. Shrama, S. Pandey, K. Chauvan, D. Shirma, B. Kumar, P.M.S.Chauvan, *J. Org. Chem.* 2012, 77, 929-937.
- [20]. M.A. Bigdeli, G. H.Mahdavinia, S. Jafari, H. Hazarkhani, *Catal.Comm.*, 2007, 8, 2229-2231.