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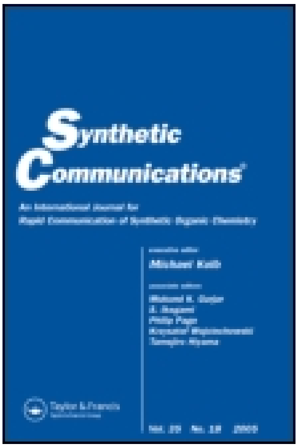

Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Simple and Efficient Method for the Preparation of Aryl Azides Using Sonication

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Accepted author version posted online: 07 Oct 2011.Version of record first published: 16 Dec 2011.

To cite this article: Vikas N. Telvekar & Kulbhushan A. Sasane (2012): Simple and Efficient Method for the Preparation of Aryl Azides Using Sonication, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 42:7, 1085-1089

To link to this article: http://dx.doi.org/10.1080/00397911.2010.535945

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Synthetic Communications®, 42: 1085–1089, 2012
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ISSN: 0039-7911 print/1532-2432 online
DOI: 10.1080/00397911.2010.535945

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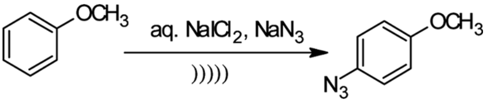
GRAPHICAL ABSTRACT



Abstract *An efficient procedure for the preparation of aryl azides using sonication is described. The convenient sonication-mediated azidation protocol is applicable to aryl compounds under mild conditions with aqueous solution of sodium dichloroiodate and sodium azide. Aryl azides were obtained in excellent yields from a variety of aryl compounds in short reaction times without affecting sensitive functional groups.*

Keywords Aryl azides; sodium azide; sodium dichloroiodate; sonication

INTRODUCTION

Azides have wide applications in organic transformations such as in conversions to heterocycles. While numerous methods are available for preparation of aliphatic azides, there is limited choice for aryl azides. The most straightforward route for the preparation of aryl azides involves replacement of amines with azide via diazotization using sodium azide or azidotrimethylsilane.[1,2] A straightforward synthesis of aryl azides from the corresponding amines is also accomplished using triflyl azide or *tert*-butyl nitrite and azidotrimethylsilane.[3–5] Alternatively, aryl amines have been transformed into aryl azides by treating the former with *para*-toluenesulfonyl azide in the presence of a Grignard reagent or strong base.[6] Aryl azides have also been prepared from arylmagnesium halides or aryl lithium reagents, generated from aryl halides, and *para*-toluenesulfonyl azide.[7] Very recently, the coupling of aromatic halides with sodium azide under catalysis with CuI-L-proline was reported to produce aryl azides in good to excellent yields.[8] However, all these transformation require long reaction time and either acidic or basic conditions, which are not compatible

Received June 18, 2010.

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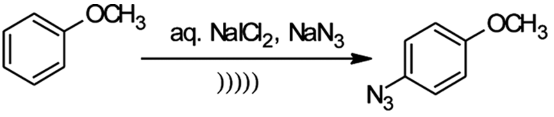


Scheme 1. Anisole converted into 4-azidoanisole using sonication.

with many functional groups present in a substrate. Thus, there is scope for alternative reagent systems for preparation of aryl azides.

Recently, interest has increased for reduced reaction time, lower costs, and simplified processes. These procedures usually combine supported reagents and microwave[9,10] or ultrasonic irradiation[11–13] to carry out a wide range of reactions in shorter reaction times and with high conversion and selectivity. A few examples using sonication are synthesis of oligomannosides,[14] condensation reaction of naphthol/aldehydes,[15] condensation reaction of aminopyrazoles/aldehydes,[16] Suzuki–Miyaura cross-coupling reaction,[17] and glycosidation in carbohydrate chemistry.[18] Our group has been working extensively on the development of novel methodologies under mild reaction conditions using various hypervalent iodine reagents. Sodium dichloroiodate is commercially available in a 50% water solution. Recently we exploited this reagent for oxidation of alcohols.[19]

While working on this reagent, we found that the aqueous solution of sodium dichloroiodate can be used for the direct preparation of aryl azides combined with sonication in a short reaction time. Initially, we carried out the reaction with anisole as a model substrate to explore the suitable reaction conditions (Scheme 1).

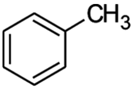
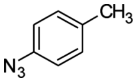
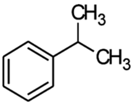
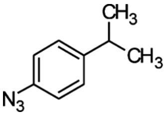
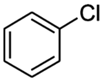
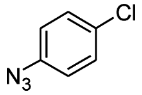
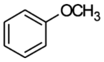
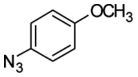
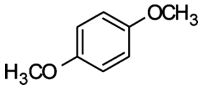
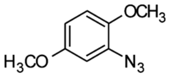
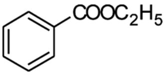
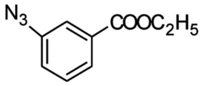
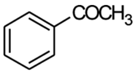
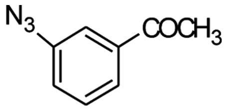
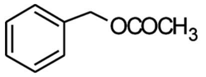
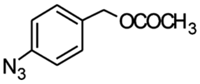
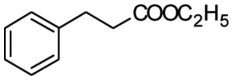
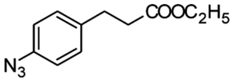
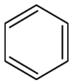
A mixture of anisole, aqueous sodium dichloroiodate solution, and sodium azide was sonicated at room temperature (25 °C). The starting material was consumed within 10 min as indicated by thin-layer chromatography (TLC) analysis. After workup and purification by silica-gel column chromatography, 4-azidoanisole was isolated in 90% yield. The reaction is in general clean, and no other product was observed in these reaction conditions. Without sonication but with stirring, the reaction did not proceed at all at room temperature, even at more than 72 h. Heating at 40–80 °C led to the formation of other unidentified products.

RESULTS AND DISCUSSION

To explore the reaction scope, a variety of aryl compounds, prepared by standard reported procedures, were converted to corresponding azides in moderate to good yields in short reaction times, and the results are summarized in Table 1.

It was found that either electron-rich or electron-deficient aryl compounds were suitable for this reaction, giving aryl azide in moderate to good yields in short reaction times (Table 1, entries 1–7). A variety of functional groups such as methoxy and acetate tolerated these reaction conditions (Table 1, entries 4, 5, 8, and 9). This feature would allow the use of the present method in the synthesis of a wide range of aryl azides. No reaction was observed in the case of benzene even after a long reaction time (Table 1, entry 10). A plausible mechanism for the aryl azidation is proposed in Scheme 2.

Table 1. Preparation of aryl azides using sodium dichloroiodate and sodium azide combination with sonication[a]

Entry	Substrate[b]	Product	Time (min)	Yield (%)[c]
1			10	82
2			10	83
3			10	85
4			10	90
5			10	88
6			15	70
7			15	72
8			15	83
9			15	82
10		—	45	NR[d]

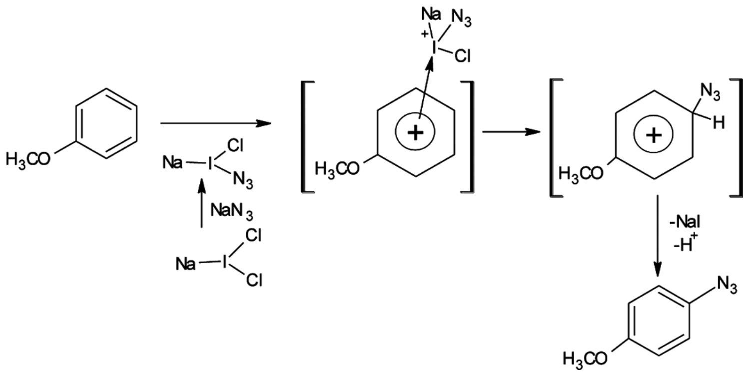
[a] Reaction conditions: Substrate (1.0 equiv), aqueous solution of sodium dichloroiodate (1.5 M, 1.01 equiv), and sodium azide (1.01 equiv) at room temperature combined with sonication.

[b] Starting compounds were prepared by standard reported procedures.

[c] Isolated yields after column chromatography and structures were confirmed by comparison of the IR and ^{1}H NMR spectra with those of authentic materials.[3,4,20–22]

[d] No reaction.

In conclusion, a new environmentally friendly reaction system using aqueous sodium dichloroiodate and sodium azide in combination with sonication has been developed. This method is capable of converting various aryl compounds into corresponding aryl azides at room temperature in short reaction times and gives moderate to good yields.



Scheme 2. Plausible mechanism for aryl azidation.

EXPERIMENTAL

Preparation of Aromatic Azides

Anisole (1 g, 9.25 mmol) and sodium azide (0.6 g, 9.4 mmol) were added to the aqueous solution of sodium dichloroiodate (6.3 mL, 1.5 M, 9.4 mmol). The resultant reaction mixture was placed in an ultrasonic bath (33 KHz) at room temperature until the starting material was completely consumed (TLC). The reaction mixture was extracted with ethyl acetate, and the organic phase was washed successively with 10% sodium bisulfate solution (2 × 20 mL), 10% sodium bicarbonate (2 × 15 mL), and water (2 × 20 mL). The organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure to give the crude product. Pure 4-azidoanisole was obtained as a brown oil after silica-gel column chromatography (10% EtOAc–hexane). ^{1}H NMR ($CDCl_3$) δ: 3.75 (3H, s,), 6.78 (2H, d, $J = 8.0$ Hz), 7.40 (2H, d, $J = 8.0$ Hz). IR (KBr) cm^{-1}: 2107, 1599.

Ethyl-3-(4-azidophenyl)propanoate (Table 1, Entry 9)

^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.26 (3H, t, $J = 8.0$ Hz), 2.53 (2H, t, $J = 7.0$ Hz), 2.90 (2H, t, $J = 7.0$ Hz), 4.10 (2H, q, $J = 8.0$ Hz), 6.98 (2H, d, $J = 8.4$ Hz), 7.18 (2H, d, $J = 8.4$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 14.1, 29.2, 33.9, 61.2, 122, 127, 136, 139, 176; EI MS (*m*/*z*) 219 [M^+]; IR (KBr) cm^{-1}: 2112, 1735, 1610.

ACKNOWLEDGMENT

K. A. S. gratefully acknowledges the Council of Scientific and Industrial Research, Delhi, India, for financial support.

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