Tetrahedron Letters 58 (2017) 3441–3445

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Iron(0) nanoparticles mediated direct conversion of aryl/heteroaryl amines to chalcogenides *via* in situ diazotization

Subir Panja, Pintu Maity, Debasish Kundu, Brindaban C. Ranu *

Department of Organic Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700032, India

ARTICLE INFO

Article history:
Received 27 June 2017
Accepted 19 July 2017
Available online 20 July 2017

Keywords:
Fe(0) nanoparticles
Chalcogenides
Aryl/heteroaryl amines
In situ diazotization
tert-Butyl nitrite

ABSTRACT

A simple procedure for the synthesis of organo-chalcogenides has been developed by the reaction of aryl/heteroaryl amines with di-aryl/heteroaryl dichalcogenides in the presence of ^{t}BuONO and Fe(0) nanoparticles. The reaction proceeds *via* in situ diazotization followed by chalcogenation. A series of functionalized diaryl/aryl heteroaryl/diheteroaryl/aryl-alkyl selenides, sulfides and tellurides have been obtained by this procedure. Significantly, using this procedure 2,4-dinitroaniline is converted to (2,4-dinitrophenyl)(phenyl)selane which is known as thioredoxin reductase (TR) and glutathione reductase (GR) inhibitor. The reaction goes by a radical pathway and a plausible mechanism has been suggested.

Introduction

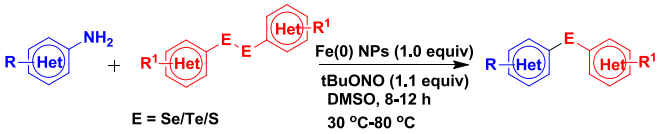
The aryl/heteroaryl chalcogenides are of much interest as they constitute the framework of many molecules having important biological activities such as anticancer, antioxidant, enzyme-inhibiting, and applications as useful materials.[1,2] They are also employed as useful intermediates in organic reactions.[3] Hence, the synthesis of chalcogenides is of continued interest and a plethora of methods have been reported. One of the widely employed procedures is the transition metal catalysed aryl-chalcogen bond formation. Several transition metals such as Pd, Ni, Cu, Fe, Co, Rh and In have been used as catalysts for the reaction of aryl halides, aryl boronic acid, aryl triflates with thiols, selenols/PhSeNa and diaryl dichalcogenides for the access to diaryl chalcogenides.[4,5] In some cases these procedures need long reaction time, higher temperature and stoichiometric or greater amount of metal catalysts and the yields were not always good.[6] Moreover, aryl halides, aryl boronic acid and aryl triflates are relatively expensive. Hence, amines being less expensive and readily available commercially, have been employed in several recent reactions. Usually aryl amines are converted to stable diazonium fluoroborates which are subsequently subjected to reaction with diaryl dichalcogenides under different conditions such as microwave irradiation,[7] ball milling[8] and in the presence of hypophosphorous acid[9] for carbon-chalcogen bond formation. However the use of aryl diazonium fluoroborate limits the substrate scope because of the practical disadvantage to diazotize the heteroaryl amines in standard acidic medium.[10] To avoid this drawback recently our group has developed an alternative route for the synthesis of diaryl/heteroaryl chalcogenides by direct use of aryl/ heteroaryl amines and ^{t}BuONO in visible light (blue LED) photocatalyzed condition.[11] Very recently Cai et al. reported synthesis of aryl sulfides from aniline using ascorbic acid as a promoter although selenides and tellurides were not addressed by this procedure.[12] We report here a more convenient and general procedure avoiding any special device such as LED, for the synthesis of aryl/heteroaryl sulfides, selenides and tellurides with a wide substrate scope by Fe(0) nanoparticles mediated direct conversion of aryl/heteoaryl amines *via* in situ diazotization using ^{t}BuONO (Scheme 1). Although there are several reports of Fe(0) mediated reactions[13] no report of its use for chalcogenide bond formation is known. Iron nanoparticles were prepared by a reported procedure and were used as such.[14]

Results and discussion

To optimize the reaction conditions a series of experiments were performed with variation of solvent, temperature and time for a representative reaction of 4-methoxy aniline and diphenyl diselenide in the presence of Fe(0) NPs.[14] The results are summarized in Table 1. Among a variety of solvents studied, dimethyl sulfoxide (DMSO) produced the best yield in the presence of Fe(0) NPs (1.0 equiv.) and ^{t}BuONO (1.1 equiv.) at 30 °C for 8 h (Table 1, entry 6). Dimethyl formamide (DMF) is also considerably effective (Table 1, entry 2) whereas, use of *N*-methylpyrrolidone (NMP) (Table 1, entry 1), CH_3CN, dimethyl carbonate, toluene and THF (Table 1, entries 7–10) led to lower yield. The change of reaction

* Corresponding author.
E-mail address: ocbcr@iacs.res.in (B.C. Ranu).

http://dx.doi.org/10.1016/j.tetlet.2017.07.070
0040-4039/



Scheme 1. Synthesis of aryl/heteroaryl selenides, tellurides and sulfides from aryl/heteroaryl amines.

temperature to 50 °C and 70 °C did not increase the yield further for this reaction (Table 1, entries 11 and 12). The reaction for longer time than 8 h (Table 1, entries 3 and 5) reduced the yield. When Fe(0) NPs was used in more than 1 equivalent no better result was obtained (Table 1, entry 13). In the absence of Fe(0) NPs, the reaction did not occur (Table 1, entry 4). The reaction produced relatively low yield (46%) in presence of Fe powder (Table 1, entry 14). In case of diphenyl ditelluride the reaction afforded the best yield in DMSO in presence of Fe(0) NPs (1.0 equiv.) and ^{t}-BuONO (1.1 equiv.) at 80 °C for 12 h (Table 1, entry 18). The lowering of temperature (50 °C and 30 °C) and time (8 h) did not give satisfactory yield of the product (Table 1, entries 15–17). For diphenyl disulfide the reaction provides the best result in DMSO in the presence of Fe(0) NPs (1.0 equiv.) and ^{t}BuONO (1.1 equiv.) at 80 °C for 8 h (Table 1, entries 19–22).

In a typical experimental procedure, a mixture of an amine and diphenyl diselenide/ditelluride/disulfide in DMSO was heated (30–80 °C) in the presence of Fe(0) NPs[14] and ^{t}BuONO for a required period of time (monitored by TLC). After evaporation of DMSO, extraction of the residue with ethyl acetate and purification by column chromatography over silica gel provided the pure product.

A wide range of substituted aryl/heteroaryl amines were subjected to reaction with substituted diphenyl diselenides by this procedure to produce the corresponding products. The results are summarized in Table 2. Both electron donating and electron withdrawing groups bearing aryl amines uniformly reacted with substituted diphenyl diselenides and provided the corresponding products (**3a, 3c, 3d, 3e, 3f, 3g, 3h, 3i, 3j, 3k, 3l, 3m, 3n, 3o, 3p, 3q, 3r**). Halogen containing aryl amines were also compatible for this reaction (**3c, 3g, 3j**) and needless to say, the presence of halogens provides scope for further funtionalization.

Heteroaryl amines successfully participated in this reaction with aryl or heteroaryl diselenides and the corresponding products (**3s, 3t, 3u, 3v**) were obtained.

Sterically hindered 2,6-dimethyl aniline also reacts with diselenides (**3i**,**3t**). Several functional groups such as –NO_2, –COMe, –CO_2Me, –OMe, –CN are sustainable with the reaction conditions. The substitution of electron donating and electron withdrawing groups on the phenyl ring of aryl amines did not have any appreciable influence on the outcome of the reaction.

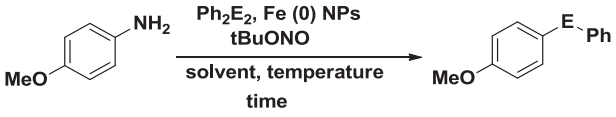
The same procedure was followed for the synthesis of diaryl tellurides and sulfides although the reactions were performed at 80 °C as optimized. All the products are summarized in Tables 3 and 4 respectively.

Several substituted aryl/heteroaryl amines have been employed for these reactions. A variety of functional groups such as –F, –NO_2, –COMe, –CN, –CHO, –OMe, –Cl, –I, –CF_3 on aryl amines are compatible for these reactions and the corresponding products were produced without any difficulty.

In general the reactions are clean and high yielding. The Fe nanoparticles were obtained by a reported procedure using $FeCl_3$ and sodium borohydride.[14] The Fe(0) NPs obtained by a different procedure using tea extract[15] without using any hydride reducing agent also provides the same result. The chalcogenides are obtained pure and properly characterized by spectroscopic data. Majority of the compounds were obtained for the first time. This procedure gives an access to diverse diaryl selenides/tellurides/sulfides in good to excellent yield. Moreover pharmaceutically potential[2] diheteroaryl selenides are also synthesized by this protocol.

2,4-Dinitroaniline reacts with diphenyl diselenide to produce (2,4-dinitrophenyl)(phenyl)selane (Scheme 2, **6a**) which is

Table 1
Standardization of reaction conditions.[a]



Entry	Ph_2E_2	Fe(0) nps (eq.)	Solvent	Time (h)	Temp (°C)	Yield %
1	Ph_2Se_2	1	NMP	12	30	30
2	Ph_2Se_2	1	DMF	12	30	70
3	Ph_2Se_2	1	DMSO	12	30	76
4	Ph_2Se_2	–	DMSO	10	30	Trace
5	Ph_2Se_2	1	DMSO	10	30	77
6[b]	**Ph_2Se_2**	**1**	**DMSO**	**8**	**30**	**82**
7	Ph_2Se_2	1	CH_3CN	8	30	30
8	Ph_2Se_2	1	DMC	8	30	65
9	Ph_2Se_2	1	Toluene	8	30	45
10	Ph_2Se_2	1	THF	8	30	49
11	Ph_2Se_2	1	DMSO	8	50	78
12	Ph_2Se_2	1	DMSO	8	70	44
13	Ph_2Se_2	2	DMSO	8	30	73
14[c]	Ph_2Se_2	1	DMSO	8	30	46
15	Ph_2Te_2	1	DMSO	8	30	21
16	Ph_2Te_2	1	DMSO	8	50	40
17	Ph_2Te_2	1	DMSO	8	80	70
18[b]	**Ph_2Te_2**	**1**	**DMSO**	**12**	**80**	**74**
19	Ph_2S_2	1	DMSO	12	30	60
20	Ph_2S_2	1	DMSO	12	80	73
21[b]	**Ph_2S_2**	**1**	**DMSO**	**8**	**80**	**81**
22	Ph_2S_2	1	DMSO	8	70	65

[a] Reaction conditions: 4-Methoxy aniline (1 mmol), diaryl dichalcogenides (0.5 mmol), ^{t}BuONO (1.1 mmol), Fe(0) NPs (1.0 mmol).
[b] Best condition.
[c] Fe powder (1 equiv.) instead of Fe(0) NPs.