Zinc-Mediated Synthesis of Diaryl Selenides from Diaryl Diselenides and Diaryliodonium Salts in Aqueous Media

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Z. Naturforsch. **61b**, 194 – 196 (2006); received November 17, 2005

An efficient synthetic method has been developed for the preparation of symmetrical and unsymmetrical diaryl selenides through a one-pot reaction of diaryl diselenides and diaryliodonium salts in the presence of Zn/AlCl₃ system in aqueous media.

Key words: Diaryl Selenides, Diselenides, Diaryliodonium Salts, Zn/AlCl₃

Introduction

The chemistry of organoselenium compounds has been growing in recent years, because of the many synthetic applications of these compounds [1]. The synthesis of diaryl selenides has attracted considerable attention due to the fact that these compounds have widespread applications. Diaryl selenides, containing amino groups, have useful antioxidative properties [2], and some biologically active molecules include diarylselenium moiety [3]. Among the useful and general methods for the preparation of symmetrical and unsymmetrical diaryl selenides, we can cite those involving the treatment of arenediazonium salts with sodium selenide [4] and with sodium benzeneselenolate [5], the reaction of electrophilic selenium species such as diselenides and selenocyanates with Grignard reagents and aryllithiums [6], the arylation of sodium benzeneselenolate with an aryl halide catalyzed by nickel (II) complex [7], photochemical reaction of simple haloarenes with sodium areneselenolate [8], the reaction of diaryl diselenides with activated halides in the presence of aminoiminomethanesulfinic acid [9], copper-catalyzed reaction of aryl iodide and diphenyl diselenide using magnesium metal [10], palladium-catalyzed reactions of phenyltributylstannyl selenide (PhSeSnBu₃) with aryl halides and triflates [11]. However, some of these methods suffer from disadvantages such as the use of toxic, hazardous, expensive or less easily available reagents, harsh reaction conditions or lower yields. In two recent reports, areneselenyl magnesium bromide [12] and diaryl diselenide [13] reacted with diaryliodonium salts to give the corresponding diaryl selenides. However, these methods were either performed under anhydrous condition and nitrogen atmosphere [12] or used unavailable titanocene hydride (Cp₂TiH) and low temperature [13]. Hence, the development of a one-step synthetic method using stable reagents under atmospheric conditions is in demand.

Results and Discussion

In the last decade, much attention has been paid to organometallic reactions in aqueous media [14]. Recently, transition metal selenolates or complexes have been widely used in synthesis of organoselenium compounds [15], but reports exploring zinc selenolates are rare [16]. In the present paper we propose a convenient one-pot method for the synthesis of diaryl selenides via reaction of diaryliodonium salts and diselenides promoted by Zn/AlCl₃ system. It has been reported earlier [16] that zinc arylselenolates can be easily generated from diaryl diselenides in the presence of Zn/AlCl₃ system. Simple stirring of diselenide 1 with metallic zinc dust in the presence of anhydrous aluminum chloride in CH₃CN-H₂O mixed solvent at 83 °C produced the zinc selenolate 2. This was followed by addition of diaryliodonium salt which gave, after work-up, the desired selenide (Scheme 1) in 52-82% yield as shown in Table 1. These diaryliodonium salts are electrophilic arylating agents and are more susceptible to nucleophilic displacement, since their positive charges should facilitate polar fission of the bonds to the aro-

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Ar	$Ar'_2I^+X^-$	Reaction time (h)	Yield (%) ^a	M.p. or b.p. [†] (°C)/Torr	
				found	reported ^b
Ph	Ph ₂ I ⁺ I ⁻	0.3	78	Oil	Oil ¹²
Ph	$(4-MeC_6H_4)_2I^+I^-$	2	80	$97 - 98^{\dagger}$	100^{6b}
Ph	$(4-ClC_6H_4)_2I^+Cl^-$	3.5	70	$139 - 141^{\dagger}$	$145 - 150^{6b}$
Ph	$(4-BrC_6H_4)_2I^+Cl^-$	3	68	$150 - 152^{\dagger}$	$158 - 161^{6b}$
4-ClC ₆ H ₄	$Ph_2I^+I^-$	1.2	80	$139 - 141^{\dagger}$	$145 - 150^{6b}$
4-ClC ₆ H ₄	$(4-MeC_6H_4)_2I^+I^-$	2.3	82	67 - 69	$71 - 73^{13}$
4-ClC ₆ H ₄	$(4-BrC_6H_4)_2I^+Cl^-$	1.25	69	98 - 100	$103 - 104^{6b}$
$3-MeC_6H_4$	$Ph_2I^+I^-$	1.5	75	$98 - 100^{\dagger}$	$100 - 102^{6b}$
$3-MeC_6H_4$	$(4-MeC_6H_4)_2I^+I^-$	3	73	$126 - 128^{\dagger}$	$129 - 134^{6b}$
1-Naphthyl	$Ph_2I^+I^-$	3.5	52	Oil	$240/0.2^7$

Table 1. Synthesis of diaryl selenides from diselenides and diaryliodonium salts in the presence of Zn/AlCl₃.

ArSe-SeAr
$$\xrightarrow{Zn/AlCl_3}$$
 $(ArSe)_2Zn$ $\xrightarrow{Ar_2l^+X^-}$ ArSeA $(CH_3CN/H_2O, 83 ^{\circ}C)$ 2 3 Scheme 1.

matic systems [17]. The reaction is found to be general and suitable for synthesis of both symmetric and unsymmetric diaryl selenides. Various diaryliodonium salts containing different substituents such as chloro, methyl, bromo and two anions, chloride and bromide, are successfully reacted.

Conclusion

In conclusion, we have developed a new general and efficient procedure for the synthesis of various diaryl selenides. The present method has the advantages of operational simplicity, mild reaction conditions, lack of toxicity, fast reaction rates, and low costs.

Experimental Section

Diaryliodonium salts were prepared by standard procedures [18]. All products were characterized by comparison of their spectral and physical data with those of known samples. ¹H (300 MHz) and ¹³C (75 MHz) NMR spectra were

recorded using a Bruker AQS-300 Avance spectrometer. IR spectra were obtained using a Shimadzu IR-460 spectrophotometer. Boiling points and melting points were determined with a Büchi B-540 melting point/boiling point capillary apparatus.

General experimental procedure

A mixture of diselenide (0.64 mmol), zinc dust (5.12 mmol), anhydrous aluminum chloride (1.92 mmol) and acetonitrile (20 ml) was stirred at 83 °C for 2 h until the zinc powder had almost disappeared; diaryliodonium salt (1.6 mmol) and water (4 ml) were then added at once to the solution and stirring was continued at that temperature for the appropriate time (Table 1) in air atmosphere. After completion of the reaction, the solution was filtered and washed with diethyl ether. The combined Et_2O/CH_3CN solution was then washed with water (3 × 20 ml), and the organic layer was dried over anhydrous sodium sulfate. The solvent was evaporated *in vacuo* to give the corresponding selenide which was purified by preparative TLC (silica gel, eluent *n*-hexane : ethyl acetate = 30:1).

Acknowledgements

The financial assistance of the K. N. Toosi University of Technology Research Council and Kermanshah Oil Refining Company is gratefully acknowledged.

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 ^a Yields of pure isolated products;
 ^b references for physical data of products.

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