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Improved Method for the Synthesis of Organic Diselenides from Organic Halides under Atmospheric Pressure

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Abstract: An improved approach to the synthesis of organic diselenides is reported. The process involves the reaction of organic halides with selenium, carbon monoxide, and water under atmospheric pressure in the presence of an inorganic base, sodium hydroxide, to afford organic diselenides in good yields.

Keywords: atmospheric pressure, carbon monoxide, organic diselenides, organic halides, selenium

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INTRODUCTION

Organic diselenides have attracted much attention as useful synthetic reagents and intermediates in organic synthesis.^[1] Much effort is being devoted to accomplishing the preparation of these compounds. The common access to these compounds is the alkylation of diselenide anions with organic halides. The diselenide anions have been prepared in many ways: the reduction of selenium with alkali metals in liquid ammonia^[2] or in the presence of an electron carrier^[3] or by ultrasound in THF,^[4] sodium hydride,^[5] or lithium aluminum hydride^[6] in THF; zinc in the presence of sodium hydroxide in DMF;^[7] samarium diiodide in THF;^[8] metal borohydrides^[9] and hydrazine^[10] in basic media; or sodium hydroxide under phase-transfer conditions.^[11] Organic diselenides also can be prepared by dimerization with selenocyanates^[12-14] or oxidation of selenols.^[15] Additionally, Sonoda also reported that elemental selenium can be readily reduced by carbon monoxide (0.5 Mpa) and water in the presence of an organic base to produce hydrogen selenide, which was successfully applied to the synthesis of organic diselenides from alkyl chlorides and acyl chlorides.^[16]

RESULTS AND DISCUSSION

In our previous studies on selenium-catalyzed reductive carbonylation of nitroaromatic compounds with carbon monoxide,^[17] we reported the synthesis of organic diselenides from aromatic and aliphatic aldehydes with Se/CO/H₂O system under atmospheric pressure.^[18] On this basis, we decided to investigate reactions of organic halides with stoichiometric selenium, carbon monoxide, and water in DMF under atmospheric pressure in the presence of the inorganic base sodium hydroxide and found that these reactions led to organic diselenides in good yields:

$$2RX + 2Se + CO (1 \text{ atm}) + H_2O + 2NaOH \xrightarrow{DMF} RSeSeR + CO_2 + 2NaX + 2H_2O.$$

When benzyl bromide (1a) was treated with equivalent selenium, carbon monoxide (bubbling), and water in DMF at 90°C for 2 h, the reductive 1a efficiently proceeded to give dibenzyl diselenide (1b) in 75% (entry 1 in Table 1). The reaction conditions for the synthesis of dibenzyl diselenide (1b) from benzyl bromide (1a) were also examined in detail and some of the results are shown in Table 1. From the Table 1 we can see that dimethylformamide (DMF) is the best solvent for this reaction (entries 1–6 in Table 1); the use of NaOAc, Et₃N, and 1,8-diazabicyclo[5,4,0]-undec-7-ene (DBU) instead of NaOH as a base led to a decreased yield of 1b (entries 7–9 in Table 1).

We next directed our attention to the preparation of organic diselenides using this method. The results of synthesis of organic diselenides from

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Table 1. Synthesis of dibenzyl diselenide (1b) from benzyl bromide (1a) under various conditions

Entry ^a	Solvent	Temperature (°C)	Base	Yield $(\%)^b$	
1	DMF	90	NaOH	75	
2	THF	90	NaOH	43	
3	CH ₃ CN	75	NaOH	68	
4	EtOH	75	NaOH	40	
5	DMSO	90	NaOH	70	
6	FP^{c}	90	NaOH	65	
7	DMF	90	NaOAc	72	
8	DMF	90	Et ₃ N	70	
9	DMF	90	DBU	62	

^aReaction conditions: benzyl bromide, 2.5 mmol; Se, 2.5 mmol; bubbling CO; solvent, 20 mL; 2.0 h.

^bIsolated yield of **1b**.

 c FP = 1-formylpiperidine.

various organic halides with the Se/CO/H₂O system under atmospheric pressure are presented Table 2. During the reaction, chlorobenzene, bromobenzene, iodobenzene, or benzoyl chloride also did not react at all (entries 1-4 in Table 2). On the contrary, benzyl halides easily reacted and gained the targeted diselenide products in good yields (entries 5-9 in Table 2). In the case of alkyl chlorides such as chlorocyclohexane, chlorocyclopentane, and n-butyl chloride, the desired diselenides were obtained in moderate yields (entries 10-12 in Table 2). When (1,2-dibromo-ethyl)-benzene was carried out under similar conditions, side reactions took place to give a complex mixture.

In conclusion, we have developed an improved method for the synthesis of organic diselenides from organic halides with a $Se/CO/H_2O$ system under atmospheric pressure in the presence of an inorganic base, sodium hydroxide. the method described here is a supplement to Sonoda's method for the preparation of organic diselenides.^[16]

EXPERIMENTAL

All melting points were recorded on a WRS-1A melting-point apparatus and were uncorrected. All ¹H NMR spectra were recorded on a 400-MHz Bruker AZ 400 spectrometer. Chemical shifts are given as δ value with reference to tetramethylsilane (TMS) as internal standard. Carbon monoxide (99.9%) was dried by zeolite 5A. Elemental selenium (>99.5%) and the reagents were received from commercial supply without purification prior to use.

Entry ^a Substrate			Product		Mp (°C)	Yield % ^b
1	PhCl	1a	No reaction			0
2	PhBr	2a	No reaction			0
3	PhI	3a	No reaction			0
4	PhCOCl	4a	No reaction			0
5	PhCH ₂ Br	5a	PhCH ₂ SeSeCH ₂ Ph	5b	87–89 (88–89.5 ^[19])	75
6	PhCH ₂ Cl	6a	PhCH ₂ SeSeCH ₂ Ph	6b	87-89 (88-89.5 ^[19])	70
7	p-BrC ₆ H ₄ CH ₂ Br	7a	p-BrC ₆ H ₄ CH ₂ SeSeCH ₂ C ₆ H ₄ Br-p	7b	96–98 (99.5–100.5 ^[11])	87
8	o-BrC ₆ H ₄ CH ₂ Br	8 a	o-BrC ₆ H ₄ CH ₂ SeSeCH ₂ C ₆ H ₄ Br-o	8b	96–97 (99–100 ^[11])	73
9	m-ClC ₆ H ₄ CH ₂ Cl	9a	m-ClC ₆ H ₄ CH ₂ SeSeCH ₂ C ₆ H ₄ Cl-m	9b	Yellow liquid ^[20]	76
10		10a	Se-Se	10b	Yellow liquid ^[21]	60
11	CI	11a	Se-Se	11b	Yellow liquid ^[21]	64
12	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ Cl	12a	CH ₃ CH ₂ CH ₂ CH ₂ SeSeCH ₂ CH ₂ CH ₂ CH ₃	12b	Yellow liquid ^[16]	62

Table 2. Synthesis of organic diselenides from organic halides under various reaction conditions

^{*a*}Reaction conditions: organic halide, 2.5 mmol; Se, 2.5 mmol; bubbling CO; H₂O, 2 mL; NaOH, 2.5 mmol; DMF, 20 mL; 2.0 h. ^{*b*}Isolated yield.

Organic Diselenides from Organic Halides

General Procedure for the Synthesis of Organic Diselenides

In a 100-mL, three-necked flask, organic halide (2.5 mmol), selenium (2.5 mmol), water (2 mL), sodium hydroxide (2.5 mmol), DMF (20 mL), and a magnetic stirring bar were placed. Carbon monoxide was introduced and bubbled into the reaction mixture with vigorous stirring at 90°C for 2 h. After the reaction was complete, CO bubbling was stopped, and the resultant mixture was stirred in air at ambient temperature for 0.5 h. Water (20 mL) was added, and the reaction mixture was extracted with diethyl ether (3 × 40 mL). The organic phase was dried over anhydrous MgSO₄ and filtered, and the solvent evaporated under reduced pressure to afford a yellow oil or crystal. Further purification by column chromatography on silica gel or recrystallization gave the pure product. All the products were identified by NMR and/or comparison with the authentic samples.

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