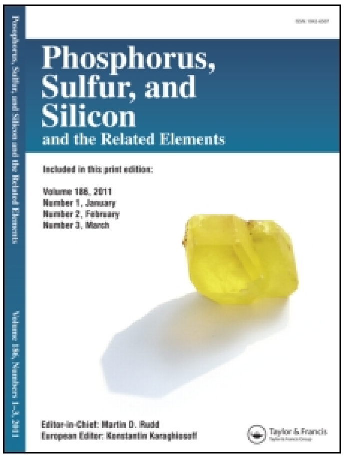

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An Improved Synthesis of Symmetrical Diselenides from Aromatic Aldehydes

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AN IMPROVED SYNTHESIS OF SYMMETRICAL DISELENIDES FROM AROMATIC ALDEHYDES

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An improved method for the synthesis of symmetrical diselenides is described. Reductive selenation of aromatic aldehydes with Se/CO/H_2O/Et_3N system in THF gave the corresponding aromatic diselenides in good yields.

Keywords Aromatic aldehydes; carbon monoxide; diselenides; selenium

INTRODUCTION

Organoselenium compounds are very important organic synthetic reagents and intermediates.[1] Among them, symmetrical diselenides are versatile reagents and potential medicinal agents.[2] Several methods have been reported for the synthesis of symmetrical diselenides.[3] For example, Nishiyama et al. found that aliphatic aldehydes and ketones can reduce selenation to aliphatic diselenides using a Se/CO/H_2O/base.[4]

RESULTS AND DISCUSSION

In the course of our studies on selenium-catalyzed reductive carbonylation of nitroaromatic compounds with carbon monoxide, we developed a new application of the Se/CO/H_2O system to convert aromatic aldehydes,[5] organic halides,[6] or imines[7] to symmetrical diselenides. However, the disadvantages of these methods are long reaction times (7–9 h) and undesirable byproducts (symmetrical urea). We report in this article an efficient method for synthesizing symmetrical diselenides (yields up to 89%) by reactions of selenium and aromatic and heterocyclic aldehydes in the presence of carbon monoxide, water, and triethylamine (Scheme 1).

Treatment of benzaldehyde (**1a**) with one equivalent selenium in THF at 100°C in the presence of carbon monoxide (3 Mpa), water, and Et_3N for 3 h led to efficient reductive

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$$\underset{\mathbf{1}}{\mathrm{ArCHO}} + \mathrm{Se} + \mathrm{CO} + \mathrm{H_2O} \xrightarrow[\mathrm{Et_3N}]{\mathrm{THF}} \underset{\mathbf{2}}{\mathrm{ArCH_2SeSeCH_2Ar}}$$

a) Ar = C_6H_5; b) Ar = *p*-MeC_6H_4; c) Ar = *m*-MeC_6H_4; d) Ar = *o*-MeC_6H_4; e) Ar = *p*-MeOC_6H_4; f) Ar = *o*- MeOC_6H_4; g) Ar = *m*- C_6H_4OH; h) Ar = 2-thienyl; i) Ar = 3-thienyl; j) Ar = 3-pyridyl

Scheme 1

selenation to give dibenzyl diselenide (**1b**) in 85% yield (Table I, entry 1). No byproduct such as benzyl alcohol or toluene was detected from the reaction mixture. Although the photochemical reaction of ketones and aldehydes with hydrogen selenide afforded alcohols,[8] acetophenone did not undergo selenation, and only a trace amount of ethylbenzene was detected in the reaction mixture (GC-MS analysis).[9] The reaction did not proceed without water or without use of base. The results with other aromatic and heterocyclic aromatic aldehydes are summarized in Table I. Increasing steric hindrance on the aromatic ring led to decreased yields, but steric effects of the substituents only slightly affect yields of the diselenides (Table I, entries 1–6). Salicylaldehyde was unchanged under the reaction conditions (Table I, entry 7). Heterocyclic-aromatic aldehydes (2-and 3-thiophenecarboxaldehydes,

Table I Synthesis of symmetrical diselenides from aromatic aldehydes[a]

Entry	Diselenide	Yield (%)	Mp (°C) (lit.)	^{1}H NMR (δ)	^{13}C NMR (δ)
1	**2a**	85[b]	92–93 (90–91)[10]	7.37–7.26 (m, 10H), 3.88 (s, 4H)	139.05, 129.04, 128.45, 127.21, 32.66
2	**2b**	89	59–60 (61–62)[11]	7.26–7.10 (s, 8H), 3.84 (s, 4H), 2.32 (s, 6H)	149.70, 129.84, 126.56, 112.44, 40.60, 32.90
3	**2c**	82	Yellow liquid[5]	7.36–7.22 (m,8H), 3.98 (s, 4 H), 2.52 (s, 6 H)	138.62, 137.54, 129.5, 128.05, 127.56, 125.82, 32.38, 21.19
4	**2d**	78	80–81 (86–86.5)[3c]	7.42–6.22 (m, 8H), 3.96 (s, 4H), 3.81 (s, 6H)	152.32, 142.85, 111.03, 108.88, 107.70, 24.86, 18.91
5	**2e**	86	72–73 (72)[12]	7.26–6.83 (m,8H), 3.83 (s,4H), 3.80 (s,6H)	138.99, 128.21, 125.82, 122.52, 26.36
6	**2f**	81	66–67 (–)[13]	7.26–6.84 (m,4H), 3.98 (s, 4H), 3.87 (s, 6H)	149.84, 148.36, 136.22, 134.52, 123.32, 28.72, 24.53
7	**2g**	—	—		
8	**2h**	82	Yellow liquid[5]	7.43–6.23 (m, 6H), 3.96 (s, 4 H)	152.23, 142.64, 111.35, 108.54, 24.52
9	**2i**	85	94–96[5] (94–96)[5]	7.27–7.02 (m, 6H), 3.86 (s, 4 H)	138.99, 128.28, 125.80, 122.52, 26.36
10	**2j**	88	77–79[5] (77–79)[5]	8.46–7.18 (m, 8H), 3.72 (s, 4H)	149.84, 148.39, 136.22, 123.32, 28.72

[a] All experimental reaction.

[b] Yield is only 32% in toluene.

and 3-pyridinecarboxaldehyde) were also efficiently transformed to their corresponding diselenides in good yields (82%–88%) (Table I, entries 8–10).

EXPERIMENTAL

All melting points were recorded on a WRS-1A melting-point apparatus and are uncorrected. All ^{1}H NMR spectra were recorded on a 400-MHz Bruker AZ 400 spectrometer. Chemical shifts are given as *d* 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.

PROCEDURE FOR SYNTHESIS OF AROMATIC DISELENIDES

The aromatic aldehyde (2.5 mmol), selenium (2.5 mmol), water (25 mmol), Et_3N (2.5 mmoL), and THF (10 mL) and a magnetic stirring bar were successively loaded into a 70-mL stainless-steel autoclave. The reactor was sealed, flushed three times with 1.0 MPa of carbon monoxide, pressurized with 3.0 MPa of carbon monoxide, and then placed in an oil bath preheated to 100°C. After the reaction was complete, the apparatus was cooled to ambient temperature, and the remaining carbon monoxide was evacuated. Then water (20 mL) was added, and the reaction mixture was extracted with diethyl ether (3 × 40 mL). The combined organic extracts were dried over anhydrous $MgSO_4$, filtered, and the solvent was evaporated under reduced pressure to afford a yellow oil. Further purification by column chromatography on silica gel or TLC gave the pure product. All the products were identified by NMR and/or comparison with authentic samples.

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