

Convenient Synthesis of Dibenzyl Diselenides under Phase Transfer Conditions

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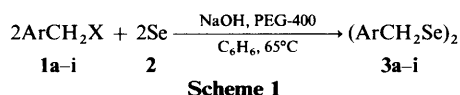
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A convenient and simple method for the synthesis of dibenzyl diselenides under phase transfer conditions is described. The process involves the reaction of selenium with sodium hydroxide at 65–70 °C and under phase transfer conditions to give sodium diselenides, which reacts with benzyl halides to afford the dibenzyl diselenides in good to excellent isolated yields. The reaction mechanism is briefly discussed.

Many methods¹ have been described for the synthesis of diaryl and dialkyl diselenides. The reaction of diselenide anion with appropriate halides is a well known method for the preparation of symmetrical diselenides.² The diselenide anion has been prepared by reaction of selenide anion with 1 equiv. of selenium,³ ultrasound-induced electrochemical synthesis^{4,5} or by reduction of selenium with 1 equiv. of reducing agent. Commonly used reagents for the reduction of selenium are alkali metals in liquid ammonia,⁶ sodium borohydride in ethanol or water,⁷ hydrazine hydrate,⁸ sodium hydroxymethanesulfinate (rongalite) in water,⁹ lithium triethylborohydride in tetrahydrofuran,¹⁰ tetraalkylammonium borohydride in toluene,¹¹ phenylhydrazine in DMF,¹² carbon monoxide in water,¹³ zinc powder¹⁴ and samarium diiodide.¹⁵ Diselenides are almost instantaneously and quantitatively prepared by oxidation of selenols (or seleninic acids¹⁶) with 30% aqueous hydrogen peroxide. Dibenzyl diselenides can also be prepared from Grignard reagents,¹⁷ sulfonic acid esters,¹⁸ and by reaction of sodium hydrogen selenide with N-substituted 1-benzotriazolylbenzyl amines in ethanol.¹⁹

Recently, we have reported the synthesis of diacyl disulfides and diaroyl diselenides from the reaction of sulfur and selenium with halides in alkaline medium under phase transfer conditions.^{20,21}

We have now used a phase-transfer method for the reaction of selenium with benzyl halides. Dibenzyl diselenides **3** can be obtained simply and in high yield, from the reaction of benzyl halides **1** with selenium **2** in a two-phase system consisting of benzene, water and a phase-transfer catalyst. The reactions are shown in Scheme 1 and the results are summarized in Table 1.



Results and Discussion

The results in Table 2 show that the phase-transfer catalyst is not only involved in production of the diselenide ion in solution, but also catalyses the substitution reaction on the benzyl chlorides. For example, in order to elucidate the mode of action of the phase-transfer catalysts, we have investigated the reaction of selenium in their absence. Selenium was treated with sodium hydroxide for 6 h at 70–80 °C, but with no evidence for the presence of brownish red diselenide dianion in the aqueous layer. When only a few drops of PEG-400 were added into the system, the aqueous layer becomes brownish red after 5 min; Table 2 shows that the yield of dibenzyl diselenide **3a** is 96%. Under the same conditions but without the addition of phase-transfer catalyst for 11 h, the yield of **3f** is only 12%.

Table 1 Dibenzyl diselenides **3a–i** prepared

Entry	Ar	X	Product	Yield (%) ^a
3a	C ₆ H ₅	Cl	(C ₆ H ₅ CH ₂ Se) ₂	96
3b	<i>p</i> -MeC ₆ H ₄	Br	(<i>p</i> -MeC ₆ H ₄ CH ₂ Se) ₂	94
3c	<i>p</i> -ClC ₆ H ₄	Br	(<i>p</i> -ClC ₆ H ₄ CH ₂ Se) ₂	73
3d	<i>p</i> -BrC ₆ H ₄	Br	(<i>p</i> -BrC ₆ H ₄ CH ₂ Se) ₂	88
3e	<i>p</i> -O ₂ NC ₆ H ₄	Br	(<i>p</i> -O ₂ NC ₆ H ₄ CH ₂ Se) ₂	75
3f	<i>o</i> -O ₂ NC ₆ H ₄	Br	(<i>o</i> -O ₂ NC ₆ H ₄ CH ₂ Se) ₂	76
3g	<i>o</i> -MeC ₆ H ₄	Br	(<i>o</i> -MeC ₆ H ₄ CH ₂ Se) ₂	83
3h	<i>o</i> -BrC ₆ H ₄	Br	(<i>o</i> -BrC ₆ H ₄ CH ₂ Se) ₂	88
3i	2-C ₁₀ H ₇	Br	(2-C ₁₀ H ₇ CH ₂ Se) ₂	81

^a Isolated yield.

We also investigated the effect of different phase-transfer catalysts on the reaction of selenium with OH⁻ and Se₂²⁻ with benzyl chlorides. It was found that the activities of the catalysts are in the following sequence: PEG-400 > PEG-600 > PEG-1500 > Bu₄NBr > CTMAB > Et₄NI > Et₄NBr > Et₄NCl. The results are summarized in Table 3.

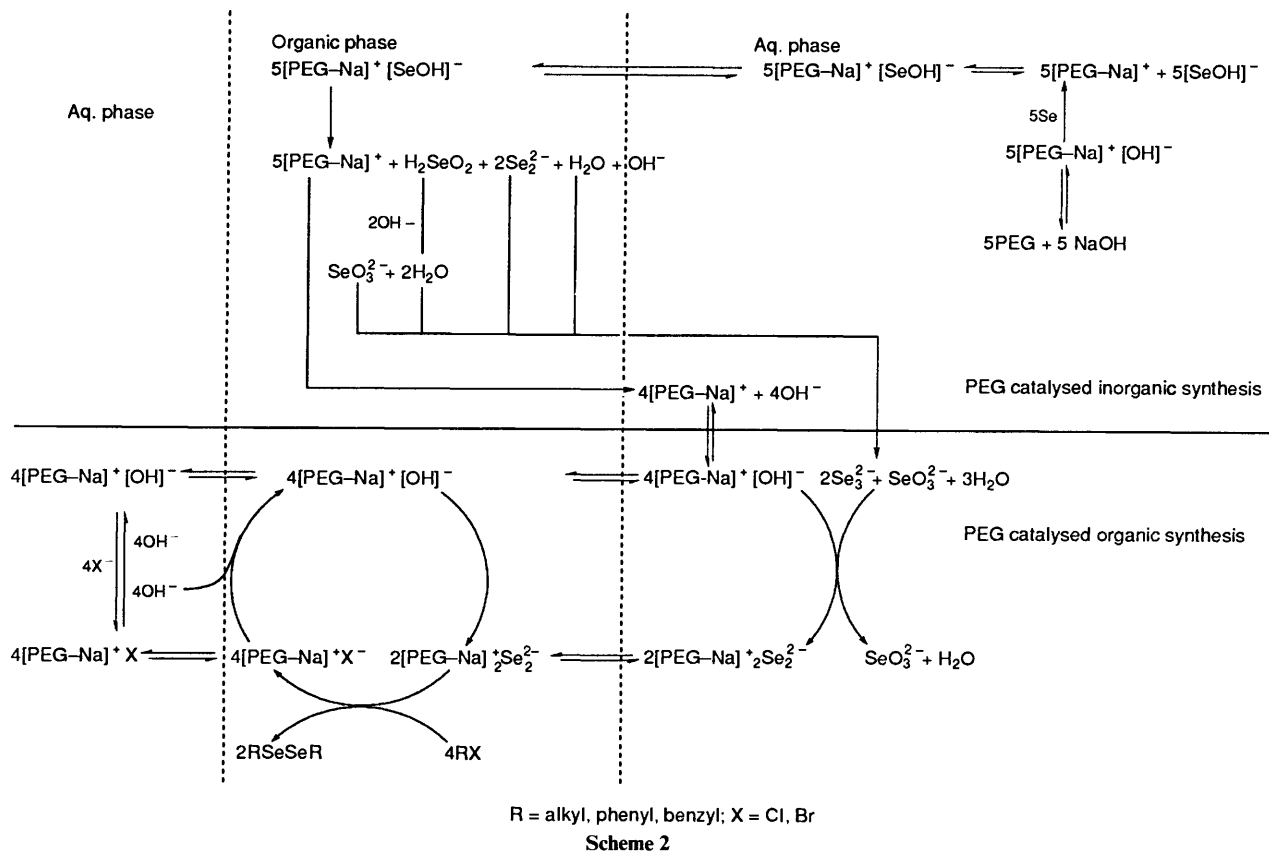
The efficiency of various solvents on the formation of dibenzyl diselenides was studied using phase-transfer catalysts. Benzene was found to be an effective solvent for the reaction. The effect of various solvents in the synthesis of dibenzyl diselenide is in the following order: benzene > tetrahydrofuran > acetonitrile > hexane.

An attempt was made to introduce phase-transfer catalysis into an inorganic reaction system by Deng and Chen.^{22,23} On the basis of our experimental results, we tentatively propose the mechanism shown in Scheme 2.

We consider that the mechanism involves two parts: inorganic synthesis and organic synthesis under phase-transfer catalysis. The PEG was chosen as the catalyst for reaction between hydroxide ions in aqueous solution and elemental selenium in the organic phase and thus generates Se₂²⁻. Reaction of PEG with NaOH forms [PEG-Na]⁺OH⁻ which, in the presence of Se₂²⁻, generates [PEG-Na]₂Se₂²⁻, which transfers to the organic phase from the aqueous phase. [PEG-Na]₂Se₂²⁻ then reacts with RX rapidly to afford the desired RSeSeR, and [PEG-Na]⁺OH⁻ is regenerated by reduction of [PEG-Na]⁺X⁻ with NaOH. The PEG is thus recycled in the reaction.

Experimental

IR spectra were measured for KBr discs using an Alpha Centauri FT-IR spectrophotometer. ¹H NMR spectra (80 MHz) were recorded in CDCl₃ using an FT-80 spectrometer.

**Table 2** Effects of PEG-400 on the yield of dibenzyl diselenide

Entry	Reagents ^a	Solvent	PTC	T/°C	t/h ^d	Yield (%) ^c
1	Se, NaOH, ^b PhCH ₂ Cl	C ₆ H ₆	PEG-400	65–70	5	96
2	Se, NaOH, ^b PhCH ₂ Cl	C ₆ H ₆	None	65–70	11	12

^a Mole ratio: C₆H₄CH₂Cl:Se:NaOH:PEG-400 = 1:1.25:10:0.000 5. ^b 10 mol dm⁻³ NaOH used. ^c Yield of isolated product. ^d The reaction was monitored by TLC on silica gel.

Table 3 Effect of phase transfer catalysts on the formation of dibenzyl diselenide

Entry	Catalyst ^b	t/h	Yield (%) ^a
1	PEG-400	5	95
2	PEG-600	5	92
3	PEG-1500	5	89
4	Bu ₄ NBr	5	88
5	CTMAB ^c	5	83
6	Et ₄ NCl	5	71
7	Et ₄ NBr	5	76
8	Et ₄ NI	5	82

^a Isolated yield. ^b C₆H₆ used as solvent. ^c CTMAB = cetyltrimethylammonium bromide.

J Values are given in Hz. Microanalyses were measured using a Carlo Erba 1106 microelemental analyser.

General Procedure.—Selenium powder (12.5 mmol) **2** was added to a mixture of PEG-400 (0.05 mmol), sodium hydroxide (10 mol dm⁻³; 10 cm³) and benzene (30 cm³) after which the reaction mixture was stirred at 65–70 °C for 3 h. The benzyl halide (10 mmol) was added and the reaction mixture was stirred under N₂ or Ar at 65–70 °C for 1 h. The aqueous layer changed from brown–red to colourless immediately. The organic layer was separated, washed with water (3 × 10 cm³) and then dried

(MgSO₄). The solvent was removed by evaporation under reduced pressure to afford the pure dibenzyl diselenides. Recrystallization from cyclohexane or benzene gave the analytically pure products.

Dibenzyl diselenide 3a. M.p. 90–91 °C (lit.,¹⁰ 90–91 °C) (Found: C, 49.5; H, 4.2. C₁₄H₁₄Se₂ requires C, 49.41; H, 4.12%); ν_{\max} (KBr)/cm⁻¹ 3041w, 2870m, 810s, 760m, 490w and 420w; δ_{H} 7.25–7.60 (10 H, m, 2 × ArH) and 3.84 (4 H, s, 2 × CH₂Se).

Bis(4-methylbenzyl) diselenide 3b. M.p. 53–54 °C (Found: C, 51.9; H, 5.1. C₁₆H₁₈Se₂ requires C, 52.17; H, 5.00%); ν_{\max} (KBr)/cm⁻¹ 3042w, 2916w, 2856w, 821m, 714m and 480m; δ_{H} 7.11–7.25 (8 H, d, 2 × ArH), 3.84 (4 H, s, 2 × CH₂Se) and 2.32 (6 H, s, 2 × CH₃).

Bis(4-chlorobenzyl) diselenide 3c. M.p. 77–78 °C (Found: C, 40.9; H, 2.8. C₁₄H₁₂Se₂ requires C, 41.07; H, 2.93%); ν_{\max} (KBr)/cm⁻¹ 3046w, 2914w, 2860w, 821m, 716m and 480m; δ_{H} 7.05–7.33 (8 H, q, 2 × ArH, *J* 8.61) and 3.82 (4 H, s, 2 × CH₂Se).

Bis(4-bromobenzyl) diselenide 3d. M.p. 99.5–100.5 °C (Found: C, 33.9; H, 2.4. C₁₄H₁₂Br₂Se₂ requires C, 33.73; H, 2.41%); ν_{\max} (KBr)/cm⁻¹ 3050w, 2942w, 2867w, 819m, 711m and 471m; δ_{H} 7.00–7.48 (8 H, q, 2 × ArH, *J* 8.42) and 3.80 (4 H, s, 2 × CH₂Se).

Bis(4-nitrobenzyl) diselenide 3e. M.p. 110–111 °C (Found: C, 39.1; H, 2.8. N, 6.5. C₁₄H₁₂N₂O₄Se₂ requires C, 39.07; H, 2.79, N, 6.51%); ν_{\max} (KBr)/cm⁻¹ 3051w, 2940w, 2869w, 853m, 752m

and 467m; δ_{H} 7.16–8.22 (8 H, q, 2 \times ArH, J 8.62) and 3.91 (4 H, s, 2 \times CH₂Se).

Bis(2-nitrobenzyl) diselenide 3f. M.p. 105–106 °C (Found: C, 39.0; H, 2.8. N, 6.4. C₁₄H₁₂N₂O₄Se₂ requires C, 39.07; H, 2.79, N, 6.51%); ν_{max} (KBr)/cm⁻¹ 3060w, 2946w, 2872w, 864m, 748m and 477m; δ_{H} 7.19–8.11 (8 H, m, 2 \times ArH) and 4.28 (4 H, s, 2 \times CH₂Se).

Bis(2-methylbenzyl) diselenide 3g. M.p. 86–86.5 °C (Found: C, 51.8; H, 5.2. C₁₆H₁₈Se₂ requires C, 52.17; H, 5.00%); ν_{max} (KBr)/cm⁻¹ 3018w, 2930w, 2860w, 764s, 722m and 485m; δ_{H} 7.12–7.33 (8 H, m, 2 \times ArH), 3.89 (4 H, s, 2 \times CH₂Se) and 2.38 (6 H, s, 2 \times CH₃).

Bis(2-bromobenzyl) diselenide 3h. M.p. 99–100 °C (Found: C, 33.8; H, 2.5. C₁₄H₁₂Br₂Se₂ requires C, 33.73; H, 2.41%); ν_{max} (KBr)/cm⁻¹ 3040w, 2940w, 2879w, 826m, 754m and 432s; δ_{H} 7.04–7.58 (8 H, m, 2 \times ArH) and 4.01 (4 H, s, 2 \times CH₂Se).

Bis(2-naphthylmethyl) diselenide 3i. M.p. 133–134 °C (Found: C, 60.3; H, 4.2. C₂₂H₁₈Se₂ requires C, 60.00; H, 4.09%); ν_{max} (KBr)/cm⁻¹ 3052w, 2940w, 2868w, 821s, 741s and 461m; δ_{H} 7.20–7.81 (14 H, m, 2 \times C₁₀H₇) and 3.93 (4 H, s, 2 \times CH₂Se).

Acknowledgements

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