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Synthesis of Bis(4-hydroxyphenyl) Selenide and Epoxide and Acrylate Monomers on This Basis

S. V. Balina, V. V. Russkikh, N. A. Orlova, L. N. Ogneva, and V. V. Shelkovnikov

Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch, Russian Academy of Sciences
pr. Akademika Lavrent'eva 9, Novosibirsk, 630090 Russia
e-mail: balina@nioch.nsc.ru

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Abstract—Reaction of $SeCl_2$ with PhOH has afforded bis(4-hydroxyphenyl) selenide, whose treatment with epichlorohydrin provides a diepoxide that is transformed in bisacrylate and further in tetraacrylate via opening of the epoxide rings with acrylic acid followed by acylation with acryloyl chloride.

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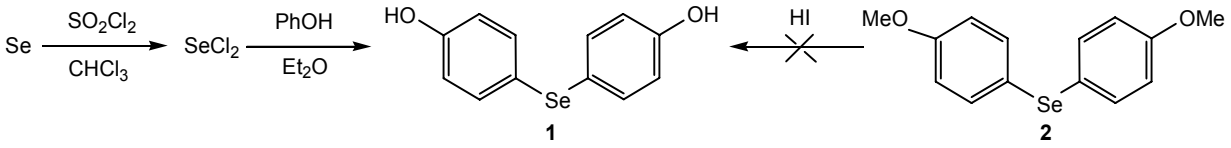
The production of polymers transparent in the visible range and characterized by a high refraction index is an important task due to their application for coating optic fibers and other optic elements [1]. One among the ways to increase the refraction index of a polymer is the introduction of highly polarizable atoms, e.g., selenium atoms, into the structure of the initial monomer [2]. As a synthetic block in the preparation of organoselenium materials capable of thermal or photopolymerization bis(4-hydroxyphenyl) selenide **1** may be used with the subsequent functionalization of the hydroxy groups.

The development of a preparative procedure for the synthesis of compound **1** interested chemists already for a long time [3]. Two-step syntheses of bis(4-hydroxyphenyl) selenide **1** were described consisting in phenol reaction with electrophilic regents ($SeOCl_2$ [3], H_2SeO_3 [4], $SeCl_4$ [5]) followed by the reduction of the primarily formed bis(4-hydroxyphenyl)-selenoxide or dichloride. A multistage synthesis of compound **1** is also known proceeding from 4-aminophenol and involving a diazotization stage; the reaction is accompanied with diselenide formation [6–8]. Our attempts to obtain selenide **1** with the use of some among these procedures showed their low efficiency, irreproducibility, and low yield of the target compound.

Recently considering the growing interest to selenium derivatives the search for new reagents for their synthesis activated. Lately a one-stage preparation of selenide **1** was described under the action on phenol of the electrophilic cation Se^{2+} [9]; the generation of Se^{2+} was performed electrochemically on a soluble graphite-selenium anode. Compound **1** was obtained in 58% yield by the reaction of elemental selenium with 4-iodophenol in the presence of Cu_2O [10]. The reaction was carried out with adding a ligand (ethylenediamine) in a system DMSO–KOH at 120°C under microwave irradiation.

Selenium dichloride $SeCl_2$ seems a promising reagent for the preparation of selenides, since it can be successfully used in reactions of electrophilic aromatic substitution [11, 12], but the best results are obtained in the synthesis of selenides from phenols substituted in the ring or their derivatives with the protected phenol groups. 2,6-Dimethylphenol reacts with $SeCl_2$ giving bis(4-hydroxy-3,5-dimethylphenyl) selenide in 62% yield [11, 12]. Bis(4-methoxyphenyl) selenide **2** was obtained by reacting $SeCl_2$ with anisole in an yield over 90% demonstrating a high regioselectivity of the process occurring with replacement of the hydrogen atom exclusively in the *para*-position of the phenyl groups. However, the preparation of selenide **1** from compound **2** requires an additional stage of removing the methyl group. Our attempts to perform the acidolysis of compound **2** by known methods [13, 14] using HI, Py·HCl failed. The application of HI at a temperature higher than 60°C resulted in the cleavage of the Se–C bond and in the formation of selenium, anisole, and bis(4-methoxyphenyl) diselenide. At the use of Py·HCl at 185–210°C along with compound **1**

Scheme 1.



formed also selenium, phenol, and bis(4-hydroxyphenyl)diselenide (Scheme 1).

In this report, we describe the procedure for preparation of diaryl selenides by reaction of $SeCl_2$ with arenes modified as compared with the method [11, 12] by using as a solvent a mixture of chloroform and ethyl ether. Phenol is brought into the reaction as a solution in Et_2O, the reaction mixture is neutralized with a water solution of Na_2CO_3, and unreacted phenol is distilled off in a vacuum.

Thus obtained bis(4-hydroxyphenyl) selenide **1** we used for the preparation of epoxide **3** and acrylate **4** and **5** monomers (Scheme 2). The sulfide analog of compound **3** described in patent [15] was produced in inert medium with the use of sodium hydride. We applied to the preparation of diglycidyl ether **3** a simpler procedure described in [16] for phenol derivative. Bis(4-glycidyloxyphenyl) selenide **3** was converted in bisacrylate **4** by the opening of the epoxy rings with acrylic acid by procedure [17]. The subsequent acylation of hydroxy groups in compound **4** with acryloyl chloride provided tetraacrylate **5**.

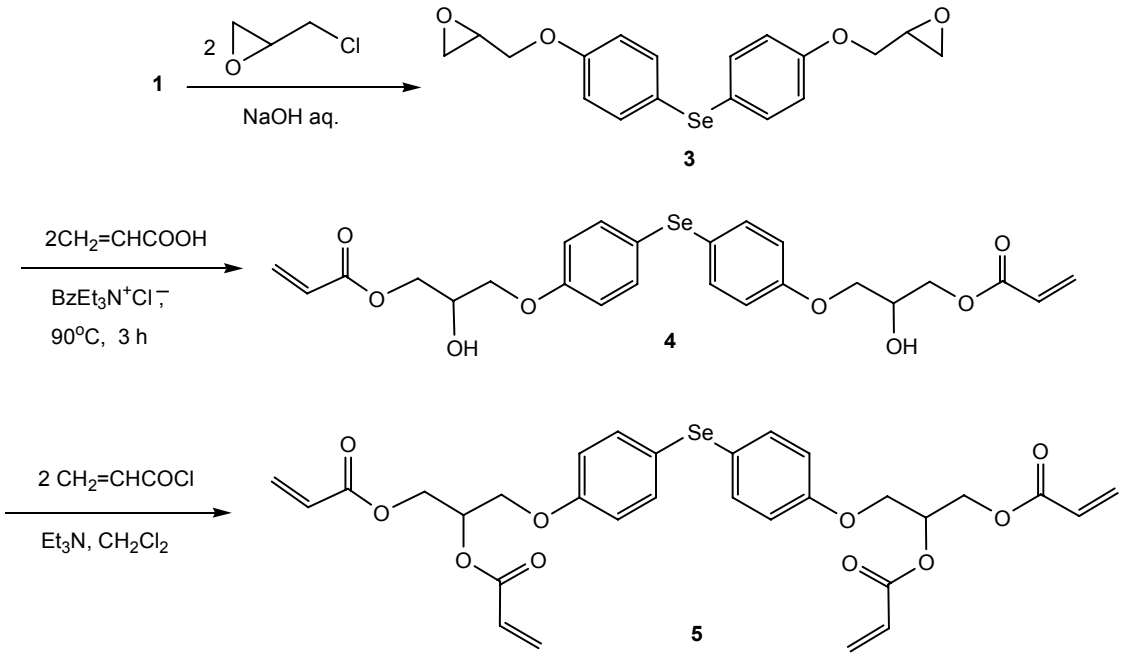
The structure of compounds **3**–**5** was established based on ^1H NMR and high resolution mass spectra.

Thus in the study a simple method was developed of the preparation of practically important synthetic block bis(4-hydroxyphenyl) selenide **1** and proceeding from the latter a synthesis was fulfilled of epoxide and acrylate monomers.

EXPERIMENTAL

NMR spectra were registered from solution in $(CD_3)_2CO$ for compound **1** and in $CDCl_3$ for compounds **3**–**5** on spectrometers Bruker AV-400, AV-300 and AV-600, operating frequencies 400.13 (^1H, internal reference the residual protons of solvents, δ 2.04 and 7.24 ppm), 75.47 (^{13}C, internal reference Me_2CO, δ 29.8 ppm), and 114.53 MHz (^{77}Se, reference Me_2Se, δ 0 ppm). Mass spectra were taken on an instrument DFS at direct admission of the sample, ionizing electrons energy 70 eV, ion source tempe-

Scheme 2.



rature 180°C. The molecular mass and elemental composition of compounds **1**, **3**, and **5** was determined from the precise values of molecular ion masses. GC-MS analysis was carried out on an instrument of Aglient Technologies.

4-(4-Hydroxyphenylselanyl)phenol [bis(4-hydroxyphenyl) selenide] (1). To a mixture of 0.79 g (0.01 mol) of selenium and 20 mL of chloroform was added a solution of 1.35 g (0.01 mol) of sulfuryl chloride in 20 mL of chloroform, and the mixture was stirred till selenium was completely dissolved. To the obtained solution 1.88 g (0.02 mol) of phenol in 20 mL of anhydrous ethyl ether was added, and the mixture was stirred at 25°C for 3 h, then a solution of 1.06 g of Na_2CO_3 in 4 mL of water was added dropwise, and the stirring was continued for 10 min till the end of CO_2 liberation. The bottom organic layer was separated from the upper water layer. The former was filtered through a bed of aluminum oxide (10 cm), the filtrate was evaporated on a water bath, the residue was diluted with 5 mL of acetone, and the formed selenium precipitate was filtered off. Acetone was distilled off from the filtrate, unreacted phenol was distilled off in a vacuum, the residue was recrystallized from chloroform. Yield 1.17 g (44%), mp 143–144°C (mp 144°C [2], 143−144°C [5]). ^{1}H NMR spectrum, δ, ppm: 6.81 d (4H_{Ar}, *J* 8.8 Hz), 7.34 d (4H_{Ar}, *J* 8.8 Hz), 8.60 s (2H, OH). ^{13}C NMR spectrum, δ, ppm: 117.49 (C^3), 121.49 (C^1), 135.76 (C^2), 158.29 (C^4). ^{77}Se NMR spectrum, δ, ppm: 380.74. Found $[M]^+$ 261.9863. $C_{12}H_{10}O_2{}^{76}Se$. Calculated *M* 261.9865.

Bis(4-methoxyphenyl) selenide (2) was obtained by procedure [9], mp 54−55°C.

Acidolysis of compound (2). *a*. To a solution of 0.29 g (1 mmol) of compound **2** in 5 mL of $CHCl_3$ was added at stirring 3 mL of HI (54% water solution), the mixture was heated at 60°C and kept for 6 h. Chloroform solution was separated from water layer and filtered. We isolated 17 mg (22%) of selenium. According to GC-MS data the chloroform solution contained anisole (41.3%), initial compound **2** (21.4%), and bis(4-methoxyphenyl) diselenide (34%).

b. A mixture of 0.29 g (1 mmol) of compound **2** and 1.16 g (10 mmol) of Py·HCl was heated at 200°C for 50 min. The melt was cooled and diluted with 10 mL of water, the precipitate was filtered off, washed with 5 mL of methanol, and dried in air to obtain 13 mg (16%) of selenium. From the filtrate the reaction products were extracted with 20 mL of $CHCl_3$. According to GC-MS data the methanol and chloroform solutions contained compound **1** (9.7, 3.6%), phenol (17.6, 24.6%), initial selenide **2** (6.1, 26.6%), and bis(4-hydroxy-phenyl) diselenide (0 and 1.1% respectively).

Bis[4-(oxiran-2-ylmethoxy)phenyl]selane (3). In 0.93 g (10 mmol) of epichlorohydrin was dissolved 1.33 g (5 mmol) of compound **1**, and to the mixture was added dropwise at vigorous stirring 1.33 g (5 mmol) of 30% water solution of NaOH. The reaction mixture was heated while stirring at 70°C for 6 h till the pH of the medium reached 7, the mixture was cooled to room temperature, the reaction products were extracted into dichloromethane (3 × 10 mL). The extract was dried with $CaCl_2$, the solvent was distilled off, the residue was chromatographed on a column packed with silica gel (eluent CH_2Cl_2), collecting the fraction with R_f 0.21 (eluent $CHCl_3$). After distilling off the eluent the residue (yellow oily substance) was dried in a vacuum. Yield 1.29 g (69%). ^{1}H NMR spectrum, δ, ppm: 2.72 d.d (2H, C$\underline{H_2}$OPh, J_1 5.0, J_2 2.6 Hz), 2.88 d.d (2H, C$\underline{H_2}$OPh, J_1 5.0, J_2 4.2 Hz), 3.32 m (2H, CH_{epoxy}), 3.89 d.d (2H, CH_2O_{epoxy}, J_1 11.2, J_2 5.7 Hz), 4.18 d.d (2H, CH_2O_{epoxy}, J_1 11.2, J_2 3.1 Hz), 6.81 d (4H_{Ar}, *J* 8.8 Hz), 7.36 d (4H_{Ar}, *J* 8.8 Hz). Found $[M]^+$ 376.0368. $C_{18}H_{18}O_4{}^{78}Se$. Calculated *M* 376.0373.

2-Hydroxy-3-[4-({4-[2-hydroxy-3-(prop-2-enoyloxy)propyloxy]phenyl}selanyl)phenoxy]propyl-prop-2-enoate (4). A mixture of 2.0 g (5.3 mmol) of diepoxide **3**, 0.9 mL (13 mmol) of acrylic acid, and 0.025 g (0.11 mmol) of triethylbenzylammonium chloride was heated while stirring at 90°C for 3 h. On cooling the reaction mixture was diluted with 50 mL of CH_2Cl_2, the organic layer was washed with water till pH 7, dried with $CaCl_2$, the solvent was distilled off on a rotary evaporator. The residue, 2.1 g of colorless oily substance containing by ^{1}H NMR data 75% of compound **4**, was without preliminary purification entered into the next stage. Yield 1.58 g (58%) (by ^{1}H NMR data). ^{1}H NMR spectrum, δ, ppm: 3.14 d (1H, OH, *J* 5.1 Hz), 3.96 m (2H, CH_2), 4.21 m (1H, CH), 4.30 m (2H, $C_6H_4OC\underline{H_2}$); 5.82 (H^A), 6.11 (H^B), 6.39 (H^C) (*ABC* system, J_{AB} 10.4, J_{AC} 1.3, J_{BC} 17.3Hz), protons of acryloyl groups, 6.76 m (2H_{Ar}), 7.33 m (2H_{Ar}).

1-[4-({4-[2,3-Bis(prop-2-enoyloxy)propoxy]-phenyl}selanyl)phenoxy]-3-(prop-2-enoyloxy)-propan-2-yl prop-2-enoate (5). To a solution of 2.1 g of the compound isolated in the previous experiment and containing 1.58 g (3 mmol) of bisacrylate **4** in 10 mL

of CH_2Cl_2 was added 2.2 mL (1.6 g, 16 mmol) of triethylamine, the mixture was cooled on an ice bath at 2 to 5°C and a solution of 1.0 mL (1.11 g, 12 mmol) of acryloyl chloride in 5 mL of CH_2Cl_2 was added dropwise at stirring. The cold bath was removed, the reaction mixture was stirred at room temperature for 4 h, diluted with 20 mL of CH_2Cl_2, washed with water (3 × 50 mL), dried with $CaCl_2$, the solvent was distilled off in a vacuum without heating. The viscous oily residue (2.7 g) was dissolved in benzene and chromatographed on a column packed with silica gel (50–160 μm), eluents benzene (fraction 1) and dichloromethane (fraction 2). Eluent was distilled off in a vacuum from fraction 2 to obtain 0.9 g (52%) of light yellow oily tetraacrylate **5**. ^{1}H NMR spectrum, δ, ppm: 4.13 d (2H, CH_2, J 5.2 Hz), 4.43 d.d (1H, CH_2, J_1 12.0, J_2 6.1 Hz), 4.51 d.d (1H, CH_2, J_1 12.0, J_2 4.0 Hz); 5.84 (H^A), 6.09 (H^B), 6.39 (H^C) (*ABC* system, J_{AB} 10.4, J_{AC} 1.3, J_{BC} 17.3 Hz), 5.86 (H^A), 6.14 (H^B), 6.44 (H^C) (*ABC* system, J_{AB} 0.4, J_{AC} 1.3, J_{BC} 17.3 Hz) – protons of two acryloyl groups, 6.80 m ($2H_{Ar}$), 7.37 m ($2H_{Ar}$). Found $[M]^+$ 628.1007. $C_{30}H_{30}O_{10}{}^{78}Se$. Calculated M 628.1008.

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