SHORT = COMMUNICATIONS

Nucleophilic Cleavage of the Ether Bond of Chlorex in the Chalcogenation with Diphenyl Dichalcogenides in the System Hydrazine Hydrate–KOH

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Abstract—The synthesis of unsymmetrical pincer ligands by reactions of diphenyl disulfide and diphenyl diselenide with bis(2-chloroethyl) ether in the system hydrazine hydrate–KOH was accompanied by the formation of 1,2-bis(phenylsulfanyl)ethane, 1,2-bis(phenylselanyl)ethane, and 1-(phenylselanyl)-2-(phenylsulfanyl)ethane as by-products with an overall yield of 23% as a result of nucleophilic cleavage of the C–O–C bond in the initial ether.

Keywords: multidentate ligands, chlorex, chalcogenation, diphenyl disulfide, diphenyl diselenide

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Dichalcogenide metal chelates represent now an important field of coordination [1, 2], catalytic [3–6], analytical [7–9], and structural chemistry. In addition, they are potential precursors to nanostructured transition metal chalcogenide films that are promising materials for electronics [10].

Bis(2-chloroethyl) ether (1, chlorex) is a very important reagent for the synthesis of pincer ligands containing several donor centers for coordination [11, 12]. We previously synthesized chromium(III) complexes with chalcogen-containing ligands derived from chlorex [13], and these complexes were used in structural studies and as components of catalytic systems for oligomerization of olefins.

Two approaches have been developed for the synthesis of multidentate ligands based on chlorex [11, 12]. The first approach is applicable to the preparation of aliphatic chalcogenide derivatives. It involves preliminary synthesis of oligomeric dichalcogenides containing a 3-oxapentamethylene fragment and their reductive at the chalcogen–chalcogen bond, followed by alkylation. The target products were thus obtained in 56–74% yield. The second approach is based on the reductive cleavage of organic dichalcogenides R_2Y_2 (R = Alk, Ar; Y = S, Se)

and subsequent reaction of the resulting chalcogenolates RY⁻ with chlorex; in this case, the yields of the target compounds were 60–68% (57–64% from Ph_2Y_2). The synthesis of ligands containing both oxygen atom and two different chalcogen atoms was described in [12]. However, only methyl derivatives were obtained in 58–72% yield [12], and the reaction was accompanied by the formation of compounds with similar chalcogen atoms. These syntheses were carried out at 60-65°C (2.5 h). When the temperature was lowered to $40-45^{\circ}\text{C}$ (1 h), products of replacement of only one chlorine atom in chlorex were identified in the reaction mixture (yield 14–15%). No compounds that could be formed as a result of cleavage of the C–O–C bond in chlorex were detected. This bond in ethers, including chlorex [14], is fairly strong. Cleavage of ethers with hydrogen iodide is well known [15]; however, ethers are stable under alkaline conditions even in the presence of strong nucleophiles.

While developing our studies aimed at synthesizing multidentate ligands with two different chalcogen atoms, an equimolar mixture of diphenyl disulfide and diphenyl diselenide was reacted with chlorex (1) under the conditions described in [11, 12] (65–70°C, 2.5 h). Surprisingly, apart from expected products 2a-2c



1 - 1 - 5 (a), 1 - 5, 1 - 5e (b), 1 - 1 - 5e

(overall yield 38% based on total Ph_2Y_2), we isolated bis(phenylchalcogenyl)ethanes **3a–3c** (overall yield 23%) which were formed as a result of cleavage of the ether bond in **1**. The reductive cleavage of Ph_2Y_2 (Y=S, Se) in the system hydrazine hydrate–KOH was carried out as described in [11] (Scheme 1). Each dichalcogenide was reduced separately, solutions of **4a** and **4b** were then combined, and chlorex was added to the resulting mixture.

The formation of 2a-2c and 3a-3c can be illustrated by Scheme 2. According to the ¹H NMR data, the 2a : 2b :2c molar ratio was 1.0 : 3.0 : 2.0, and the ratio 3a : 3b :3c was 1.0 : 2.8 : 1.8, which indicates higher reactivity of PhSe⁻ ions in both substitution of chlorine in 1 and ether bond cleavage. Taking into account that separate reactions of 4a and 4b with chlorex under similar temperature conditions did not produce compounds 3a and 3c even when the reaction time was prolonged to 5 h (only traces of 3a or 3c were detected), cleavage of the ether bond according to Scheme 2 is likely to require simultaneous action of PhS⁻ and PhSe⁻ ions. The nature and mechanism of the synergistic effect of these anions on the ether bond cleavage is the subject of a separate study.

Compounds **2a** and **2c** were described previously [11]. Unsymmetrical bischalcogenide **2b** was previously unknown and was characterized by a set of spectral methods (¹H, ¹³C, and ⁷⁷Se NMR, IR, and GC/MS) in a mixture with **2a** and **2c**. Signals in the NMR spectra were assigned using heteronuclear shift correlation experiments (HMBC ⁷⁷Se and HSQC ¹³C) [16].

Bischalcogendes **3a–3c** were synthesized previously via multistep procedures or from 1,2-dibromoethane [6, 17]. Their ¹H and ¹³C NMR spectra were given in [6]. It should be noted that no compounds **3a–3c** were formed when 1,2-dichloroethane was directly reacted with **4a** and **4b** in N₂H₄·H₂O–KOH.

Thus, the reaction of chlorex with a mixture of diphenyl disulfide and diphenyl diselenide in the system hydrazine

hydrate–potassium hydroxide gives not only products of substitution of chlorine atoms in chlorex but also products of ether bond cleavage, which opens a synthetic route to difficultly obtainable bis(phenylchalcogenyl)ethanes.

Reaction of diphenyl disulfide and diphenyl diselenide with chlorex (1) in the system hydrazine hydrate-KOH. Diphenyl disulfide, 5.46 g (0.025 mol), was added in portions to a solution of 6.72 g (0.12 mol) of KOH in 30 mL of hydrazine hydrate, and the mixture was stirred for 1.5 h at 80-85°C. Likewise, a solution of 7.8 g (0.025 mol) of diphenyl diselenide was prepared in a separate vessel. The obtained solutions were cooled to 25°C and mixed together, 5.9 mL (0.05 mol) of chlorex (1) was added to the mixture, and the mixture was stirred for 1.5 h at 65–70°C. After cooling, the organic layer (6.65 g) was separated, and the aqueous hydrazine layer was extracted with diethyl ether (2×50 mL). The extract was dried, and the solvent was distilled off to leave 0.95 g of the residue. GC/MS analysis showed the presence of compounds 2a-2c and 3a-3c (~85%) and volatile impurities (15%) which were not identified. By vacuum distillation (2 mm Hg) we succeeded in separating only volatile components of the residue and obtaining fractions enriched in either 3a–3c or 2a–2c.

The ¹H, ¹³C, and ⁷⁷Se NMR spectra of **2a** and **2c** were fully identical to those reported in [11]. Their mass spectral data are given for the first time: m/z 290 (**2a**), 386 (⁸⁰Se, **2c**).

Phenyl{2-[2-(phenylselanyl)ethoxy]ethyl}sulfane (**2b**) was characterized in a mixture with other products. ¹H NMR spectrum (CDCl₃), δ , ppm: 2.95 m (2H, CH₂Se), 2.99 m (2H, CH₂S), 3.53 m and 3.62 m (4H, CH₂O), 7.21–7.55 m (10H, Ph). ¹³C NMR spectrum (CDCl₃), δ_{C} , ppm: 26.62 (CH₂Se), 33.08 (CH₂S), 69.36, 70.38 (CH₂O), 126.12–135.86 (Ph). ⁷⁷Se NMR spectrum (CDCl₃): δ_{Se} 270.25 ppm. Mass spectrum: *m/z* 338 (⁸⁰Se).

RUSSIAN JOURNAL OF GENERAL CHEMISTRY Vol. 90 No. 9 2020

1,1'-(Ethane-1,2-diyldisulfanediyl)dibenzene (3a). Hereinafter, chemical shifts reported in [6] are given in parentheses. ¹H NMR spectrum (CDCl₃), δ , ppm: 3.00 s (3.08 s) (4H, CH₂S), 7.21–7.55 m (7.22–7.65 m) (10H, Ph). ¹³C NMR spectrum (CDCl₃), δ_{C} , ppm: 33.26 (33.34) (CH₂S), 126.12–135.86 (126.0–132.9) (Ph). Mass spectrum: *m/z*: 246.

Phenyl-[2-(phenylselanyl)ethyl]sulfane (3b). ¹H NMR spectrum (CDCl₃), δ, ppm: 2.95 m (3.01–3.08 m) (2H, CH₂Se), 3.00 m (3.12–3.19 m) (2H, CH₂S), 7.21– 7.55 m (7.16–7.61 m) (10H, Ph). ¹³C NMR spectrum (CDCl₃), $\delta_{\rm C}$, ppm: 26.40 (26.5) (CH₂Se), 33.06 (34.2) (CH₂S), 126.12–135.86 (126.5–135.1) (Ph). ⁷⁷Se NMR spectrum (CDCl₃): $\delta_{\rm Se}$ 323.61 ppm. Mass spectrum: *m/z* 294 (⁸⁰Se).

1,1'-(Ethane-1,2-diyldiselanediyl)dibenzene (3c). ¹H NMR spectrum (CDCl₃), δ, ppm: 3.04 s (3.16 s) (4H, CH₂Se), 7.21–7.55 m (7.26–7.65 m) (Ph). ¹³C NMR spectrum (CDCl₃), $\delta_{\rm C}$, ppm: 27.16 (27.2) (CH₂Se), 126.12–135.86 (127.2–133.1) (Ph). NMR spectrum ⁷⁷Se (CDCl₃): $\delta_{\rm Se}$ 341.91 ppm: Mass spectrum: *m/z* 342 (⁸⁰Se).

The ¹H, ¹³C, and ⁷⁷Se NMR spectra were recorded on a Bruker DPX-400 spectrometer at 400.13, 100.62, and 76.31 MHz, respectively, using tetramethylsilane (¹H, ¹³C) and dimethyl diselenide (⁷⁷Se) as internal standards. The mass spectra were run on a Shimadzu GCMS-QP5050A instrument (SPB-5 capillary column, 60 m×0.25 mm; quadrupole mass analyzer, electron impact, 70 eV; ion source temperature 190°C; a.m.u. range 34–650).

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CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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