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Reviews

Synthesis of organochalcogen compounds in basic reducing systems

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The review surveys the data on the synthesis of organosulfur, -selenium, and -tellurium compounds in basic reducing systems. Good prospects of the hydrazine hydrate—alkali system are demonstrated.

Key words: chalcogens, chalcogenides, dichalcogenides, thiocols, selenocols, basic reducing systems, dithiols, diselenols, bis(alkylchalcogeno)alkanes, bis(alkylchalcogeno)methylene chalcogenide.

Introduction

The development of the chemistry of organic compounds of sulfur, selenium, and tellurium is dictated by continuous extension of their use in practice and in theoretical studies.[1—3] This, in turn, stimulates the development and perfection of the synthetic routes to organochalcogen compounds, as indicated by the large number of reviews devoted to this topic.[4—10] However, in our opinion, these studies do not pay adequate attention to the use of basic reducing systems in the synthesis of organochalcogen compounds (OCC). Using these systems, it is possible to prepare OCC from elemental chalcogens and their simple, readily available inorganic and organic derivatives. The direct reaction of chalcogens with organic compounds proceeds most easily for sulfur[11] and less easily for selenium[12] and tellurium.[13] Most often, these reactions are carried out at elevated temperatures. In recent years, the tendency for microwave activation of the reactions has appeared, especially in the synthesis of organosulfur compounds.[14,15] The chemical activation of chalcogens and some of their derivatives involves their transformation into anionic species such as alkali metal chalcogenides, polychalcogenides, hydrochalcogenides, or organylchalcogenides (M_2Y, M_2Y_x, MYH, MYR, where M is alkali metal, x = 2—4, R is an organic substituent, Y = S, Se, Te). The subsequent direct reaction of these anions with electrophiles gives the desired OCC. The syntheses are carried out as one-pot protocols without isolation of intermediate chalcogen derivatives. The transition of chalcogens (or their oxides, dichalcogenides, and polychalcogenides) into chalcogenide anions is a redox reaction, which requires the presence of a reducing agent and a basic medium (basic reducing system). The most

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substantial achievements made in recent years refer to this type of OCC synthesis.

Redox properties of chalcogens and their derivatives

Unlike oxygen, the sulfur-group elements possess a broad range of valence states[16] in which the number of outer electrons is eight (for chalcogenides and polychalcogenides), six (for free chalcogens, Y^0), two (Y^{4+} in chalcogen dioxides or tetrahalides), or 0 (Y^{6+}). The change in the chalcogen valence state is accompanied by electron transfer and refers to redox reactions. These reactions, especially those with sulfur, are highly significant for the biochemistry of living organisms[17] and often reflect the mechanism of action of some sulfur-containing drugs.[18] The thiol $\rightleftharpoons$ disulfide redox transformations in living organisms are necessary for the provision of vital functions; therefore, despite the marked advances made in this field,[19] they remain the subject of keen attention of researchers.[20,21] The role of selenium and tellurium for microbes, plants, animals, and humans is beyond doubt; nevertheless, redox processes that take place with these elements in living organisms are less studied.[22,23]

The diversity of chalcogen valence states determines their dual redox nature in the elemental state and in polychalcogenides and, hence, the capacity for disproportionation, which readily occurs on treatment with alkaline reagents.[16] The reactions under these conditions yield two types of compounds, one with a positive and one with a negative oxidation state of the chalcogen. Usually, these reactions are carried out in aqueous solutions; sulfur can thus be converted into sulfides and polysulfides as well as, depending on the process conditions, alkali metal sulfites, thiosulfates, or sulfates.[16] This type of generation of polysulfide anions from elemental sulfur is used to prepare diorganyl disulfides[24] and thiocols.[25] Selenium and tellurium disproportionate more unambiguously in alkaline media (Scheme 1)[26].

Scheme 1

$$3\,Y + 6\,KOH \longrightarrow 2\,K_2Y + K_2YO_3 + 3\,H_2O$$

Y = Se, Te

The dissolution of selenium in aqueous alkali starts at an alkali concentration no lower than 0.5 *N*, whereas tellurium dissolves only in a 9 *N* solution. The reaction is reversible for both elements; therefore, aqueous alkaline solutions of selenium and tellurium have not found application in the OCC synthesis.

The introduction of polar aprotic solvents (DMSO, HMPTA) into an aqueous solution is favorable for the activation of elemental halogens. The use of organic solvents facilitates the subsequent reaction of the resulting anions with electrophiles. Using systems of this type, chalcogens have been converted into unsaturated chalcogenides and many their derivatives.[27—29] Highly thermally stable polyarylene selenides have been synthesized in the NaOH—HMPTA system.[30] Microwave radiation is used to increase the efficiency of the process.[14]

For organic dichalcogenides, redox disproportionation in the presence of alkali has been studied under phase transfer catalysis conditions in THF taking diaryl dichalcogenides as examples[31—33] (Scheme 2).

Scheme 2

$$2\,ArYYAr \xrightarrow{4\,OH^-} 3\,ArY^- + ArYO_2^- + 2\,H_2O$$

Y = S, Se, Te

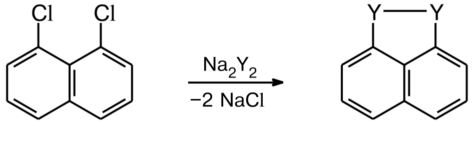
The ArY^- anions generated in this way were used successfully for the synthesis of alkyl aryl chalcogenides.

The methods for OCC synthesis based on disproportionation have not found wide use, mainly due to the fact that some of the chalcogen is irretrievably lost as derivatives with positive oxidation state, which, moreover, complicate the subsequent reaction of the anions with electrophiles and give rise to large amounts of polluted waste water. More often, chalcogens and organic polychalcogenides are activated in the presence of a reducing agent.

Chalcogen activation in basic reducing systems

Alkali metals are efficient reagents for the activation of chalcogens; however, direct fusion of the reactants for synthetic purposes is seldom used.[34] The use of aprotic solvents markedly extends the scope of the method. The reaction of sulfur (selenium) with sodium in HMPTA followed by treatment with 1,8-dichloronaphthalene resulted in the synthesis of naphtho[1,8-*cd*]-1,2-dithiole and naphtho[1,8-*cd*]-1,2-diselenole[35] (Scheme 3).

Scheme 3



Y = S, Se

Tetrahydrofuran is also suitable as the solvent for the reaction of chalcogens with metals.[36—38] In this solvent, ditellurides were reduced with lithium metal with subsequent synthesis of alkyl aryl tellurides.[37]

In practice, solutions of metals in ammonia are used most often. This reaction is especially suitable for the synthesis of acetylene derivatives of chalcogens.[39] The reaction of sodium acetylenide with elemental sulfur in liquid ammonia affords polyene polysulfides of a complex composition with various sulfur-containing polymer blocks, which are formed through spontaneous polymerization of intermediate thioketene.[40]

When reacting with chalcogens and organic dichalcogenides, alkali metal hydrides and complex hydrides create a basic reducing medium and, hence, they are successfully used for OCC synthesis. The synthesis is carried out in a one-pot system using water[41] or an organic solvent, most often, aprotic.[42,43] Sodium borohydride is used to reduce diaryl dichalcogenides to give ArY^- anions, which are then used for nucleophilic addition to multiple bonds.[44,45] The reaction of $ArTe^-$ with aryltellurium iodides (ArTeI) gave unsymmetrical diaryl tellurides.[46] An anion exchange resin[6] containing BH_4^- anions has been used as the reducing agent for the synthesis of dialkyl diselenides.

Chalcogens are reduced with tin dichloride in aqueous alkali. The overall reaction is shown in Scheme 4 (see Ref. 47).

Scheme 4

$$Y + 6\,KOH + SnCl_2 \longrightarrow K_2Y + K_2SnO_3 + 2\,KCl + 3\,H_2O$$

The use of divalent tin compounds as reducing agents in phase transfer-catalyzed reactions has been surveyed in a review.[8] Volatile alkyl selenium and tellurium compounds have been obtained in high yields in chalcogen—H_2O—$SnCl_2$—KOH systems in the presence of DMSO or without addition of organic solvents or catalysts.[48]

Of organometallic compounds, lithium derivatives are successfully used in the synthesis of OCC. 2,2-Dipyridyl diselenide and 2,2-dipyridyl ditelluride and unsymmetrical chalcogenides based on them have been prepared using these reagents.[49] Certain difficulties in the work with organometallic compounds hamper their wide use in the preparation of OCC.

In alkaline media, some organic reducing agents are used to generate chalcogenide anions (rongalite[50] and thiourea dioxide[51]). However, these reagents are easily oxidized; therefore, they have not found wide use in the synthesis of OCC.

Electroreduction of chalcogens and organic dichalcogenides is also possible. The reduction at the cathode is accompanied by an increase in the pH, *i.e.*, a basic reducing system is formed directly in the process of electrolysis. Methods for the synthesis of diorganyl diselenides and diorganyl ditellurides using selenium-[52] or tellurium-containing[53] cathodes in an aprotic solvent in the presence of alkali have been developed. The additional use of ultrasound in the electrochemical process resulted in generation of the Se^{2-} and Te^{2-} anions apart from the dichalcogenide anions.[54] The RY^- anions are also generated electrochemically from organic dichalcogenides[55] and used in the OCC synthesis.

The polysulfide anions are formed in the reaction of sodium sulfide with sulfur.[56] Since the oxidation states of both the elemental sulfur and the sulfide anion change, this is also a redox process. Usually, sulfur is activated in an aqueous medium by means of sodium sulfide (the systems formed in this way are used in the industrial synthesis of thiocols[25]). If azeotropic distillation of water is carried out during this synthesis, the anhydrous polysulfides in DMSO or DMF obtained in this way are used for the synthesis of polysulfide oligomers from polychloroethylenes.[57,58] However, a similar reaction of tetrachloroethylene with sodium trisulfide in DMF affords a monomeric product, dimethylthioacetamide, which is formed with participation of DMF.[58]

The hydrazine hydrate—base system, which we developed, proved to be the most versatile for OCC synthesis. This system is considered in detail below.

Hydrazine is a rather weak base ($pK_b = 6.5$)[59] but a rather strong reducing agent in alkaline media.[60] The redox process is accompanied by the transformation of hydrazine into nitrogen and water, which is very important from the environmental standpoint (Scheme 5).

Scheme 5

$$N_2H_4 + 4\,OH^- - 4\,e \longrightarrow N_2 + 4\,H_2O$$

The hydrazine hydrate—base system readily converts chalcogen molecules into the Y_n^{2-} anions (Scheme 6). The n value depends on the reactant ratio (mainly on the Y : base ratio), the presence of the solvent, and other factors.

Scheme 6

$$2n\,Y + N_2H_4 + 4\,OH^- \longrightarrow 2\,Y_n^{2-} + N_2 + 4\,H_2O$$

Y = S, Se, Te; $n = 1$—4

The sodium (or potassium) chalcogenides obtained in this way are made to react with electrophiles without isolation, giving rise to diverse OCC. This reaction underlay the development of a number of systems for sulfur dissolution[61] meant for the removal of sulfur deposits from pipelines and communications at the plants producing or using elemental sulfur. Solutions of sulfur obtained in this way are efficient catalysts for wood delignification.[62,63]

Hydrazine molecules are highly prone to association with other molecules, to give, for example, hydrazine hydrate[16,59] or to self-association to give dimers.[64] If association involves the hydrazine hydrogen atoms, this increases the nucleophilicity of the hydrazine molecule. Perhaps, for this reason, the reaction of hydrazine with carbonyl compounds is markedly facilitated in the presence of polysulfide anions.[65]

The hydrazine hydrate—alkali system cleaves also Y—Y bonds in organic dichalcogenides[66] (Scheme 7).

Scheme 7

$$2\ \mathrm{RYYR} + \mathrm{N_2H_4} + 4\ \mathrm{OH^-} \longrightarrow 2\ \mathrm{RY^-} + \mathrm{N_2} + 4\ \mathrm{H_2O}$$

Hydrazine is a product of ammonia oxidation[59] and, apart from reducing properties, it may exhibit the properties of an oxidant, especially when made to react with a potent reducing agent such as hydrogen sulfide.[67] This affords polysulfides, for example:

$$\mathrm{N_2H_4} + 2\ \mathrm{H_2S} \longrightarrow (\mathrm{NH_4})_2\mathrm{S_2}.$$

The *n* value in the resulting S_n anion depends on the presence of a base and its nature (this value decreases with an increase in the medium basicity). Therefore, for selective generation of monochalcogenide anions in the chalcogen—hydrazine hydrate—base system, an excess of alkali is used.

Hydrazine has long attracted attention of researchers for OCC synthesis.[68—70] However, the reactions of chalcogens with its aqueous or other solutions without an excess of the base resulted in generation of mainly dichalcogenide anions. The use of the hydrazine hydrate—base system without a solvent made it possible to synthesize organic monochalcogenides and other OCC having various structures.

Synthesis of OCC in a hydrazine hydrate—base system

Reactions of chalcogens with monoelectrophiles

The polysulfide anions generated from sulfur in this system as an aqueous solution are alkylated at room temperature with various alkyl halides to give diorganyl polysulfides[71] (Scheme 8).

Scheme 8

$$2\ \mathrm{RX} + \mathrm{S}_n^{\ 2-} \longrightarrow \mathrm{R_2S}_n + 2\ \mathrm{X^-}$$

R = Alk; X = Cl, Br, I; n = 2—4

The *n* value for the reaction products is determined by the S : MOH ratio (M = K, Na). When the ratio is close to unity, disulfide is formed as the major reaction product (yield 60—87%). When excess sulfur is used, the yields of tri- and tetrasulfides increase (the overall yield is 70—85%). An increase in the length of the alkyl chain is accompanied by a decrease in the selectivity of formation of the disulfides.

Selenium and tellurium generate Y^{2-} anions in a hydrazine hydrate—alkali system without a solvent (Y : KOH = 1 : (2—4)). Their subsequent alkylation with alkyl halides results in diorganyl selenides or diorganyl tellurides whose yield reaches 95% (Scheme 9).[72]

Scheme 9

$$\mathrm{K_2Y} + 2\ \mathrm{RX} \longrightarrow \mathrm{R_2Y} + 2\ \mathrm{KX}$$

Y = Se, Te; R = Me, Et, Pr, $\mathrm{Pr^i}$, $\mathrm{Bu^i}$, *etc.*; X = Cl, Br, I

The target reaction products are readily isolated from the reaction mixture as an organic layer or crystals. In the absence of alkali, hydrazine hydrate reacts with chalcogens to give polychalcogenide anions with great *n* values, which are alkylated to give unstable dialkyl polyselenides and dialkyl polytellurides.[73]

Diorganyl disulfides are efficiently reduced in the hydrazine hydrate—alkali system without a solvent to give organylthiolate anions. The alkylation of the thiolate anions with alkyl halides furnishes unsymmetrical sulfides[74] whose yield reaches 80—95%. The system in question is convenient for the preparation of unsymmetrical sulfides starting from thiols.[74] In this case, hydrazine hydrate prevents the thiols from oxidation and thus increases the process selectivity.

On the basis of reactions of dialkyl diselenides and dialkyl ditellurides with alkyl halides in the hydrazine hydrate—alkali systems, a method for the synthesis of unsymmetrical diorganyl selenides and diorganyl tellurides has been proposed.[66] The synthesis is carried out in two steps (Scheme 10).

Scheme 10

$$2\ \mathrm{R_2Y_2} + \mathrm{N_2H_4 \cdot H_2O} + 4\ \mathrm{KOH} \longrightarrow 4\ \mathrm{RYK} + \mathrm{N_2} + 5\ \mathrm{H_2O}$$

$$\mathrm{RYK} + \mathrm{R'X} \longrightarrow \mathrm{RYR'} + \mathrm{KX}$$

Y = Se, Te; R = Alk, Ar; R′ = Alk

The reduction of dichalcogenides takes place at a temperature of 80—90 °C at the reactant ratio R_2Y_2 : KOH = 1 : (2—3), and alkylation is carried out at 20—25 °C.

The reaction of tellurium with the hydrazine hydrate—KOH system can be directed toward the predominant formation of potassium ditelluride, which is readily alkylated giving rise to dialkyl ditellurides. Conditions for the isolation of these unstable compounds from the reaction mixture have been selected.[75,76] However, for the synthesis of unsymmetrical dialkyl tellurides, diorganyl ditellurides can also be used without isolation.[77]

In the aqueous hydrazine—alkali system, the activation of a mixture of chalcogens introduced either simultaneously or successively has been also carried out. The type of the anions formed (including mixed anions such as sulfidoselenides, sulfidotellurides, or selenidotellurides) was determined by treating them with ethyl bromide followed by identification of the diethyl polychalcogenides.[78] Mixed sulfidoselenides were noted to be formed most easily.

Allyl halides have also been employed for the preparation of unsymmetrical diorganyl chalcogenides in a hydrazine hydrate—alkali system. Most often, allylic chalcogen derivatives were obtained in high yields and the reactions were not accompanied by side processes.[79] However, in some cases, especially at high alkali concentrations (molar ratio R_2Y_2 : KOH = 1 : (6—10)), the allyl—propenyl rearrangement took place[80] (Scheme 11).

Scheme 11

$$\mathrm{2\,Ph_2Y_2 + N_2H_4 \cdot H_2O + 4\,KOH} \longrightarrow$$

$$\longrightarrow \mathrm{4\,PhYK + N_2 + 5\,H_2O}$$

$$\mathrm{PhYK + CH_2{=}CHCH_2Br} \longrightarrow \begin{cases} \longrightarrow \mathrm{PhYCH_2CH{=}CH_2} \\ \longrightarrow \mathrm{PhYCH{=}CHMe} \end{cases}$$

Y = S, Se, Te

The ratio of the isomers depends on the nature of the element Y, the degree of isomerization decreasing in the sequence S (95%) > Se (53%) > Te (3%), all other factors being equal. The total yield of the allyl and propenyl chalcogenides amounts to 80—90%. This rearrangement occurs directly during the synthesis of allyl chalcogenide when the RY^- anion reacts with allyl bromide. Indeed, the rearrangement does not take place on keeping of allyl chalcogenides in the hydrazine hydrate—KOH system at 90—110 °C. Propenyl chalcogenides are formed as mixtures of *Z*- and *E*-isomers with the *Z*-isomer predominating (*Z* : *E* = 3 : 1 for sulfur and 5 : 4 for selenium). A mechanism for the rearrangement has been proposed.[80]

Diallyl selenide can be obtained in 95% yield in the Se—$N_2H_4 \cdot H_2O$—KOH system from allyl chloride only in the absence of atmospheric oxygen.[81] In the presence of oxygen, a partial hydrogenation product, allyl propyl selenide, is formed[81,82] in a yield of up to 38%. Hydrogenation is performed by the diimide, which is produced from hydrazine and oxygen.

The preparation of allyl 2-thienyl chalcogenides (Y = S, Se) in the basic reducing system under consideration involves the Claisen rearrangement, which is more characteristic of allyl selenide.[83]

The reactions of activated chalcogen forms with polyelectrophiles in a hydrazine hydrate—base system

The use of polyelectrophiles in reactions with chalcogen solutions in basic reducing systems resulted in the development of new synthetic routes to OCC, in particular, to oligomeric or polymeric compounds.

Poly(alkylene polysulfides) (thiocols) are usually prepared by the reaction of dihaloalkanes with solutions of sodium polysulfides, which are generated by heating sulfur with an aqueous solution of sodium hydroxide or by the reaction of sodium sulfide with sulfur.[25,84] The use of basic reducing systems underlay the development of new methods for the synthesis of poly(alkylene polysulfides) based on the alkylation of solutions of sulfur with polyelectrophiles. In the synthesis of poly(methylene polysulfides), dichloromethane, formaldehyde, paraformaldehyde, and urotropin have been utilized as polyelectrophiles.[85] The reaction of methylenating agents with sodium polysulfide generated by the reaction of sodium sulfide with elemental sulfur (without hydrazine) furnishes oligomeric poly(methylene polysulfides) in up to 12% yield, whereas the use of a sulfur—hydrazine hydrate—alkali system affords oligomeric polysulfides in up to 90% yield (the product yield and the sulfur content depend on the nature and the ratio of the reactants used).[85] For example, the following products have been obtained (Scheme 12).

Scheme 12

$$n\,\mathrm{Na_2S_2} + (n+1)\,\mathrm{CH_2Cl_2} \longrightarrow$$

$$\longrightarrow \mathrm{Cl}\!\left[\mathrm{CH_2S_2}\right]_n\!\mathrm{CH_2Cl} + 2n\,\mathrm{NaCl}$$

$$\left[\mathrm{CH_2O}\right]_{2n} + n\,\mathrm{Na_2S_3} \xrightarrow{\mathrm{H_2O}}$$

$$\longrightarrow \left[\mathrm{CH_2OCH_2S_3}\right]_n + 2n\,\mathrm{NaOH}$$

The addition of sodium bicarbonate to bind the alkali being evolved facilitates the formation of poly(methylene polysulfide) in the highest possible yield.

The use of dihaloalkanes with longer polymethylene chain (*m* = 2—6) gave poly(alkylene polysulfides) of various structures in high yields[86,87] (Scheme 13).

Other bis-electrophiles used include glycerol dichlorohydrins[87] and compounds with the formula

Scheme 13

$$n\ X^1(CH_2)_mX^2 + n\ Na_2S_x \longrightarrow$$

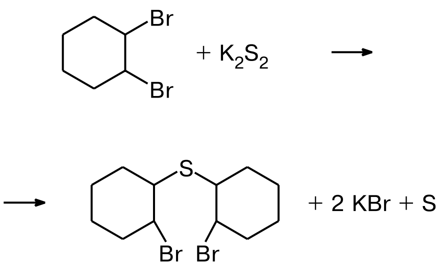
$$\longrightarrow X^1\!\left[S_x(CH_2)_m\right]_{n-1}S_x(CH_2)_mX^2$$

X^1, X^2 = Cl, Br

$(ClCH_2CH_2)_2Y$ (Y = O, S),[88] which were converted into polymeric polysulfides of the thiocol type containing oxygen bridges (in the case of Y = O).

The reaction of 1,2-dibromocyclohexane with sodium or potassium disulfide gives (probably, due to steric hindrance) only bis(2-bromocyclohexyl) sulfide (40%)[87] (Scheme 14).

Scheme 14



The alkylation of sodium polysulfide with 1,2,3-trichloropropane in an aqueous hydrazine—alkali system affords a dendrimer-like polymer.[89]

Chloroacetyl chloride reacts effectively with sulfur in the hydrazine hydrate—NaOH system in water to give N,O,S-containing polymers (Scheme 15)[90].

Scheme 15

$$NH_2NH_2 + 2\ ClCH_2COCl \xrightarrow[-2\ HCl]{}$$

$$\longrightarrow ClCH_2CONH{-}NHCOCH_2Cl$$

$$n\ ClCH_2CONH{-}NHCOCH_2Cl + n\ Na_2S_m \longrightarrow$$

$$\longrightarrow \left[CH_2CONH{-}NHCOCH_2S_m\right]_n + 2n\ NaCl$$

$m = 2$—2.5, $n = 4$—6

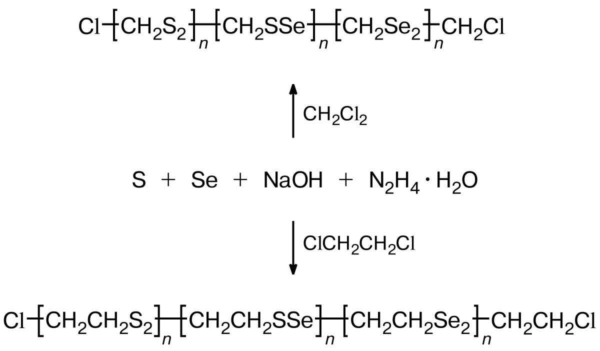
Chloroacetyl chloride reacts with sodium disulfide generated from sodium sulfide and sulfur in aqueous alcohol giving rise to polysulfide oligomers containing carbonyl groups[90] (Scheme 16).

Scheme 16

$$n\ ClCH_2COCl + Na_2S_2 \longrightarrow \left[CH_2COS_2\right]_n$$

Poly(methylene selenides) and poly(methylene diselenides) are formed in the reaction of dichloromethane with a selenium solution in hydrazine hydrate—alkali systems.[91] Poly(alkylene polyselenides) with a longer methylene chain in the bis-electrophile molecule were prepared only for 1-chloro-3-bromopropane.[92] No selenium-containing oligomers were formed with 1,2-dihaloehanes, 1,4-dibromobutane, or 1,5-dichloropentane. Mixed sulfur- and selenium-containing oligomers were prepared from dichloromethane and 1,2-dichloroethane[93] (Scheme 17).

Scheme 17



$$Cl\left[CH_2S_2\right]_n\left[CH_2SSe\right]_n\left[CH_2Se_2\right]_nCH_2Cl$$

$$\uparrow CH_2Cl_2$$

$$S + Se + NaOH + N_2H_4 \cdot H_2O$$

$$\downarrow ClCH_2CH_2Cl$$

$$Cl\left[CH_2CH_2S_2\right]_n\left[CH_2CH_2SSe\right]_n\left[CH_2CH_2Se_2\right]_nCH_2CH_2Cl$$

The combined activation of sulfur and tellurium in the hydrazine hydrate—NaOH system and the subsequent reaction of the resulting solution with dichloromethane yield an oligomer with ditelluride bridges containing virtually no sulfur, which was assigned the following structure:[93]

$$Cl\left[CH_2Te_2(CH_2Te_2)_2CH_2STe(CH_2Te_2)_2CH_2Te_2\right]_nCH_2Cl$$

The combined activation of selenium and tellurium followed by alkylation with dichloromethane gives a polymer whose chain contains diselenide and ditelluride bridges.[93]

$$Cl\left[CH_2Te_2CH_2Te_2CH_2Se_2CH_2Se_2\right]_nCH_2Cl$$

Alkylene dihalides react also with the RS^- and RSe^- anions generated from diorganyl disulfides and diorganyl diselenides in a hydrazine hydrate—alkali system. A convenient method for the preparation of bis(organylthio)alkanes[94] and bis(organylselenio)alkanes[95] has been developed. The synthesis is performed as a two-step one-pot process (Scheme 18).

When diphenyl and bis(2-thienyl) disulfide is used in the reaction with 1,2-dichloroethane, unsymmetrical chloro-substituted sulfides are formed apart from

Scheme 18

$$2\ R_2Y_2 + N_2H_4 \cdot H_2O + 4\ MOH \longrightarrow$$

$$\longrightarrow 4\ RYM + N_2 + 5\ H_2O$$

$$2\ RYM + X^1(CH_2)_nX^2 \longrightarrow RY(CH_2)_nYR + MX^1 + MX^2$$

R = Me, Et, Pr, Ph, 2-thienyl, 8-quinolyl;
Y = S, Se; M = Na, K; n = 1—5; X^1, X^2 = Cl, Br

bis(organylthio)ethanes[94] (in the case of other disulfides, these products are not formed) (Scheme 19).

Scheme 19

$$RSM + ClCH_2CH_2Cl \longrightarrow RSCH_2CH_2Cl + MX$$

R = Ph, 2-thienyl

Unsaturated sulfides were obtained from dimethyl disulfide and bis(8-quinolyl) disulfide with an excess of alkali[94] (Scheme 20).

Scheme 20

$$RSCH_2CH_2Cl \longrightarrow RSCH{=}CH_2$$

R = Me, 8-quinolyl

Unlike disulfides, thiols react with dichloroalkanes in a hydrazine hydrate—alkali system to give mainly unsymmetrical chlorine-containing sulfides.[96] When 1-chloro-3-bromopropane is used in this reaction, the bromine atoms are completely substituted (to give chloropropyl sulfide), while in the case of dibromoalkanes, only the corresponding bis(organylthio)alkanes were produced.

The difference between the reaction patterns of thiols and disulfides with dichloroalkanes in basic reducing systems is attributable to different degrees of hydrazine solvation of the thiolate anions generated from these reagents, which is confirmed to a certain extent by quantum-chemical calculations.[97]

In the synthesis of bis(ethylseleno)alkanes from dichloro- or dibromoethane or dibromopropane, the target products are formed in minor amounts.[95] As the dihaloalkane carbon chain becomes longer, the yields of bis(ethylseleno)alkanes increase. This is due to the formation of a cyclic transition state involving a hydrazine molecule, which may lead to regeneration of diethyl diselenide and formation of a olefin (especially, ethylene and propylene).[95]

A simple route to bisethylthio(polymethylene sulfides), difficult to obtain by other methods, has been developed based on the reaction of dichloromethane with simultaneously the EtS^- and S^{2-} anions generated in the hydrazine hydrate—alkali system from diethyl disulfide and sulfur (separate activation) or from diethyl trisulfide[98] (Scheme 21).

Scheme 21

$$Et_2S_3 + N_2H_4 \cdot H_2O + 4\ KOH \longrightarrow$$

$$\longrightarrow 2\ EtSK + K_2S + N_2 + 5\ H_2O$$

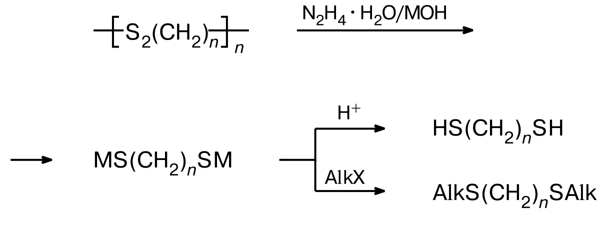
$$2\ EtSK + n\ K_2S + n\ CH_2Cl_2 \xrightarrow[-KCl]{} EtS(CH_2S)_nEt$$

Poly(methylene sulfides) with n = 1—4 were isolated and identified, although the formation of products with greater n was also noted.

Reductive synthesis of di- and polythiols, diselenols, and their derivatives

The S—S bonds in the synthesized poly(alkylene polysulfides) (thiocols) readily undergo reductive cleavage in a hydrazine hydrate—alkali system. The reduction yields dithiolates whose mild acidification results in alkanedithiols, while treatment with alkylating reagents affords bis(alkylthio)alkanes[86—88] (Scheme 22).

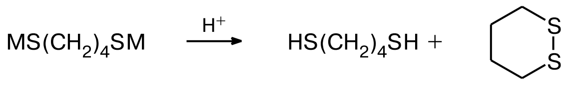
Scheme 22



M = Na, K

When 1,4-butanedithiol is synthesized by this procedure, 1,2-dithiane is produced together with the target product (Scheme 23).

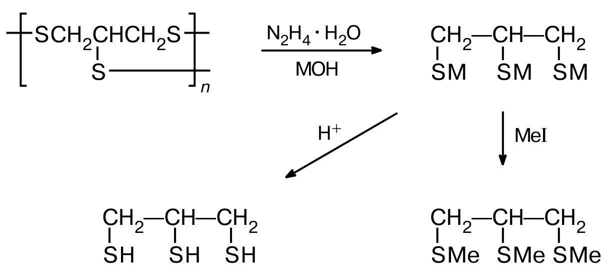
Scheme 23



M = Na, K

The reduction of thiocols prepared from 1,3-dichloro-2-hydroxypropane and 1,2-dibromo-3-hydroxypropane yields in both cases two dithioglycerol isomers, which may be attributed to migration of the hydroxy group.[87] The dendrimer polysulfide oligomer prepared from 1,2,3-trichloropropane was converted into trithioglycerol and its trimethyl derivative[89] (Scheme 24).

Scheme 24



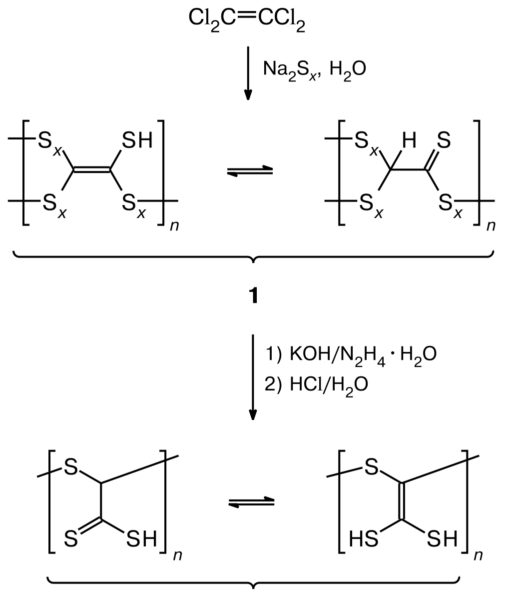
M = Na

For the reduction of thiocols to alkanepolythiols, selenophenol can also be used as the reducing agent. During the reaction, this reagent is converted into crystalline diphenyl diselenide, which markedly facilitates the product isolation.[99]

The synthesis of alkanepolythios *via* polysulfide oligomers was used to develop new in principle approaches to the utilization of mustard gas[87] and some organochlorine wastes of epichlorohydrin production.[100,101]

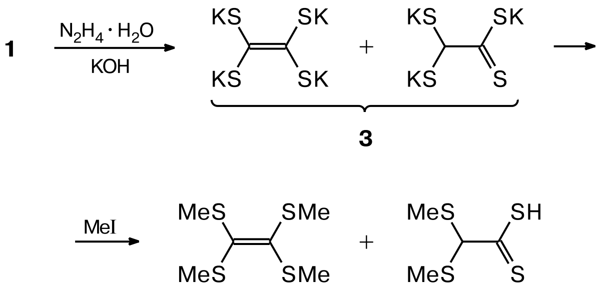
The reductive cleavage, in a hydrazine hydrate—alkali system, of the polymeric product obtained from tetrachloroethylene and sodium polysulfide in DMSO gives, after acidification of the reaction mixture, a sulfur-containing polymer of a different composition[102] (Scheme 25).

Scheme 25



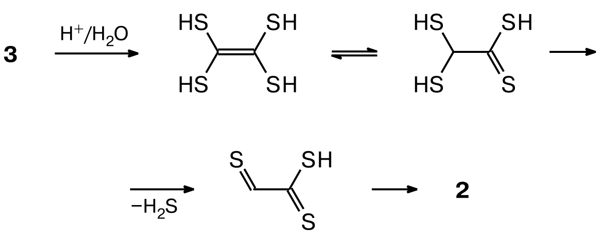
Treatment of the reaction mixture obtained after reductive cleavage with methyl iodide gives two products (Scheme 26).

Scheme 26



This confirms the proposed[102] route for the transformation of the starting polymer in a hydrazine hydrate—alkali system (Scheme 27).

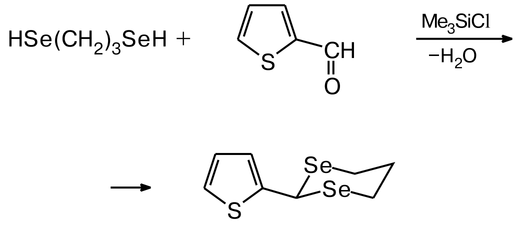
Scheme 27



Poly(methylene polysulfides) undergo complete decomposition in a hydrazine hydrate—alkali system with both the reductive cleavage of the S—S bonds and with easy cleavage of the C—S bonds [103] (which are not cleaved in the reduction of other polysulfides). The monosulfide polymers are thus converted into methane and sodium sulfide and, in addition, nitrogen, hydrogen, and ammonia are evolved. Disulfide polymers give sodium sulfide and disulfide, while trisulfide polymers decompose to sodium disulfide and trisulfide. The formation of the corresponding anions was confirmed by isolation of their alkylation products (after treatment with ethyl bromide).

Easy reductive cleavage with the hydrazine hydrate—alkali system was also observed for selenocols.[92] Under these conditions, 1,3-propanediselenol was synthesized[92] and characterized for the first time[92] by modern physicochemical methods. The formation of diselenol

Scheme 28



was additionally confirmed by isolating the product of its condensation with thiophene-2-carbaldehyde, namely, 2-(1,3-diselenan-2-yl)thiophene[104] (Scheme 28).

Conclusion

The considered data demonstrate that the synthesis of organic chalcogen derivatives in basic reducing systems, especially in the systems containing hydrazine hydrate is successfully developing. The reactions of monoelectrophiles with a variety of chalcogen-containing anions generated in these systems are described in sufficient detail in the literature. The reactions with polyelectrophiles and substrates containing functional groups, either inert or reactive with respect to hydrazine, are less studied. Study of these reactions will essentially contribute, beyond doubt, to the development of the chemistry of OCC, which in turn would extend the scope of their applications not only for practical purposes but also for solving theoretical problems of organic chemistry. We hope that these methods of synthesis would attract attention of researchers due to their simplicity, versatility, and the ease of isolation of the target product.

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