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Chalcogenisation of unsaturated organohalogen compounds by elemental chalcogens and their metal derivatives

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Abstract: The presented review addresses the prospects for application of organochalcogen compounds in various fields of technology, medicine, agriculture and organic synthesis. The unsaturated chalcogenisation products appear to be of much greater interest compared to their saturated analogues, especially in organic synthesis. This study observes halogen derivatives of ethene, propene, propyne and butene subjected to chalcogenisation as unsaturated substrates. The indicated reagents are related either to large-tonnage products of industrial organochlorine synthesis or waste products of organochlorine production with their disposal presenting an important environmental task. According to analysed publications, chalcogenisation processes are based on the application of elemental chalcogens (sulphur, selenium, and tellurium) or their available metal derivatives (Na_2S , etc.). In the reactions of chalcogens with unsaturated halogen derivatives, the elements both in an accessible form and in a free state are subjected to reductive activation resulting in the formation of anionic nucleophilic reagents. Complex metal hydrides, chalcogenide anions and rongalite are exemplified for application in terms of reducing agents. The review emphasises the prospects of basic reduction systems based on hydrazine hydrate in activation processes. Special aspects in the introduction of caustic alkalis and an monoethanolamine organic amine as bases in these systems are described. For the considered chalcogenisation processes, conditions are specified providing the most optimal yield of certain products. In some particular cases, the stereochemistry of the obtained compounds is presented considering the formation conditions for the stereoisomers of a certain configuration. For a number of the obtained compounds, the prospects of practical application are provided. In general, the current review is intended for specialists working in the field of organic synthesis and application of organochalcogen compounds.

Keywords: organochalcogen compounds, chalcogenisation, chalcogens, unsaturated organohalogen compounds, hydrazine hydrate-base systems

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Халькогенирование ненасыщенных галогенорганических соединений элементными халькогенами и их металлическими производными

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Резюме: В представленном обзоре рассмотрены вопросы, касающиеся перспектив использования халькогенорганических соединений в медицине, сельском хозяйстве, в различных областях техники и в органическом синтезе. Показано, что ненасыщенные продукты халькогенирования представляют

гораздо больший интерес по сравнению с их насыщенными аналогами, особенно при использовании в органическом синтезе. В качестве ненасыщенных субстратов, подвергаемых халькогенированию, представлены галогенпроизводные этена, пропена, пропиена и бутена. Указанные реагенты относятся либо к многотоннажным продуктам промышленного хлорорганического синтеза, либо являются отходами хлорорганических производств, утилизация которых является важной экологической задачей. Проанализированные публикации отражают процессы халькогенирования, базирующиеся на использовании элементных халькогенов (серы, селена и теллура) или их доступных металлических производных (Na_2S и др.). Для осуществления реакций халькогенов с ненасыщенными галогенпроизводными элементы в доступной форме в свободном состоянии подвергают восстановительной активации, в результате которой образуются анионные нуклеофильные реагенты. В качестве восстановителей показаны примеры использования комплексных гидридов металлов, халькогениданионов и ронгалита. В обзоре подчеркнуты перспективы применения для целей активации основно-восстановительных систем на базе гидразингидрата. Показаны особенности введения в качестве оснований в эти системы едких щелочей и органического амина – моноэтаноламина. Для рассмотренных процессов халькогенирования указаны условия, обеспечивающие наиболее оптимальные выходы определенных продуктов. В необходимых случаях представлена стереохимия получаемых соединений и рассмотрены условия образования стереоизомеров определенной конфигурации. Для некоторых получаемых соединений показаны перспективы практического применения. Материал обзора будет полезен специалистам в области органического синтеза и практического использования халькогенорганических соединений.

Ключевые слова: халькогенорганические соединения, халькогенирование, халькогены, ненасыщенные галогенорганические соединения, системы гидразингидрат-основание

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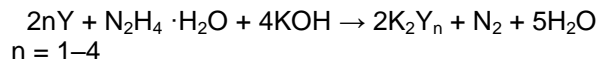
INTRODUCTION

The scope of organic chalcogen compounds can be seen to be constantly expanding. Although sulphur and its organic derivatives have been applied by humans since ancient times, more recent uses include unique medicines created on their basis, including antibiotics, anticancer drugs, drugs for human immunodeficiency, as well as protector drugs against ionising radiation. The technological application of organosulphur compounds is associated with the development of rubber vulcanisation agents, dyes, photographic materials, complexing agents, flotation reagents and extractants, polymerisation process regulators, as well as with the creation of corrosion protection agents and new types of polymeric materials, in particular for new generation chemical current sources and others directions [1]. The use of selenium and tellurium compounds was clearly indicated only in the second half of the last century and was associated, first of all, with their technical application in obtaining ligands for complex formation, organic semiconductors and electrically conductive polymers [2, 3]. However, in recent decades, numerous data have been obtained on the biological role of selenium and tellurium organic derivatives [4–6]. A detailed study for the structure of organochalcogen compounds (OCC) served as an impetus for the development of many theoretical concepts in

organic chemistry [7–9]. An important direction in the application of OCCs involves their use as precursors in contemporary organic synthesis [10–12]. By virtue of these precursors, new nanomaterials, analogues of natural compounds are obtained along with typically unstable, highly reactive compounds. Thus, the synthesis and use in modifying drugs of this class of compounds presents a specific task in modern organic chemistry.

The development and improvement of methods for OCC synthesis is constantly stimulated by the continuous expansion in the scope of their application. The most universal method of introducing a chalcogenyl substituent into the structure of an organic molecule involves the nucleophilic substitution of halogen. Chalcogen-containing anions manifest themselves as nucleophiles in these reactions (Y^{2-} , Y_n^{2-} , RY^\cdot with $\text{Y} = \text{S}, \text{Se}, \text{Te}$ and R denoting an organic radical). The specified anionic forms are included in some commercial chemicals, mainly sodium sulphide, applied in the form of nanohydrate ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$). The application of the considered chalcogenide reagents is directly related to the possibility of their generation from accessible, storage-stable elemental chalcogens. In order to introduce them into a nucleophilic substitution reaction, simple substances are converted into an anionic form by chemical activation carried out due to the reductive splitting of $\text{Y}-\text{Y}$ bonds in elemental

chalcogens. Currently, although a wide range of reducing systems is available for application, their use is typically associated with the involvement of explosive reagents (organic derivatives of metals, hydrides and complex hydrides), toxic and combustible solvents, compounds of heavy metals in



In this reaction, the value of n is determined by the Y: KOH ratio.

Here, the resulting chalcogenide and polychalcogenide anions are reacting in the synthesis directly in the hydrazine hydrate solution without being isolated in an individual state. Using this activation method, a large number of saturated OCCs have been synthesised, including chalcogen-containing polymers and heterocyclic systems, some of whose unique properties have been described (see, for example, [14]).

From a practical point of view, OCCs with multiple structural bonds are of particular interest due to their significant expansion of the synthetic potential and practical significance of the studied compounds. In order to synthesise them, reactions of chalcogen-containing nucleophiles with unsaturated organohalogen compounds can be applied. In the substrates under consideration, halogen atoms can be attached to carbon atoms in both the sp^3 hybridisation state, characterised by nucleophilic reactions to proceed fairly easy, and the sp^2 hybridisation state. In the latter case, nucleophilic substitution may be hindered [15]. When the conditions change, halogen vinyl fragments in the resulting products enter into further chemical transformations, ensuring cascade reactions allowing valuable OCCs to be obtained.

The present review provides the main research results with the objects of study consisting in organohalogen derivatives of ethylene, propylene, pro-

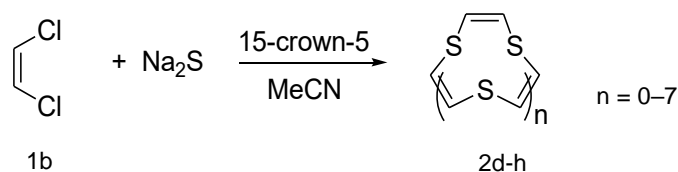
pyne and butylene. In addition, such derivatives are to be highlighted as relating either to large-tonnage organochlorine products or substances generated from organochlorine production wastes.

Halcogenisation of ethylen chlorinated derivatives. Thiylolation of vinyl halides or their derivatives, having a halogen atom attached to the sp^2 -hybridised carbon atom, is carried out either using photochemical and thermal assistance [16, 17] or by means of aprotic highly polar solvents [17]. In nucleophilic reactions, only di- and polyhalogen derivatives of ethene were studied.

The ethylene dichloro-derivatives 1,1-dichloroethene (vinylidene chloride) (1a) and 1,2-dichloroethene (*E*- and *Z*-isomers) (1b) present commercially available monomers and reagents. The unsaturated organochalcogen compounds obtained on their basis open up wide possibilities for the synthesis of polyfunctional n , π -ligands for complexation with transition metal ions.

The work [18] describes the photochemical reaction of atomic sulphur with 1,2-dichloroethene (1b), resulting in a low yielded dichlorothiirane. However, when the *Z*-1b compound and sodium sulphide nonahydrate reacts in acetonitrile with the presence of 15-crown-5 interphase transfer catalyst (0.4 equiv.), a mixture of cyclic unsaturated sulphur-containing compounds – unsaturated thiacycrocrown esters (2a-h) – was obtained at room temperature in 45 h with a total yield of 40 % [19] (Scheme 1).

Scheme 1
Схема 1



$n = 0$, 2a (44 %)*; $n = 1$, 2b (3 %); $n = 2$, 2c (traces); $n = 3$, 2d (4 %); $n = 4$, 2e (18 %); $n = 5$, 2f (16 %); $n = 6$, 2g (10 %); $n = 7$, 2h (5 %).

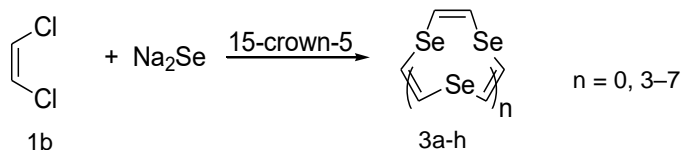
* product concentration in the mixture, according to 1H NMR data.

X-ray diffraction data were obtained for the synthesised thiacycrocrown esters, presenting all sulphur atoms in the cycle to be directed inward (endodentate ligand), i.e. totally *Z*-configured.

The dimensions of the cavities for the (2d-h) joints consistently increase from 1.76 to 5.36 Å.

In the treatment of *Z*-1b dichloroethene by sodium selenide obtained from selenium, sodium hydroxide and reducing agent of rongalite (sodium hydroxymethylsulphinate), six unsaturated selenocrown esters (3a-f) were synthesised (total yield of 29 %) using 0.1 eq. of 15-crown-5 ether additives [20] (Scheme 2).

Scheme 2
Схема 2



$n = 0$, 3a (24 %)*; $n = 3^{**}$, 3b (6 %); $n = 4$, 3c (22 %); $n = 5$, 3d (20 %); $n = 6$, 3e (16 %); $n = 7$, 3f (12 %).

* product concentration in the mixture, according to ^1H NMR data.

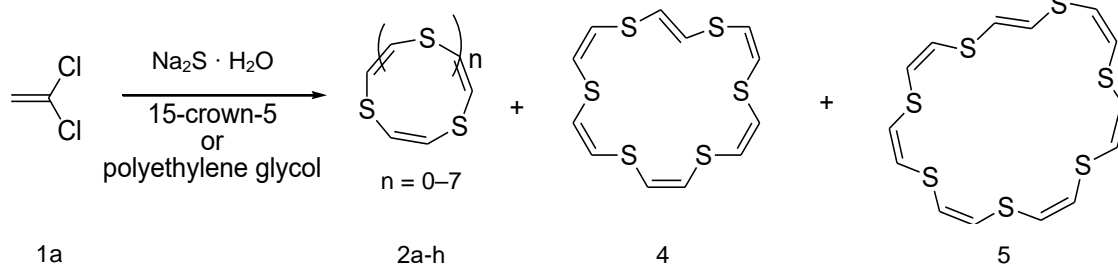
** no traces of $n = 1$ and 2 compounds were detected in the mixture.

As an example, the complexation of crown ether selenium with silver ions is presented in [20].

Type 2 unsaturated thiocrown ethers were also synthesised in the reaction of vinylidene chloro-

ride (1a) with sodium sulphide nonahydrate in acetonitrile with the presence of catalysts: 15-crown-5 or polyethylene glycol with a molecular weight of 300, 750 and 2000 units [21]. In this case, an interesting feature of the reaction consists in the formation of 18-membered (4) and 21-membered (5) cycles with *E*-configuration of one of the double bonds in addition to the formation of (2a-h) cycles with exclusively *Z*-configuration of sulphur atoms in the double bond (Scheme 3).

Scheme 3
Схема 3



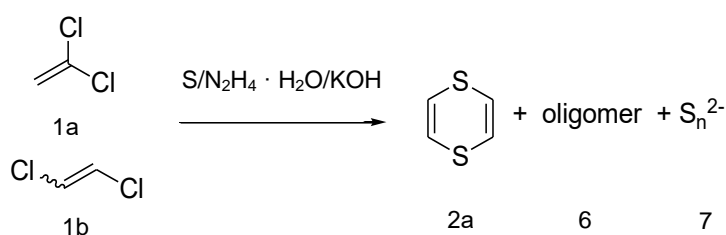
2a – 39 %*; 2b – 4 %; 2c – no traces; 2d – 6 %; 2e – 21 %; 2f – 13 %; 2g – 9 %; 2h – 5 %; 4 – 2 %; 5 – 2 %. Product concentration in the mixture, according to ^1H NMR data (0.4 equiv. of 15-crown-5 catalyst, room temperature, duration of 48 hours). In the case of applying the polyethylene glycol (0.1–0.5 equiv.) as a catalyst, a mixture of thiocrown ethers of approximately the same composition was obtained with a maximum yield of 15 %.

According to the work [21], in the product mixture, the absence of compounds with a geminal arrangement of sulphur atoms relative to the double bond carbons is accounted for mechanism involving the isomerisation of the geminal intermediate into a vicinal product. The considered scheme of the mechanism illustrates the formation of *E*-configura-

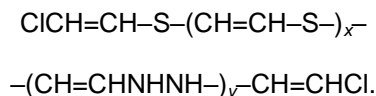
ted cycles. However, according to the authors, the initial act of the process is presented by direct nucleophilic substitution of chlorine atoms in vinylidene chloride (1a), leading to contradiction in the inertness notion of halogen atoms attached to a double bond.

Using the "sulphur-hydrazine hydrate-KOH" system generating exclusively S^{2-} anions at a KOH:S ratio exceeding 2, the thiylation of (1a) and (1b) dichloroethenes easily proceeds at a temperature of 23 °C and results in a mixture of three product types: 1,4-dithiin (2a) (16–31 and 14–46 % of yield, when using the (1a) and (1b) compounds, respectively), the (6) oligomer (26–75 %) and the (7) product of oxidative condensation of sulphur, i.e. a mixture of polysulphide anions S_n^{2-} (S_2^{2-} , S_3^{2-} and even traces of S_4^{2-}) (Scheme 4) [22].

Scheme 4
Схема 4



In the case of applying (1a) dichloride and (1b) compound, the molecular weight of the resulting (6) oligomeric product comprises 2260–6120 and 1750–2000 units, respectively. Based on the elemental analysis data, the following structure was assigned to the oligomer:

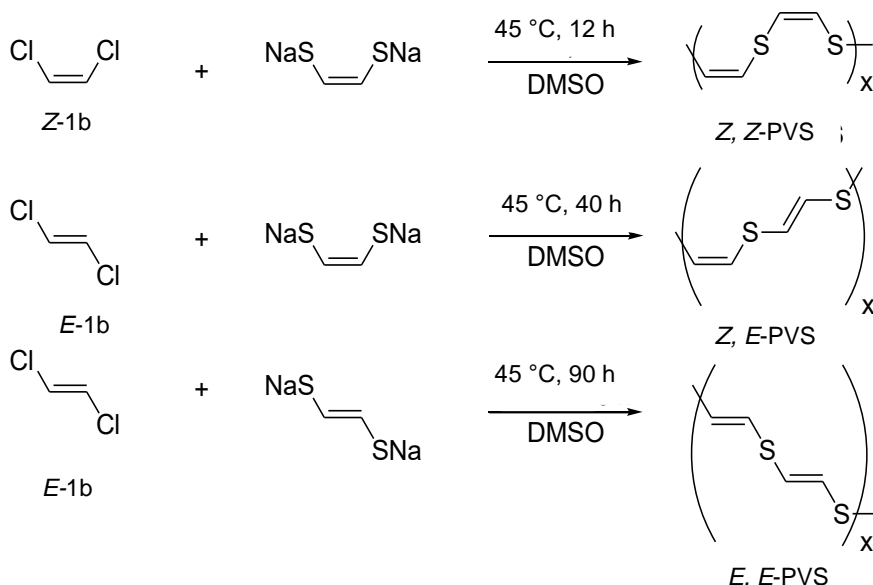


For oligomers obtained using the (1a) compound, the value of x and y was equal to 30–88 and 6–15, respectively. In the case of using the

(1b) dichloride, the above values were 22–24 and 1–6, respectively. According to IR spectroscopy and taking the results of the *E*- and *Z*-polyvinyl sulphide (PVS) studies into account, the vinylene units in the oligomer chain are exclusively *Z*-configured [23]. In current study, PVSs were obtained by polycondensation of *E*- and *Z*-1b dichlorides with *E*- and *Z*-isomers of hardly accessible sodium 1,2-ethanedithiolate (Scheme 5).

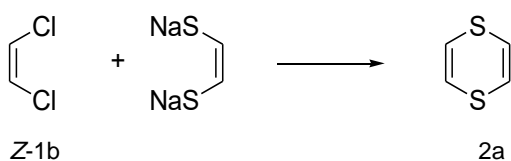
The electrical conductivity of obtained PVS is also examined by the authors of work [23], and *E*, *E*-PVSs are demonstrated to possess higher conductivity in comparison with *Z*,*Z*-polymer with the $\lg \sigma$ value ranging approximately from -4,5 to -6 S/cm).

Scheme 5
Схема 5



For 1,4-Ditiin (2a) in the reaction represented by Scheme 4, the substantially higher yield is observed in comparison with the data, obtained by the authors of works [19, 21], and its separation from other reaction products proceeds quite easily. A slightly higher yield of 47 % was established in the study for the reaction of *Z*-1b dichloride with *Z*-1,2-sodium ethanedithiolate in dry DMSO [24] (Scheme 6).

Scheme 6
Схема 6

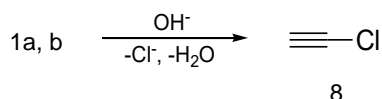


The (2a) compound involves an important object for structural studies, making the development of preparatively available methods for its preparation to be an important synthetic task.

After the separation of (2a) and (6) products, the formation of (7) polysulphide anions in the remaining aqueous hydrazine solution was confirmed by their alkylation by 1-bromopropane with the isolation and identification of dipropyl polysulphides.

The formation of the monotypic products presented in Scheme 4 under application of vinylidene chloride (1a) or both isomers of 1,2-dichloroethene (1b), as well as the participation of hydrazine in the formation of (6) oligomers, allowed the authors of [22] to propose a scheme for product formation having the primary key act consisting in the dehydrochlorination of (1) compounds with the formation of highly reactive chloroacetylene (8) (Scheme 7).

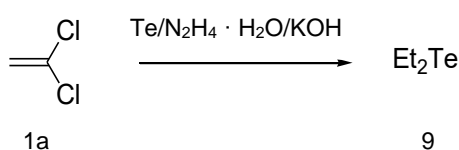
Scheme 7
Схема 7



The presence of excess hydrazine in the reaction medium prevents the formation of macrocyclic structures presented in [19, 21] and, with the participation of (8) reagent and S^{2-} anions, results in the formation of nitrogen containing oligomers.

During the reaction of selenium and tellurium with (1a) vinylidene chloride under conditions similar to sulphur application, no analogues of 1,4-dithiine were isolated [25]. In the case of tellurium, the presence of diethyl telluride (9) is convincingly proved by the authors of this work with the formation accounted for the reductive hydrogenation of multiple bonds with the participation of hydrazine and telluride anions (Scheme 8).

**Scheme 8
Схема 8**



Tetrachloroethylene, a derivative of ethylene having four chlorine atoms, is the subject of large-scale industrial production. Having relatively stable

characteristics, this compound is widely applied in terms of a solvent for dry cleaning of textile materials and degreasing metal surfaces. The works [26, 27] describe only the interaction of tetrachlorethylene with sodium polysulphide Na_2S_x formed upon activation of sulphur with sodium sulphide $Na_2S \cdot H_2O$ (Scheme 9) [27].

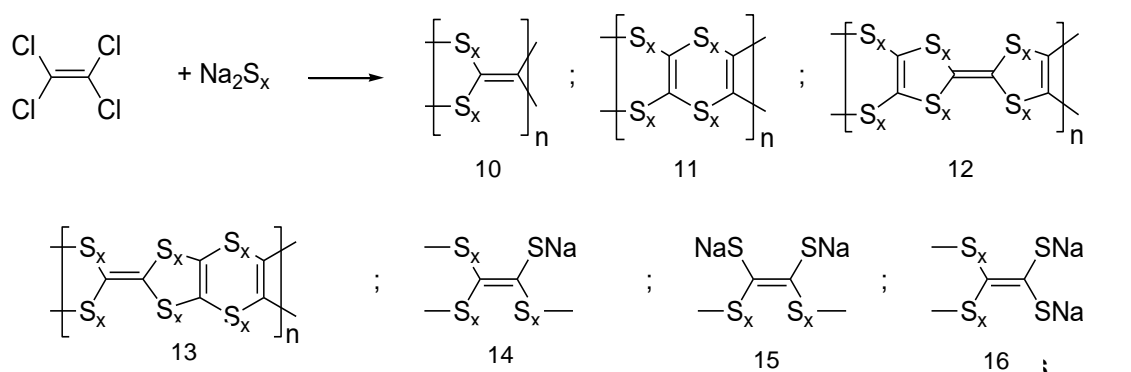
**Scheme 9
Схема 9**



In order to obtain an anhydrous polysulphide, water is removed by azeotropic distillation using octane.

The obtained anhydrous polysulphide ($x=2-5$) reacts with tetrachlorethylene in a DMSO medium and a temperature of 90–110 °C (1.5–3 h) and forms polysulphide polymers having semiconductor properties (when doped with iodine, the electrical conductivity is 10^{-8} S/cm) [26]. According to the authors of this work, the obtained polymer is assumed to contain fully polycondensed structures (10–13), as well as fragments with incomplete polycondensation (14–16) (Scheme 10).

**Scheme 10
Схема 10**



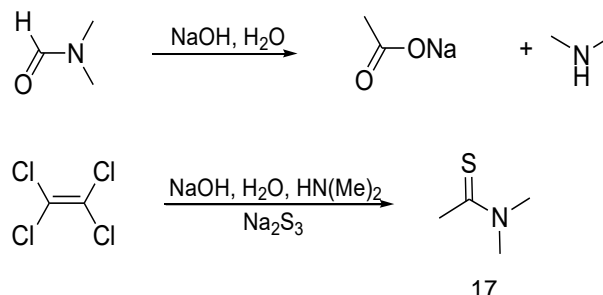
The structure of fragments (10–15) was confirmed by reductive cleavage of polymers by the "hydrazine hydrate-alkali" system and subsequent methylation of cleavage products.

Although the reaction of tetrachlorethylene with Na_2S_4 and Na_2S_5 in aqueous alkaline DMF also results in polymer products, the Na_2S_3 trisulphide in this reaction forms an individual compound of dimethylthioacetamide (17) with the participation of dimethylamine resulting from the alkaline hydrolysis of DMF [28] (Scheme 11).

The simplest chlorine derivative of propene, 3-chloropropene (allyl chloride), present a multi-ton product of industrial organochlorine synthesis. The high mobility of halogen in the allyl position ensures the production of a wide range of allyl chalcogenides [see, for example, 29, 30] studied in the *chalcogen* Claisen rearrangement of allylaryl (heteroaryl) chalcogenides [31, 32], identification the

chalcogen atom characteristics affecting the allyl rearrangement in the series of allylphenylchalcogenides [33], as well as in the synthesis of various heterocyclic structures [34].

**Scheme 11
Схема 11**

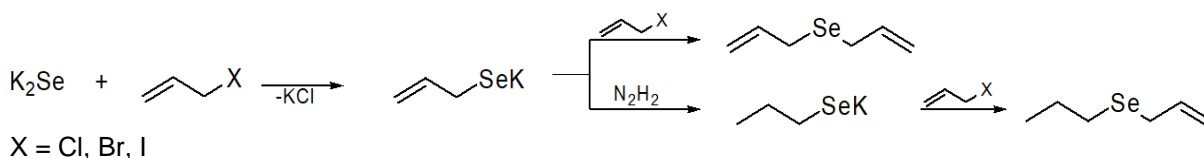


Halogen derivatives of propene and propyne

By application of AlX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) and elemental chalcogens in the hydrazine hydrate/ KOH system, all three diallyl chalcogenides were obtained [35]. As expected, allyl iodide is the most reactional, followed by bromide and chloride. When AlI_3 is introduced in the synthesis of diallyl selenide, the by-product of allyl propyl selenide is

formed due to the participation of hydrazine and atmospheric oxygen, in other words, hydrogenation of one double bond is observed [35, 36]. In the presence of atmospheric oxygen in an alkaline medium, hydrazine forms a highly reactive diimide hydrogenating the intermediate-generated potassium allyl selenolate contained in the aqueous hydrazine phase (Scheme 12).

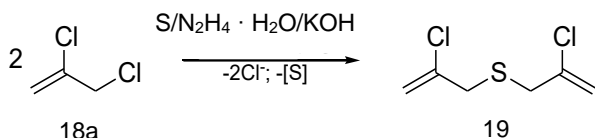
**Scheme 12
Схема 12**



In parallel, the formed diallyl selenide and the allyl propyl selenide obtained by hydrogenation transits into the organic phase, avoiding further reduction. In the case of using allyl bromide, the reaction of diallyl selenide formation proceeds quickly and potassium allyl selenate transits from the aqueous hydrazine phase without hydrogenation [35].

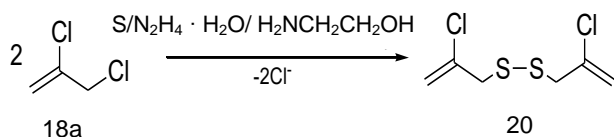
The chalcogenisation of the dichloro-derivative of propene, 2,3-dichloropropene-1 (18a), was studied only in the hydrazine hydrate-base system. Dichloropropene (18a) with a S_2^{2-} disulphide anion, generated in the hydrazine hydrate- KOH system at a ratio of $\text{KOH} : \text{S} = 1 : 1$ and yielded in 78 %, forms not an expected disulphide, but rather a monosulphide derivative (19) [37] (Scheme 13).

**Scheme 13
Схема 13**



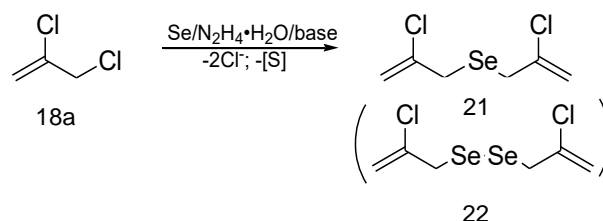
The corresponding disulphide (20) was obtained in the yield of 70 % by generating an anion disulphide in the hydrazine hydrate-monoethanolamine system [38] (Scheme 14).

**Scheme 14
Схема 14**



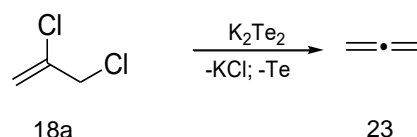
The diselenide anion obtained both in the hydrazine hydrate- KOH system and in the hydrazine hydrate-monoethanolamine system forms a monoselenide derivative (21) in a reaction with dichloride (18a) (72–70 % yield). However, in the latter case, diselenide (22) was identified with the yield of 7 % [39] (Scheme 15).

**Scheme 15
Схема 15**



No tellurium-containing products are formed by tellurium in the K_2Te or K_2Te_2 with dichloride forms (18a). The products of the reaction turned out to be propadiene (23) (78 %) and regenerated elemental tellurium [40] (Scheme 16).

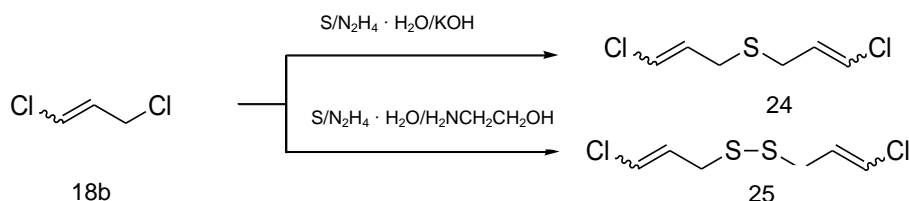
**Scheme 16
Схема 16**



The proposed reaction can serve as a convenient preparative method for producing propadiene, which is widely used in various organic synthesis processes [41].

1,3-Dichloropropene (18b) presents an isomer of dichloride (18a) with the chlorine atoms located in the 1,3-positions. Commercial product (18b) consists of *E*- and *Z*-isomers mixture with a proportion of 1.1 : 1. According to the work [42], in a reaction with (sulphur-hydrazine hydrate-base) systems, with either KOH or monoethanolamine is used as the base, dichloropropene (18b) behaves similarly to the 18a compound. In the first system, monosulphide (24) (72 % yield, a mixture of three geometric isomers) is formed during the generation of S_2^{2-} anions (Scheme 17). When monoethanolamine is used as the base (also generating anions S_2^{2-} [13]), the corresponding disulphide (25) is quantitatively isolated.

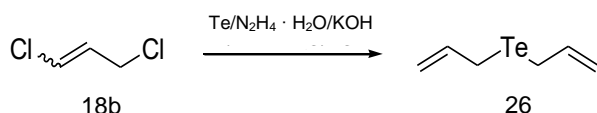
Scheme 17
Схема 17



When applying selenium, a complex mixture of products is formed in both systems with the possibility of isolating the corresponding selenide in a yield of up to 15 % [42].

The reaction of dichloropropene (18b) with tellurium in the hydrazine hydrate-KOH system appears to be completely different from the corresponding reaction of the isomer (18a) provided in Scheme 16. As a result of the interaction of dichloride (18b) with tellurium activated to K_2Te , diallyl telluride (26) was obtained with a yield of 57 % (Scheme 18) [42]. This work discusses the mechanism of reductive cleavage of the C-Cl bond with sp^2 -hybridised carbon atom.

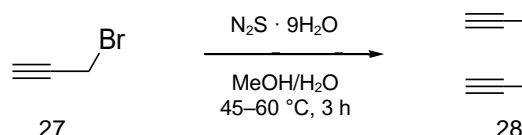
Scheme 18
Схема 18



The method of obtaining diallyltelluride (26), presented in Scheme 18, turns to be preparatively more effective than the synthesis of this compound by allyl iodide.

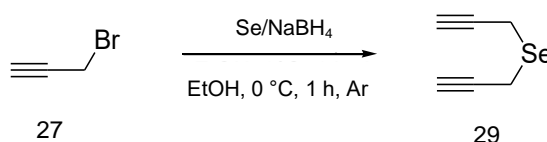
Among the halogen derivatives of propyne, propargyl bromide (27) is most often applied in laboratory practice. By applying it under the action of sodium sulphide nanohydrate, dipropargyl sulphide (28) is obtained with a yield of 48 % [43] (Scheme 19).

Scheme 19
Схема 19



Dipropargyl selenide (29) is formed with a 61–70 % yield in the reaction of two equivalents of propargyl bromide (27) with sodium selenide (Scheme 20), obtained during the reduction of selenium by $NaBH_4$ in ethanol [44].

Scheme 20
Схема 20



With the substitution of propargyl bromides, the corresponding substituted propargyl sulphide and selenide were obtained, some of which were successfully applied in the synthesis of heterocyclic compounds [45].

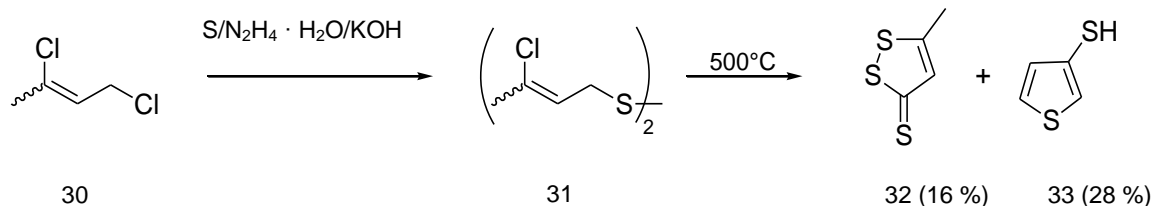
No dipropargyl telluride was obtained due to its extreme instability.

Chlorinated derivatives of butene

1,3-Dichlorobut-2-ene (30) was studied in the chalcogenisation reactions as a C_4 unsaturated halogenated hydrocarbon. Dichloride (30) presents a waste product of chloroprene production. Using the (sulphur-hydrazine hydrate-KOH) system (sulphur is activated to anions S_2^{2-}), the corresponding disulphide (31) was obtained from dichlorobutene (30) in 84 % yield and successfully used in obtaining heterocyclic compounds: 5-methyl-1,2-dithiol-3-thione (32) and 3-thiopheniol (33) (Scheme 21) [46].

So far from this example, despite the fact that the dichloride (30) is a homolog of 1,3-dichloropropene (18b), its behaviour in chalcogenisation reactions appears to be significantly different.

Scheme 21
Схема 21



CONCLUSION

The presented research data demonstrate the possibility of obtaining valuable organochalcogen

compounds using simple unsaturated halogen derivatives and elemental chalcogens with the simultaneous action of basic reduction systems. Due

to the availability of precursors, the ease of implementation of the proposed methods and the high practical significance of the obtained products, the considered methods are a powerful tool in the development of organochalcogen synthesis and the expanded scope of OCC applications. For preparative purposes, the prospects and advantages

of using basic reduction systems based on hydrazine hydrate for chalcogen activation are presented in a particularly informative form. The authors hope the presented results will attract the attention of researchers involved in the synthesis, structural study and practical application of OCC.

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Igor B. Rozentsveig, Valentina S. Nikonova, Nikolai A. Korchevin analyzed the data, summarized the material and wrote the manuscript. Igor B. Rozentsveig, Valentina S. Nikonova, Nikolai A. Korchevin have equal author's rights and bear equal responsibility for plagiarism.

Conflict of interests

The authors declare no conflict of interests regarding the publication of this article.

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