Review
Recent Advances in Design and Synthesis of Diselenafulvenes, Tetraselenafulvalenes, and Their Tellurium Analogs and Application for Materials Sciences

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Abstract: The first organic metals were obtained based on tetrathiafulvalene. The most significant advance in the field of organic metals was the discovery of superconductivity. The first organic superconductors were obtained based on tetramethyltetraselenafulvalene. These facts demonstrate great importance of tetraselenafulvalenes and their precursors, diselenafulvenes, for materials sciences. Derivatives of 1,4-diselenafulvene and 1,4,5,8-tetraselenafulvalene are useful building blocks for organic synthesis and donor units for the preparation of charge-transfer complexes and radical ion salts, the construction of organic metals, superconductors, organic Dirac materials, semiconductors, ferromagnets, and other conductive materials. This review covers the literature on the design, synthesis, and application of 1,4,5,8-tetraselenafulvalenes and 1,4-diselenafulvene and their tellurium analogs over the past 15–20 years. These two classes of compounds are interconnected, since the main part of methods for the synthesis of tetraselenafulvalenes is based on the diselenafulvene derivatives as starting compounds. Special attention is paid to the development of novel efficient synthetic approaches to these classes of compounds. Conducting properties and distinguishing features of materials based on tetraselenafulvalenes and their tellurium analogs as well as examples of materials with high conductivity are discussed.

Keywords: diselenafulvenes; tetraselenafulvalenes; ditellurafulvenes; tetratellurafulvalenes; heterocycles; materials sciences; superconductors

1. Introduction

Historically, the first organic metals based on 1,4,5,8-tetrathiafulvalene (TTF) were discovered. The preparation of a conducting TTF salt was described in 1972 [1] and the synthesis of first organic metal, a complex of TTF with tetracyanoquinodimethane (TCNQ), was reported in 1973 [2]. The TTF-TCNQ complex behaved as a metal over a large temperature range and had by far the largest maximum electrical conductivity of any organic compound known at that time [2].

The discovery of organic metals gave impetus to the development of synthetic approaches to a variety of structural modifications of TTF, which have been carefully studied in search of organic metals with high conductivity [3–5]. As the replacement of skeletal sulfur atoms of TTF by more polarizable selenium atoms has been generally recognized as an effective approach to superior electron donors with enhanced intermolecular interactions, selenium analogs of TTF, 1,4,5,8-tetraselenafulvalene (TSF), have received much attention and have been intensively studied as electron donors for the preparation of conducting materials [4–6].

The most significant advance in the field of organic metals has been the discovery of their superconductivity. The first organic superconductor was synthesized by Bechgaard et al. based on tetramethyltetraselenafulvalene (TMTSF) [6]. It was obtained in the form of single-crystal salts with a composition of 2:1, (TMTSF)$_2$PF$_6$, by electrochemical oxidation of
TMTSF in the presence of the corresponding tetraalkyl ammonium salts. Later, a number of similar salts, which exhibit superconductivity, were synthesized based on TMTSF and were named Bechgaard’s salts [6]. These historical facts demonstrate great importance of TSF derivatives and their precursors, 1,4-diselenafulvene, for materials sciences.

The Bechgaard’s salts have the general formula (TMTSF)$_2$X, where X$^-$ is a monovalent anion. The formation of the charge transfer salts includes the transfer of one electron from two TMTSF molecules to one X molecule.

Derivatives of 1,4-diselenafulvene and 1,4,5,8-tetraselenafulvalene are of great interest as important heterocyclic building blocks and scaffolds for organic synthesis. These two classes of compounds are interconnected, since the methods for the synthesis of tetraseleenafulvalenes are considerably based on diselenafulvene derivatives. The tetraseleenafulvalene derivatives serve as donor units for the preparation of charge-transfer complexes and radical ion salts, the construction of organic metals [7–11], semiconductors [12–14], superconductors [15–22], ferromagnets [23], and other conducting materials [24–32]. It should be noted that the bis(ethylenedithio)tetraseleenafulvalene (BETS) derivatives yielded more organic metals and superconductors than other TSF derivatives [20–22]. The unsymmetrical analog of BETS, bis(ethylendithio)dithiadiselenafulvalene (BEDT-STF), is also an important donor. Various new molecular conductors including organic Dirac materials and magnetic conductors have been developed based on the BETS and BEDT-STF salts [20–22,31,32].

In 2004, the journal “Chemical Reviews” published an issue devoted to the preparation and properties of organic conductors and superconductors, as well as methods for the synthesis of their molecular components, in which significant place was given to the TSF derivatives [28–30]. The tellurium analogs, 1,4-ditellurafulvene and 1,4,5,8-tetratellurafulvalene derivatives, are also of high interest, as it can be seen from a 2003 review [33], which is devoted to the synthesis and physicochemical properties of 1,4-dichalcogenafalvenes and 1,4,5,8-tetrachalcogenafalvenes.

However, since then and to the present, a number of novel synthetic approaches to 1,4-diselenafulvene and TSF derivatives have been developed and new data for material sciences have been obtained that require processing and rationalization. This article presents a review of the literature on 1,4-diselenafulvene and TSF derivatives, as well as on tellurium analogs of these compounds, mainly for the last 15–20 years.

### 2. The 1,4-Diselenafulvene and 1,4,5,8-Tetraselenafulvalene Derivatives

#### 2.1. Non-Condensed 1,4-Diselenafulvenes

1,4-Diselenafulvene 1 was obtained based on available and inexpensive industrial starting reagents, selenium and acetylene, in the KOH-HMPTA-H$_2$O system (100–140 °C, 10–15 atm). The proposed route for the formation of compound 1 includes the generation of the acetylide anion from acetylene and potassium hydroxide, its insertion reaction with selenium, followed by heterocyclization of the resulting ethyneselenolate anions (Scheme 1) [34].

![Scheme 1. Synthesis of 1,4-diselenafulvene 1 from acetylene and selenium [34].](image)

Heterocycle 1 is an important intermediate in organic synthesis as well as the starting material for preparation of 1,4,5,8-tetraselenafulvalene 2. The latter is the electron donor for the synthesis of organic metals: charge transfer complexes and radical ion salts with high electrical conductivity.
(E)-2-Benzylidene-4-phenyl-1,3-diselenole 3 is a promising product, which exhibits antioxidant, hepatoprotective, and anticonvulsant activity [35–37]. Protonation of lithium phenylalkyneselenolate 4 leads to dimerization and the formation of 1,3-diselenole 3 in 64% yield. Phenylacetylene was deprotonated with n-BuLi in THF solution at low temperature (−78 °C) in order to obtain lithium phenylalkyneselenolate 4. This lithium derivative was used in situ in the insertion reaction with elemental selenium producing compound 4 in 94% yield (Scheme 2) [38,39].

![Scheme 2](image)

Scheme 2. The preparation of (E)-2-benzylidene-4-phenyl-1,3-diselenole 3 from phenylacetylene and selenium [38,39].

Diselenole 3 was previously obtained in 94% yield by the one-pot efficient method based on the reaction of phenylacetylene with elemental selenium in the system KOH-HMPA-H₂O [40].

Selenoketones are promising intermediates for the synthesis of selenium-containing heterocycles [41–43]. The reaction of selenourea with benzoylbromoacetylene in the presence of triethylamine led to the formation of 3,5-dibenzoyl-1,4-disеленafortvene (5) in 60% yield (Scheme 3) [41].

![Scheme 3](image)

Scheme 3. The synthesis of 3,5-dibenzoyl-1,4-diselenafullene (5) by the reaction of selenourea with benzoylbromoacetylene in the presence of triethylamine [41].

Lithiation of ethyl propiolate with lithium hexamethyldisilazide in THF followed by selenium insertion reaction gives ethyl 2-(2-ethoxy-2-oxoethylidene)-1,3-diselenole-4-carboxylate in 75% yield as a mixture of E- and Z-isomers (6a,b) (Scheme 4) [44].

![Scheme 4](image)

Scheme 4. The preparation of ethyl 2-(2-ethoxy-2-oxoethylidene)-1,3-diselenole-4-carboxylate as a mixture of E- and Z-isomers (6a,b) [44].

The recrystallization of this mixture made it possible to obtain pure Z-isomer 6b suitable for X-ray diffraction analysis. Diselenoles 6a,b turned out to be interesting crystalline compounds that exhibit an unusual coordination between the oxygen atom of the oxoethylidene group and the nearest selenium atom [44]. It is interesting to note that, under the action of the daylight, the E-isomer 6a in solution was completely converted to the Z-isomer 6b (Scheme 4), presumably through a photochemically induced isomerization mechanism. This conversion did not occur in the dark [44].

The reaction of 2-methylene-1,3-dimethylimidazolidine with selenium monochloride followed by treatment with triethylamine gave 2-(1,3-dimethylimidazolidinium) diselenocarboxylate (7) in 48% yield as thermo stable crystals. This compound reacted with two equivalents of dimethyl- and diethyl acetylenedicarboxylates in dichloromethane at room temperature to afford 1:2 adducts 8a,b in 67% and 60% yields, respectively (Scheme 5) [45].
The synthesis of 4-(2-naphthyl)-2-[1-(2-naphthyl)methylidene]-1,3-diselenole 14 in 90% yield upon protonation (Scheme 7) [47,48].

Diselenafulvene 14 was also obtained by treating a dioxane solution of compound 12 with an ethanolic potassium hydroxide solution [47,48].
2.2. Condensed 1,4-Diselenafulvenes and 1,4,5,8-Dithiadiselenafulvalenes

A new method for the synthesis of 4,5-alkylene-diseleno-1,3-diselenole-2-thiones 15a,b was developed without using the highly toxic reagent carbon diselenide (CSe₂). The reaction of lithiated thione 16 with bis(selenocyanato)methane or 1,2-bis(selenocyanato)ethane was carried out at low temperature in dry THF leading to products 15a,b. The latter compounds were readily converted to the corresponding ketones 17a,b in 59% and 89% yields, respectively, by the conventional method using Hg(OAc)₂/acetic acid/chloroform (Scheme 8) [49].

\[
\begin{align*}
16 & \xrightarrow{i} 15a (34\%); 15b (21\%) & 17a (59\%); 17b (89\%)
\end{align*}
\]

\(i: \text{NCSe(CH}_2)_n\text{SeCN (n = 1 (a), n = 2 (b)) (1,2–2.0 eq.), then LDA (2.5–3.0 eq.), –78––65 °C; ii: Hg(OAc)₂, AcOH–CH}_2\text{O}_3\)

Scheme 8. The synthesis of 1,3-diselenole-2-thiones 15a,b and methylene- and ethylenediselenole derivatives 17a,b [49].

Methylene- and ethylenediselenole derivatives 17a,b are valuable precursors for the preparation of a wide range of tetraselenafulvalenes.

It was found that the cross-coupling of 4,5-ethylenedioxy-1,3-dithiol- and -1,3-diseleno-2-thione (18 and 19) with compound 20 in the presence of triethylphosphite in refluxing toluene or benzene proceeded with abnormal ring opening giving 2-(thioxomethylidene)- and 2-(selenoxomethylidene)-1,3-diselenoles (21 and 22) in 30% and 52% yields, respectively (Scheme 9) [50]. In the reaction of thione 18 with ketone 20, along with compound 21, the expected product, ethylenedioxy-1,3-diselene-1,3-dithiafulvalene (23) in 37% yield was formed, while the reaction of thione 19 with ketone 20 proceeded without the formation of the corresponding tetraselenafulvalene (Scheme 9). The proposed pathway for the formation of heterocycles 21 and 22 included the attack of triethylphosphite on the thiacarbonyl group of compounds 18 and 19, which promoted the breaking of neighboring C-S and C-Se bonds, followed by cross-coupling of the formed intermediates with ketone 20 [50].

\[
\begin{align*}
18, 19 & + 20 \xrightarrow{\text{benzene or toluene}} 21 (30\%); 22 (52\%) \\
18, 21: X = S & R = \text{CO}_2\text{Me} \\
19, 22: X = \text{Se} & R = \text{CO}_2\text{Me}
\end{align*}
\]

Scheme 9. The synthesis of compounds 21, 22, and 23 [50].

New functionalized diselenafulvene 27 was synthesized in 78% yield based on 1,3-diselenole-2-selone and zinc complex of intermediate compound, cyanoethylsulfanylstituted ethylenedioxytetrathiafulvalene 24, which was obtained by cross-coupling of 4,5-ethylenedioxy-1,3-dithiol-2-thione 18 with 4,5-bis(2-cyanoethylthio)-1,3-dithiol-2-one (25) in the presence of triethylphosphite (Scheme 10) [51].
valene (BEDT-STF)ated with diiodomethane to afford the expected product, methylene diselenadithi-}

Scheme 10. The synthesis of diselenafulvene 27, an electron donor [51].

Studies of the electrochemical properties of the compound 27 showed that it is a good electron donor, which can be used to obtain conducting materials [51].

The synthesis of dimethyl-, bis(methylthio)-, and ethylenedithio derivatives of dithiadiselenafulvalene 28a-c is outlined in Scheme 11 [52]. The first of these three-step pathways was a cross-coupling reaction between 4-methylthio-5-(2-methoxycarbonylthio)-1,3-diselenole-2-selone and 1,3-dithiole-2-chalcogenones 30a-c in the presence of trimethylphosphite. Yields of cross-coupling products 31a-c were 29%, 78%, and 73%, respectively. At the second stage, compounds 31a-c were subjected to deprotection of the 2-methoxycarbonylthio group with cesium hydroxide in a DMF solution and in situ treatment with bromochloromethane to give the corresponding 2-methylthio-3-chloromethylthio derivatives of dithiadiselenafulvalene 32a-c in 87%, 52%, and 61% yields, respectively. The ring closing reaction via transalkylation at the sulfur atom was initiated by treatment with sodium iodide to obtain derivatives 28a-c in 37%, 57%, and 66% yields, respectively. The resulting compounds were found to have good electron-donating properties. A radical cation salt with AsF$_6^-$ anion, which exhibited semiconductor properties, was obtained based on compound 28c [52].

Scheme 11. The synthetic approach to derivatives of 2,3-cyclohexylenedithio-1,4-dithia-5,8-diselenafulvalene [52].

One of the most important donors, unsymmetrical bis(ethylendithio)diselenadithiaful-

cule (BEDT-STF) 33, can be obtained by the method depicted in Scheme 12 [53]. The cross-coupling reaction of 4,5-ethylenedithio-1,3-diselenole-2-one 34 with 4,5-ethylendithio-1,3-dithiol-2-thione 30c proceeded in triethylphosphite at 110–120 °C for 30 min in a nitrogen atmosphere affording product 33 in 46% yield. The yield of product 33 was significantly lower (7%) in the case of using 4,5-ethylendithio-1,3-dithiol-2-one 35 (Scheme 12) [53].

Scheme 12. The synthesis of bis(ethylendithio)diselenadithiafulvalene 33 [53].

While most organic compounds require high pressures to exhibit Dirac-cone-type band structures, the organic charge-transfer complex (33)$_2$I$_3$ exhibits unique properties to form Dirac electron states under ambient pressure [32,53–57].
The efficient synthesis of 2,3-cyclohexylenedithio-1,4-dithia-5,8-diselanafulvalene 36 was developed based on the cross-coupling reaction of 4,5-cyclohexylenedithio-1,3-dithiole-2-thione 37 with 1,3-diselenole-2-ketone 38 (Scheme 13) [58]. The reagents were heated at 110 °C in the presence of triethylphosphite for 2 h. After cooling the mixture to room temperature, removing the solvent, and the purification by column chromatography, the target product 36 was obtained in 62% yield.

![Scheme 13](image)

Scheme 13. The efficient synthesis of 2,3-cyclohexylenedithio-1,4-dithia-5,8-diselanafulvalene 36 [58].

The product 36 revealed donor properties and was used for the preparation of a new maleonitrile dithiolate nickel complex, 36·Ni[(SCN)C=C(CN)S]2. It was found, however, that this complex had usual mixed donor-acceptor stacks and exhibited dielectric properties [58].

The synthetic approach to 5-H-(1,3-diselenole-2-ylidene)-1,3-dithia-4,6-diselenapentalene 39 is shown in Scheme 14 [59]. The cross-coupling reaction of 1,3-diselenole-2-one 39 and 4,5-bis[(2-methoxy carbonyl)ethylseleno]-1,3-dithiol-2-thione 40 gave 2,3-bis[(2-methoxycarbonyl)ethylseleno]diselenadithiafulvalene 41 in 68% yield. Then, deprotection of the methyl propionate group in compound 41 with cesium hydroxide led to the formation of diselenadithiafulvalene diselenolate dianion 42, which was realylated with diiodomethane to afford the expected product, methylene diselenadithiadiselenafulvene 39 in 75% yield (Scheme 14) [59].

![Scheme 14](image)

Scheme 14. The synthetic routes to 5-H-(1,3-diselenole-2-ylidene)-1,3-dithia-4,6-diselenapentalene 39 and 5-H-(1,3-dithiole-2-ylidene)-1,3,4,6-tetraselenapentalene 43 [59].

The preparation of 5-H-(1,3-dithiol-2-ylidene)-1,3,4,6-tetraselenapentalene 43 was carried out according to a modified procedure using 4,5-bis(methoxycarbonyl)-1,3-dithiol-2-thione 44 instead of the original 1,3-dithiol-2-thione 35 (Scheme 14) [59].

The cross-coupling of thione 44 with compound 45 gave the desired unsymmetrical intermediate product 46 in 69% yield. The formation of the selenium-containing ring was carried out in the same way as for the synthesis of compound 39. However, in this case, a mixture of the reaction products, diester 47a and monooester 47b, was formed. The latter compound was a partially deesterified product, the formation of which was probably caused by the action of cesium iodide. Precursors 47a and 47b were converted to product 43 using standard deesterification conditions (Scheme 14) [59].

The compounds 39 and 43 exhibited fairly good electron-donor properties among the selenium-modified series of methylenedithio tetrathiafulvalenes. Based on these new donors, electrorcrystallization in the presence of tetrabutylammonium salts (n-Bu4NX, X = Br, AuI2, I3) gave radical-cationic salts 1.26·(39)2Br, 1.26·(39)2I1.26, (43)2(AuI2)0.44, and (43)1.26. All the obtained salts showed metallic properties down to a temperature of 1.5 K [59].
The cross-coupling reaction of 4,5-trimethylene-1,3-dilennole-2-one 48 with 4,5-bis(2-cyanoethylthio)-1,3-dithiol-2-one 25 in the presence of trimethyl phosphite at 110 °C gave trimethylenediselenadithiafulvalene 49 in 12% yield. The diselenadithiafulvalene 49 was used in the synthesis of components of single metal complexes. Further deprotection of compound 49 and its treatment with a methanol solution of NiCl₂·6H₂O or HAuCl₄·4H₂O in the temperature range from –78 °C to room temperature led to nickel-gold complex 50a and 50b, which afforded one-component metal complexes 51a and 51b after electrocrystallization (Scheme 15) [59].

![Scheme 15](image)

Scheme 15. The synthesis of trimethylenediselenadithiafulvalene 49 and its complexes with nickel 50a,b and gold 51a,b [59].

The obtained one-component molecular conductors with diselenadithiafulvalene skeletons 51a,b showed high three-dimensional conductivity at room temperature [60,61].

The compound dimethyldiselenadithiafulvalene 52, the analog of diselenadithiafulvalene 49, was obtained by a similar way outlined in Scheme 16. The resulting nickel unsymmetrical complex 53 exhibited a strong third-order non-linear optical response in the visible and near-infrared regions of the spectrum and was regarded as a possible photoconductor [62].

![Scheme 16](image)

Scheme 16. The synthesis of nickel unsymmetrical complex 53 [62].

Bis(1,3-dithiole-2-thione-4,5-dithiolato)nickelate, Ni(dmit)₂, having the complex 53-like structure, was studied by Naito and colleagues and showed photochemical properties in the composition with N,N'-ethylene-2,2'-bipyridinium [63] and methyl viologen salts [64].

The compound 58 was obtained in 67% yield from 5,6-dibromo-4,7-diethylbenzotriselenole 55 via intermediate compound, 4,5-(o-xylylenediseleno)-3,6-diethyl-1,2-dibromobenzene (56) (Scheme 17) [65]. The latter compound, after removing the o-xyylene protecting group, was involved in the reaction with carboxyldiamidazole. The reaction of compound 58 with 4,5-bis(butylthio)-1,3-dithiol-2-thione in triethylphosphite at 120 °C for 3 h led to 3,6-diethylphthalonitride 59, containing the dithiadiselenafulvalene moiety. The dithiadiselenafulvalene tetramer-octamethylphthalocyanine 60 was obtained in 33% yield by the treatment of compound 59 with lithium alkoxide at 120 °C. The compound 60 was involved in the reaction with nickel acetate at 155 °C affording a nickel complex 61 (Scheme 17) [65].
A mixture of compounds 64 and 65 was heated in triethylphosphite at 120 °C in a nitrogen atmosphere for 2 h. The target product 62 was isolated in 75% yield (Scheme 18) [66]. This method is applicable to the synthesis of 1,3-diselenoles containing exotic substituents (such as the pyrazine ring), which are sensitive to some highly reactive reagents used in the classical Wittig reaction.

Diselenadithiafulvalene 63, condensed with the pyrazine cycle, was synthesized from pyrazino-1,3-diselenole-2-one 64 and 4,5-bis(methylthio)-1,3-dithiol-2-thione 65 (Scheme 19) [67]. A mixture of compounds 64 and 65 was heated in triethylphosphite at 120 °C in a nitrogen atmosphere for 2 h. The copper complexes CuCl2(63)2 and [Cu2Br2S(63)] were obtained by the method of vertical diffusion. The first complex exhibited the dielectric properties, whereas the second complex showed the properties of semiconductor (Scheme 19) [67].

The synthesis of 5-(1,3-diselenole-2-ylidene)-1,3,4,6-tetrahtiapentaline (66) in 28% yield by the cross-coupling reaction between 1,3-dithiol-2-one derivative 67 condensed with diselenadithiafulvalene and 4,5-bis(methylthio)-1,3-dithiol-2-thione (30b) was developed by refluxing the reagents in toluene in the presence of trimethylphosphite (Scheme 20) [68]. The radical-cationic salt (66)PF6 was studied by the voltammetric method and showed metallic properties down to 5 K.
Molecules 2022, 27, x FOR PEER REVIEW 10 of 34

was developed (Scheme 21) [69]. Compound 63 was obtained in 62% yield by cross-coupling reaction between the product 62 and benzyl propection by treatment with BF3·Et2O and BuSH. Subsequent re-protection with tert-butyldimethylsilyl group gave compound 71 in 53% yield. Finally, the target compound 68 was obtained in 62% yield by cross-coupling reaction between the product 71 and ketone 34 in triethylphosphite followed by deprotection of the tert-butylidimethylsilyl group in compound 72 (Scheme 21) [69].

Scheme 21. The efficient synthesis of dithiadiselenafulvalene derivatives 68 and 72, condensed with catechol [69].

Selenium-containing tetrathiapentalene condensed compounds with the fulvalene moiety 73a–f were synthesized by three successive cross-coupling reactions (Scheme 22) [70,71]. Iodine salts (73a)(I3)5/3 and (73b)(I3)5/3 showed high conductivity at room temperature [70], whereas salts based on arsenic fluoride (73c)(AsF6)0.32 and (73f)(AsF6)0.35 exhibited semiconductor properties [71].

Two new donor molecules of the tetrathiapentalene type, compounds 74a,b, containing two selenium atoms and six sulfur atoms in the heterocyclic skeleton, were synthesized by the cross-coupling reaction depicted in Scheme 23 [72]. This combination of the sulfur and selenium atoms in the heterocyclic scaffold results in a particular type of resistivity: flat resistivity over a wide temperature range for the PF6 and AsF6 salts of 74a,b, which showed good conductivity [72].
Selenium-containing tetrathiapentalene condensed compounds with the fulvalene moiety were synthesized by the cross-coupling reaction depicted in Scheme 23 [72]. This combination of containing two selenium atoms and six sulfur atoms in the heterocyclic skeleton, were synthesized by three successive cross-coupling reactions (Scheme 22) [73]. The intermediate compound, tetrahydrothiophen-2-one -extended donors, the products 76a,b were synthesized by the cross-coupling of 4,5-ethylenedithio-1,3-diselenole-2-one with succinic thioanhydride in the presence of triethylphosphite.

It was found that the PF₆, AsF₆, and SbF₆ salts of the product 76b exhibited metallic properties down to 2 K, while the PF₆ and AsF₆ salts of compound 76a showed semiconducting behavior.

2.3. Halogenated 1,4-Disenefulvenes and 1,4,5,8-Dithiodisenefulvalenes

Halogenated sulfur and selenium-containing fulvalenes have attracted much attention in respect to the unique crystal and electronic structures of their cation radical salts [74–76]. In contrast to the other halogenated fulvalenes, iodinated diselenafulvalenes have special ability to construct an intermolecular “iodine bond” by interaction of the iodine atom with other functional groups. The physical properties of materials such as organic conductors depend considerably on the crystal structure properties, and introduction of an “iodine bond” is one of the most effective methods of design and crystal engineering in organic conductors [74–76].

A new efficient multistep method for the synthetic preparation of 1,3-disenefole-2-thione 16 in 76% yield without the use of toxic carbon diselenide (CSe₂) was developed (Scheme 25) [74]. Dicyclopentadienyl dichlorotitanium and readily available elemental...
selenium were used as starting materials in this synthesis. The resulting diselenafulvene 16 was converted into iodo derivatives 78 and 79. In order to introduce efficiently the iodine atoms and to obtain compounds 78 and 79 in good yields (51% and 97% yields, respectively), a 17-fold excess of perfluorobutyl iodide (PFBI) and a 6-fold excess of lithium diisopropylamide were used (Scheme 25) [74]. The products 78 and 79, in turn, were regarded as valuable starting compounds for the synthesis of various tetraselenafulvene derivatives.

Scheme 25. The synthetic route to the products 78 and 79 [74].

The iodine-substituted analog of dithiadiselenafulvalene, compound 80, was synthesized in 72% yield by successive iodination of the starting 1,2-dithiol-2-thione with iodine monochloride and the cross-coupling reaction of product 81 with ketone 34 (Scheme 26) [75]. The salt (80)₄[Fe(CN)₅NO] was prepared by electocrystallization from a solution of the corresponding donor dithiadiselenafulvalene 80 in dichloromethane and bis(tetraphenylphosphonium)nitroprusside, (PPh₄)₂[Fe(CN)₅NO], which was used as an electrolyte. It is worth noting that the salt (80)₄[Fe(CN)₅NO] exhibited semiconducting properties [75].

Scheme 26. The synthesis of the product 80 [75].

New halogenated diselenadithiafulvalenes 82 and 83, containing both chlorine and iodine atoms, were synthesized in 44% and 83% yields, respectively, by the reaction sequence shown in Scheme 27 [76]. Intermediate compound 84 was obtained by successive lithiation by lithium diisopropylamide, chlorination with hexachloroethane, and iodination of the lithium derivative of 1,2-dithiol-2-thione with iodine monochloride. Compound 84 was converted to ketone 85 using the Hg(OAc)₂-CHCl₃-AcOH system. Intermediate compounds 84 and 85 were further involved in the cross-coupling reactions with the corresponding ketone 34 and thione 86. Studies of the properties of compounds 82 and 83 showed that the chlorine atom mainly contributes to the electronic properties within one molecule, and the iodine atom to intermolecular interaction through the iodine bond. Appropriate application of the different roles of halogen atoms can be useful for the development of new supermolecular organic conductors based on these compounds (Scheme 27) [76].
The cross-coupling reaction of 4,5-dibromo-1,3-dithiol-2-thione 87 with 4,5-ethylenedithio-1,3-diselenene 34 afforded 4,5-dibromo-4',5'-ethylenedithiodiselenadithiafulvalene 88 in 80% yield (Scheme 28) [77]. Compound 88 exhibited electron-donating properties. A charge-transfer complex of compound 88 with tetracyanoquinodimethane, (88)2[TCNQ], was obtained by slow evaporation of dichloromethane from a solution of these compounds [77].

The authors noted that bromo derivatives of selenafulvalenes were more available compounds compared to the analogous iodo derivatives. However, the bromo derivatives also display donor abilities and can be used for the preparation of charge-transfer complexes [77].

2.4. Non-Condensed 1,4,5,8-Tetraselenafulvalenes

Convenient and practical synthetic procedures for the preparation of diselenafulvene 1 and tetraselenafulvalene 2 based on selenium and sodium acetylide were developed (Scheme 29) [78]. This approach has the advantage of using cheap, non-toxic selenium powder as the selenium source and commercially available sodium acetylide in xylene light mineral oil.

The authors emphasized that only two steps were required for the synthesis of the target compound by this method, which was suitable for laboratory-scale preparation, about 7 g of diselenafulvene 1 and more than 2 g of fulvalene 2 can be obtained by these two experiments under laboratory conditions [78]. The authors also noted that in combination with previously developed methods (the functionalization of tetraselenafulvalene 2 as protected thiolate or selenolate moieties followed by their deprotection/realkylation chemistry), the present approach paved a practical way to various heterocycle-fused tetrase-
lenafulvalene type donors, which can be used to produce superconducting radical cation salts (Scheme 29) [78].

Electrochemical oxidation of tetraselenafulvalene 2 in the presence of potassium nitroprusside $K_2[Fe(ONO)_2(CN)_5] \cdot 2H_2O$ and 18-crown-6 using nitrobenzene as a solvent gave a new single-crystal radical cationic salt $(2)_{7}[Fe(NO)(CN)]_2$, which showed the properties of a conductor at room temperature and 130 K [79].

Efficient syntheses of tetramethyltetraselenafulvalene (89) were developed in the last century [4–6]. An interesting method for the preparation of tetramethyltetraselenafulvalene, doubly labeled with $^{13}$C isotope at the positions 2 and 2′ (4,4′,5,5′-tetramethyl $\Delta^{2,2}$-bis-1,3-diselenole $89^*$) was described (Scheme 30) [80]. Labeled with $^{13}$C isotope carbon diselenide was obtained from $^{13}$C-dichloromethane at 580–600 °C. The $^{13}$C-carbon diselenide, after cooling to room temperature and dissolving in pentane, was reacted with piperidine at 0 °C leading to piperidinium 1-piperidino $^{13}$C-diselenocarbamate $90^*$ in 33% yield.

The single-site $^{13}$C-enriched tetramethyltetraselenafulvalene was synthesized by the classical method: the cross-coupling reaction in the presence of triethylphosphite (Scheme 30) [80].

The reaction of cyclooctyne with carbon diselenide in the presence of red selenium and 18-crown-6 using nitrobenzene as a solvent gave a new single-crystal radical cationic salt $(2)_{7}[Fe(NO)(CN)]_2$, which showed the properties of a conductor at room temperature and 130 K [79].

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The reaction of compound $90^*$ with 3-chloro-2-butanone in DMF for 1 h at room temperature gave 1-piperidino $^{13}$C-carbodiselenoic acid, 1-methyl-2-oxopropyl ester $91^*$ in quantitative yield (Scheme 30) [80]. Diselenocarbamate $91^*$ was successively treated with concentrated $H_2SO_4$ and 60% aqueous HPF$_6$ at 0 °C to form 2-(1-piperidino)-2-($^{13}$C)-4,5-dimethyl-1,3-diselenole hexafluorophosphate $92^*$ in 86% yield. Labeled with $^{13}$C isotope 4,5-dimethyl-1,3-diselenolene-2-selone $93^*$ was prepared in 53% yield by the reaction of compound $92^*$ with hydrogen selenide in ethanol. The target product $89^*$ in 61% yield was obtained by the classical method: the cross-coupling reaction in the presence of triethylphosphite (Scheme 30) [80].

The single-site $^{13}$C-enriched tetramethyltetraselenafulvalene was obtained starting from 4,5-dimethyl-1,3-diselenolene-2-one [81]. Correlation between non-Fermi-liquid behavior and antiferromagnetic fluctuations in superconducting (TMTSF)$_2$PF$_6$ salt was studied using $^{13}$C-NMR spectroscopy [81].

A series of tetraselenafulvalene compounds $95$ ($n = 1–15$) was synthesized in up to 84% yield by a one-step reaction of dialkyl disulfides $94$ with tetralithiated tetraselenafulvalene $2$ (Scheme 31) [82]. Compounds $95$ were found to be weak electron-donating molecules and to show low dark conductivity. At the same time, as the number of methylene groups increased, the electrical conductivity increased due to the presence of high-dimensional conduction paths. The resulting compounds were highly soluble in organic solvents [82].

\[
\begin{align*}
\text{Scheme 30. The synthetic route to 4,4′,5,5′-tetramethyl } & \Delta^{2,2}\text{-bis-1,3-diselenole } 89^*, \text{ doubly labeled with } ^{13}\text{C isotope [80].} \\
\text{Scheme 31. The synthesis of tetraselenafulvalene compounds } & \text{95} \text{ (n = 1–15) from TSF and dialkyl disulfides 94 [82].}
\end{align*}
\]
The authors noted that the compounds 95 were good candidates for the field-effect transistor channel based on the advantageous features: low dark conductivity, low donor ability, on-site Coulomb repulsion energy, high-dimensional $\pi$-electron structure, and high solubility in organic solvents [82].

The use of one equivalent of phenylselenadiazole 96 and three equivalents of selenadiazole 97 in the reaction in a mixture of THF and tert-butanol at $0 \degree C$ in the presence of sodium hydride led to diselenafulvene 98 in 46% yield. The latter compound was successfully formulated with the formation of compounds 99 and 100 by the Vilsmeier-Haack reaction (Scheme 32) [83].

![Scheme 32. The synthesis of compounds 99–101 [83].](image)

The products 99 and 100, bearing the aldehyde group, can serve as precursors of the vinylogs of tetraselenafulvalene derivatives. The iodine-morpholine reagent was used to convert fulvene 98 to diphenyltetraselenafulvalene 101 (a mixture of $E$- and $Z$-isomers) in 28% yield (Scheme 32) [83].

### 2.5. Condensed 1,4,5,8-Tetraselenafulvalenes

The reaction of cyclooctyne with carbon diselenide in the presence of red selenium in boiling dichloromethane afforded cycloocteno[1,2-$d$]1,3-diselenole-2-selone 102 (59% yield), which was converted into tetraselenafulvalene 103 in 94% yield by the treatment with trimethylphosphite in boiling benzene (Scheme 33) [84]. The formation of selone 102 can be rationalized by addition of carbon diselenide to cyclooctyne to form 1,3-diselenole-2-yldene 104, which then reacts with elemental selenium or can capture selenium atom from the carbon diselenide molecule yielding compound 102 (Scheme 33) [84]. This reaction successfully competed with the carbene dimerization with the formation of tetraselenafulvalene 103 if the process was carried out in the absence of elemental red selenium.

![Scheme 33. The synthesis of tetraselenafulvalene 103 [84].](image)

The convenient synthesis of bis(ethylenedioxy)tetraselenafulvalene 105 without the use of toxic reagents such as carbon diselenide and hydrogen selenide was developed (Scheme 34) [85]. The key intermediate 106 was synthesized by the reaction between lithium selenolate 107 and $N,N$-dimethylselencarbamoyl chloride 108 in THF at $0 \degree C$ under argon. Both compounds 107 and 108 can be prepared based on elemental selenium powder. Diselencarbamate 106 was quantitatively converted to iminium salt 109, which was used to prepare selone 110 in the NaSeH-AcOH system. The synthesis of the target tetraselenafulvalene 105 (30% yield) was carried out by a coupling reaction under very mild conditions in benzene using hexamethylphosphorous triamid (HMPA) at room tem-
perature under argon (Scheme 34) [85]. The new donor compound 105 exhibited sufficient solubility in common organic solvents and the ability to form CH...O hydrogen bonds. Its electrochemical properties were found to be promising for obtaining new organic metals, including superconductors [85].

![Scheme 34](image)

**Scheme 34.** The convenient synthetic approach to bis(ethylenedioxy)tetraselenafulvalene 105 [85].

A condensed derivative of tetraselenafulvalene, ethylenothio-1,4,5,8-tetraselenafulvalene 111, was synthesized as a new promising electron donor (Scheme 35) [86]. The key intermediate was the 1,3-diseleneno-2-selone derivative 112, easily prepared from commercially available tetrahydroprynyl-protected 3-butyn-1-ol. Using a conventional cross-coupling reaction with 1,3-diseleneno-2-selone, the desired product 113 was obtained in 37% yield. Then, the tetrahydroprynyl-protecting group of compound 113 was removed by treatment with dilute hydrochloric acid, and the resulting alcohol 114 (71% yield) was converted into tosyolate 115 in 95% yield.

![Scheme 35](image)

**Scheme 35.** The synthetic route to ethylenothio-1,4,5,8-tetraselenafulvalene 111 [86].

The formation of the dihydrothiophene ring was achieved by a transalkylation reaction at the sulfur atom in the presence of sodium iodide in DMF, which resulted in the desired ethylenethiotetraselenafulvalene 111 in 81% yield (Scheme 35) [86]. The use of electrosolubility in common organic solvents and the ability to form CH...O hydrogen bonds. Its electrochemical properties were found to be promising for obtaining new organic metals, including superconductors [85].

![Scheme 36](image)

**Scheme 36.** The synthetic approach to bis(ethylenothio)-1,4,5,8-tetraselenafulvalene 116 [87].

A three-stage synthesis of new donors, dimethyl and bis(methylthio) derivatives of methylenedithiotetraselenafulvalene 117a,b, was developed (Scheme 37) [52]. Cross-coupling reactions between 1,3-diseleneno-2-selones 118a,b and 4-methylthio-5-(2-methoxy carbonylthio)-1,3-diseleneno-2-selone 29a in the presence of trimethylphosphite gave intermediate products 119a,b...
in 42% and 35% yields, respectively. Removing the protective 2-methoxycarbonylthiophenylthio group in compounds 119a, b with cesium hydroxide in DMF solution and in situ treatment with bromochloromethane led to the corresponding 2-methylthio-3-chloromethylthio derivatives of tetralselenafulvalene 120a, b in 85% and 57% yields, respectively. The transalkylation at the sulfur with the ring-closure reaction were carried out by treatment with sodium iodide to give derivatives 117a, b in 47% and 62% yields, respectively (Scheme 37) [52].

![Scheme 37. The preparation of derivatives 117a, b [52].](image)

The obtained compounds showed good electron-donating properties. Based on compound 117a, three radical cation salts were obtained. Salts with I\₂Br\⁻ and AsF\₆\⁻ anions exhibited semiconducting properties, while the PF\₆\⁻ salt displayed metallic conductivity down to 130 K [52].

A general synthetic approach to a series of alkylenedithio- (121a–c, 65%, 75%, and 66% yields, respectively) and bis(alkylenedithio)tetralselenafulvalenes 122a–c (50%, 52%, and 61% yields, respectively) was developed (Scheme 38) [88]. Key intermediate compounds 123 and 124 were readily prepared by phosphite-activated reactions of 4-methylthio-5-(2-methoxycarbonylthiophenylthio)-1,3-selenole-2-selone 29a. The latter compound was obtained in 88% yield from a fairly stable, readily available, and cheap reagent, 1,2-dichloro-1-methylthioethane, by treating it with butyl lithium in situ to form lithium 2-methylthioacetylide, followed by the reaction of the acetylide with selenium, methyl-3-thiocyanatopropionate and carbon diselenide (Scheme 38) [88].

![Scheme 38. The synthesis of tetralselenafulvalene derivatives 121a–c and 122a–c [88].](image)

The obtained compounds were found to be excellent electron donors for the preparation of organic conductors [88]. Benzoquinone-fused ethylenedithiotetraselenafulvalene 125 was synthesized by the reaction sequence depicted in Scheme 39 [89]. The key intermediate compound 128 was obtained in 73% yield by a four-step synthesis from catechol: protection of two hydroxyl groups with tert-butylidiphenylsilyl groups, diiodination, the Stille cross-coupling reaction with Bu\_3SnSe(CH\_2)\_2CN followed by treatment with NaH and Bu\_3SnCl\_2. In the presence of AlMe\_3, the reaction of compound 128 with methyl ester 129 obtained from ketone 34 and subsequent deprotection of hydroxyl groups gave catechol-condensed tetralselenofulvalene 130 in 52% yield. Electrochemical oxidation of compound 130 in the presence of 2,2′-bipyridine afforded ortho-benzoquinone-fused ethylenedithiotetraselenafulvalene 125 in quantitative yield (Scheme 39) [89].
Nitrilotophenyl benzaldehyde 131 with sodium nitrate in concentrated sulfuric acid giving 4-bromo-3-nitrobenzaldehyde and reduction of the nitro group by subsequent Sandmeyer reaction made it possible to obtain 3,4-dibromobenzaldehyde 132 in 73% yield (Scheme 40) [90]. The aldehyde 132 was quantitatively converted to 2-(3,4-dibromophenyl)-1,3-dioxolane 133 to protect the formyl group in further reactions. Poly(diselenide) 134 was prepared by the reaction between dibromo compound 133 and sodium diselenide in DMF. The reduction of polymer 134 with sodium tetrahydroborate followed by treatment with thiophosgene made it possible to obtain the key 5-(1,3-dioxolan-2-yl)-benzo-1,3-diselenole-2-thione 135. The cross-coupling reaction between thione 135 and 4,5-(ethylenedithio)-1,3-diselenole-2-one 34 in triethylphosphite led to tetraselenafulvaleneacetal derivative 136, which was hydrolyzed to produce formyl derivative 137. The latter compound was involved in the reaction with 2,3-dimethyl-2,3-bis(hydroxyamino)butane in the presence of its sulfuric acid salt as a catalyst giving cyclic bis(hydroxylamine) 138 in 86% yield as a radical precursor. Compound 138 was converted by oxidation with lead dioxide into a new organic spin-polarized donor 139 in 79% yield, which exhibited ferromagnetic properties (Scheme 40) [90].

New tetraselenafulvalenes derivatives find application in the synthesis of organic spin-polarized donors [90].

The efficient approach to new fused heterocycles, bis(propylenethio)tetraselenafulvalene 140a (60% yield) and bis(propyleneseleleno)tetraselenafulvalene 140b (30% yield) based on tetrahydropyran-protected pent-4-yn-1-ol as the starting compound is outlined in Scheme 41 [91,92].
Scheme 41. The efficient approach to new fused heterocycles 140a and 140b [91,92].

Various types of highly conductive radical-cationic salts were prepared based on tetraselenafulvalenes 140a,b. For example, the PF$_6^-$, AsF$_6^-$, and FeCl$_4^-$ salts retained metallic properties down to the liquid helium temperature [91,92].

Tetraselenafulvalene derivative 141 was obtained in 56% yield using tetrahydropropargyl-protected acetylene containing a thioethyl fragment as the starting compound by the approach illustrated in Scheme 42 [92,93].

Scheme 42. Synthesis of tetraselenafulvalene derivative 141 from tetrahydropropargyl-protected acetylene [92,93].

The efficient and practical synthetic method for the preparation of condensed electron donors of the tetraselenafulvalene type 144a,b and 145a,b in up to 94% yield was developed by the approach depicted in Scheme 43 using tetrabutylammonium [94].

Scheme 43. The efficient and practical synthetic method for the preparation of condensed electron donors of the tetraselenafulvalene type 144a,b and 145a,b [94].

The obtained compounds 144a,b and 145a,b served as efficient electron donors for preparation of organic conducting materials [94].

A new very interesting donor compound, 2-(1,3-diselenole-2-ylidene)-5-(1,3-dithiol-2-ylidene)-1,3-diselena-4,6-dithiapentalene 146, containing tetrathiafulvalene structure condensed with the tetraselenafulvalene scaffold, was synthesized in 49% yield (Scheme 44) [95]. The TSF derivative 147 was sequentially treated with CsOH·H$_2$O, with ZnCl$_2$, n-Bu$_4$NBr, and then with triphosgene to obtain compound 148 (40% yield). The cross-coupling reaction between 148 and 4,5-bis(methoxy-carbonyl)-1,3-dithiol-2-thione (149, two equivalents) in the presence of trimethyl phosphate at reflux in toluene gave bis(methoxy-carbonyl) derivative 150a in 79% yield. The product 146 was obtained in 49% yield by demethoxy-carbonylation of compound 150a with excess LiBr·H$_2$O in hexamethylphosphorous triamide.
The radical cationic salt (146)ReO₄ exhibited low conductivity with a high activation energy.

![Scheme 44. Synthesis of compound 146, containing tetrathiafulvalene structure condensed with the tetracenefulvalene scaffold [95].](image)

A number of derivatives of bis-condensed donors 150a–d and 151, as well as their vinyl analogs 152a,b and 153a, were synthesized in 32–73% yields using corresponding intermediate zincates (Scheme 45) [96].

![Scheme 45. The synthesis of donor compounds 150a–d, 151, 152a,b and 153a [96].](image)

The donor compounds 150a, 152a, and 153a form highly conductive complexes with tetracyanoquinodimethane (TCNQ) and salts with I₃ with very low activation energies of 0.0094–0.040 eV (Scheme 45) [96].

### 2.6. Other 1,4-Selenafulvene and 1,4,5,8-Selenafulvalene Derivatives

The intermediate 2-(1,1-diformylmethylene)-1,3-diselenole 154 was obtained in 70% yield from 2-methylene-1,3-diselenole 1 by the Vilsmeyer–Haack reaction (Scheme 46) [97]. The dialdehyde 154 was further condensed with dithiolium phosphonium bromides and dithiolium phosphonates in the presence of a base. As a result, a number of polycyclic selenium-containing tetrathiafulvalene vinylogues of the dendralene type 155a–c, 156a–d, 157, and 158 bearing a 1,3-diselenole moiety were obtained in good yields by the Wittig and Wittig–Horner reactions (Scheme 46) [97]. The obtained products showed electrochemical activity.

![Scheme 46. Synthesis of bicyclic and polycyclic compounds 155a–c, 156a–d, 157, and 158 including vinylogues of the dendralene type [97].](image)
The selenoketenones 160 were obtained by deprotonation of aromatic diynes 159 with n-BuLi, subsequent addition of elemental selenium at 0 °C, and reaction with water in the temperature range from −55 °C to room temperature for 3 h (Scheme 47) [98]. The resulting intermediates 160 in situ were subjected to cycloaddition polymerization to produce electron-donating π-conjugated polymers 161a–c with a 1,4-diselenafulvene moiety in 95%, 85%, and 68% yields, respectively.

![Scheme 47. Synthesis of electron-donating π-conjugated polymers 161a–c [98].](https://example.com/scheme47.png)

The solubility of the polymers depends on their structure. The attachment of long alkyl chains enhances solubility in non-polar solvents. The resulting polymers exhibited electron-donating properties, as did their soluble charge-transfer complexes with tetracyanoquinodimethane [98].

Two-bridged tetraseleunalfulvenophanes 163a,b were efficiently synthesized from trimethylsilylacetylene by the synthetic approach presented in Scheme 48 [99]. Using sequential deprotection and realkylation of the bis-thiolate tetraseleunalfulvalene building block 162 (51% yield), two-bridged tetraseleunalfulvenophanes 163a,b were efficiently synthesized in 25% and 20% yields, respectively (Scheme 48) [99]. The radical cationic salt 163b with the Au(CN)₂⁻ anion exhibited very high conductivity at room temperature.

![Scheme 48. The synthetic approach to two-bridged tetraseleunalfulvenophanes 163a,b from trimethylsilylacetylene [99].](https://example.com/scheme48.png)

The synthesis of 4,5-dicarbomemethoxy-1,3-diselenole-2-thione 165 in 43% yield was developed from the intermediate titanocene pentaseleunide 164 and elemental selenium, avoiding the use of highly toxic carbon diselenide (Scheme 49) [100].

![Scheme 49. The synthetic route to triselenathiafulvalene 167 [100].](https://example.com/scheme49.png)

The cross-coupling of two half-blocks of compound 165 in the presence of triethylphosphite led to the unsymmetrical derivative tetracarbomethoxytriselenathiafulvalene derivative 166 in 40% yield. As a result of the sulfur-selenium “scrambling” in the presence of the
electron-withdrawing group in the positions 4 and 5 of the diselenole ring, a mixed thiase-
lenafulvene core was generated. Unsubstituted triselenatiafulvalene 167 was obtained in
37% yield by decarbomethoxylation of compound 166 (Scheme 49) [100].

The charge transfer complex of triselenatiafulvalene 167 with tetracyanoquinodimeth-
ane showed a high degree of anisotropic conductivity in the polycrystalline sample, which
decreased with increasing temperature [100].

3. The Synthesis of 1,4-Ditellurafulvene and 1,4,5,8-Tetratellurafulvalene Derivatives

The efficient synthetic approaches to 1,4-ditellurafulvenes and 1,4,5,8-tetratellurafulval-
enes are less developed than to the corresponding selenium derivatives and a number of
the obtained derivatives of these two classes of organotellurium compounds is significantly
smaller than that of known 1,4-diselenafulvenes and 1,4,5,8-tetraselenafulvalenes.

The cross-coupling reaction of 1,3-selenatellurole-2-selone 168 and trimethylsilyl
derivative of 1,3-diselenole-2-selone 169 gave triselenatellurafulvalene with trimethylsi-
lyl group 170, which was separated by gel permeation chromatography in 11% yield
(Scheme 50) [101]. The trimethylsilyl group was then easily removed by the desilylation re-
action with potassium fluoride in an aqueous THF solution giving triselenatellurafulvalene
171 in 86% yield. The complex of the product 171 with tetracyanoquinodimethane showed
high conductivity at room temperature and retained metallic properties at 85 K [101].

\[
\text{Scheme 50. The convenient synthesis of triselenatellurafulvalenes 170 and 171 based on trimethylsi-
lylacetylene [101].}
\]

The thermal reaction between phenyliodoacetylene and powdered tellurium gave a
mixture of \((E)-1,4\text{-ditellurafulvene derivative 172 and its iodinated isomer (Z)-1,1\text{-diiodo}-
1,4\text{-ditellurafulvene 173 by refluxing the reaction mixture in toluene for 6 h. After the chro-
nomographic separation of these two isomers, (Z)-1,1\text{-diiodo}-1,4\text{-ditellurafulvene 173 was
reduced by aqueous solution of sodium thiosulfate to corresponding (Z)-ditellurafulvalene
173 with the retention of stereoconfiguration (Scheme 51) [102].}

\[
\text{Scheme 51. The synthesis of 1,4-ditellurafulvene derivative 172, 173, and 174 from phenyliodoacety-
lene and tellurium [102].}
\]

Reduction of poly(o-phenylene ditelluride) 175 with the hydrazine hydrate/sodium
hydroxide system in DMF led to generated disodium o-benzenditellurolate 176, which re-
acted with benzylidene chloride or dibromomethane to give 2-phenylbenzo-1,3-ditellurol
177 or benzo-1,3-ditellurol 178 in 32% and 58% yields, respectively (Scheme 52) [103].
The carbonylation of compound 179 with methyl iodide. The reaction of 2-lithiobenzo-1,3-ditellurole 180 in THF was added to this suspension (Scheme 54) [105]. A solution of lithium dicyclohexylamide in THF, 2-methylbenzo-1,3-ditellurole (180) and benzo-l,3-ditellurole-2-carboxylic acid 181 [103].

In contrast to benzo-1,3-dithiole and its 2-substituted derivatives, which can be lithiated with butyllithium, the C-Te bond in benzo-1,3-ditellurole 178, as well as in its noncyclic analogs, diorganyl tellurides, R₂Te, is cleaved by butyllithium. As a result of the reaction of heterocycle 178 with n-BuLi, even at low temperatures, a complex mixture of various diorganyl tellurides is formed [103].

Although 2-lithiobenzo-1,3-ditellurole 179 was generated in rather low yield by treating a solution of heterocycle 178 with lithium dicyclohexylamide in THF, 2-methylbenzo-1,3-ditellurole (180) was obtained in 38% yield by the reaction of 2-lithiobenzo-1,3-ditellurole 179 with methyl iodide. The carbonylation of compound 179 with carbon dioxide gave benzo-l,3-ditellurole-2-carboxylic acid 181 in 27% yield (Scheme 52) [103].

The successful synthesis of dendralenic ditellurole-containing compounds including dendralenes was developed based on trimethylsilylacetylene and elemental tellurium (Scheme 53) [104]. Trimethylsilylacetylene was lithiated with butyllithium and lithium trimethylsilylacetylide reacted with tellurium to give tellurolate, which was protonated leading to unstable intermediate 182. Crude compound 182 was subjected to the Vilsmeier-Haack reaction to afford stable desired dialdehyde 183. The latter compound was condensed with malononitrile and carbomethoxymethyl phosphorane to give products 184 and 185 in 45% and 70% yields, respectively. Dialdehyde 183 was efficiently reacted with 4,5-dicarbomethoxy-1,3-dithiole phosphorane in the presence of sodium hydride to produce dendrale 186 in 63% yield. In like fashion, phosphonates 187 and 188 afforded dendralenes 189 and 190 in 38% and 43% yields, respectively, upon condensation with dialdehyde 183 in the presence of a base (Scheme 53) [104].

A systematic study of the synthesis of the π-donor tetratelluralfulvalene 191 made it possible to increase the yield of the purified fulvalene product from about 12% to quite reproducible values reaching 26% (if tetrabromoethene is used at the final stage of cyclization). The optimized procedure for the synthesis of tetratelluralfulvalene 191 is as follows (Scheme 54) [105]. A solution of n-BuLi in hexane was added to a suspension of distannan 192, tellurium, and LiCl in THF cooled to −78 °C over 30 min in an argon atmosphere. After additional stirring for 45 min, tetrabromoethene in THF was added to this suspension containing ditellurolate 193 over 1 h followed by stirring at −78 °C for 2 h. The crude product, after isolation from the reaction mixture, was purified by column chromatography on silica gel under argon giving tetratelluralfulvalene 191 in 26% yield (Scheme 54) [105].
In contrast to benzo-1,3-dithiole and its 2-substituted analogs, 1,4-di- 
selefulvene derivatives serve as main building blocks for the con- 
struction of 1,4,5,8-tetraselenafulvalenes, which find augmenting appli- 
cation in the preparation of materials with varying degrees of conductivity and various properties.

This method of synthesis makes it possible to reliably obtain useful amounts of compound 191 and allowed to 
contribute to the development of studying the radical cation complexes and charge-transfer salts based on tetratellurafulvalene and to investigate its potential as a building block for the preparation of functionalized electron donor compounds [105].

4. Application of 1,4,5,8-Tetraselenafulvalene Derivatives and Their Tellurium Analogs for Materials Sciences

As shown by the literature data, 1,4-diselenafulvene derivatives serve as main building blocks for the con- 
struction of 1,4,5,8-tetraselenafulvalenes, which find augmenting application in the preparation of materials with varying degrees of conductivity and various properties.

The well-known and frequently used tetraselenafulvalene \( \pi \)-donors molecules are bis(ethylenedithio)diselenadithiafulvalene 33, tetramethyltetraselenafulvalene 89, bis(ethyl enedithio)tetraselenafulvalene 122b, and dimethyl(ethylenedioxy)tetraselenafulvalene 194 (Scheme 55).

Compound 33 (BEDT-STF) is a very important unsymmetrical donor that was used to obtain the organic charge-transfer complex (33)\(_2\)I\(_3\) exhibiting unique properties to form Dirac electron states under ambient pressure [20–22,31,32,53–57].
Recently, much attention has been paid to Dirac electronic systems. However, most of these studies are theoretical (e.g., quantum chemical calculations by DFT methods) due to the limited availability of the relevant materials. The Dirac electron systems (DES) are characterized by massless electrons with relativistic behavior and high speed (1/100–1/1000th of the velocity of light). Previously, similar relativistic behavior of electrons was observed in graphene. In fact, DES were initially found in graphene and some inorganic compounds [22,55]. It should be noted that organic DES exhibit important advantages over their inorganic counterparts. For example, in contrast to inorganic DES, most organic DES are characterized by a clearly defined crystal structure and chemical stoichiometry. However, the majority of organic DES shows the properties of Dirac electron states only under high pressure. In contrast to this observation, the organic charge-transfer complex \((33)_2\) exhibits unique properties to form Dirac electron states under ambient pressure [32, 53–57]. Based on studies of the electrical, magnetic, optical, and structural properties of \((33)_2\) under ambient pressure, it was established that this salt possesses a band structure characterized with Dirac cones, which was in good agreement with the quantum chemical calculations [20–22,31,32,53–57]. In fact, this salt is a unique object for research, which can provide an important insight into the properties of the Dirac electrons by measurements of various physical properties under ambient pressure.

New conductors \((89)_2[3,3'-Co(1,2-C_2B_3H_11)_2]\) and \((89)_2[3,3'-Fe(1,2-C_2B_3H_11)_2]\) were synthesized based on tetramethyltetraselenafulvalene \(89\) by anodic oxidation under galvanic conditions in the presence of \(\text{Na}[3,3'-\text{Co}(1,2-C_2B_3H_11)_2]\) and \((\text{Me}_3\text{NH})[3,3'-\text{Fe}(1,2-C_2B_3H_11)_2]\) [106,107].

Semiconductors \((89)_3[\text{Re}_2\text{Cl}_8]_2\text{CH}_3\text{CN}\) and \((89)_3[\text{Re}_2\text{Cl}_8]_2\cdot 6\text{CH}_2\text{Cl}_2\) were obtained by electrochemical oxidation at room temperature in the presence of \((n-\text{Bu}_4\text{N})_2[\text{Re}_2\text{Cl}_8]\) in acetonitrile or dichloromethane [108], also known are superconductors such as \((89)_3\text{PF}_6\) and \((89)_2\text{ClO}_4\) [109–111] and the organic charge-transfer complex \((89)\text{TCNQ}\), which is an intrinsic semiconductor [112,113].

The compound \(89\) and triftluormethyltetrayanotriquinodimethane \((\text{CF}_3\text{TCNQ})\) form two types of charge transfer complexes, \((89)_2(\text{CF}_3\text{TCNQ})\) and \((89)(\text{CF}_3\text{TCNQ})(\text{PhCl})_{1/2}\) (from chlorobenzene solution). The first one is semiconductor and the second is a strong donor, i.e., it exhibited metallic properties [114].

Tetramethyltetraselenafulvalene \(89\) forms radical cationic salts with weakly coordinating anions such as tetrakis(3,5-trifluoromethylphenyl)borate \((\text{BArF})\), dodecamethylcarbocarane \((\text{Me}_{12}\text{CAR})\), and hexabromocarocene \((\text{Br}_6\text{CAR})\), which showed a high tendency to \(\pi\)-dimerization. The radical cationic salt \((89)(\text{Me}_{12}\text{CAR})\) was obtained by mixing a solution of dodecamethylcarbocarane in pentane and a solution of selenafulvalene \(89\) in dichloromethane in a 1:1 molar ratio. Radical-cationic salts \((89)(\text{BArF}), (89)(\text{BArF})(\text{CH}_2\text{Cl}_2)_{1/2}\) and \((89)(\text{Br}_6\text{CAR})\) were obtained by mixing a solution of selenafulvalene \(89\) in dichloromethane with tris(p-bromophenyl)aminium cation-radical of tetrakis(3,5-trifluoromethylphenyl)borate or hexabromocarobane taken as salts. The obtained radical-cationic salts are promising for the use in molecular rotors and switches, in which molecular motion is associated with \(\pi\)-bonding between opposite parts and depends on the strength of such interactions [115].

The compound \(89\) is also used in multisensor matrices for the detection of analytes in the gas or liquid phase, which includes, along with tetraselenafulvalene \(89\), tetrahalogenated tetraselenafulvalene and other tetrachalcogenoalkalvaline derivatives that can individually change their physicochemical properties when exposed to analytes or to mixtures of analytes, and these changes can be detected by a sensor or by a set of sensors [116].

Based on bis(ethylenedithio)tetraselenafulvalene \(122b\) and \((\text{AsPh}_4)_2(\text{Cu}_2\text{Cl}_6)\), the \(\kappa-(122b)\) and \(\theta-(122b)\) salts were obtained by diffusion electrolysis of solutions in a mixture of chlorobenzene-ethanol solvents. The obtained salts \(\kappa-(122b)\) and \(\theta-(122b)\) exhibited metal-like behavior down to 40 K and 4 K, respectively, and the salt \(122b\) (CuCl) salt showed dielectric properties [117].

The \((122b)_3[\text{Cu}_2(\text{C}_2\text{O}_4)_3](\text{CH}_3\text{OH})\) salt, which was obtained by electrochemical oxidation of neutral bis(ethylenedithio)tetraselenafulvalene \(122b\) in the presence of
[(C₂H₅)₃NH]Cu₂(C₂O₄)₂ in a solution of a mixture of solvents chlorobenzene-methanol, demonstrated antiferromagnetic properties [118].

The lead-containing salts, (122b)₂PbBr₃ and (122b)₂Pb₂Br₅, exhibited metallic resistivity at low temperature [119]. These salts were prepared by electrochemical galvanostatic oxidation of bis(ethylenedithio)tetratellurafulvalene 122b in the presence of Bu₄NPbBr₃ or [Bu₄NPbBr₃ + Bu₄NB].

Electrocrystallization of compound 122b gave θ-(122b)₂[Fe(CN)₅NO], (122b)₂[RuBr₅NO] and (122b)₂[RuCl₃NO] salts using the nitroprusside anion or its corresponding ruthenium halides ([Fe(CN)₅X]²⁻ or [RuX₅NO]²⁻, where X = Cl or Br) and auxiliary electrolytes as a mixture of solvents (1,1,2-trichloroethylene/ethanol (10 vol%), nitrobenzene/1,2-dichloroethylene (40 vol%)/ethanol (10 vol%) and benzonitrile/ethanol (10%), respectively). The θ-(122b)₂[Fe(CN)₅NO] salt exhibited metallic properties down to 40 K, the (122b)₂[RuBr₅NO] salt behaved like a semiconductor, and the (122b)₂[RuCl₃NO] salt was an insulator [120].

Based on the Keggin polyoxometalate [(SMo₁₂O₄₀)⁰⁻] and compound 122b, the semiconductor (122b)₄[(SMo₁₂O₄₀)₃·10H₂O, was obtained, which shows increased conductivity at elevated pressure [121]. The bimetallic oxolate complex (122b)₃[MnCr(C₂O₄)₃(CH₂Cl₂)] exhibited the hybrid properties of a ferromagnet at temperatures below 5.3 K and metal-like conductivity at ambient temperature [122]. Obtained by electrocrystallization, two-dimensional organic metals (122b)₄MBr₄(PhBr) (M = Cd, Hg) with differently oriented conducting layers in the plane of the conducting layer demonstrated metallic properties, and across the layers-semiconductor behavior, which depends on temperature [123]. Also known are superconductors such as κ-(122b)₂TiCl₄ [124], κ-(122b)₂Hg₂Br₄[FeCl₄] [125], λ-(122b)₂Fe₄Ga₁-C₁₄ (x = 0.45) [126], and λ-(122b)₂Fe₄Cl₅Br₂ (x = 0.4, 0.5 and 0.7) [127] and organic metals such as κ-(122b)₄Hg₃Cl₈) [125], θ-(122b)₄Ni(CN)₄ [128], and κ-(122b)₂Mn[N(CN)₂]₃ [129].

Dimethyl(ethylenedioxy)tetratellurafulvalene 194 was synthesized by the cross-coupling of 4,5-dimethyl-1,3-diseleno-2-selone and 4,5-ethylenedioxy-1,3-diseleno-2-selone [130]. The superconductors κ-(194)₂[Au(CN)₄](solv.) (solv. = 1,3-dioxolane, 2,5-dihydrofuran, tetrahydropryan, 1,3-dioxane, 3,4-dihydro-2H-pyran or 1,4-dioxane) [130,131] and radical cationic salts of the general formula (194)₂X (X = PF₆, AsF₆, SbF₆) with metallic properties [132] were obtained based on compound 194.

The well-known tellurium-containing fulvalenes effective as π-donors are tetratellurafulvalene 191, hexamethylenetetratellurafulvalene 195, and tetrachlorotetratellurafulvalene 196 (Scheme 56).

Scheme 56. Well-known tetratellurafulvalenes, which are effective as electron-donor compounds and used for the preparation of conductive materials.

Tetratellurafulvalene 191 in the form of a charge transfer complex with tetracyanoquinodimethane is used in the production of modified electrically conductive thin graphene films [133].

Tetratellurafulvalene 191 and hexamethylenetetratellurafulvalene 195 are used in photovoltaic conversion functional devices as substrates in the form of charge transfer complexes that exhibit near-IR absorption [134]. In addition, fulvalenes 191, 195, and tetramethylthiotetralurafulvalene are used in electroluminescent devices as electron carriers and electron donors. Such organic electroluminescent devices show low operating voltage and high luminescence intensity due to the low resistance of the organic layer [135].

Based on hexamethylenetetralurafulvalene 195, single-crystal complexes with 2,5-diethyltricyanoquinodimethane (Et₂TCNQ) and bis-1,2,5-thiadiazolotetracyanoquinodimethane (BTDA-CNQ), which have a packing structure with alternately stacked donor-acceptor molecules, were prepared. These two complexes showed high conductivity despite
their disadvantageous packing method, which usually leads to materials with dielectric properties [136].

The complex of fulvalene 195 with 2,5-diethyl-tetracyanoquinodimethane, (195)(Et2TCNQ)(THF)x (x = 0.5–1), is metallic at temperatures above 200 K [137], while its complex with trifluoromethyl-tetracyanoquinodimethane (195)(CF3TCNQ)3 is a semiconductor [114].

Tetrachlorotetratellurafulvalene 196 is used in multisensor matrices for the detection of analytes in the gas or liquid phase [116].

5. Conclusions

The derivatives of 1,4-diselenafulvene and 1,4,5,8-tetraselenafulvalene and their tellurium analogs are important scaffolds and valuable heterocyclic building blocks for organic synthesis and donor units for the preparation of charge-transfer complexes and radical ion salts. The 1,4,5,8-tetraselenafulvalene derivatives and its tellurium analogs have shown themselves to be useful electron donors for the preparation of various conducting materials including Dirac electronic systems [31,32,53–57], superconductors [4–6,8–11,15–22,24,47,75,78,85,106,107,109–111,124–127], semiconductors [52,67,71,73,75,108,120,121,123] and compounds with ferromagnetic properties [7,15,23,48,76,118,122]. Well-known tetraselena- and tetratellurafulvalenes, which are effective as electron-donor compounds and most commonly used for the preparation of conductive materials, are outlined in Schemes 55 and 56.

Regarding the synthesis of 1,4,5,8-tetraselenafulvalene and its derivatives, the efficient approaches based on cross-coupling reactions of 1,3-selenole-2-one, 1,3-selenole-2-thione and 1,3-selenole-2-selone, which usually proceed in the presence of triethylphosphite, have frequently been used. These methods have been successfully developed and improved.

However, some efficient methods deserve to be mentioned. The method for preparation of diselenafulvene 1 and tetraselenafulvalene 2 based on selenium and sodium acetylide is a convenient and practical synthetic approach (Scheme 29) [78]. This approach, as well as the method depicted in Scheme 1 [34], have the advantages of using cheap, non-toxic selenium powder as the selenium source and commercially available acetylene or sodium acetylide.

Very important is a general synthetic approach to a series of alkylenedithio-121a–c and bis(alkylenedithio)tetratellurafulvalenes 122a–c (Scheme 38) [88]. Tetraselenafulvalenes 122a–c (especially compound 122b, Scheme 55) have frequently been used for preparation of various conducting materials including organic metals and superconductors [117–129].

The efficient approach to a number of polycyclic selenium-containing tetrathiafulvalene vinylogues of the dendralene type 155a–c, 156a–d, 157, and 158 bearing a 1,3-diselenole moiety using Vilsmeyer–Haack and Wittig–Horner reactions is worth mentioning (Scheme 46) [97].

A valuable synthesis of tetratellurafulvalene 191 in 26% yield by the optimized procedure with the use of tetrabromoethene at the final stage of cyclization is also very important (Scheme 54) [105]. This approach makes it possible to reliably obtain sufficient amounts of compound 191, which can be used for investigation of its potential as a building block for the preparation of functionalized electron donor compounds and the preparation of novel radical cation complexes and charge-transfer salts based on tetratellurafulvalene [105].

Obviously, the possibilities of 1,4-diselenafulvenes, 1,4,5,8-tetraselenafulvalenes, and their tellurium analogs for use in organic synthesis and in the preparation of conductive materials are far from being exhausted. Further research will lead to the synthesis of previously unknown complex compounds and preparation of novel conductive materials with new useful combinations of physicochemical properties.
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