2.13 Selenophenes

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2.13.1 INTRODUCTION
The scope of this chapter was first defined at the beginning of Chapter 3.16 in the first edition of Comprehensive Heterocyclic Chemistry (CHEC-I). Since then, a general review on selenium heterocycles has been published (B-86M1 213-01). A few more specific works have also appeared
concerning: the chemistry of selenophenes \(82\text{AH}(30)127,\) B-85\text{MI} 213-01, B-86\text{MI} 213-03, \(88\text{PS}(38)149,\) 9\text{PHC}(370), the ring opening of chalcogenophenes by means of lithiation reactions \(\text{B-83}\text{MI} 213-01\), the molecular motions in metal carbonyl derivatives \(\text{83}\text{MI} 213-04\), and the electrical and optical properties of conductive polychalcogenophenes and their applications \(\text{87}\text{MI} 213-01\). This chapter will cover the literature through to 1993 (e.g., \textit{Chemical Abstracts}, volume 118) with the same order of appearance of the material as in CHEC-I.

2.13.2 THEORETICAL METHODS

Numerous theoretical studies have been realized on selenophenes in order to compare them with their chalcogeno congeners. Indeed in this case the series is complete from oxygen to tellurium derivatives. One of the most fascinating and controverted parameters is the aromatic character. A new index \(I_s\) based upon a statistical evaluation of the deviations in peripheral bond orders (derived readily from experimental bond length) has been proposed for aromaticity quantization \(\text{85}\text{TI}(409)\). The values for the furan series are: O: 43; S: 66; Se: 59; Te: 48, and so show a reasonable parallelism with A, the aromaticity parameter obtained from the dilution shifts method. More recently, this index has been improved \(\text{92}\text{T}(335)\), and the values of \(I_s\) are the following: O: 53; Te: 59; Se: 73; S: 81.5 (compared with benzene: 100).

The characterization by \textit{ab initio} molecular orbital theory of chalcogen isosteres of benzene \(88\text{JA}(420)\) has allowed the prediction of structures with a precision of 0.04 \AA for the bonds and 2° for the angles. In this approach, the selenophene series shows important delocalization. New theoretically derived and energy-based criteria for aromaticity were proposed \(\text{90}\text{J}(843, \text{90PHC}(2)50)\).

The extent of transmission of substituent effects in selenophene and several condensed derivatives was deduced from \textit{CND}2 quantum chemical calculations on C-protonated forms or \(\sigma\) complexes \(\text{82CS}(75, \text{82CS}(208)\). Quantum chemical calculations \(\text{CND}2\text{(S)}\) of spectroscopic parameters of selenophene and several condensed derivatives have been used to determine their ionization potentials \(\text{86}\text{ZV}(225)\).

Several physicochemical parameters (first electron affinity, valence ionization potential, and photoionization cross-section) were determined by the Green’s function \(\text{82}\text{MI} 213-02\). The SCF-INDO perturbation theory calculations established the contributions of Fermi contact, orbital-dipole, and spin-dipole to \(1\text{H}^-\text{C}^-\text{Se}\) in several selenophene derivatives \(\text{82}\text{MI} 213-03\). The PRMO-SCPT-INDO of chalcogenophenes indicates that spin couplings are transmitted through the \(\sigma\) network and that orbital dipole interactions play a lesser role than in benzene \(\text{83}\text{MI} 213-02\). In a similar way, SCPT-INDO calculations of spin–spin coupling constants in selenophene show a good correlation with the experimental values \(\text{85}\text{MI} 213-02\). Force field calculation procedures were developed with the aim of getting information about the influence of substituent effects on the aromatic ring force field in 2-bromo- and 2-chloroselenophenes \(\text{87}\text{CPL}(138)244, \text{88}\text{MI} 213-01\). Numerical values of force field constants, refined from experimental frequencies, show as previously established, a noticeable variation of aromaticity in the chalcogenophene series \(\text{85}\text{SA}(A)679)\).

Comparison of the calculated geometries, ionization energies, dipole moment, and net atom charges indicated that the 3-21G basis should include a \(\Delta\) polarization function on selenium \(\text{89}\text{MI} 213-01\). Physicochemically-based semiempirical MO calculations showed a fair correlation between the average \(\nu_{C-O}\), the average ionization energy of the carbonyl lone pair orbitals, and the \(\delta^+\text{C}^-\text{C}^-\text{O}\) for seleno and tellurophthalic anhydrides. Their dipole moments in benzene at 25°C are respectively, 3.30 D (Se) and 2.71 D (Te) \(\text{82}\text{SA}(A)185)\).

2.13.3 EXPERIMENTAL STRUCTURAL METHODS

2.13.3.1 Molecular Structure

Several x-ray structures of complexed selenophene derivatives have been published: \((\text{C}_8\text{H}_6\text{Se})_2\text{Hg}^+\text{Cl}^-\) \(\text{86AX}(C)1449\); \((\text{C}_8\text{H}_6\text{Se})_2\text{HgBr}_2\) \(\text{88AX}(C)253\); \(\text{Cp}(\text{CO})_2\) \text{Re} selenophene \(\text{90JA}7811, \text{91JA}5651\). Complete characterization of a selenium analogue (I) of proton sponge has been achieved by a crystal structure determination \(\text{88TL}(1905)\).

X-ray diffraction shows that the 2-lithiobenzo[b]selenophene–TMEDA complex is dimeric, where the diamine acts as chelating ligand between the lithium-bridged benzo[b]selenophenes \(\text{89OM}(1)688\). Oxygen and sulfur analogues behave similarly.
Trinuclear carbonyl clusters of Ru, Fe, and Os react with selenophene in an insertion manner to give products whose structures have been determined by x-ray diffraction \( \langle 91 \text{JOM}(419)63 \rangle \) and which decompose at high temperature.

Dimethyl ethynedicarboxylate and elemental selenium react with \( \eta^2 \)-cyclopentadienyl-dicarbonylcobalt to give several selenophene derivatives, whose structures have been confirmed by x-ray diffraction, among them the unexpected 2,3,4,5-tetramethoxy carbonyl–selenophene \( \langle 92 \text{PS}(68)37 \rangle \).

Electronic and structural modifications of polyselenophenes during electrochemical doping were studied by \textit{in situ} x-ray spectroscopy \( \langle 86 \text{MI} 213-05 \rangle \). Microwave spectra of various \( \alpha \)-deuterated selenolanes allowed the establishment of their molecular structure \( \langle 92 \text{MI} 213-01 \rangle \).

### 2.13.3.2 NMR Spectroscopy

Besides routine structure determinations, NMR spectroscopy has been used for structure correlations and chemical shift predictions.

The total structure of selenophene has been determined by NMR (\( ^1 \text{H}, ^13 \text{C}, \) and \( ^77 \text{Se} \) on the liquid crystal medium \( \langle 82 \text{OMR}(19)173 \rangle \)). The same study carried out on benzo[b]selenophene evidenced, besides its structure, a significant solvent effect on \( ^1 \text{H} \) chemical shifts \( \langle 84 \text{JOM}(277)359 \rangle \).

As expected, substituent effects on \( \delta ^{13} \text{C} \) and \( \delta ^{1} \text{H} \) in the chalcogenophene series led to a qualitative determination of four different substituent classes depending on the heteroatom, and its interaction with the substituent. This method allows the prediction of chemical shifts \( \langle 90 \text{MRC}397 \rangle \).

From values of \( ^{13} \text{C}--^{13} \text{C} \) in 25 selenophene derivatives, it appeared that the \( \sigma \)-electronic effects are the most important factors governing the observed values \( \langle 88 \text{ZOR}2268 \rangle \). Moreover, a quantitative measurement of \( \pi \)-electron deficiency or excessiveness \( ^5 \Delta \) was proposed from \( ^{13} \text{C} \) values. For the chalcogenophene series \( ^5 \Delta \) is as follows: O: 1.31; S: 1.35; Se: 1.43; Te: 1.83 (compared with benzene: 1). It allows a more accurate prediction of \( ^{13} \text{C} \) chemical shifts in substituted heteroaromatic compounds \( \langle 82 \text{OMR}(19)192 \rangle \). Spin–spin coupling pathways in chalcogenophenes were analyzed by the polarization propagation method \( \langle 86 \text{MI} 213-02 \rangle \).

There is a good correlation between the NMR chemical shifts (\( ^1 \text{H}, ^{13} \text{C}, \) and \( ^77 \text{Se} \)) of selenophenes and those of their [b]benzocondensed analogues \( \langle 81 \text{CSI}447 \rangle \) as well as with the CND0 calculated electron densities \( \langle 82 \text{OMR}(18)33 \rangle \). An increments-based evaluation of substituent effects in other heterocondensed selenophenes was made by means of the same technique \( \langle 83 \text{CS}22 \rangle \). An excellent linear relationship of \( \delta ^{77} \text{Se} \) and \( \delta^{125} \text{Te} \) in several heterocycles is found and its slope is discussed on a theoretical basis. Experimental \( ^{77} \text{Se} \) chemical shifts and \( ^{1} \text{H}^{77} \text{Se}--^{77} \text{Se} \) in alkylselenolselenophenes \( \langle 87 \text{MRC}129 \rangle \) are discussed in relation to aromaticity and substituents \( \langle 87 \text{CS}359 \rangle \). The structure of pivaloylchalcogenophenes was established by routine NMR techniques \( \langle 85 \text{ZN}(A)1329 \rangle \). Selenolane ylides (2) were studied by \( ^{77} \text{Se} \) NMR \( \langle 82 \text{ZOR}119 \rangle \).

\[
\text{Me}_2N \quad \text{NMe}_2
\]

\[
\text{Se} \quad \text{Se}
\]

(1)

Data from \( ^1 \text{H} \) NMR show that selenolame salt (3) exists in solution as diequatorial conformers \( \langle 86 \text{ZOR}1553 \rangle \). Complexes of selenolane with \( \text{PdX}_2 \) were examined by dynamic NMR \( \langle 86 \text{JCS}(D)205 \rangle \). Surprisingly, \( ^{19} \text{F} \) chemical shifts of trifluoromethyl sulfone derivatives of chalcogenophenes are rather insensitive to the substitution pattern and to the nature of the heterocycle \( \langle 87 \text{JFC}(36)439 \rangle \). A NMR kinetic study of the Meisenheimer adducts formed by nitro-selenophenes and methoxide anion showed the following order of decreasing stability \( S > O > Se \) \( \langle 88 \text{CS}349 \rangle \). The conformation of nitro-
3,3'-biselenenyliyls was deduced from NMR measurements using induced cholesteric mesophases \(<86\text{ST}307\>). Proton and \(^{13}\text{C}\) NMR spectroscopy are also useful for the characterization of polymeric selenophenones \(<82\text{JPS(A)1697}\>.

2.13.3.3 Ultraviolet, Infrared, Raman, and Photoelectron Spectroscopy

Ultraviolet spectra of chalcogenophenones were investigated with the aim of exploring the Rydberg transitions terminating at the \(3\sigma\) orbital \(<88\text{CS331}\>). Pivaloylselenophenones and their oxygen and sulfur containing congeners were routinely examined by IR and UV spectroscopy \(<85\text{ZN(A)1329}\>). Low lying excited electronic states have been identified for the dibenzochalcogenophene series \(<89\text{MI 213-03}\>.

The phosphorescence spectra of benzo[b]- and dibenzochalcogenophene series were analyzed at 77 K in ethanol and n-pentane \(<89\text{ZN(A)205, 89\text{ZN(A)}1116}\>). The rate constants of both radiative (\(K_{\text{PT}}\)) and nonradiative (\(K_{\text{CT}}\)) deactivation of the lower triplet correlate linearly with \(\Sigma kC^2\zeta^2\) (where \(C_k\) denotes the Hückel AO coefficients in the HOMO of the carbon atoms bound to the heteroatom, and \(\zeta\) is the spin orbit coupling constant of the heteroatom present). A linear correlation is observed between \(K_{\text{PT}}\) and \(K_{\text{CT}}\) as an example for the Orlandi–Siebrand rule.

The UV and luminescence spectra of benzo[b]selenophene-doped naphthalene show that the properties of localized excitation states are different \(<83\text{MI 213-03}\>). Charge transfer complexes of selenophene and some condensed derivatives were examined by UV, IR, and photoelectron spectroscopy and the experimental ionization potentials are in agreement with the calculated ones \(<82\text{CS214}\>.

The isomerization potential of selenoindigo was obtained from its electronic spectra \(<87\text{PC1317}\>). The fluorescence decay of the same molecule as an impurity in benzoic acid crystals has been observed and probably involves a double proton transfer \(<86\text{CPL(131)44}\>.

Oxidation potentials of oligomeric 2-thienyl and seleniyls, obtained by classical palladium(II) coupling, were determined by UV spectroscopy \(<88\text{CC988, 89PS(42)171, 90PS(48)239}\>). Photoluminescence has been observed also in polyselenophenones \(<89\text{SMC295}\>). Luminescence spectra of polychalcogenophenones depend on the temperature and for polyselenophene the phenomenon disappears at high temperatures \(<90\text{MI 213-01}\>). Fundamental vibrations in the IR and Raman spectra for benzo[b]selenophene and tellurophene were completely assigned and modes proposed. Their evolution with chalcogen change has been analyzed \(<83\text{SA(A)1033}\>.

Molecular vibrational constants and chemical bonding allowed the establishment of a ground state aromaticity \((S > Te > Se > O)\), whereas this order is modified when the reactivity in electrophilic substitution is considered \((O > S > Te > Se)\) (see Section 2.13.2 for comparison) \(<85\text{MI 213-04}\>.

Due to the high quality of the spectra, FT–Raman is claimed as the preferred technique for routine vibrational spectroscopy \(<92\text{OM(430)37}\>). Dynamic disorder in tricarbonylchromium selenophenes has been characterized by low frequency vibrational spectra \(<82\text{SA(A)1163}\>). The principal bands for polyselenophenones (H or D) have been assigned \(<89\text{SM317}\>). \textit{Ab initio} calculations of electron bonding energies obtained from photoelectron spectroscopy of substituted selenophenes in the gaseous phase are well correlated with the Hammett substituent parameters \(<83\text{CS209}\>.

The electron transmission spectra of selenophene have been observed and discussed \(<84\text{CPH455}\>.

The nonplanarity of 2-arylselenophenes has been demonstrated by photoelectron spectroscopy \(<88\text{ZOB450}\>). This technique has also shown an inversion of the HOMO upon [b]benzo condensation of selenophene \(<88\text{IZV2616}\>). The system C==Se==C==C has been studied by photoelectron spectroscopy and quantum chemical methods. There is a linear correlation for \(\sigma_-\sigma_-\text{-MO}\) energies for C==C==Se==C==C and selenophene \(<91\text{IZV2317}\>.\) Comparison of the photoelectron spectra of dibenzochalcogenophenones and LCAO calculations shows as expected the planarity of these systems \(<83\text{ST(102)183}\>). Photoelectron spectra of the dibenzochalcogenophene series \(<88\text{ZOB1409}\>) and MO calculations identified a \(b_1\) symmetry for the first HOMO for these compounds. The first ionization potential decreases in the order \(O > S > Se > Te\). The second HOMO has \(a_2\) symmetry and the
second ionization potential is fairly constant. In order to evaluate substituents effects in selenophene, selenium 3d core electron shifts were correlated with the Cl shifts of the ring carbon atoms and with Hammett $\sigma$ constants $\langle86\text{MI} 213-07\rangle$.

2.13.3.4 Mass Spectrometry

Polyselenophenes were analyzed by laser desorption/FT mass spectrometry $\langle86\text{MI} 213-04, 86\text{MI} 213-06\rangle$. Appearance potentials for the formation of negative ions in resonance electron capture of chalcogenophenes have been reported $\langle91\text{IZV}590\rangle$.

2.13.3.5 Electron Spin Resonance

Anion radicals generated electrochemically from 29 derivatives of chalcogenophenes were examined by ESR and the results were discussed $\langle83\text{IST}(102)183\rangle$. An ESR study of radical ions in the 2,5-diphenylselenophene series has been published $\langle90\text{JOM}(389)301\rangle$. These spectra belong to systems conformationally rigid on the ESR timescale as evidenced by the nonequivalence of the ortho and meta-proton hyperfine coupling constants. For the O, S, and Se congeners, the spectra show the expected symmetry of the parent LUMO and antisymmetry for the HOMO.

2.13.3.6 Dipole Moments

Anisotropic molecular polarizabilities, dipole moments, and quadrupole moments of the selenophene series have been discussed in terms of comparison of experimental results and $ab\ initio$ calculations. The results elucidate the electronic charge distributions in these molecules $\langle92\text{JPC}7301\rangle$. The group dipole moments of 2- and 3-substituted selenophenes, depend upon the $\sigma$-acceptor and $\pi$-donor ability of the substituted heteroaryl moieties $\langle85\text{ZOR}203\rangle$. The preferred conformation of some 2-acylselenophenes was deduced from their dipole moment analysis $\langle85\text{ZN}(A)1338\rangle$. Measurements of the infinite dilution (in cyclohexane) molar field gradient birefringence constants, Kerr constants, and Cotton–Mouton constants for the chalcogenophenes series led to an estimate of the position of the effective quadrupole center of these molecules $\langle83\text{JCS}(F2)539\rangle$.

2.13.3.7 Miscellaneous

Theoretical and experimental investigations into resonance hybridization between benzo[b]-selenophene and naphthalene in benzoselenophene-doped naphthalene systems provided evidence for two nonequivalent centers for the impurity $\langle85\text{MI} 213-03\rangle$. Chromatographic structural analysis by adsorption on graphitized thermal carbon black was used for the determination of conformation in 2-phenylchalcogenophenes $\langle87\text{MI} 213-02\rangle$. The adsorption of selenophene on various solid phases allowed its direct observation by EXAFS $\langle91\text{MC}6\rangle$.

Polyselenophenes were examined by NEXAFS and compared with the ISEELS spectra of selenophenes $\langle89\text{JC}1819, 90\text{MI} 213-04\rangle$. The presence of polarons and bipolarons may explain the experimental data on the evolution of optical and magnetic properties upon doping polyselenophenes $\langle88\text{MI} 213-02\rangle$. A compilation (250 pages) of spectral parameters associated with triplet–triplet absorption of organic molecules and in condensed media has been published $\langle86\text{MI} 213-08\rangle$.

2.13.4 THERMODYNAMIC CONSIDERATIONS

Several thermodynamics constants ($\Delta H^0_{\text{comb.}}, \Delta H^0_{\text{form.}}, \Delta H^0_{\text{evap.}}, \Delta H^0_{\text{atom.}}$) were determined by calorimetry for selenophene and its benzo[b]derivatives $\langle89\text{DOK}(307)1139\rangle$. The existence of stable and metastable phases in crystalline selenophene has been demonstrated by thermodynamic evidence $\langle91\text{CR}(C)701\rangle$. The glass transition temperatures (Tg) were measured for selenophene copolymers and their
dependence upon the length of the lateral chain was discussed \( \langle 89 \text{MI } 213-04 \rangle \). Low energy resonance states of molecular anions were determined for the chalcogenophene series \( \langle 90 \text{KGS276, 90MCLC459} \rangle \).

A compilation of thermodynamic parameters for heterocycles has been published \( \langle 90 \text{MI } 213-05 \rangle \). Selenophene has been observed in the gasification of spiked coal by ICP \( \langle 86 \text{JC465} \rangle \).

### 2.13.5 Reactivity of Fully Conjugated Rings

#### 2.13.5.1 Thermal and Photochemical Reactions

Electron withdrawing groups on di-1,2-(3-selenienyl)ethenes show a thermally irreversible photochemical cyclization with relative high quantum yield \( \langle 90 \text{OC2592} \rangle \) giving (4).

![Chemical structure of selenium compound](image)

Photochemical reaction of selenophene with 3-iodocoumarin afforded the 3-(2-selenienyl)coumarin \( \langle 90 \text{KGS1469} \rangle \). Selenophene has been used for MOCVD deposition of ZnSe \( \langle 84 \text{EUP106537, 84MI } 213-02 \rangle \). The structural quality of these thin films has been studied by cross-sectional high resolution transmission electron microscopy and cathodoluminescence \( \langle 85 \text{MI } 213-05 \rangle \).

In the presence of Fe\(_2\)(CO)\(_9\) and Me—CHBrCO—CHBrMe, selenophene undergoes photochemical addition leading to the 2-substituted derivative (5) and the 1,5-dihydrobicyclic compound (6) \( \langle 85 \text{PS245} \rangle \).

Theoretical and experimental investigations into resonance hybridization between benzo[b]-selenophene and naphthalene in benzoselenophene-doped naphthalene systems provided evidence for two nonequivalent centers for the impurity.

![Chemical structure of selenium compound](image)

#### 2.13.5.2 Electrophilic Substitutions

The perchloric acid catalyzed acylation of selenophene with acetic anhydride is claimed to give solely 2-acetyl selenophene \( \langle 81 \text{MI } 213-01 \rangle \). Ethoxal chloride reacts at the same position \( \langle 83 \text{BEP896054} \rangle \). Reaction with trifluoromethylsulfonyl chloride and stannic chloride gives 2-trifluoromethylthioselenophene, and addition of trifluoromethanesulphonic acid promotes formation of the 2,5-bis(trifluoromethylthio) derivative \( \langle 83 \text{JFC23525} \rangle \).

Electrophilic substitution on 2-(2-selenienyl)benzimidazole \( \langle 88 \text{JCS(P1)1033} \rangle \) takes place in the selenophene moiety \( \langle 83 \text{KGS1531, 87KGS1636} \rangle \). New selenium containing D,L-amino acids were obtained by reacting selenium containing substrates with \( \alpha \)-hydroxy Cbz glycine. With benzo[b]-selenophene, only the 3-isomer was isolated and the reaction failed with selenophene \( \langle 81 \text{JHC1605} \rangle \).

Treatment of selenoindoxyl in its enol form (3-hydroxybenzo[b]selenophene) with trifluoroacetic acid (Scheme 1) leads to a trimeric condensed compound (7) beside dimeric compounds \( \langle 86 \text{CS287} \rangle \).

Conventional palladium(II)-catalyzed coupling methodology allowed the formation of a number of oligo 2-thienyl or selenienyls \( \langle 90 \text{H30645} \rangle \). The thallation reaction of selenophene affords the 2-thallated species which give 2-iodoselenophene upon iodination \( \langle 90 \text{MI } 213-06 \rangle \).
2.13.5.3 Reactions on the Selenium Atom

Much work has been devoted to the formation of complexes where selenophene acts as a ligand. For example, with first row transition metals selenenylthienylmethane forms stable molecular species \( \langle 83\text{MI }213-05 \rangle \). The effect of substitution of either cyclopentadienyl or selenophene rings on the structure of \( \eta^- \) and \( \eta^1 \)-selenophene (sel) complexes \( \text{Cp(CO)}_2\text{Re(sel)} \) has been discussed \( \langle 91\text{JA5651} \rangle \).

Clusters are formed of \( \text{Os}_3(\text{CO})_{10} \) (MeCN)\(_2 \) with selenophene of composition \( \text{Os}_3(\text{CO})_{10} \text{C}_4\text{H}_4\text{Se} \) by both C—H and C—Se insertions, the latter affording compounds \( \langle 90\text{CC1568} \rangle \). Substituted selenophenes were also studied \( \langle 92\text{JOM351} \rangle \).

\[
\text{Os(CO)}_3(\text{OC})_4\text{Os}(\text{8})
\]

Salts readily obtained from dibenzochalcogenophenes \( \langle 9 \rangle \) are powerful methylation agents \( \langle 9a \rangle \), even in water as solvent \( \langle 89\text{TL7293} \rangle \), or trifluoromethylating electrophiles \( \langle 9b \rangle \) (Scheme 2) \( \langle 90\text{EUP382206, 90TL3579} \rangle \).

\[
\text{CF}_3\text{SO}_3^- \quad \text{CY}_3
\]

\( \langle 9a \rangle \) \( Y = \text{H} \)

\( \langle 9b \rangle \) \( Y = \text{F} \)

\( X = \text{S, Se, Te} \)

The reactivity depends on the aromaticity of the heterocycle and decreases in the order \( \text{S} > \text{Se} > \text{Te} \) \( \langle 93\text{JA2156} \rangle \). The \( \text{NiCl}_2 \) catalyzed reaction of Grignard reagents induces the ring opening of chalcogenophenes, with the loss of the chalcogen atom, giving the corresponding \( s\text{-cis}-1,3\)-butadiene (Equation (1)) whose structure has been proved by high resolution \( ^1\text{H} \) and \( ^{13}\text{C} \) NMR spectroscopy. The yields decrease in the series from \( \text{Te} \) to \( \text{O} \) \( \langle 84\text{CC617} \rangle \).

\[
\begin{align*}
\text{CF}_3\text{Br} & \xrightarrow{\text{NiCl}_2} \text{CF}_3 \rightarrow R-\text{CF}_3 \\
\text{C}_6\text{H}_5\text{NH}_2 & \xrightarrow{\text{NaI}} \text{H}_2\text{N}-\text{C}_6\text{H}_4\text{F}_3 \text{ (9a, p)} \\
\end{align*}
\]

Some benzo[\( b \)]selenophenes have been used as models for catalytic dihydrodesulfuration studies \( \langle 91\text{DIS(B)5302} \rangle \).

2.13.5.4 Nucleophilic Substitutions

Nucleophilic substitution of halogen in \( 2-(3)\text{halo}-3-(2)\text{formylbenzo[\( b \)]selenophenes} \) by nitrogen-containing nucleophiles is the first step for the formation of new tricyclic compounds \( \langle 83\text{HC49} \rangle \).
The role of Meisenheimer complexes was studied in the nucleophilic substitution of the nitro group by methoxide anion in 2- and 3-trifluoromethylsulfanyl-4- and 5-nitroselenophenes \( \langle 83\text{JCR(S)}58 \rangle \). The use of potassium thiocyanate and selenocyanate as nucleophiles with 3-bromo-2-nitroselenophene has allowed the elaboration of several condensed bicyclic selenophenes \( \langle 83\text{JHC113} \rangle \) as shown in Structures (10) and (11).

As an example of general methods for the synthesis of arylacetic acids, selenophene has been metallated by Bu\(^{+}\)Li. Transmetallation afforded the corresponding zinc compound which was coupled with good yields, with ethyl bromoacetate \( \langle 83\text{OM598} \rangle \) or bromoacetonitrile \( \langle 87\text{S40} \rangle \). A new class of compounds (12) have been synthesized, starting from 2,5-dilithioselenophene, as potential electron donors or acceptors \( \langle 91\text{TL4313} \rangle \).

The classical nucleophilic ring opening of condensed selenophenes has been generalized to more complex compounds. The C—Se bond is preferentially cleaved by MeLi in heterocycles (13)–(16) \( \langle 83\text{BSB53}, \text{83CS177} \rangle \). However, heterocycle (16) undergoes ring opening with S—N bond cleavage \( \langle 87\text{BSB407} \rangle \). These reactions afford diversely substituted selenophenes that can be further transformed.

2.13.5.5 Radicals and Electrochemical Reactions

One electron electrochemical reduction of 2-NO\(_2\) chalcogenophenes becomes progressively easier when going from oxygen to selenium \( \langle 83\text{MI 213-07} \rangle \). Selenophene-3-carboxylic acid is electrochemically reducible to its 2,3-dihydroderivative but the corresponding furan is not reduced under the same conditions \( \langle 83\text{IZV944} \rangle \).

Oxidation of benzo[b] and dibenzoselenophene in nonaqueous media leads to the formation of the corresponding oxide \( \langle 92\text{MI 213-02} \rangle \), whereas 1,2-dibenzodiselenin first looses a selenium atom forming dibenzoselenophene before undergoing oxidation \( \langle 92\text{MI 213-03} \rangle \).

Like thiophene, selenophene derivatives react with dimethyl diazomalonate in the presence of rhodium acetate to give ylides (17) which are less stable than their sulfur-containing congeners \( \langle 84\text{CS253} \rangle \).

Due to potential industrial applications, important studies (see Section 2.13.9) have been made on polyselenophenes and similar compounds which can be prepared by electrochemical polymerisation \( \langle 83\text{MI 213-08} \rangle \). Electrochemical study (cyclic voltametry and chronocoulometry) shows that poly(3-methylselenophene) is a very good electrode material \( \langle 88\text{SM77} \rangle \).
2.13.5.6 Cycloaddition Reactions

The mechanism of the photochemical addition of benzophenone to selenophene derivatives has been studied and in some cases an oxetane is isolable <82MI 213-01, 83MI 213-06>. The [2 + 2] photoaddition of 2,3-dimethylmaleic anhydride to benzo[b]selenophene and heteroaryl-condensed selenophenes furnished cycloadducts whose structure was established. Selenophene does not react under these conditions <83JHC1465>. 1,2,3-Triphenylnaphthalene is obtained when reacting selenophene with E-stilbene <91ZOR1364>, probably through a cycloaddition pathway. Inverse electron demand [4 + 2] cycloadditions of selenophene across 1,2,4,5-tetrazines gave 5,6-diazabenzo[b]selenophene derivatives <89CZ17>.

2.13.6 REACTIVITY OF NONCONJUGATED RINGS

Investigation of the kinetics and mechanism of ligand substitution in the formation of complexes \( \eta^2-C_6H_5Nb(CO)_3C_6H_4X \) shows that the stability of these complexes increases from \( X = O \) to Te <91OM256>. The comparative thermolysis of several benzylselenenides has shown that the 1,3-dihydrobenzo[c]selenophene (18) is more stable than expected for a dibenzylselenide since it is produced by the reaction shown in Equation (2) <82BCJ182>.

\[
\begin{array}{c}
\text{Se-} \quad \text{Se} \\
\text{Se} \quad \text{Se} \\
\end{array} \xrightarrow{\Delta T} \quad \begin{array}{c}
\text{Se} \\
\end{array}
\]

Reduction of 1,3-dihydrobenzo[c]selenophenium salts with magnesium leads to ring opening and the formation of selenide (19) (Equation (3)) <89TL981>.

\[
\begin{array}{c}
\text{Se-} \quad \text{Me} \\
\end{array} \xrightarrow{\text{Mg}} \quad \begin{array}{c}
\text{Se} \quad \text{Me} \\
\end{array}
\]

Vinylselenonium salts derived from selenolane were obtained by hydrobromic acid elimination from \( \beta \)-bromoalkylselenonium salts <88ZOR355>. Generation of dinitrocarbene is possible through electrochemical oxidation of the ylide (20) <89IJV356>.

\[
\begin{array}{c}
\text{Se} \\
\end{array} \quad \begin{array}{c}
\text{O} \quad \text{N} \\
\end{array}
\]

Classical reactions of 2,3-dihydrobenzo[b]selenophene-3-one (selenoindoxyl) with various amines followed by cyclization have been used to give several condensed polycyclic compounds <85IZV861>. The oxidation of selenoindoxyl gives its rather unstable selenium oxide <89LA811>. The attempted photochemical rearrangement of 2-diazoselenoindoxyl afforded the 2-methoxy derivative instead of the expected benzoselenete <89JOC240>. Charge transfer complexes of 2,5-dihydroselenophene have been described <87JOM(330)337>.

Oxidation of selenolane by chloramine T in the presence of amides or sulfonamides afforded the corresponding selenenamides <81PS(10)153>. The Se—Br bond of Se-dibromoselenolane adds across double bonds in a regio- and stereospecific manner <84ZOR2480, 87ZOR949>.

2.13.7 REACTIVITY OF SUBSTITUENTS

The (\( E \)) alkene (21) was obtained from 2-iodoselenophene as an example of a general coupling reaction between iodoarenes and vinylsilanes <86JOC5286>. Bromine–lithium interconversion reactions of 3,4-dibromoselenophene were the starting steps for
the synthesis of nonclassical selenolothiophenes (22) \textsuperscript{82CS176} as well as selenolotetrathiafulvalene (23) \textsuperscript{84JOC1117}.

![Structure 22](image)

![Structure 23](image)

The selenium analog (24) of TCNQ was synthesized from 2,5-dibromoselenophene \textsuperscript{88CL1179}.

![Structure 24](image)

Selenophene-3-carbaldehyde (25) has been transformed by classical ways into the tricyclic compound (26) (Equation (4)) \textsuperscript{83T819}.

![Equation 4](image)

The formation of nonclassical selenothiophene and selenophenes (27) has been achieved by traditional transformation of bis-3,4-chloromethylselenophene (28) \textsuperscript{84CS53}. The Schollkopf methodology and rhodium catalyzed reduction allowed the enantioselective synthesis of 2- and 3-selenienylalalines \textsuperscript{87CS249}.

![Structure 27](image)

![Structure 28](image)

Application of a general synthesis of 4-hydroxycoumarins allowed the synthesis of tricyclic compound (30) from ester (29) (Equation (5)) \textsuperscript{86UKZ1082}.

![Equation 5](image)

### 2.13.8 RING SYNTHESIS

#### 2.13.8.1 Formation of One Bond

##### 2.13.8.1.1 C–Se

When applied to benzylselenides of the type shown in Structure (31), the Barton radical based methodology afforded selenolane (Equation (6)) \textsuperscript{92CC57}.
The easy generation of radicals from benzylselenides also leads to benzo[h] derivatives (33) from compounds (32) contained in (Equation (7)) (92TL5137).

\[
\text{(32)} \xrightarrow{\text{AIBN, } \text{TiCl}_4, \text{Zn}} \text{(33)}
\]

\[
\text{(32)} \xrightarrow{\text{TiCl}_4, \text{Zn}} \text{(35)} \xrightarrow{\Delta T} \text{(36)}
\]

\[
\text{(37)} \xrightarrow{\Delta T} \text{(38)}
\]

The electrophilic cyclization of selenide (39) led to the benzo[h]selenophene derivative (40) which has been transformed into the corresponding quinone (41) (Scheme 4) (92H341749).
2.13.8.2 Formation of Two Bonds

2.13.8.2.1 Selenium plus C₄ unit

This is the easiest and most studied route because it uses inorganic derivatives of selenium. New examples of the ring closure of arylalkynes by means of SeX₄ have been published (81KGS1283). By this method 2-aminomethylbenzo[b]selenophene (42) are obtained (Equation (9)) (90KGS1331).

\[
\begin{align*}
\text{NMe}_2 & \quad \xrightarrow{\text{SeBr}_4} \quad \text{Br} \quad \text{NMe} \\
\text{SeBr}_4 & \quad \xrightarrow{} \quad \text{SeBr}_4
\end{align*}
\]

(9)

In a similar way, SeBr₄ adds across allylbenzene in an anti-Markovnikoff manner and gives 2-bromomethyl-2,3-dihydrobenzo[b]selenophene (82KGS911).

A new synthesis of selenophene derivatives (44) has been developed by Japanese chemists (Equation (10)). It consists of the oxidation by SeO₂ of conjugated alkenes (43).

\[
\begin{align*}
\text{R}_1&\xrightarrow{\text{SeO}_2} \text{R}_1 \quad \text{Se} \quad \text{CO}_2\text{R} \\
\text{SeO}_2 & \quad \xrightarrow{} \quad \text{R}_1 \quad \text{Se} \quad \text{CO}_2\text{R} + \text{R}_1 \quad \text{Se} \quad \text{CO}_2\text{R}
\end{align*}
\]

(10)

The furan analogue (45) is formed at the same time with higher yields (86TL2643, 87BCJ1807). Similar oxidation of isoprenoid dienes affords mixtures of substituted selenolanes as well as six- and seven-membered selenium-containing heterocycles (86DOK289114, 86IZV2514). The SeO₂ oxidation of stilbazole with the formation of 2-(2 pyridyl)benzo[b]selenophene (46) is claimed to be an analytical procedure for the quantization of SeO₂, even in water (89MI213-02).

\[
\begin{align*}
\text{Se} & \quad \text{N} \\
\text{Se} & \quad \text{Se}
\end{align*}
\]

(46)

Phosphorylated allenes react with methylselenenyl chloride to give, after cyclization, phosphonic acid derivatives (47) (83PS15373, 88PS3535) or (48) (85H23543) with 60–70% yields.

\[
\begin{align*}
\text{Se} & \quad \text{O} \quad \text{P} \quad \text{OR} \\
\text{Se} & \quad \text{O} \quad \text{P} \quad \text{OR}
\end{align*}
\]

(47)

(48)

Numerous examples of an organometallic based methodology for the formation of selenophenes have been discussed. In these cases, a selenolate anion is formed in situ followed by cyclization. The application to selenophenes is due to the Brandsma group (83TL2203). Indeed, when hydrocarbon (49) is first metallated and then treated with selenium, a mixture of (50) (46%) and (51) (42%) is formed after hydrolysis (Equation (11)). The base catalyzed isomerization of (50) to (51) is quantitative.
Selenophenes

In a quite similar reaction, benzo[h]selenophene is available from phenylethyne (52) via a double metallation reaction (Equation (12)) \(\langle 85RTC226 \rangle\).

\[
\begin{array}{c}
\text{Ph} - \text{C}_2\text{H}_2 \quad \text{i-iv} \quad \text{Se} \\
\text{Me} \\
(52)
\end{array}
\]

\(\text{i, Bu}^+\text{Li; ii, Bu}^+\text{OK; iii, red Se; iv, H}_2\text{O}^+\)

The dianionic intermediate is quenchable with several electrophiles. Dibenzoselenophene derivatives (54) are also available from suitably substituted 2,2'-dibromobiphenyls (53) (Equation (13)). In that case, Engman has shown that the chalcogen may be introduced in its elemental form as well as its halide (SeX₄) \(\langle 84JHC413 \rangle\). The corresponding diselenide (55) is isolable and can be transformed into dibenzoselenophene (54).

\[
\begin{array}{c}
\text{Br} - \text{Br} \quad \text{i, Bu}^+\text{Li} \quad \text{Se} \quad \text{Br} - \text{Br} \\
\text{R} \\
(53)
\end{array}
\]

\[
\begin{array}{c}
\text{R} \quad \text{i, Bu}^+\text{Li} \quad \text{Se} \quad \text{Br} - \text{Br} \\
\text{R} \\
(54)
\end{array}
\]

\[
\begin{array}{c}
\text{Se} \quad \text{Br} - \text{Br} \quad \text{ii, Se or SeX}_4, \text{Na}_2\text{S}_2\text{O}_3 \\
\text{R} \\
(55)
\end{array}
\]

The same reaction has been extended to 2,2'-dibromo-1,1'-binaphthyl \(\langle 91JHC433 \rangle\) which affords dinaphthoselenophene (Equation (14)). The dibenzoselenophene analogue (56) of proton sponge has been obtained (7% yield) following the same methodology (Equation (14)) \(\langle 88TL1905 \rangle\). Its \(pK_a\) has a value of 11.8 ± 0.1 close to that of proton sponge itself (\(pK_a\): 12.1).

\[
\begin{array}{c}
\text{Br} - \text{Br} \quad \text{i, Bu}^+\text{Li} \quad \text{NMe}_2 \quad \text{Br} - \text{Br} \\
\text{Me}_2\text{N} \\
(56)
\end{array}
\]

The first organoselenoate complex (57) has been obtained by a Br–Li exchange and fully characterized (Equation (15)) \(\langle 92JA7937 \rangle\).

\[
\begin{array}{c}
\text{Br} - \text{Br} \quad \text{i, Bu}^+\text{Li} \quad \text{Se} \quad \text{Br} - \text{Br} \\
\text{Me}_2\text{N} \\
(57)
\end{array}
\]

The transmetallation of zirconium five-membered heterocycles by elemental selenium also affords selenophene derivatives with yields up to 50% \(\langle 88JA2310 \rangle\). Classical thermal displacement (210°C) of SO₂ by selenium allowed the synthesis of 3,4-di-t-butylselenophene from the corresponding thiophene dioxide \(\langle 90TL4473 \rangle\).

Selenophene derivatives are also available from selenide anion. Phase transfer catalysis improved the yield of selenolane from Na₂Se and 1,4-dibromobutane \(\langle 89SR1931 \rangle\). The reaction of sodium
selenolate with alkyne (58) affords a mixture of two compounds (60) and (59) which can be transformed easily into (60) by acidic treatment (Equation (16)) <87PS(34)119>.

\[
\begin{align*}
\text{R}^1\text{C}≡\text{Cl} & \xrightarrow{\text{NaSeH}} \text{R}^1\text{Se} & \text{H}^+ & \xrightarrow{\text{quant.}} \text{R}^2\text{Se} \\
\text{(58)} & & \text{(59)} & \text{(60)}
\end{align*}
\]

Using the Diels adduct between anthracene and maleic anhydride, it is possible to obtain a complex selenolane. Its flash thermolysis affords the previously unknown 3-selenolene, which has been fully characterized <86JCR(S)98>.

Lithium selenide reacts with o-chloroacetophenone in aprotic medium to give unexpectedly a significant amount (25%) of selenoindoxyl <88TL6119>. Reaction of H₂Se with ketoepoxide (61) gives 12% of the selenolane derivative besides a tetrahydroselelenopyran derivative (Equation (17)) <91ZOR942>.

\[
\begin{align*}
\text{O} & \xrightarrow{\text{H}_2\text{Se} \text{DMF}} \text{O} \\
\text{(61)} & \text{(62)}
\end{align*}
\]

The thermolysis of the selenadiazole derivative (62) follows an unexpected course and affords 15% yield of 2,3-dihydrobenzo[b]selenophene (Equation (18)) <85CB198>. Bis(allenic) compounds (63) even react with selenium to give benzo[b]selenophenes (64) (Equation (19)) <88TL1935>.

\[
\begin{align*}
\text{Cu, 180 °C} & \xrightarrow{\text{Ar, 180 °C}} \text{Ar} + \text{Ar} \\
\text{(62)} & \text{(63)} \text{(64)}
\end{align*}
\]

Bis(alkynes) react similarly <90MI 213-08, 92URP1721053>. Less reactive 1,3-butadienes (65) require more drastic conditions to afford selenophenes (66) (Equation (20)) <89S181>.

\[
\begin{align*}
\text{R}^1 & \xrightarrow{\text{Se, dbu} \text{DMF}} \text{R}^2 \\
\text{(65)} & \text{(66)}
\end{align*}
\]

The selenation of cinnamaldehyde with a substituted borylseleinide leads to a 2-selenolene derivative <92CL1843>.

### 2.13.8.2.2  Se—Cₓ—Cᵧ plus Cᵧ—Cₜ

Several products were formed by addition of phenylselenolate anion to DMAD <82ZOR281>. Among them, modest yields of 2,3-di(methoxycarbonyl)-4-phenylselenophene and 3-methoxy-carbonyl-2,4-diphenylselenophene are obtained. The study of the photochemical addition of
diphenyldiselenide to alkynes (Equation (21)) has shown the formation of benzo[b]selenophene derivatives (67) among other photoproducts (88JOC2533).

\[
R = \begin{array}{c}
\text{CO}_2\text{Me} \\
\end{array} \quad \text{(PhSe)}_2 \quad \text{hv} \quad \begin{array}{c}
\text{CO}_2\text{Me} \\
\end{array}
\]

\[ \text{Se} \quad R \]

\[ \text{(67)} \]

\[ \text{(21)} \]

2.13.8.2.3 $C_x-\text{Se}-C_y$ plus $C_x-\text{Selenium}$

The classical Hinsberg synthesis of thiophenes has been applied to the preparation of 2,5-dicarbonylselenophenes (68) (87H(26)909) as shown in Equation (22).

\[
\begin{array}{c}
\text{OHC-CHO} \\
\end{array} + \begin{array}{c}
\text{Se} \\
\end{array} \quad \text{B}^- \quad \begin{array}{c}
\text{Se} \\
\end{array}
\]

\[ \begin{array}{c}
\text{(68)} \\
\end{array} \]

\[ \text{(22)} \]

2.13.8.3 Formation of Three Bonds

Russian chemists have developed the synthesis of selenophenes from alkynes and (or) alkenes and elemental selenium. A 25% yield of selenophene is obtained when selenium and KOH are treated with a mixture of ethyne and ethene at 120°C in DMSO (82T713). In the transformation HMPT may also be used as a cosolvent (84ZOR484). An improved yield of 58% of selenophene (Se, Al₂O₃, ethyne) has been reported (83JOC2544) and the method has been patented (83JAP(K)59227881). All the parameters of the reaction (83ZOR276) have been optimized. It has also been claimed that using dimethylselenide instead of elemental selenium gives higher yields (85URP1231055), even up to 96% (87KGS279). With diphenyldiselenide, benzo[b]selenophene derivatives are also formed (89MI 213-06, 90MI 213-07). In the same way, when heated neat at 210°C with elemental selenium substituted, alkynes afford substituted selenophenes (69) (87H(26)2215, 87NKK1424, 92H(34)1487).

\[
R = \begin{array}{c}
\text{Se} \\
\end{array} \quad \text{Se} \quad \text{(69)} \\
\]

\[ \text{(23)} \]

The general synthesis of chalcogenophene derivatives has been extended to aminoselenophenes (70) (Equation (24)) (92M455).

\[
\begin{array}{c}
\text{NC} \\
\end{array} \quad \begin{array}{c}
\text{CN} \\
\end{array} \quad \begin{array}{c}
\text{Ph} \\
\end{array} \quad \begin{array}{c}
\text{Cl} \\
\end{array} \quad \text{Cl} \quad \begin{array}{c}
\text{R} \\
\end{array} \quad \text{NaSeH} \quad \text{base} \quad \begin{array}{c}
\text{NC} \\
\end{array} \quad \begin{array}{c}
\text{Ph} \\
\end{array} \quad \begin{array}{c}
\text{Se} \\
\end{array} \quad \begin{array}{c}
\text{R} \\
\end{array} \quad \text{NH}_2 \]

\[ \text{(70)} \]

\[ \text{(24)} \]

2.13.8.4 Ring Transformations

The ring opening reaction of 3-lithioselenopyran-4-one (Structure (71)) gives a 10% yield of the 2,3-dihydroselephene (72) (Scheme 5) (88JOC1203).

A general transformation of furan into selenophene is possible by action of hydrogen selenide on the oxygen heterocycle (82KGS418, 83KGS219) in the presence of strong acid (HClO₄). The mechanism has been elucidated (89KGS1458). Yields of up to 80% are attainable with 2,5-disubstituted seleno-
**Selenophenes**

![Scheme 5](image)

phene (84KGS1606). Even with 2,3-dihydrofuran, 2-selenolene is obtained in 20% yield by the action of H₂Se at 300°C on Zeocarb 2 (86KGS1478).

Ring contraction is observed as a result of classical oxidation of selenopyran derivatives (73) with formation of selenophenes (74) (Equation (25)) (89KGS767).

![Equation 25](image)

Some selenazoles may be transformed into selenophenes by dipolar additions, for example, Equation (26) (91CL2043).

![Equation 26](image)

The preparation of sterically highly congested 1,9-disubstituted dibenzo seleniumenes (76) has been described from selenanthrene Se-oxide (75). When treated in concentrated H₂SO₄, these compounds afforded new dications (77) (Scheme 6) (92CL675).

![Scheme 6](image)

### 2.13.9 IMPORTANT COMPOUNDS AND APPLICATIONS

#### 2.13.9.1 Compounds of Biological Interest

A large variety of compounds have been prepared in which a selenium atom replaces an oxygen, a sulfur, or a nitrogen one. These compounds were synthesized in order to try to improve the existing bioactivity. Among them selenolevamisole analogues are described (83JHC523). The palladium(0) catalyzed coupling of selenenylationboronic acids has been realized with halopyrimidines (86CS305), halouracils (90JHC2165), halocytosines (91JHC1613), halo-2-deoxyuridine, and cytidine (92MI 213-04). The antiviral activity of all these molecules has been evaluated.
Selenophenes

The antiviral character of 2-selenienyl nucleosides has been patented (90MIP8912061) as well as the antiallergic activity of ketone (78) (90GEP(O)4037187).

(78)

Homo-Ebselens (80) were synthesized from selenolactones (79) in a multistep pathway (Equation (27)). Unfortunately these molecules are highly photosensitive and their antiinflammatory activity is too low compared with Ebsele (92TL3863).

(79) R1 = H, Me; R2 = H, Me, Bn, Ph (80)

Starting from dibromoisophthalaldehyde (81), a new multistep methodology (Equation (28)) has been designed for the synthesis of all the sulfur and selenium analogues of psoralene (82) (92H(34)1119). These compounds seem to be promising with regard to their bioactivity (94MI213-01).

(81) (82) X, Y = S, Se

The synthesis of the selenium analogue (85) of the hallucinogen psilocin is described from 6-methoxyanthranilic acid (83). The key intermediate is 4-methoxyselenoindoxyl (84) (Scheme 7). The bioactivity is not mentioned (92H(34)1737).

(83) (84) (85)

Scheme 7

A new synthesis of dibenzoselenophene (86) is the key step for the formation of selenoellipticine (87) (Scheme 8) (93ACS(B)208).

(86) (87)

Scheme 8

The auxin-like activity of benzo[b]selenienyl-3-acetic acid has been confirmed (83P2657, 85MI213-06). The phototoxicity of α-terthienyl is claimed to be higher against yeast alcohol dehydrogenase than α-tertelenieryl (84MI213-03).
2.13.9.2 Compounds with Potential Technical Utility

Since the mid-1980s, more than 60 patents concerning selenophene derivatives have been filed. They generally deal with polyselenophenes that can be used in two important directions: electroconductive films and photosensitive materials. In such a matter, it is not possible to be exhaustive and we will summarise the more significant features. The polymerization of selenophene may be effected chemically (84SM389, 85MI 213-07, 87JAP(K)62106923), or electrochemically (83JAP(K)58187432, 84JAP(K)59191727, 85JAP(K)6050194, 86SM281, 87MI 213-04).

New long chain alkyl selenophenes were synthesized (90PS(47)35) and the effects of the position (85MCLC235, 87MI 213-05), and of the length of the alkyl chain (89MI 213-05) have been established. An optimization of the electrosynthesis of polyselenophene has been claimed (90MCLC459). Mixed thienyl–selenienyl polymers were prepared and their properties investigated by cyclic voltammetry and chronocoulometry (93SM115). Poly-2-vinylselenophene are claimed to have a higher conductivity than their sulfur analogues (92CL155), whereas iodine doped 2,5-polyselenophenes show an unexpectedly low conductivity (84MI 213-01). Some interesting applications seem to be possible with such polymeric materials. They are useful in: electric devices (84JAP(K)5943060), dry batteries (88JAP(K)6322415), microporous membranes with selective gas permeability (89JAP(K)0138125, 89JAP(K)0111139), printed circuits (90EUP413109), and antistatic coatings (90MIP463516). It is claimed that 2-azoderivatives of selenophenes are photosensitive (84JAP(K)59223433, 91JAP(K)03141362), as well as selenophene ketohyrazones (89JAP(K)0165557). The incorporation of selenophene derivatives in low percentages improves the storage properties of photographic materials (88JAP(K)63175853).

Charge transfer complexes of dibenzoselenophene and naphthoquinones have colouring properties (88DP343). A new catalyst containing the selenophene moiety (88) has been devised for the formation of polyurethanes (87MI 213-03).

\[
\text{Se} \quad \text{O} \quad \text{O}
\]

(88)