Synthesis of Selenophenes

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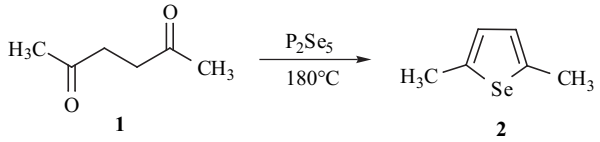
Abstract: The preparation of selenophenes is here reviewed. Although it does not include the synthesis of fused rings systems with selenophenes, the entire range of reactions is covered: from acetylenes, olefins, β-diketo compounds, furan, imine, amide, cycle contraction using sodium selenide, cycloaddition, radical cyclisation and much more.

Keywords: Selenophenes, heterocycles, selenium, ring closure, selenide, cyclisation.

I. GENERAL INTRODUCTION

Previously published work on the synthesis, reactions and applications of selenophenes has been reviewed in several monographs, series and articles [1-25].

The first preparation of the selenophene series was the 2,5-dimethylselenophene **2**, synthesised by Paal [26] in 1885, by heating acetonylaceton **1** in a sealed tube with phosphorus pentaselenide (Scheme **1**).



1 **2**

Scheme 1.

The selenophene series follows the usual rules of nomenclature of heterocyclic compounds by analogy of the corresponding thiophene derivatives using the name *selenophene*, instead of *thiophene,* for the fully unsaturated ring system containing one atom of selenium.

The analogy between these two heterocycles [27] can also be extended to the dipole moment (μ = 0.52 D) which is between tellurophene (μ = 0.46 D) and thiophene (μ = 0.54 D) [28], and also for the NMR properties [29-31]. Even if some differences can be seen on the chemical shifts for these two five-membered heterocycles [32], they are similar (-0.50ppm for 2 and 5-H, -0.23 for 3 and 4-H, -5.4ppm for C2 and C5, -1.5ppm for C3 and C4) [33,34].

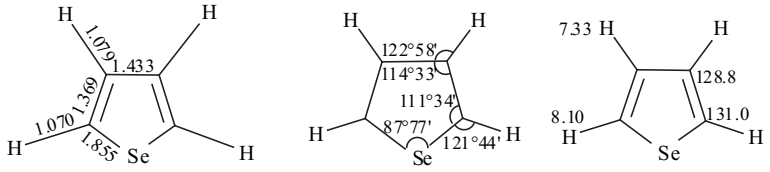
The aromatic π-electron system is obtained by the interaction of the π-electron of two carbon-carbon double bonds with the lone-pair of the selenium atom. The study of the electronic structure of five-membered heterocycles is considerably assisted by knowledge of their geometry. Mass spectrometry is a very useful tool for the identification and characterisation of selenophenes, knowing its behaviour under electronic impact [36].

The stability of selenophene can be observed in basic, soft acidic conditions and moderate oxidising agents. Nakayama [37] *et al*. found in 1996, that the atom of selenium can be oxidised to give a 1,1-dioxide selenophene like the thiophene moiety.

Selenophenes show the same typical reactivity of the electrophilic substitutions than furans or thiophenes, which occur more readily in the α- than in the β-position [38].

II. APPLICATIONS AND UTILITY OF SELENOPHENES

The applications of the organo-selenium compounds and especially selenophenes, have gained importance since this last decade. They can be found in several areas of investigations such as polymers [39], new luminescent materials [40,41], a new class of high-performance semiconductors [42], organic field-effect transistors [43], electrically conductive polymer microcapsules for ink [44], non-linear optical polyselenophene [45], cancer



Scheme 2.

Selenophene is described in the literature as a pale yellow oil (mp -38°C, bp 110°C, d 1.6003 kg.L^{-1}, n_D^{20} 1.571). Physical details such as bonds lengths (Å) and angles (°) have been determined by microwave spectral data (Scheme **2**) [35].

chemoprevention [46], selenaporphyrin [47], cholinergic ligands and modulators of monoamine receptors and transporters [48], seleno-analogue of L-tryptophan essential for the biosynthesis of proteins, hormones and alkaloids [49].

The discovery of high conductivity in some organo-selenium compounds has initiated a whole era of research. The first and most used acceptor molecule is 7,7,8,8-tetracyanoquinomethane. A selenophene [50] and a

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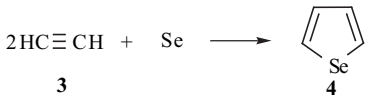
biselenophene [51] analogue has been prepared, starting from 2,5-dibromoselenophene, which shows a promising future [52]. A seleno analogue of tetrathiafulvalene has been found to be a good electron donor forming conducting molecular complexes [53]. Selenophenes β-diketons can be used as extractants for the separation and isolation of some metals such as zirconium, thorium or neodymium.

III. SYNTHESIS OF SELENOPHENES DERIVATIVES

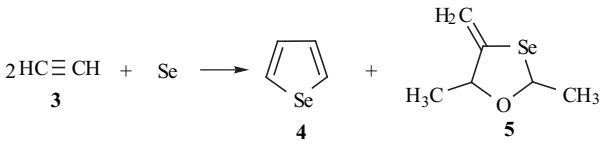
1. From Acetylenes

As indicated previously, acetylene **3** heated with elementary selenium gives the non-substituted selenophene **4** [54-61], which is the most commonly used for big amount (Scheme **3**).



Scheme 3.

In 1933, McMahon [62] described the output of this preparation by using a catalyst made up of a mixture of bauxite and aluminium selenide, improved later by Mohmand [63], by replacing sand by alumina. Gurasova [64] also described the reaction of elementary selenium with acetylene **3** in an aqueous basic medium, giving two major products of selenophene **4**. It also produced numerous seleno derivatives **5** [65].



Scheme 4.

In 1987, Voronkov [66] *and coll*. carried out a synthesis of selenophene in gas phase by the reaction of acetylene **3** with dimethyl selenide or diselenide **5** which gave 78-96% selenophene (Scheme **5**). Korchevin [67] has described a synthesis of selenophene **4** by using diphenyl diselenide **6**, and also two equivalents of acetylene in a high temperature reaction (500-580°C) [68].

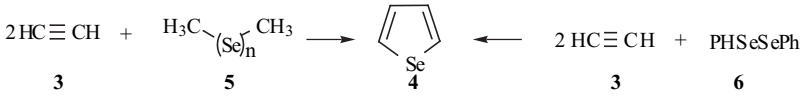
Perveev [69] *and coll*. obtained alkyl, vinyl and hydroxyl selenophenes in a reaction of hydrogen selenide with acetylenic, vinylacetic and hydroxyacetic epoxides (Scheme **6**).

The 2,5-disubstituted selenophenes were synthesised by the reaction of hydrogen selenide on a diyn-system catalysed by silver or copper ions [70-72]. About thirty other by-products formed at the time of this reaction were identified [73,74]. Another synthesis of 2,5-disubstituted selenophenes is based on the condensation of a keto-acetylenic ester with hydrogen selenide [75].

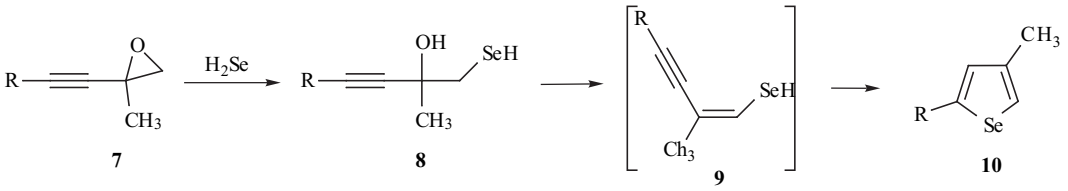
A more general synthesis of selenophenes derivatives starting from diacetylenics compounds and sodium hydrogen selenide NaHSe in methanol at 40°C has been described by Curtis (Scheme **8**) [76].

In a semi-micro synthesis, the selenophene is prepared with bis(trimethylsilyl)-3-butadiyne and hydrogen and sodium selenide generated *in situ* by Se and $NaBH_4$ in aqueous DMF [77,78]. Selenophenes were obtained as major compound in the reaction between vinylacetylene and the selenide anion, generated from elemental selenium in DMSO at 100-120°C. The reaction of the acetylenic compound with the elemental selenium at 220°C gave the selenolo[3,2-*b*]selenophene [79].

Trofimov [80] described the preparation of an unexpected selenophene by the reaction of a butenyne compound with sodium selenide anion in a basic medium.



Scheme 5.



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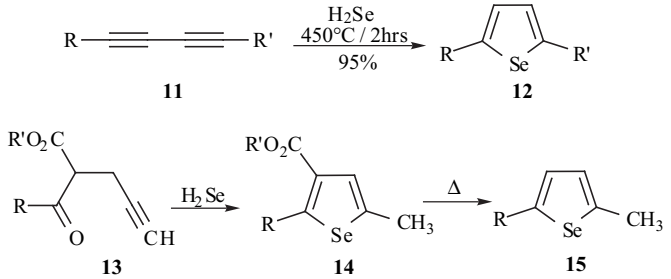

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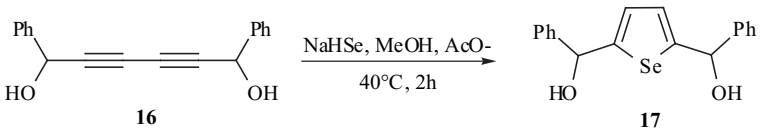
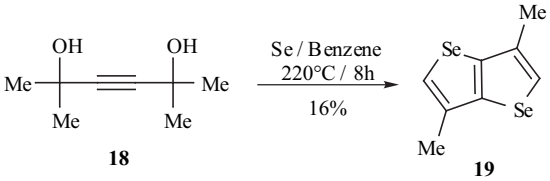


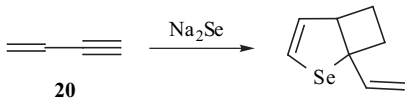
16 **17**

Scheme 8.



18 **19**

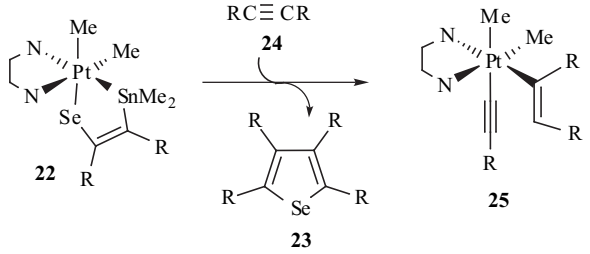
Scheme 9.



20 **21**

Scheme 10.

The platinum complex reacted with an excess RCCR to give a mixture of organoselenium compounds and an unexpected organoplatinum(IV) complex (Scheme **11**) [81].



22 **23** **25**

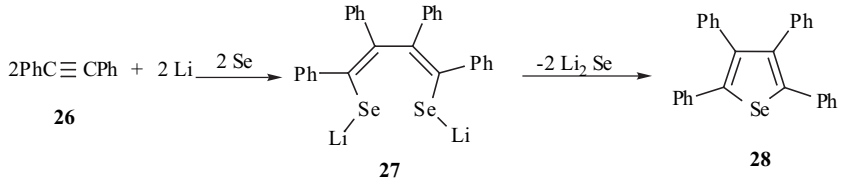
Scheme 11.

The reaction of diphenylacetylene **26** with lithium, generate *in situ* the dilithiated diphenylbutadiene, followed by the addition of elemental selenium that gives the selenophene **28** by the insertion of selenium, and followed by elimination of lithium selenide Li_2Se (Scheme **12**) [82].

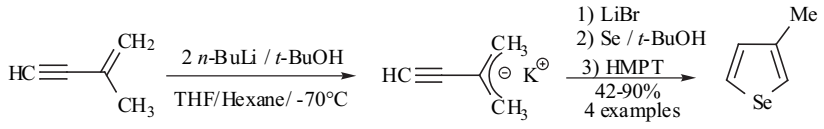
Addition at -70°C of a solution of 30g tBuOH in 50mL of THF yielded a mixture of **29** (0.10mol) and 1 eq. of n-BuLi in 110mL of THF. The temperature is allowed to rise -5°C before adding LiBr (0.25mol) which gives a slight-yellow precipitate. Powdered red selenium (0.11 mol) was introduced in one portion at -45°C. Temperature is raised to 0°C and t-BuOH is added at -20°C, followed by hexamethylphosphoric triamide at 0°C. The mixture is stirred for 45 to 90 min. Subsequent addition of water (500mL) followed by usual work-up give 3-methyl selenophene in 42 to 90 % after a purification on silica gel using hexane as eluant. This synthesis described by Brandsma [83] in 1983 has been confirmed by Catel [84] in 1987 (Scheme **12**).

Nakayama [85] *and coll*. reported the preparation of an intermediate tetraethylethanediselenoamide **33** in 81% and its reaction with DMAD in refluxing chlorobenzene, followed by the thermal extrusion of selenium to produce dimethyl 4,5-bis(diethylamino)selenophene-2,3-dicarboxylate **35** in 87%.

Zafrani [86] *et al*. described the conversion of the propargylic selenides **36** to isomeric selenophenes **37** and **38** by the reaction with *t*-BuOK in dry THF at room temperature in 21% overall yield (ratio 2:3) (Scheme **14**).

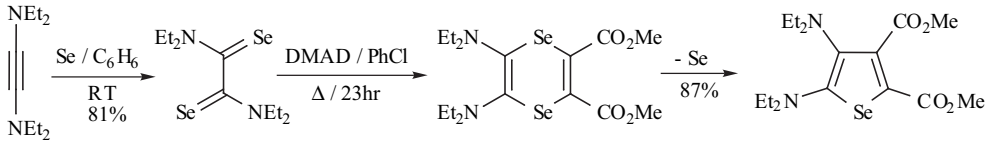


26 **27** **28**



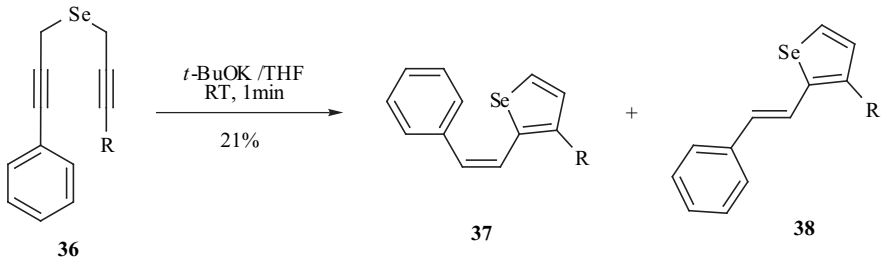
29 **30** **31**

Scheme 12.



32 **33** **34** **35**

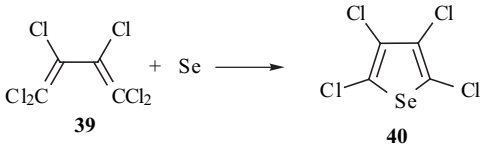
Scheme 13.



Scheme 14.

2. From Olefins

Yur'ev and Kmel'nitskii [87] have developed a synthesis of selenophene and analogues by the reaction of paraffins, olefins or conjugated dienes with selenium dioxide in the presence of chromic acid on alumina at 450-500°C. Arbusov and Kataev [88,89] have used methylated analogues starting from conjugated dienes and elemental selenium at 380-420°C. Tetrachloroselenophene is formed by the reaction of selenium with an equimolar quantity of hexachlorobutadiene at 250°C [90].



Scheme 15.

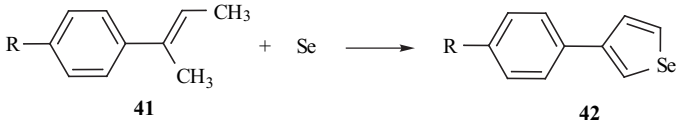
Monoarylselenophenes **42** can be prepared by interaction between a styrene derivative **41** with elemental selenium [91].

Okuma has demonstrated that the reaction of tetracyanoethylene **44** (TCNE) with the seleno derivative **43**, affords an unexpected selenophene **45** in refluxing toluene (Scheme **17**) [92].

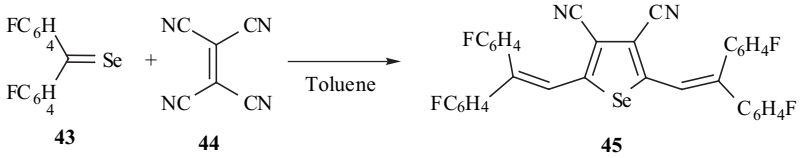
As described in a German patent, fusion of tetraphenylcyclopentadienone **46** with elemental selenium gives the tetraphenylselenophene **47** (Scheme **18**) [93].

A more recent synthesis of 3,4 dimethylselenophene **49** is described by Paulmier [94]. The 2,3-dimethyl-1,3-butadiene **48** is introduced by a nitrogen stream in a glass tube heated at 450°C and containing gaseous selenium and fragments of pyrex. Starting from the same butadiene, Mamedov has realised a synthesis of 2,3-disubstituted selenophene by using selenium dioxide SeO_2 and a rare zeolite catalyst [95].

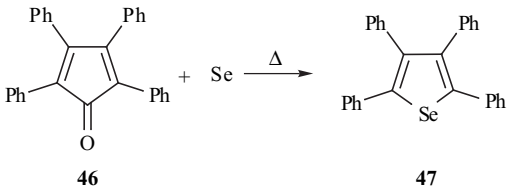
Treatment of cinnamaldehyde **50** with a diboron selenide **51** and 2,3-dimethyl-1,3-butadiene **48** gives a dihydro selenophene **52** (Scheme **20**) [96].



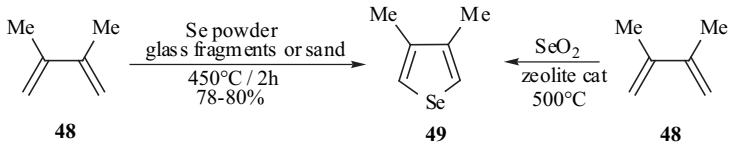
Scheme 16.



Scheme 17.



Scheme 18.



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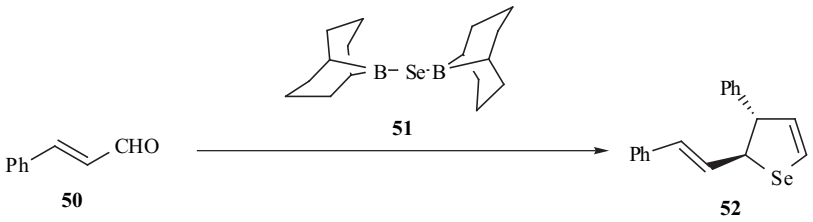
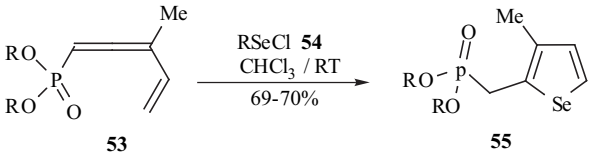


Scheme 20.

Angelov [97] has synthesised a phosphated selenophene **55** by the reaction of a selenochloride derivative **54** and a phosphated compound **53** (Scheme **21**) [98].



Scheme 21.

Potapov hypothesised that the formation of 2,5-diphenylselenophene **57** proceeds according to a radical chain mechanism. A possible route to this synthesis includes homolytic rupture of the Se-C bond with the formation of a radical intermediate (Scheme **22**) [99].

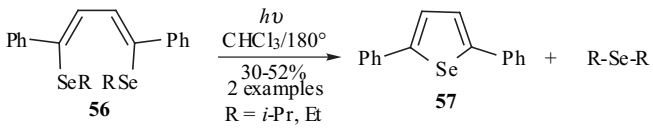
The tetraphenylselenophene **28** has been obtained from the 1,4-dilithiotetraphenylbutadiene **58** and Se_2Br_2, and from the 1,4-diiodotetraphenylbutadiene **59** and lithium selenide [100]. This reaction may work by using directly elemental selenium instead of Se_2Br_2 [101].

The bis-γ,γ-dimethylallenyl selenide **60** is converted by spontaneous cycloaromatisation in 3-isopropenyl-4-isopropylselenophene **61** (Scheme **24**) [102,103].

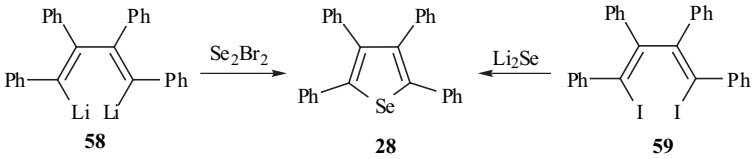
The dimethyl-4-arylselenophene-2,3-dicarboxylate **63** has been isolated with other by-products from the reaction of a solution of potassium 2-*p*-tolylethyneselenolate **62** and dimethyl acetylenedicarboxylate (DMAD) in tetrahydrofuran at room temperature for 2hrs (Scheme **25**) [104].

Voronkov has shown that a cyclisation can occur when vinyl selenide **64** is heated at 450°C to afford the corresponding non-substituted selenophene **4** (Scheme **26**) [105].

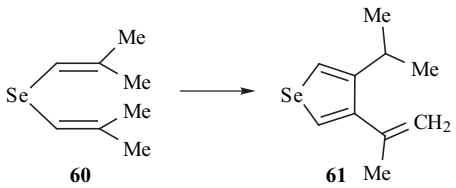
3-(phenylsulfinyl)-selenophene **66** was obtained with 62% overall yield from the reaction of the 1,3,4-alkatrienyl



Scheme 22.



Scheme 23.



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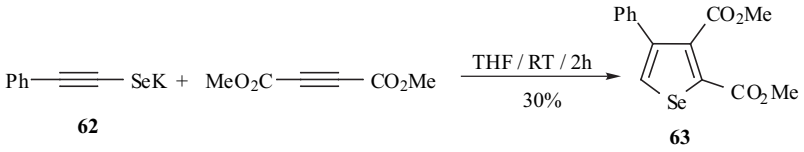
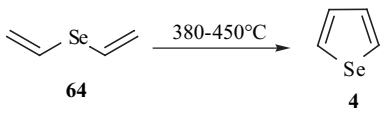
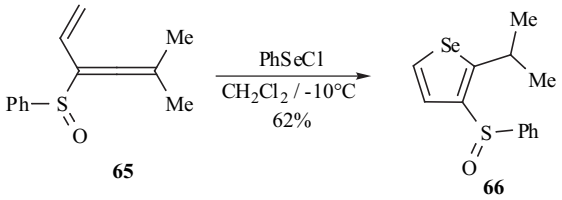


Scheme 25.



Scheme 26.

sulfoxide **65** with phenylselenyl chloride in dry dichloromethane at -10°C (Scheme **27**) [106].



Scheme 27.

3. From β-Diketo Compounds

3,4-Diarylselenophenes **69** were synthesised by condensation of the selenodiacetic methyl ester **67** with dibenzoyl **68**, followed by hydrolysis and decarboxylation (Scheme **28**) [107,108]. A similar synthesis has been described by Cava for 3,4-dihydroxyselenophenes **73** [109]. Selenodiacetic diethyl ester **71**, condensed with diethyl-oxalate **72** in a basic mixture of sodium ethylate in ethanol and gave the corresponding 3,4-hydroxy derivative.

Phosphorous pentaselenide (or triselenide [110]), prepared from amorphous red selenium, can give a cyclisation of 1,4-diketon **74** to obtain 2,3,4,5-substituted selenophenes **75** with good yields (Scheme **29**) [111-114].

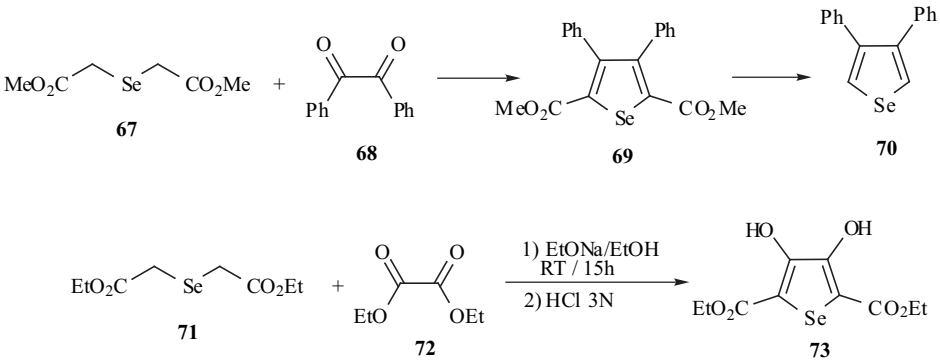
The trimer glyoxal **77** can react in a basic media with a selenide **76** to give a dibenzoylselenophene **78** [115].

The synthesis of selenophenes using the titan tetra-chloride, inducts, a coupling reaction of pinacol to form a diol derivate. Heating this above diol **80** with a catalytic amount of *p*-toluenesulfonic acid in refluxing toluene for 1 hr, afforded the corresponding selenophene **81** (Scheme **31**) [116,118].

A recent synthesis of 5-alkyl-2-selenophenecarboxylate, *via* the direct oxidation of 2,4-alkadienoïc ester with the selenium dioxide, has been described by Tsuboi [119].

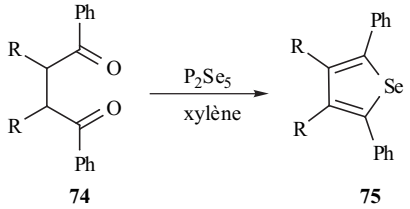
4. Cycle Transformation

Yur'ev [120] has shown that furans **82** can be converted in selenophenes **4** by using hydrogen selenide in the presence of magnesium oxide at 450°C. This mechanism has been studied by Kharchenko, who gives a diketo compound as intermediate (Scheme **32**) [121].

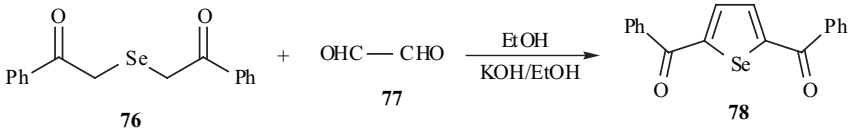


Scheme 28.

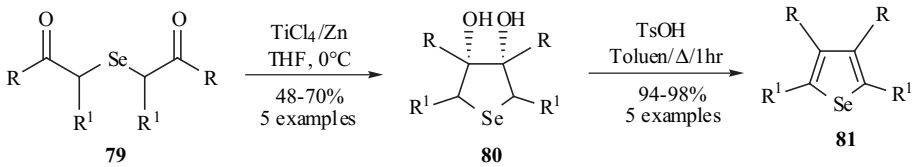
The selenopyran ring system **83** is a good precursor of selenophene by its oxidation with selenium oxide [122], by



Scheme 29.

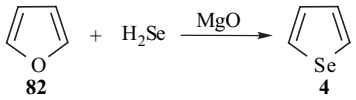


Scheme 30.

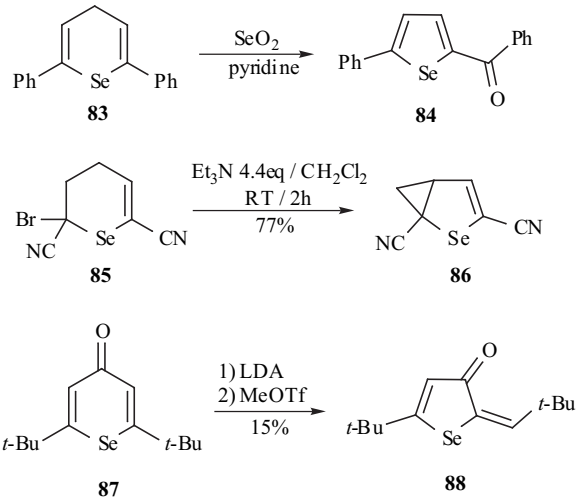


Scheme 31.

a rearrangement (**85** to **86**) [123], and by a lithiation of **87** with LDA, followed by quenching with methyl triflate in 15% yield (Scheme **33**) [124].

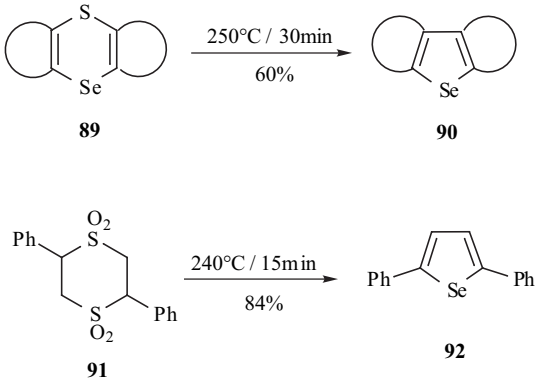


Scheme 32.



Scheme 33.

A selenophene compound **90** can be smoothly obtained from the corresponding 1,4-diselenin derivatives **89** on pyrolysis at 250°C [125]. Heating 2,5-diphenyl-1,4-dithiin 1,1,4,4-tetroxide **91** with elemental selenium at 240°C for 15 min, afforded the 2,5-diphenyl-selenophene **92** in 84% yield [126].



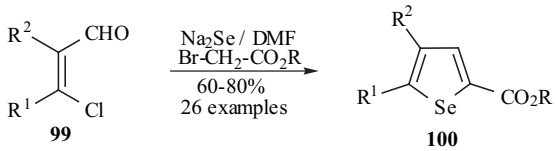
Scheme 34.

The reaction of 4-phenyl- or (2-thienyl)-1,2,3-selenadiazoles **93** with 10 equivalents of arylacetylenes **94** leads to the formation of 2,5-diarylselenophenes **95** in moderate to good yield and 1,4-diraylbuta-1,3-diynes as by-products (Scheme **35**) [127,128].

Nakayama *and coll.* [129] have developed a synthesis of nitrogenated, oxygenated and selenated heterocycles **98**, starting from thiophene **96** by oxidation of the atom of sulfur followed by an extrusion of a molecule of SO_2, in order to replace it by elemental selenium (Scheme **36**).

5. Using Sodium Selenide Na_2Se

Kirsch has found a general method of synthesis of 2,3,4-substituted-selenophenes **100** by a Fiesselmann's reaction implying a β-chloroacrolein **99**, an aldehyde, sodium selenide and an alkyl bromoacetate (Scheme **37**) [130,131].



Scheme 37.

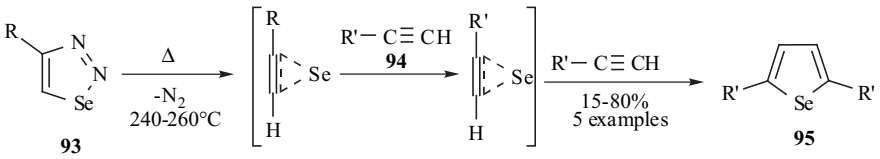
Kirsch has extended this way of synthesis of 2,3,4-selenophenes **102** by using halogeno-benzyls bearing electron withdrawing group, still starting from β-chloroacroleins [132].

A bitellurophene containing a bisacetylenic spacer **103** can react with freshly prepared sodium selenide and cyclise to give the selenophene bi-tellurophene **104** (Scheme **39**) [133].

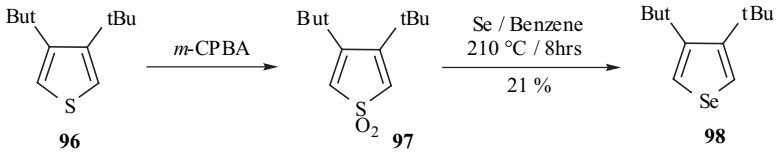
A solution of the dichloride **105** in tetrahydrofuran stirred for 16h with sodium selenide, afforded the corresponding selenophene **106** (Scheme **40**) [134].

Successive reactions of β-cinnamonitrile with sodium selenide, produced *in situ* with elemental selenium and sodium borohydride, and α-chloro-keto compounds have been used for the preparation of 5-substituted-4-amino-2-phenylselenophene-3-carbonitrile [135].

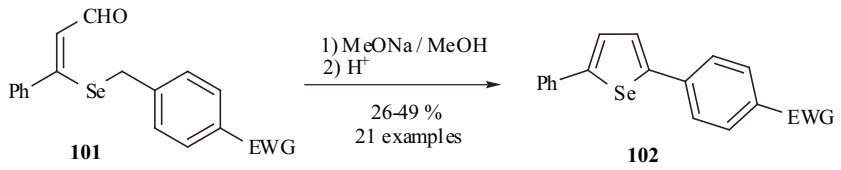
A racemic mixture of 1,3-butadiene diepoxide **107** was allowed to react with a freshly prepared aqueous solution of



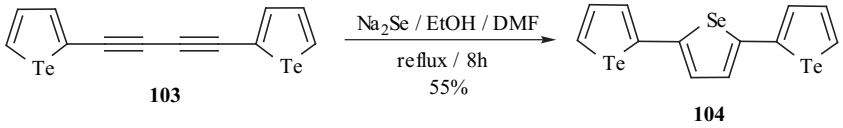
Scheme 35.



Scheme 36.

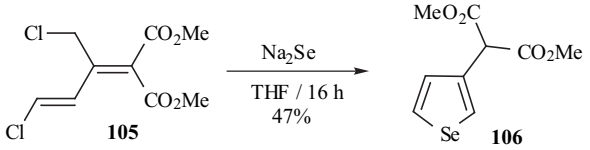


Scheme 38.

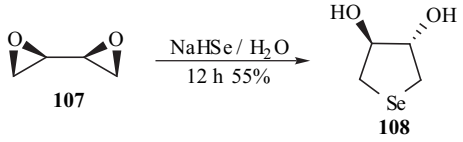


Scheme 39.

sodium hydrogenoselenide in water, to give a 3,4-hydroxy tetrahydroselenophene **108** (Scheme **41**) [136].

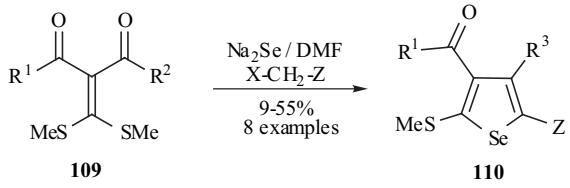


Scheme 40.



Scheme 41.

A very useful method of synthesis of selenophenes series is to use ketene dithioacetals **109** as starting material. These are easily prepared from a β-diketo compounds and carbon disulfide in a basic media, followed by the addition of methyl iodide. A freshly prepared suspension of sodium selenide in DMF is added at room temperature, followed by an activated methylen compound and a soft base such as potassium carbonate. The seleno intermediate undergoes a Dieckman-type cyclisation to give selenophenes **110** in moderate yield [137].

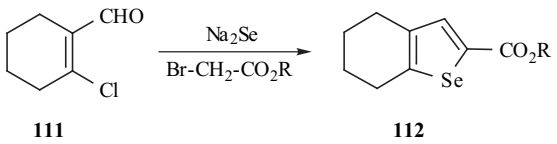


R^1 = Me, Ph, OEt; R^2=Me, Ph, OEt; Z=CO_2R, CN, Ac, Bz

Scheme 42.

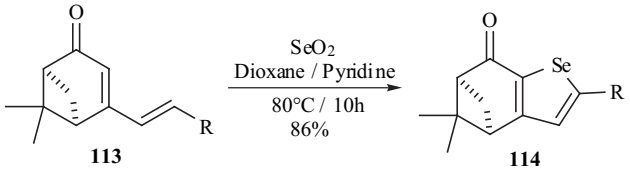
6. Tetrahydrobenzo[*b*]selenophene

Sodium selenide reacts with chloroacrolein **111** to remove the atom of chlorine and condense with activated methylene which undergoes a Dieckmann-type cyclisation to give the selenophene **112** (Scheme **43**) [138].



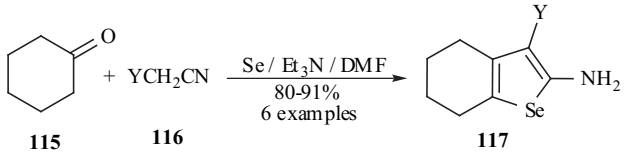
Scheme 43.

Another synthesis of tetrahydrobenzo*[b]*selenophene **114** has been set up, starting from a diene **113**, bearing a keto group at the position C-1 with selenium dioxide [139].



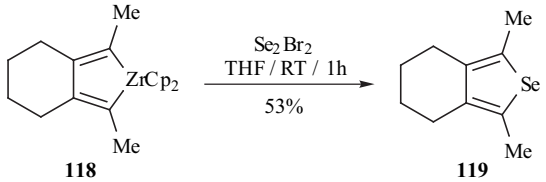
Scheme 44

In the Gewald's reaction, generally used for the preparation of thiophenes, can also lead to selenophene. Cyclohexanone **115**, ethyl cyanoacetate **116** and selenium, in the presence of a base, give the corresponding selenophene **117** [140,141].



Scheme 45.

A transfer of zirconium can be carried out of a metal cycle to the corresponding selenophene in a one-pot reaction [142]. The synthesis of selenium-containing analogues nicely demonstrate that the zirconacycle **118** need not be isolated and one-pot synthesis can be handled. The zirconacycle can be generated *in situ* and then treated by Se_2Br_2 to give selenophene **119** in 53% yield (Scheme **46**) [143].

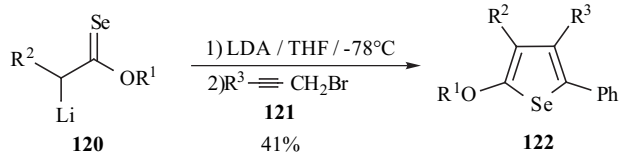


Scheme 46.

7. From Selenoester

The reaction of propargyl bromide **121** with lithium 1-alkoxyselenolate **120** was found to proceed through a propargylic rearrangement to generate an allenic selenoic O-

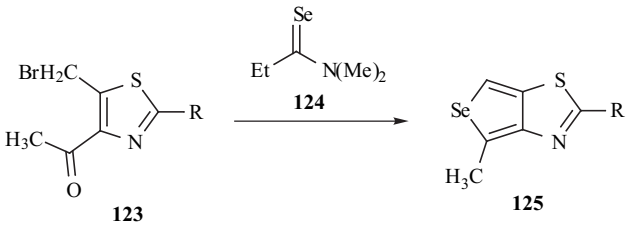
ester which led to poly substituted selenophenes **122** in moderate yields under reflux [144].



120 **121** 41% **122**

Scheme 47.

The selenolothiazole **125** is prepared starting from commercial thiazole **123** which can react with the *N,N*-diethylselenopropionamide **124** (Scheme **48**) [145].



123 **124** **125**

Scheme 48.

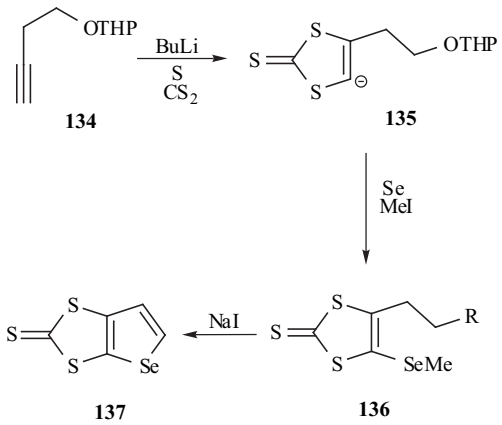
Selenothioic acids S-alkyl esters **126** were treated with triethylamine and cadmium acetate to give symmetrically substituted selenophenes **127**, whereas the similar reaction in the presence of alkyl halides afforded ketene selenothio-acetals in moderate yields [146,147].

N'-selenoacylamidines **128** can react with many dienophiles. When the Diels-Alder's reaction is made at 0°C, the intermediate 4*H*-1,3-selenazine **129** is formed. This product, after thermolysis in refluxing dichloromethane, gives another seleno intermediate **130**, which rearranges and affords the selenophene **131** by heating in ethanol [148].

8. Fused Systems

The selenium oxychloride reacts on the diacetonitrile compound **132** to form the dinitrile selenophene **133** (Scheme **51**) [149].

The organolithiated compound **135** formed starting from butyl lithium and CS_2 reacts with elemental selenium followed by addition of methyl iodide to give the intermediate **136**. The latter cyclise in DDQ to afford the fused selenophene **137** [150].

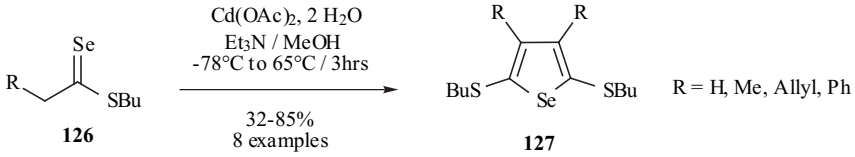


134 **135** **137** **136**

Scheme 52.

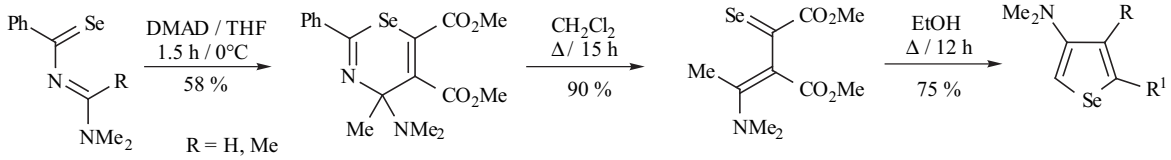
The reaction between selenomethyl-selenophene **138** and methyl bromoacetate give the selenoloselenophene **139** (Scheme **53**) [151].

The thiophene **140** endowed with two halomethyl groups in the position 3 and 4 can react with sodium selenide to give the selenolo[3,4-*c*]thiophene **141** [152].



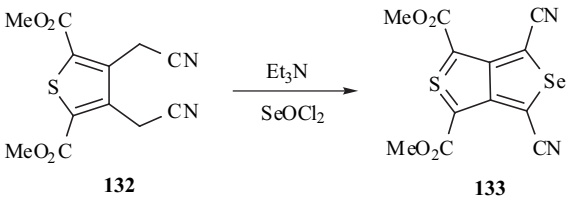
126 **127**

Scheme 49.



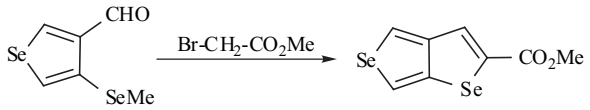
128 **129** **130** **131**

Scheme 50.



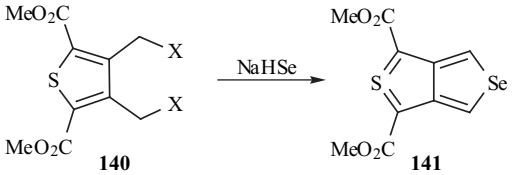
132 **133**

Scheme 51.



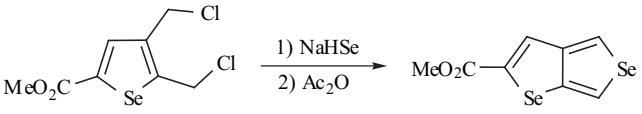
138 **139**

Scheme 53.



140 **141**

Scheme 54.

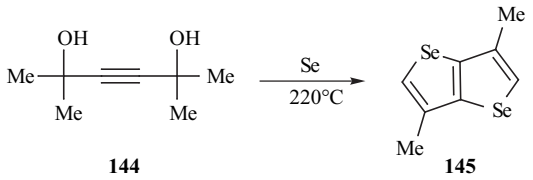


142 **143**

Scheme 55.

Gronowitz has developed a similar synthesis of selenolo[3,4-*b*]selenophene **143** from 2,3-dichoromethylene-selenophene **142** and sodium hydrogenselenide [153].

The acetylenic compound **144** condenses with elemental selenium at 220°C to produce the selenolo[3,2-*b*]seleno-phene **145** (Scheme **56**) [154].



144 **145**

Scheme 56.

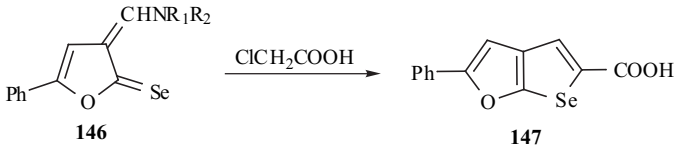
Treatment of furan **146** with 2-chloro-acetic acid followed by the elimination of an amino group gives the selenolo[2,3-*b*]furan **147** [155].

The selenophene moiety can be also built from a five-membered heterocycle **148** if bearing a methylsulfanyl group in α-position combined with one or two electronwith-drawing group. Selenolo[2,3-*b*]selenophenes and thiophenes **149** have been synthesised by this way from selenophenes (Scheme **58**) [156].

9. Cycloaddition

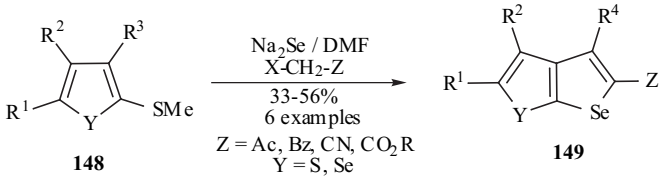
The cycloaddition of selenide **150** with DMAD in dry dioxane kept at 120°C for 42h gives a dihydroselenophene **151** in 55% yield [157].

Treatment of cyclopentadienyldicarbonylcobalt **152** with DMAD in toluen at reflux, in the presence of elemental selenium produce three products from which selenophene **153** (Scheme **60**) [158].



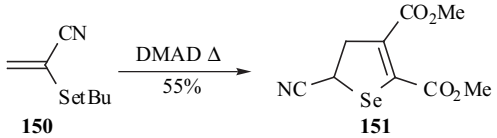
146 **147**

Scheme 57.



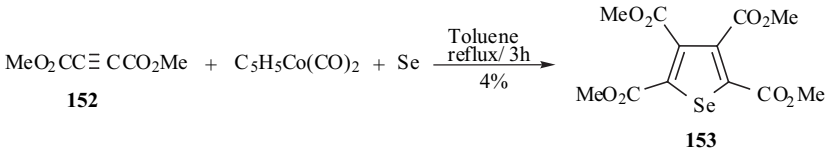
148 **149**

Scheme 58.



150 **151**

Scheme 59.



152 **153**

Scheme 60.

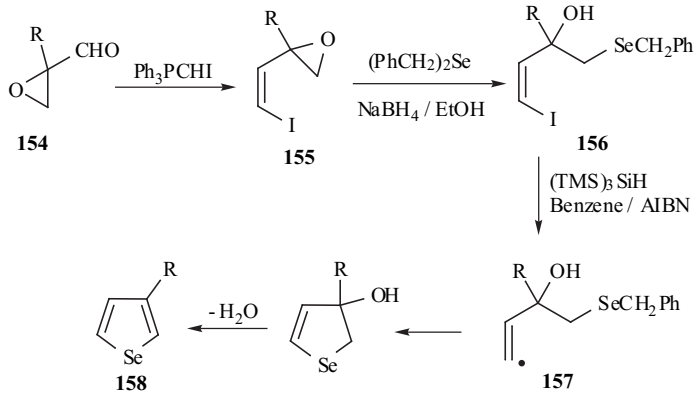
10. Radicals

In an attempt to expand the synthetic utility of homolytic substitution chemistry, the intramolecular attack on vinyl and aryl radicals at the selenium atom in alkyl selenides have been investigated [159]. Vinyl and aryl iodides react with (trimethylsilyl)silane (TTMSS) to afford selenophenes and benzoselenophenes in excellent yield. When the seleno precursor **156** is treated with TTMSS in benzene at 80°C (AIBN initiator), quantititive conversion to 3-substituted selenophene **158** is observed (Scheme **61**).

The tiohydroxamic ester procedure has been chosen to generate the radical, without the need for chain carriers such as tri-n-butyltin or (trimethylsilyl)sylil radicals, species known to attack both alkyl selenides and alkyl bromides. When the hydroxamic ester **158** was dissolved in [$^2He_6$]benzene in an NMR experiment, and the sample irrradiated with a 150W tungsten lamp, the solution became colourless after 5 min. 270MHz NMR spectroscopy indicated the formation of tetrahydroselenophene **160** in 79% yield, clearly demonstrating the efficiency of the homolytic substitution process on selenium (Scheme **62**) [160].

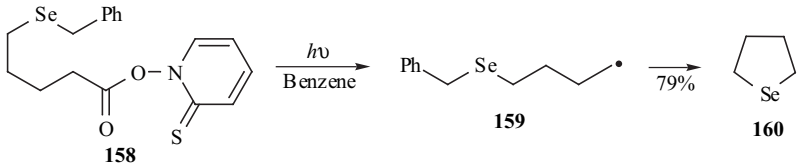
11. From Imines

2,4-Diarylselenophenes **162** were synthesised by amalgamating imines **161** and aromatic ketones with elemental selenium at 240°C (Scheme **63**) [161-163].



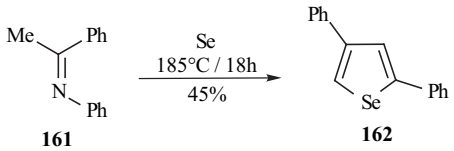
154 **155** **156** **157** **158**

Scheme 61.



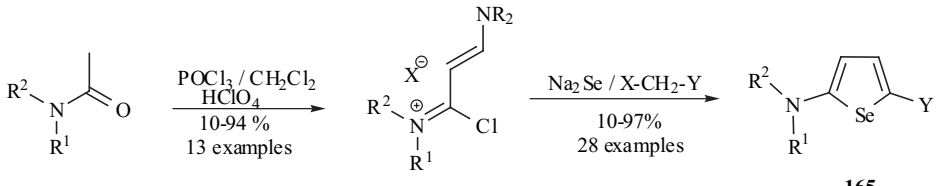
158 **159** **160**

Scheme 62.



161 **162**

Scheme 63.



163 **164** **165**

Scheme 64.

12. From Amides

Hartmann and Zug have developed a synthesis of thiophenes and selenophenes starting from an amide **163**. A Vilsmeier-Haack reaction followed by an addition of sodium selenide gives an *N,N'*-presubstituted-3-aminothioacrylamide **164**. This compound is allowed to react with activated methylen compounds to produce aminoselenophenes **165**, substituted at positions 2 and 5 (Scheme **64**) [164-166].

IV. GENERAL CONCLUSION AND OUTLOOK

To conclude on this article, I would say that the synthesis of selenophenes can be made in a lot of different pathways. Elemental selenium has been widely used when combined with acetylenes in early century and, nowadays, less toxic reagents like sodium selenide or metal eneselenolate [167] take place to prepare safely selenium-containing heterocycles. On the basis of this knowledge, selenophenes can be used as good precursors of a wide variety of organoselenium compounds, some of which are of great interest from a synthetic and as depicted in paragraph II, biological and pharmaceutical point of view. Although further synthetic approach may not be studied, selenophene ring system constitutes a very useful tool in applied heterocyclic chemistry, and we will see some of these results in the near future.

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