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PERSPECTIVE

New development of synthesis and reactivity of seleno- and tellurophenes

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Due to the many new and remarkable findings and applications that have been published in recent years in seleno- and tellurophene chemistry, this review revisits the different aspects of this chemistry, including synthesis, reactivity and applications in the field of heterocycles.

1. Introduction

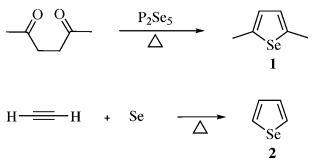
Chalcogenides are widely studied agents with a diverse array of biological effects.[1] In this context, the introduction of chalcogen group compounds into organic molecules has found wide utility because of the extraordinary number of very different reactions. Chalcogenides are attractive synthetic targets because of their chemo-, regio-, and stereo-selective reactions,[2] their use in a wide variety of functional groups, avoiding protection group chemistry, and their useful biological activities.[3] The chalcogen group can be introduced in an organic substrate *via* both nucleophile and electrophile reagents. After introduction into an organic substrate, the organochalcogen groups are easily removed by selenoxide *syn* elimination[4] and [2,3] sigmatropic rearrangement.[5] The carbon–chalcogen bond can also be replaced by a carbon–hydrogen,[6] carbon–halogen,[7] carbon–lithium,[8] or carbon–carbon bond.[9]

Among chalcogenides, heterocycles containing chalcogen atoms play an important role in organic synthesis, especially in the development of methodologies for the synthesis and reactivity of substituted telluro- and selenophenes.[10] One reason for this is their widely varied synthetic organochemical potential. The chalcogen atom exercises a stabilizing effect on neighboring positive as well as negative charges. This makes the carbon responsive towards both nucleophilic and electrophilic attack, an extremely useful feature in organic synthesis. In addition, chalcogenophene heterocycles (Se, Te) have numerous uses in the fields of biochemistry, physical organic chemistry, materials chemistry and organic synthesis. For example, selenophene oligomers are compounds of current interest because many show photoenhanced biological activities[11] and crystalline polymerizations.[12] Thus, a wide variety of oligomers and related chalcogen compounds, including mixed chalcogen–pyrrole oligomers, have been synthesized mainly with the expectation of obtaining excellent precursor compounds for molecular devices and electroconductive polymers.[13] In addition, chalcogenophenes are widely studied agents with a diverse array of biological effects, these include antioxidant action,[14] antinociceptive[15] and antiinflammatory properties[16] as well as efficacy as maturation inducing agents.[17]

Due to the growing importance and utility of these heterocycles in organic synthesis and due to the many remarkable findings and applications recently published, the purpose of this review is to revisit different aspects of seleno- and tellurophenes chemistry, including their reactivity and applications in the field of heterocycles.

2. Selenophenes

Selenophene heterocycles are an important class of compounds because of their excellent biological effects, including, antitumoral,[18] anticonvulsant,[19] and other medicinal applications,[20] as well as being biologically active substances exhibiting hepatoprotective,[21] antinociceptive,[22] antihypertensive,[23] and fungicidal properties.[24] In addition, these compounds are very useful synthetic intermediates and can function as suitable building blocks to synthesize other biologically active compounds, such as natural products. Many synthetic methods, including electrophilic cyclization and transition metal catalyzed intramolecular cyclization, have been successfully employed in the synthesis of these selenium-heterocycles. One of the first preparations in the selenophene series was 2,5-dimethylselenophene **1**, reported by Paal in 1885 *via* reaction of hexane-2,5-dione with phosporus pentaselenide in a sealed vessel at high temperatures (Scheme 1).[25] Nowadays, the most user-friendly system for the production of non-substituted selenophene **2**, on a large scale, is the heating of acetylene with selenium powder. This low cost system provides selenophene in good yields and high purity (Scheme 1).[26] Starting from acetylene, the construction of selenophene was developed by McMahon, in 1933, employing bauxite and aluminium selenide as the catalyst.[27] Lately, this method was improved using alumina as a catalyst.[28]



Scheme 1

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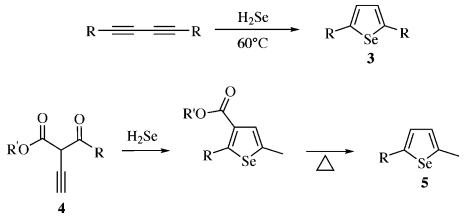
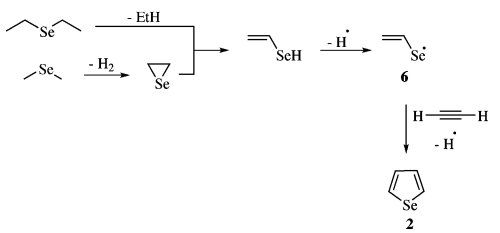
Similar protocol was reported by Gurasova who described the preparation of selenophene by reaction of acetylene with elemental selenium in aqueous basic medium.[29]

Starting from diyn-system, the construction of selenophenes **3** was developed employing hydrogen selenide and copper or silver as catalysts (Scheme 2). In a typical experiment, ethanol (40 ml) containing sodium ethoxide (0.02 mol) and silver acetate (5 mg) was saturated with hydrogen selenide at room temperature. After that, diyn (0.01 mol) was added and the mixture was warmed on a water bath at 60 °C to obtain selenophene derivatives in yields of 46% to 97%.[30] In addition, keto-acetylenic esters **4** were converted to the corresponding 2,5-disubstituted selenophenes **5** *via* a condensation reaction with hydrogen selenide (Scheme 2).[31]



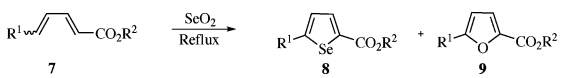
Scheme 2

Selenophene synthesis was achieved under high temperatures (from 400 to 600 °C) in a gas-phase reaction of dimethyl and diethyl selenides with acetylene. Nevertheless after an initial period of reaction an accumulation of elemental selenium in the reactor hampered the isolation of selenophene in a pure state decreasing the yields. The addition of 10–50 mol% of methanol stabilized the operation for several hours increasing the yield from 72% to almost quantitative yields. It was proposed that the thermal reaction of dialkyl selenide gives the vinylselenyl radical **6** which is trapped by acetylene ot obtain the desired selenophene (Scheme 3).[32]



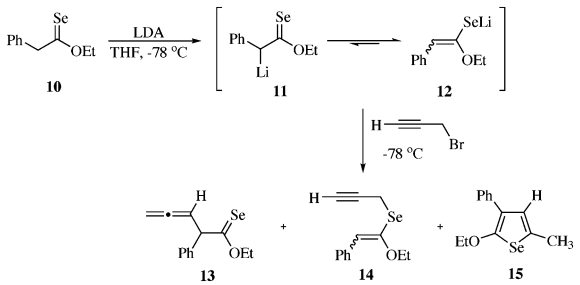
Scheme 3

Functionalized selenophenes **8** were prepared from 2,4-alkadienoic esters **7** by oxidation reaction with SeO_2 (1.1 equivalent) in benzene at reflux. In most cases, the formation of furan derivatives **9**, as side product, was observed. It is important to point out that the reaction time was crucial for the outcome of the oxidation. While a short reaction time (0.5 h) gave selenophenes **8** in moderate yields, a longer reaction time (2 h) gave predominantly furan derivatives **9** (Scheme 4).[33]



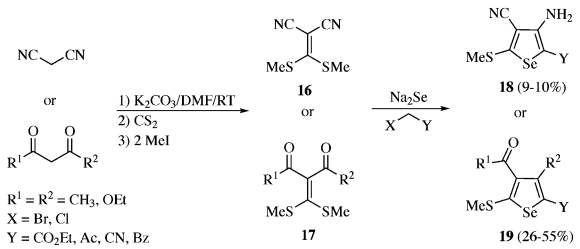
Scheme 4

Poly-substituted selenophene **15** was synthesized by lithium enolate nucleophile chemistry. Lithium 1-alkoxyeneselenolate **11**, which disclosed an equilibrium between eneselenol **12**, was readily prepared by the treatment of selenoester **10** with lithium diisopropylamide (LDA). The treatment of the nucleophile **11**/**12** with propargyl bromide at −78 °C formed the selenophene **15** as the major product together with selenoester **13** and propargyl selenides **14** (Scheme 5).[34]



Scheme 5

A significant study for the synthesis of substituted selenophenes **18** and **19**, involving a two-step reaction using sodium selenide,[35] ketene dithioacetals **16** and **17** and ethyl bromoacetate was developed by Kirsch and co-workers.[36] The reaction is believed to proceed *via* an addition-elimination pathway before cyclization and is performed on a large scale (10 mmol) (Scheme 6).

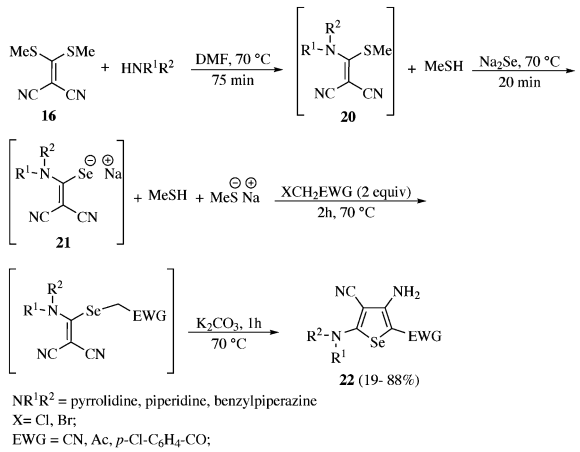


Scheme 6

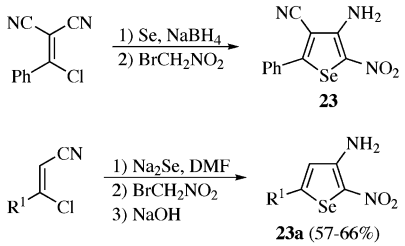
This successful protocol was also extended for the reaction between dithioacetals **16** and a secondary amine. Initially this reaction formed the intermediate ketene *N*,*S*-acetals **20**, adding sodium selenide gave the intermediate selenolate **21** and liberated 1 equivalent of methyl thiolate in the reaction media. The first equivalent of ethyl bromoacetate was consumed by the methyl thiol so that 2 equivalents of the activated halide were required. Finally, potassium carbonate was added to obtain the selenophenes **22** (Scheme 7).[37]

The same group provided a variation of the previous study, adding β-chloroacrylonitriles to a freshly prepared sodium selenide using DMF as a solvent at 60 °C. After the formation of the selenolate, the bromonitromethane was added dropwise at 0 °C then heated to 60 °C for 2 h. The addition of sodium hydroxide to the reaction gave the cyclized 3-amino-2-nitroselenophenes product **23** in moderate to good yields (Scheme 8).[38]

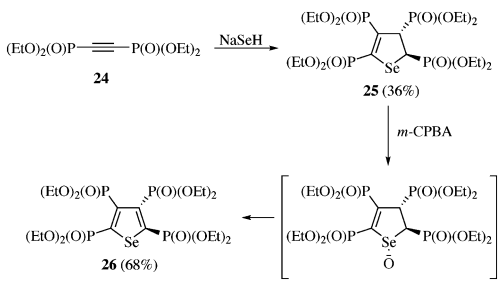
Sasaki and co-workers published a very straightforward synthesis of phosphoryl attached selenophenes. In this work, exploring the reactivity of diphosphorylacetylene **24** with sodium hydroselenide they obtained 2,3-dihydrotetraphosphorylselenophene **25**. Further oxidation with *m*-CPBA, followed by dehydratation led to tetraphosphorylselenophene **26** in 68% yield (Scheme 9).[39]



Scheme 7



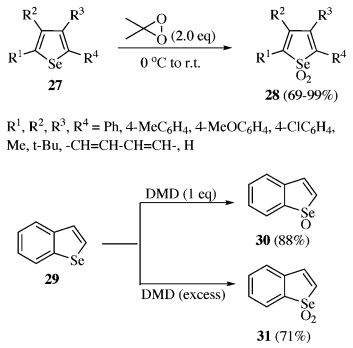
Scheme 8



Scheme 9

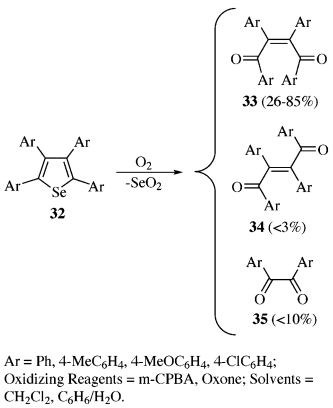
Following their work on the oxidation of selenophenes Nakayama and co-workers reported the first synthesis of selenophene 1,1-dioxides **28** employing dimethyldioxirane (DMD) as the oxidizing agent.[40] Treatment of tetraphenylselenophene **27** with DMD (2.2 equivalents) in acetone for 1 h at 0 °C allowed the corresponding oxide in 66–99% yield (Scheme 10). The reaction scope was extended to different substituents affording the respective selenoxides with reasonable to good yields. Oxidation of selenophenes **29** with 1 equimolar amount of DMD resulted in almost quantitative convertion to **30**, which was not isolated due its labile character. Nevertheless the oxidation of benzoselenophene **29** with different reaction times and using different molar amounts of DMD enabled the isolation of the benzoselenophene 1-oxide **30** and benzoselenophene 1,1-dioxide **31** in 88% and 71% yields, respectively (Scheme 10).

In a closely related investigation, the same group reported that selenophenes **32** experienced oxidative ring opening when *m*-chloroperbenzoic acid was used instead of dimethyldioxirane. Thus, selenium dioxide elimination occurred to give a *cis*/*trans*

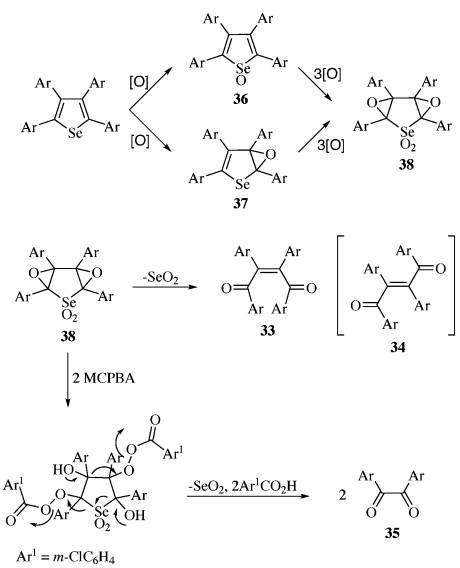


Scheme 10

mixture of 1,2-dibenzoyl-1,2-diphenylethylenes **33** and **34** and traces of benzyl **35** as products (Scheme 11).[41] The mechanism proposed for this reaction included the formation of seloxides **36** (oxidation to give the epoxide **37** can also be considered), which was then oxidized by three equivalents of *m*-chloroperbenzoic acid to give **38**. Selenium dioxide elimination from **38** affords the mixture of *cis*/*trans* product **33** and **34**. Additional oxidation of **38** followed by terminal decomposition gave benzyl **35** (Scheme 12).

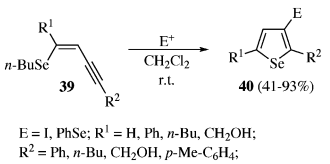


Scheme 11



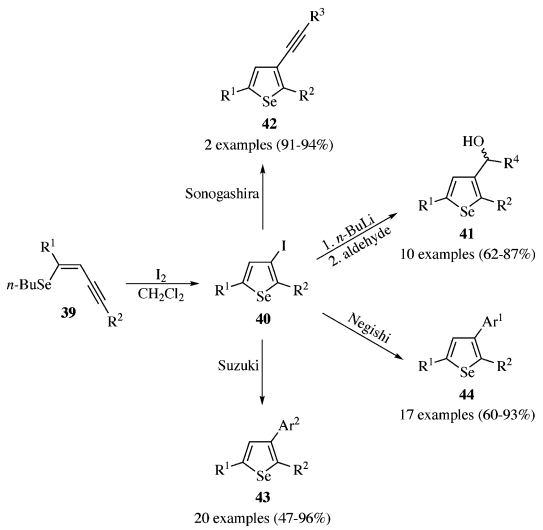
Scheme 12

In 2007, we described a general approach to the preparation of 3-substituted selenophenes **40** *via* electrophilic cyclization reaction of (*Z*)-selenoenynes **39** (Scheme 13).[42] We observed that the nature of solvent and structure of (*Z*)-selenoenyne were important to the cyclization reaction. Regarding the influence of the solvent, better results were achieved using CH_2Cl_2, which furnished the desired product in high yields, after a very short reaction time. When THF, Et_2O, MeOH, hexane and MeCN were used as solvent, good yields were also obtained; however, these reactions proceeded more slowly. In addition, our results also demonstrated that the efficiency of the selenophene formation was significantly dependent on the steric effects and that this cyclization reaction occurred only with selenoenynes having a Se–C sp3 bond. In order to complete our investigation and to further prove the potential of 3-iodoselenophene derivatives **40** as precursors for increasing molecular complexity, we tested the reactivity of these compounds for the preparation of more highly substituted selenophenes. For instance, 3-iodoselenophene **40** was treated under metal–halogen exchange conditions with *n*-BuLi and intermediates trapped with aldehydes provided the corresponding secondary alcohols **41** in good yields (Scheme 14). Conversely, using palladium or copper catalyzed cross-coupling reactions with terminal alkynes, boronic acids and organozinc compounds we were able to convert 3-iodoselenophene to Sonogashira **42**, Suzuki **43** and Negishi **44** type products, respectively, in good yields (Scheme 14).[43]



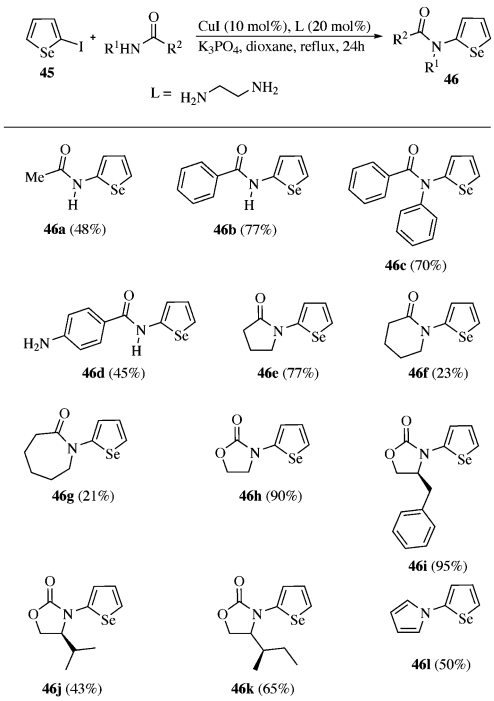
E = I, PhSe; R^1 = H, Ph, *n*-Bu, CH_2OH;
R^2 = Ph, *n*-Bu, CH_2OH, *p*-Me-C_6H_4;

Scheme 13



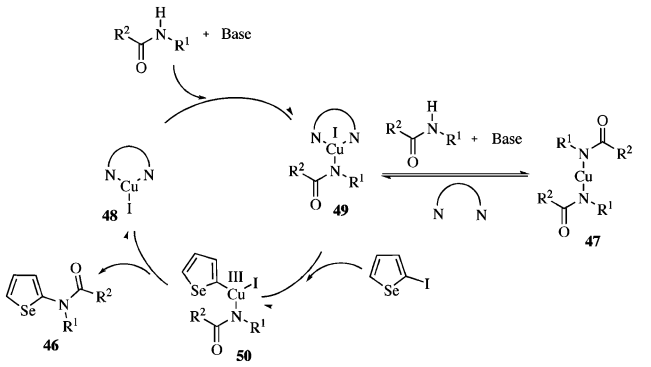
Scheme 14

As an alternative to the reactivity of selenophenes we described a carbon–nitrogen bond formation *via* a coupling reaction of 2-iodo-selenophene **45** and amides catalyzed by Cu(I) in the presence of a base and an inexpensive ligand, and established the first route to obtaining 2-nitrogen–selenophene derivatives **46** (Scheme 15).[44] The reaction worked well with oxazolidinones, lactams, and aliphatic and aromatic amides, as nitrogen sources, in the absence of any supplementary additives. In addition, the reaction proceeded cleanly under mild reaction conditions and was sensitive to the ratio of amide/2-iodo-selenophene, as well as the nature of the ligand, base, and solvent. Thus, the careful analysis of the optimized reaction revealed that the optimum conditions for this carbon–nitrogen coupling were: Cu(I) (10 mmol %) in 1,4-dioxane (3 ml) with K_3PO_4 (0.6 mmol) as the base, ethylenediamine as the ligand (20 mmol%), amide (0.6 mmol), and 2-iodo-selenophene **45** (0.5 mmol). Reflux for 24 h, afforded the *N*-functionalized selenophenes **46a–n** in moderate to good yields (Scheme 15). Although details of the mechanism explaining the carbon–nitrogen bond formation using 2-iodo-selenophene with copper catalysts are not yet known, an approximation of this reaction is shown in Scheme 16. This hypothesis is proposed on the basis of an analogous catalytic process of the amidation of aryl iodide.[45] Reaction pathways leading to selenophene derivative products seem to depend on the amount of both amide substrate and ligand, since the excess amide can inhibit the coupling reaction, probably because of the formation of an unreactive cuprate complex **47** which inhibits the catalytic process. Thus, the catalytic cycle starts with a Cu(I) diamine complex **48**. The mechanism includes three main steps: (a) formation of the intermediate Cu(I) amidate **49**, formed either through amide coordination to **48**, followed by depronotation or through the ethylenenediamine association and the subsequent amide dissociation from **47**; (b) addition of 2-iodoselenophene to generate the Cu(III) species, **50**; (c) reductive elimination leading to the final amination product **46** (Scheme 16).



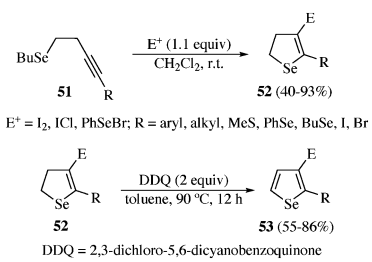
Scheme 15

The synthetic study of a partially saturated version, 2,3-dihydroselenophene derivatives of selenophenes, has been limited.



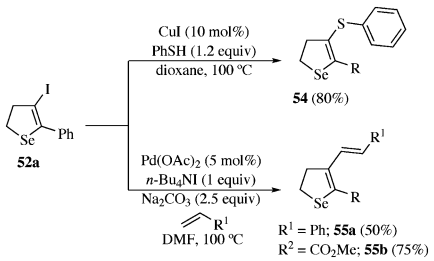
Scheme 16

Thus we aimed to explore approaches for the synthesis of 2,3-dihydroselenophenes **52** and examine their ability as precursors of 3-iodoselenophenes. In our study, we observed that 2,3-dihydroselenophenes **52** were formed from homopropargylic selenides **51** through electrophilic cyclization *via* a simple process employing I_2, ICl and PhSeBr, as electrophilic source, in CH_2Cl_2 as solvent and at room temperature (Scheme 17).[46] To identify the solvent potentially suitable for cyclization, we first chose MeOH, hexane, MeCN, THF and CH_2Cl_2. For this process, CH_2Cl_2 was the most effective solvent giving cyclized product in high yields. The study to screen the nucleophilic source showed that ICl and PhSeBr gave the target products in lower yields than I_2. The cyclization turned out to be general with respect to a diverse array of functionalities. Experiments showed that electrophilic cyclization of substrate, having an aromatic ring directly bonded to the terminal alkyne, was not sensitive to the electronic effects of the substituent. For example, the aromatic ring having either a neutral, electron donating or electron withdrawing substituent gave the cyclized products in very similar yields. In contrast, when the reaction was carried out with homopropargyl selenides with a hydrogen atom or an alkyl group in the terminal position, little decrease in the yields was observed, and the cyclized products were obtained in moderate yields. We also found that the reaction of 2,3-dihydroselenophenes **52** (1 equivalent) with DDQ (2 equivalents) in toluene at 90 °C gave the selenophene derivatives **53** in good yields (Scheme 17). In addition, 2,3-dihydroselenophene derivatives **52a** were submitted to a copper-catalyzed thiol cross-coupling reaction and Heck-type reaction giving the desired products **55a** and **55b**, respectively, in moderate to good yields (Scheme 18).



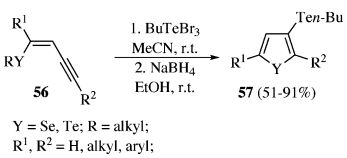
Scheme 17

In a further work to prepare selenophenes, we reported the use of butyltellurium tribromide as electrophilic source for the electrophilic cyclization of (*Z*)-chalcogenoenynes **56** to 3-



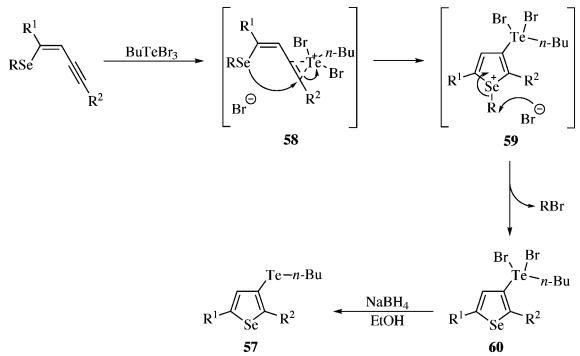
Scheme 18

(butyltelluro)chalcogenophenes **57** (Scheme 19).[47] This study focused on the introduction of a butyltelluro group at the C3 of the selenophenes to use as a substrate in palladium-catalyzed reactions.[48] We found that butyltellurium bromide species did not work as electrophilic sources, and as a consequence, 3-(butyltelluro)selenophene was not obtained. From these disappointing results we turned our attention to butyltellurium tribromide (*n*-BuTeBr$_3$), a tellurium(IV) species, more electrophilic and more stable than *n*-BuTeBr. Thus, the reaction of 1.0 equivalent of (*Z*)-selenoenyne, 1.1 equivalents of *n*-BuTeBr$_3$, using MeCN as the solvent at room temperature, and afterwards treatment with $NaBH_4$ and EtOH gave the desired chalcogenophenes in high isolated yields. We believe that the mechanism of this tellurium cyclization reaction involves the following: (i) coordination of the carbon–carbon triple bond to *n*-BuTeBr$_3$ to generate a telluronium intermediate **58**, (ii) *anti* attack of the selenium atom on the activated telluronium intermediate to produce the salt **59**, and (iii) facile removal of the alkyl group by the bromine anion present in the reaction mixture to generate the corresponding 3-[dibromo(butyl)tellanyl]selenophene **60** and one molecule of *R*Br. The reduction of **60** with $NaBH_4$ in EtOH gave the corresponding 3-(butyltellanyl) selenophene **57** as the product (Scheme 20). An advanced application of these tellurium compounds was carried out using palladium-catalyzed cross-coupling. For example, compound **61** was successfully obtained in a 71% isolated yield by Suzuki cross-coupling of **57a** with phenylethynyl trifluoroborate (Scheme 12). In a similar manner, the cross-coupling of **57a** with 4-methoxyphenyl trifluorborate gave the corresponding selenophene derivative **62** in 68% yield (Scheme 21). These results are considered acceptable when compared to iodine analogues.[49]

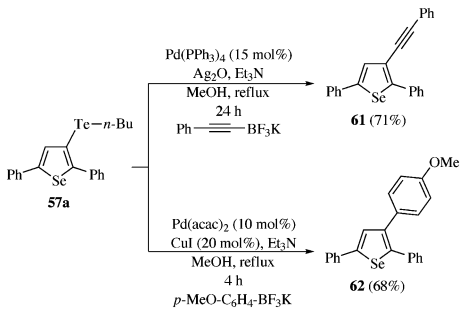


Scheme 19

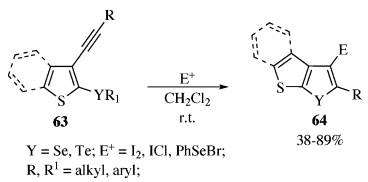
We also prepared a range of fused 4-iodo-selenophene[2,3-*b*]thiophenes **64** by electrophilic cyclization of 2-alkylchalcogen-3-alkynylthiophenes **63** (Scheme 22).[50] Thus, optimized reactions revealed that the optimum condition for this electrophilic cyclization reaction is the combination of 2-butylseleno-3-alkynylthiophenes (1 equivalent), electrophilic source (1.1 equivalent) using CH_2Cl_2 (5 ml) as the solvent, at room temperature. Since the success of this reaction is probably dependent on the nature of the group directly linked to the selenium atom, we explored this influence using different alkyl, aryl and benzyl groups. The results revealed



Scheme 20



Scheme 21

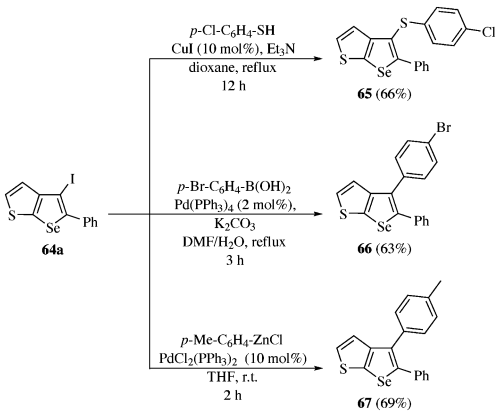


Scheme 22

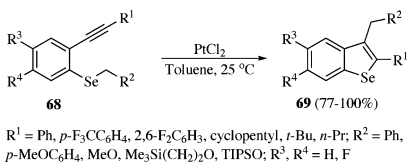
that butyl and ethyl groups bonded at the selenium atom resulted in the formation of products in high yields after very short reaction times. The 2-benzylseleno-3-alkynylthiophene also gave the product in moderate yield, however, with higher reaction time. Nonetheless, performing the reaction with 3-alkynylthiophene, having a phenyl group bonded at the selenium atom, the desired product was not observed, even after a long reaction time. The 4-iodo-selenophene[2,3-*b*]thiophene products can be further functionalized by palladium-catalyzed coupling reactions. In this way, the reaction of **64a** with aryl thiols, using just Cu(I) as catalyst, in dioxane, afforded the resultant product **65**, in 66% isolated yield. In a similar manner, the reaction of **64a** with organoboron and organozinc species gave the corresponding Suzuki **66** and Negishi **67** products in 63% and 69% yields, respectively (Scheme 23).

3. Benzoselenophenes

The synthesis and characterization of benzoselenophenes are of current interest owing to their potential applications as organic semiconductors for various optoelectronic devices. Thus, a convenient method for the preparation of benzoselenophenes **69** through a one step platinum catalyzed procedure by the direct cyclization of *ortho*-alkynylaryl selenides **68** was recently described by Nakamura and co-workers (Scheme 24).[51] A plausible mechanism to explain the formation of the benzoselenophenes

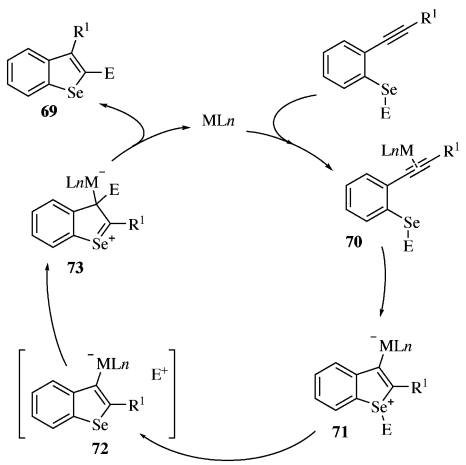


Scheme 23



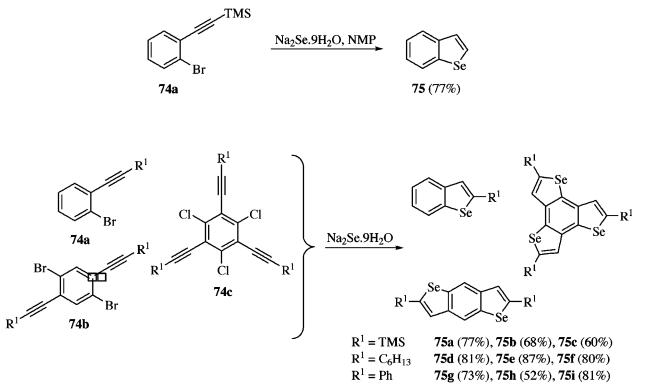
Scheme 24

69 was based on the key intermediate **71**, which is formed by initial coordination of platinum to the triple bond of the *ortho*-alkynylaryl selenides to produce complex **70**. Nucleophilic attack of the selenium atom gives the cyclized intermediate **71**. The 1,3 migration from the carbon atom bonded to the metal, *via* ion pair **72**, gives the intermediate **73**. The elimitaion of the catalyst from intermediate **73** delivers the product **69** (Scheme 25).



Scheme 25

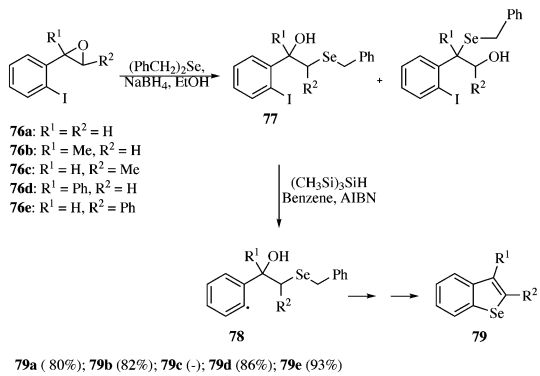
Intramolecular cyclization of *o*-halo-substituted ethynylbenzenes using sodium chalcogenides as nucleophile reagents to prepare benzoselenophene **75** was described by Takimiya and co-workers (Scheme 26).[52] The reaction was carried out *via* the addition of sodium selenide reagent (generated *in situ* from sodium borohydride and selenium powder in ethanol) to a solution of *o*-bromo ethynylbenzenes **74** in *N*-methyl-2-pyrrolidone (NMP) maintaining the reaction at 180 °C for 12 h. It was observed that ethynylbenzenes with a trimethylsilyl group at the terminal position of the alkynes gave the unsubstituted benzo[*b*]selenophene



Scheme 26

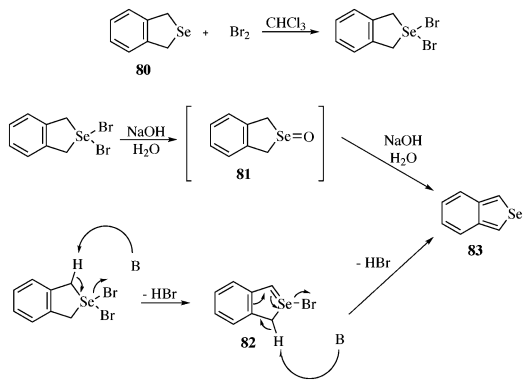
as product. Probably, in this cases sodium selenide acts as a nucleophile cleaving the carbon–silyl bond to form the selenophene ring (Scheme 26).

Substituted and unsubstituted 2-(benzylseleno)-l-(2-iodopheny1)ethanols **77**, prepared *via* reaction of benzylselenolates with epoxides **76**, reacted smoothly with tris(trimethylsily1)silane in benzene at 80 °C (AIBN initiator conditions) to afford benzoselenophenes **79** in excellent yield (82–93% yields). This reaction presumably involves intramolecular homolytic substitution by aryl radicals **78** at the selenium atom with the expulsion of benzyl radical followed by facile dehydration to afford the aromatic selenophene ring system (Scheme 27).[53]



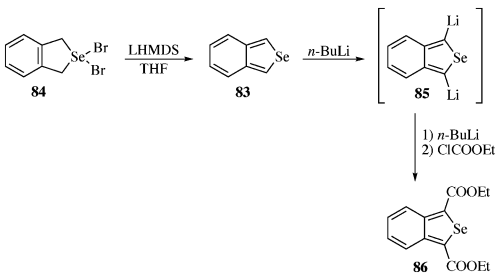
Scheme 27

Benzo[*c*]selenophenes **84** were efficiently prepared *via* bromination/dehydrobromination followed by oxidation of the 1,3-dihydrobenzo[*c*]selenophene **80** *via* intermediates **81** and **82**. Afterwards the benzo[*c*]selenophene generated was lithiated *in situ* and treated with ethyl chloroformate to give a functionalized benzoselenophene diester . Thus, dihydrobenzo[*c*]selenophene **80** was converted to the dibromo derivative **84** in quantitative yield by reaction with 1 equivalent of bromine at room temperature. When the dibromide **84** was treated with 40% aqueous sodium or with nonaqueous bases, such as 1,5-diazobicyclo[3.4.0]nonene (DBN) or lithium hexamethyldisilazide (LHMDS) in THF, it gave the benzo[*c*]selenophene **83** *via* the selenoxide intermediate or *via* dehydrohalogenation, respectivelly (Scheme 28). Thus, the preparation of benzo[*c*]selenophene **83** under anhydrous conditions provided a good route for the *in situ* preparation of the diester derivative **86**. In this way, the dilithium intermediate **85** was prepared by addition of excess of *n*-butyllithium to **83**



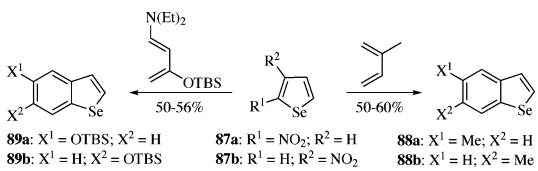
Scheme 28

followed by reaction of the dianion **85** with ethyl chloroformate (Scheme 29).[54]



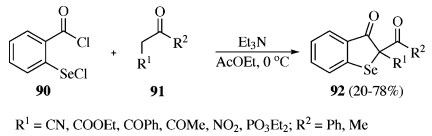
Scheme 29

Mancini and co-workers described an efficient synthesis of benzoselenophenes *via* Diels–Alder reaction, using nitroselenophenes **87a** and **87b** as dienophile and isoprene and 1-diethyl-amino-3-*tert*-butyldimethyl-siloxy-1,3-butadiene (Rawal's diene) as the diene. The reaction of **87** with isoprene proceeded *via* thermal extrusion of nitrous acid giving the mixture (1 : 1) of isomeric cycloadducts **88a** and **88b** in moderate yields. When 1-diethyl-amino-3-*tert*-butyldimethyl-siloxy-1,3-butadiene was reacted with **87a** it generated the aromatic cycloadducts **89a** and **89b** with loss of the nitro group. Similarly, in the reaction of Rawal's diene with 3-nitroselenophene **87b** the benzoselenophene **89b** was obtained with moderate yield and complete regioselectivity (Scheme 30).[55]



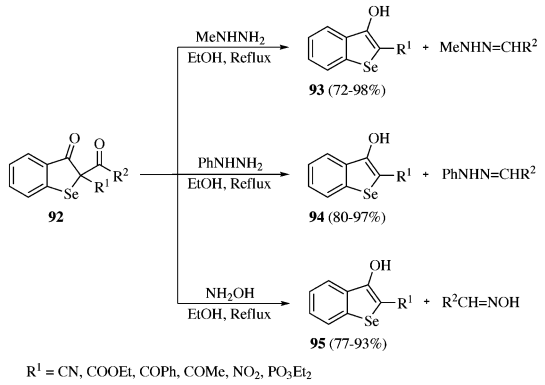
Scheme 30

2-(Choroseleno)benzoyl chlorides **90** were found by Lisiak and Mlochowski to undergo cyclization in the presence of carbonyl compounds **91** by reaction with excess triethylamine, followed by hydrazines to afford hydroxybenzoselenophenes **93–95** (Scheme 31). The reaction of 2-(chloroseleno)benzoyl chlorides **90** with carbonyl compounds having a C–H acid, such as benzoylacetonitrile, α-nitroacetophenone and ethyl benzoylacetate, with triethylamine, using ethyl acetate at 0 °C gave dihydro benzo[*b*]selenophenones **92** in good yields. Thus, the reaction of dihydro selenophenones **92** with hydroxylamine or phenyl-,

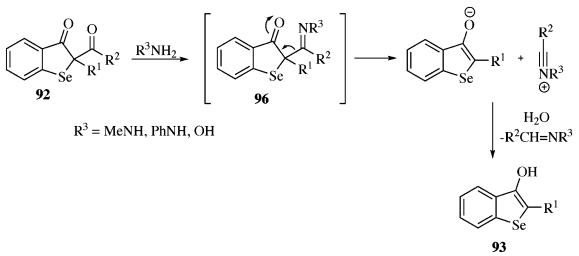


Scheme 31

methylhydrazine in ethanol as solvent under reflux for 3 h gave the hydroxybenzo[*b*]selenophenes **93–95** in high yields (72–98%) (Scheme 32). The mechanism proposed by the authors is that the unstable hydrazone **96** is the key intermediate for hydroxybenzo[*b*]selenophenes formation (Scheme 33).[56]

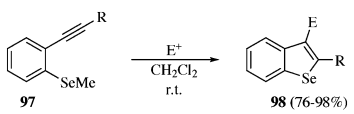


Scheme 32

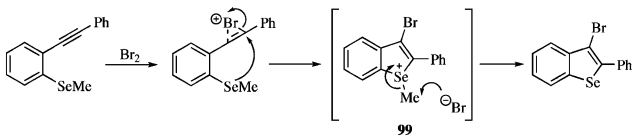


Scheme 33

Larock and co-workers reported an elegant study for the preparation of 2,3-disubstituted benzo[*b*]selenophenes **98** by electrophilic cyclization of various 1-(1-alkynyl)-2-(methylseleno)arenes **97** using Br_2, NBS, I_2, ICl, PhSeCl and PhSeBr as electrophile sources (Scheme 34).[57] This reaction tolerated many functional groups, including nitrile, hydroxyl, silyl, nitro, methoxyl, and ester. In this study, Larock and co-workers also evaluated the mechanistic details of the electrophilic cyclization. To determine the advanced intermediates of the reaction, the authors monitored the reaction by ^{1}H NMR spectroscopy. From the ^{1}H NMR spectroscopy the most relevant data obtained for the proposed mechanism is shown in Scheme 35, in which the first



Scheme 34

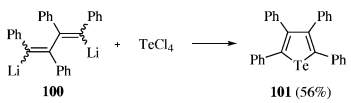


Scheme 35

step is electrophile coordinated with the triple bond, followed by nucleophilic attack by selenium to generate the cationic intermediate **99** detected by ^{1}H NMR. The cationic intermediate **99** then undergoes facile removal of the methyl group *via* S_N2 displacement by the counterion bromide, generated *in situ* during the cyclization, to give MeBr (detected by ^{1}H NMR) and the cyclized product (Scheme 35).

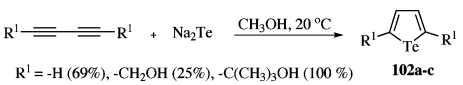
4. Tellurophenes

Increasing interest in tellurophene in recent years is explained by the discovery of a series of derivatives with clearly defined biological activity. The effect of a tellurophene fragment in the porphyrin macrocycle on anticancer activity was studied, and it was established that the glycosylated derivatives of tellurophene act as inhibitors of inosine 5′-monophosphate dehydrogenase.[3] In addition, tellurophene derivatives have also received increased attention, as potential components of advanced materials[58] and as substrates for the laser-induced chemical vapor deposition (CVD) of tellurium metal films.[59] To our knowledge, the first report of the preparation of an tellurophene was described in 1961. Braye, Hubel and Caplier prepared tetraphenyltellurophene **101** by reacting 1,4-dilithiotetraphenylbutadiene **100** (prepared by the reaction of diphenylacetylene with lithium metal) with tellurium tetrachloride (Scheme 36). The reaction gave a large scale (5.35 g) of tellurophene in 53% yield based on $TeCl_4$ amount.[60]



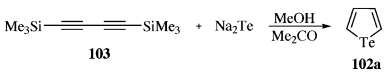
Scheme 36

In 1966, Mack was the first to show the preparation of tellurophene having no substituent **102a** or 2,5 disubstituted derivatives **102b–c**. This method has been shown to be the most useful, and the tellurophenes were achieved in moderate to good yields by reaction of a solution of sodium telluride with equivalent quantity of the diacetylenes (Scheme 37).[61] Forty years later, we consider that this procedure is quite general and is efficiently used with success to prepare tellurophenes with different substituents. However, the yields are generally improved using the complete experimental details described by Fringuelli and Taticchi.[62] It was noted by the authors that water and oxygen must be rigorously excluded, butadiyne must be used directly after purification, commercial metallic grey tellurium must be used and at the end of the reaction the solvent must not be concentrated under vacuum to avoid loss of tellurophene.



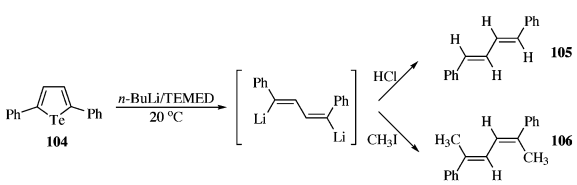
Scheme 37

When employing bis(trimethylsilyl)-1,3-butadiyne **103** to avoid the external generation of butadiyne, Barton and Roth reported the preparation of a non-substituted tellurophene **102a** in 37% yield by the reaction of a commercial methanolic solution of sodium telluride (Scheme 38).[63] A considerable improvement in the yield by this method was achieved by Praefcke and Lohner using *in situ* prepared sodium telluride.

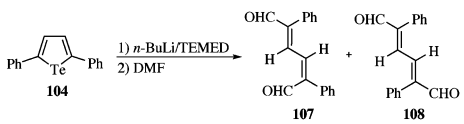


Scheme 38

1,4-Substituted phenyl butadienes **105** with *E*,*E* configuration were easily synthesized *via* the direct treatment of tellurophene **104** with *n*-butyllithium in the presence of tetramethylethylenediamine (TEMED) and dimethyl ether as the solvent at room temperature.[64] Alternatively, 2,5-diphenyl hexadiene **106** was obtained as the *E*,*E* isomer exclusively in 47% yield when the reaction was quenched with methyl iodide instead of HCl (Scheme 39). On the other hand, the major *E*,*Z* isomer **107** was observed when the quench was performed with dimethylformamide, however, after a long time, the *E*,*Z* isomer **107** converted itself to the *E*,*E* isomer **108**, quantitatively (Scheme 40).



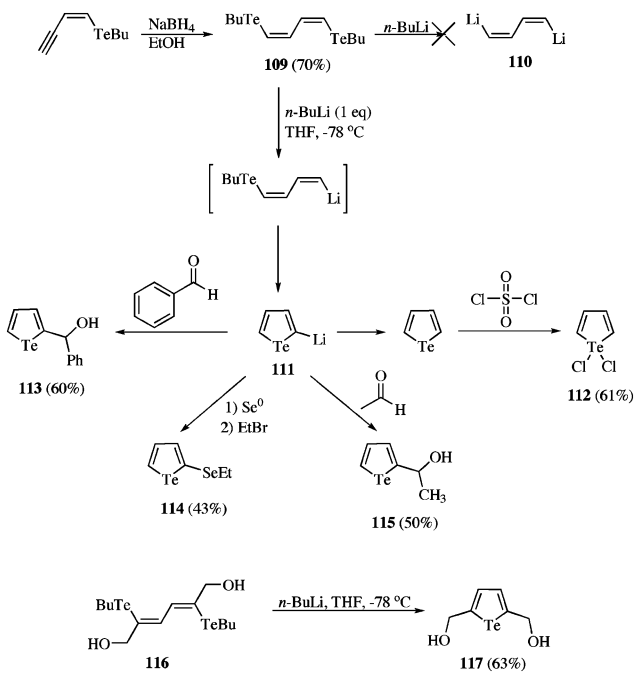
Scheme 39



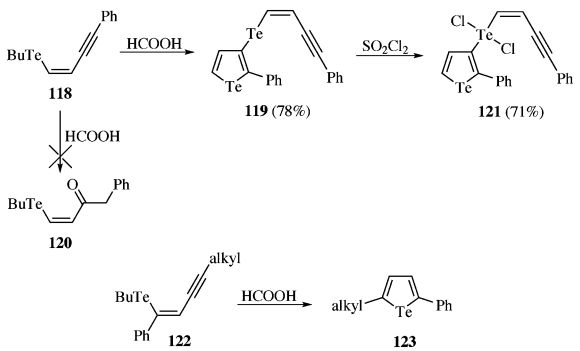
Scheme 40

Furthermore, reaction of *n*-butyllithium with 1,4-bis(butyltelluro)-1,3-butadiene **109** did not afford the 1,4-dilithium species **110** as expected, rather, a ring closure to form tellurophene **111** was observed (Scheme 41).[65] The first tellurium–lithium exchange occurs, and before the second exchange takes place, the tellurium atom is intramolecularly attacked by the vinyl anion, and the aromatic heterocycle is formed. A second equivalent of *n*-butyllithium is assumed to deprotonate the α-position of tellurophene. This fact is supported by the addition of different elecrophile sources to the reaction mixture, affording 2-substituted tellurophenes **112–115** in moderate to good yields (Scheme 41). In addition, 2,5-disubstituted tellurophene **117** was prepared by the reaction of bis(butyltelluro)-1,3-butadiene **116** with *n*-butyllithium in THF in 63% yield (Scheme 41).

Under Rupe reaction conditions, Dabdoub and co-workers reported the unexpected formation of disubstituted tellurophenes **119** (Scheme 42).[66] Attempting to convert the 1-butyltelluro-4-phenyl-1-buten-3-yne **118** in the correspondent α,β-unsaturated β-telluro-substituted ketone **120**, they treated **118** with 50% or



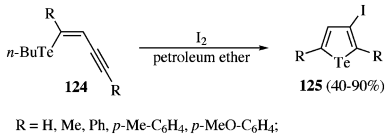
Scheme 41



Scheme 42

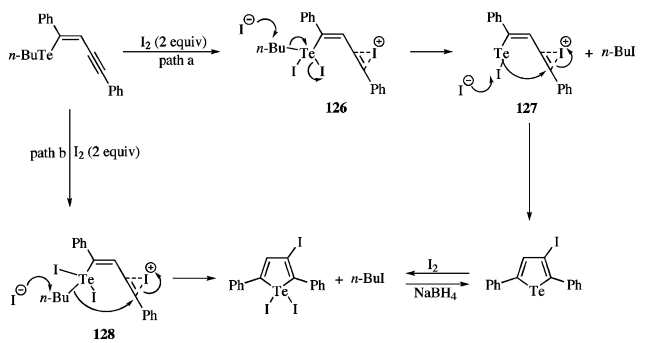
85% aqueous solutions of formic acid. Nonetheless, instead of the expected ketone, they observed the formation of the telluro-substituted enynetellurophene **119** in a *cis* : *trans* ratio of 74 : 26. The proposed structure was confirmed by X-ray diffraction from the *cis* isomer of **121**, obtained as yellow crystals after a derivatization of **119** by treatment with sulfuryl chloride at room temperature, followed by recrystalization from hexane. Since the reactions with alkyl substituted tellurobutenynes **122** furnished the expected telluro-α,β-unsaturated ketones **120**, the authors suggested that the phenyl groups of the starting telluride are intrinsically responsible for the formation of the tellurophene.

By studying the chemistry and application of the vinylic tellurides **124**, Daddoub and co-workers discovered that they underwent cleavage of the Te–C sp^3 bond by reaction with iodine to produce 3-iodo-tellurophenes **125** as main products.[67] The reaction was applicable to a series of tellurobutenynes and the corresponding 3-iodo tellurophenes **125** were isolated in good to excellent yields (Scheme 43). A mechanistic proposal provided by the authors consisted of initial reaction of butyltelluroenyne with iodine to generate the iodonium intermediate **126**. The reaction with iodide gave rise to iodobutane and tellurenyl iodide **127**,



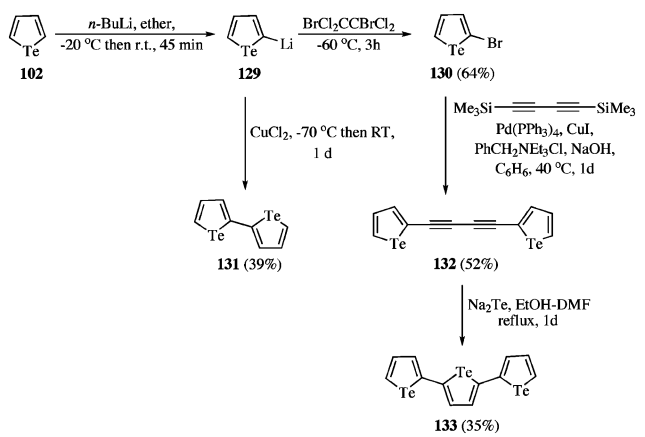
Scheme 43

which underwent attack by iodide at the iodine atom, followed by ring closure through opening of the iodonium ion (pathway *a*, Scheme 44). In another possibility, a direct ring closure can happen to give the dihalogenated tellurophene and iodobutane *via* intermediate **128** (pathway *b*, Scheme 44).



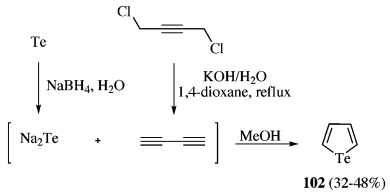
Scheme 44

Conjugated tellurophenes are potential candidates to study electrical conductivity like their polythiophene analogues.[68] Otsubo and co-workers related a sequential protocol to obtain bitellurophene **131** and tertellurophene **133** (Scheme 45).[58] The tellurophene monomer **102** was first treated with *n*-butyllithium giving the 2-lithiated intermediate **129**. Thus the addition of copper(II) chloride to a solution containing 2-(lithium)tellurophene gave the bitellurophene **131** in 39% yield (Scheme 45). Addition of 1,2-dibromotetrachloroethane to **129** led to the formation of 2-bromotellurophene **130**, which underwent palladium catalyzed coupling with bis(trimethylsilil)butadiyne to afford 1,4-bis(tellurophen-2-yl)butadiyne **132** in 52% yield. Finally treatment of **132** with sodium telluride prepared from tellurium powder with Rongalite and sodium hydroxide in ethanol–DMF solvent system led to the formation of tertellurophene **133** in 35% yield.



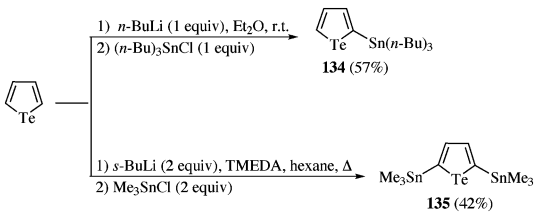
Scheme 45

Investigating a new simple way to large scale synthesis of tellurophene, Stephens and Sweat reported a modified synthesis of tellurophene involving the *in situ* generation of sodium telluride by reduction of tellurium powder with $NaBH_4$ in water.[69] Sodium telluride formation was easily observed by the violet color reaction solution, obtained through the addition of tellurium into an aqueous/methanolic solvent system containing sodium borohydride. Thus, the addition of diacetylene, *via* gas line, prepared in a separate flask by heating 1,4-dichloro-2-butyne with KOH, to the sodium telluride produced the non substituted tellurophene **102** in moderate yield (Scheme 46).

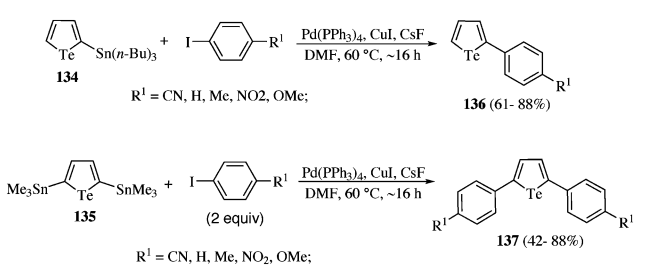


Scheme 46

The same research group described an advanced application of this methodology for the synthesis of mono- and di-stannyl tellurophenes. Thus, standard monolithiation of tellurophene **102** using *n*-butyllithium in diethyl ether at room temperature, followed by quenching with tributyltin chloride, gave the desired monostannyl tellurophene **134** in 57% yield. Simply by changing the standard procedure to *sec*-butyllithium (2.1 equivalent) using hexane as solvent at reflux, with the identical substrate, gave di-stannyl tellurophenes **135** in 42% yields (Scheme 47).[70] The potential of mono- and di-stannyl tellurophenes obtained as precursors for increasing molecular complexity *via* palladium catalyzed reactions was also briefly investigated. In this study, 2-aryl **136** and 2,5-diaryltellurophenes **137** were convenient prepared, in moderate to good yields, by Stille coupling[71] of mono- **134** and di-stannyl tellurophenes **135** with aryl iodides, using the mixed copper–palladium catalyst system, with caesium fluoride as additive (Scheme 48).



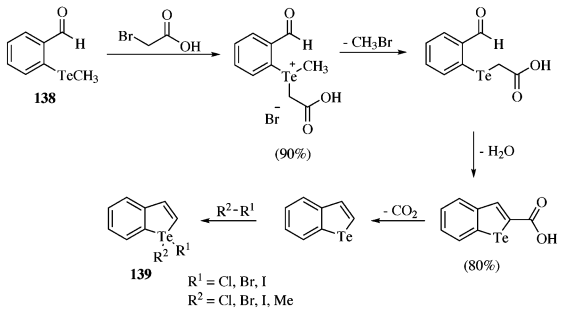
Scheme 47



Scheme 48

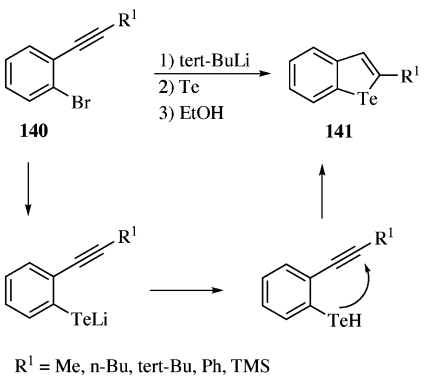
5. Benzotellurophenes

In 1971, Piette and Renson reported the first synthesis benzo[*b*]tellurophene **139** in 54% overall yield using a four-stage synthesis from *o*-(methyltelluro)benzaldehyde **138** and bromoacetic acid (Scheme 49).[72]



Scheme 49

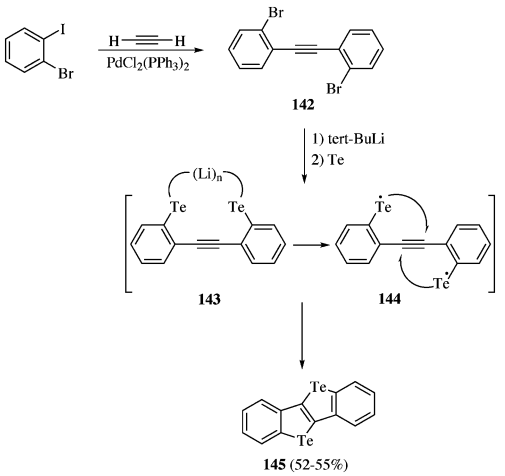
Using *o*-bromoethynylbenzenes **140** as key starting materials, Sashida and co-workers prepared benzo[*b*]tellurophenes **141** in a one-pot procedure.[73] Based on previous reports in which the tellurolate anion was added *via trans*-fashion to acetylenic compounds[74] to afford *Z*-vinyl tellurides, they first performed a Sonogashira coupling of bromoiodobenzene with 1-substituted acetylenes to obtain 2-alkynyl-arylbromine **140**. The bromolithium exchange reactions in the aryl compounds with sequential addition of tellurium powder and after an ethanolic workup, provided benzotellurophenes **141** as single product in good yields (Scheme 50).



Scheme 50

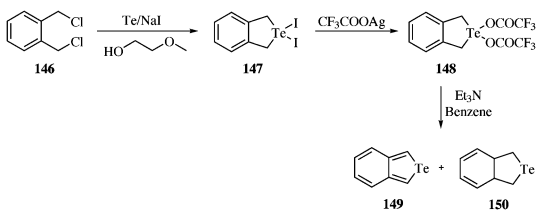
Simultaneously to that work in obtaining benzo[*b*]tellurophenes **141**, the same group also synthesised [1]benzotelluro[3,2-*b*][1]-benzotellurophenes.[75] The reaction of *o*-bromoiodobenzene with acetylene was catalyzed by bis(triphenylphosphine)palladium dichloride to give 2,2′-dibromodiphenyl acetylene **142** which in turn was lithiated with *tert*-butyllithium in anhydrous tetrahydrofuran at −80 °C, and followed by addition of tellurium powder to give tellurophene **145** in 55% yield (Scheme 51). Since the reaction was carried out in the absence of a proton source, the authors assumed that the mechanism involved a radical pathway through intermediates **143** and **144**.

Cava and co-workers reported the synthesis of benzo[*c*]tellurophenes **149** in a systematic approach involving

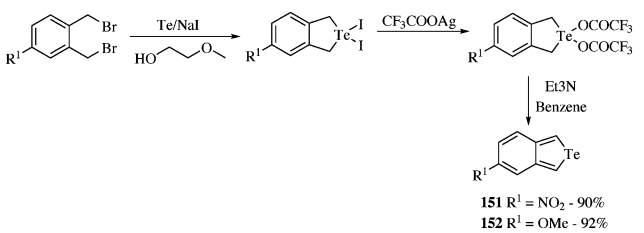


Scheme 51

iodination of the tellurium atom (Scheme 52).[76] The synthesis started with the reaction between 1,2-bis(chloromethyl)-benzene **146** and tellurium and sodium iodide to give 1,3-dihydro-2,2-diiodobenzo[*c*]-tellurophene **147**. Since dehydroiodination gave low yields of benzo[*c*]-tellurophene **149**, the iodine atoms were changed for trifluoroacetate and then treated with tetrahydrotellurophene trifluoroacetate **148** and triethylamine to afford benzo[*c*]tellurophene **149** and tetrahydrotellurophene **150** in the ratio 8 : 1 (Scheme 52). In addition to unsubstituted 1,2-bis(chloromethyl)-benzene, the aromatic ring having either electron-withdrawing (NO_2) or electron-donating group (MeO) was also converted to benzo[*c*]tellurophenes **151** and **152** in 90 and 92% yields, respectively (Scheme 53).

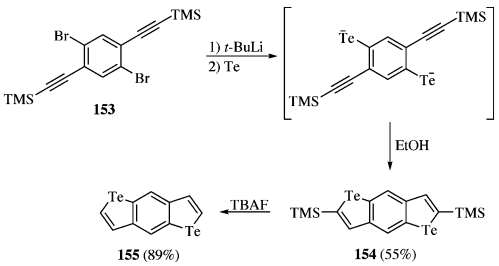


Scheme 52



Scheme 53

1,4-Dibromo-2,5-bis(2-trimethylsilylethynyl)benzene **153** was also utilized as a starting material for the preparation of benzotellurophene **155** (Scheme 54).[77] In this process 1,4-dibromo-2,5-bis(2-trimethylsilylethynyl)benzene **153** was first synthesized by Sonogashira coupling between 1,4-dibromo-2,5-diiodobenzene and trimethylsilylacetylene. Sequentially, to the solution of **153**, in ether, was added *tert*-butyllithium (4 equivalents) at −78 °C and tellurium powder (2 equivalents) at room temperature, followed by



Scheme 54

the addition of ethanol gave 2,6-bis(trimethylsilyl)benzo[1,2-*b*:4,5-*b*′]-ditellurophene **154** which was then desilylated by treatment with tetrabutylammonium fluoride (TBAF) to give benzo[1,2-*b*:4,5-*b*′]ditellurophene **155** in 89% yield.

Conclusions

Although, the widespread use of chalcogen compounds by synthetic organic chemists or as a tool in organic synthesis, mainly in the application to total synthesis, has been hampered because of the bad reputation attributed to these compounds, there has been an impressive increase in the number of publications in the chalcogenophenes field appearing in the literature. Much effort has been devoted to developing chalcogenophene chemistry which has transformed it into a very broad and exciting field with many opportunities for research and development of applications. Future developments in the synthesis and reactivity of chalcogenophenes, mainly in the study of carbon–carbon formation and use in transition metal-catalyzed coupling reactions is expected as well as studies into toxicological and pharmacological aspects. Thus, in this review we hope to have demonstrated the chalcogenophenes as valuable tools for synthetic strategies and have shown a new dimension within the field, particularly in polyvalent chemistry.

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