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Synthesis of Vinyl Selenides

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1. Introduction

The versatility and utility of vinyl chalcogenides in organic synthesis is well documented through the publication of a number of review articles[1] and books.[2] The development of new methods for the preparation and applicability of vinyl sulfides,[3a−c] sulfones,[3d] and tellurides[4] was recently revised.

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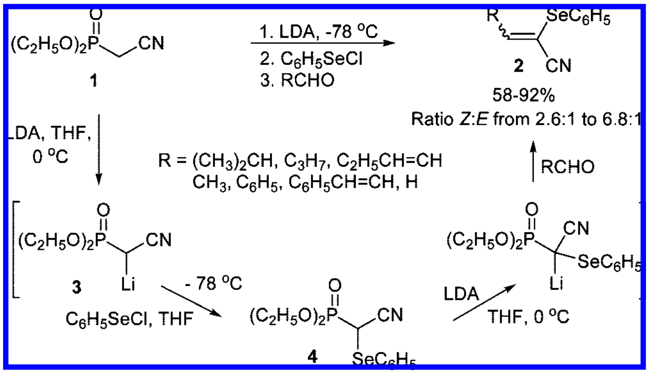
During the preparation of this review, a very interesting microreview by Beletskaya and Ananikov appeared in the literature,[5] covering the mechanistic aspects of the use of transition metal catalysis in the preparation of vinyl sulfides and selenides. The most recent review article extensively discussing the preparation, chemical properties, and applications of vinyl selenides dates from 1997.[1a] Since then, several important improvements have been described, including new, more general, cleaner, and more selective methodologies for the synthesis of these compounds. In this review, we will provide an update of available methods for the synthesis of vinyl selenides developed in the past decade, although some important and original findings reported earlier will be also included. Aspects of reactivity and use of vinyl selenides for the elaboration of more complex compounds, as well as the preparation of vinyl selenonium and aromatic cyclic vinyl selenides, will not be covered, except for some specific examples.

Our aim here is to describe the new methodologies, based on the structure of the starting materials, to discuss the scope and limitations and to comment on the stereochemistry and yields of the reactions. To facilitate discussion, the range of synthetic methodologies for the preparation of vinyl selenides has been divided here into five major groups: (a) via Horner, Wittig and correlated reactions, (b) methods starting from acetylenic selenides, (c) methods starting from alkynes, (d) methods starting from allenes and alkenes, and (e) via multicomponent reactions.

2. Vinyl Selenides via Horner, Wittig and Correlated Reactions

Since the pioneering works using Wittig-type reactions to prepare vinyl selenides, a number of new and general methods have been described.[1h] A limitation of these reactions is their low atomic efficiency, with a high amount of residues at the end of the process. The main advantage of this approach is the preparation of vinyl selenides with chain elongation and with different substitution patterns, although

Scheme 1



a mixture of (*E*)- and (*Z*)-alkenes is obtained in almost all of the described examples.

2.1. Vinyl Selenides via a Horner Olefination

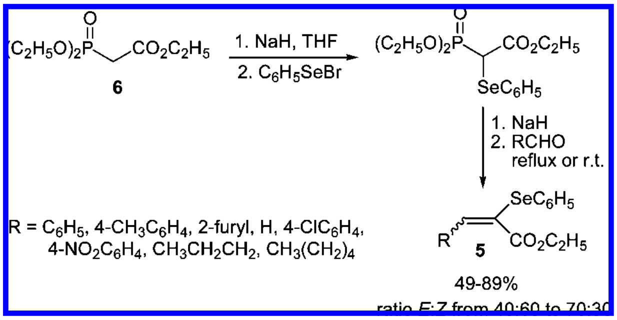
Although the Horner olefination of selenophosphonates for preparation of vinyl selenides is a well-described reaction and was reported in a recent review,[1h] there have been more recent improvements worthy of note. Silveira and co-workers have described the preparation of functionalized vinyl selenides by the Horner reaction.[6−8] Thus, the reaction of cyanomethylphosphonate **1** with phenylselenenyl chloride, followed by reaction with aromatic and aliphatic aldehydes under basic conditions, afforded α-phenylselenoacrylonitriles **2** in 58−92% yields, preferentially with *Z* configuration (Scheme 1).[6]

A typical procedure consists of treatment of cyanomethylphosphonate **1** with LDA to generate the lithiated species **3**, which, upon reaction with phenylselenenyl chloride in THF, affords the α-phenylseleno(cyano)phosphonate intermediate **4**, as depicted in Scheme 1. Intermediate **4** was easily transformed into the desired vinyl selenide **2** using LDA in excess, followed by reaction with aldehydes. The α-phenylselenoacrylonitriles **2** reacted with dienes in the presence of $C_2H_5AlCl_2$, furnishing the corresponding Diels−Alder adducts, while selective reduction of the cyano group with DIBAL-H resulted in the α-phenylseleno-α,*β*-unsaturated aldehydes in good yields. The authors also used the vinyl selenides **2** as Michael acceptors toward the reaction with amines, producing corresponding highly functionalized α-phenylseleno-*β*-amino nitriles.

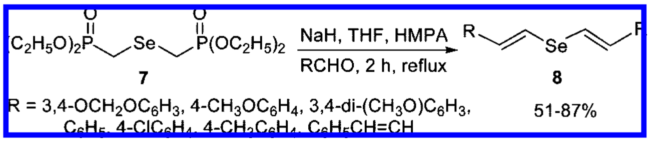
Several α-phenylseleno-α,*β*-unsaturated esters **5** were synthesized by a similar procedure, starting from triethylphosphonate **6**, using NaH as the base and phenylselenenyl bromide as the electrophilic selenium source.[7] The reaction was performed with aliphatic and aromatic aldehydes, and the *E* isomer was obtained preferentially in most of the cases in 49−89% overall yields (Scheme 2). Similar to the vinyl selenides **2**, the vinylselenoesters **5** were efficiently converted to functionalized cyclohexenes in good yields by reaction with dienes. In this case, $ZnBr_2$ was used as a Lewis acid to catalyze the Diels−Alder reaction.

Selenium bis-phosphonate **7** was employed by Silveira and co-workers in the synthesis of the very utile divinyl selenides **8**, via reaction with aromatic aldehydes in the presence of NaH.[8] This method is 100% regioselective, affording exclusively (*E*)-divinyl selenides in 51−87% yields after refluxing for 2 h (Scheme 3). The divinyl selenides were successfully converted to (*E*)-alkenes by nickel-catalyzed cross-coupling with Grignard reagents. The advantage of using divinyl selenides instead vinyl selenides lies in both the former organyls linked to selenium being transferred in coupling reactions.

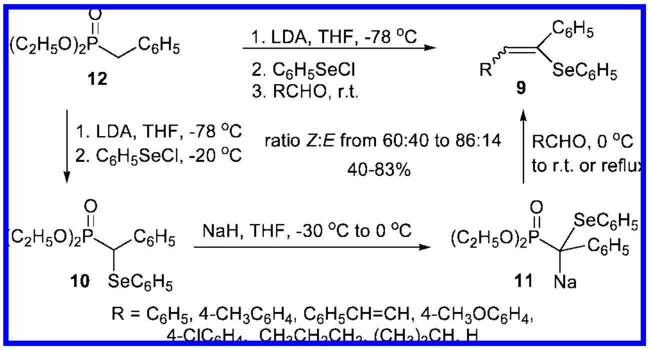
Scheme 2



Scheme 3



Scheme 4

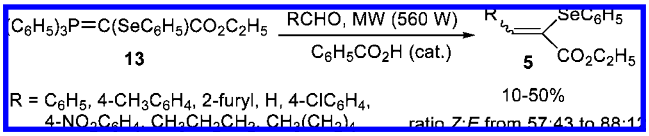


Recently, our group described a new and efficient method of preparation of α-phenylseleno *β*-substituted styrenes **9** by the reaction of diethyl α-phenylselenobenzylphosphonate **10** with NaH and aldehydes (Scheme 4).[9] The treatment of **10** with NaH generated the anion **11** which, upon reaction with aliphatic and aromatic aldehydes, afforded the desired product **9** with the *Z* isomer being the main product. Alternatively, the vinyl selenides **9** can be obtained directly from **12** by sequential reactions with LDA, phenylselenenyl chloride, and the aldehyde in a one-pot process, as depicted in Scheme 4. The α-phenylselenostyrenes **9** were subjected to several transformations, such as the selenium−lithium exchange, to afford vinyl lithium species, which were captured with aldehydes and DMF, yielding, respectively, (*Z*)-allyl alcohols and (*E*)-α-phenyl-α,*β*-unsaturated aldehydes in good yields. The hydrolysis of **9** in the presence of $TiCl_4$ resulted in the corresponding α-aryl acetophenones.

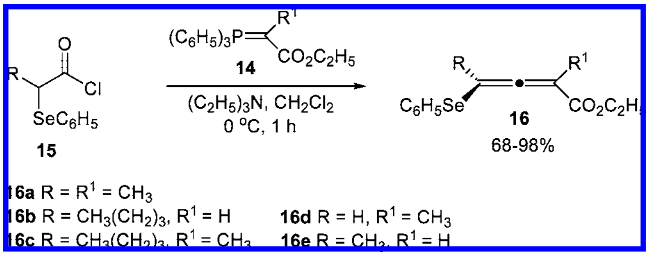
2.2. Vinyl Selenides by Wittig-type Reactions

The use of the Wittig reaction for the preparation of α-phenylseleno-α,*β*-unsaturated esters **5** starting from phosphoranes with low reactivity **13** was described by Silveira and co-workers (Scheme 5).[7] The authors were able to successfully prepare several functionalized vinyl selenides using microwaves as a nonclassical energy source, with the *Z* isomer being the main product (*Z*:*E* ratio from 57:43 to 88:12). Although the products have been obtained in low

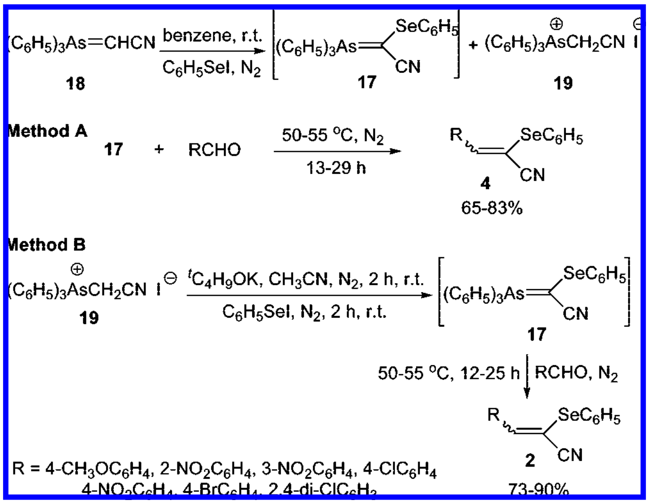
Scheme 5



Scheme 6



Scheme 7



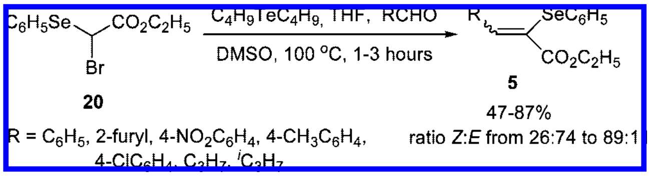
yields (10−50%), this procedure is an alternative method to the Horner reaction described above.[7]

Similarly, the stabilized phosphoranes ethyl 2-(triphenylphosphoranylidene)acetate or propionate **14** were subjected to reaction with α-phenylseleno ketenes, generated in situ by the reaction of α-phenylseleno acid chloride **15** with triethylamine in dichloromethane. The reaction is fast and occurs under mild conditions (1 h at 0 °C), and the corresponding 4-phenylseleno allenic esters **16** were obtained in 68−98% yields (Scheme 6).[10]

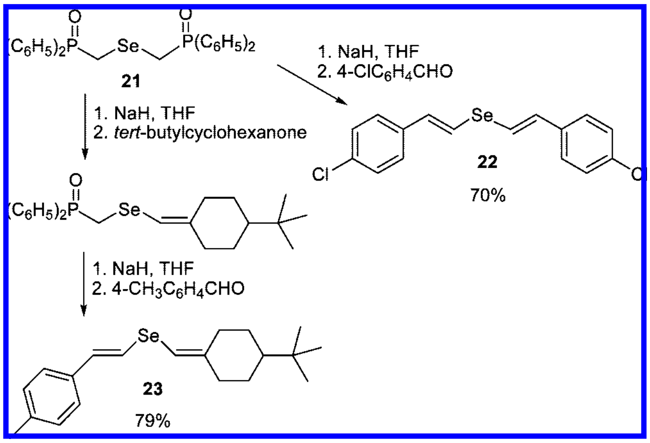
The very unstable α-phenylselenenyl cyanomethylene triphenylarsorane **17**, obtained in situ from treatment of cyanomethylene triphenylarsorane **18** with phenylselenenyl iodide, was used in a Wittig-type reaction with aromatic aldehydes to afford a mixture of (*Z*)- and (*E*)-α-phenylselenoacrylonitriles **4** in good yields (Scheme 7 - Method A).[11] Alternatively, the triphenylarsorane **17** can be obtained from the treatment of arsonium iodide **19** with 1 equiv of $^{t}C_4H_9OK$, followed by capture with 0.5 equiv of phenylselenenyl iodide (Scheme 7 - Method B).

Silveira and co-workers described the use of stabilized telluronium salts as phosphonium equivalents to perform the preparation of several α-phenylseleno-α,*β*-unsaturated esters **5** in good yields (47−87%) and with *Z* preferential stereochemistry in most of the studied examples (Scheme 8).[12] The tellurium ylides were prepared in situ at neutral conditions by the reaction of α-bromo-α-phenylseleno acetate **20** with dibutyl telluride (1 equiv) and aldehyde in THF/DMSO at 100 °C for 1−3 h.

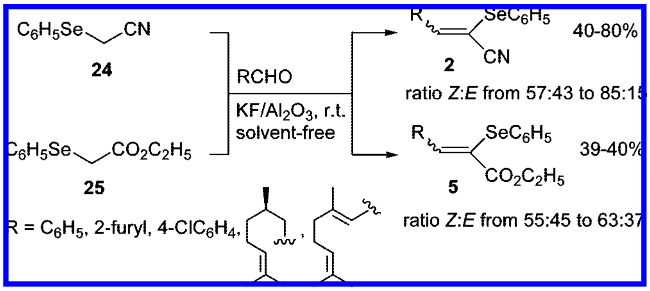
Scheme 8



Scheme 9



Scheme 10



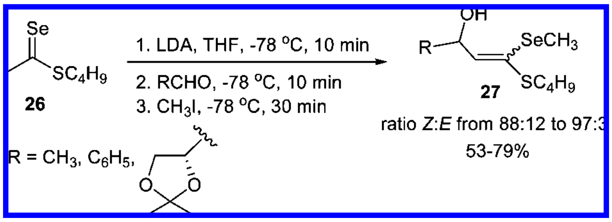
More recently, the same group[13] described a detailed study of the preparation and reactivity of chalcogenyl phosphonates and phosphane oxides (S, Se, and Te). The bis(methyldiphenylphosphane oxide) selenides **21** were successfully used in the selective preparation of symmetrical and unsymmetrical (*E*)-divinylic selenides **22** and **23** in 70 and 79% yields, respectively (Scheme 9).

2.3. Vinyl Selenides by Knoevenagel Reaction and Condensation Reactions

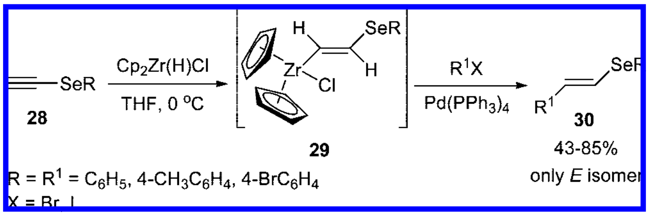
A cleaner and more atom efficient protocol to prepare α-phenylselenoacrylonitriles **2** and α-phenylseleno-α,*β*-unsaturated esters **5** with *Z* preferential stereochemistry was described by Perin and co-workers through the solvent-free Knoevenagel reaction between aldehydes and phenylselenoacetonitrile **24** or ethyl(phenylseleno)acetate **25**, respectively (Scheme 10).[14] The functionalized vinyl selenides were obtained in moderate to good yields (39−80%) after 4−5 h of stirring the mixture in the presence of KF/Al_2O_3 under solvent-free conditions at room temperature, and the method can be used for both aromatic and aliphatic aldehydes.

Murai and co-workers[15] described the aldol-type condensation reaction of selenothioacetic acid *S*-butyl ester **26** with aldehydes, followed by treatment with methyl iodide, to afford a mixture of (*E*)- and (*Z*)-ketene selenothioacetals **27**

Scheme 11



Scheme 12



in 53−79% yields (Z:E ratio = 88:12 to 97:3, Scheme 11). The reaction occurs via a β-hydroxy eneselenolate intermediate, and three different selenothioacetals **27**, derived from benzaldehyde, 2-isopropylidene-D-glyceraldehyde, and acetaldehyde, were synthesized.

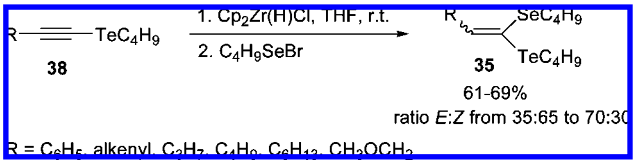
3. Preparation of Vinyl Selenides from Acetylenic Selenides

3.1. Vinyl Selenides by Hydrozirconation of Acetylenic Selenides

Methods starting from terminal, functionalized, or conjugated alkynes are the most important and widely employed strategies for the selective preparation of vinyl selenides. Among the methods recently described, the hydrozirconation of terminal acetylenic selenides **28** with Schwartz reagent [$Cp_2Zr(H)Cl$], followed by a cross-coupling of the β-zirconated vinyl selenide **29** with aryl halides in the presence of $Pd(PPh_3)_4$, was used by Huang and Zhu to prepare, exclusively, (E)-vinyl selenides **30** in moderate to good yields (43−85%), as depicted in Scheme 12.[16]

Since the work of Huang and Zhu, several articles have appeared in the literature describing new routes for access of vinyl selenides by hydrozirconation of internal and terminal alkynyl selenides, followed by the capture of the respective α- or β-zirconated intermediates with an electrophile. Thus, Dabdoub and co-workers[17] described the synthesis of several Z-vinyl selenides **31** in good yields (64−89%) by the reaction of **32** with 2 equiv of $Cp_2Zr(H)Cl$ in THF at room temperature, followed by quenching with water (Scheme 13). The use of 2 equiv of Schwartz reagent was crucial for the selectivity of the reaction, and only the Z isomer was obtained.

Scheme 14

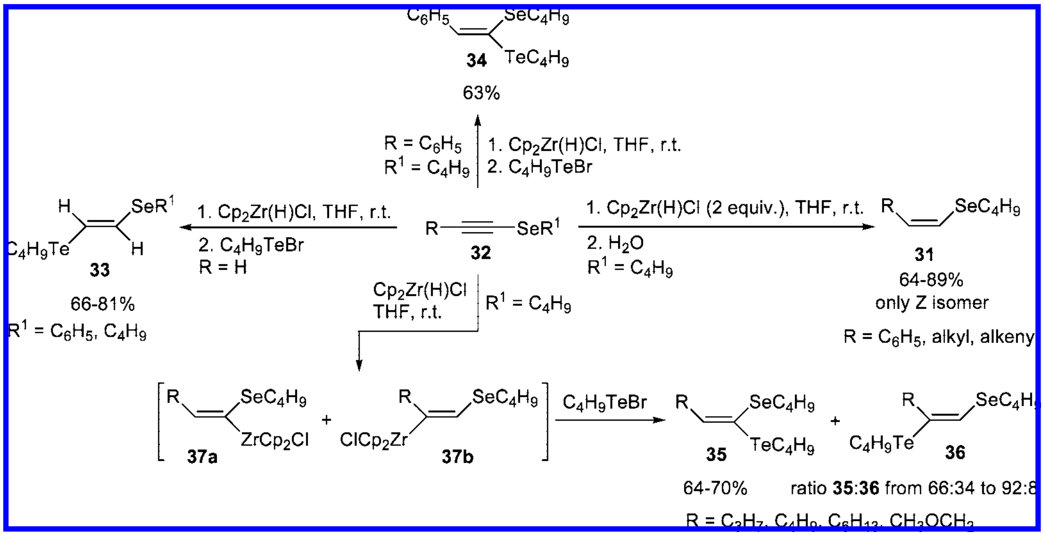


When C_4H_9TeBr was used as the electrophile, (E)-1-butyltelluro-2-organylselenoethenes **33** were obtained in good yields (66−81%) and 100% selectivity from terminal butylselenoalkynes **32** (R = H), while a mixture of selenotelluroethenes **35** and **36** (64−70% yield; **35**:**36** ratio = 66:34 to 92:8) was obtained from 1-butylseleno-2-alkylethynes **32**.[17] This occurs because the hydrozirconation of internal acetylenic selenides **32** affords a mixture of α- and β-zirconated vinyl selenides **37a** and **37b**, which, by reaction with butyltellurenyl bromide, afforded the isomers **35** and **36** (Scheme 13). In a similar fashion, the authors synthesized selenotelluroketeneacetals **35** starting from telluroacetylenes **38**, which, after hydrozirconation, were treated with C_4H_9SeBr, to afford a mixture of (Z)- and (E)-**35** in good yields (61−69%, Scheme 14).

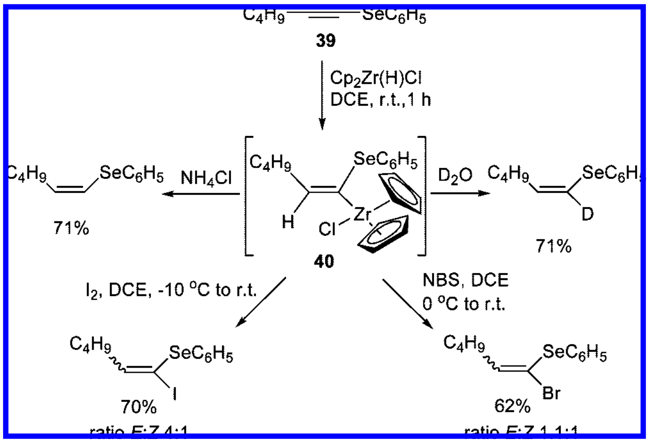
The hydrozirconation of 1-phenylselenohex-1-yne **39** using 1.2 equiv of $Cp_2Zr(H)Cl$ was described by Markó and co-workers,[18] affording the α-zirconated intermediate **40**, which was captured with several electrophiles to afford a mixture of (Z)- and (E)-1-vinyl selenides in good yields (around 70%), but with low selectivity (E:Z ratio =1.1:1 to 4:1, Scheme 15). The authors circumvented the problem of lack of selectivity in an elegant way, using a hydroalumination reaction of a new volumous selenoacetylene that will be discussed later in this review in Scheme 20.

The hydrozirconation of internal acetylenic selenides **32** in THF at room temperature was used by Zhong and Guo in

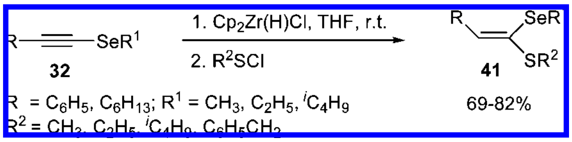
Scheme 13



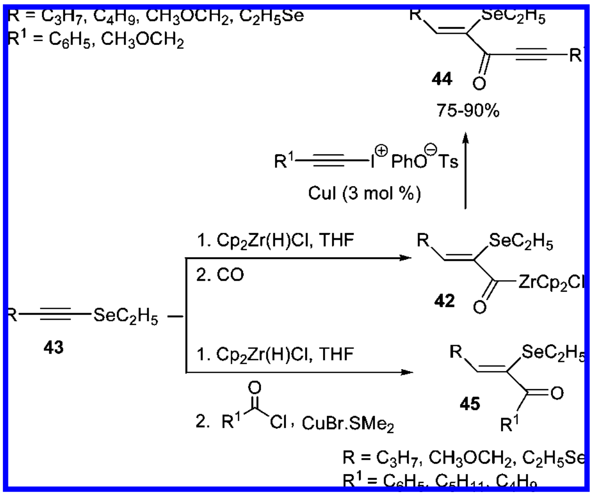
Scheme 15



Scheme 16

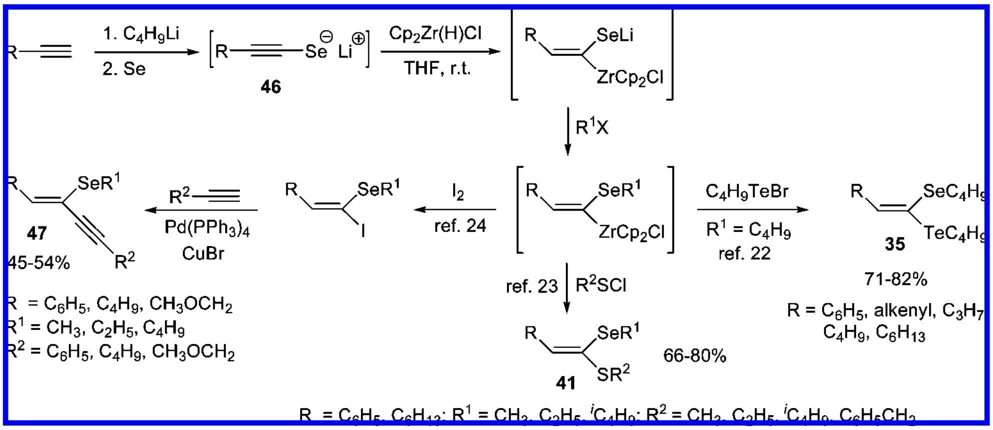


Scheme 17



the selective preparation of (*Z*)-selenothioketeneacetals **41** in good yields (69−82%).[19] In this reaction, the α-zirconated intermediate **40** was trapped with alkyl and benzylthio chlorides (Scheme 16). This is a more selective method to (*Z*)-ketene selenothioacetals, as compared with that developed by Murai (see Scheme 11),[15] starting from *S*-butyl selenoesthers.

Scheme 18



In a variant of the hydrozirconation of alkynyl selenides, Huang and Sun prepared a series of stable (*Z*)-α-selanylvinylacylzirconocene chlorides **42** through a sequential treatment of 1-ethylseleno alkynes **43** with $Cp_2Zr(H)Cl$ and carbon monoxide (Scheme 17).[20] The copper-catalyzed coupling of (*Z*)-α-selanylvinylacylzirconocene chlorides **42** with alkynyliodonium tosylates at room temperature in THF afforded, selectively, (*Z*)-α-selenylvinylalkynyl ketones **44** in good yields (75−90%). If acyl chloride is used instead of carbon monoxide, (*Z*)-α-ethylseleno-α,*β*-unsaturated ketones **45** are selectively obtained (Scheme 17).[21]

3.2. Vinyl Selenides by Hydrozirconation of Lithium Alkynyl Selenolates

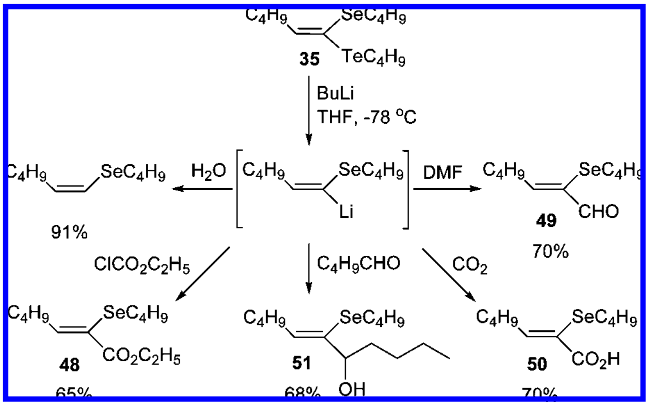
As described above, the hydrozirconation of internal acetylenic selenides and tellurides can be used for the preparation of several functionalized vinyl selenides and ketene selenochalcogenoacetals. However, in contrast to the hydrozirconation of terminal selenoalkynes, in this case a mixture of α- and *β*-zirconated intermediates is generated, and, consequently, (*Z*)- and (*E*)-vinyl selenides are obtained. This drawback can be eliminated if alkynylselenolate anion **46**, generated in situ from the reaction of an alkyne with C_4H_9Li and elemental selenium, is used instead of the internal acetylenic selenide **32** (Scheme 18).[22−24]

The method described in Scheme 18 was originally employed by Dabdoub and co-workers to prepare several (*Z*)-selenotelluroketeneacetals **35** ($R = C_4H_9$), which were selectively transmetalled with C_4H_9Li.[22] The authors explored the higher reactivity in the chalcogen/metal exchange reaction of the organotellurium moiety to prepare α-butylseleno ester **48**, aldehyde **49**, carboxylic acid **50**, and *β*-hydroxi vinyl selenides **51**, all with (*Z*)-configuration (Scheme 19). The hydrozirconation of alkynylselenolate anion was later used by Zhong and Huang to prepare, selectively, (*Z*)-selenothioketeneacetals **41**[23] and (*Z*)-2-alkylselenobut-1-en-3-ynes **47** (Scheme 18).[24] The enynes **47** were deselenylated with C_4H_9Li, followed by treatment with water to afford, selectively, (*E*)-but-1-en-3-ynes, or they were cross-coupled with C_6H_5ZnBr in the presence of $NiCl_2(PPh_3)_2$ to generate a new C−C bond in the conjugated alkenyne.

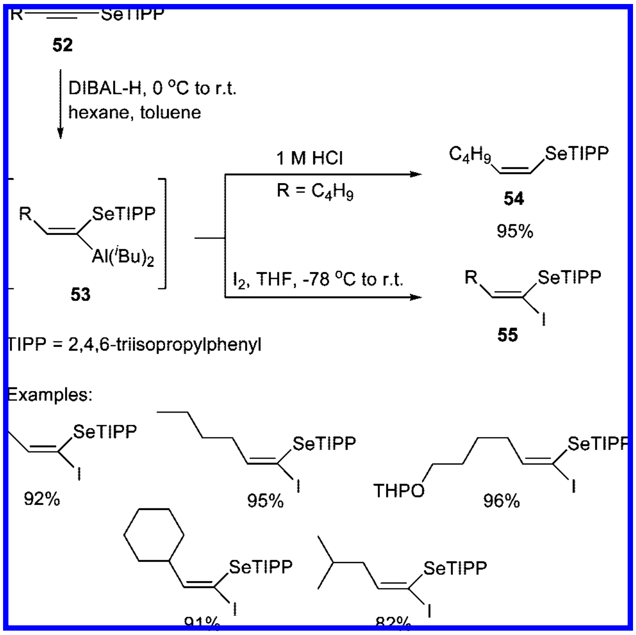
3.3. Vinyl Selenides by Hydroalumination of Acetylenic Selenides

The hydroalumination of selenoacetylenes, first described by Dabdoub and co-workers[25] and subsequently used by Al-

Scheme 19



Scheme 20



Hassan,[26] is an efficient method for α-vinylseleno alanes, which can be trapped with diluted HCl to afford, exclusively, (*Z*)-vinyl selenides in good yields. When an appropriate electrophile is used, functionalized vinyl selenides can be accessed. A drawback of this reaction, however, is the formation of a significant amount of diphenyl diselenide as coproduct, in view of the competitive spC-Se bond cleavage by the DIBAL-H. This parallel reaction limits the amount of vinyl selenide obtained. As mentioned before, Markó and co-workers have been successful in increasing the yields of the hydroalumination approach by using 1-(2,4,6-triisopropylphenyl)selenylhex-1-yne **52** as the starting material.[18] In fact, when **52** was hydroaluminated with DIBAL-H, and the vinyl alane intermediate **53** was quenched with 1 M HCl, the (*Z*)-vinyl selenide **54** was obtained in 95% yield without any amount of the diaryl diselenide (Scheme 20). The method was extended to others electrophiles (Br_2 and I_2) to afford α-halo vinylselenides, but with a loss of selectivity for Br_2 (80−90%). The authors synthesized five different (*E*)-1-iodo-1-alkylselenoalkenes **55** (82−96% yields), but the method failed completely for the selenoalkyne derived from phenylacetylene.

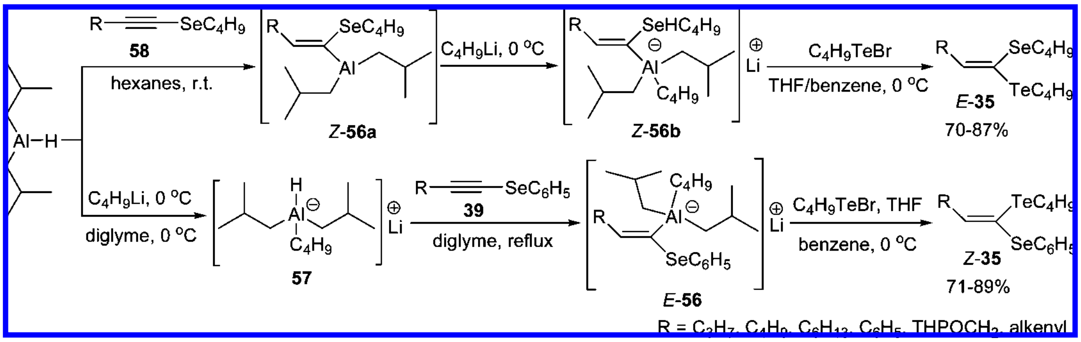
The 1-iodo-1-selenoalkenes **55** were submitted to a sequential functionalization of both heteroatom positions, with 100% of retention of the configuration at the double bond after the overall process, indicating that **55** is a convenient 1,1-dianion synthon for the stereoselective synthesis of trisubstituted alkenes. First, the more labile C−I bond was replaced by a new C−C bond, either via a Pd-catalyzed cross-coupling with organozinc derivatives or by an I−Li exchange, followed by capture of the 1-seleno-1-lithio-alkene intermediate with several electrophiles, such as aldehydes, acid anhydrides and chlorides, epoxides, etc. In the sequence, the organyl selenium group was replaced by a second C−C bond using the Se−Li exchange with LDBB or the Ni-catalyzed cross-coupling with Grignard reagents.

While this review was in production, a variation of the hydroalumination of selenoacetylenes was described by Guerrero Jr. and co-workers[27] for the selective preparation of (*E*)- and (*Z*)-selenotelluroketeneacetals **35**. Intending to increase the reactivity of the (*Z*)-butylseleno vinyl alanes **56a**, the reactants were treated with C_4H_9Li to give the respective (*Z*)-butylseleno vinyl alanates **56b**, which, after capture with C_4H_9TeBr (4 equiv), afforded the respective (*E*)-1-butyltelluro-1-butylseleno-2-organylethenes **35** in good yields (Scheme 21). On the other hand, when the Zweifel's reagent **57** was added to the selenoacetylene **39**, the anti addition adducts, (*E*)-phenylselenovinylalanate intermediates *E*-**56**, were obtained exclusively and, after capture with C_4H_9TeBr, afforded the (*Z*)-1-butyltelluro-1-phenylseleno-2-organylethenes **35** in good yields.

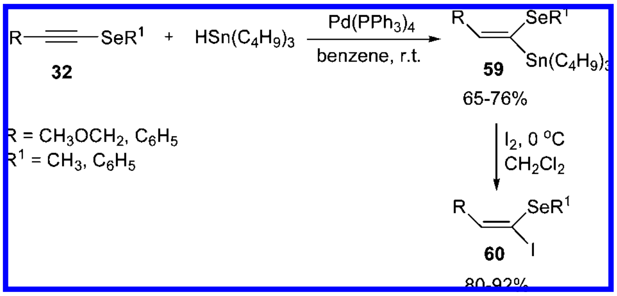
3.4. Vinyl Selenides by Hydrostannation of Acetylenic Selenides

The reaction of acetylenic selenides **32** with tributyltin hydride catalyzed by $Pd(PPh_3)_4$ in benzene at room temperature gave, selectively, (*E*)-α-selanylvinylstannanes **59** in good yields.[28] The hydrostannation of five different acetylenic selenides (R = CH_3OCH_2, C_6H_5; R^1 = CH_3, C_6H_5) was studied, and the treatment of **59** with iodine at 0 °C for 2 h

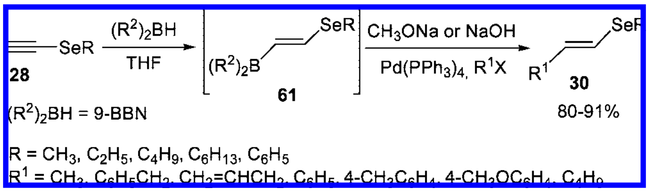
Scheme 21



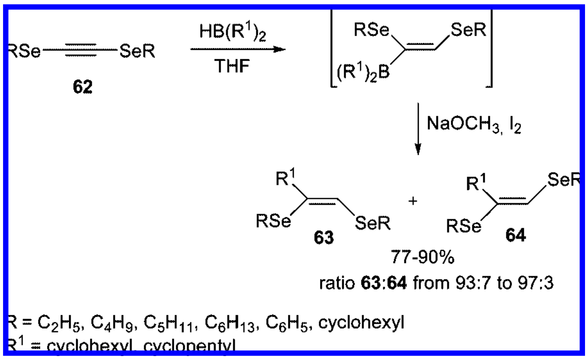
Scheme 22



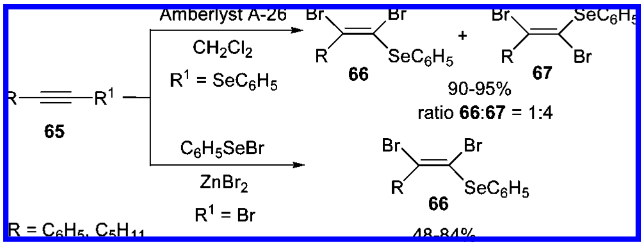
Scheme 23



Scheme 24



Scheme 25



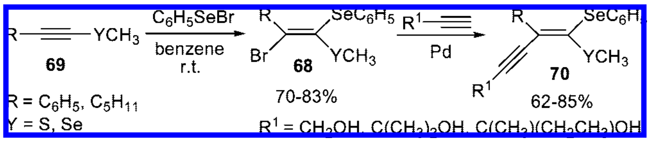
afforded the corresponding (*E*)-α-iodo vinylselenides **60** in 80−92% yields (Scheme 22).

3.5. Vinyl Selenides via Hydroboration of Acetylenic Selenides

The hydroboration of terminal acetylenic selenides **28**, followed by the reaction with alkyl halides in the presence of a catalytic amount of $Pd(Ph_3)_4$ and sodium methoxide or hydroxide, was employed for the synthesis of several (*E*)-vinyl selenides **30** in good yields (80−91%).[29] Thus, for example, the (*E*)-*β*-methylselenovinylborane **61** (R = CH_3) prepared by the hydroboration of terminal methylselenoacetylene **28** with 9-borabicyclo-[3,3,1]-nonane (9-BBN) in THF, reacted with benzyl bromide (R^1 = $C_6H_5CH_2$) in the presence of 3 mol % of $Pd(PPh_3)_4$ and 3 equiv of MeONa for 5 h under reflux to afford, exclusively, (*E*)-1-methylseleno-2-benzylethene **30** in 87% yield (Scheme 23).

When 1,2-dialkylselenoacetylenes **62** where submitted to the hydroboration with dicycloalkylboranes, followed by iodination under basic conditions, (*Z*)-1,2-dialkylseleno-1-cycloalkylethenes **63** were obtained, along with a minor amount of the (*E*)-isomer **64** (*Z*:*E* ratio = 93:7 to 97:3), in good yields (77−90%, Scheme 24).[30] The stereochemistry of **64** was established via a sequential Ni-catalyzed cross-coupling reaction with allyl zinc bromide, affording the respective (*Z*)-1-ethylseleno-1,4-dienes, and then reduction with $LiAlH_4$ followed by protonolysis, resulting in the (*E*)-alkene with retention of the configuration.

Scheme 26



3.6. Vinyl Selenides from Bromination of Acetylenic Selenides

Braga and co-workers[31] described the use of perbromide ion-exchange resin Amberlyst A-26 for the bromination of acetylenic selenides **65** (R^1 = C_6H_5Se), affording a mixture of (*Z*)- and (*E*)-1,2-dibromovinyl selenides **66** and **67** in 90−95% yields (Scheme 25). When bromine was used instead of the resin, only 20% yield was obtained. Alternatively, the authors reacted alkynyl bromides (R^1 = Br) with C_6H_5SeBr under catalysis of $ZnBr_2$, obtaining only the (*Z*)-isomer **66** in 48−84% yields.

3.7. *β*-Bromovinyl Ketene Chalcogenoacetals (Se,Se and Se,S) from Chalcogeneacetylenes

Zeni and co-workers[32] described the preparation of several *β*-bromovinylchalcogenoketene acetals **68** by the stereoselective addition of phenylselenenyl bromide to methylseleno- and methylthioalkynes **69**. The reaction was clean and afforded the trans adducts in 70−83% yields after stirring for 2 h at room temperature in benzene (Scheme 26). The chalcogenoketene acetals **68** were cross-coupled with terminal alkynes in presence of Pd(0) to afford chalcogenoenynes **70** in 62−85% yields. To determine the geometry of the chalcogenoenynes **70**, the authors used the Se/Li selective exchange, followed by capture of the lithium intermediate with NH_4Cl, affording the respective selenium-free 1-methylthiobut-1-en-3-ynes with retention of the configuration.

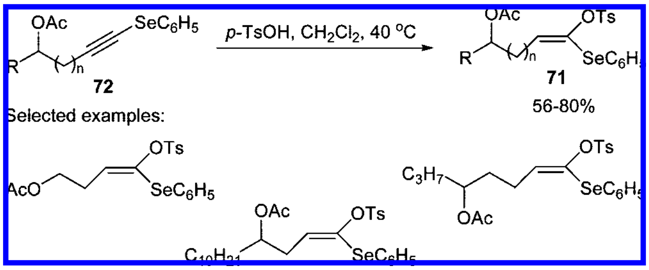
3.8. Vinyl Selenides via Hydrotosylation of Selenoalkynyl Protected Alcohols

Tiecco and co-workers[33] prepared several protected hydroxyl-(*Z*)-α-(phenylseleno)vinyl *p*-toluenesulfonates **71** from the treatment of alkynyl phenylselenides **72** with dry *p*-toluenesulfonic acid in CH_2Cl_2 at 40 °C. Only the *Z* isomer was isolated in 56−80% yields (Scheme 27). The authors used the functionalized (*Z*)-vinyl selenides to prepare α-phenylseleno *γ*- and *δ*-lactones (six examples), through an intramolecular cyclization promoted by phenylselenenyl sulfate.

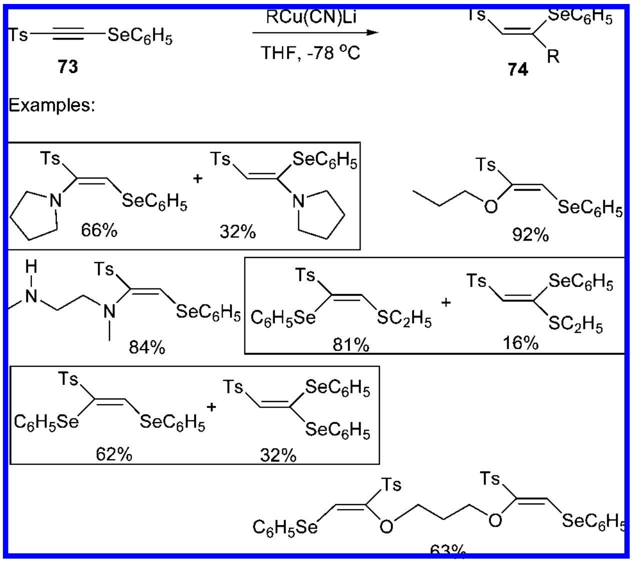
3.9. Vinyl Selenides from 1-Phenylseleno-2-(*p*-toluenesulfonyl)ethyne

Back and co-workers described a detailed study of the reactivity of new 1-phenylseleno-2-(*p*-toluenesulfonyl)ethyne

Scheme 27



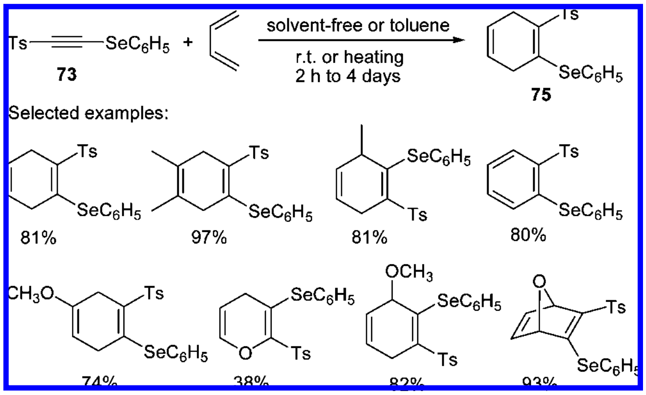
Scheme 28



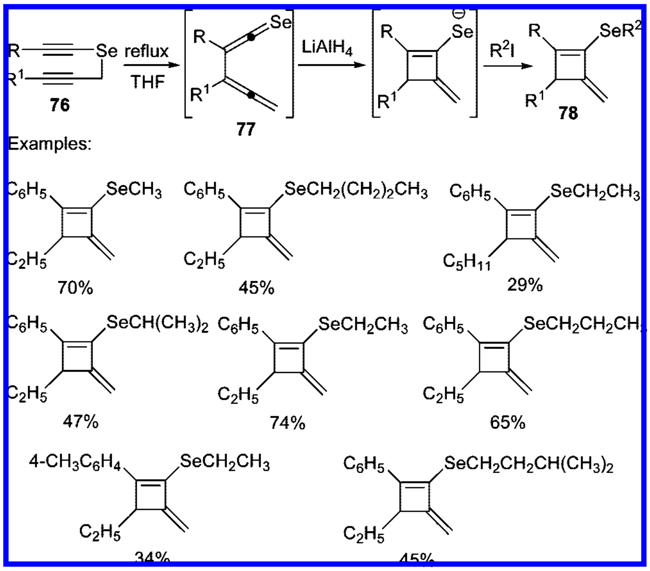
$\mathbf{73}$ against organocopper reagents, affording the anti-Michael adducts, (*Z*)-*β*-(phenylseleno)vinyl sulfones **74**, with formation of the new carbon−carbon bond at the selenium-containing carbon (Scheme 28).[34] On the other hand, when heteroatom nucleophiles (R_2NH, C_6H_5SeNa, and C_2H_5SNa) were added to **73**, the preferential formation of the Michael adduct was observed. The authors suggest that the phenylseleno group can be remarkably effective as an activating group in conjugated additions, competing effectively with the *p*-toluenesulfonyl group in some cases. In the same study, phenylselenoacetylene **73** was subjected to addition of several hard and soft nucleophiles, such as pyrrolidine, CH_3ONa, C_2H_5SNa, and C_6H_5SeNa, affording, exclusively, (*Z*)-*β*-(phenylseleno)alkenes in good yields after refluxing for 30 min (for C_6H_5SeNa) to 36 h (CH_3ONa, C_2H_5SNa). Selenoxide *syn*-elimination of vinyl selenide **74** using *m*-CPBA afforded the corresponding allenic sulfones, while reaction with $R^1Cu(SeC_6H_5)Li$ resulted in substitution of the phenylseleno group in **74** for R^1, with total retention of configuration. The functionalized vinyl selenides (R = $N(R^2)_2$, OR^2, SR^2, and SeR^2) were also subjected to several transformations, such as the nickel boride-mediated deselenylation and acidic hydrolysis.

The phenylselenoacetylene **73** is also an effective dienophile and dipolarophile for Diels−Alder reaction with a variety of symmetrical and unsymmetrical dienes, affording the respective cycloaddition adducts, vinyl selenides, in good yields (Scheme 29).[35] The cycloadditions proceed under mild conditions in the presence of an excess of diene, without the need for Lewis acid catalysis. For unsymmetrical dienes with an electron-donating group, an anomalous regiochemistry was observed, with formation of the respective 1,3-cycloadducts. The authors performed a sequence of reactions in the cyclic vinyl selenides and observed that **75** can be used as ketene equivalent in Diels−Alder reactions. Selenoxide and *p*-toluenesulfinic eliminations, nickel boride-promoted deselenylation, and cross-coupling with $CH_3Cu(SeC_6H_5)Li$ were reactions described using the vinyl selenide cyclodienes prepared.

Scheme 29



Scheme 30



3.10. Vinyl Selenides via Allenyl Selenoketene, Generated from Acetylenic Selenides

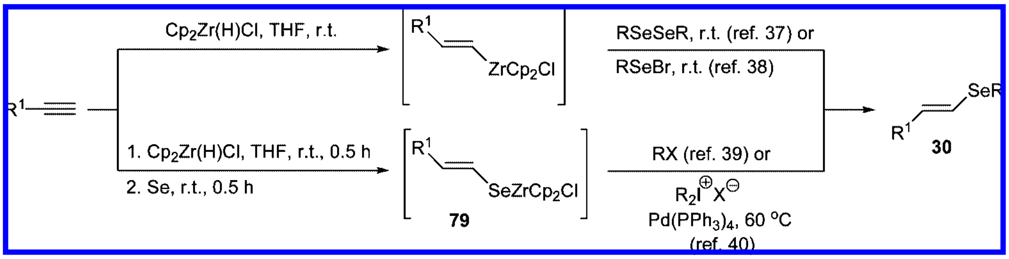
The reaction of 2-alkynyl arylethynyl selenide **76** with alkyl iodides in the presence of lithium aluminum hydride afforded, via allenyl selenoketene **77**, eight new cyclic vinyl selenides **78** in 29−74% yields (Scheme 30).[36] The generation of allenyl selenoketene intermediate **77** was confirmed by heating the selenide **76** in a React IR probe and monitoring the typical absorbance for the allenyl group.

4. Preparation of Vinyl Selenides from Alkynes

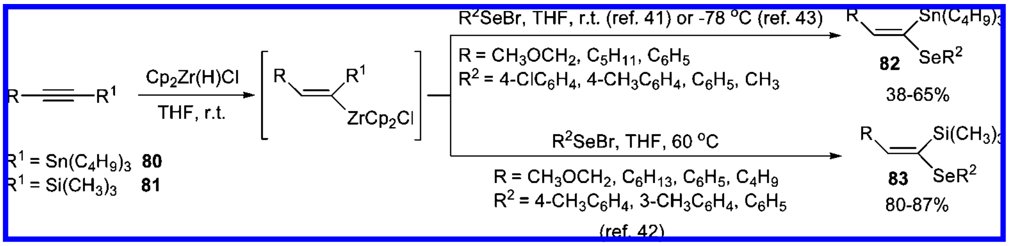
4.1. Vinyl Selenides via Zr/Se Exchange

Since the publication in 1996 by Huang and Zhu of the hydrozirconation of alkynes with Schwartz reagent, followed by capture of the zirconated alkene with diaryl diselenides[37] or arylselenenyl bromides,[38] to afford (*E*)-vinyl selenides with 100% selectivity, this reaction has been largely used for

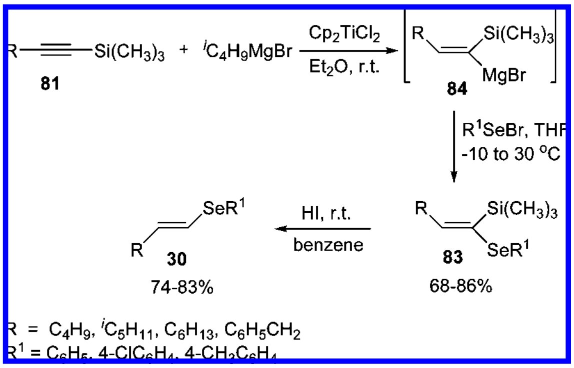
Scheme 31



Scheme 32



Scheme 33



preparation of functionalized vinyl selenides (Scheme 18). The same group published, some years later, reports of the insertion of elemental selenium into the Csp^2−Zr bond of alkenylchlorozirconocenes, affording (*E*)-vinylseleno zirconocenes **79**, which, after treatment with alkyl halides, gave the respective (*E*)-alkylvinyl selenides **30** in reasonable to good yields (38−75%).[39] The method was extended to preparation of (*E*)-arylvinyl selenides **30** via coupling of the intermediate **79** with diaryliodonium salts (Scheme 31).[40]

When 1-stannyl alkynes **80**[41] and 1-trimethylsilyl alkynes **81**[42] were employed, (*Z*)-α-selenylvinylstannanes **82** and (*E*)-2-alkyl-1-trimethylsilyl vinyl selenides **83** were obtained, respectively, in moderate to good yields (Scheme 32). In their detailed study of the hydrozirconation of stannyl alkynes aimed at the synthesis of ketene stannyl(chalcogeno) acetals, Dabdoub and Baroni[43] observed that the yield of the (*Z*)-α-selenylvinylstannanes **82** was increased when the addition of the C_6H_5SeBr was performed at a low temperature instead of at room temperature (Scheme 32). The (*E*)-2-alkyl-1-trimethylsilyl vinyl selenides **83** were regioselectively coupled with Grignard reagents in the presence of CuI to give the respective (*Z*)-1,2-dialkyl vinyl silanes in good yields.

4.2. Vinyl Selenides via Mg/Se Exchange

As an alternative to the aforementioned method, vinyl selenides **83** were stereoselectively synthesized by the hydromagnesiation of 1-trimethylsilyl alkynes **81**, followed by the reaction with arylselenenyl bromides (Scheme 33).[44] The hydromagnesiation reaction of alkynylsilanes at 25 °C in ether gave, after 6 h, the (*Z*)-α-silylvinyl Grignard reagent **84**, which reacted with selenenyl bromides in THF to afford exclusively the (*E*)-vinyl selenides **83** in 68−86% yields. The authors selected the (*E*)-vinyl selenides **83** and subjected then to the desilylation reaction with HI, affording (*E*)-vinyl selenides **30** in good yields (79−83%).

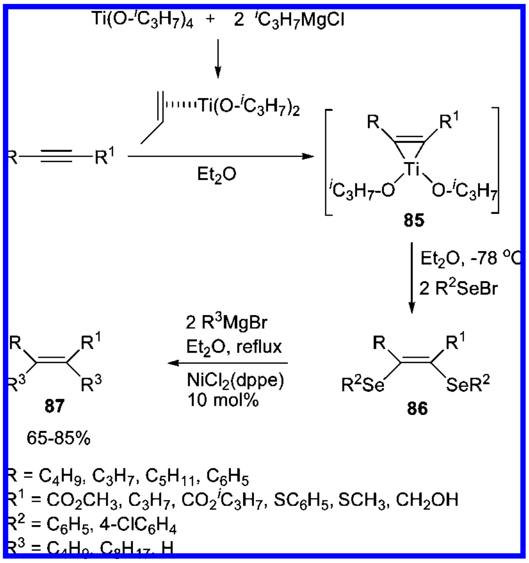
4.3. Vinyl *vic*-bis(Arylselenides) via Ti/Se Exchange

Silveira and co-workers described the reaction of alkyne-titanium complexes **85**, prepared in situ by the reaction of internal alkynes with Ti(O-$^iC_3H_7$)$_4$/2 $^iC_3H_7MgCl$, with R^2SeBr, to afford selectively (*Z*)-vinyl tetrasubstituted *vic*-bis(selenides) **86** in good yields (54−73%).[45] The method was used to prepare highly functionalized tetrasubstituted vinyl selenides, such as, α,*β*-unsaturated esters, ketene thioselenoacetals, and allyl alcohols. The *vic*-bis(selenides) **86** are very interesting in organic synthesis, as demonstrated by the authors, in that they are easily converted to tetra- and trisubstituted olefins **87** by cross-coupling with Grignard reagents under nickel catalysis (Scheme 34). This coupling reaction is similar to that used by Martynov and co-workers for the selective preparation of (*Z*)-vinyl selenides and (*Z*)-alkenes starting from (*Z*)-1,2-bis(ethylseleno)ethene.[46]

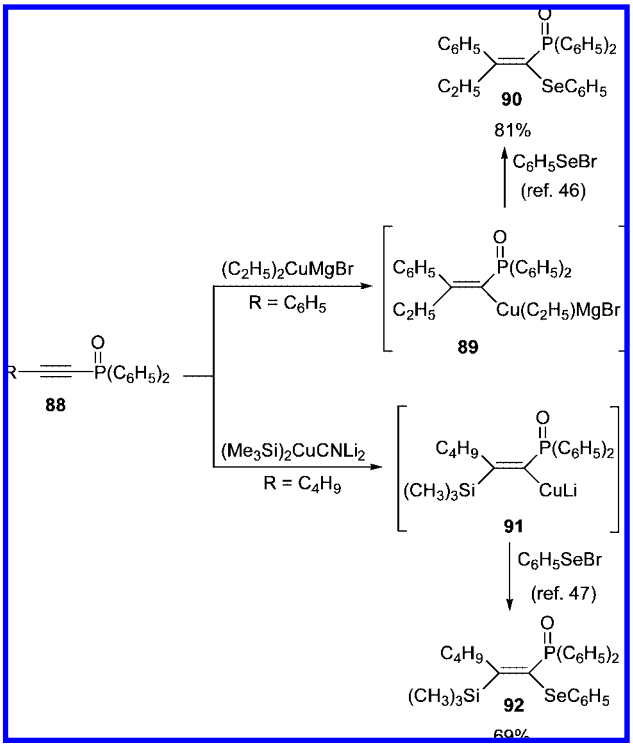
4.4. Vinyl Selenides via Cu/Se Exchange

The carbocupration of acetylenic phosphine oxides **88** (R = C_6H_5) with organocopper(I) reagents, prepared in situ from CuI and 2.0 equiv of alkylmagnesium bromide, afforded the vinylcopper(I) species **89**, which was trapped with C_6H_5SeBr to afford, selectively, the α-phenylseleno vinylphosphine oxide **90**.[47] Similarly, the authors performed the silylcupration of **88** (R = C_4H_9) with organosilylcopper(I) reagents and trapped the dimetallated intermediate **91** with C_6H_5SeBr, affording the respective (*Z*)-1-phenylseleno vinylphosphine oxide **92** in 69% yield (Scheme 35).[48] The authors used several other electrophiles instead C_6H_5SeBr, such as, alkyl halides, I_2, NBS, NCS, and PhTeI.

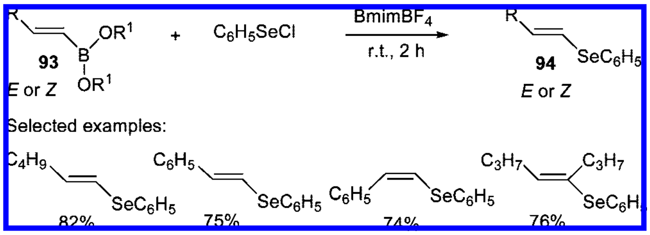
Scheme 34



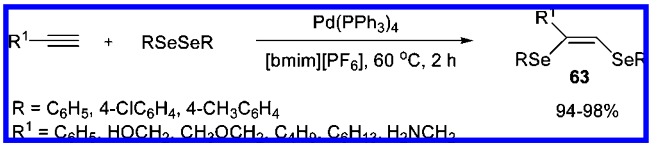
Scheme 35



Scheme 36



Scheme 37



4.5. Vinyl Selenides via B/Se Exchange

The hydroboration of alkynes proceeds stereoselectively to generate (*E*)-vinylboranes **93**. The stereospecific displacement of the boron moiety in (*E*)-vinylboronic acids and esters with C_6H_5SeCl in the presence of ionic liquid bmimBF_4 was used to synthesize (*E*)-vinyl selenides **94** in good yields (71−84%).[49a] The reaction occurs at room temperature after 2 h, and the products were easily isolated by washing the mixture with ethyl ether. The ionic liquid was reused without significant loss in yields. The reaction works also with (*Z*)-vinylboronic ester, affording the respective (*Z*)-vinyl selenide **94** in good yield (Scheme 36). Taniguchi prepared (*E*)-*β*-phenylselenostyrene in 89% yield (only one example) by the copper-catalyzed coupling of diphenyl diselenide with the organoboronic acid derived from phenylacetylene in DMSO/H_2O (2/1).[49b]

4.6. Vinyl *vic*-bis(Arylselenides) via Pd Catalyzed Diaryl Diselenide Addition

As described in the introduction of this review, the use of transition metals as catalyst in coupling reactions, focusing on the preparation of vinyl chalcogenides, including the selenium ones, was already reviewed. However, there are several Pd-catalyzed reactions that appeared after the publication of those reviews that are worthy of note. These new reports include a green version of the catalytic diaryl diselenide addition to terminal alkynes, recently described by Cai and co-workers.[50] The authors observed that the $Pd(PPh_3)_4$-catalyzed addition reaction of diaryl diselenides to terminal alkynes proceeded smoothly in the presence of ionic liquid bmimPF_6 to afford stereoselectively the corresponding (*Z*)-1,2-bis(arylseleno)-1-alkenes **63** in excellent yields (94−98%) after stirring for 2 h at 60 °C (Scheme 37). The method works with a variety of terminal acetylenes, such as propargyl amine and propargyl alcohol, alkyl and arylacetylenes. The ionic liquid/catalyst system was reused up to four times without loss of activity.

4.7. Vinyl Selenides via Addition of Nucleophilic Selenium Reagents to Alkynes

The most frequently employed method for preparation of (*Z*)-vinyl selenides is the hydroselenation of terminal and internal alkynes using nucleophilic organylselenolate anions, which can be generated in situ starting from the respective diorganyl chalcogenide in the presence of a reducing agent,[1a,2a] or from elemental selenium in the presence of alkyl lithium.[51]

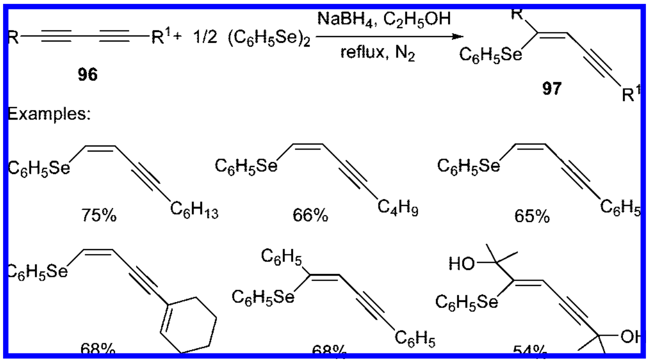
4.7.1. Hydroselenation Using (RSe)$_2$/NaBH$_4$/EtOH

The hydroselenating agent $C_6H_5Se^-$, first described by Sharpless and Lauer in 1973,[52] is easily prepared by reduction of $(C_6H_5Se)_2$ with $NaBH_4$ in ethanol and is the most commonly used nucleophilic organoselenium reagent for insertion of an organylselenium moiety into organic substrates. In their studies of reactivity of nucleophilic selenium species with different electrophiles, Miyashita and co-workers have shown that the real structure of the mild nucleophilic selenium species is the sodium phenylseleno(triethoxy)borate complex 95, which is slightly less nucleophilic than the naked selenolate anion $C_6H_5Se^-$ (Scheme 38).[53]

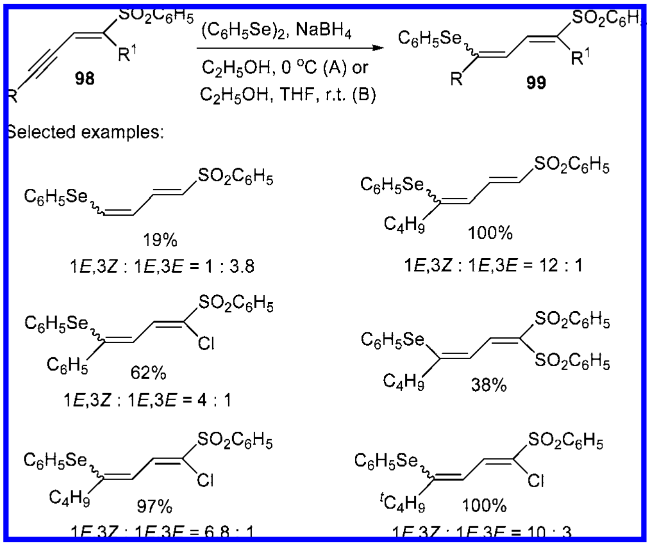
Scheme 38

$$C_6H_5SeSeC_6H_5 + 2\ NaBH_4 \xrightarrow[C_2H_5OH]{6\ C_2H_5OH} \underset{\mathbf{95}}{2\ Na[C_6H_5SeB(OC_2H_5)_3]} + 7\ H_2$$

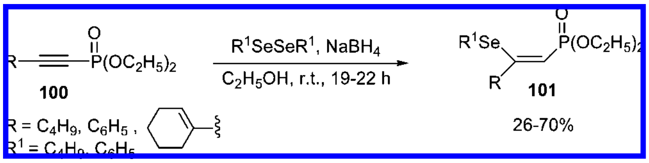
Scheme 39



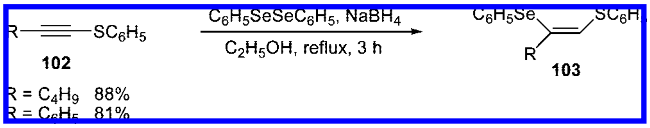
Scheme 40



Scheme 41



Scheme 42



Although the detailed studies of Miyashita and co-workers show the real entity of the nucleophile acting in the $(RSe)_2/NaBH_4/C_2H_5OH$ systems, almost all of the works involving the in situ generation of nucleophilic selenium as above use the simplified "RSeNa" notation. Intending to preserve the fidelity of the original papers, we will reproduce their descriptions. However, the reader needs to be aware of the experimental conditions used to generate the selenium species.

4.7.1.1. Addition to Conjugated 1,3-Diacetylenes. Since the publication of Comasseto's review in 1997, reporting the synthesis and reactivity of vinyl selenides, several articles appeared in the the literature showing the use of the $(RSe)_2/NaBH_4/C_2H_5OH$ system to generate in situ the nucleophilic selenium species. The main improvements or modifications in this methodology through the last years consist, especially, of the use of functionalized alkynes, such as buta-1,3-diynes, but-1-en-3-ynes, propargylamine, and propargyl alcohols derivatives, Michael acceptors (esthers, ketones, nitriles, phosphine oxides, etc.), and 1-chalcogene alkynes.

The hydroselenation of symmetrical and unsymmetrical 1,4-diorganylbuta-1,3-diynes **96** using $(C_6H_5Se)_2/NaBH_4$ in C_2H_5OH was described by Dabdoub and co-workers[54] and results in the regio-, stereo-, and chemoselective formation of the (*Z*)-1-phenylseleno-4-organyl-1-buten-3-ynes and (*Z*)-1-phenylseleno-1,4-diorganylbut-1-en-3-ynes **97** in good yields (54−75%). The authors observed that the terminal triple bond of unsymmetrical 1,3-diacetylenes **96** is more reactive than alkyl and aryl substituted ones, while the propargylic triple bond (alcohol derivative) presents an intermediary reactivity against the hydroselenation (Scheme 39).

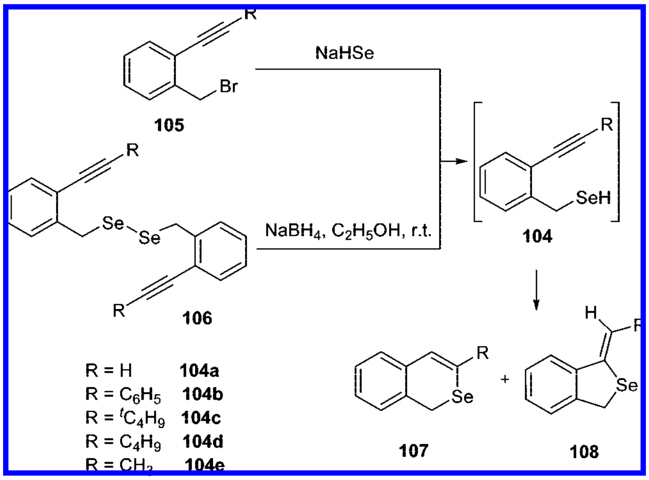
4.7.1.2. Addition to Electron-deficient Enynes. The hydroselenation of electron-deficient enyne sulfones **98** to afford the highly functionalized 4-phenylseleno-1-sulfonylbuta-1,3-dienes **99** was exhaustively studied by Yoshimatsu and Hasegawa.[55] The authors generated the nucleophilic selenium species using $NaBH_4/C_2H_5OH$ at 0 °C (Method A) or $NaBH_4/THF/C_2H_5OH$ at room temperature (Method B) (Scheme 40). In all the tested examples, a high selectivity for the product of anti addition to the δ-position was observed. This article's importance was in raising the issue of the actual nucleophile generated in the $NaBH_4/EtOH/(C_6H_5Se)_2$ system because the chemical behavior of the selenium species was unexpected when compared with the alkoxy and thiolate anions (RONa and RSNa, Scheme 40).

4.7.1.3. Addition to Michael Acceptor Alkynes. The hydroselenation of electron-deficient triple bonds (Michael acceptors) has been used to prepare highly functionalized trisubstituted vinyl selenides, precursors of tri- and tetrasubstituted alkenes. Braga and co-workers[56] reacted sodium organylseleno(triethoxy)borates, generated in situ by the reaction of diorganyl diselenide with $NaBH_4$ in C_2H_5OH as depicted in Scheme 38, with alkynylphosphonates **100** to give diethyl 2-organoselenenyl-2-organylvinylphosphonates **101** in reasonable to good yields (Scheme 41). The reaction was performed by addition of alkynylphosphonates to a solution of the nucleophilic selenium species at room temperature. When diphenyl diselenide was used as a starting material, the *Z*-vinyl selenide was obtained in modest yields (26−40%), while for dibutyl diselenide, a mixture of *E* and *Z* isomers was obtained (E:Z ratio = ~30:70) in good yields (68−70%).

4.7.1.4. Addition to 1-Chalcogene Alkynes. Dabdoub and co-workers[57] used the hydroselenation of phenylthioacetylenes **102** to prepare, selectively, (*Z*)-1-phenylseleno-2-phenylthio-1-organylethenes **103** (Scheme 42). The sodium phenylseleno-(triethoxy)borates were generated in situ under refluxing ethanol, as described above. The authors observed that the phenylthio group acts as a directing and activating group for the nucleophilic addition of the nucleophilic selenium species. In the same article, the authors prepared (*Z*)-1-organylteluro-2-phenylthio-1-organylethenes, using C_6H_5TeNa and C_4H_9TeNa as nucleophilic species.

4.7.1.5. Intramolecular Cyclization of o-Ethynylbenzyl Selenols. *o*-Alkynylbenzyl selenols **104**, obtained from reaction of *o*-alkynylbenzyl bromide **105** with NaHSe or by

Scheme 43



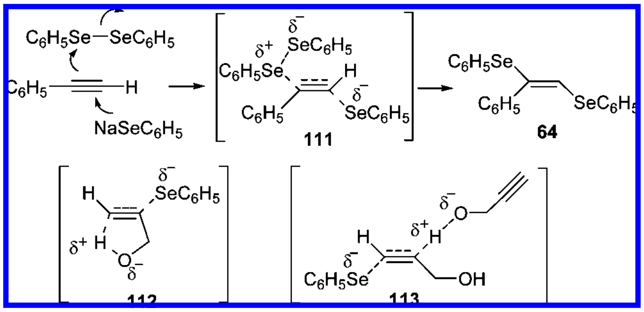
the cleavage of the diselenide **106** with NaBH$_4$/C$_2$H$_5$OH, easily cyclized to afford a mixture of the respective isoselenochromenes **107** and (*Z*)-1-methylidene-2-selenaindanes **108** in 56−81% yields (**107**:**108** ratio = 49:22 to 60:14, Scheme 43).[58,59] The terminal *o*-ethynylbenzylselenol **104a** regioselectively cyclized to isoselenochromene **107a** in 56% yield. On the other hand, the phenyl substituted selenol **107b** cyclized only via a 5-*exo*-*dig* reaction, giving only the benzylidene-2-selenaindane **108b** in 66% yield. The isoselenochromenes **107** were transformed into the corresponding 2-benzoselenopyrylium tetrafluoroborates by treatment with $(C_6H_5)_3C^+BF_4^-$ in excellent yields. These selenonium salts were used by the authors in an X-ray study and were also reacted with hydrazines to afford 5*H*-2,3-benzodiazepines in one-pot synthesis at mild conditions and in moderate yields.

4.7.2. Hydroselenation Using (RSe)$_2$/NaBH$_4$ under Solvent-free Conditions

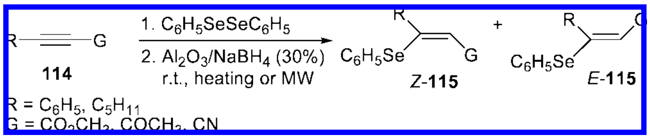
Recently, our group described a clean approach to hydroselenation of terminal alkynes using diphenyl diselenide and NaBH$_4$ supported on alumina under solvent-free conditions (Scheme 44).[60] When the alkynols **109** ($R^1 \neq C_6H_5$) reacted under our conditions at room temperature, a mixture of Markovnikov **110** and anti-Markovnikov adducts **94** was obtained in good yields after 48 h. The reaction time was drastically reduced when microwave radiation was employed as a nonclassical energy source, and the vinyl selenides with preferential (*Z*)-configuration were obtained in comparable yields after 10−15 min.

The solvent-free procedure for hydroselenation does not work with alkyl acetylenes. However, when phenyl acetylene ($R^1 = C_6H_5$) was used as the starting alkyne, 1,2-bis-(organylseleno) alkenes **64** were obtained in very good yields after several hours (stirring at room temperature) or minutes (under microwaves) with preferential (*E*)-stereochemistry (Scheme 44). A possible mechanism explaining the formation of the (*E*)-bis-(seleno)alkenes from phenyl acetylene is depicted in Scheme 45 and involves the intermediate **111**. A free-radical chain addition mechanism may also be involved. However, the fact that propargyl alcohols do not afford the respective bis-(seleno)alkenes suggests that the intermediates **112** and **113** are involved in the formation of **110** and **94**, respectively.

Scheme 45



Scheme 46

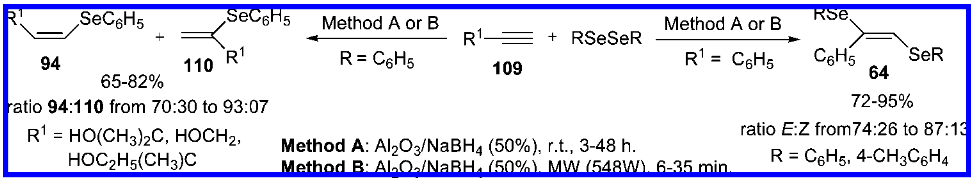


The solvent-free procedure using NaBH$_4$/Al$_2$O$_3$ for the cleavage of the Se−Se bond to generate the nucleophilic selenium species was also used by our group in the preparation of several functionalized trisubstituted vinyl selenides **115** (Scheme 46).[61] This cleaner procedure was employed in the hydroselenation of several Michael acceptors, such as alkynyl esters, ketones and nitriles **114**, affording the respective *β*-phenylseleno-α,*β*-unsaturated esters, ketones and nitriles **115** in good yields (60−83%) and preferentially with *Z*-configuration (*Z*:*E* ratio = 85:15 to 96:4). We observed that, when microwaves were used as a nonclassical energy source, the reaction time was reduced from hours to several minutes, with comparable yield and selectivity.

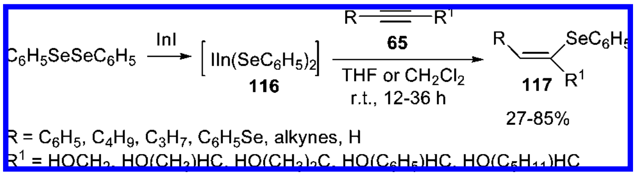
4.7.3. Hydroselenation Using Selenium−Indium Reagents

A highly selective hydroselenation of propargyl alcohol and internal alkynes **65** was achieved by Peppe and coworkers[62] using bis(phenylseleno)iodo-indium(III) **116**, easily obtained from the reaction of indium(I) iodide and diphenyl diselenide. The reaction afforded exclusively the Markovnikov adducts with (*Z*)-stereochemistry **117** in modest to good yields, but it failed with terminal alkyl acetylenes (Scheme 47). This reaction is important because it circumvents a limitation of the hydroselenation of propargyl alcohols previously described, which is the formation of a mixture of Markovnikov and anti-Markovnikov adducts, depending on the bulky substituents in the starting alkynol.

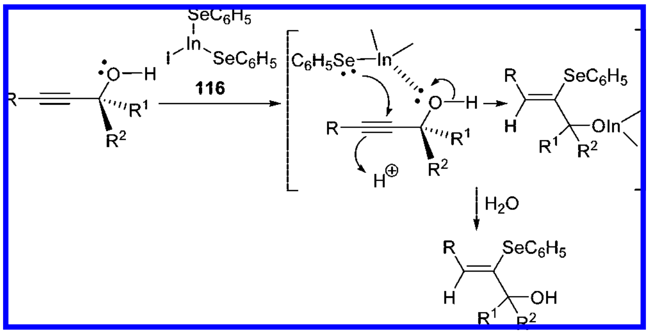
Scheme 44



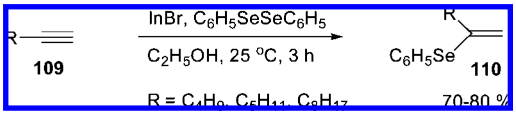
Scheme 47



Scheme 48



Scheme 49



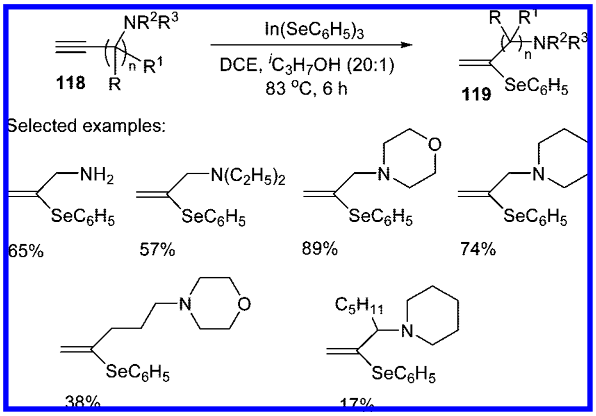
Similarly, for the solvent-free reaction using $NaBH_4/Al_2O_3$, the authors observed that the indium−selenium reagent **116** did not react with hept-1-yne and ethyl propiolate in anhydrous conditions, and they proposed a possible mechanism showing that the presence of a hydroxyl group in the alkyne is essential to the reaction (Scheme 48). Aiming to expand the scope of indium promoted hydroselenation of alkynes, the authors studied the reaction of bis(phenylseleno)bromo-indium(III), generated in aqueous ethanol (95%) and in the complete absence of oxygen, with terminal 2-alkyl-1-alkynes. Exclusive formation of the Markovnikov vinyl selenides **110** was observed after 3 h at room temperature (Scheme 49).[63] On the other hand, when phenylacetylene **109** (R = C_6H_5) was employed, a mixture of (*E*)- and (*Z*)-1,2-bis(phenylseleno)styrene (*E*:*Z* ratio = 9:1) was obtained in 20% yield, indicating that, in this case, a radical mechanism involving C_6H_5SeH, generated in situ, is involved.

Indium(III) benzeneselenolate, $In(SeC_6H_5)_3$, was efficiently used as an alternative, halide-free, selenating agent in the regioselective Markovnikov hydroselenation of terminal aminoalkynes **118**, affording the respective α-phenylseleno allylic amines **119** in moderate to good yields (Scheme 50).[64] By varying the solvent and temperature, the authors were able to control the regiochemistry of the reaction, which afforded exclusively the Markovnikov adduct when a mixture of dichloroethane (DCE) and $^iC_3H_7OH$ (20:1) was used as the solvent at 83 °C. The new Se−In bond containing reagent was easily obtained by heating metallic indium and diphenyl diselenide in high-boiling aromatic solvents, such as toluene or xylenes.

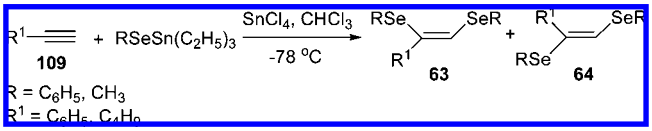
4.7.4. Vinyl Selenides using Selenium−Tin Reagents

1,2-Bis(organylseleno)-1-organylethenes **63** and **64** were also obtained by Martynov and co-workers[65,66] in moderate yields (12−59%) when they reacted organylselenotriethylstannanes, $RSeSn(C_2H_5)_3$ (R = CH_3, C_6H_5), with hex-1-yne and phenylacetylene in the presence of $SnCl_4$. Unlike the reaction of diselenides with acetylenes, which is stereoselective for the anti addition, with selenostannanes a mixture of *Z* and *E* ethenes was obtained, with the respective diselenides and chlorotriethylstannane (Scheme 51). The authors observed that, when using 5% KOH instead of water in the quench of the reaction, the hydroselenation adduct, 1-methylseleno-1-phenylethene, was obtained in 26% yield from the reaction of $CH_3SeSn(C_2H_5)_3$ with phenylacetylene.

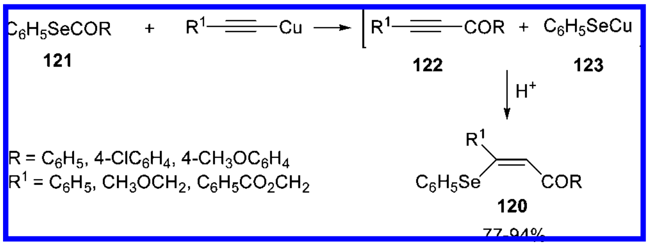
Scheme 50



Scheme 51



Scheme 52



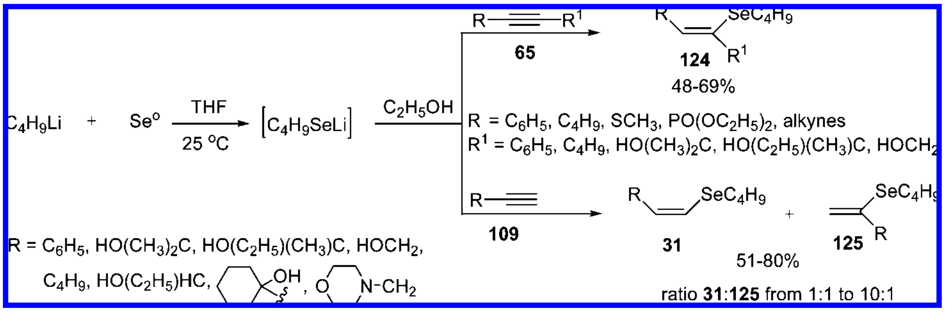
4.7.5. Hydroselenation using Selenium−Copper Reagents

(*Z*)-*β*-Arylseleno-α,*β*-unsaturated ketones **120** were selectively obtained in good yields (77−94%, only *Z* isomer was isolated) by the selenocarbonylation addition of aryl selenoesters **121** to terminal alkynes under copper(I) catalysis.[67] The method works with a variety of terminal acetylenes, such as propargyl ether, alkyl, and arylacetylenes. The first step of the reaction is believed to involve the α,*β*-alkynone **122** intermediate and the nucleophilic C_6H_5SeCu species **123**, which, after acidification, was converted to the respective arylselenol and added to the alkynyl ketone **122** (Scheme 52).

4.7.6. Hydroselenation Using Selenium−Lithium Reagents

As mentioned above, the nucleophilic species of selenium can also be generated in situ, starting from elemental selenium and C_4H_9Li in THF at room temperature. In this case, the C_4H_9SeLi anion is the effective nucleophile. This important improvement, described by Zeni and co-workers,[51] avoids the previous preparation of diorganyl diselenides or even the use of malodorous selenophenol as the selenium

Scheme 53



Scheme 54

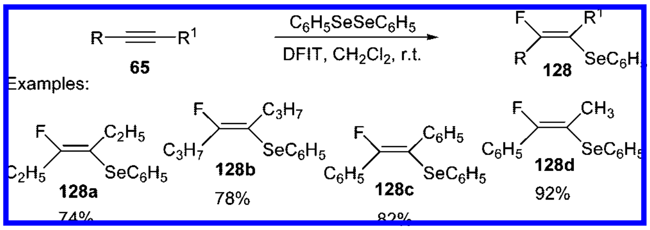
source. Using this new approach, the hydroselenation of several internal **65** and terminal alkynes **109** was described, affording the corresponding vinyl selenides **124**, **31**, and **125** in moderate to good yields (Scheme 53). The method was extended to symmetrical and unsymmetrical 1,3-diacetylenes **65** and other functionalized alkynes, such as 1-alkynyl phosphonate and 1-methylthio acetylene. Except for the hydroselenation of phenylacetylene, which affords exclusively the (*Z*)-2-butylselenostyrene **31**, in all the tested examples a mixture of *Z*- and *E*-isomers (for internal alkynes and 1,3-diacetylenes) or (*Z*)- and geminal vinyl selenides (for terminal alkynes) was obtained. The authors also described the use of their new methodology in the preparation of tetrasubstituted vinyl selenides, based on hydroselentation followed by trapping of the vinyllithium intermediate with benzaldehyde instead of water. The highly functionalized vinyl selenide **126** was obtained in 78% yield from the 1-alkynyl phosphonate **127** (Scheme 54). Potapov and coworkers[68] prepared two unsymmetrical divinyl selenides with *Z*-configuration starting from elemental selenium, acetylene, and phenylacetylene (63%) or propargyl alcohol (57% yield). By this protocol it was possible to prepare also the tellurium analogues. Alternatively, the nucleophilic species C_6H_5SeLi could be generated in situ from diphenyl diselenide and $LiAlH_4$ in THF. This protocol was used in the selective synthesis of 1,2-dichlorovinyl phenyl selenide (43% yield), starting from dichloroacetylene.[69]

4.8. Vinyl Selenides via Addition of Electrophilic Selenium Reagents to Alkynes

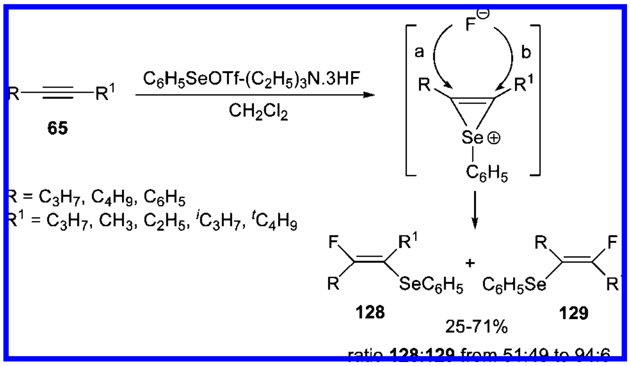
4.8.1. Vinyl Selenides via Phenylselenofluorination of Alkynes

The preparation of the very utile, highly functionalized, tetrasubstituted (*E*)-fluoro(phenylselenoalkenes) **128** can be achieved via several pathways using different C_6H_5Se-F equivalents, such as $(C_6H_5Se)_2$/difluoroiodotoluene (DFIT),[70] $C_6H_5SeOTf\text{-}(C_2H_5)_3N.3HF$, $C_6H_5SeSbF_6\text{-}(C_2H_5)_3N.3HF$,[71] or by the electrochemical fluorochalcogenation of alkynes with C_6H_5SeF generated in situ.[72] For all the studied examples, the (*E*)-1-phenylseleno-2-fluoroalkenes **128** were exclusively obtained. With the recent improvements of the selective fluoroselenylation of alkynes and the use of the system $(C_6H_5Se)_2$/DFIT for the generation of the reactive species, C_6H_5SeF was added to symmetrical and unsymmetrical

Scheme 55



Scheme 56



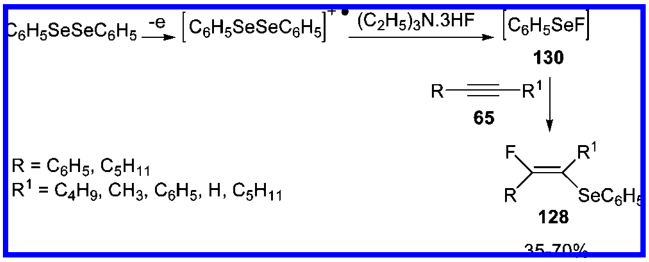
internal alkynes in good yields (Scheme 55).[70] When 1-phenylprop-1-yne was used, only the (*E*)-*β*-phenylseleno derivative **128d** was obtained in 92% yield. The authors observed, however, that the method did not work with terminal alkynes, which afforded, exclusively, phenylselenoalkynes, with hydrogen substitution by C_6H_5Se.

The use of novel reagents $C_6H_5SeOTf\text{-}(C_2H_5)_3N\cdot 3HF$ and $C_6H_5SeSbF_6\text{-}(C_2H_5)_3N\cdot 3HF$[71] as PhSeF equivalents in the fluoroselenylation of symmetrical and unsymmetrical internal alkynes afforded (*E*)-phenylselenofluoroalkenes **128** and **129** in reasonable to good yields (25−71%). For the unsymmetrical alkynes, steric factors are important in the regiochemistry of the addition (Scheme 56).

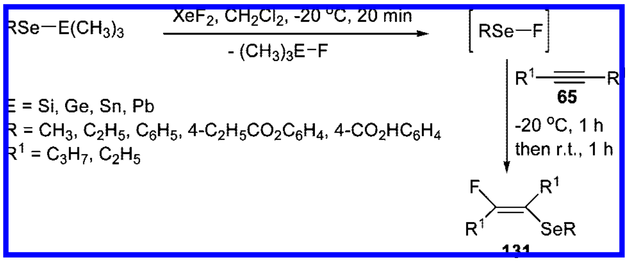
The electrochemical oxidation of $(C_6H_5Se)_2$ can generate an electron-deficient intermediate $(C_6H_5SeSeC_6H_5)^+$, which reacts with HF, leading to C_6H_5SeF.[72] The addition of **130** to internal alkynes produced the corresponding (*E*)-1-phenylseleno-2-fluoroalkenes **128** in modest to good yields (35−70%). However, when 1,2-diphenylacetylene **65** ($R = R^1 = C_6H_5$) and the terminal phenylacetylene **65** were used, only a 10% yield of **128** was achieved (Scheme 57).

Several RSeF species were efficiently generated in situ by Poleschner and co-workers through the cleavage of selenides of the type RSe-E$(CH_3)_3$ (E = Si, Ge, Sn, Pb) with xenon difluoride.[73] To prove the formation of the reactive fluoroselenylating species, the authors synthesized selectively (*E*)-organylselenofluroalkenes **131** in moderate to good yields

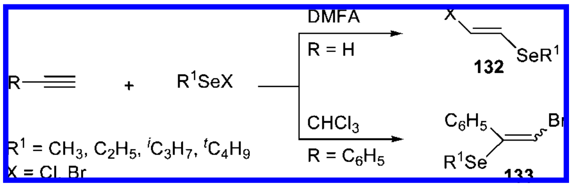
Scheme 57



Scheme 58



Scheme 59



by reacting RSeF with symmetrical internal alkynes oct-4-yne and hex-3-yne (Scheme 58). The best yields of **131** were obtained starting from RSe-Si$(CH_3)_3$ (72−82%), while RSe-Sn$(CH_3)_3$ derivatives were less reactive (26−71%). For all the abovementioned selenides, the reaction with XeF_2 was fast (20 min at −20 °C in CH_2Cl_2), and the addition step was done in one pot with stirring for additional 2 h in the presence of the alkyne.

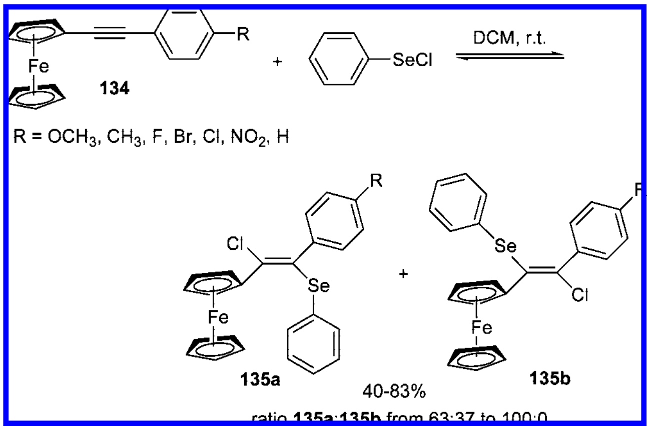
4.8.2. Vinyl Selenides via Selenochlorination and Selenobromination of Alkynes

Potapov and co-workers synthesized several (*E*)-alkyl-2-halovinyl selenides **132** (X = Cl, Br) by the anti addition of akylselenenyl chlorides and bromides to acetylene.[74] When phenylacetylene was used as the starting alkyne in the reaction with alkylselenenyl bromide in $CHCl_3$,[74a] a mixture of (*E*)- and (*Z*)-1-alkylseleno-2-bromo-1-phenylethenes **133** was obtained (Scheme 59). The authors claim a high yield and emphasize the simple procedure of their method.

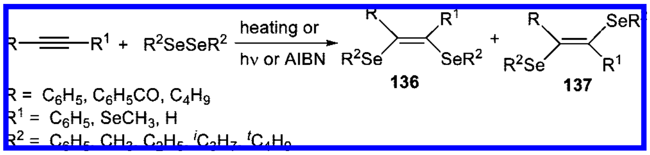
More recently, the same group described the use of an equimolar amount of benzeneselenamide and $SnCl_4$ as a new selenochlorinating system instead C_6H_5SeCl for preparation of (*E*)-3-chloro-4-(phenylselanyl)hex-3-ene.[75] In this case, the effective electrophilic species of selenium is generated in situ, via chlorination of selenamide. In the same work, several examples of vinyl sulfides were synthesized using the sulfur-analogue benzenesulfenamide.

Floris and co-workers[76] described the regioselective electrophilic addition of C_6H_5SeCl to arylferrocenylalkynes **134** in dichloromethane (DCM) at room temperature, affording a mixture of two regioisomers (*E*)-1-chloro-1-ferrocenyl-2-phenylseleno-2-arylethene **135a** and (*E*)-2-chloro-1-ferrocenyl-1-phenylseleno-2-arylethene **135b** in 40−83% yields and a **135a**:**135b** ratio from 63:37 to 100:0 (Scheme 60). The authors believe that the preferential formation of adduct **135a** is probably due to a favorable iron−selenium interaction, as suggested by a semiempirical calculation.

Scheme 60



Scheme 61



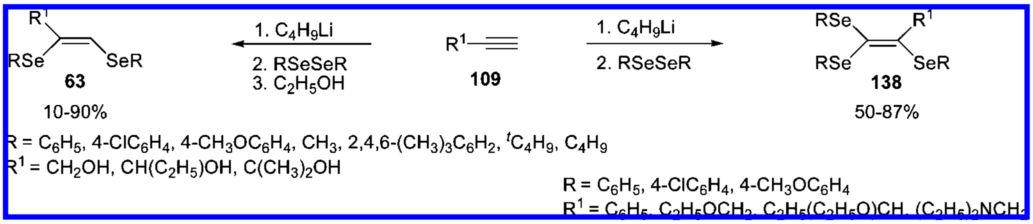
The selenochlorination of acetylene using $SeCl_4$ in ether for preparation of (*E*,*E*)-bis(2-chlorovinyl) selenide was described by Martinov and co-workers.[77] When the reaction was performed in the presence of $SnCl_4$ and CH_2Cl_2, (*E*)-2-chlorovinyl 1,2,2-trichloroethyl selenides was obtained in 62% yield after 3 h.

4.9. Vinyl Selenides via Thermal Addition of Dialkyl Diselenides to Alkynes

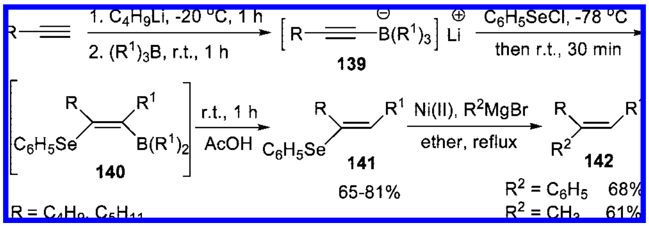
Potapov and co-workers[78] described a study of thermal addition of several dialkyl diselenides to nonactived terminal alkynes to afford a mixture of *Z*- and *E*-1,2-bis(alkylseleno)-ethenes **136** and **137** in good yields (78−96%). When a mixture of the dialkyl diselenide and phenylacetylene was heated at 140 °C in a sealed tube, the *E*-isomers predominated over the *Z*-ones. This is in acordance with a radical mechanism and is contrary to the results of the palladium catalyzed syn addition, where the *Z*-isomer is the major product.[79] The same group realized a detailed study of the thermal, photoinitiated, and AIBN-induced reactions of diorganyldiselenides to acetylenes, affording *Z*- and *E*-1,2-bis(organylseleno)-ethenes **136** and **137** (Scheme 61).[80] The authors studied the reactivity of different diselenides and acetylenes and concluded that the reactivity order of diselenides is $(C_6H_5Se)_2 \cong (CH_3Se)_2 \geq (C_2H_5Se)_2 > (^iC_3H_7Se)_2 \gg (^tC_4H_9Se)_2$ and for the acetylenes is $C_6H_5C{\equiv}CH > C_6H_5COC{\equiv}CH > C_4H_9C{\equiv}CH > C_6H_5C{\equiv}CSeCH_3 > C_6H_5C{\equiv}CC_6H_5$. However, when $CHCl_3$ was used as the solvent in the presence of $SnCl_4$, syn addition of dialkyl diselenide to phenylacetylene was observed at room temperature, affording preferentially *Z*-1,2-bis(alkylseleno)-ethenes **136**.[81]

The same authors studied the thermal addition of dimethyl diselenide to trimethylsilyl acetylene.[82] In contrast to the addition to nonactived alkynes described above, in this case

Scheme 62



Scheme 63



the major product was (*Z*)-1,2-bis(methylseleno)-1-trimethylsilylethene obtained in 70% yield (*Z*:*E* ratio = 95:5) at 150 °C.

4.9.1. Vinyl Selenides via Addition of Diphenyl Diselenides to Alkynyl Lithium

Recently, Zeni and co-workers[83] described an exhaustive study of a catalyst-free addition of dichalcogenides to terminal alkynyl lithium to afford selectively bis-**63** and tris-chalcogenoalkenes **138** in good yields. Zeni's method avoids a priori preparation of the selenoacetylene and produces exclusively the *Z* isomers in good yields and under mild reaction conditions (Scheme 62). The authors observed that the selectivity control was governed by the effective participation of the hydroxyl group of propargyl alcohols. When acidic hydroxyl group protons are present in the alkyne, (*Z*)-bis-vinyl selenides **63** were obtained, while alkynes with no potentially acidic hydroxyl group protons at propargyl positions gave exclusively tris-vinyl selenides **138**. The method was successfully extended to diorganyl sulfides, but failed with the tellurium analogues.

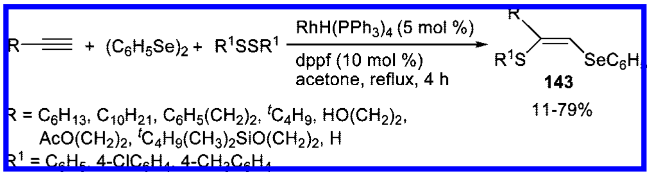
4.10. Vinyl Selenides via Selenium Electrophile Addition to 1-Alkynyltrialkyl Borates

Hevesi and Gerard[84] described the reaction of 1-alkynyltrialkyl borates **139** with phenylselenenyl chloride, affording selectively (*Z*)-β-phenylseleno alkenylboranes **140** in good yields (Scheme 63). When the alkenyl boranes were subjected to protodeborylation with acetic acid in a one pot sequence, 1,2-disubstituted vinyl selenides **141** were obtained in good yields and high selectivity. The authors also performed a Ni-catalyzed coupling of **141** with Grignard reagents, affording trisubstituted alkenes **142** in good yields and with high regio- and stereoselectivity.

4.11. Vinyl Selenides via Selenothiolation of Alkynes

Yamaguchi and co-workers[85] described the rhodium complex, RhH(PPh$_3$)$_4$, and 1,1′-bis(diphenylphosphino)ferrocene, dppf-catalyzed regio- and stereoselective addition of diaryl disulfides and diaryl diselenides to terminal alkynes, affording (*Z*)-1-arylseleno-2-arylthio-1-alkenes **143** in 11−79% yields after refluxing in acetone for 4 h (Scheme 64).

Scheme 64



Alternatively, the selenothiolation of acetylene can be performed under base-catalyzed conditions (KOH/DMSO/H$_2$O), with good selectivity for the (*Z*)-**143** (R^1 = CH$_3$, C$_6$H$_5$; SeC$_6$H$_5$, SeC$_4$H$_9$, SeCH$_3$).[86]

4.12. Vinyl Selenides from Phenyl Propargyl Selenides

Yoshimatsu and co-workers[87] developed a four-carbon homologation process for the selective synthesis of 4-ethoxy-2-(organylthio)-1-phenylselenobuta-1,3-dienes **144a**,**b** in good yields starting from phenyl propargyl selenide **145** (Scheme 65). The reaction is believed to proceed via the allene intermediate **146**, which undergoes the addition of the sulfenyl group to afford the 1-selenyl-2-sulfenyl alkenes **147a**,**b**. The selenobutadienes **144** were conveniently converted to the respective highly functionalized conjugated dienals and trienals **148** in a two step sequence.

5. Preparation of Vinyl Selenides from Allenes and Alkenes

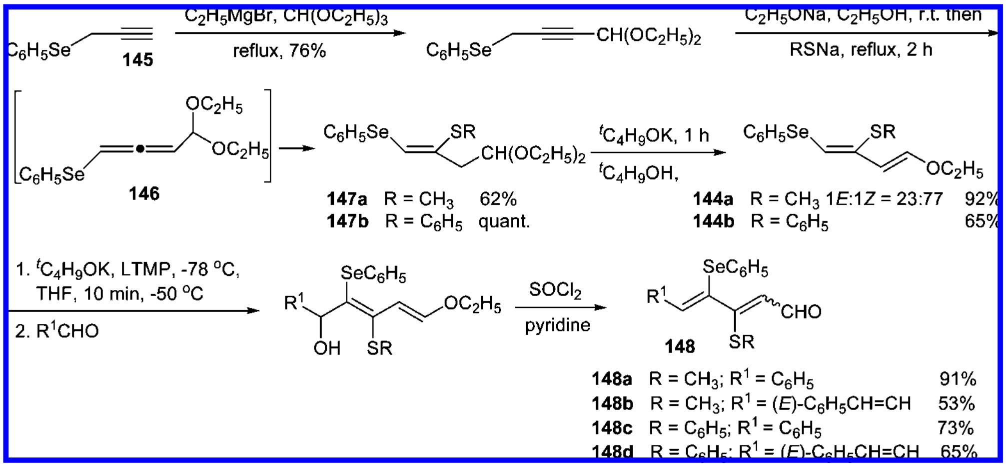
5.1. Vinyl Selenides from Vinyl(phenyl)iodonium Salts

(*E*)-(β-Organylvinyl)phenyliodonium salts **149** readily react with sodium arylseleno(triethoxy)-borate, generated in situ from the reaction of (ArSe)$_2$ with NaBH$_4$/C$_2$H$_5$OH at 0 °C, to give the respective vinyl selenides **30** instantaneously and in good yields (Scheme 66).[88] When (*E*)-(β-phenylvinyl)phenyliodonium tetrafluoroborate **149** was used, (*E*)-vinyl selenides **30** were the only observed products, with retention of the configuration. On the other hand, when (*E*)-(β-butylvinyl)phenyliodonium tetrafluoroborate **149** reacted under the same conditions, the (*Z*)-vinyl selenide **30**, with complete inversion of the configuration of the starting alkene, was obtained exclusively. The authors suggested that the first case, the retention of the configuration, occurs via an addition−elimination or a ligand coupling mechanism, while the inversion of the configuration could be related to an S$_N$2 transition state.

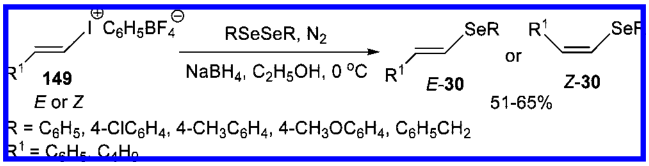
5.2. Vinyl Selenides from Vinyl Bromides

The first synthesis of vinyl selenides by nucleophilic vinylic substitution of unactived vinyl halides was described by Tiecco and co-workers.[89a] In their pioneering work, the authors used the RSe$^-$ anion (R = CH$_3$ or aryl) as a

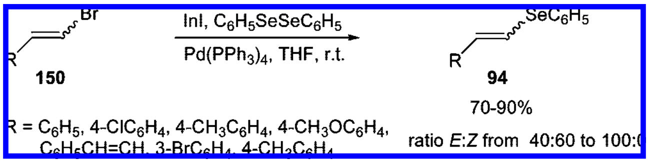
Scheme 65



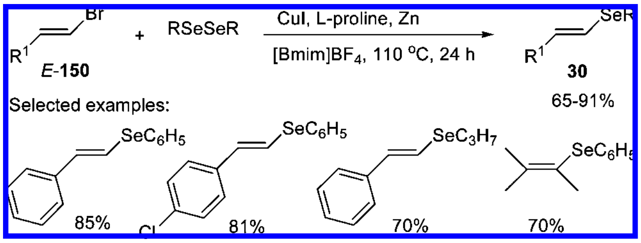
Scheme 66



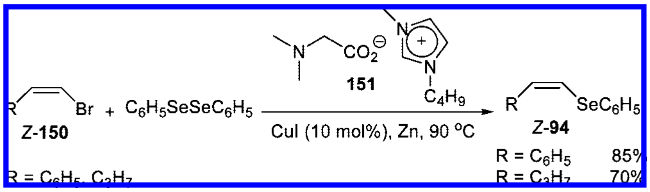
Scheme 67



Scheme 68



Scheme 69



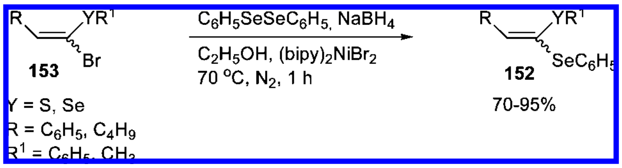
nucleophilic selenium species, which was generated in situ using Na/DMA or Na/DMF. This method is a simple and efficient route to obtain selectively (*E*)- or (*Z*)-vinyl selenides, and in the past few years different nucleophilic species of selenium have been used in this reaction.[89] Recently, Gavrilova and Amosova described a novel method for preparation of vinyl selenides using sodium etheneselenolate, generated in situ by the reaction of divinylselenide with Na/NH_3.[3c] The authors prepared several functionalized vinyl selenides in good yields starting from vinyl or aryl bromides. The nucleophilic species of selenium generated by the reaction of indium(I) iodide with diphenyl diselenide [bis(phenylseleno)-iodo-indium(III)], originally described by Peppe and co-workers,[62] was employed by Ranu and co-workers[90] for the selective preparation of several (*E*)-vinyl selenides **94** in good yields starting from vinyl bromides **150** (Scheme 67). The substitution reaction was catalyzed by palladium(0) [$Pd(PPh_3)_4$] and was 100% stereoselective for (*E*)-vinyl bromides, while the (*Z*)-starting vinyl bromides afforded a mixture of (*Z*)- and (*E*)-vinyl selenides (*Z*:*E* ratio = 40:50 to 70:30).

Recently, Chang and Bao[91] described the CuI/L-proline-catalyzed zinc-promoted coupling reaction of vinyl bromides with diorganyl diselenides in the presence of the ionic liquid (IL) [bmim]BF_4 (Scheme 68). The reaction proceeds at 110 °C for 24 h. Using this recyclable metal-catalyzed procedure, the authors prepared several (*E*)-β-organylselenostyrenes **30** in good yields starting from (*E*)-β-bromostyrenes **150**, without formation of any (*Z*)-isomer. When (*Z*)-1-bromopent-1-ene was used instead of (*E*)-β-bromostyrenes, the coupling occurred with slight isomerization (*Z*:*E* ratio = 95:5). The authors reused the metal catalysts immobilized in IL up four times with little effect on the rate or yield of the reaction in each cycle.

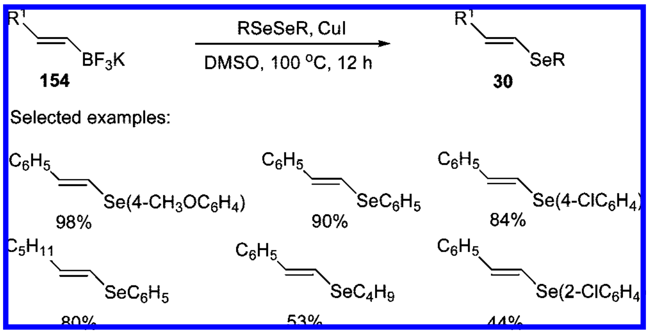
Bao and co-workers[92] also described the use of ILs based on amino acids, such as *N*,*N*-dimethylglycine, [bmim]Gly **151**, to promote the coupling of diphenyl diselenide with (*Z*)-vinyl bromides **150** catalyzed by CuI/Zn, affording the respective (*Z*)-vinyl selenides **94** in good yields (Scheme 69). The method was applied to the hydrothiolation reaction with a series of thiols. Only two examples of this reaction were studied, using selenium starting from (*Z*)-β-bromostyrene (85% yield, *Z*:*E* ratio = 98:2) and (*Z*)-1-bromo-1-pentene (70% yield, *Z*:*E* ratio = 96:4). Similar to the method described in Scheme 68, the metal catalysts immobilized in **151** can be reused up four cycles. The new IL plays multiple roles in this reaction, acting not only as the solvent but also as the base and promoter for the Cu(I) catalyzed coupling.

The substitution of bromine or iodine atoms by phenylselenolate anion was explored by Stefani and co-workers for the preparation of several selenoketeneacetals **152** (Scheme 70).[93] In this case, 1-chalcogene-1-haloalkenes **153**,[94,95] were used as the starting material and $(bipy)_2NiBr_2$ was used as the catalyst for the substitution reaction. The nucleophilic selenium species was generated as described before in this section, using $(C_6H_5Se)_2/NaBH_4/C_2H_5OH$.

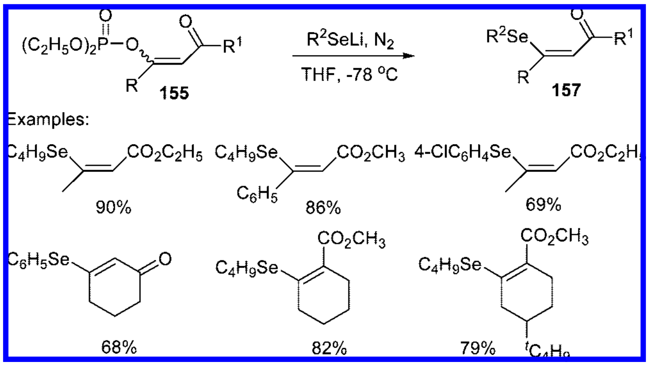
Scheme 70



Scheme 71



Scheme 72



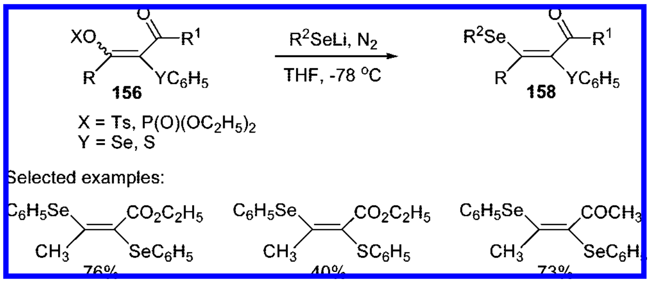
5.3. Vinyl Selenides from Potassium Vinyltrifluoroborates

Beside the methods involving vinylic boron precursors, such as vinylboranes and vinylboronic acids and esthers, described in section 4.5, potassium vinyltrifluorobarate salts **154** were recently used by Braga and co-workers as a new precursor in the selective synthesis of (*E*)-vinyl selenides (Scheme 71).[96] The CuI-catalyzed coupling reaction was performed in DMSO at 100 °C and, after 12 h, the (*E*)-vinyl selenides **30** were isolated in 44−98% yields. The method is general and works well with both aromatic and aliphatic diselenides, as well as with (*E*)-*β*-styryl and (*E*)-*β*-alkylvinyltrifluoroborates. This approach is valuable because the available methods for the selective preparation of (*E*)-vinyl selenides are not trivial.

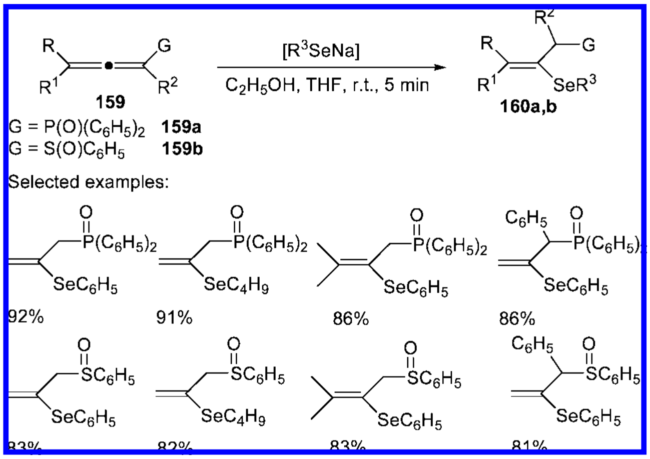
5.4. Vinyl Selenides from Enol Phosphates and Enol Tosilates

Silveira and co-workers[97] described the reaction of enol phosphates **155** of *β*-dicarbonyl compounds with lithium organoselenolates to give *β*-organoseleno (*Z*)-α,*β*-unsaturated carbonyl compounds **157** in good yields (Scheme 72). When the reaction was performed at −78 °C, only the *Z* isomer **157** was obtained, even starting from a *Z*/*E* mixture of the enolphosphate **155**. This vinylic substitution-based method was also used for the preparation of 1,2-bis(organochalcogenium)alkenes **158** in moderate to good yields and with high preference for the *E* isomer (*E*:*Z* ratio = 90:10 to 100:0, Scheme 73).

Scheme 73



Scheme 74

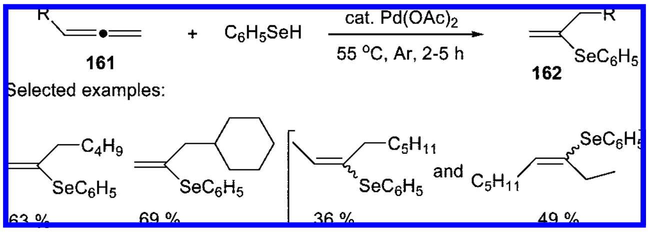


5.5. Vinyl Selenides via Hydroselenation of Allenes

Huang and co-workers[98] described the selective hydroselenation of 1,2-allenylphosphine oxides[98a] **159a** and 1,2-allenylsulfoxides[98b] **159b** to afford, respectively, *β*-organoselenium allyl phosphine oxides **160a** and *β*-(organoseleniumallyl)phenylsulfoxides **160b** in good yields (Scheme 74). The authors used the system $NaBH_4/(R^3Se)_2/C_2H_5OH$ to generate the nucleophilic species of selenium. The reaction is very fast (5 min) and affords the desired products at room temperature and with the addition of the selenium exclusively at the *β*-position. The authors believe that this selectivity is due to the mechanism of the addition, which involves a conjugated addition of R^4Y^- to functionalized allenyl at the *β*-position to afford an allyl carbanion stabilized by the sulfoxide[98a] and phosphine oxide[98b] groups. The procedure was also successfully extended to tellurium and sulfur analogues.

Ogawa and co-workers[99] described a method for the hydroselenation of deactivated allenes **161**, using palladium(II) acetate [$Pd(OAc)_2$] as catalyst (Scheme 75). In contrast to the oxygen-induced radical addition of C_6H_5SeH to terminal allenes, which occurs preferentially at the terminal double bond, this palladium-catalyzed hydroselenation affords the internal adduct **162** as the major product (63−64% yield), being a complementary method to prepare vinyl selenides from allenes. The reaction is performed at 55 °C under argon atmosphere for 3.5 h, and the product is filtered off in Celite and the solvent is evaporated. Internal

Scheme 75



cyclohexylallene (76% yield) and asymmetric pentylmethylallene (85% yield) were also employed as starting materials.

In contrast, dialkyl diselenides were reacted with allenes **161** in the presence of a rhodium-phosphine complex and trifluoromethanesulfonic acid to give a mixture of (*E*)-2-alkylseleno-1,3-dienes **163** and (*E*)-2-alkylseleno-2-alkenes **164** (59−70% yield; **163**:**164** ratio = 56:44 to 67:33, Scheme 76).[100] The reaction is selective for the diene formation, but a small amount of the Markovnikov adduct **165** (4−17%) was also isolated. The authors also observed that only alkyl diselenides afforded satisfactory yields, while diphenyl diselenide gives only 18% overall yield of the respective vinyl selenides.

The highly strained and reactive vinylidenecyclopropanes **166** reacted with diaryl diselenide to afford the corresponding addition adducts **167** in moderate to good yields (Scheme 77).[101,102] Good yields were obtained with both, electron-withdrawing and electron-donor groups, at the aryl substituents in the starting allene **166**. The reaction can be catalyzed both by the radical initiator 2,2′-azobis(2-methylpropionitrile) (AIBN) or by iodosobenzene acetate [$C_6H_5I(OAc)_2$], a hypervalent iodine reagent. The adduct **168** is obtained via a radical mechanism with the participation of the radical **B** in presence of AIBN (5 mol%) and in refluxing benzene for 10 h, while the ionic intermediate selenonium cation **C** is believed to participate in the iodine promoted reaction (Schemes 78[101] and 79[102]).

5.6. Vinyl Selenides from Methylenecyclopropanes

The reaction of the highly strained methylenecyclopropanes (**169**, MCPs) with phenylselenenyl chloride was observed to occur smoothly at 0 °C in dichloromethane to give a mixture of (cyclobut-1-enylselanyl)benzene **170** along with the ring opening adduct **171** in good overall yields (75−88%, **170**:**171** ratio from 53:47 to 0:100, Scheme 80).[103] When diphenyl diselenide was employed as selenating agent, it was necessary to heat the reaction at 150 °C for 3 h to afford the respective ring opened vinyl selenides **172** in good yields (59−89%).[104] If unsymmetrical MCP was used as the starting material, a 1:1 mixture of *Z*- and *E*-vinyl selenides was obtained. When *gem*-aryl disubstituted MCPs reacted with diaryl diselenides in the presence of iodosobenzene diacetate [$C_6H_5I(OAc)_2$] at 35−40 °C in DCE for 30−40 h,[105] the corresponding ring-opening products 1,2-bis(arylselanyl)-3,3-diarylcyclobut-1-enes **173** were obtained in good yields (40−78%, Scheme 80). The vinyl selenides **173** ($R = R^1 = C_6H_5$) and **172** were submitted to oxidative cyclization with *m*-CPBA and H_2O_2 at room temperature in CH_2Cl_2, furnishing, respectively, 3-phenylselenenyl-2,5-dihydrofuran derivatives in moderate yields (after three steps) and 4-oxo-2,2-diphenyl-1-(phenylselanyl)cyclobutyl 3-chlorobenzoate.

5.7. Vinyl Selenides from Electron-Deficient Olefins

Berlin and Engman[106] have prepared several α-phenylseleno-α,*β*-unsaturated esters, amides, ketones, nitriles, and sulfones **174** in good yields (53−90%) by the zinc chloride-promoted chloroselenation/dehydrochlorination of the corresponding α,*β*-unsaturated compounds **175**. The method affords preferentially the *E*-olefins and is suitable both for terminal and substituted electron-deficient alkenes (Scheme 81). The functionalized vinyl selenides obtained were employed in the preparation of *exo*-methylene pyrrole **176** and dihydropyrrole derivative **177** via a radical cyclization route.

Abe and co-workers[107] described the preparation of cyclic (*Z*)-*β*-organylseleno-α,*β*-unsaturated nitrocycloalkenes **178** in good yields (57−97%) by the addition−elimination reaction of nucleophilic selenium to *β*-sulfinyl-α,*β*-unsaturated cyclic nitroalkenes (**179**, Scheme 82). The authors used phenylselenol and methylselenol, generated in situ from the respective trimethylsilyl selenides in methanol. When the alicyclic sulfoxide **180** reacted with $C_6H_5SeSi(CH_3)_3$, a mixture of (*Z*)-1-nitro-2-phenylselenoprop-1-ene **181** and the (*E*)-isomer **182** was obtained in 71% yield (**181**:**182** ratio = 9:1).

6. Preparation of Vinyl Selenides via Multicomponent Reactions

6.1. Palladium-Catalyzed Four-Component Reactions

Knapton and Meyer[108] described the atom-economic regio- and stereoselective preparation of (*Z*)-*β*-phenylseleno-acrylamides **183** in good yields (45−95%) by a one-pot four-component coupling reaction catalyzed by $Pd(PPh_3)_4$. Thus, when sulfenamides, terminal aliphatic alkynes, carbon monoxide, and diphenyl diselenide were in contact in benzene at 80 °C, in the presence of 3% $Pd(PPh_3)_4$, the corresponding (*Z*)-3-phenyseleno-acrylamides **183** were obtained with 100% regiospecificity for the *β* position and 100% stereoselectivity for the *Z* isomer (Scheme 83).

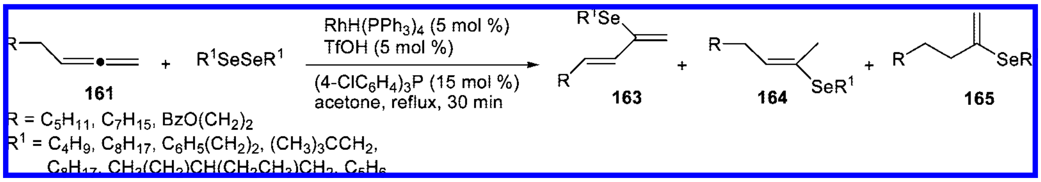
6.2. Three-Component Reactions Starting from Acetylenic Sulfones

Huang and Xie[109] synthesized several *β*-phenylseleno-α-tolylsulfonyl-substituted alkenes **184** via a three-component conjugate-nucleophilic addition reaction of acetylenic sulfones, phenylselenomagnesium bromide, and carbonyl compounds (aldehydes and ketones) at −20 °C in presence of THF/DCM (Scheme 84). The Michael-aldol tandem adducts **184** were obtained in moderate to good yields (50−90%) and with high regio- and stereoselectivity for the *β* position (100%) and the *Z* isomer (*Z*:*E* ratio = 96:4 to 99:1). The adducts **184** obtained from aliphatic acetylenic sulfones were readily converted to heteroatom substituted 1,3-dienes in high yield and high stereoselectivity by a reaction with $Ac_2O/BF_3 \cdot (C_2H_5)_2O$.

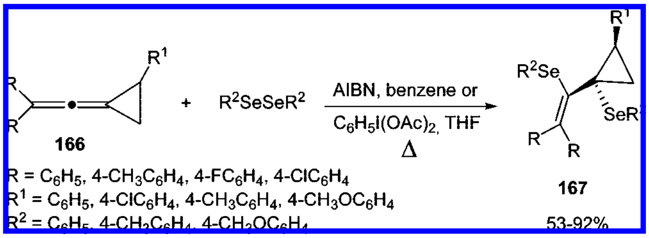
6.3. Three-Component Reactions Starting from Acetylenic Selenides

Huang and Sun[110] developed an efficient method for the regio- and stereoselective preparation of (*E*)-3-chloro-2-

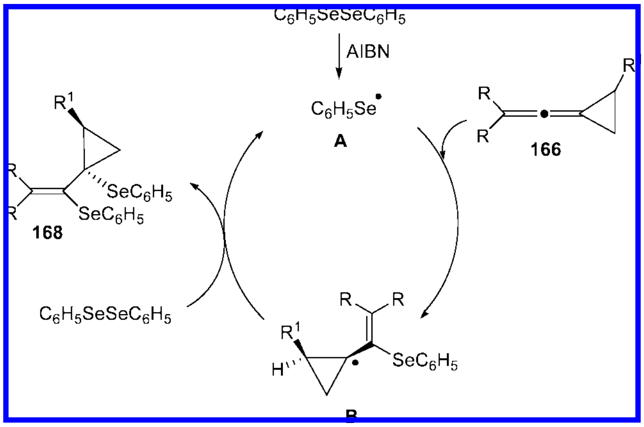
Scheme 76



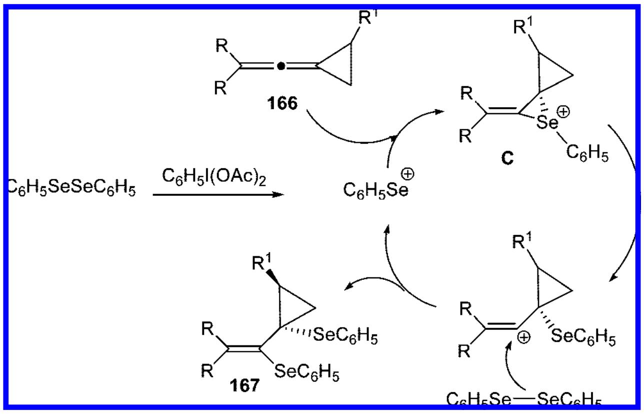
Scheme 77



Scheme 78



Scheme 79



organylseleno-3-phenylacrylates **185** in good yields (60−95%) by the reaction of 2-phenylethynyl selenides **32** (R = C_6H_5) with carbon monoxide, alkyl alcohols, and $CuCl_2$ in benzene, catalyzed by $PdCl_2$ (Scheme 85). When 2-alkylethynyl selenides **32** were used instead of the 2-phenylethynyl ones, the stereochemistry of the reaction was directly opposite, selectively affording the respective (*Z*)-3-chloro-2-organylseleno-3-phenylacrylates **186** in 67−86% yields. Remarkably, when a heteroatom was present in the acetylenic selenides **32**, such as pyridine and $THPOCH_2$, the chlorocarbonylation adducts were not formed, possibly due the coordination of the heteroatom with palladium. To prove the regio- and the stereochemistry of formed products, the authors treated the (*E*)-3-chloro-2-organylseleno-3-phenylacrylates **185** with $LiAlH_4$ and DIBAL-H, affording respectively (*E*)-cinnamyl alcohol and (*Z*)-3-chloro-2-ethylselenooct-2-en-1-ol in good yields.

6.4. Radical Three-Component Reactions

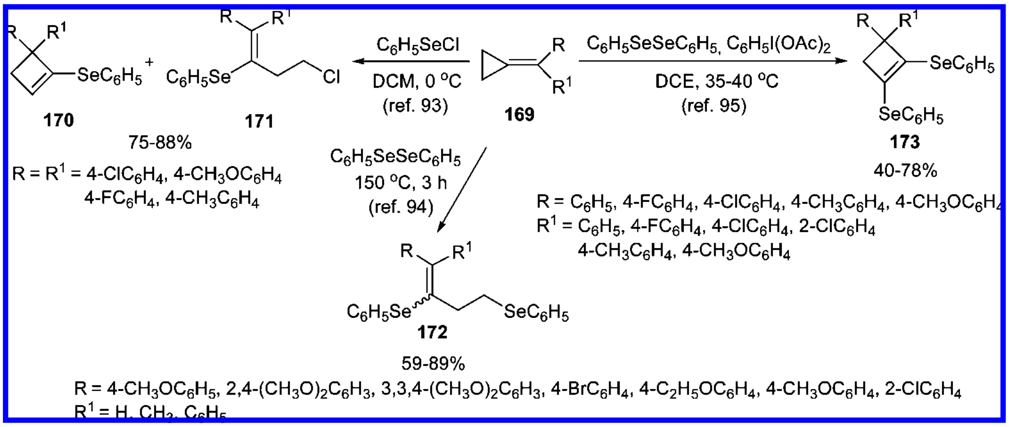
Ogawa and co-workers[111] developed a selective three-component coupling of alkynes, alkenes, and diphenyl diselenide under visible-light irradiation to afford functionalized (*Z*)-vinyl selenides **187** in good yields (Scheme 86). The authors described in a first study the three-component coupling using several radical precursors and they found that the right strength of carbon-radical trapping by diphenyl diselenide facilitates its selective coupling with an electron-poor alkyne and an electron-rich alkene.[111a] The three-component reaction is kinetically controlled, and the $(C_6H_5Se)_2$ facilitates the sequential addition and inhibits the polymerization of the unsaturated compounds. The same procedure was employed using vinylcyclopropanes as the alkene component with good results (Scheme 87).[111b] When the vinyl selenides **187** were coupled with lithium dialkylcuprate, selective alkylation at the *β*-position was observed, with selective cleavage of the C_6H_5Se group at the carbon sp^2 bond and total retention of the stereochemistry at the double bond.

6.5. Photoinduced Thio- and Telluroselenation Reactions

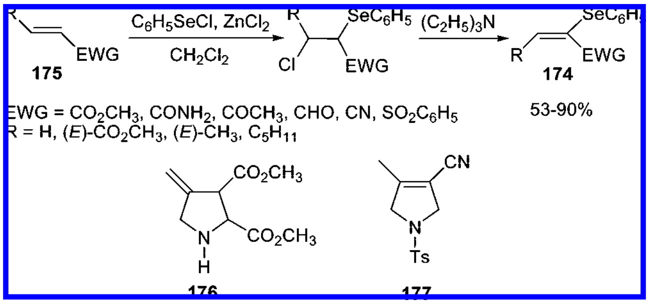
The photoinduced thioselenation of several allenes **161** using the $(C_6H_5S)_2$-$(C_6H_5Se)_2$ binary system was described by Sonoda and co-workers,[112] affording selectively the respective *β*-(vinylseleno)allylsulfides **188** in good yields (71−99%, Scheme 88). Thus, when the allene was subjected to reaction with a mixture of diphenyl disulfide and diphenyl diselenide in $CDCl_3$ at room temperature for 3−5 h, a mixture of *Z*- and *E*-vinyl selenides, with predominance of the *Z*-isomer (*Z*:*E* ratio from 60:40 to 78:22), was obtained. The authors observed that the selenium radical $C_6H_5Se•$ preferentially attacks at the allene, affording the adduct **189**, which is converted into the thioselenation product **188** via the selective displacement of the terminal phenylseleno group (Scheme 89).

The same authors described the use of the protocol depicted in Scheme 86 using acetylene **65** instead allene[113] and the $(C_6H_5Te)_2$-$(C_6H_5Se)_2$ binary system instead of the $(C_6H_5S)_2$-$(C_6H_5Se)_2$ one.[114] In the first case, when phenylacetylene was subjected to radical thioselenation using equimolar amounts of diphenyl disulfide and diphenyl diselenide, the reaction proceeded smoothly to afford exclusively (*E*)-α-(phenylseleno)-*β*-(phenylthio)styrene **190** in 96% yield (Scheme 90).[113] The method was successfully used with others terminal and internal alkynes, producing the respective vinyl selenides in good yields, although the reaction required prolonged irradiation and was accompanied by the formation of the *Z*-isomer (31−87% yield, *E*:*Z* ratio = 58:42 to 95:5). When conjugated enynes were used, the

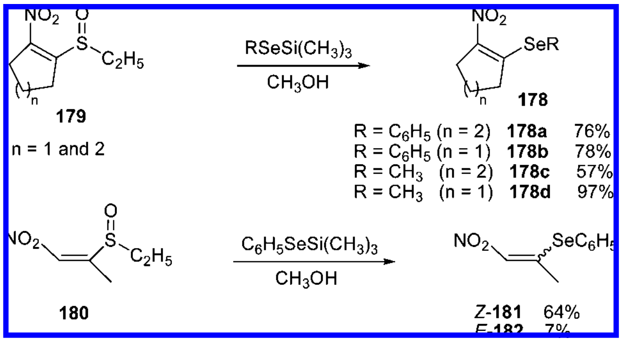
Scheme 80



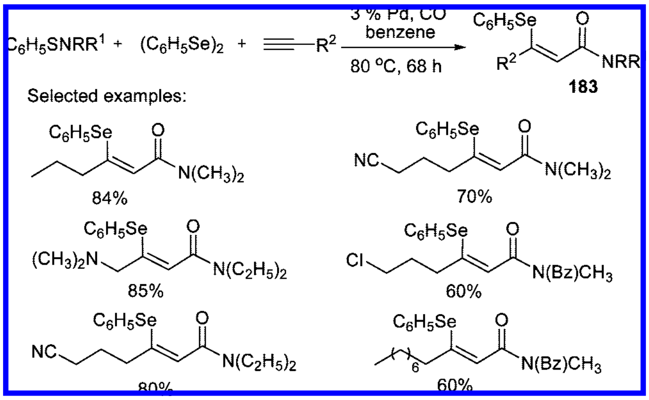
Scheme 81



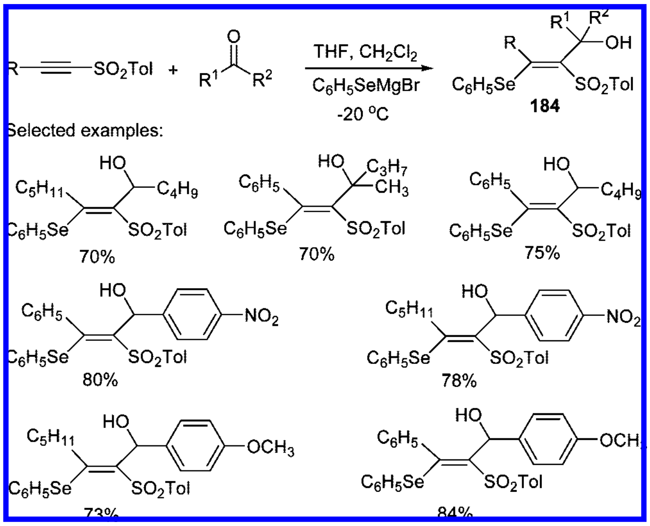
Scheme 82



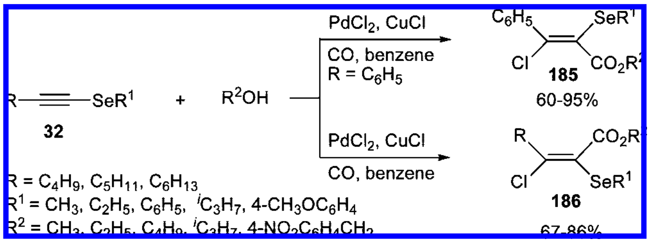
Scheme 83



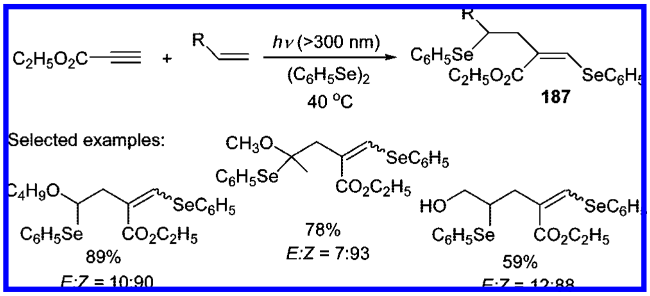
Scheme 84



Scheme 85



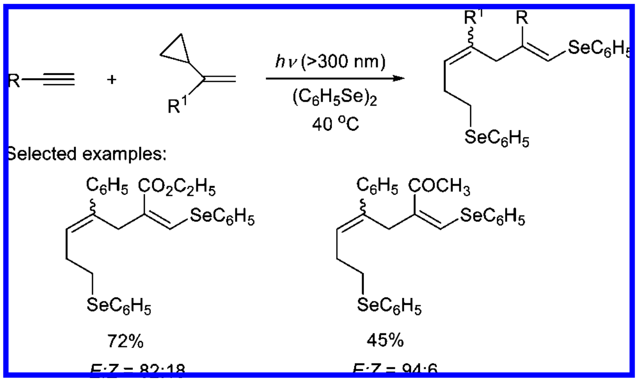
Scheme 86



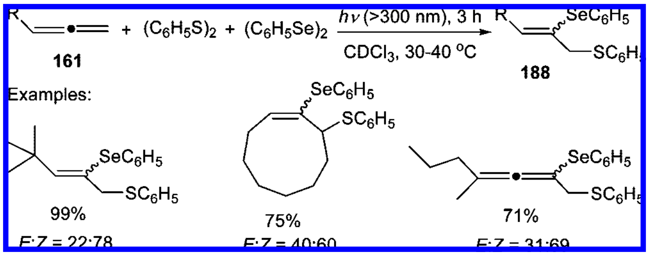
stereochemistry of the new double bond was inverted, and the internal phenylselenobutadienes **190d** and **190g** were obtained in 71 and 90% yields and E/Z ratios of 17:83 and 30:70, respectively.

Similarly, (E)-α-(phenylseleno)-β-(phenylteluro)-styrene **191a** was selectively obtained in 95% yield (E:Z ratio = 90:10) after irradiation for 2 h of an equimolar mixture of phenylacetylene, $(C_6H_5Te)_2$ and $(C_6H_5Se)_2$ in $CDCl_3$. When oct-1-yne was used, (E)-α-(phenylseleno)-β-(phenyltelluro)octene **191b** was exclusively obtained in 29% yield. (Scheme 91).[114]

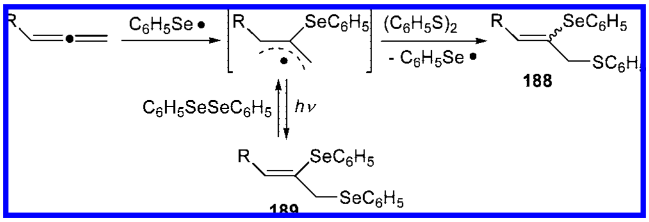
Scheme 87



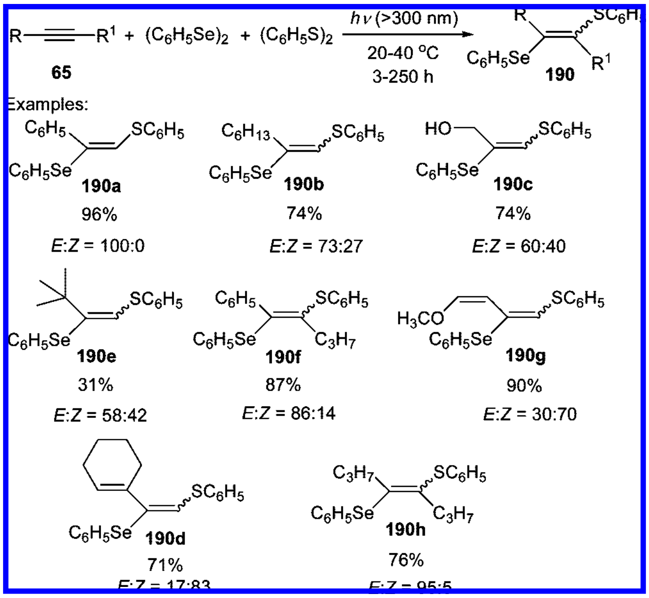
Scheme 88



Scheme 89



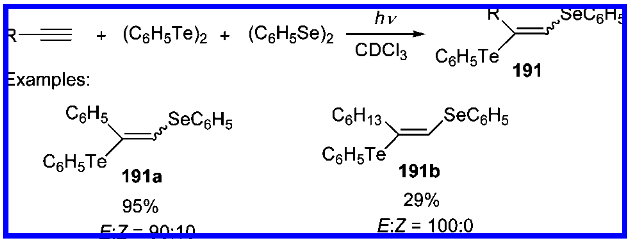
Scheme 90



7. Conclusions

During the past decade, significant progress has been made in the development of new, improved chemoselective and regioselective methods for the synthesis of vinyl selenides. More recently, a lot of novel structures of organoselenium compounds with unique biological properties and low toxicity were described.[115] On the basis of these findings, we hope that this review can give ample and updated information on the different methodologies for the synthesis of vinyl selenides with a large variety of strucutures. Thus, we intended that the vinyl selenides can be explored not only as a versatile synthetic intermediate in total synthesis but also in studies of their pharmacological and toxicological aspects.

Scheme 91



8. Acknowledgments

We thank all whose names that appear in the references, for their contributions to our own work described herein. We are also grateful to CAPES, CNPq, and FAPERGS for financial support of our research. R.B.P. thanks CAPES for a PRODOC-fellowship. G.P., E.J.L., and R.G.J. are recipients of CNPq fellowships.

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