Synthetic Methods

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Formation and Reactivity of Phosphorus–Selenium Rings

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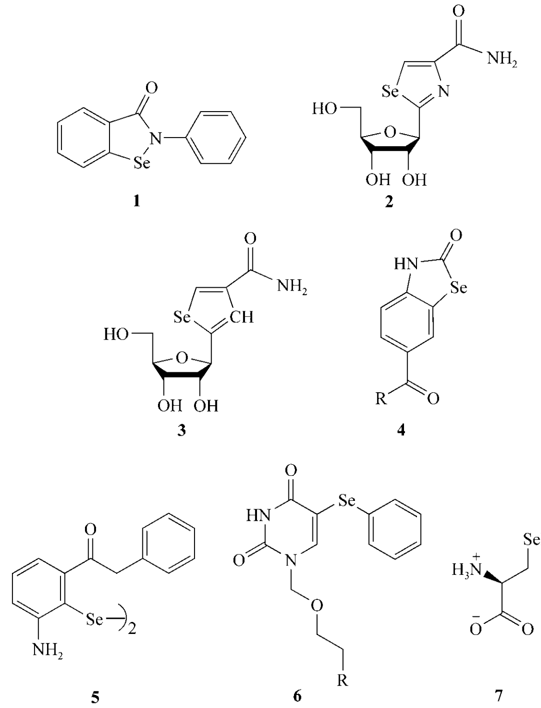
heterocycles · phosphorus · selenium · synthetic methods

Phosphorus–selenium ring chemistry has developed to include the synthesis of some exciting new motifs and provided organic chemists with a new reagent, [PhPSe$_2$]$_2$, which has become known as Woollins' reagent.

1. Introduction

There is a clear need for useful, readily handled reagents for the insertion of selenium into molecules and materials.[1,2] Selenium-containing reagents have enabled important synthetic transformations to be performed simply and in high yield.[2] Because of its high polarizability, selenium is being inserted into molecular materials (analogues of tetrathiafulvalene (TTF) etc.). Selenium is an essential element for life; for example, selenocysteine is viewed as the 21st amino acid in the natural repertoire, and the importance of selenium-containing enzymes in redox processes has become increasingly recognized.[3] Many organoselenium compounds have been studied as biological models that are capable of simulating catalytic functions demonstrated by natural enzymes.[4] For example, ebselen (**1**, Scheme 1) has been shown to act as a glutathione peroxidase (GP$_x$) mimic and as a scavenger of peroxynitrite, and the activity of the sulfur analogue of ebselen was 15-fold lower than that of ebselen.[4b,c] It appears that ebselen blocks the activity of several enzymes by reacting with the critical SH groups of the enzymes. Some photoactive organoselenium compounds have been used as sensitizers in photodynamic therapy.[4d–f] Selenazofurin **2** has been reported to be a potent inhibitor of phlebovirus infections.[4g] Selenophenfurin **3** has been shown to exhibit antiproliferative activity and to inhibit inosine 5′-monophosphate dehydrogenase. Leukotrienes such as leukotriene B$_4$ (LTB$_4$) are known as important mediators of asthma, allergy, arthritis, psoriasis, and inflammatory bowel disease.[4h,i] Galet et al. reported that benzoselenazolinones of type **4** and the corresponding diselenides **5** dramatically decrease the formation of LTB$_4$.[4j] Phenylseleno-substituted pyrimidines of type **6** exhibit significant inhibition of uridine phosphorylase and thymidylate synthase. In an earlier study, selenium-methylated selenocysteine **7** was found to be an antitumor agent, and it has been shown that β-elimination is important for this activity.[4k]



Scheme 1. Some biologically active selenium compounds.

Typical compounds used for the preparation of organoselenium systems include SeO$_2$, PhSeO$_2$H, PhSeCl, PhSe$^-$,[5–7] and in coordination chemistry selenoethers and phosphine selenides.[8] P–S heterocycles have been well established; Lawesson's reagent is widely used,[9] and a number of analogues and larger rings are also known.[10,11] There is a fundamental interest in P–Se rings and cages, as they are fairly unusual molecules. This Minireview briefly illustrates how the area has recently developed with the use of P–Se systems as reagents for organic transformations. One leading compound has been so successfully developed that it is now commer-

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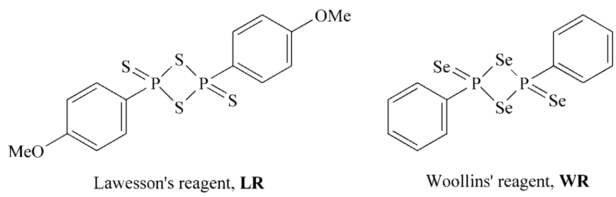
cially available from Sigma–Aldrich as "Woollins' reagent" (Scheme 2).

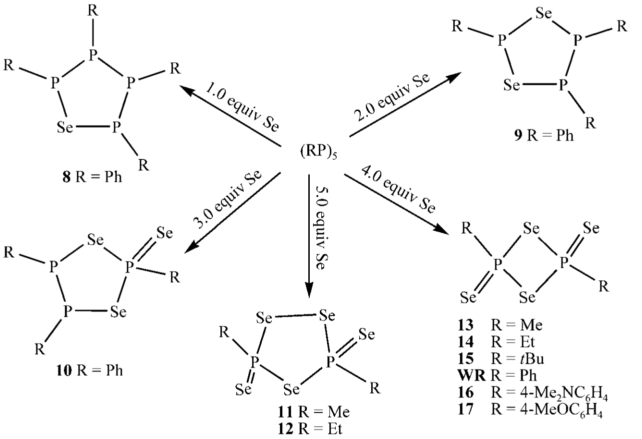


Scheme 2. Structures of Lawesson's reagent (**LR**) and Woollins' reagent (**WR**).

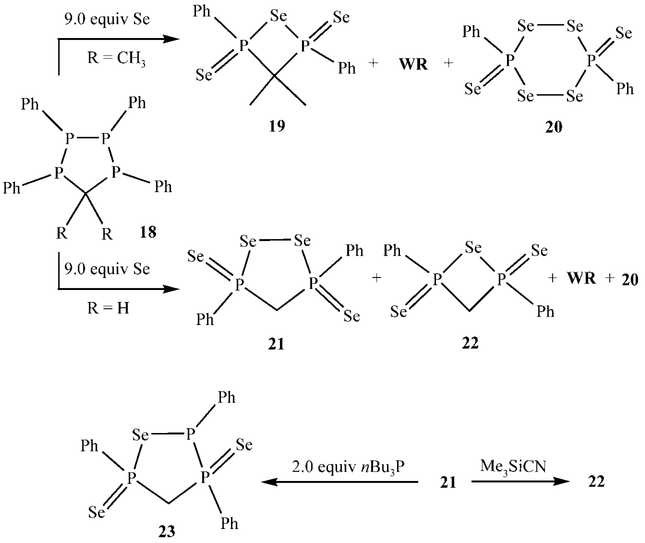
2. Synthesis of $(RP)_xSe_y$ Rings

The first examples of $(RP)_xSe_y$ rings were obtained by Karaghiosoff et al.[12,13] and Woollins et al.[14,15] from reactions of cyclophosphines $(PR)_{5,6}$ (R = Me, Et, 4-$Me_2NC_6H_4$, 4-$MeOC_6H_4$, Ph) with selenium. The formation of these compounds **8**–**17** and **WR** involves the formal replacement of RP by Se and in some cases the additional oxidation of P^{III} to P^V=Se at some phosphorous centers (Scheme 3).

Around the same time, Shore et al. reported the synthesis of $(tBuPSe_2)_2$ from *tert*-butyldichlorophosphine and Li_2Se_2.[16] Although this compound was studied crystallographically, its potential chemistry has been overlooked. Hahn et al. were able to obtain this compound, as well as its methyl and phenyl analogues, from the reaction of the silyl esters of the corresponding triselenophosphonic acids and DMSO, although no detailed experimental procedure or spectroscopic data was reported.[17] The synthesis of mixed P-Se-C rings **18**–**23** and **WR** based on similar methodologies has also been investigated (Scheme 4).[18]

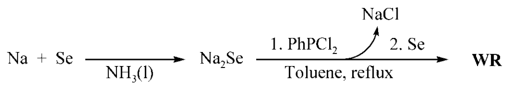


Scheme 3. Synthesis of $(RP)_xSe_y$ from the corresponding cyclopentaphosphine and elemental selenium.



Scheme 4. Examples of mixed P–Se and P-Se-C rings.

More recently, a larger-scale route to prepare **WR**, which can be conveniently scaled up to approximately 150 g, has been successfully realized. This method starts with the formation of Na_2Se in liquid ammonia and uses $PhCl_2$ (Scheme 5).[19]

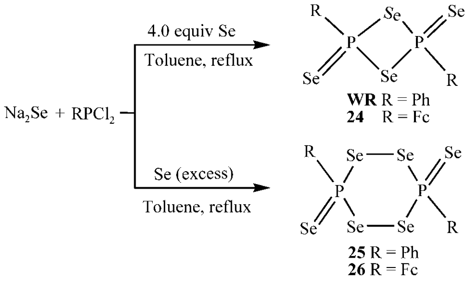


Scheme 5. Large-scale synthesis of **WR**.

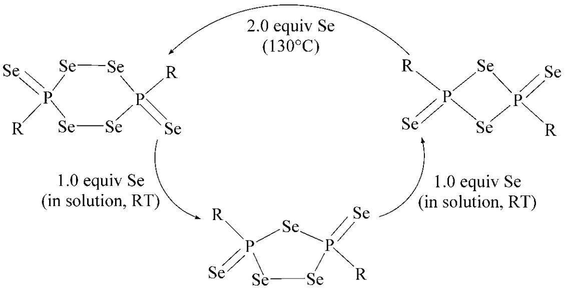
Guoxiong Hua received his B.Sc. at Hubei University (1985) and M.Sc. at Dalian University of Technology (1988). After spending several years as experimental officer and lecturer in Liaoning University of Petroleum & Chemical Technology, he worked in the chemical industry (1992–1999). He moved to the UK for Ph.D. work under the supervision of J. D. Woollins at the University of St. Andrews (1999–2003). After a short research period with I. Singleton at the University of Newcastle (2003–2005), he returned to St. Andrews as a postdoctoral fellow.

J. Derek Woollins studied for his degree and Ph.D. at the University of East Anglia (Norwich). After postdoctoral research in Vancouver (UBC, with W. R. Cullen), Michigan (MSU with B. Rosenberg), and Leeds (N. N. Greenwood), in 1983 he was appointed as lecturer at Imperial College London. In 1994 he moved to Loughborough as Professor of Inorganic Chemistry and in 1999 to the University of St. Andrews as Chair in Synthetic Chemistry. His research interests are centered around synthetic and structural chemistry of Groups 15 and 16.

The range of P–Se heterocycles was extended by using dichlorophosphanes with other substituents at the phosphorus atom, for example, $FcPCl_2$ (Fc = ferrocenyl), and an excess of elemental selenium, resulting in the formation of other selenium-rich systems **24**–**26** (Scheme 6).[20] The interconversion of these rings involves a complex set of equilibria and rearrangements (Scheme 7).

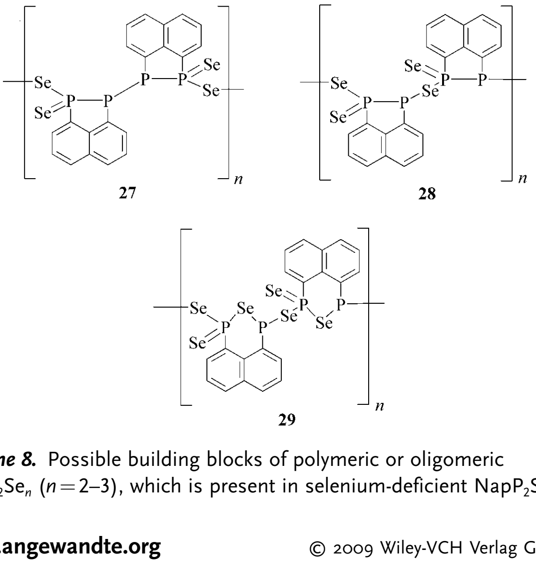


Scheme 6. Synthesis of selenium-rich rings.



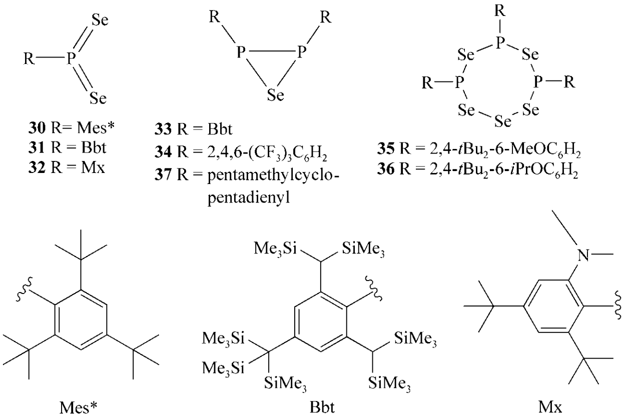
Scheme 7. Ring expansion and contraction in compounds $(RP)_xSe_y$ (R = Ph or Fc).

Selenium-deficient systems are also accessible, and very recently a naphthalene-backbone system $NapP_2Se_4$ (Nap = naphthalene-1,8-diyl), which appears to contain significant amounts of oligomeric or polymeric materials **27**–**29** with low selenium content, has also been prepared (Scheme 8).[21]



Scheme 8. Possible building blocks of polymeric or oligomeric $NapP_2Se_n$ (n = 2–3), which is present in selenium-deficient $NapP_2Se_4$.

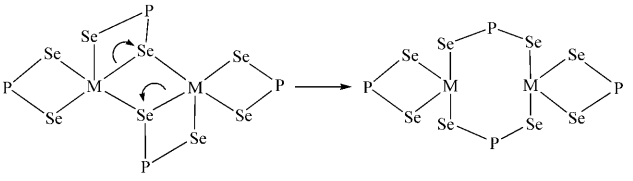
The presence of extremely bulky organic substituents results in either monomeric diselenoxophosphoranes **30**–**32** with a three-coordinate pentavalent phosphorus atom,[22–24] three-membered rings **33** and **34**,[22,25] or eight-membered rings **35** and **36**.[26] One selenadiphosphirane containing the pentamethylcyclopentadienyl substituent, which is neither particularly bulky nor electronically stabilizing, was isolated as stable species **37** and crystallographically characterized (Scheme 9).[27]



Scheme 9. Examples of P–Se systems obtained using sterically demanding R groups.

3. Formation of Metal Complexes

The main focus of this Minireview is organic reactivity, but it is worth mentioning some interesting coordination chemistry. Baxter et al. used **WR** to selenate the carbonyl-containing complexes $[ML(\eta^2\text{-OCCR})(CO)(Tp)]$ (M = W, Mo; L = PMe_2Ph, PPh_3, $P(OMe)_3$; R = anisyl; Tp = hydrotris(pyrazol-1-yl)borate), leading to the selenoketenyl complexes $[ML(\eta^2\text{-SeCCR})(CO)(Tp)]$.[28] Some new metal complexes have been prepared by Woollins et al. and notably by Rothenberger et al. The reaction of **WR** with *cis*-$[PtCl_2(PR_3)_2]$ (PR_3 = 1/2 1,2-bis(diphenylphosphino)ethane (dppe), PEt_3, PMe_2Ph, and PPh_2Me) in THF gave the complexes *cis*-$[Pt(Se_3PPh)(PR_3)_2]$.[29] Reaction of **WR** with NaOR (R = Me, Et, *i*Pr) led to the diselenophosphonate anions $[Ph(RO)PSe_2]^-$, which can be complexed to a range of metals. The nickel complex $[Ni\{Ph(MeO)PSe_2\}_2]$ adopts a square-planar ML_2 structure, while the cadmium complex $[Cd\{Ph(MeO)PSe_2\}_2]$ displays a dimeric M_2L_4 structure. Two different lead complexes **38** and **39** can be obtained. One structure consists of PbL_2 units joined by Pb···Se interactions to form distinct but conventional dimeric pairs. The other structure is a novel dimer built around a central four-membered Pb_2Se_2 ring. The relationship between these two motifs is illustrated below (Scheme 10).[30] The successful use of **WR** in the synthesis of polynuclear metal selenium clusters by Rothenberger and co-workers is described in reference [31]

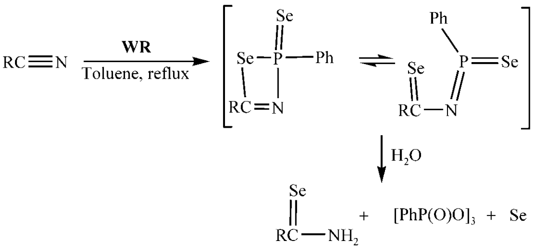


38 **39**

Scheme 10. The relationship between two structural motifs for [$M_2\{Ph(MeO)PSe_2\}_4$] complexes (M = Pb, Cd).

4. Preparation of Organoselenium Compounds

A wide range of organoselenium compounds has been prepared using **WR**. Selenoamides and selenoaldehydes were obtained by simple oxygen–selenium exchange or by reaction with arylnitriles (ArCN) and subsequent hydrolysis. Thus, the reaction of arylnitriles with **WR** in toluene heated at reflux and subsequent addition of water afforded a variety of primary arylselenoamides **40–57** in 60–100% yield (Scheme 11).[32] **WR** was also used to convert secondary and tertiary amides into the corresponding selenoamides **58–64** in 30–70% yield and indolizine-3-aldehydes into selenoaldehydes **65–67** in 40–62% yield at room temperature (Scheme 12).[33,34] The first crystallographically characterized example of an indolizine-3-selenoaldehyde, 2-*tert*-butylindolizine-3-selenoaldehyde (**66**) has also been reported.[34]



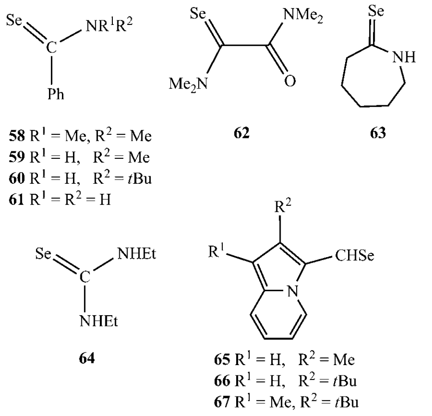
40 R = C_6H_5
41 R = 3-MeC_6H_4
42 R = 4-MeC_6H_4
43 R = 2,6-$Cl_2C_6H_3$
44 R = 4-$(NC)C_6H_4$
45 R = 3-$(NC)C_6H_4$
46 R = 4-$(O_2N)C_6H_4$
47 R = 3,4-$(H_3CO)_2C_6H_3$
48 R = 2,4-$(H_3CO)_2C_6H_3$
49 R = 2,3-$(H_3CO)_2C_6H_3$
50 R = 4-$(H_3CO)C_6H_4$
51 R = 3-$(H_3CO)C_6H_4$
52 R = 2-$(H_3CO)C_6H_4$
53 R = 4-ClC_6H_4
54 R = 3-ClC_6H_4
55 R = 2-ClC_6H_4
56 R = 4-FC_6H_4
57 R = 4-BrC_6H_4

Scheme 11. Synthesis of a variety of arylselenoamides using **WR**/H_2O.

Bethke et al. have also found **WR** to be an effective selenation reagent in the synthesis of selenocarbonyl compounds; a series of selenoamides **68–81** were isolated in 77–85% yield from the room-temperature reaction of formamides and **WR** in benzene (Scheme 13).[35]

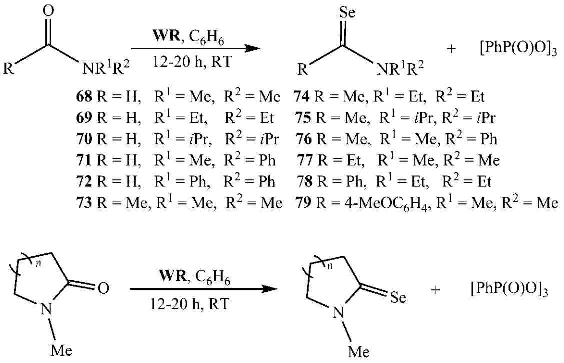
The synthesis of 1,3-diarylbenzo[*c*]selenophenes **82–92** involves a selenium transfer reaction of benzo[*c*]furan using **WR** (Scheme 14).[36]

Upon treatment with **WR** in toluene solution, carboxylic acids are converted into selenocarboxylic acids **93–95** (Scheme 15). The latter (generated in situ) are versatile reagents for the introduction of selenium into organic structures and for amidation, especially in cases when the nucleophilicity of the corresponding thiocarboxylic acid is insufficient.[37]



58 R^1 = Me, R^2 = Me
59 R^1 = H, R^2 = Me
60 R^1 = H, R^2 = *t*Bu
61 R^1 = R^2 = H
62
63
64
65 R^1 = H, R^2 = Me
66 R^1 = H, R^2 = *t*Bu
67 R^1 = Me, R^2 = *t*Bu

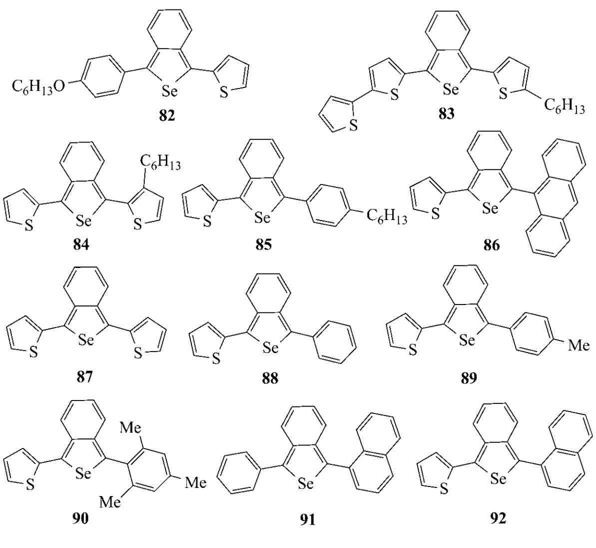
Scheme 12. Selenocarbonyl compounds prepared using **WR**.



68 R = H, R^1 = Me, R^2 = Me
69 R = H, R^1 = Et, R^2 = Et
70 R = H, R^1 = *i*Pr, R^2 = *i*Pr
71 R = H, R^1 = Me, R^2 = Ph
72 R = H, R^1 = Ph, R^2 = Ph
73 R = Me, R^1 = Me, R^2 = Me
74 R = Me, R^1 = Et, R^2 = Et
75 R = Me, R^1 = *i*Pr, R^2 = *i*Pr
76 R = Me, R^1 = Me, R^2 = Ph
77 R = Et, R^1 = Me, R^2 = Me
78 R = Ph, R^1 = Et, R^2 = Et
79 R = 4-$MeOC_6H_4$, R^1 = Me, R^2 = Me

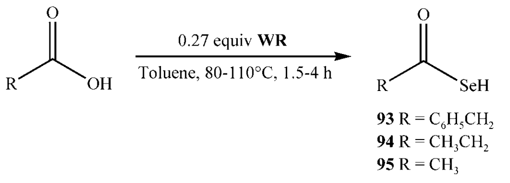
80 *n* = 1
81 *n* = 2

Scheme 13. Synthesis of selenoamides using **WR**.



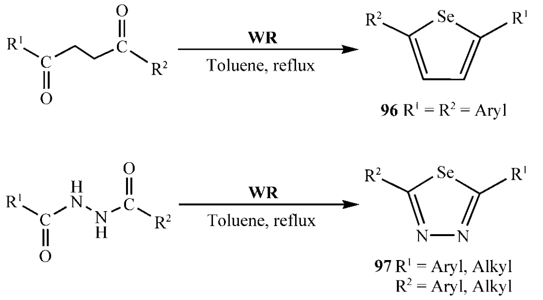
Scheme 14. Selenation products from the reaction of **WR** with benzo[*c*]furans.

More recently, **WR** has been used in the synthesis of a variety of 2,5-disubstituted selenophenes **96** and selenazoles



Scheme 15. Synthesis of selenocarboxylic acids using **WR**.

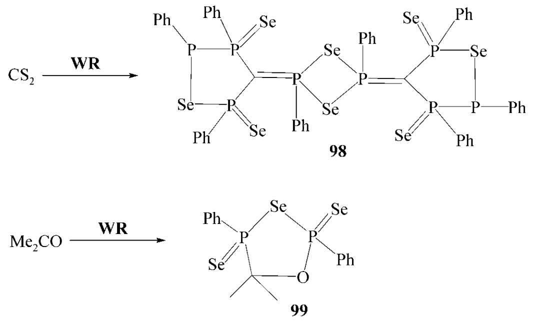
97 in excellent yield (90–99%) from the corresponding 1,4-diketones ($R^1C(O)CH_2CH_2C(O)R^2$, $R^1 = R^2 =$ aryl) and 1,4-diamides ($R^1C(O)NHNHC(O)R^2$, $R^1 =$ aryl or alkyl, $R^2 =$ aryl or alkyl; Scheme 16).[38]



Scheme 16. Synthesis of 2,5-disubstituted selenophenes and selenazoles using **WR**.

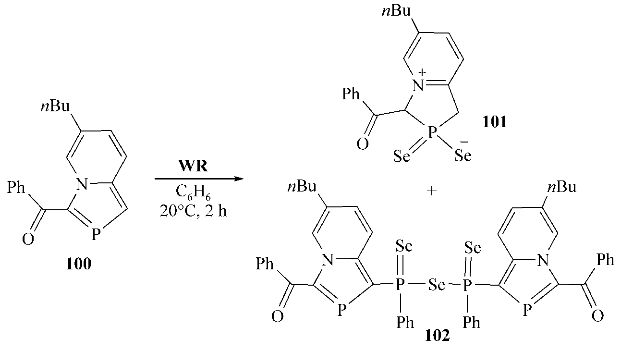
5. Synthesis of P–Se Heterocycles

The synthesis of a range of phosphorus–selenium heterocycles by the use of **WR** has been explored by Woollins' and others' groups. The synthesis of **98** and **99** by the action of acetone or CS_2 on **WR** were the earliest examples (Scheme 17).[14a,b]

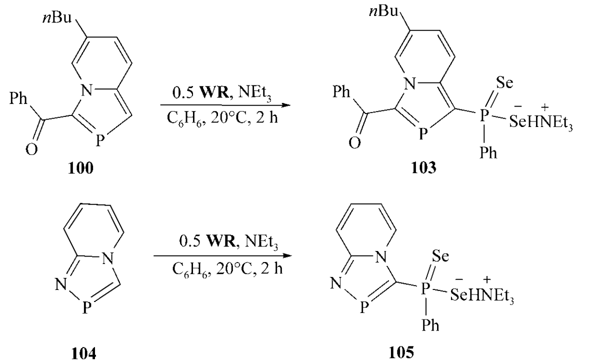


Scheme 17. Synthesis of four- and five-membered P–Se heterocycles using **WR**.

When phosphaindolizine **100** reacts with **WR** in benzene at room temperature, no oxygen–selenium exchange was observed. Instead, two new products were obtained: the pale yellow crystalline air- and moisture-sensitive pyridinium diselenophosphinate **101** (27% yield of isolated product) and the selenoanhydride **102**, which was identified by ^{31}P NMR spectroscopy and consists of a nearly 1:1 mixture of two diastereomers (Scheme 18).[39] However, with NEt_3 and the appropriate stoichiometry, the diselenophosphinate **103** was obtained as the only reaction product in 87% yield from the reaction of phosphaindolizine **100** and **WR**. Similarly, the diselenophosphinate **105** was obtained in 42% yield from the reaction of **WR** and 1-aza-2-phosphaindolizine (**104**; Scheme 19).



Scheme 18. Reaction of a phosphaindolizine with **WR**.

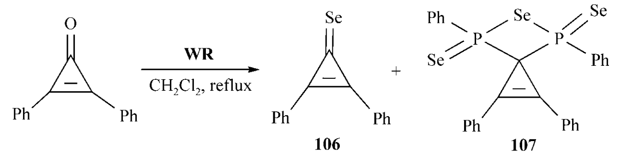


Scheme 19. Synthesis of new diselenophosphinate using **WR**.

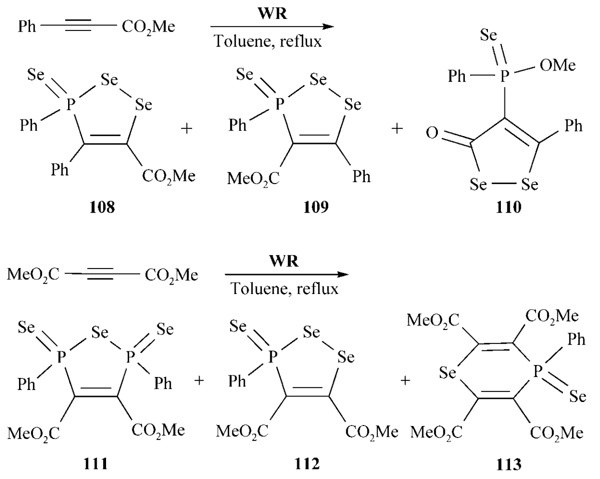
A far more extensive series of P–Se heterocycles was obtained by the reaction of **WR** with a wide range of organic substrates containing reactive unsaturated $C{=}O$, $C{=}C$, and $C{\equiv}C$ bonds. For example, the spirocyclic heterocycle **107** with a four-membered P_2SeC ring was obtained together with the selenocarbonyl derivate **106** from the reaction of **WR** with diphenylcyclopropenone (Scheme 20).[19]

Reactions of **WR** with alkynes led to several new heterocycles **108–113** in 20–26% yield of isolated product (Scheme 21).[19,40]

The reaction of **WR** with norbornene in toluene heated at reflux proceeds with cleavage of the P_2Se_2 ring to give a 1,2-

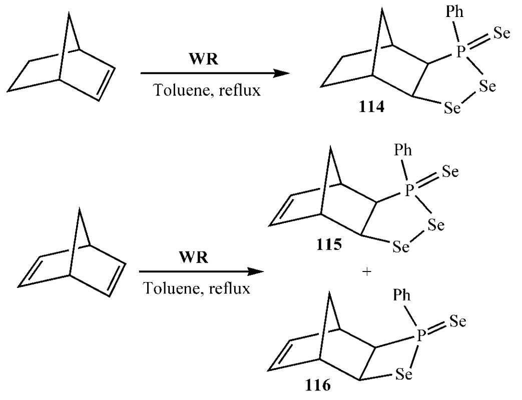


Scheme 20. Synthesis of a spirocyclic heterocycle using **WR**.



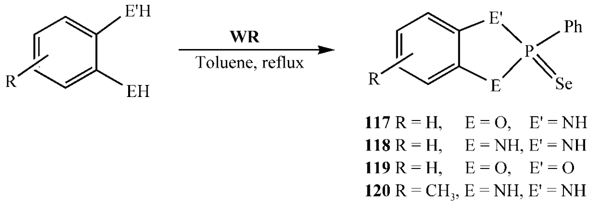
Scheme 21. Synthesis of new P–Se heterocycles using **WR**.

diselena-3-phospholane **114** containing a five-membered C_2PSe_2 ring (confirmed by X-ray crystallography), which was isolated in 20% yield.[41] However, the reaction of **WR** with norbornadiene proceeds somewhat more completely than with norbornene to yield the analogous product **115** with a C_2PSe_2 ring as well as the heterocycle **116** with a four-membered C_2PSe ring analogous to thiaphosphetane (C_2PS) rings (Scheme 22).[42]



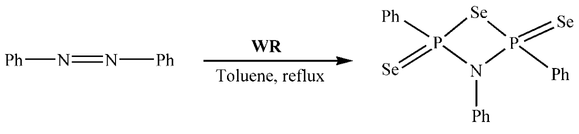
Scheme 22. Reaction of **WR** with norbornene and norbornadiene.

Treatment of **WR** with 2-aminophenol, 1,2-phenylenediamine, catechol, or 3,4-diaminotoluene led to the rupture of the dimer, giving **117**–**120**, respectively (Scheme 23).[43]



Scheme 23. Formation of simple heterocycles using **WR**.

The reaction of **WR** with azobenzene proceeds with cleavage of the N=N bond and substitution of a bridging selenium atom in **WR** by an NPh unit, giving the first crystallographically characterized selenaazadiphosphetane **121** (Scheme 24).[41]



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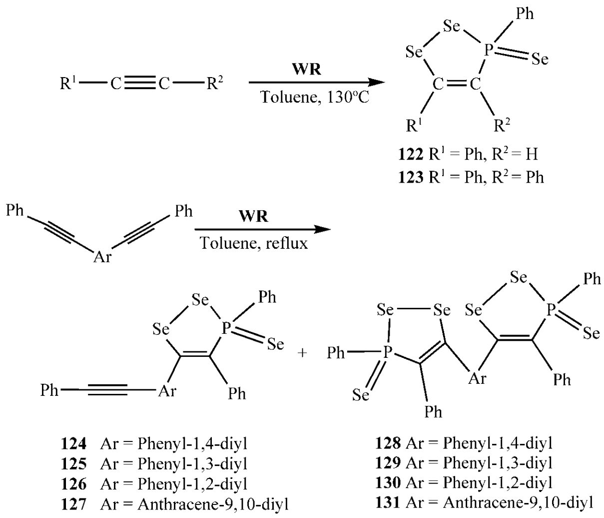
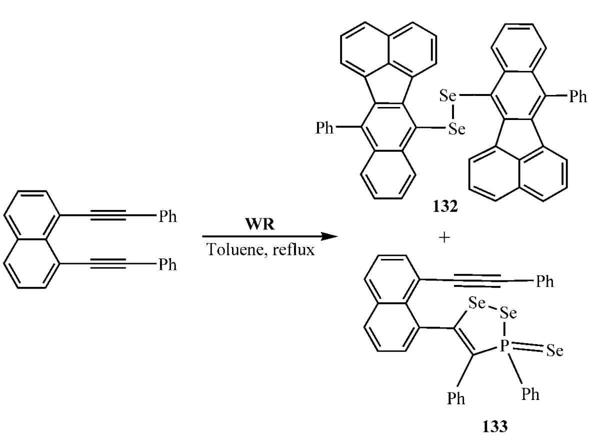
Scheme 24. Synthesis of a selenaazadiphosphetane using **WR**.

Several other novel five-membered PSe_2C_2 heterocycles **122**–**131** were synthesized from **WR** and alkynes by formal addition of a Ph(Se)PSe_2 fragment to the alkyne triple bond (Scheme 25). An unusual diselenide **132**, formed by an intramolecular cycloaddition/rearrangement reaction along with a five-membered PSe_2C_2 heterocycle **133**, was obtained when a sterically constrained naphthalene dialkyne was used (Scheme 26).[40,44]

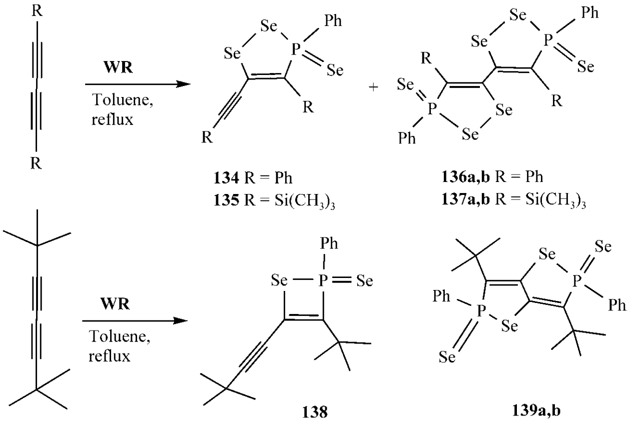


Scheme 25. Synthesis of five-membered PSe_2C_2 rings using **WR**.



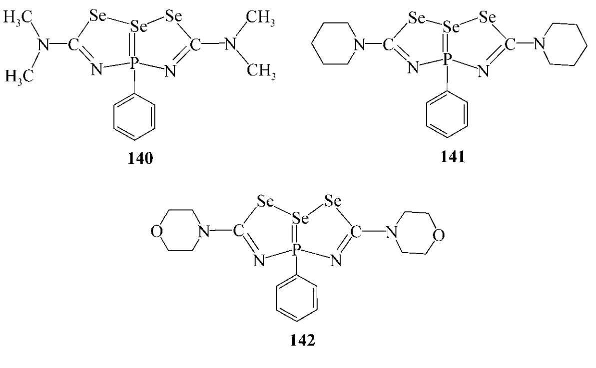
Scheme 26. Unexpected diselenide formation from the reaction of a bis(alkyne) with **WR**.

Similarly, heating **WR** at reflux with symmetrically disubstituted diynes (RC≡C−C≡CR, R = Ph, Si(CH$_3$)$_3$) in 2:1 molar ratio in toluene gave two products: five-membered P(Se)Se$_2$C$_2$ heterocycles **134** and **135** with one unreacted triple bond and diheterocycles **136** and **137** (as pairs of diastereomers) with two five-membered P(Se)Se$_2$C$_2$ rings connected through a C−C single bond. However, **WR** and *t*BuC≡C−C≡C*t*Bu react differently to afford the four-membered P(Se)SeC$_2$ heterocycle **138** with one unreacted triple bond and the heteropentalene **139** (also as a pair of diastereomers) with two P(Se)SeC$_3$ rings fused at the central two carbon atoms of the original diyne system (Scheme 27).[45]



Scheme 27. Reaction of diynes with **WR**.

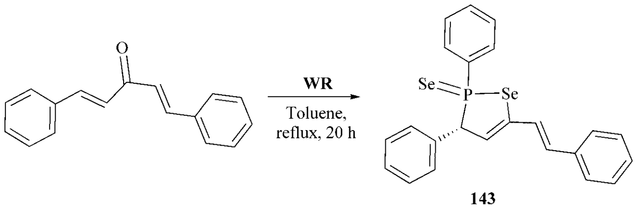
Heating a toluene solution of **WR** at reflux with a ten-fold excess of dialkylcyanamides R$_2$NCN (R$_2$ = Me$_2$, -CH$_2$CH$_2$OCH$_2$CH$_2$-, or -(CH$_2$)$_5$-) led to the heteropentalenes **140**–**142** in approximately 5 % yield (Scheme 28).[46]



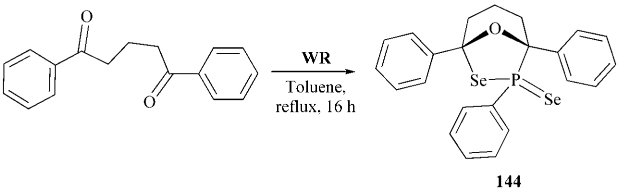
Scheme 28. 1,6,6γ^4-Triselena-3a-phospha-3,4-diazapentalenes obtained from the reaction of **WR** with dialkylcyanamides.

WR reacts with dibenzylideneacetone in toluene heated at reflux for 20 h to form the heterocycle **143** with a planar C$_3$P(Se)Se ring in 56 % yield (Scheme 29).[47]

A fused heterocyclic [3,2,1]tricycle **144** has been prepared by the reaction of **WR** with 1,5-diphenylpentane-1,5-dione in toluene heated at reflux. The product was isolated in 22 % yield (Scheme 30).[48]

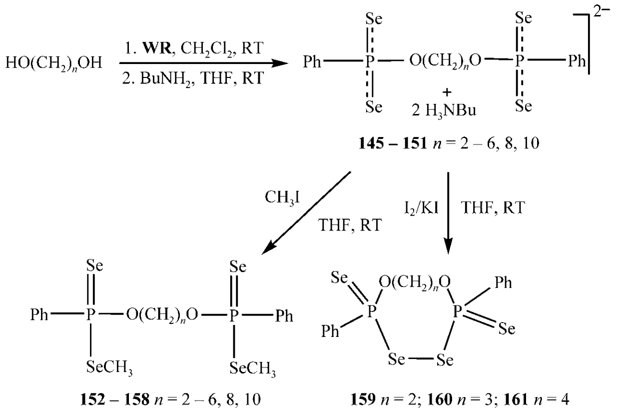


Scheme 29. Synthesis of 2,3-diphenyl-5-phenylvinyl-[1,2]selenaphosphole-2-selenide using **WR**.



Scheme 30. Synthesis of new P–Se heterocyclic [3,2,1]tricycles using **WR**.

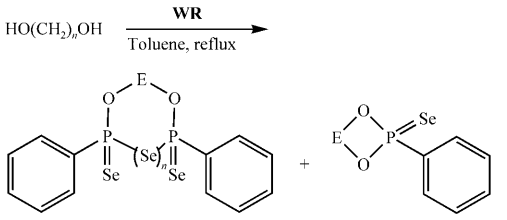
Recently, the reaction of diols HO(CH$_2$)$_n$OH (n = 2–6, 8, 10) with **WR** in dry dichloromethane and subsequent treatment with butylamine in THF at room temperature has been shown to afford the corresponding ammonium salts **145**–**151** in excellent yield (91–97 %). These salts react with methyl iodide to afford dimethyl esters of bis(diselenophosphonic acids) **152**–**158** in moderate to excellent yield (50–86 %) and react with I$_2$/KI in THF at room temperature to give eight-, nine-, and ten-membered-ring diselenides **159**–**161** in good to excellent yield (70–90 %; Scheme 31).[49,50]



Scheme 31. Synthesis of ammonium salts and dimethyl esters of bis(diselenophosphonic acids) and eight-, nine-, and ten-membered rings using **WR** and the corresponding diols.

Interestingly, heating a toluene solution of **WR** at reflux with ethylene glycol led to new ring systems: a seven-membered triselenapyrophosphonate **162** and a five-membered 1,3-dioxaphosphorinane-2-selenide **165**. However, under the same reaction conditions, 1,3-propanediol and 1,4-butanediol react with **WR** to give cyclic tetraselenapyrophosphonates **163** and **164** and 1,3-dioxaphosphorinane-2-selenides **166** and **167**. Surprisingly, only 1,3,2-dioxaphosphorinane-2-phenyl-2-selenide **168** was obtained in 69 % yield as a pale yellow solid by the reaction of pinacol with one equivalent of **WR** in toluene heated at reflux (Scheme 32).[49]

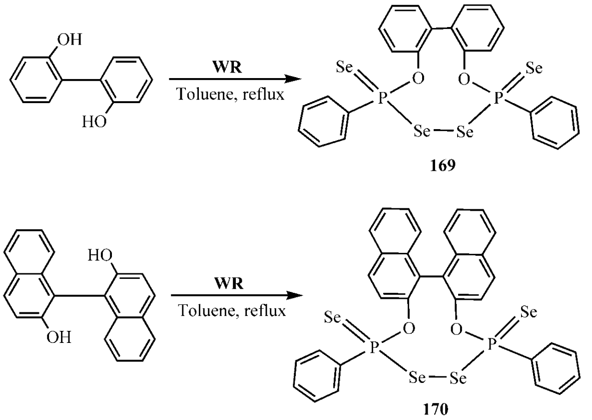
Heating equimolar amounts of aromatic diols and **WR** in toluene at reflux for 15 h afforded solely diselenides **169** and **170** as white crystals in 61 and 65 % yield, respectively (Scheme 33).[50]



162 E = $(CH_2)_2$, $n = 1$
163 E = $(CH_2)_3$, $n = 2$
164 E = $(CH_2)_4$, $n = 2$

165 E = $(CH_2)_2$
166 E = $(CH_2)_3$
167 E = $(CH_2)_4$
168 E = $C(CH_3)_2C(CH_3)_2$

Scheme 32. Reaction of **WR** with diols.

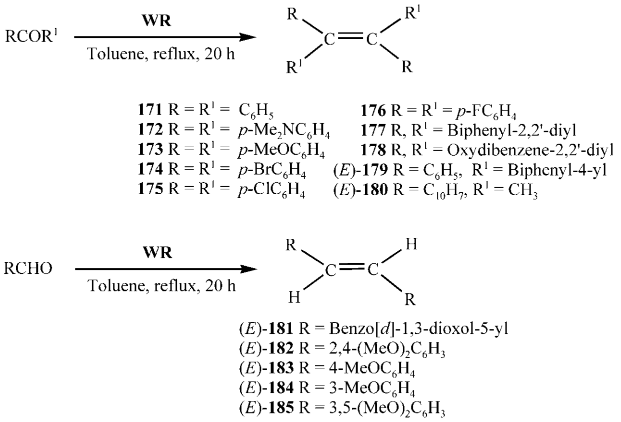


Scheme 33. Synthesis of ten-membered rings from the reaction of **WR** with aromatic diols.

6. Application as a Coupling and Deoxygenation Reagent

Reductive dimerization of a wide range of ketones and aldehydes was achieved by treatment with **WR** in toluene heated at reflux, which yields symmetrical and unsymmetrical *E*-olefins **171**–**185** in 53–100 % yield (Scheme 34).[51] This method has potential for a variety of systems and may prove especially beneficial when base-sensitive substituents are present. The proposed mechanism for this reaction involves a Wittig-like reaction intermediate.

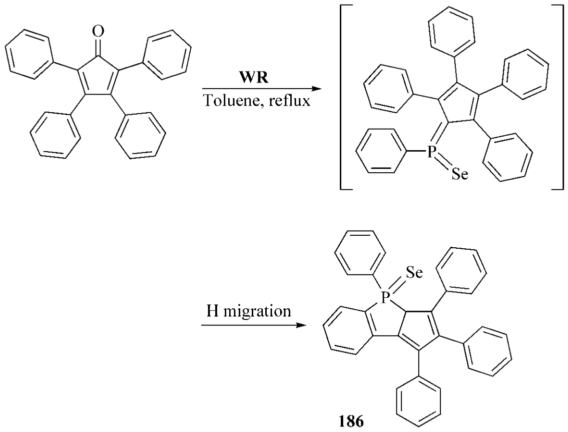
An unexpected product was obtained in an attempt to synthesize the reductive dimerization product from the reaction of tetraphenylcyclopentadienone with **WR**, which resulted in a stable five-membered heterocycle **186**. The steric hindrance was thought in this case to prevent the intermediate from being attacked by another tetraphenylcyclopentadienone molecule. Instead, hydrogen migration occurs to give the new phosphorous heterocycle (Scheme 35).[51]



171 R = R^1 = C_6H_5
172 R = R^1 = p-$Me_2NC_6H_4$
173 R = R^1 = p-$MeOC_6H_4$
174 R = R^1 = p-BrC_6H_4
175 R = R^1 = p-ClC_6H_4
176 R = R^1 = p-FC_6H_4
177 R, R^1 = Biphenyl-2,2'-diyl
178 R, R^1 = Oxydibenzene-2,2'-diyl
(*E*)-**179** R = C_6H_5, R^1 = Biphenyl-4-yl
(*E*)-**180** R = $C_{10}H_7$, R^1 = CH_3

(*E*)-**181** R = Benzo[*d*]-1,3-dioxol-5-yl
(*E*)-**182** R = 2,4-$(MeO)_2C_6H_3$
(*E*)-**183** R = 4-$MeOC_6H_4$
(*E*)-**184** R = 3-$MeOC_6H_4$
(*E*)-**185** R = 3,5-$(MeO)_2C_6H_3$

Scheme 34. Reductive dimerization of ketones or aldehydes promoted by **WR**.



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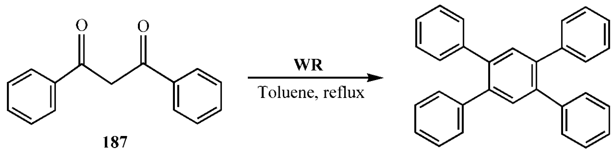
Scheme 35. Reaction of tetraphenylcyclopentadienone with **WR**.

A particularly interesting aromatic compound **188** was obtained when 1,3-diphenylpropane-1,3-dione (**187**) was used as starting material rather than an olefin (Scheme 36). It can be anticipated that this reaction could be extended to a wide variety of β-diketones and perhaps even to heterocyclic systems to provide entry to a range of new heterocycles.[51]

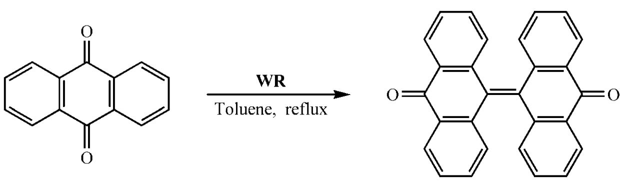


187

188

Scheme 36. Reaction of 1,3-diphenylpropane-1,3-dione with **WR**.

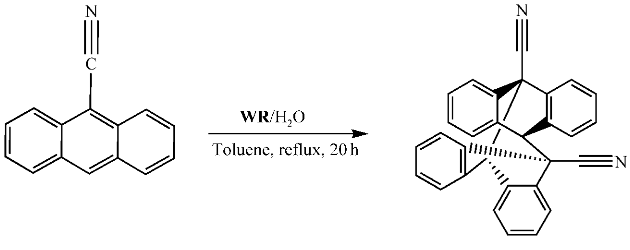
Similarly, the reaction of **WR** with anthracene-9,10-dione afforded 9,9′-bianthracene-10,10′-dione **189** in 90% yield (Scheme 37).[52]



189

Scheme 37. Reaction of anthracene-9,10-dione with **WR**.

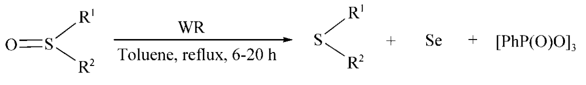
Surprisingly, heating a toluene solution of **WR** at reflux with 9-cyanoanthracene and subsequent treatment with water gave as the only isolable compound the dimerization product 9,9′-dicyanodianthracene **190** in 29% yield, in which the C≡N group was retained (Scheme 38).[52]



190

Scheme 38. Product obtained from 9-anthracenecarbonitrile with **WR**/H_2O.

The deoxygenation of a series of sulfoxides to the corresponding sulfides **191–202** was effectively promoted by **WR** under relatively mild conditions in good to excellent yield (81–99%; Scheme 39).[53] The reaction was found to be a very useful approach in organic synthesis because of the easy workup, mild conditions, high selectivity, and high conversion of substrates.



191 $R^1 = R^2 = C_6H_5$
192 $R^1 = R^2 = 4\text{-}ClC_6H_4$
193 $R^1 = R^2 = C_6H_4CH_2$
194 $R^1 = 4\text{-}O_2NC_6H_4CH_2$, $R^2 = C_6H_5$
195 $R^1 = C_6H_4CH_2$, $R^2 = 4\text{-}MeC_6H_4$
196 $R^1 = R^2 = 4\text{-}MeC_6H_4$
197 $R^1 = C_6H_4CH_2$, $R^2 = C_6H_5$
198 $R^1 = C_6H_4CH_2$, $R^2 = 4\text{-}ClC_6H_4$
199 $R^1 = 4\text{-}MeC_6H_4CH_2$, $R^2 = C_6H_5$
200 $R^1 = 4\text{-}MeC_6H_4$, $R^2 = CH_3$
201 $R^1 = C_{12}H_{25}$, $R^2 = CH_3$
202 $R^1 = R^2 = C_4H_9$

Scheme 39. Deoxygenation of sulfoxides to sulfides using **WR**.

7. Conclusions

Woolins' reagent has proven to be a very useful reagent for the synthesis of a variety of P–Se heterocycles containing four- to ten-membered rings and for the preparation of some simple metal complexes and polynuclear clusters. Reaction of **WR** with compounds containing a variety of functional groups such as diols, amides, nitriles, ketones, aldehydes, olefins, and alkynes provides synthetic chemists with a tool to easily introduce selenium or selenium and phosphorus into organic compounds. Deoxygenation of sulfoxides to sulfides and reductive dimerization of ketones and aldehydes to the corresponding symmetrical and unsymmetrical *E*-olefins are further useful applications of **WR**.

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