Organo Phosphorus-Selenium Heterocycles Derived from Haloalkanols and Alkenes

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Abstract: Treating Woollins’ reagent (WR) with an equimolar amount of sodium 2-bromoalkanolate (which were prepared in situ from the reaction of bromoalkanol and NaH) in THF gave five- or six-membered PSeOC₅n (n = 2 or 3) phosphorus-selenium heterocycles 3 and 4 in good yields. WR reacting with one equivalent of conjugated 1,3-dienes led to the formation of different end products: with 1,4-diphenylbuta-1,3-diene giving a five-membered 2,3,5-triphenyl-4-styryl-1,2,5-selenadiphospholane 2,5-diselenide 5; however, with 2,3-dibenzyl-1,3-butadiene affording 4,5-dibenzyl-2-phenyl-3,6-dihydro-2H-1,2-selenaphosphinine 2-selenide 6 as a major isolable product. Refluxing WR with one equivalent of unconjugated 2,5-dimethyl-1,5-hexadiene in toluene produced P-Se heterocyclic compound 7 with the same five-membered C₂P(Se)SeP(Se) motif as 5. Furthermore, heating a toluene solution of WR with an equimolar amount of N-allylaniline gave rise of a five-membered C₃N³P(Se)Se heterocycle 8; carrying out a reaction of cinnamitride with an equivalent of WR under identical conditions did not give any air-stable product, however, selenoamide 11 was isolated in 95% yield after treatment with water. Three demonstrative X-ray structures are reported.

Key words: Woollins’ reagent; Phosphorus-selenium heterocycles; Alkenes; Haloalkanols; Selenoamide.

Selenium-containing heterocyclic compounds have been attracting considerable attention due in part to their interesting reactivities and potential pharmaceutical properties, applications as new materials as well as reagents and catalysts. However, the synthesis of selenium-containing organic heterocycles is not always easy because of the inconvenience of typical selenium reagents such as H₂Se, NaHSe, (Me₂Si)₃Se, potassium selenocyanate and tetraethylammonium tetrathioenotungstate [Et₄N]₂WSe₄, each exhibiting its own problems including toxicity, solubility, difficulty in handling and poor reactivity. 2,4-Bis(phenyl)-1,3-dihydrodiphenylphosphine-2,4-diselenide [PPh(Se)(μ-Se)]₂, known as Woollins’ reagent, WR, is an efficient selenating reagent in synthetic chemistry. WR has been widely utilized as a selenation reagent for the synthesis of a wide range of selenium containing and non-selenium containing compounds as well as for the synthesis of a variety of phosphorus-selenium heterocycles. In continuation of our studies investigating the reactivity of WR towards different organic substrates as precursors or building blocks, herein, we report the synthesis and characterization of six small phosphorus-selenium heterocycles and one selenium containing heteroatom compound from the reaction of WR with alkenes or haloalkanols and three representative X-ray structures.

Heating 1-bromoethanol or 1-bromopropanol with equi-molar amount of NaH in THF at 70 °C for 2 h, followed by treating with a half-molar amount of WR at room temperature for 24 h gave the corresponding five- or six-membered phosphorus-selenium heterocycles 3 and 4 in 91% and 86% yields, respectively (Scheme 1). Apparently, WR reacts with sodium 2-bromoalkanolates first producing the intermediates 1 and 2 as salts, followed by intramolecular cyclization to give the final products 3 and 4. However, when bromoalkanols with long alkenene chain (n ≥ 4) were used, the reactions were too complex to isolate any pure product.

![Scheme 1 Synthesis of phosphorus-selenium heterocycles 3 and 4.](image-url)

Compounds 3 and 4 are air and moisture stable for several months without any decomposition, and soluble in normal organic solvents. Compounds 3 and 4 were fully characterised by multinuclear NMR and IR spectroscopy and accurate mass measurement. Both compounds showed the anticipated molecular ion peaks [M+H]⁺, and were confirmed by satisfactory accurate mass measurements. ³¹P ⁷⁷Se NMR spectra of 3 and 4 showed sharp singlets at 88.4 and 68.4 ppm, respectively flanked by two pairs of selenium satellites with ³¹P ⁷⁷Se coupling constants of 390/381 Hz and 852/832 Hz, indicating the presence of both P-Se single bond and P-Se double bonds in these heterocyclic compounds. This was further supported by the ⁷⁷Se NMR spectra which showed two doublets at 342.5/370.4 ppm and -0.4/-40.5 ppm with matching ³¹P ⁷⁷Se coupling constants.

Refluxing a toluene solution of 1,4-diphenylbuta-1,3-diene with an equimolar amount of WR led to new five-membered 2,3,5-triphenyl-4-styryl-1,2,5-selenadiphospholane 2,5-diselenide 5 with one C=C double bond unreacted in 36.2% yield via the cleavage of four-membered [P(Se)(μ-Se)]₂ ring as shown in Scheme 2. Carrying on the reaction of WR with two or more equivalents of 1,4-diphenylbuta-1,3-diene under identical conditions furnished the same product with a slight improvement of yield. Prolonged reactions had no impact on the yield. Furthermore, to investigate the reactivity of the remaining C=C double bond in compound 5 towards WR, the reaction of compound 5 with one equivalent of WR was performed in refluxing toluene. As expected, no new products were isolated with recovery of the starting materials.
materials, compounds 5 and WR. The result suggests that the steric hindrance effectively shields the further reaction of WR with the remaining pendant C=C double bond.

![Scheme 2 Synthesis of heterocycle 5 from the selenation of 1,4-diphenylbuta-1,3-diene](image1)

Surprisingly, WR reacting with an equimolar amount of 2,3-dibenzyl-1,3-butadiene in refluxing toluene led to 4,5-dibenzyl-2-phenyl-3,6-dihydro-2H-1,2-selenaphosphine 2-selenide 6 in 45.6% yield as a unique product rather than a five-membered ring as compound 5 (Scheme 3). Once again, we carried on the reaction of the product 6 with one more equivalent of WR under identical conditions, but no new product was identified.

![Scheme 3 Synthesis of heterocycle 6 from the selenation of 2,3-dibenzyl-1,3-butadiene](image2)

The above results prompted us to investigate related reactions. Unconjugated 2,5-dimethyl-1,5-hexadiyne reacted with an equimolar amount of WR in refluxing toluene resulting in a unique P-Se heterocyclic compound 7 with five-membered C$_2$P(Se)SeP(Se) motif in 46.1% isolated yield after work-up (Scheme 4). Once more, the remaining unconjugated C=C double bond in the heterocycle 7 remained unreacted. The product was further treated with another equivalent of WR under identical conditions leading to recovery of the starting materials.

![Scheme 4 Synthesis of heterocycle 7 from the selenation of 2,5-dimethyl-1,5-hexadiyne](image3)

Compounds 5 – 7 were spectrally characterised by multinuclear NMR and IR spectroscopy and accurate mass measurement. All of new compounds showed the anticipated molecular ion peaks [M+H]$^+$, and were confirmed by satisfactory accurate mass measurements. The phosphorus atoms in compounds 5 – 7 are potentially stereogenic centres. In fact, two stereoisomers were observed by multinuclear NMR in compounds 5 and 7. $^{31}$P NMR spectra of 5 – 7 showed sharp singlets in the range of 43.0 – 61.8 ppm, flanked by two pairs of selenium satellites with $^{77}$Se coupling constants in the ranges of 333 – 416 Hz and 756 – 803 Hz, indicating the presence of both P-Se single bond and P=Se double bond in these heterocyclic compounds. This was further supported by the $^{77}$Se NMR spectra which showed one set of triplets at 364.1 and 469.1 ppm for 5 and 7 respectively and two doublets in the range of -179.0 – -103.1 ppm with matching $^{31}$P-$^{77}$Se coupling constants, and displayed two pairs of doublets at 286.5 and -133.6 ppm with matching $^{31}$P-$^{77}$Se coupling constants in compound 6. The IR spectra of compound 6 showed a strong bond at 2009 cm$^{-1}$, indicating the presence of an unconjugated C=C supporting the formation of the six-membered heterocycle.

The X-ray structure of 5 is shown in Figure 1$^{16}$. The newly formed ring is non-planar and there is a trans arrangement of two phenyl groups being inclined each other by 16.6° and a trans arrangement of two exo-selenium atoms bonded to the phosphorus atoms. The P⋯P cross-ring distance (3.27 Å) is approximately midway between the P-P single bond (2.20 Å) and van der Waal’ separation (3.80 Å). The distances of P-Se double bonds [2.0914(16) and 2.0944(17) Å] and P-Se single bonds [2.273(2) and 2.2768(15) Å] are similar to P=Se and P-Se bond lengths previously observed in other related compounds containing the P(Se)(μ-Se) unit.$^{17-19}$

![Figure 1 X-ray structure of 5 (Hydrogen atoms omitted for clarity).](image4)

Selected bond lengths (Å) and angles (°) (esds in parentheses): Se(1)-P(1) 2.0914(16), Se(2)-P(2) 2.0944(17), Se(3)-P(1) 2.273(2), Se(3)-P(2) 2.2768(15), P(1)-C(1) 1.872(5), P(1)-C(17) 1.810(6), P(2)-C(23) 1.801(7), P(2)-C(2) 1.846(6), C(1)-C(2) 1.517(9), P(1)-P(2)-Se(1) 91.75(6), Se(1)-P(1)-Se(3) 112.55(8), Se(1)-P(1)-C(1) 116.26(19), Se(1)-P(1)-C(17) 114.23(18), Se(3)-P(1)-C(1) 101.6(2), Se(3)-P(1)-C(17) 106.9(2), C(1)-P(1)-C(17) 104.1(2), Se(2)-P(2)-Se(3) 116.88(7), Se(2)-P(2)-C(2) 114.1(2), Se(2)-P(2)-C(23) 114.69(19), Se(3)-P(2)-C(23) 98.19(17), Se(3)-P(2)-C(2) 105.66(19), C(2)-P(2)-C(23) 111.14(1).
We tested other organic substrates with C=C double bonds in reactions with WR. Surprisingly, five-membered heterocycle 8 was obtained in 72% yield when N-allylaniline reacted with an equivalent of WR in refluxing toluene solution (Scheme 5). Compound 6 represents a symmetric cleavage product of WR rather than the expected five-membered ring diphosphorus species. A two-step reaction mechanism can be proposed for the formation of 8. The first step is that N-allylaniline reacts with the true reactive species PhPSe$_2$ (I) from WR in elevated temperature leading to the intermediate II. Then, an intra-molecular [2 + 2] addition resulting in the ring closure of intermediate II gives five-membered heterocycle 8.

![Scheme 5 Synthesis of heterocycle 8 from the selenation of N-allylaniline](image)

Treating cinamnitrile with an equivalent of WR in refluxing toluene did not lead to any stable isolable product. However, when the resulting reaction mixture was treated with water, selenoamide II was isolated in 95% yield (Scheme 6). We propose that the heterocyclic compound 10 was readily formed via a [2 + 2] cycloaddition of PhPSe$_2$ from WR with the triple bond C≡N of cinamnitrile (due to the double bond C=C being less reactive than the triple bond C≡N towards WR). However, the intermediate 10 is not isolable and easily decomposed to selenoamide II after hydrolysis. This might be following a similar mechanism that suggested in the previous report of the preparation of primary arylselenoamides.

![Scheme 6 Synthesis of selenoamide II from the selenation of cinamnitrile](image)

The proposed structures of 8 and II are based on their spectral analyses and accurate mass measurement. Both compounds 8 and II showed the anticipated molecular ion peaks [M+H]$^+$, and their formulae were confirmed by satisfactory accurate mass measurements. For 8, two stereoisomers were found in ca. 2 : 1 intensity ratio in multi-NMR spectra. The $^{31}$P NMR spectrum of 8 comprises sharp singlets at 60.8 / 59.8 ppm, the singlet in each case being flanked by two pairs of selenium satellites with $^{77}$Se coupling constants of 379 / 379 Hz and 806 / 806 Hz, indicating both P-Se single bond and P=Se double bond characters. This was further confirmed by the $^{77}$Se NMR exhibiting double doublets at 482.2 / 465.9 ppm with matching $^{31}$P - $^{77}$Se coupling constants. For 9, the IR spectra showed a strong band at 1630 cm$^{-1}$ from the C=C double bond, and intense bands at 746 cm$^{-1}$ and medium bands at 372 cm$^{-1}$ are characteristic of the C=Se group. $^{31}$ $^{77}$Se NMR spectrum displayed a singlet signal at 592.3 ppm which is typical of selenoamides.

Compounds 8 and II were crystallized by slow diffusion of hexane into dichloromethane solutions to give transparent, colourless cubic crystals.

![Figure 2. X-ray structure of 8 (Hydrogen atoms omitted for clarity).](image)

There are two independent molecules in the asymmetric unit. Selected bond lengths (Å) and angles (˚) (esds in parentheses) (dimensions for one independent molecule in square parentheses): Se(1) - N(3) 1.797(5) [1.792(6)], N(3) - P(2) 2.2263(19) [2.2263(19)] A˚2.12

$^{31}$P - $^{77}$Se coupling constants of 379 / 379 Hz and 806 / 806 Hz, indicating both P-Se single bond and P=Se double bond characters. This was further confirmed by the $^{77}$Se NMR exhibiting double doublets at 482.2 / 465.9 ppm with matching $^{31}$P - $^{77}$Se coupling constants. For 9, the IR spectra showed a strong band at 1630 cm$^{-1}$ from the C=C double bond, and intense bands at 746 cm$^{-1}$ and medium bands at 372 cm$^{-1}$ are characteristic of the C=Se group. $^{31}$ $^{77}$Se NMR spectrum displayed a singlet signal at 592.3 ppm which is typical of selenoamides.

Compounds 8 and II were crystallized by slow diffusion of hexane into dichloromethane solutions to give transparent, colourless cubic crystals. 8 crystallises in the triclinic space group P$ar{1}$ with two crystallographically independent molecules in the asymmetric unit (Figure 2) and confirms the presence of the five-membered heterocyclic ring. 8 adopts an envelope conformation with the Se(1)-P(2) bond 2.2263(19) [2.2263(19)] A˚, and Se(2)-P(2) bond 2.0855(17) [2.0915(17)] A˚. The P-Se single bond length [P(2)-N(3)] 1.693(5) [1.693(6)] A˚ is appropriate for a P-N single bond. The geometry around P(2) [Se(1)-P(2)-Se(2) 114.42(9) [113.99(6)]] is a distorted tetrahedron due to the steric hindrance of the phenyl groups. One of two phenyl rings is co-planar with the newly formed five-membered ring with two phenyl rings oriented cis to one another being inclined by 83.2° [76.8°] to each other.

![Figure 2. X-ray structure of 8 (Hydrogen atoms omitted for clarity).](image)

There are two independent molecules in the asymmetric unit. Selected bond lengths (Å) and angles (˚) (esds in parentheses) (dimensions for second independent molecule in square parentheses): Se(1)-P(2) 2.2263(19) [2.2263(19)], Se(2)-P(2) 2.0855(17) [2.0915(17)], Se(1)-C(5) 1.983(8) [1.983(8)], P(2)-N(3) 1.693(5) [1.693(6)], P(2)-C(7) 1.797(5) [1.792(6)], N(3)-C(13) 1.4249(1) [1.4108(8)], N(3)-C(4), 1.427(8) [1.472(8)], C(4)-C(5) 1.462(11) [1.462(11)]. P(2)-Se(1)-C(5) 88.5(2) [88.0(2)], Se(1)-P(2)-Se(2) 114.42(9) [113.99(6)], Se(1)-P(2)-C(7) 106.1(2) [108.6(2)], Se(2)-P(2)-C(7) 111.96(19) [111.8(2)], Se(1)-P(2)-N(3) 96.5(2) [96.75(16)], Se(2)-P(2)-N(3) 120.06(18) [118.8(2)], N(3)-P(2)-C(7) 106.0(2) [108.6(2)], P(2)-N(3)-C(4) 117.8(5) [117.3(4)], N(3)-C(4)-C(5) 114.5(5) [115.3(7)], Se(1)-C(5)-C(4) 106.7(5) [107.2(5)].
selenoamide. The C=Se double bond length (1.861(7) Å) is marginally longer that in arylselenoamides [1.820(4)–1.848(2)\textsuperscript{20,26}] due to the seleocarbonyl group being stabilised by conjugation with the free electron pairs at the nitrogen and the conjugated C=C double bond. A similar C=Se double bond distance (1.837(4) Å) was found in $N,N'$-diethyl-2-methyl-3,3-diphenylprop-2-eneseleolamoid.\textsuperscript{28} The shortness of the C–N bond length in which the C–N bonds are adjacent to the C=Se double bond [1.337(10) Å], compared to the normal C–N bond distances [1.45–1.48 Å],\textsuperscript{28} suggests some multiple bonding character. It should be noted that N(1)–C(1)–C(2)–C(3) adopts is approximately co-planar with the phenyl ring, while Se(1) lies 0.182 Å out of this plane.

![Figure 3. X-ray structure of II. Selected bond lengths (Å) and angles (°) (esds in parentheses): Se(1)–C(1) 1.861(7), N(1)–C(1) 1.337(10), C(1)–C(2) 1.440(12), C(2)–C(3) 1.339(11), C(3)–C(4) 1.446(11); Se(1)–N(1) 1.48 Å, C(1)–C(2) 1.337(10) Å, Se(1)–C(1) 1.337(10) Å.](image)

**Experimental Section**

Unless otherwise stated, all reactions were carried out under on oxygen free nitrogen atmosphere using pre-dried solvents and standard Schlenk techniques, subsequent chromatographic and work up procedures were performed in air. $^1$H (270 MHz), $^{13}$C (67.9 MHz), $^{31}$P–$^1$H (109 MHz) and $^{77}$Se–$^1$H (51.4 MHz referenced to external Me$_2$Se) NMR spectra were recorded at 25 °C (unless stated otherwise) on a JEOL GSX 270. IR spectra were recorded as KBr pellets in the range of 4000 - 250 cm$^{-1}$ on a Perkin–Elmer 2000 FTIR/Raman spectrometer. Mass spectrometry was performed by the EPSRC National Mass Spectrometry Service Centre, Swansea and the University of St Andrews Mass Spectrometry Service. X-ray crystal data for 5 were collected using Rigaku SCX Mini Mercury CCD system and for 8 and 11 using the Rigaku STANDARD system.\textsuperscript{29} Intensity data were collected using $\phi$ steps accumulating area detector images spanning at least a hemisphere of reciprocal space. All data were corrected for Lorentz polarization effects. Absorption effects were corrected on the basis of multiple equivalent reflections or by semi-empirical methods. Structures were solved by direct methods and refined by full-matrix least-squares against F$^2$ by using the program SHELXTL.\textsuperscript{30} Hydrogen atoms were assigned riding isotropic displacement parameters and

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In conclusion, Woolfins’ reagent (WR) reacting with equimolar amount of sodium 2-bromoalkanlates gave the corresponding five- or six-membered phosphorus-selenium heterocycles in good yields. WR reacting with dienes resulted in the formation of different end products: with conjugated 1,4-diphenylbuta-1,3-diene and unconjugated 2,5-dimethyl-1,5-hexyldiene affording diphorous species heterocycles with a C2P(Se)SrP(Se) motif; however, with 2,3-dibenzyl-1,3-butadiene producing a monophorous species heterocycle with a C4P(Se)Se motif. Treating WR with N-allylaniline under identical conditions resulted in a new five-membered C$_2$N(P(Se))Se heterocycle. Reaction of cinnamolitrile with an equivalent of WR under identical conditions did not give any isolable product apart from selenoamide, which was isolated in 95% yield after treatment with water. The structures of all new compounds have been elucidated by using $^1$H, $^{13}$C, $^{31}$P, $^{77}$Se NMR spectroscopy and accurate mass measurement in conjunction with single crystal X-ray crystallography of three structures.

**General procedure for the synthesis of heterocycles 3 and 4.** A white suspension of 2-bromoalkanol (2.0 mmol) and 0.16 g of NaH (4.0 mmol) in 50 mL of THF was heated at 70°C for 2 h. Upon cooling to room temperature and removing unreacted solid, the filtrate was added to WR (0.54 g, 1.0 mmol) and the mixture was stirred at room temperature for 24 h. After removing unreacted solid by filtration and evaporating solvent in vacuo, the residue was purified by column chromatography on silica gel (1:9 ethyl acetate/dichloromethane) to give the compounds 3 and 4.

2-Phenyl-1,3,2-oxazolophospholane 2-selenide (3): 0.275 g as a yellow oil (91% yield). Selected IR (KBr, cm$^{-1}$): 1435(m), 1259(m), 1185(w), 1100(s), 1016(s), 983(s), 925(m), 745(s), 688(m), 547(s), 549(s), 520(m). $^1$H NMR (CD$_2$Cl$_2$, δ, 8.00–7.87 (m, 2H, ArH), 7.52–7.49 (m, 3H, ArH), 4.82–4.64 (m, 2H, OCH$_2$), 3.78–3.60 (m, 2H, SeCH$_2$) ppm. $^{31}$C NMR

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(CD$_2$Cl$_2$, δ), 136.9 (d, J(PC) = 93.0 Hz), 133.2 (d, J(PC) = 3.1 Hz), 131.0 (d, J(PC) = 12.5 Hz), 128.6 (d, J(PC) = 14.5 Hz), 72.7, 34.8 ppm. 31P NMR (CD$_2$Cl$_2$, δ) 88.4 (s, J(PSe) = 390 Hz, J(PSe) = 852 Hz) ppm. 77Se NMR (CD$_2$Cl$_2$, δ) 342.5 (d, J(PSe) = 390 Hz), -0.4 (d, J(PSe) = 852 Hz) ppm. Accurate mass measurement [FI$^+$, m/z]: 303.8773 [M$^+$], calculated mass for C$_3$H$_6$OP$_2$Se$_2$: 303.8770.

2-Phenyl-1,3,2-oxaselenaphosphinane 2-selenide (4): 0.280 g as a yellow oil (86% yield). Selected IR (KBr, cm$^{-1}$): 1434(m), 1258(m), 1183(m), 1104(s), 979(vs), 895(m), 864(m), 742(s), 688(m), 583(s), 547(vs), 524(s). 1H NMR (CD$_2$Cl$_2$, δ) 8.08-8.00 (m, 2H, ArH), 7.55-7.50 (m, 3H, ArH), 4.90-4.76 (m, 2H, OCH$_2$), 4.29-4.14 (m, 2H, SeCH$_2$), 3.08-3.02 (m, 2H, CH$_2$) ppm. 13C NMR (CD$_2$Cl$_2$, δ) 135.0 (d, J(PC) = 93.4 Hz), 133.2 (d, J(PS) = 3.1 Hz), 131.0 (d, J(PC) = 12.5 Hz), 128.7 (d, J(PS) = 14.5 Hz), 68.2, 27.1, 23.7 ppm. 31P NMR (CD$_2$Cl$_2$, δ) 504.5 (s, J(PS) = 381 Hz, J(PS) = 832 Hz) ppm. Accurate mass measurement [FI$^+$, m/z]: 317.8924 [M$^+$], calculated mass for C$_3$H$_6$IOP$_2$Se$_2$: 317.8926.

Synthesis of 2,3,5-triphenyl-4-styryl-1,2,5-selenadiphospholane 2,5-selenide (5). A solution of 1,4-diphenyl-1,3-butadiene (0.21 g, 1.0 mmol) and WR (0.54 g, 1.0 mmol) in 20 mL of toluene was refluxed for 24 h. Upon cooling to room temperature, the resulting red suspension disappeared and the residue was extracted with dichloromethane (2 mL) and purified by column chromatography on silica gel (elucent dichloromethane) to give 0.315 g as a pale yellow paste in 62.8% yield. Selected IR (KBr, cm$^{-1}$): 2009 (vs, C=C), 1492(m), 1433(m), 1090(s), 1027(m), 976(m), 730(s), 726(m), 695(s), 537(m), 514(m). 1H NMR (CD$_2$Cl$_2$, δ) 7.99-7.92 (m, 2H, ArH), 7.49-7.46 (m, 3H, ArH), 7.36-7.03 (m, 10H, ArH), 3.83 (s, 2H, CH$_2$), 3.67-3.53 (s, 2H, CH$_2$), 3.28-3.10 (m, 4H, CH$_2$) ppm. 13C NMR (CD$_2$Cl$_2$, δ) 138.9, 138.3, 138.2, 136.2, 136.0, 134.2, 133.4, 132.6 (d, J(PC) = 12.5 Hz), 132.2, 132.1, 131.8 (d, J(PC) = 3.1 Hz), 129.1, 129.0, 128.7, 128.4 (d, J(PC) = 12.5 Hz), 126.6 (d, J(PC) = 12.5 Hz), 105.5, 45.2 (d, J(PC) = 29.1 Hz), 39.4 (d, J(PC) = 81 Hz), 39.3 (d, J(PC) = 83 Hz), 28.3 (d, J(PC) = 73 Hz) ppm. 31P NMR (CD$_2$Cl$_2$, δ) 48.1 (s, J(PS) = 416 Hz, J(PS) = 756 Hz), 48.0 (s, J(PS) = 416 Hz, J(PS) = 756 Hz) ppm. 77Se NMR (CD$_2$Cl$_2$, δ) 286.5 (d, J(PS) = 415 Hz), -133.6 (d, J(PS) = 756 Hz) ppm. MS (Cl$^+$, m/z), 503 [M+H]$^+$. Accurate mass measurement (Cl$^+$, m/z): 502.9941 [M+H]$^+$. Calculated mass for C$_3$H$_3$P$_2$Se$_2$: 502.9946.

Synthesis of 3-benzyl-2,5-diphenyl-3-(3-phenylprop-1-en-2-yl)-1,2,5-selenadiphospholane 2,5-selenide (6). A mixture of 2,3-dibenzyl-1,3-butadiene (0.24 g, 1.0 mmol) and WR (0.54 g, 1.0 mmol) in 150 mL of toluene was refluxed for 24 h. The red suspension disappeared and a yellow solution with some black solid formed. Upon cooling to room temperature, the solvent was removed under reduced pressure and the organic residue was extracted with dichloromethane (2 mL) and purified by column chromatography on silica gel (elucent dichloromethane) to give 0.315 g as a pale yellow paste in 62.8% yield. Selected IR (KBr, cm$^{-1}$): 2009 (vs, C=C), 1492(m), 1433(m), 1090(s), 1027(m), 976(m), 730(s), 726(m), 695(s), 537(m), 514(m). 1H NMR (CD$_2$Cl$_2$, δ) 7.99-7.92 (m, 2H, ArH), 7.49-7.46 (m, 3H, ArH), 7.36-7.03 (m, 10H, ArH), 3.83 (s, 2H, CH$_2$), 3.67-3.53 (s, 2H, CH$_2$), 3.28-3.10 (m, 4H, CH$_2$) ppm. 13C NMR (CD$_2$Cl$_2$, δ) 138.9, 138.3, 138.2, 136.2, 136.0, 134.2, 133.4, 132.6 (d, J(PC) = 12.5 Hz), 132.2, 132.1, 131.8 (d, J(PC) = 3.1 Hz), 129.1, 129.0, 128.7, 128.4 (d, J(PC) = 12.5 Hz), 126.6 (d, J(PC) = 12.5 Hz), 105.5, 45.2 (d, J(PC) = 29.1 Hz), 39.4 (d, J(PC) = 81 Hz), 39.3 (d, J(PC) = 83 Hz), 28.3 (d, J(PC) = 73 Hz) ppm. 31P NMR (CD$_2$Cl$_2$, δ) 48.1 (s, J(PS) = 416 Hz, J(PS) = 756 Hz), 48.0 (s, J(PS) = 416 Hz, J(PS) = 756 Hz) ppm. 77Se NMR (CD$_2$Cl$_2$, δ) 286.5 (d, J(PS) = 415 Hz), -133.6 (d, J(PS) = 756 Hz) ppm. MS (Cl$^+$, m/z), 503 [M+H]$^+$. Accurate mass measurement (Cl$^+$, m/z): 502.9941 [M+H]$^+$. Calculated mass for C$_3$H$_3$P$_2$Se$_2$: 502.9946.
Synthesis of 5-methyl-2,3-diphenyl-1,3,2-
selenazaphospholidine 2-selenide (8). A mixture of N-allylamine (0.135 g, 1.0 mmol) and WR (0.54 g, 1.0 mmol) in 10 mL of dry toluene was refluxed for 7 h. The red suspension disappeared and a colorless solution was formed. After removing the solvent in vacuum the residue was purified by silica gel column (toluene as eluent) to give 0.288 g as a pale yellow solid in 89.7% yield. Selected IR (KBr, cm⁻¹): 1595(s, C=O), 1490(s), 1435(s), 1267(s), 1248(s), 1091(s), 880(s), 757(s), 688(vs), 608(s), 526(s), 491(s). Two stereoisomers were found in ca. 2:1 intensity ratio. 

1H NMR (CD2Cl2, δ): 8.14-8.05 (m, 2Hx, ArH), 7.52-7.48 (m, 3Hx, ArH), 7.22-6.61 (m, 5Hx, ArH), 5.57-5.17 (m, 1Hx, CH2), 4.42-3.75 (m, 2Hx, CH2), 1.90-1.67 (m, 3Hx, CH3) ppm. 31P NMR (CD2Cl2, δ): 142.1, 142.0, 135.7, 132.7, 132.5, 132.1, 131.6, 131.5, 131.4, 131.3, 128.9, 128.8, 128.5, 128.4, 128.3, 124.3, 124.2, 123.1, 122.7, 63.2, 63.1, 41.3, 21.0, 18.3 ppm. 31P NMR (CD2Cl2, δ): 60.8 (s, J(13P-1Se) = 285 Hz, J(P=Se) = 806 Hz); 59.8 (s, J(13P-1Se) = 379 Hz, J(P=Se) = 806 Hz) ppm. 77Se NMR (CD2Cl2, δ): 482.8 (d, J(13P-1Se) = 379 Hz); 465.9 (d, J(13P-1Se) = 379 Hz); -20.7 (d, J(13P-1Se) = 806 Hz); -83.6 (d, J(13P-1Se) = 806 Hz) ppm. MS (CI⁺, m/z): 322 [M+H]⁺. Accurate mass measurement (CI⁺, m/z): 322.0260 [M+H]⁺, calculated mass for C14H17NPSe2⁺: 322.0264.

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synlett.

Synthesis of 2-phenylprop-2-eneselenoamide (11). A mixture of trans-cinnamonic acid (0.13 g, 1.0 mmol) and WR (0.54 g, 1.0 mmol) in 20 mL of toluene was refluxed for 6 h. The red suspension disappeared and a red solution was formed. Upon cooling to 90°C, 1.0 mL of water was added and the mixture was refluxed for another 1 h. After cooling to room temperature the solvent was removed in vacuo and the organic residue was extracted with dichloromethane and purified by column chromatography on silica gel (1:5 ethyl acetate/dichloromethane as eluent) to afford 0.200 g as a red solid in 95.2% yield. Selected IR (KBr, cm⁻¹): 1664(m, C=C), 1630(vs, C=C), 1426(vs), 1292(m), 1250(m), 1019(m), 968(s), 740(vs), 688(s), 372(m). 1H NMR (CD2Cl2, δ): 8.53 (dw, 2H, NH), 7.84-7.38 (m, 5H, ArH), 6.88 (d, J(H,H) = 7.0 Hz, 1H, CH), 5.90 (d, J(H,H) = 7.0 Hz, 1H, CH) ppm. 13C NMR (CD2Cl2, δ): 202.4, 144.9, 130.5, 129.3, 129.2, 128.4, 128.0 ppm. 77Se NMR (CD2Cl2, δ): 592.3 ppm. MS (ES⁺, m/z): 233 [M+Na]⁺. Accurate mass measurement (ES⁺, m/z): 233.9795 [M+Na]⁺, calculated mass for C14H15SeNa: 233.9798.

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References and notes


(16) Crystallographic data for compound 5: C$_2$H$_4$P-Se$_2$, $M$ = 659.33, Monoclinic, space group P2$_1$/c, $a = 13.065(3)$, $b = 19.737(3)$, $c = 11.192(2)$ Å, $\beta = 112.23(4)$, $U = 2671.4(9)$ Å$^3$, $Z = 4$, $\mu = 1.639$ mm$^{-1}$, 16123 reflections, 4685 unique ($R_{int} = 0.061$); $R_1 = 0.0659$, $wR_2 = 0.1073$.


(23) Crystallographic data for compound 8: C$_2$H$_4$NP-Se$_2$, $M$ = 399.19, Triclinic, space group P-1, $a = 8.785(4)$, $b = 9.7406(19)$, $c = 19.590(11)$ Å, $\alpha = 76.22(4)$, $\beta = 87.46(5)$, $\gamma = 69.26(4)$, $U = 1521.2(11)$ Å$^3$, $Z = 4$, $\mu = 1.743$ mm$^{-1}$, 16169 reflections, 5291 unique ($R_{int} = 0.043$); $R_1 = 0.0515$, $wR_2 = 0.1389$; Crystallographic data for compound 11: C$_2$H$_4$NSe, $M$ = 210.14, Monoclinic, space group P2$_1$/c, $a = 20.158(10)$, $b = 5.509(3)$, $c = 7.846(4)$ Å, $\beta = 98.756(12)$, $U = 861.1(8)$ Å$^3$, $Z = 4$, $\mu = 1.621$ mm$^{-1}$, 4686 reflections, 1509 unique ($R_{int} = 0.055$); $R_1 = 0.0628$, $wR_2 = 0.2568$.


Reactions Of Woollins’ Reagent

This work describes a new entry into a range of CPSe Rings via simple reactions with WR.

• Statement of significance of work.

Reaction of Woollins Reagent leads to a new group of five-membered CPSe rings or when allylaniline is used the five membered PNSeC₂ ring shown.