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Formation of new organoselenium heterocycles and ring reduction of 10-membered heterocycles into seven-membered heterocycles

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ABSTRACT

Reacting 2,4-bis(phenyl)-1,3-diselenadiphosphetane-2,4-diselenide [{PhP(Se)(μ-Se)}$_2$], Woollins' reagent**,** with an equivalent of aromatic diol in refluxing toluene afforded 10-membered phosphorus–selenium heterocycles **1** and **2** with an O–P(Se)–Se–Se–P(Se)–O linkage. Two equivalents of aromatic diol and Woollins' reagent in refluxing toluene gave seven-membered phosphorus–selenium heterocycles **3** and **4** with an O–P(Se)–O linkage together with 10-membered phosphorus–selenium heterocycles **1** and **2**. It was also found that the diphosphorus species O–P(Se)–Se–Se–P(Se)–O rings **1** and **2** could be readily ring contracted into the monophosphorus rings **3** and **4** in almost quantitative yields via further reaction with another equivalent of corresponding aromatic diol. One representative X-ray structure is reported.

1. Introduction

Organoselenium chemistry has been a very useful approach in the hands of synthetic chemists [1]. Organoselenium heterocyclic compounds have attracted considerable interest in the past several decades due to their unique properties [2] and applications as potential pharmaceuticals [3], new materials [4] as well as reagents and catalysts [5]. However, the synthesis of selenium-containing organic heterocycles is not always easy due to the inconvenience of traditional selenium reagents such as H_2Se, NaHSe, $(Me_3Si)_2Se$, potassium selenocyanate and tetraethylammonium tetraselenotungstate $[Et_4N]_2WSe_4$, each having its own problems including toxicity, solubility, difficulty in handling and poor reactivity. In recent years, 2,4-bis(phenyl)-1,3-diselenadiphosphetane-2,4-diselenide [{PhP(Se)(μ-Se)}$_2$], Woollins' reagent**,** has become a very useful selenium source or selenation reagent in synthetic chemistry [6] due to its less unpleasant chemical properties and ready preparation and easy handling [7]. Herein, we report the easy preparation of seven- and 10-membered phosphorus–selenium heterocycles from the reaction of Woollins' reagent with aromatic diol. Furthermore, the seven-membered monophosphorus species could be obtained by the ring contraction of 10-membered diphosphorus species via reacting with another molar equivalent of aromatic diol.

2. Experimental

2.1. General and physical measurements

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_2Se) NMR spectra were recorded in $CDCl_3$ 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. Microanalysis was performed by the University of St. Andrews microanalysis service. Mass spectrometry was performed by the EPSRC National Mass Spectrometry Service Centre, Swansea and the University of St. Andrews Mass Spectrometry Service.

2.2. Preparation of the compounds**1–4**

CARE: The following reactions may evolve H_2Se which is highly toxic. Reaction must be performed in an efficient fume hood and reaction outlets should be scrubbed with aqueous copper sulfate solution.

2.2.1. Reaction of Woollins reagent with two equivalents of aromatic diol

A suspension of 2,2′-diphenol or 1,1′-bi(2-naphthol) (2.0 mmol) with Woollins' reagent (0.54 g, 1.0 mmol) in 20 mL of dry toluene

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was refluxed for 7 h. The red suspension disappeared and a yellow solution formed. Upon cooling to room temperature, the solvent was removed *in vacuo*, the residue was purified by chromatography column (silica gel, toluene as eluent) to give **1** (180 mg, 25% yield) or **2** (179 mg, 22% yield) and **3** (260 mg, 70% yield) or **4** (354 mg, 75% yield).

*2.2.2. Reaction of **1** or **2** with an equivalent of aromatic diol*

A mixture of **1** or **2** (1.0 mmol) and an equivalent of 2,2′-diphenol or 1,1′-bi(2-naphthol) in 20 mL of toluene was refluxed for 7 h. A red suspension disappeared and a yellow solution formed along with some grey elemental selenium. Upon cooling to room temperature, the solvent was removed in vacuum, the residue was purified by silica gel chromatography column (toluene as eluent) to give **3** (735 mg, 99% yield) and **4** (920 mg, 98%).

*2.2.3. Compound **3***

Yellow solid. Selected IR (KBr, cm^{-1}): 3058(w), 2949(w), 1497(m), 1474(m), 1433(s), 1243(m), 1195(s), 1112(m), 1093(m), 912(vs), 777(s), 748(m), 687(m), 609(m), 560(m). ^1H NMR (CD_2Cl_2, δ), 7.91–7.82 (m, 4H, ArH), 7.63–7.57 (m, 4H, ArH), 7.49–7.36 (m, 5H, ArH), 7.09–7.02 (m, 4H, ArH) ppm. ^{13}C NMR (CD_2Cl_2, δ), 148.5 (d, J(P,C) = 12.5 Hz), 133.5 (d, J(P,C) = 2.1 Hz), 132.7, 131.6, 131.5, 130.9, 130.4, 129.9, 129.7, 128.5, 128.3, 126.7, 122.4 (d, J(P,C) = 3.1 Hz) ppm. ^{31}P NMR (CD_2Cl_2, δ), 108.6 (s, J(P,Se $_{exo}$) = 937 Hz) ppm. ^{77}Se NMR (CD_2Cl_2, δ), −239.8 (d, J(P,Se $_{exo}$) = 937 Hz) ppm. Mass spectrum (CI^+, m/z): 373 $[M+H]^+$. Elemental *Anal.* Calc. for $C_{18}H_{13}O_2PSe$: C, 58.2; H, 3.5. Found: C, 58.3; H, 3.5%.

*2.2.4. Compound **4***

Yellow solid. Selected IR (KBr, cm^{-1}): 3056(w), 2961(w), 1587(m), 1509(m), 461(m), 1436(m), 1324(m), 1219(s), 1191(m), 1112(m), 1068(m), 943(vs), 837(s), 746(s), 724(s), 609(s). ^1H NMR (CD_2Cl_2, δ), 8.13 (d, J(H,H) = 8.8 Hz, 2H, NaphH), 8.03 (d, J(H,H) = 8.2 Hz, 2H, PhH), 7.93 (d, J(H,H) = 8.2 Hz, 2H, PhH), 7.84–7.67 (m, 4H, NaphH + PhH), 7.59–7.29 (m, 5H, NaphH + PhH), 6.93 (d, J(H,H) = 8.8 Hz, 2H, NaphH) ppm. ^{13}C NMR (CD_2Cl_2, δ), 148.5 (d, ^2J(P,C) = 15 Hz), 146.1 (d, ^2J(P,C) = 9.3 Hz), 133.6, 132.6, 132.6, 132.5, 132.1, 131.8, 131.6, 130.9, 130.8, 128.7, 128.6, 128.5, 128.2, 127.2, 127.0, 126.8, 125.9, 122.0 (d, ^3J(P,C) = 2.1 Hz), 121.0 (d, ^3J(P,C) = 2.1 Hz) ppm. ^{31}P NMR (CD_2Cl_2, δ), 108.7 (s, J(P,Se_{exo}) = 939 Hz) ppm. ^{77}Se NMR (CD_2Cl_2, δ), −236.0 (d, J(P,Se_{exo}) = 939 Hz) ppm. Mass spectrum (CI^+, m/z): 473 $[M+H]^+$. Elemental *Anal.* Calc. for $C_{26}H_{17}O_2PSe$: C, 66.25; H, 3.64. Found: C, 65.62; H, 3.64%.

2.3. Crystal structure determination

X-ray crystal data for compound **4** were collected using the St. Andrews Robotic diffractometer (Saturn724 CCD) at 125 K with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) [8,9]. Intensity data were collected using ω 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 [10,11]. Hydrogen atoms were assigned riding isotropic displacement parameters and constrained to idealized geometries.

*2.3.1. Crystallographic data for **4***

$C_{26}H_{17}O_2PSe \cdot CH_2Cl_2$, M = 556.29, triclinic, space group $P\bar{1}$, a = 8.456(3), b = 11.254(3), c = 14.314(3) Å, U = 1198.6(6) $Å^3$, Z = 2, μ = 1.541 mm^{-1}, 12 626 reflections, 4168 unique (R_{int} = 0.0810); R_1 = 0.0736, wR_2 = 0.2387.

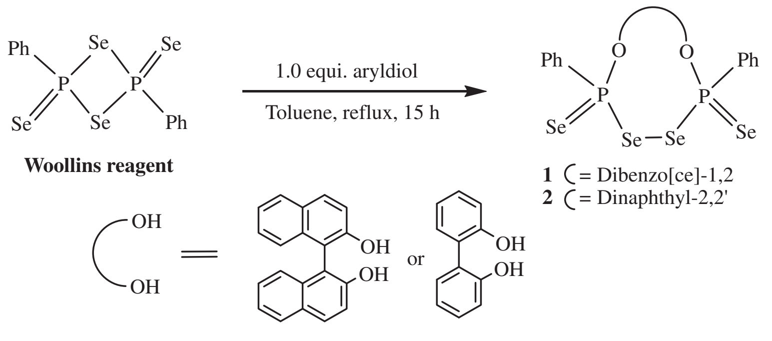
3. Results and discussion

*3.1. Syntheses of compounds **1–4***

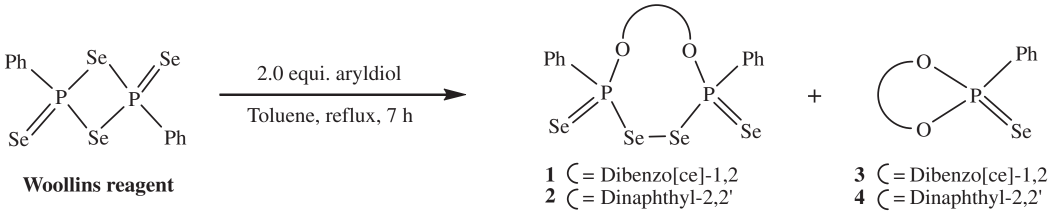
Treating one equivalent of aromatic diol [2,2′-diphenol or 1,1′-bi(2-naphthol)] and Woollins' reagent in refluxing toluene solution for 15 h generating 10-membered diselenides **1** and **2** with an O–P(Se)–Se–Se–P(Se)–O linkage has been reported previously (Scheme 1) [12]. However, reacting Woollins' reagent with two molar equivalents of aromatic diol at reflux in toluene for 7 h gave rise to, after work-up in the air, seven-membered monophosphorus species **3** and **4** with an O–P(Se)–O linkage in 70% and 75% yield together with 10-membered diphosphorus species **1** and **2** in 25% and 22% yield (Scheme 2).

We suggest that mechanistically the reactions to give **1–4** could proceed through the following reaction paths in Scheme 3. First, the reaction of Woollins' reagent with one molecule of aromatic diol affords **C** via a nucleophilic substitution followed by proton transfer. Intermediate **C** cyclises and eliminates one molecule of hydrogen gas to give **D** (diphosphorus species **1** or **2**). **D** repeats the same nucleophilic substitution with another equivalent of aromatic diol to generate **E** by with proton transfer and loss of one molecule of selenium. Intermediate **E** collapses into two molecules of **G** (monophosphorus species **3** or **4**), one formed straightforwardly, another from the intermediate **F** by spontaneous loss of a molecule of hydrogen selenide.

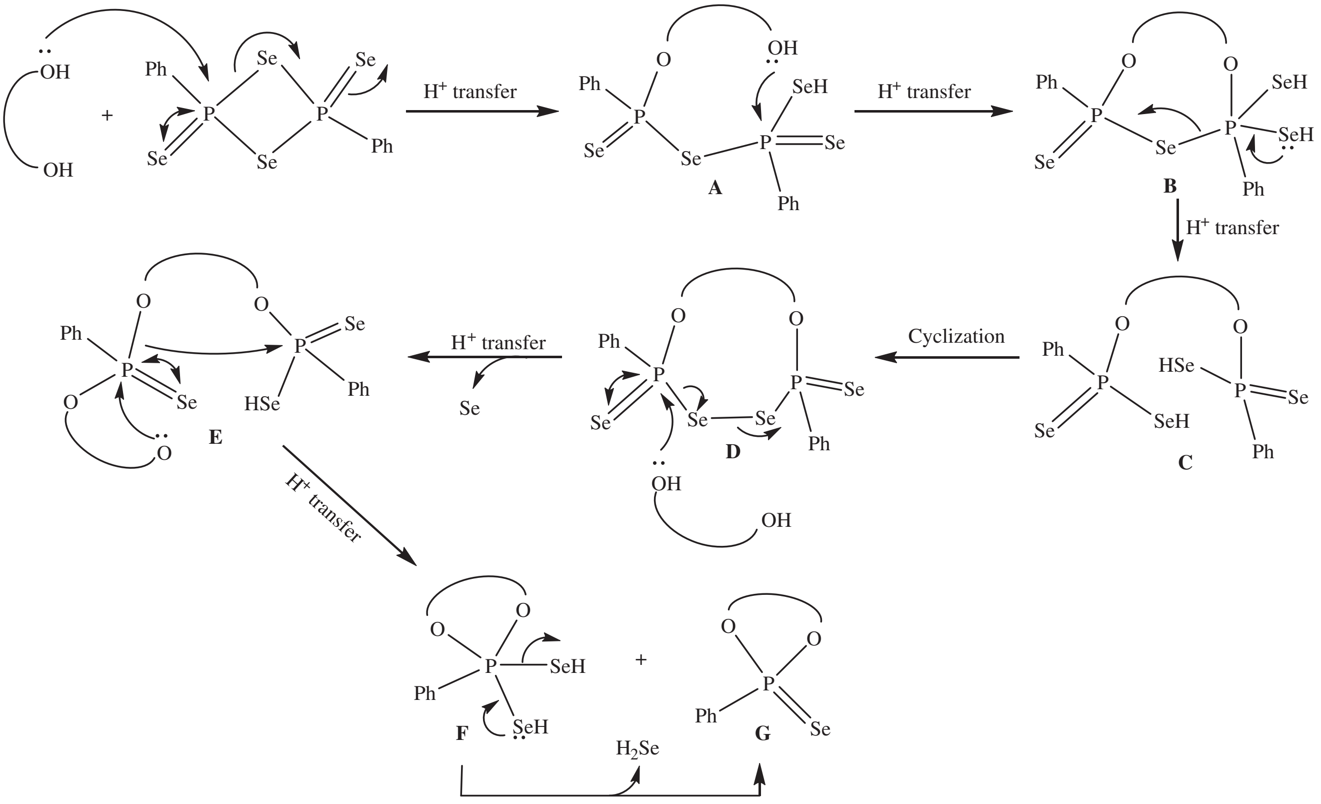
To confirm the mechanism, the isolated diphosphorus species **1** and **2** were reacted with another molar equivalent of corresponding aromatic diol under similar condition. Monophosphorus species **3** or **4** formed in almost quantitative yield (99% and 98%) in this way (Scheme 4). Black selenium was found in the resulting mixture and the release of H_2Se in the reaction was observed in the bubbler which connects the N_2 line and the top of the



Scheme 1. Reaction of Woollins' reagent with one molar equivalent of aromatic diol.



Scheme 2. Reaction of Woollins' reagent with two molar equivalents of aromatic diol.



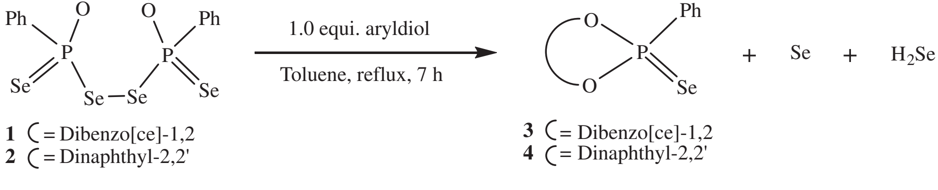
Scheme 3. Possible mechanism for the formation of heterocycles **1–4**.

condenser (and could be trapped by sodium hydroxide as sodium selenium after the bubbler).

Monophosphorus **3** and **4** are soluble in organic solvents and are air-stable. The ^{31}P NMR spectra of **3** and **4** exhibit sharp singlets at 108.7 and 108.6 ppm, which are accompanied by one set of satellite for the exocyclic selenium atoms (^{1}J(P,Se$_{exo}$): 937 Hz for **3** and 939 Hz for **4**), thus indicating the presence of only double P=Se bonds in each compound. The ^{77}Se NMR spectra for **3** and **4** contain signals arising from exocyclic ($\delta = -239.8$ and -236.0 ppm; ^{1}J(P,Se$_{exo}$) = 937 and 939 Hz), further confirming the presence of the only P=Se double bond in both **3** and **4**. The elemental microanalyses of **3** and **4** were satisfactory, and all compounds showed the anticipated [M]$^+$ or [M+H]$^+$ peak in their mass spectra.

3.2. X-ray structure of compound 4

Attempt to crystallize compound **3** were unsuccessful. Compound **4** co-crystallized with one molecule of dichloromethane and contains a highly puckered seven-membered $C_4O_2P(Se)$ ring in Fig. 1. The exocyclic P=Se distance [2.058(2) Å] is similar to those in other compounds which contain the P(Se)(μ-Se) unit



Scheme 4. Ring reduction of diphosphorus species into monophosphorus species.

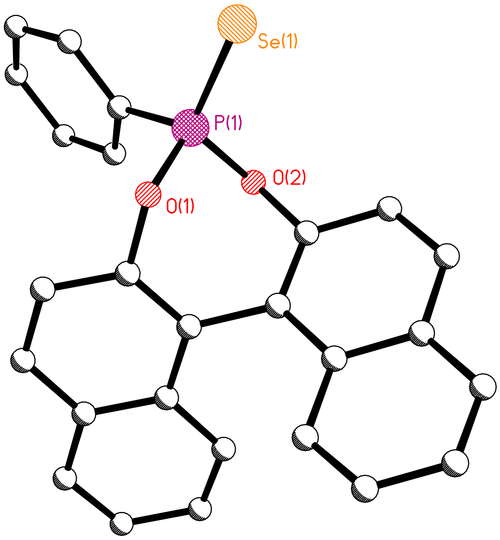


Fig. 1. Single crystal X-ray structure of **4** (hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (°) (esds in parentheses): Se(1)–P(1) 2.058(2), P(1)–O(1) 1.625(4), P(1)–O(2) 1.602(6), P(1)–C(21) 1.788(7), O(1)–C(1) 1.417(9), O(2)–C(11) 1.413(9); Se(1)–P(1)–O(1) 109.4(2), Se(1)–P(1)–O(2) 117.65(16), Se(1)–P(1)–C(21) 116.5(2), O(1)–P(1)–O(2) 102.8(2), P(1)–O(1)–C(1) 117.8(4), P(1)–O(2)–C(11) 115.9(4).

[13–16]. The O–P–O angle of the highly puckered seven-membered P–O–C–C–C–C–O ring, 102.8(2)° is distorted tetrahedral angle at P(1), while the exocyclic Se=P—O angle is [109.4(2)°] is nearly normal tetrahedral.

4. Conclusions

Ten-membered or seven-membered phosphorus–selenium heterocycles with an O–P(Se)–Se–Se–P(Se)–O or O–P(Se)–O linkage have been successfully prepared from the selenation of aromatic diol by Woollins' reagent. The large diphosphorus species O–P(Se)–Se–Se–P(Se)–O rings could be readily contracted into the small monophosphorus species O–P(Se)–O rings via further treatment with one equivalent of aromatic diol. The structures of the novel heterocycles have been elucidated by using ^{1}H, ^{31}P, ^{77}Se NMR spectroscopy and microanalysis in conjunction with single-crystal X-ray crystallography.

Acknowledgments

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Appendix A. Supplementary data

CCDC 766221 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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