

# SYNLETT Spotlight 289

## Woollins' Reagent

Compiled by María Ángeles López-García



This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

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### Introduction

Woollins' Reagent {WR, 2,4-diphenyl-1,3-diselenadi-phosphetane-2,4-diselenide,  $[\text{PhP}(\text{Se})(\mu\text{-Se})_2]$ } is a selenium analogue of the well-known Lawesson's reagent,  $[\text{4-MeOC}_6\text{H}_4\text{P}(\text{S})(\mu\text{-S})_2]$ . Compared to other selenium reagents, the deep-red crystals of WR have less unpleasant chemical properties, are easy to prepare, and safely handled in air.<sup>1</sup> WR is used in the synthesis of selenium-containing organic compounds and P–Se heterocycles.<sup>2</sup>

Woollins and co-workers initially prepared WR from the pentamer  $(\text{PhP})_5$ ,<sup>3</sup> which is an air-sensitive compound with a lingering stench. For this reason, they have developed a new method preparing WR producing material of high purity in high yield.<sup>4</sup> This compound is now commercially available.

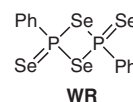
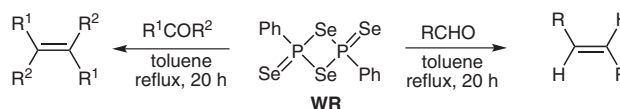


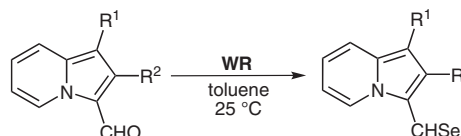
Figure 1

### Abstracts

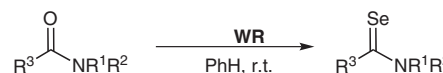
(A) *Stereoselective Synthesis of Olefins by a Reductive Coupling Reaction.* Aromatic ketones and aldehydes were converted into symmetrical and asymmetrical *E*-olefins by reaction with WR in 53–100% yield. A mechanism involving a Wittig-like reaction intermediate has been proposed.<sup>5</sup>



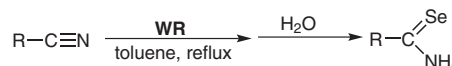
(B) *Selenocarbonyl Synthesis.* The treatment of indolizine-3-aldehydes with WR gave access to the corresponding selenoaldehydes in 40–59% yield.<sup>6</sup>



(C) *Synthesis of *N,N*-Disubstituted Selenoamides by O–Se Exchange.* The selenation of *N,N*-disubstituted amides using WR provided a general and straightforward route to the corresponding selenoamides. This reaction was carried out under mild conditions and afforded the selenoamides in higher yields (21–85%) than using other selenation reagents. The yield decreased with the bulkiness of the nitrogen substituents.<sup>7</sup>



(D) *Synthesis of Primary Arylselenoamides.* Woollins and co-workers have developed a new method for the synthesis of primary arylselenoamides, which were obtained by the reaction of aryl nitriles with WR and subsequent addition of water in moderate to excellent yields (60–100%).<sup>8</sup>



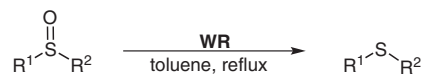
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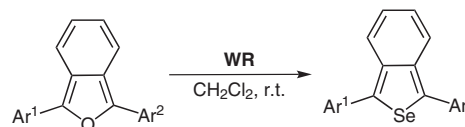
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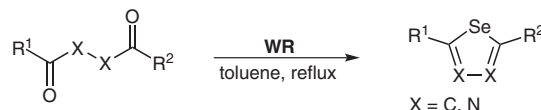
(E) *Synthesis of Sulfides by Deoxygenation of Sulfoxides.* Woollins' reagent allowed the deoxygenation of a series of sulfoxides to sulfides in good to excellent yields (81–99%). The reaction proceeded by refluxing a toluene suspension of the cited reagent and the corresponding sulfoxides. The reaction has been found to be a very useful approach in organic synthesis because of the simple work-up, mild conditions, high selectivity and high conversion of substrates.<sup>1</sup>



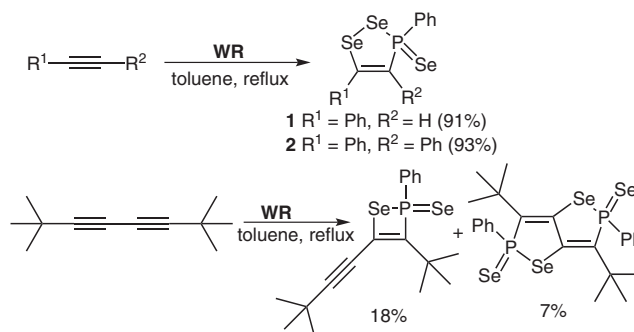
(F) *Synthesis of 1,3-Diarylbenzo[c]selenophenes.* The reaction of benzo[c]furans with WR has been used in the synthesis of a series of 1,3-diarylbenzo[c]selenophenes in 55–70% yield involving a selenium transfer reaction.<sup>9,10</sup>



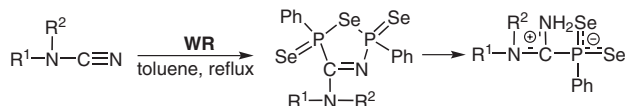
(G) *Synthesis of 2,5-Disubstituted 1,3,4-Selenadiazoles and Selenophenes.* Recently, Woollins and co-workers have described an efficient method for the synthesis of 2,5-disubstituted 1,3,4-selenadiazoles by the reaction of WR and 1,2-diacylhydrazines.<sup>11</sup> Similarly, 2,5-disubstituted selenophenes were obtained from 1,4-diketones.<sup>2</sup>



(H) *Synthesis of Vinylic P–Se Heterocycles and Bis-Heterocycles.* Five-membered P(Se)Se<sub>2</sub>C<sub>2</sub> heterocycles have been synthesized by insertion of a Ph(Se)PSe<sub>2</sub> fragment from WR into the alkyne triple bonds.<sup>12</sup> On the contrary, the reaction of WR with 1,4-di-*tert*-butyl-1,3-diyne gave an unusual four-membered P(Se)SeC<sub>2</sub> ring and a fused bis-heterocyclic compound with two five-membered rings.<sup>13</sup>



(I) *Synthesis of Selenazadiphospholaminediselenides.* Woollins and co-workers have synthesized selenazadiphospholaminediselenides by the reaction of phenylalkylcyanamides with WR in moderate yields (42–43%). The novel heterocycles were hydrolyzed to the unusual zwitterionic cabamidoyl(phenyl)phosphinodiselenic acid in high yields (96–98%).<sup>14</sup>



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