SYNLETT
Spotlight 289

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

Woollins' Reagent

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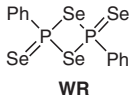
Introduction

Woollins' Reagent {WR, 2,4-diphenyl-1,3-diselenadiphosphetane-2,4-diselenide, $[PhP(Se)(\mu\text{-}Se)]_2$} is a selenium analogue of the well-known Lawesson's reagent, $[4\text{-}MeOC_6H_4P(S)(\mu\text{-}S)]_2$. 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.[1] WR is used in the synthesis of selenium-containing organic compounds and P–Se heterocycles.[2]

Woollins and co-workers initially prepared WR from the pentamer $(PhP)_5$,[3] 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.[4] This compound is now commercially available.

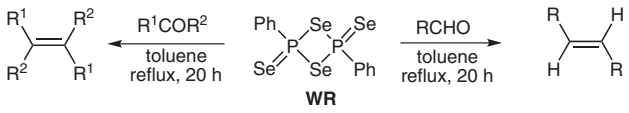


WR

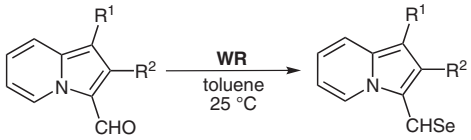
Figure 1

Abstracts

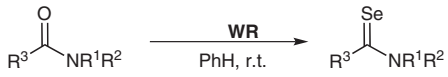
(A) *Stereoselective Synthesis of Olefins by a Reductive Coupling Reaction.* Aromatic ketones and aldehydes were converted into symmetrical and asymmetrical *E*-olefins by reaction with WR in 53–100% yield. A mechanism involving a Wittig-like reaction intermediate has been proposed.[5]



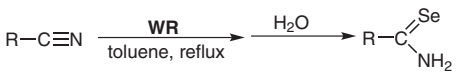
(B) *Selenocarbonyl Synthesis.* The treatment of indolizine-3-aldehydes with WR gave access to the corresponding selenoaldehydes in 40–59% yield.[6]



(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.[7]



(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 arylnitriles with WR and subsequent addition of water in moderate to excellent yields (60–100%).[8]



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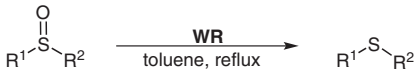
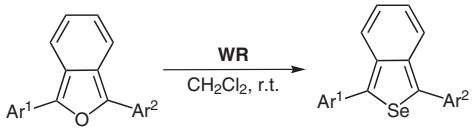
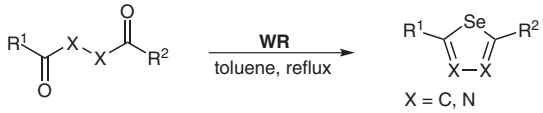
(E) *Synthesis of Sulfides by Deoxygenation of Sulfoxides.* Woollins' reagent allowed the deoxygenation of a series of sulfoxides to sulfides in good to excellent yields (81–99%). The reaction proceeded by refluxing a toluene suspension of the cited reagent and the corresponding sulfoxides. The reaction 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.[1]



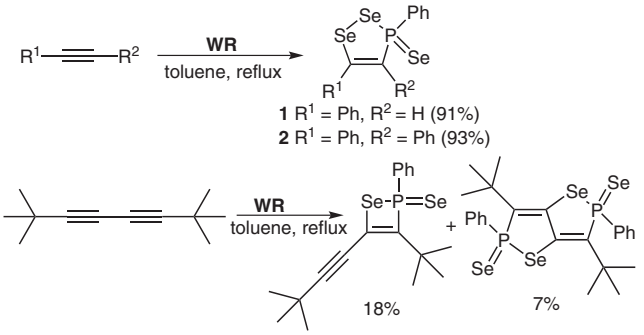
(F) *Synthesis of 1,3-Diarylbenzo[c]selenophenes.* The reaction of benzo[*c*]furans with WR has been used in the synthesis of a series of 1,3-diarylbenzo[*c*]selenophenes in 55–70% yield involving a selenium transfer reaction.[9,10]



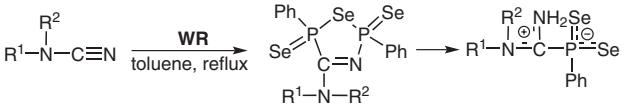
(G) *Synthesis of 2,5-Disubstituted 1,3,4-Selenadiazoles and Selenophenes.* Recently, Woollins and co-workers have described an efficient method for the synthesis of 2,5-disubstituted 1,3,4-selenadiazoles by the reaction of WR and 1,2-diacylhydrazines.[11] Similarly, 2,5-disubstituted selenophenes were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



(H) *Synthesis of Vinylic P–Se Heterocycles and Bis-Heterocycles.* Five-membered $P(Se)Se_2C_2$ heterocycles have been synthesized by insertion of a $Ph(Se)PSe_2$ fragment from WR into the alkyne triple bonds.[12] On the contrary, the reaction of WR with 1,4-di-*tert*-butyl-1,3-diyne gave an unusual four-membered $P(Se)SeC_2$ ring and a fused bis-heterocyclic compound with two five-membered rings.[13]



(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)phosphinodiselenoic acid in high yields (96–98%).[14]



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