Woollins’ Reagent

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Introduction

Woollins’ Reagent [WR, 2,4-diphenyl-1,3-diselenadi-phosphetane-2,4-diselenide, \([\text{PhP(Se)}(\mu-\text{Se})]_2\)] is a selenium analogue of the well-known Lawesson’s reagent, \([4-\text{MeOC}_6\text{H}_4\text{P}(\mu-\text{S})]_2\). 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 \((\text{PhP})_5\),\(^3\) 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.

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 reaction of arylnitriles with WR and subsequent addition of water in moderate to excellent yields (60–100%).\(^8\)
(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 Vinylc P–Se Heterocycles and Bis-Heterocycles. Five-membered P(Se)SeC2 heterocycles have been synthesized by insertion of a Ph(Se)PSe2 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)SeC2 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

References