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The syntheses of sulfides by deoxygenation of sulfoxides using Woollins' reagent

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Abstract—Woollins' reagent (**WR**) acts as a deoxygenation reagent for a wide range of sulfoxides affording the corresponding sulfides in good to excellent yields (up to 99% isolated yield) under mild conditions.

The reduction of sulfoxides to the corresponding sulfides is an important reaction that has found considerable utility in organic synthesis and in biochemical reactions.[1,2] So far, various methods for the deoxygenation of sulfoxides have been developed, such as using metal hydride reagents ($LiAlH_4$, $NaBH_4$, etc.), low-valent metallic species ($SnCl_2$, VCl_3, etc.), halide ions (HI, TMSI, TiI_4, etc.)[3,4] and phosphines combined with Lewis acids.[5,6] However, most of the methods suffer from serious disadvantages including the use of expensive reagents that are difficult to handle, functional group incompatibility, difficult work up procedures or harsh reaction conditions such as low pH, high temperature, or long reaction time.[4d,7] Thus, there is still considerable interest in the development of highly efficient reagents for this transformation.

2,4-Diphenyl-1,3-diselenadiphosphetane-2,4-diselenide $[PhP(Se)(\mu\text{-}Se)]_2$, known as Woollins' reagent (**WR**), is a selenium counterpart of the well-known Lawesson's reagent, $[p\text{-}MeOC_6H_4P(S)(\mu\text{-}S)]_2$. Compared with other selenium reagents, the deep-red crystals of **WR** have less unpleasant chemical properties and are easily prepared/safely handled in air.[8] **WR** acts as an efficient selenium source for the synthesis of a wide range of selenoamides and selenoaldehydes by a simple oxygen/selenium exchange reaction or reaction with ArCN followed by hydrolysis, as well as being a useful reagent for the synthesis of a variety of P–Se heterocycles.[9–12]

We have recently found that **WR** is also an efficient coupling reagent for syntheses of symmetrical and (*E*)-olefins from ketones or aldehydes.[13] In studies related to this coupling reaction, we attempted the reaction of **WR** with diphenyl sulfoxide (PhS(O)Ph, **1a**). Surprisingly, we obtained the deoxygenated product diphenyl sulfide (**1b**) in 99% isolated yield. Similarly we obtained sulfides **1b**–**12b** by refluxing a toluene suspension of **WR** (1 mmol) and the corresponding sulfoxides (2 mmol) for 6–20 h under nitrogen. During this period, the suspended **WR** gradually disappears and a yellow solution is formed along with a grey elemental selenium precipitate. Flash chromatography on silica (eluting with toluene) gives **1b**–**12b** (identified by comparison with literature spectroscopic data) as pale pink/yellow solids or colourless oils in good to excellent yields (Table 1).

All substrates including those bearing electron-withdrawing groups, for example, NO_2 gave excellent yields. Alkyl sulfoxides react rapidly with **WR**, however, aryl and benzylic sulfoxides need much longer reaction times.

Attempts to convert aryl or alkyl sulfones into the corresponding sulfides with **WR** were unsuccessful even when the reaction was lengthened up to 72 h. No product was observed and only the starting material was recovered.

The $^{31}P\{^1H\}$ NMR spectrum of the crude mixture from the reaction of PhS(O)Ph with **WR** in toluene-d_8 (after 20 h reflux) contains multiplets centred at 3.3 and

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Keywords: Woollins' Reagent; Sulfoxide; Sulfide; Deoxygenation; Reduction.

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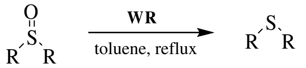
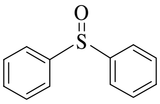
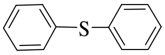
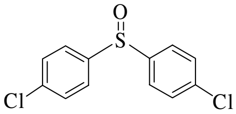
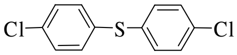
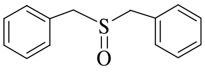
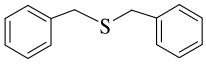
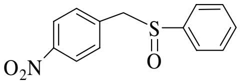
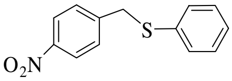
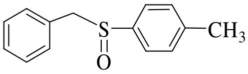
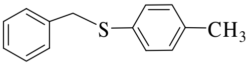
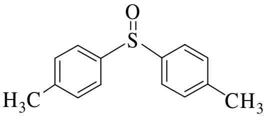
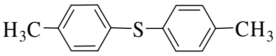
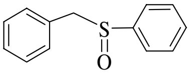
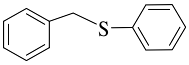
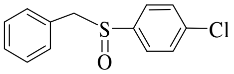
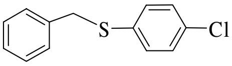
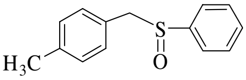
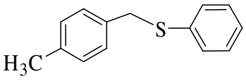
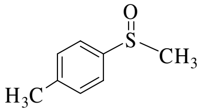
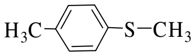
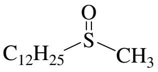
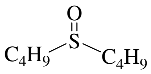
Table 1. The deoxygenation of sulfoxides using **WR**

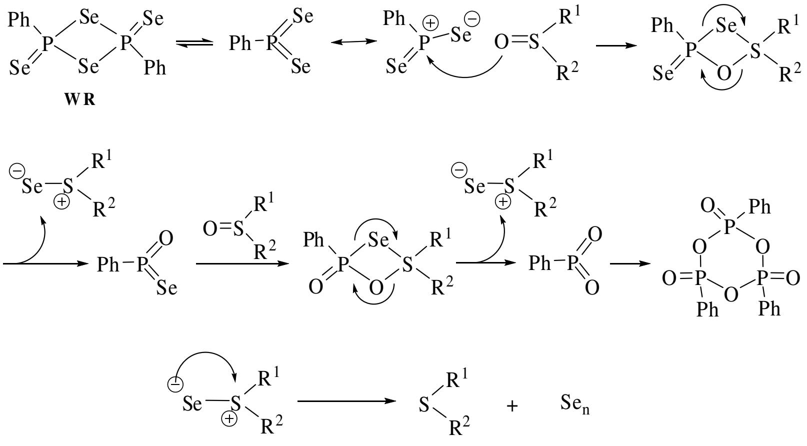


Entry	Substrate	Product	Time (h)	Yield[a] (%)
1	**1a** 	**1b** 	20	99
2	**2a** 	**2b** 	20	93
3	**3a** 	**3b** 	20	99
4	**4a** 	**4b** 	20	81
5	**5a** 	**5b** 	20	97
6	**6a** 	**6b** 	20	99
7	**7a** 	**7b** 	20	99
8	**8a** 	**8b** 	20	97
9	**9a** 	**9b** 	20	99
10	**10a** 	**10b** 	20	99
11	**11a**  $C_{12}H_{25}S(O)CH_3$	**11b** $C_{12}H_{25}$–S–CH_3	10	99
12	**12a**  $C_4H_9S(O)C_4H_9$	**12b** C_4H_9–S–C_4H_9	6	99

[a] Isolated yields.

1.0 ppm but no ^{77}Se{^{1}H} NMR signal was observed for this crude mixture. The ^{31}P–^{31}P coupling constants (37–40 Hz) suggest a P(O)–O–P(O) linkage, indicating the formation of the $(PhPO_2)_3$ trimer which has been previously reported by Bethke et al.[9e] (A_2B type spectrum, $\delta_A = 1.6$, $\delta_B = 3.5$, $^2J = 39.9$ Hz).

The mechanism of the reactions can be explained as follows (Scheme 1). At elevated temperatures **WR** is in equilibrium with a diselenaphosphorane $PhPSe_2$, which is the true reactive species in refluxing solution.[12] First, the sulfoxide attacks a phosphorus atom to give a four-membered cyclic intermediate [PhP(Se)(μ-Se)(μ-O)SR^{1}R^2], which then eliminates [PhP(O)Se]. PhP(O)Se can react further with the sulfoxide to give another four-membered cyclic intermediate [PhP(O)(μ-Se)(μ-O)SR^{1}R^2], which eliminates [PhP(O)O], that transforms into stable $(PhPO_2)_3$. Obviously, we would anticipate that the bond strength between the sulfur and selenium atom in the intermediate Se=S(R^1)R^2 is very weak and



Scheme 1.

thus in refluxing toluene elemental selenium would be expelled to give stable sulfides (**1b**–**12b**).

In conclusion, the deoxygenation of a series of sulfoxides to sulfides was effectively promoted by **WR** under mild conditions in a good to excellent yield. The reaction was found to be a very useful approach in organic synthesis because of the easy work-up, mild conditions, high selectivity and high conversion of substrates.

Acknowledgement

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2007.03.132.

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