Efficient Synthesis of 2,4-Bis(phenyl)-1,3-diselenadiphosphetane-2,4-diselenide (Woollins’ Reagent)

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ABSTRACT: An improved approach for the preparation of 2,4-bis(phenyl)-1,3-diselena-2,4-diphosphetane-2,4-diselenide (Woollins’ reagent) is described. Reacting dichlorophenylphosphine with Na₂Se which was in situ prepared from the reaction of elemental selenium and metal sodium in the presence of naphthalene in refluxing tetrahydrofuran generated Woollins’ reagent with excellent purity and a yield of up to 96.4%.

INTRODUCTION

The chemistry of 2,4-bis(phenyl)-1,3-dilena-2,4-diphosphetane-2,4-diselenide (PhPSe₂)₂ has received attention since it was suggested to be named as Woollins’ reagent (WR).1 WR has been used for a range of transformations and heterocycle syntheses for the past 2 decades.2−14 It has been successfully applied as an efficient building unit or block to synthesize a series of 8-, 9-, and 10-membered selendophosphorus heterocycles with the P–Se–Se–P linkage15 and unique octasele-nocyclododecane with four carbon atoms and eight selenium atoms in this 12-membered cycle.16 Another attractive application has been its ability to act as a highly chemoselective reagent, such as in the reduction of a wide range of 1,4-enediones and 1,4-yndiones in methanol, which led to saturated 1,4-diketones,17 and the selective reduction of the double bond of 2-α,β-unsaturated thiazo and selenazolidinones, which gave the corresponding saturated heterocycles in good yields.18 WR has also been used as a reducing reagent to transform porpholactone into dihydro-porpholactone in 40% yield or into adjacent tetrahydroporpholactone in 75% isolated yield.19 We have previously reported the synthetic method of WR involving liquid ammonia.20

RESULTS AND DISCUSSION

Here, we report a modified method for the synthesis of WR, which does not involve the use of liquid ammonia. We hope that this procedure will help facilitate further development of WR. The following procedure may be scaled down 5-fold or 10-fold with no loss of yield. The method involves the use of the unpleasant dichlorophenylphosphine; however, it avoids the handling of potentially hazardous liquid ammonia. In addition, the method produces a product of high purity in a higher yield and by a cleaner process, and the major advantage of this method is that it can be achieved on a large scale and at high quality by using normal glassware.

EXPERIMENTAL SECTION

Caution. This reaction involves toxic selenium powder, highly reactive sodium metal, and extremely malodorous P₃P₂-dichlorophenylphosphine. The reactions should be carried out in a well-ventilated fume cupboard, and gloves should always be worn. The procedure should be performed under an inert atmosphere.

Sodium metal (in small pieces, 14.75 g, 640 mmol) was added to a solution of dry tetrahydrofuran (THF) (750 mL) and naphthalene (8.2 g, 64 mmol) at room temperature, resulting in a black suspension. Selenium (25.2 g, 320 mmol) was added, and the suspension was refluxed for 24 h to give Na₂Se as an off-white solid after THF was removed in vacuo. Toluene (750 mL) was added, PhPCl₂ (45.5 mL, 640 mmol) was added, and the mixture was refluxed further for 24 h. The reaction mixture was cooled to under 100 °C and filtered by passing through a thick layer of dry Celite to remove the NaCl (or using a filter cannula method). A second portion of selenium (42.1 g, 540 mmol) was added, and the suspension was refluxed for 24 h to give Na₂Se as an off-white solid after THF was removed in vacuo. Toluene (750 mL) was added, PhPCl₂ (45.5 mL, 640 mmol) was added, and the mixture was refluxed further for 24 h. The reaction mixture was cooled to under 100 °C and filtered by passing through a thick layer of dry Celite to remove the NaCl (or using a filter cannula method). A second portion of selenium (42.1 g, 540 mmol) was added, and the mixture was refluxed for another 24 h. A second portion of PhPCl₂ (20 mL, 281 mmol) was added, and the mixture was refluxed further for another 24 h. Upon cooling to room temperature, WR (81.65 g, 96.4%) was collected by filtration.

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and washing with cold dry toluene (100 mL × 3) and dry diethyl ester (100 mL) as a reddish-brown powder. Found (calcd for C_{12}H_{10}P_{2}Se_{4}): C 27.12 (27.09), H 1.82 (1.89) %. 31P NMR (solid state): δ = 18.7 (s) ppm. Mass spectrum (ESI+): M+ 534. Powder X-ray diffraction (PXRD) is a useful method for checking for any impurities (Figure 1). The reaction may be scaled down 10-fold with no significant loss in yield.

**PROPERTIES**

WR is insoluble in a normal organic solvent but dissolves in toluene at elevated temperatures and can be stored in a fume cupboard at room temperature for several months without apparent decomposition.

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Notes

The authors declare no competing financial interest.

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