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Communication

# Convenient Synthesis of Triphenylphosphine Sulfide from Sulfur and Triphenylphosphine

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**Abstract:** Elemental sulfur ($S_8$) was found to react very rapidly (<1 min) with a stoichiometric amount of triphenylphosphine at rt in sufficient amount of solvent (0.2–0.5 mL of solvent/1 mmol of $PPh_3$). Compared to the previously described methods, the present procedure constitute excellent access to triphenylphosphine sulfide.

**Keywords:** elemental sulfur; triphenylphosphine; triphenylphosphine sulfide; green chemistry

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## 1. Introduction

In recent years, the development of new synthetic process methodologies which are inexpensive, high-yielding, highly atom efficient and eco-friendly have attracted great interest due to the growing concerns about environmental pollution and depletion of natural resources. As a waste produced annually, about 70 MT by the oil and gas refining industry, elemental sulfur, existing as a yellow octatomic solid, is an abundant and inexpensive raw material. With its low atomic weight along with its user-friendliness, including low toxicity to humans, odorlessness, low volatility, high stability at ambient conditions and non-hygroscopic nature, this element could be conveniently served as an ideal direct sulfur precursor for the synthesis of sulfur-containing compounds. Such a strategy is obviously in line with the requirements for greener processes by transforming waste to high value additional products.

Due to the fact that elemental sulfur can adopt diverse oxidation states ranging from −2 in sulfide to +6 in sulfuric acid as well as in sulfate salts, esters and sulfamides, sulfur-containing compounds have a wide range of applications in everyday life, such as agrochemicals, pharmaceuticals, and organic materials. Compounds containing P=S bonds are increasingly common in the scientific literature with a wide array of applications ranging from medicinal chemistry, ligands, organic n-semiconductors to receptors of transition and heavy metal ions [1–4]. Therefore, the synthesis of P=S analogues is of considerable interest. Consequently, different strategies were developed based on the reaction of phosphines or phosphine oxides with elemental sulfur [5] or sulfur-containing compounds [6–8] as sulfur donors.

Although the direct reaction of triphenylphosphine with sulfur leading to triphenylphosphine sulfide was known, this reaction was described to proceed slowly at rt or require heating at high temperatures. Very recently, the rotary ball mill technique (at 400 rpm) was applied to this reaction to lower the reaction temperature to rt with shortened reaction time (4 h) [9]. However, in this case, although solvents were not used during the reaction, extraction of the product from the apparatus required a significant amount of solvent. It should also be noted that although this technique could be useful in some cases, it is not suitable as a common synthetic method for any synthetic organic laboratory due to the high price of the apparatus (varying from many thousands to tens of thousands of dollars for typical laboratory models).

In this context, the simplification of reaction conditions by lowering the solvent amounts, using standard and inexpensive laboratory glassware and purifying the obtained products by simple filtration and washing should be an excellent approach to valorize and promote the widespread application of the developed synthetic procedure.

Herein we report a very rapid reaction of a stoichiometric mixture of triphenylphosphine with sulfur (reaction time less than 1 min) under very simple conditions of shaking.

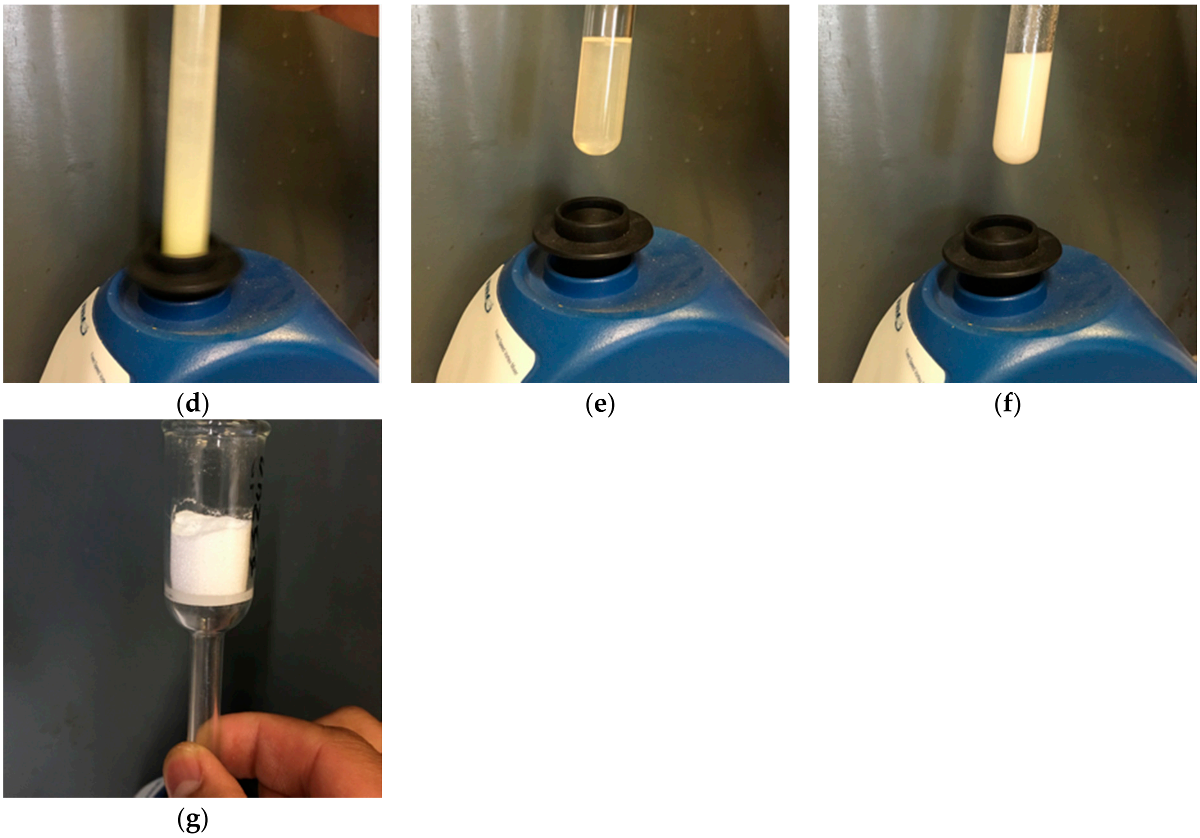
During the course of our study on new reactivities of elemental sulfur applied to organic synthesis [10–12], we have noticed that some reactions with this element proceeded very efficiently in highly concentrated media or even in the absence of solvent. When the reactions were performed at high temperatures, the reaction media were in general liquid, and the stirring was possible without any difficulty [13–15]. However, if the reactions were carried out with solid starting materials (including solid sulfur), the addition of an inert or weakly interacting solvent could be performed to facilitate the stirring. Such solvents should be used in sufficient quantity to avoid excessive dilution, which in turn reduces the reactivity significantly.

## 2. Experiments

Our reaction is visualized in Figure 1. The reaction could be performed in a test tube, although larger reactors could be used for larger scales (100 mmol). Equimolar amounts (10 mmol) of solid triphenylphosphine (as flakes) **1a** and sulfur were added to a test tube (Figure 1a,b). The solvent (5 mL was added) (Figure 1c). We noticed that common laboratory solvents such as $CH_2Cl_2$, $CHCl_3$, toluene … were all suitable for this reaction. The reaction tube was shaken vigorously with a vortex mixer. The reaction mixture became rapidly homogeneously with a slight increase in temperature (about 40 °C). The solid triphenylphosphine sulfide product was precipitated out after 40 s of shaking as a white crystalline powder. The reaction mixture cooled down to rt was filtered, washed with methanol (2 mL × 3) and dried to afford the product as a white crystalline solid triphenylphosphine sulfide **2a** (yield = 2.59 g, 88%). The filtrate could be concentrated to provide a pure product. The purity of the product could be confirmed by $^{1}H$, $^{31}P$ and $^{13}C$ NMR spectra as well as by elemental analysis. Compared to $^{31}P$ NMR of the starting $PPh_3$ (7.32 ppm in $CDCl_3$), the chemical shift of the corresponding $PPh_3S$ is significantly different (43.3 ppm). Compared to known methods, ours is highlighted by its high atom-efficiency with short reaction time (<1 min) under room temperature conditions with a very small amount of moderately polar solvents such as chloroform, $CH_2Cl_2$, toluene and its easy purification by simple filtration.


(**a**) (**b**) (**c**)

**Figure 1.** *Cont.*



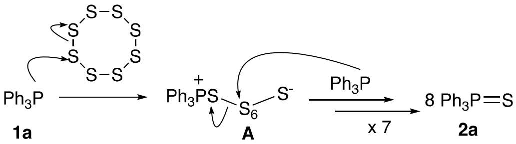
(**d**) (**e**) (**f**)

(**g**)

**Figure 1.** Description of the procedure. (**a**) Commercially available flake triphenylphosphine (2.62 g, 10 mmol); (**b**) Addition of yellow sulfur (320 mg, 10 mmol); (**c**) Addition of $CH_2Cl_2$ (5 mL), t = 0; (**d**) The reaction mixture was shaken vigorously with mechanical shaker; (**e**) Both solid materials disappeared progressively. At t = 30 s, the reaction mixture became nearly homogeneous to yield a pale-yellow solution; (**f**) t = 40 s, triphenylphosphine sulfide precipitated as a white solid; (**g**) The reaction mixture was filtered, the precipitate was washed with MeOH (2 mL × 3) and dried. Yield = 2.59 g (88%).

## 3. Results and Discussion

Mechanistically, the reaction could be initiated by a nucleophilic attack of triphenylphosphine to $S_8$ molecules to provide zwitterion **A** (Scheme 1), as previously proposed by Bartlett and Meguerian [5]. A cascade of seven-time attacks of the other seven molecules of $Ph_3P$ would consume all the polysulfide chain. The first step could be rate determining and depends on the concentration of both starting materials. This suggests that the reaction is best performed under highly concentrated conditions. Since sulfur is not well soluble in common protic polar solvents such as alcohol (methanol or ethanol) or dipolar aprotic solvents (DMF, DMSO), the reaction performed in these solvents did not succeed in the same manner or required longer reaction times.



**Scheme 1.** Proposed reaction mechanism.

The reaction conditions could also be extended to other analogs as exemplified by two derivatives of triphenylphosphines bearing a *para* substituent such as chloro (**1b**) or methoxy (**1c**). In both cases tested, the reactions on a smaller scale (1 mmol) could be conveniently performed in a 7-mL test tube with magnetic stirring and provided the corresponding products **2b**-**2c** in quantitative yields (See Supplementary Material).

## 4. Conclusions

In conclusion, we have developed an efficient method for the synthesis of triphenylphosphine sulfide from triphenylphosphine and elemental sulfur. While the reaction was well studied a long time ago and recently reinvestigated using some state-of-the-art techniques, effort to simplify the reaction conditions by using cheap and readily available laboratory glassware while shortening the reaction time and providing purification is usually neglected, overlooked or even forgotten.

The salient aspects of our developed synthetic procedure are its high atom-efficiency, its short reaction time (<1 min), its room temperature conditions, the involvement of only a very small amount of moderately polar solvents such as halogenated solvents (chloroform, $CH_2Cl_2$) or aromatic hydrocarbon solvents (toluene, xylenes) and its easy purification by simple filtration.

As a matter of fact, the purification step, especially in large-scale production, may be time-consuming, difficult or even impossible using other chromatography techniques than simple washing with solvents. This purification technique is once again demonstrated to be easily achieved. Previously, some organic reactions with elemental sulfur leading to complex scaffolds could be purified by applying the same technique [16–20].

We hope that this procedure will be useful not only for those who work with P=S bond containing compounds but also for organic chemists exploring new and useful chemical behaviors of elemental sulfur.

**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/cleantechnol4020013/s1, File S1: Characterization and copies of $^{1}H$, $^{31}P$ and $^{13}C$ NMR spectra of the products triphenylphosphine sulfides **2a**-**2c**.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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