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► **To cite this version:**

Thanh Binh Nguyen. Convenient Synthesis of Triphenylphosphine Sulfide from Sulfur and Triphenylphosphine. *Clean Technologies*, 2022, 4 (2), pp.234-238. 10.3390/cleantechnol4020013 . hal-03787432

HAL Id: hal-03787432

<https://hal.science/hal-03787432v1>

Submitted on 18 Nov 2022

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1 Communication

2 Convenient Synthesis of Triphenylphosphine 3 Sulfide from Sulfur and Triphenylphosphine

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8 Received: date; Accepted: date; Published: date

9 **Abstract:** Elemental sulfur (S₈) was found to react very rapidly (<1 min) with a stoichiometric
10 amount of triphenylphosphine at rt in sufficient amount of solvent (0.2-0.5 mL of solvent/1 mmol of
11 PPh₃). Compared to the previously described methods, the present procedure constitute excellent
12 access to triphenylphosphine sulfide.

13 **Keywords:** elemental sulfur; triphenylphosphine; triphenylphosphine sulfide; green chemistry
14

15 1. Introduction

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

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

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

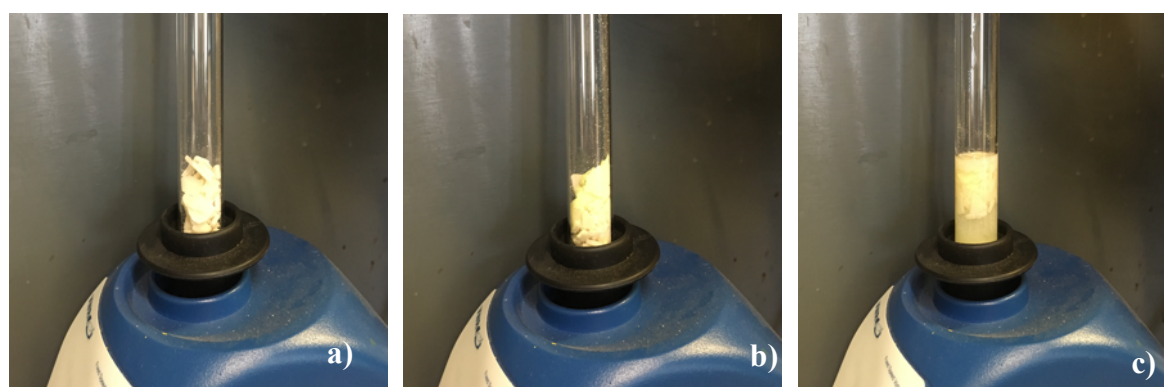
44 In this context, simplification of reaction conditions by lowering the solvent amounts, using
45 standard and inexpensive laboratory glass wares and purifying the obtained products by simple
46 filtration and washing should be an excellent approach to valorize and promote the widespread
47 application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

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

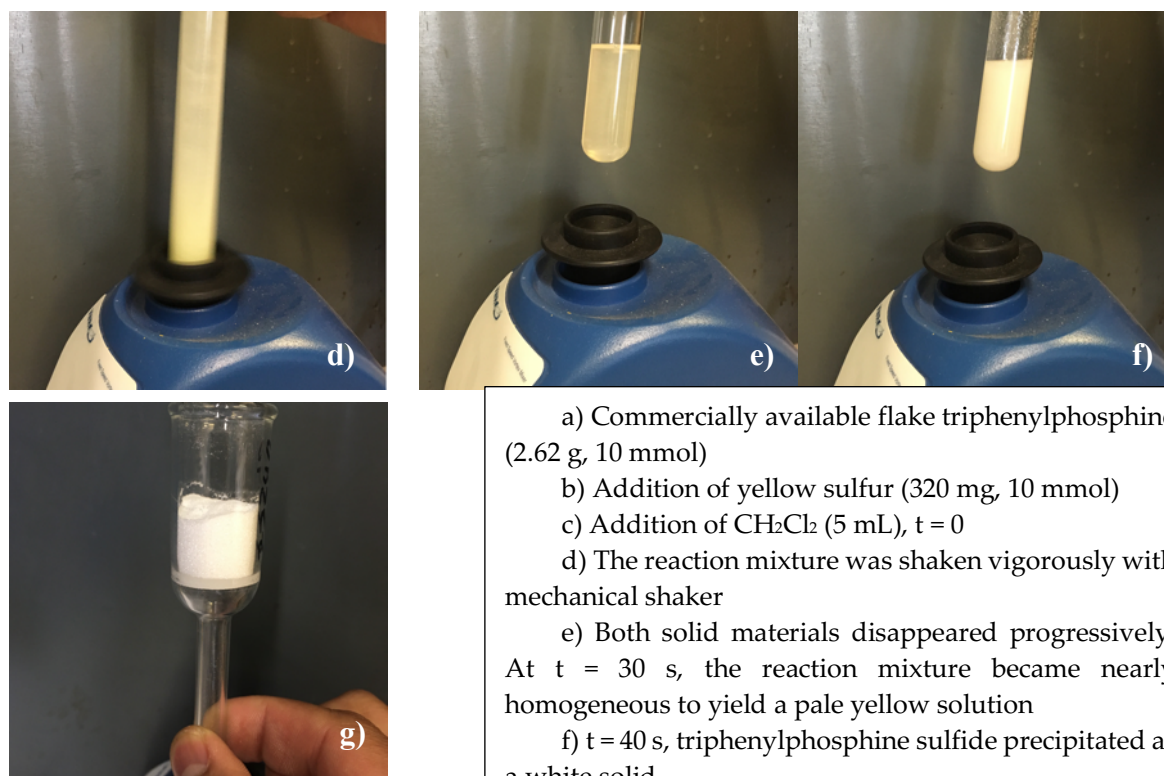
50 During the course of our study on new reactivities of elemental sulfur applied to organic
51 synthesis,^{[10]-[12]} we have noticed that some reactions with this element proceeded very efficiently in
52 highly concentrated media or even in the absence of solvent. When the reactions were performed at
53 high temperature, the reaction media were in general liquid and the stirring was possible without
54 any difficulty.^{[13]-[14]} However, if the reactions were carried out with solid starting materials (including
55 solid sulfur), addition of an inert or weakly interacting solvents could be done to facilitate the stirring.
56 Such solvents should be used in sufficient quantity to avoid excessive dilution, which in turn reduces
57 significantly the reactivity.

58 2. Experiments

59 Our reaction was visualized in Figure 1. The reaction could be performed in a test tube although
60 larger reactors could be used for larger scales (100 mmol). Equimolar amounts (10 mmol) of solid
61 triphenylphosphine (as flakes) **1a** and sulfur were added to a test tube (Figure 1a-b). The solvent (5
62 mL was added) (Figure 1c). We noticed that common laboratory solvent such as CH₂Cl₂, CHCl₃,
63 toluene... were all suitable for this reaction. The reaction tube was shaken vigorously with a vortex
64 mixer. The reaction mixture became rapidly homogeneously with slight increase in temperature
65 (about 40 °C). The solid triphenylphosphine sulfide product was precipitated out after 40 s of shaking
66 as a white crystalline powder. The reaction mixture cooled down to rt was filtered, washed with
67 methanol (2 mL × 3) and dried to afford the product as a white crystalline solid triphenylphosphine
68 sulfide **2a** (yield = 2.59 g, 88%). The filtrate could be concentrated to provide pure product. The purity
69 of the product could be confirmed by ¹H, ³¹P and ¹³C NMR spectra as well as by elemental analysis.
70 Compared to ³¹P NMR of the starting PPh₃ (7.32 ppm in CDCl₃), the chemical shift of the
71 corresponding PPh₃S is significantly different (43.3 ppm). Compared to known methods, ours is
72 highlighted by its high atom-efficiency with short reaction time (< 1 min) under room temperature
73 conditions with a very small amount of moderately polar solvents such as chloroform, CH₂Cl₂,
74 toluene and its easy purification by simple filtration.
75



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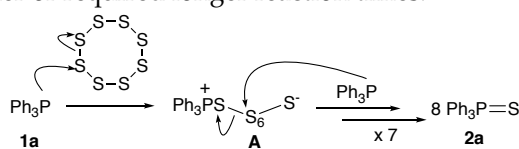


a) Commercially available flake triphenylphosphine (2.62 g, 10 mmol)
 b) Addition of yellow sulfur (320 mg, 10 mmol)
 c) Addition of CH_2Cl_2 (5 mL), $t = 0$
 d) The reaction mixture was shaken vigorously with mechanical shaker
 e) Both solid materials disappeared progressively. At $t = 30$ s, the reaction 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 \times 3) and dried. Yield = 2.59 g (88%).

Figure 1. Description of the procedure

3. Results and Discussion

Mechanistically, the reaction could be initiated by a nucleophilic attack of triphenylphosphine to S_8 molecule to provide zwitterion **A** (Scheme 1) as previously proposed by Bartlett and Meguerian.^[5] A cascade of seven-time attack of 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 solvent 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 be also 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 in 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 Supporting information).

4. Conclusions

In conclusion, we have developed an efficient method for the synthesis of triphenylphosphine sulfide from triphenylphosphine and elemental sulfur. While the reaction is well studied 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 glass wares while shorten the reaction time and purification is usually neglected, overlooked or even forgotten.

102 The salient aspects of our developed synthetic procedure are its high atom-efficiency, its short
103 reaction time (< 1 min), its room temperature conditions, the involvement of only a very small amount
104 of moderately polar solvents such as halogenated solvents (chloroform, CH₂Cl₂) or aromatic
105 hydrocarbon solvents (toluene, xylenes) and its easy purification by simple filtration.

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

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

114 **Supplementary Materials:** The following are available online at www.mdpi.com/xxx/s1, Characterization and
115 copies of ¹H, ³¹P and ¹³C NMR spectra of the products triphenylphosphine sulfides **2a-2c**.

116 **Author Contributions:** T.B.N.

117 **Funding:** No funding available for this research.

118 **Conflicts of Interest:** The authors declare no conflict of interest. The funders had no role in the design of the
119 study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to
120 publish the results.

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