Registry No.—**1**, 42245-85-2; **2a**, 62016-00-6; **2b**, 62016-12-0; **3**, 123-54-6; **4**, 141-97-9; **5**, 62016-01-7; **6a**, 62016-02-8; **6a** di-*N*-oxide, 62016-03-9; **6b**, 62016-04-0; **6b** di-*N*-oxide, 62016-05-1; **7**, 62016-06-2; **8**, 62016-07-3; **9**, 62016-08-4; **10**, 62016-09-5; **11**, 62016-10-8; **12**, 62016-11-9.

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Friedel–Crafts Type Preparation of Triphenylphosphine[1a]

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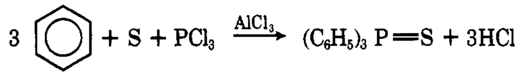
Triarylphosphines, of which triphenylphosphine is the most widely employed member, are generally prepared through organometallic precursors, such as the reaction of phenylmagnesium halides or phenyllithium with phosphorus trihalides.[2]

We now wish to describe a convenient, simple Friedel–Crafts type preparation of triphenylphosphine. The reaction of phosphorus trichloride with benzene under Friedel–Crafts conditions has been widely studied, but only phenyldichlorophosphine and diphenylchlorophosphine have been obtained as products, and under no conditions could the reaction be directed to yield triphenylphosphine (probably owing to an unfavorable disproportionation equilibrium).[3] Phosphorus oxychloride also fails to give triphenylphosphine oxide. Phosphorus sulfochloride ($PSCl_3$), on the other hand, yields triphenylphosphine sulfide upon reaction with benzene and excess aluminum chloride.[4] As triphenylphosphine sulfide offers the possibility of being desulfurized (reduced) to give triphenylphosphine this reaction path offered a good possibility to the simplified Friedel–Crafts type preparation of triphenylphosphine without recourse to organometallic reagents.

We have now found a greatly simplified method to prepare triphenylphosphine sulfide in 71% yield directly from benzene by reacting it with sulfur, phosphorus trichloride, and aluminum chloride. Various methods can be applied for the desulfurization of triphenylphosphine sulfide.[5-7]



We have found the preferred method to be the reduction with sodium naphthanide,[7] giving 89% yield, although desulfurization with iron filings (80%) is also convenient. The reaction with Raney nickel,[6] however, gave considerably lower (15%) yields.

$$Ph_3P = S \underset{-Na_2S}{\xrightarrow{\text{Na(naphth), THF}}} Ph_3P$$

Experimental Section

Preparation of Triphenylphosphine. Into a 500-mL round-bottom flask fitted with a reflux condenser and drying tube under nitrogen purge were added $AlCl_3$ (64 g, 0.48 mol), PCl_3 (16.55 g, 0.12 mol), S (3.85 g, 0.12 mol), and excess benzene (150 mL), to serve both as a reactant and solvent. The solution was stirred magnetically while being heated to reflux for a period of 8 h. Thereafter, to the cooled solution 125 mL of ice water was added. The organic layers were separated and the water layer extracted three times with benzene. The combined benzene solution was dried over Na_2SO_4, and after evaporating solvent left a yellow solid. Recrystallization from acetone–water yielded 25 g (71%) of pure triphenylphosphine sulfide, $Ph_3P{=}S$, mp 158–160 °C. Desulfurization of triphenylphosphine sulfide can be carried out by method A or B.

A. With Sodium Naphthanide.[7] To a 50-mL flask fitted with a reflux condenser and nitrogen purge were charged 25 mL of THF, 6.1 g of naphthalene (0.05 mol), and 1.1 g of Na (0.05 mol). To the deep green solution was added slowly with stirring 4.6 g of triphenylphosphine (0.02 mol). After the addition was complete, the solution was refluxed for 4 h. The cooled solution was quenched with water. Steam distillation followed by extraction with ether and recrystallization from ethanol gave 3.69 (89%) of pure triphenylphosphine, mp 79–81 °C.

B. With Iron Filings.[4] To a 250-mL round-bottom flask fitted with reflux condenser and thermometer and under nitrogen purge were added 25 g of triphenylphosphine sulfide (0.1 mol) and 0.1 g of Fe filings (0.15 mol). The reaction mixture was heated to 370 °C for 2 h. After cooling the crude product was dissolved in ethanol and filtered, and after evaporation of solvent recrystallized from fresh ethanol to give 18.0 g (8) of triphenylphosphine, mp 79–81 °C.

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Registry No.—Triphenylphosphine, 603-35-0; benzene, 71-43-2; PCl_3, 7719-12-2; triphenylphosphine sulfide, 3878-45-3; sulfur, 7704-34-9.

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