

The Reaction of $\text{Ph}_3\text{P}^+\text{SR}$ with Thiols: A Simple, Efficient Synthesis of Unsymmetrical Disulphides

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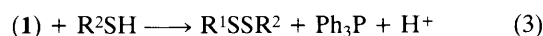
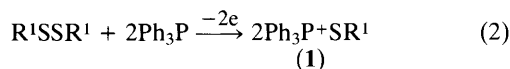
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Reaction of $\text{Ph}_3\text{P}^+\text{SRCIO}_4^-$, prepared electrochemically from RSSR and Ph_3P , with thiols in n-hexane at room temperature gave unsymmetrical disulphides in excellent yields with recovery of Ph_3P .

Various methods for synthesizing unsymmetrical disulphides have been developed,^{1,2} and the difficulties in the synthesis are well documented. Among the conceivable stoichiometries for the disulphide formation, equation (1) is one of the



most attractive routes. We have formally effected equation (1) by the reaction of electrochemically prepared alkylthio- and arylthio-triphenylphosphonium ions^{3†} (**1**) with thiols [equations (2) and (3)]. Although the formation of phosphonium



ions of type (**1**) has been postulated in the reaction of disulphides with triphenylphosphine, their subsequent reaction with thiolate ions has been shown to give sulphides and triphenylphosphine sulphide.^{1,4}

A typical preparation of an unsymmetrical disulphide is as follows. A mixture of $\text{Ph}_3\text{P}^+\text{SMcClO}_4^-$ (29 mmol), c-C₆H₁₁SH (29 mmol), and Et₃N (30 mmol) in n-hexane (75 ml) was stirred for 7 h at room temperature. The crystals

† The preparation of (**1**) reported in ref. 3 involves a difficult controlled-potential electrolysis in a two-compartment cell with NaClO₄ as supporting electrolyte. However, constant current electrolysis in an open beaker with HClO₄ instead of NaClO₄ has proved much easier and effective, and a large amount of (**1**) (>20 g) can be readily prepared in a single run.

Table 1. Reaction of $\text{Ph}_3\text{P}^+\text{SR}^1\text{ClO}_4^-$ with R^2SH .^a

R ¹	R ²	Reaction time/h	Yield of R ¹ SSR ² /%
Me	PhCH ₂	2	90
Me	Furfuryl	2	87
Me	<i>p</i> -MeC ₆ H ₄	0.5	95
Me	Bu ⁿ	4	100
Me	Bu ^t	7	77
Me	c-C ₆ H ₁₁	6	76
PhCH ₂	Bu ⁿ	3	92
Ph	Bu ⁿ	3	90

^a In n-hexane (5 ml) containing Et₃N (1.0 mmol) at room temperature: (**1**), 1.0 mmol; R²SH, 1.0 mmol; c-C₆H₁₁ = cyclohexyl. ^b Determined by g.l.c. on the reaction mixture without removing Ph₃P. The disulphides were characterized by elemental analysis, ¹H n.m.r., and mass spectrometry.

(Et₃NHClO₄) deposited were filtered off, and the filtrate was washed with water and dried (MgSO₄). The resulting solution, after being concentrated *in vacuo* to ca. 20 ml, was cooled to -20 °C. The Ph₃P deposited was filtered off, and c-C₆H₁₁SSMe was obtained by vacuum distillation (70%). Results of other smaller scale preparations are summarized in Table 1. Formation of R¹SR² was not detected at all, and the yields of other possible products, R¹SSR¹ and R²SSR², were <1%.

At present, it is not clear why the reaction of (**1**) with thiols proceeds as observed. However, when the reaction of (**1**, R¹ = Me) with PhCH₂SH (see Table 1) was carried out in tetrahydrofuran (THF), THF-H₂O (1 : 1, v/v), and methanol, the yield of PhCH₂SSMe decreased to 86, 74, and 38%,

respectively; in methanol, considerable amounts of $(\text{PhCH}_2\text{S})_2$ and $(\text{MeS})_2$ were formed. These findings suggest that the instability of the ion pair, $[\text{Ph}_3\text{PSR}^1]^+\text{R}^2\text{S}^-$, might be the driving force of the reaction. Such an ion pair has been suggested as the intermediate in the reaction of Ph_3P and a disulphide.¹

The present method is versatile and has advantages over the other methods reported; the phosphonium ions (**1**) are easy to prepare and stable, the route to the unsymmetrical disulphides requires only simple and mild conditions, and, particularly, Ph_3P is recovered and can be used repeatedly to prepare (**1**).

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