The Reduction of Aryl Disulfides with Triphenylphosphine and Water

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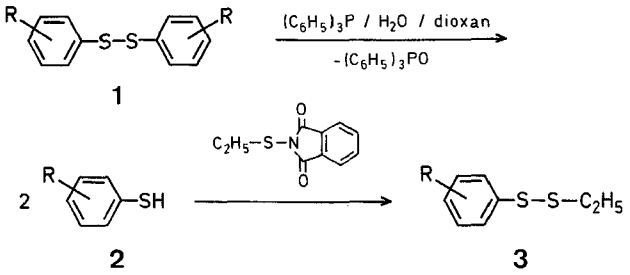
We wish to report that treatment of symmetrical aryl disulfides with triphenylphosphine in aqueous dioxane is a good method for the preparation of benzenethiols (**1**→**2**), and is often more convenient than other existing methods[1]. The benzenethiol product is easily separated from triphenylphosphine oxide by either extraction with aqueous base or by distillation. Triphenylphosphine reduction appears particularly useful for the *in situ* preparation of readily oxidizable benzenethiols, since the triphenylphosphine oxide by-product often does not interfere with subsequent reactions.



For example using a modification of the recently reported sulfenamide disulfide synthesis[2], unsymmetrical ethylaryl disulfides have been prepared in high yields from the corresponding symmetrical aryl disulfides without isolation of intermediates (**1**→**2**→**3**). Symmetrical aryl disulfides are convenient starting materials for the preparation of **3** since they are often more readily available, and are easier to purify and to store than the corresponding benzenethiols. In fact we have found *in situ* reduction by triphenylphosphine to be an excellent method for preparation of benzenethiol samples for accurate pKa and spectral measurements[3].

The reduction of an aryl disulfide by triphenylphosphine and water was first reported in 1935 by Schönberg, who obtained a 30% yield of thiophenol (isolated as the benzoate)

when phenyl disulfide was refluxed with one equivalent of triphenylphosphine in "wet" benzene[4]. In dioxane/water the reaction appears to be general for a wide variety of *o*-, *m*-, and *p*-substituted aryl disulfides. The rate of reduction is dependent on the substitutent R, being faster for electron withdrawing R groups, and the overall reaction is susceptible to both acid and base catalysis[3]. These and other aspects of the mechanism of this novel reduction reaction will be discussed in a future publication.

General Reduction Procedure; Benzenethiol (2a):
A solution of phenyl disulfide (**1a**, 4.10 g, 0.019 mol) and triphenylphospline (5.24 g, 0.020 mol) in a mixture of dioxane (60 ml) and water (15 ml), containing two drops of concentrated hydrochloric acid, was stirred at 40° under nitrogen for 20 min (until **1a** was no longer detectable by G.L.C.). The solvent was removed in vacuo and the residue taken up in ether and dried with magnesium sulfate. Concentration and short-path distillation afforded **2a**; yield 2.8 g (68%); b.p. 164–168°. The uncatalyzed reduction occurs more slowly: 3 hr half-life at 100°.

Ethyl 3-Nitrophenyl Disulfide (3d):
A solution of 3-nitrophenyl disulfide (**1d**; 3.08 g, 0.010 mol) in a mixture of dioxane (40 ml) and water (10 ml) was treated with solid triphenylphosphine (2.62 g, 0.010 mol). After stirring under nitrogen for 10 min, the solvent was then evaporated in vacuo (35–50°), and a solution of *N*-(ethylthio)phthalimide[5] (4.76 g, 0.020 mol) in benzene (25 ml) was added. Phthalimide soon began to precipitate and this mixture was stirred at reflux under nitrogen for 12 hr. After cooling to 5°, phthalimide and triphenylphosphine oxide were removed by filtration, the filtrate concentrated in vacuo, and the residue distilled to afford **3d**; yield 3.38 g (77%); b.p. 104–106°/0.04 torr.

$C_8H_9NO_2S$	calc.	C 44.63	H 4.21	N 6.51	S 29.79
(215.3)	found	44.38	4.32	6.33	30.05

I.R. (neat): ν_{max} = 1520, 1340, 803, 730 cm^{-1}.

^{1}H-N.M.R. (CCl_4): δ = 8.53–7.28 (m, 4H), 2.81 (q, 2H, J = 7 Hz), 1.32 ppm (t, 3H, J = 7 Hz).

Table. Benzene Thiols and Ethyl Aryl Disulfides from Symmetrical Aryl Disulfides

	R	Benzene Thiol (**2**) Conditions	Yield (%)	Ethylaryl Disulfide (**3**) b.p.	Yield (%)
a	H	40° (20 min)[b]	69	66°/0.1 torr	83
b	2-$COOCH_3$	40° (60 min)[b]	70	[c]	73
c	4-NO_2	40° (10 min)	77	136°/0.2 torr	78
d	3-NO_2	40° (10 min)	81	105°/0.04 tor	77

[a] All new compounds showed I.R. and N.M.R. spectra consistent with the indicated structures and correct combustion analyses. Except where indicated the products were purified by distillation.
[b] A catalytic amount of concentrated hydrochloric acid was added.
[c] Purified by chromatography on Silica Gel.

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