

A New One-step Synthesis of Sulphenamides from Alkyl and Aryl Disulphides

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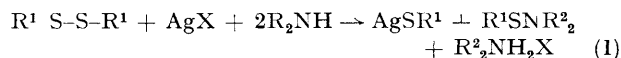
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Summary The reaction of an alkyl or aryl disulphide with silver(I) ion and alkyl or aryl amines gives good yields of the corresponding sulphenamides.

THERE are few general synthetic methods for the preparation of alkyl and aryl sulphenamides. The procedure most widely used involves the condensation of an alkyl¹ or

aryl² sulphenyl chloride with an amine, less successful methods involve the reaction of metal mercaptides with chloroamines,³ oxidative condensation of thiols with amines⁴ and the displacement of amines on alkanesulphenylthiocyanates⁵ and on alkyl esters of thiosulphonic S-acids.⁶

We report a ready one-step synthesis of sulphenamides from aryl or alkyl disulphides according to equation (1)



R^1 and R^2 = alkyl or aryl

$X = NO_3$ for aryl derivatives and AcO for alkyl derivatives

For the preparation of sulphenamides derived from aromatic disulphides the best procedure was the following. To a solution of silver nitrate (1 equiv) in methanol the disulphide (1 equiv) and then the amine (2 equiv) were added. The mixture was stirred at room temperature for 15 h and then filtered. Evaporation gave a residue which

than those *via* the corresponding sulphenyl chloride method (84 and 77% *vs* 40 and 59%, respectively).

The sulphenamides derived from aliphatic disulphides were unstable in the presence of silver nitrate-methanol, so the following procedure was devised. To a solution of disulphide (1 equiv) in ethyl acetate was added silver acetate (2 equiv), and excess of amine (8 equiv), and the mixture was stirred at room temperature for 22 h. The work-up procedure was identical to that for the aromatic systems. The results are summarized in the Table.

Recently, one of us reported¹¹ that disulphides are readily cleaved by methanesulphinic acid in the presence of silver nitrate to produce thiosulphonate S-esters in high yield. We feel that both this reaction and the sulphenamide reaction are members of a mechanistic class, recently described by Kice,¹² in which co-operative assistance by an electrophile and a nucleophile results in sulphur-sulphur bond cleavage. The present reaction would thus be initiated by formation of a complex between Ag^+ and a non-bonding electron pair on one sulphur atom of the $R-S-S-R$ system, followed by nucleophilic displacement on the adjacent sulphur atom by amine.

TABLE

Preparation of sulphenamides from aryl and alkyl disulphides

Disulphide	Amine	Reaction time (h)	Sulphenamide	Properties
Bis (2 benzothiazolyl) disulphide	$PhNH_2$	15 0	2-Benzothiazolesulphenamide (77%)	Ref 8
	Piperidine	15 0	N-Piperidyl-2-benzothiazolesulphenamide (90%)	Ref 9
	Pr^iNH_2	15 0	N-Isopropyl 2 benzothiazolesulphenamide (90%)	Ref 10
$(m-NO_2 C_6H_4 S)_2$	$PhNH_2$	15 0	<i>m</i> -Nitrobenzenesulphenamide (82%)	Ref 7
	$EtNH_2$	15 0	N-Ethyl <i>m</i> -nitrobenzenesulphenamide (94%)	B p 111° at 0.05 mmHg
$(Ph CH_2 S)_2$	Et_2NH	22 0	NN-Diethylbenzenesulphenamide (58%)	B p 79–82° at 0.6 mmHg
	Pr^iNH_2	22 0	NN-Diisopropylbenzenesulphenamide (50%)	B p 88° at 0.7 mmHg
$(Ph \cdot S)_2$	Pr^iNH_2	22 0	N-Isopropylbenzenesulphenamide (73%)	B p 61–61.5 at 0.4 mmHg
	Pr^i_2NH	22 0	NN-Diisopropylbenzenesulphenamide (76%)	B p 71.5–73° at 0.35 mmHg

Satisfactory elemental analyses, i.r. spectra and ¹H n.m.r. spectra were obtained for all new compounds.

was dissolved in ether, washed with water, and dried. After removal of ether the sulphenamide was purified by chromatography, distillation or crystallization. The yields of 3-nitrobenzenesulphenamide⁷ and 2-benzothiazolesulphenamide⁸ *via* the silver nitrate method were much better

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