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LEAD DITHIOLATES: THEIR USE IN THE SYNTHESIS OF CYCLIC DISULPHIDES

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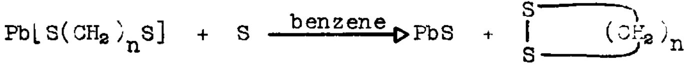
There has been considerable interest in the synthesis and chemistry of cyclic disulphides due to the importance of compounds such as lipoic acid. We therefore wish to report a general and convenient synthesis of cyclic disulphides in high yields and under mild conditions.

Lead dithiolates, obtained by the almost instantaneous reaction of a dithiol and an aqueous solution of lead acetate in near quantitative yields, react readily with sulphur to give lead sulphide and the corresponding cyclic disulphide (equation 1.).



(n = 3,4,5 and 6)

The reactions were carried out in approximately 0.1 molar solution of benzene. After mixing the reactants for a few minutes the yellow mixture turned black and after thirty minutes lead sulphide was filtered off and on removal of the solvent the cyclic disulphide was obtained in high yield. This method was previously attempted by Field[1] but was found to be successful only in the preparation of dithiacyclohexane. Some idea of the generality of this method of cyclic disulphides can be seen by the examples given in table I. We have been able to prepare a whole series of cyclic disulphides without the vast dilution required by the dithiol oxidation, described by Schoberl[2], using ferric chloride. Selenium, Chlorine and iodine, table II, all react with lead butanedithiolate to give high yields of dithiacyclohexane. The mass spectrum of the product formed by the selenium oxidation showed that selenium was not involved in the disulphide product. One specific application of this synthesis could be the preparation of derivatives of 1,2-dithiacyclopentane. For example 1,2-dithia-4-

hydroxy-pentane, which was stable towards distillation, was obtained in high yields although polymerised on standing after a few days.

References

1. L. Field and R. B. Barbee, J. Org. Chem., 1963, 34, 157.
2. A. Schoberl and H. Grafje, Ann, 1958, 614, 66.

Table I

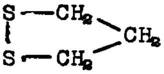
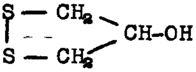
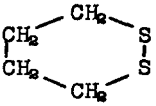
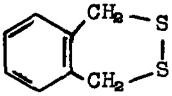
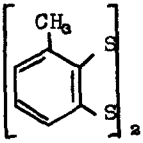
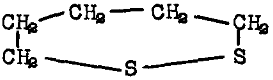
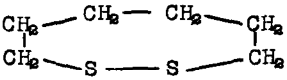
Cyclic Disulphide	% Yield
	90
	79
	96
	88
	74
	82
	86

Table II

Effect of various oxidants on the formation of 1,2-dithiacyclohexane

Oxidant (X)	% Yield
S	96
Se	98
Cl_2	87
I_2	73