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REDUCTIVE DESULFURIZATION OF THIOLSULFONATES: A NOVEL SYNTHESIS OF ALICYCLIC SULFINATE ESTERS[1]

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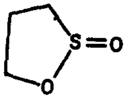
While cyclic sulfonic acid esters, sultones, have been studied extensively[3], the cyclic esters of the lower oxidation state sulfur acids, sulfinate esters, have remained relatively unknown. To date, only six alicyclic sulfinate esters have been reported[4]; two via thermal isomerization of thietane dioxides at 300-400°[4a], while more recently, two esters have been synthesized by controlled chlorine oxidation of the corresponding mercapto-alcohols[4a], and two by the action of thionyl chloride on 3-butene-1-ols[4b]. In all cases, the esters prepared were highly substituted; the parent members of these heterocycles are unknown.

We wish to report a novel synthesis of these parent compounds, 1,2-oxathiolane-2-oxide (1) and 1,2-oxathian-2-oxide (2). We have found



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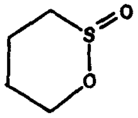

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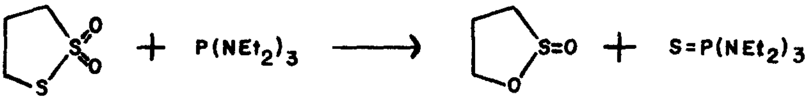
that alicyclic thiolsulfonates, on treatment with tris(diethylamino)-phosphine (3), a highly reactive trivalent phosphorus compound[5], undergoes a reductive desulfurization affording alicyclic sulfinate esters in high yield.

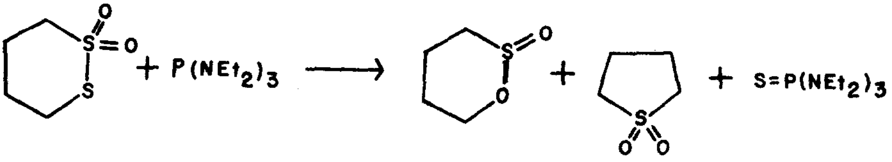
Addition of the aminophosphine 3 to a benzene solution of the thiolsulfonate, 1,2-dithiolan-1,1-dioxide (4) effects an exothermic



4 3 1

reaction which on chromatographic workup provides the desired 1,2-oxathiolan-2-oxide 1 in 92% yield.

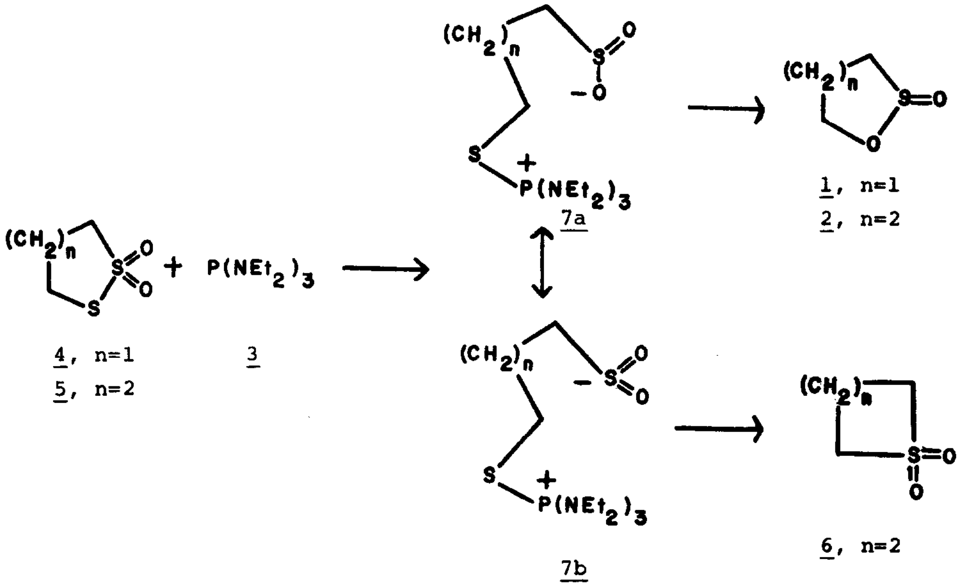
Similarly, the reaction of 1,2-dithian-1,1-dioxide (5)[6] with the phosphine 3 in benzene gives a mixture consisting of 10% tetrahydrothiophene-1,1-dioxide (6) and 90% 1,2-oxathian-2-oxide 2. This alicyclic sulfinate ester was subsequently isolated in 62% yield[7].



5 3 2 6

Proof of structure of sulfinates 1 and 2 obtains from their ready oxidation by permanganate to the corresponding sultones. The presence of a strong infrared band at 1120 cm^{-1} (-O-SO-) further confirmed the presence of a sulfinate ester grouping. In addition, N.M.R. and mass spectra were consistent with the proposed structures[8].

The formation of both sulfone 6 and sulfinate 2 during desulfurization of 5 would indicate that the reaction proceeds



via an ionic intermediate of the type 7 which, because of the ambident nature of the sulfinate anion[9], may cyclize through either sulfur or oxygen. The preferential cyclization through oxygen (resonance contributor 7a) is in agreement with the known Arbuzov rearrangement of thiolsulfonates with trialkyl phosphites[10]. The formation of a sulfone from thiolsulfonate 5 but not from 4 may reflect the influence of ring size on the course of reaction.

Acknowledgements:

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References:

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5. This phosphine readily desulfurizes a wide variety of disulfides; see ref. 1.
6. Thiosulfonates 4 and 5 were prepared by oxidation of the corresponding dimercaptans.
7. Satisfactory elemental analyses were obtained for compounds 1, bp 48°(0.2mm); 2, bp 60°(0.6mm); 4, mp 24.5-26°; 5, mp 54-55°.
8. A study of the NMR and mass spectra of these and similar compounds is underway and will be reported separately.
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