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A NEW SYNTHESIS OF 2-OXATHIOLONE

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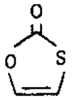
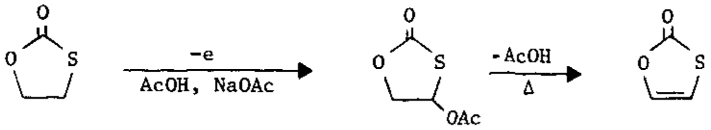
Abstract —— A convenient synthesis of 2-oxathiolone starting from ethylene monothiocarbonate is described.

2-Oxathiolone **A** is structurally related to vinylene carbonate. It is a potential new monomer for producing poly(1-mercapto-2-hydroxyethylene). In addition, it is also a potential component for thermal [4+2] or photo [2+2] cycloaddition. The resulting cycloaddition adducts can be hydrolyzed to cis-β-mercaptoalcohols which are not accessible by conventional methods. Substituted 2-oxathiolones have been prepared by heating an appropriate 1-thiocyanato-3-buten-2-one in the presence of an acid,[1] by heating a dialkyl ketone with carbonylchlorosulfenyl chloride[2] or by cyclization of an α,α'-dibromoketone with $EtOCS_2K$[3]. 4,5-Unsubstituted 2-oxathiolone can be prepared by dehydrogenation of ethylene thiocarbonate with N-bromosuccinimide.[4] In this communication, we will describe an electrochemical approach to 2-oxathiolone **A**.



A

The anodic oxidation of sulfides in acetic acid has been investigated by Nokami et al. and shown to give mainly α-acetoxy sulfides.[5] We have found that the anodic oxidation of ethylene monothiocarbonate in acetic acid using sodium acetate as a supporting electrolyte yields 4-acetoxyethylene monothiocarbonate. The subsequent pyrolysis affords 2-oxathiolone in 40-50% overall yield from ethylene monothiocarbonate. A typical reaction carried out was



as follows. Into a 40 ml undivided electrolysis cell fitted with two platinum (2 x 2 cm^2) electrodes were placed 5.2 g (0.05 mole) of ethylene monothiocarbonate, 0.15 g (0.018 mole) of sodium acetate as a supporting electrolyte and 30 ml of acetic acid as a solvent. The mixture was electrolyzed without cooling by passing a constant current (0.5A) through the cell. After two Faradays/mol of electricity had passed, acetic acid was removed under reduced pressure. The residue was washed with aqueous sodium bicarbonate and extracted with ether. After removal of the ether, the mixture was distilled (120-130°C, 10 mm Hg) to give 4-acetoxyethylene monothiocarbonate[6] in >90% yield. A mixture of 4-acetoxyethylene monothiocarbonate (2.0 g) and a catalytic amount of sodium acetate were placed into a 25 ml round bottom flask fitted with a distillation head and heated with stirring to 200°C. After removal of the acetic acid, 2-oxathiolone was isolated in >50% yield by distillation. 2-Oxathiolone: bp 190-200°C [lit.[4] 70-72°C/12 mm Hg], IR (neat) 1800 (C=O), 1510 (C=C), ^{1}Hnmr ($CDCl_3$) δ6.30 (d, 1H), 6.85 (d, 1H). Anal. Calcd for $C_3H_2O_2S$: C, 35.28; H, 1.97; S, 31.40. Found: C, 35.11; H, 2.01; S, 31.62.

REFERENCES AND NOTES

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6. ^{1}Hnmr ($CDCl_3$) δ2.14 (s, 3H), 4.56 (d, 2H), 6.30 (dd, 1H).

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