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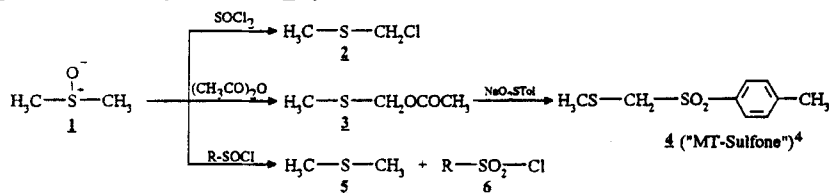
## THE SULFINATE-SULFONE PUMMERER REARRANGEMENT

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**Abstract:**  $\alpha$ -CH acidic sulfoxides with additional electron-withdrawing substitution at C- $\alpha$  afford generation of  $\alpha$  sulfonyl thioethers during reaction with sulfinyl chlorides. Some reaction details as well as a mechanistic proposal are presented.

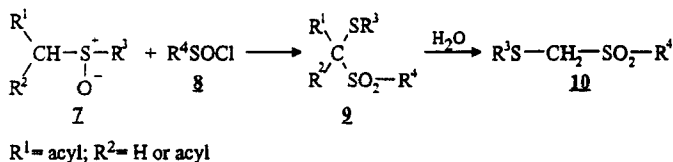
### Introduction

The PUMMERER rearrangement is an acid catalyzed intramolecular redox reaction of CH acidic sulfoxides which leads to reduction at sulfur and to oxidation of  $\alpha$  carbon<sup>1</sup>. A suchlike formed OH-group can be easily replaced by other nucleophilic groups. Thus, conversion of DMSO (**1**) i.e. with acyl chlorides leads to acyloxy sulfonium chlorides which are in equilibrium with chloro sulfonium carboxylates presumably via tetravalent sulfur intermediates<sup>2</sup>. Since on the one hand conversion of DMSO with thionyl chloride yields directly chloromethyl methyl sulfide<sup>3</sup> (**2**), and MT-sulfone **4** is easily available from DMSO, acetic acid anhydride and sodium 4-toluene sulfinate<sup>4</sup> via Pummerer reaction, sulfinyl chlorides on the other hand are oxygenated to sulfonyl chlorides **6** by sulfoxides<sup>5</sup>:

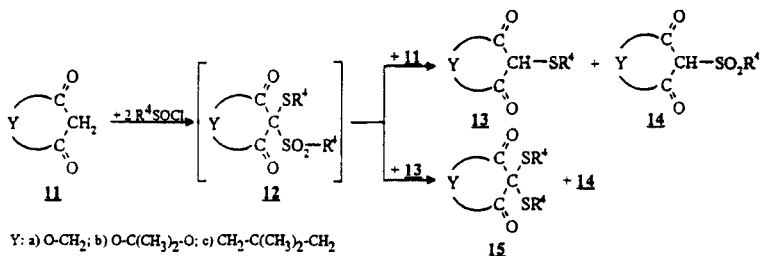


### Results

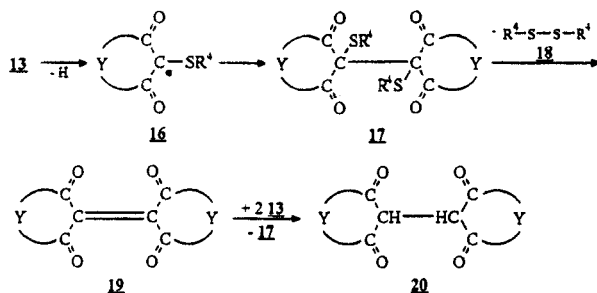
Additional enhancement of sulfoxide  $\alpha$ -CH acidity by electron withdrawing groups rendered possible sulfone formation via sulfinate-sulfone Pummerer rearrangement<sup>6</sup>:



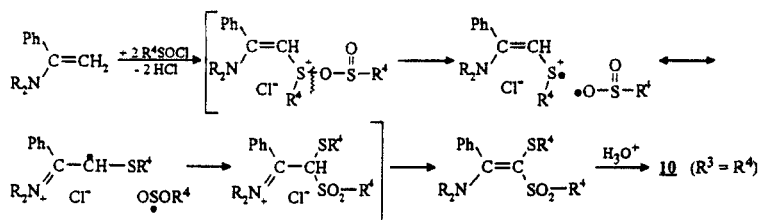
Because of high CH acidity of open-chain 1,3-dicarbonyl compounds application of the aforementioned scheme by use of two mols of sulfinyl chloride **8** yields the corresponding  $\alpha$  sulfonyl thioethers **10**<sup>6,7</sup>. This reaction sequence, however, fails with particularly strong acidic cyclic 1,3-dicarbonyl compounds **11** because their bis-sulfur substituted derivatives **12** represent very efficient sulfonylating agents which attack all suitable nucleophiles present in the reaction mixture<sup>8</sup>:



Additionally, intermediacy of **13** gives rise to formation of capto-dative substituted radicals **16** which dimerize to give dimers **17** and subsequent products (**18-20**):



The related geminal  $\beta$ -dithiofunctionalization of  $\alpha$ -morpholino styrene<sup>9</sup> is of particular importance for mechanistic interpretation of this type of Pummerer rearrangement because it suggests sulfonyl radical migration within an radical cation-radical-pair rather than sulfinate formation:



In these cases a one-pot procedure affords directly i.e. MT-sulfone.

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