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Rearrangements in Spiro- λ^4 -sulfane Chemistry

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The reactions of possible spiro- λ^4 -sulfane precursor diaryl sulfoxides with dehydrating agents have been studied resulting in the formation of cyclic anhydride, spiro- λ^4 -sulfane, cyclic sulfonium-ylide, lactam-sulfoxide, cyclic sulfonimide and cyclic sulfilimine type of intermediates or products. The structures of the intermediates or products depend on the functional groups attached to the aryl rings at *ortho* positions and on the reaction conditions applied.

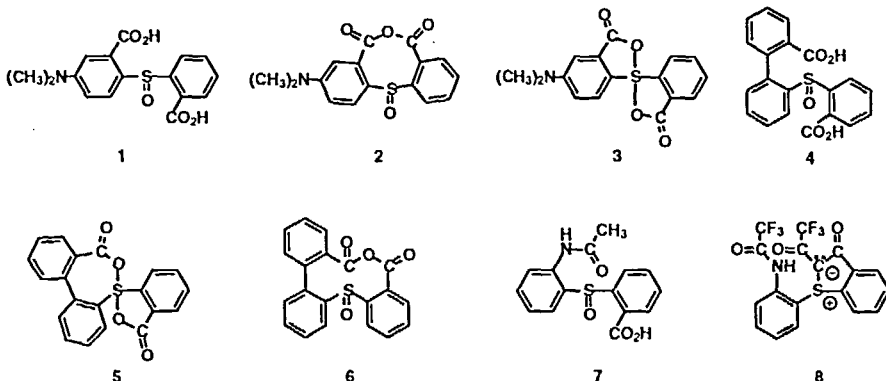
Key words: sulfoxide, spiro- λ^4 -sulfane, cyclic anhydride, cyclic sulfonium-ylide, lactam-sulfoxide, cyclic sulfonimide, cyclic sulfilimine.

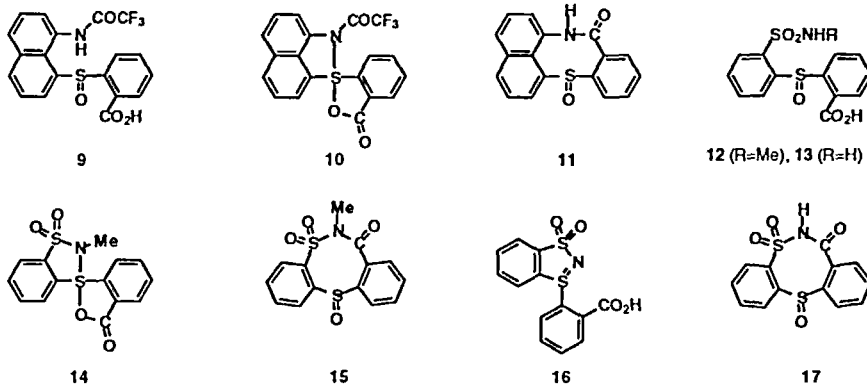
INTRODUCTION

As a part of our program designed to study the reactions involving λ^4 -sulfanes as intermediates or products we have prepared possible spiro- λ^4 -sulfane precursor diarylsulfoxides with carboxy-, N-acylamino-, N-methylsulfonamido- and sulfonamido groups and investigated their reactions with dehydrating agents (e.g. DCC, acid anhydrides). By the isolation of the intermediates or products we have found novel reactions which might be important in the spiro- λ^4 -sulfane chemistry.

RESULTS

Starting sulfoxides, intermediates and products:





The dehydration of sulfoxide 1 with DCC yielded the isolable cyclic anhydride 2, which could be transformed into the diaryldiacetoxy- λ^4 -sulfane 3 by short heating in 1,2-dichloro-ethane solvent.¹

When sulfoxide 4 was treated with acetic anhydride in pyridine after heating for a short time at 100 °C a mixture of the spiro- λ^4 -sulfane 5 and cyclic anhydride 6 could be isolated.^{2,3}

The diarylsulfoxide 7 could be converted to acyl-stabilized cyclic sulfonium-ylide 8 by heating with trifluoroacetic anhydride in DMF.⁴

The treatment of diarylsulfoxide 9 with trifluoroacetic anhydride gave the spiro- λ^4 -sulfane 10; the heating of this reaction mixture followed by addition of water resulted in the formation of lactame sulfoxide 11.^{5,6}

From the reaction mixture of sulfoxide 12 and acetic anhydride at room temperature the spiro- λ^4 -sulfane 14 crystallized out immediately, when this mixture was refluxed for 3 h the cyclic sulfonimide 15 could be isolated exclusively.⁷

The treatment of sulfoxide 13 with acetic anhydride in pyridine at 100 °C for 3 h gave the cyclic sulfilimine 16. The cyclic sulfonimide 17 also can be transformed into 16 under these conditions.⁷

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