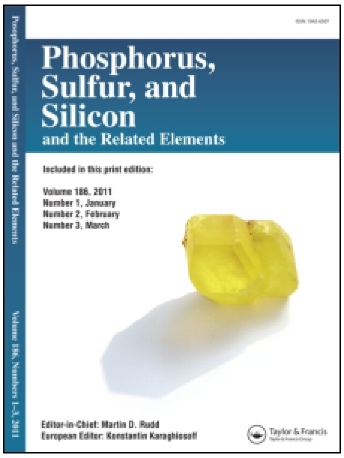

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Rearrangements in Spiro-λ^4-sulfane Chemistry

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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.

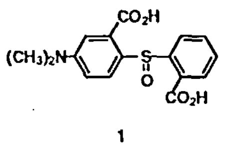
Key words: sulfoxide, spiro-λ^4-sulfane, cyclic anhydride, cyclic sulfonium-ylide, lactam-sulfoxide, cyclic sulfonimide, cyclic sulfilimine.

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: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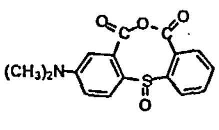
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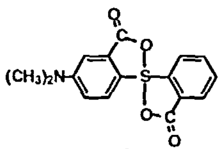
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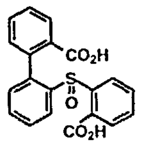
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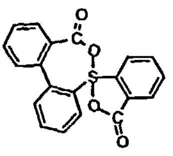
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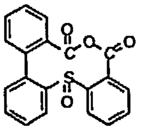
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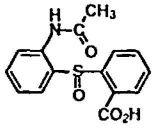
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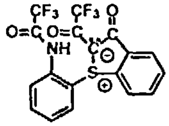
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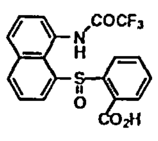

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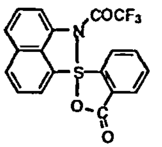

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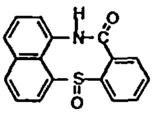

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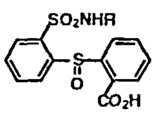
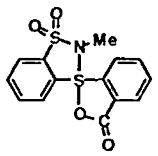


12 (R=Me), 13 (R=H)



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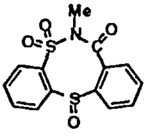

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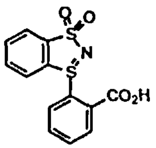

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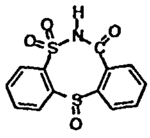

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The dehydration of sulfoxide 1 with DCC yielded the isolable cyclic anhydride 2, which could be transformed into the diaryldiacyloxy-λ^4-sulfane 3 by short heating in 1.2-dichloro-ethane solvent.[1]

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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