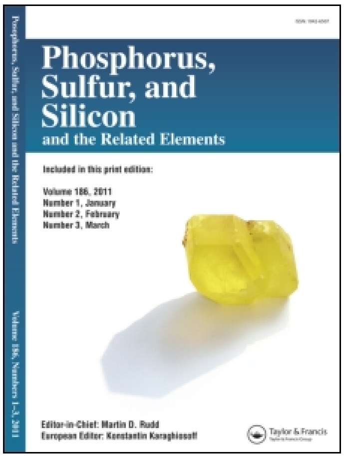

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# Chemistry and Structure of Thiophenium S,C-Ylides

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# CHEMISTRY AND STRUCTURE OF THIOPHENIUM S,C-YLIDES

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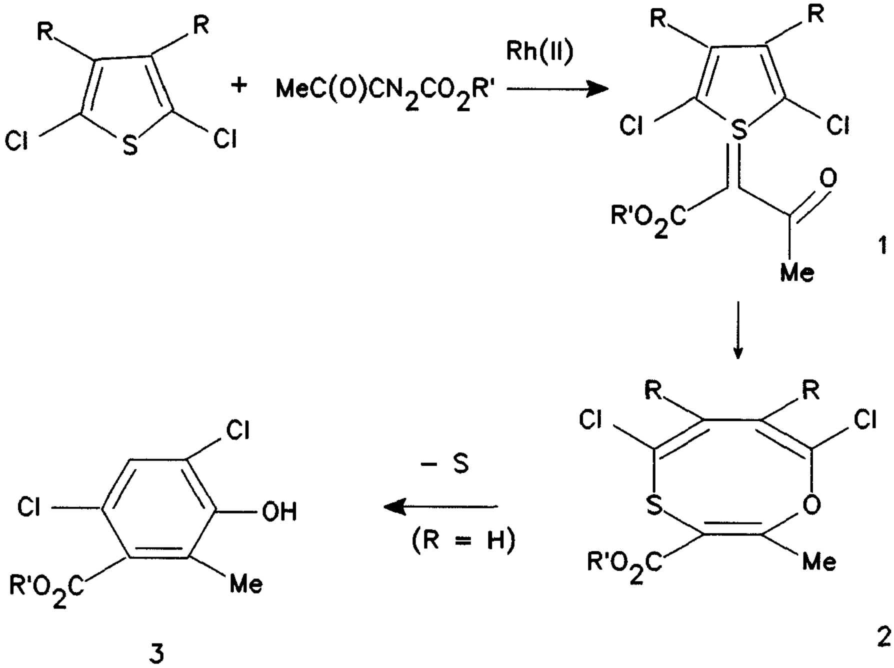
Abstract Thiophenium S,C-ylides were prepared from substituted thiophenes and dicarbonyldiazocompounds and their rearrangements were studied. NMR studies indicate restricted rotation about the ylidic bond.

Porter and coworkers demonstrated that thiophene reacts with dimethyl diazomalonate in the presence of rhodium catalyst yielding the corresponding thiophenium S,C-ylide (**1**) which can undergo thermally induced S→C shift to a 2-substituted thiophene.[1] We have found that ylides **1**, substituted at positions 2 and 5, rearrange thermally to the corresponding 1,4-oxathiocines (**2**).[2] A number of ylides **1** were prepared from polysubstituted thiophenes and diazoalkanes derived from dialkyl malonates, alkyl acetoacetates, and dimedone, and their thermal reactivity was studied. Thiophenium S,C-ylides vary greatly in their stability; some of them are reasonably stable, while other cannot be isolated and rearrange spontaneously to the oxathiocines **2**.

When *both*, 3, and 4 positions in the parent thiophene were unsubstituted, the corresponding 1,4-oxathiocines were capable of further transformation, involving sulfur extrusion and the 1,2-shift of chlorine, yielding tetrasubstituted phenols (**3**).[3] The reactions sequence is presented in the Scheme. The mechanism for the transformations **1**→**2** abd **2**→**3** is proposed.

A series of new S,C-ylides derived from benzo[b]thiophene and *β*-dicarbonyldiazocompounds were also prepared and characterised.[4] NMR ($^1H$, $^{13}C$) studies revealed that ylides substituted additionally at position 2 of the thiophene ring can exist as pairs of diastereomers, not interchangable at room temperature. The slow exchange between two sites results from the restricted rotation about the ylidic C—S bond. The crystal structure of one ylide demonstrated different molecular environment for the two parts of the *β*-dicarbonyl ylidic substituent with respect to the benzothiophene ring. The benzo[b]thiophene ylides were found to be much less reactive than those derived from thiophene.



**Scheme**

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