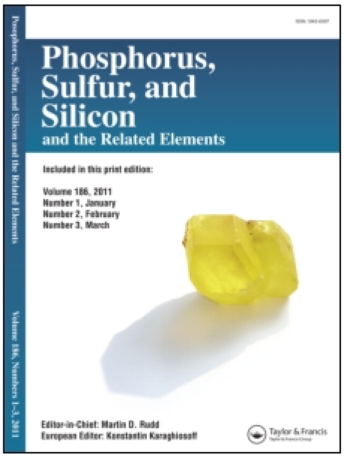

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THERMAL AND PHOTOCHEMICAL REARRANGEMENTS OF 1-METHYL-1-BENZOTHIEPINIUM SALTS

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THERMAL AND PHOTOCHEMICAL REARRANGEMENTS OF 1-METHYL-1-BENZOTHIEPINIUM SALTS

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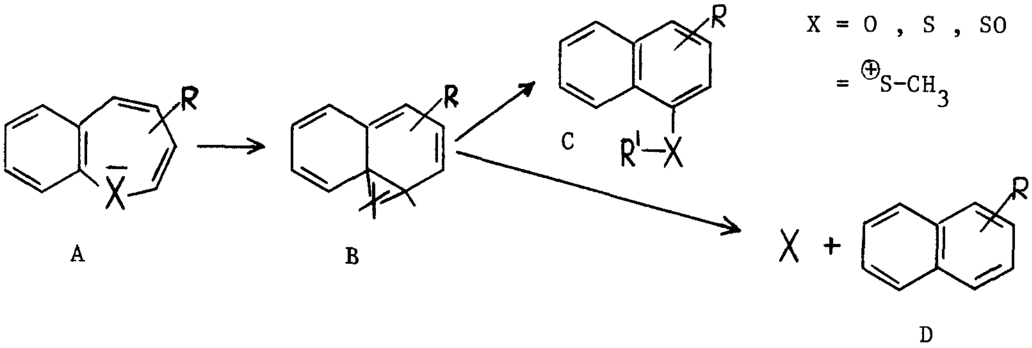
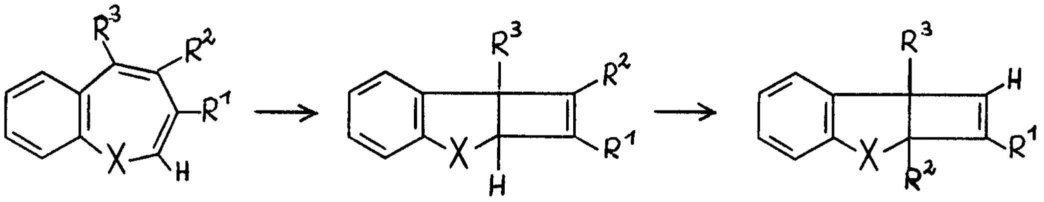
The THERMAL REARRANGEMENT of the benzo-anellated seven-membered heterocycles A begins with the valence bond isomerization A→B . The very unstable B itself cannot be detected because of its fast rearrangement to the stable naphthalene derivatives C respectively D . The reaction rates A→B are strongly affected by the nature of the substituents R and the function X and determine moreover, owing to the high energies of activation, the rates of the whole reaction sequences A→C or A→D . If the thermal lability of the 1-benzoxepins (X = O),



1-benzothiepins (X = S) and 1-benzothiepin-1-oxides (X = SO) is compared a remarcable increase in the series X = O < S < SO can be observed. Since the ability of X to serve as leaving group rises in the same order, we find at the same time a turn of the reaction products from type C to type D . There are good reasons to anticipate, that the 1-METHYL-1-BENZOTHIEPINIUM SALTS (X = $^{\oplus}$S-CH$_3$) should be thermally more stable than the 1-benzothiepins, but less stable than the 1-benzoxepins and that they should rearrange to products of the type C . In this communication these reasons are briefly discussed and the expectations confirmed by several examples. The reaction products and kinetics are described as well as the influence of the substituents R upon the reaction rates and the results are compared with the properties of the corresponding A with X = O , S , SO . Furthermore some details of the probable reaction mechanism are alleged.

The PHOTOCHEMICAL REARRANGEMENT of the various A leads to the appropriate hetero-bicycloheptadienes E . In the case of X = S or SO an additional isomerization of E occurs yielding F . We show that 1-METHYL-1-BENZOTHIEPINIUM SALTS (X = $^{\oplus}$S-CH$_3$) undergo the photochemical ring closure A$\rightarrow$E but not the isomerization to the corresponding F .



A

X = O, S, SO, $^{\oplus}$S-CH$_3$

E

F

only X = S, SO

The compounds E with X = $^{\oplus}$S-CH$_3$ are received as mixtures of both diastereomers, which could be separated. The arguments to establish their structures are discussed.