

This article was downloaded by:

On: 30 January 2011

Access details: Access Details: Free Access

Publisher Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

### THERMAL AND PHOTOCHEMICAL REARRANGEMENTS OF 1-METHYL-1-BENZOTHIPIPIUM SALTS

Hans Hofmann<sup>a</sup>; Attila Molnar<sup>a</sup>

<sup>a</sup> Institut für Organische Chemie der Universität Erlangen-Nürnberg, Erlangen

**To cite this Article** Hofmann, Hans and Molnar, Attila(1979) 'THERMAL AND PHOTOCHEMICAL REARRANGEMENTS OF 1-METHYL-1-BENZOTHIPIPIUM SALTS', Phosphorus, Sulfur, and Silicon and the Related Elements, 6: 1, 133 – 134

**To link to this Article:** DOI: 10.1080/03086647908080340

**URL:** <http://dx.doi.org/10.1080/03086647908080340>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

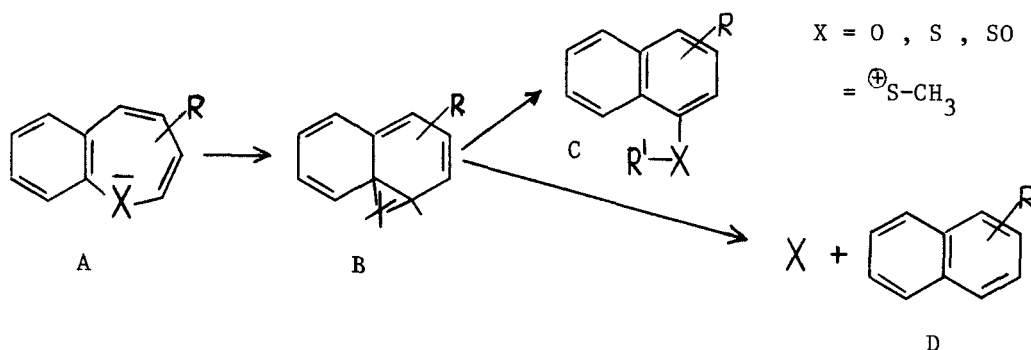
The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

# THERMAL AND PHOTOCHEMICAL REARRANGEMENTS OF 1-METHYL-1-BENZOTHIPIPIUM SALTS

Hans Hofmann and Attila Molnar

Institut für Organische Chemie der Universität Erlangen-Nürnberg,  
Henkestraße 42 , D-8520 Erlangen

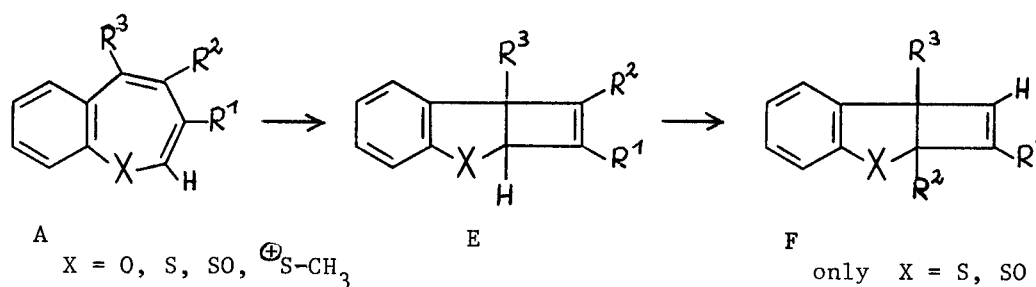
The THERMAL REARRANGEMENT of the benzo-anellated seven-membered heterocycles A begins with the valence bond isomerization  $A \rightarrow B$ . The very unstable B itself cannot be detected because of its fast rearrangement to the stable naphthalene derivatives C respectively D. The reaction rates  $A \rightarrow B$  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  $A \rightarrow C$  or  $A \rightarrow D$ . If the thermal lability of the 1-benzoxepins ( $X = O$ ),



1-benzothiepins ( $X = S$ ) and 1-benzothiepin-1-oxides ( $X = SO$ ) is compared a remarkable 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-BENZOTHIPIPIUM SALTS ( $X = \text{S}^+\text{-CH}_3$ ) 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-BENZOTHIPIPIUM SALTS ( X =  $\oplus$ S-CH<sub>3</sub> ) undergo the photochemical ring closure A  $\rightarrow$  E but not the isomerization to the corresponding F .



The compounds E with X =  $\oplus$ S-CH<sub>3</sub> are received as mixtures of both diastereomers, which could be separated. The arguments to establish their structures are discussed.