

THE HOMOTHIOPYRYLIUM IONS

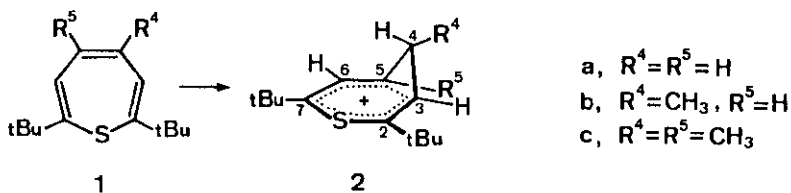
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In contrast to the vast amount of literature concerning the preparation and characterization of the carbocyclic homoaromatic ions, no direct observation of the corresponding heterohomoaromatic ions has been reported so far. In view of the precedent that on protonation cyclooctatetraene easily converted into the homotropylium ion, the thiepins **1a**, **1b**, and **1c** are expected to be promising candidates for the formation of the homothiopyrylium ions such as **2a**, **2b**, and **2c**, respectively.

Treatment of a CD_2Cl_2 solution of 2,7-di-*t*-butylthiepin (**1a**) with a solution of FSO_3H in SO_2 at -78°C gave the 2,7-di-*t*-butyl-3,5-homothiopyrylium ion (**2a**) (as an orange solution). The ^1H NMR spectrum of the solution indicates (i) charge delocalization over the six-membered ring framework, (ii) fairly large chemical shift difference ($\Delta\delta = 2.5$ ppm) between two methylene protons ($\text{H}_{4\text{o}}$ and $\text{H}_{4\text{i}}$), (iii) geminal coupling constant of 11.6 Hz for these protons. These findings are consistent with the homothiopyrylium ion structure **2a**. The same ion was also formed when **1a** was dissolved in conc. H_2SO_4 . The ^1H NMR spectrum of this solution at room temperature shows essentially the same signals except methylene protons which appear at δ 2.66 as a broad singlet. The ^1H NMR spectrum of **2a** is temperature dependent due to the ring flipping. The $\Delta G^\ddagger$ value for the ring flipping is found to be 13.0 kcal/mol.



On protonation, **1b** and **1c** also converted to the corresponding homothiopyrylium ions, **2b** and **2c**, respectively. Protonation of 1-benzothiepin will also be discussed.