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5*H*-BENZO[*b*]THIEPINIUM AND 3*H*-BENZO[*b*]THIEPINIUM IONS

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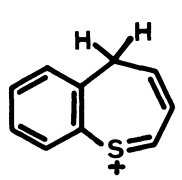
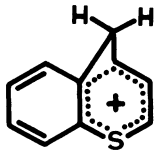
Both 5*H*-benzo[*b*]thiepinium and 3*H*-benzo[*b*]thiepinium ions were generated in strong acidic media and characterized by ^{1}H- and ^{13}C-NMR spectra: the former ion can be regarded as benzohomothiopyrylium ion whereas the latter is postulated to have localized sulfonium ion structure.

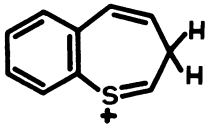
Recently it has been claimed that the homothiopyrylium ions were generated from the corresponding monocyclic thiepins on protonation.[1] Our extension of the original work now indicates that the annelation of a benzene ring to a thiepinium ion controls and competes with the corresponding homothiopyrylium ion structure. We wish to report that the 5*H*-benzo[*b*]thiepinium ion (**1**) exists in a delocalized benzohomothiopyrylium ion structure (**1b**) whereas the 3*H*-benzo[*b*]thiepinium ion (**2**) has a localized sulfonium ion structure (**2a**) instead of a delocalized one **2b**.



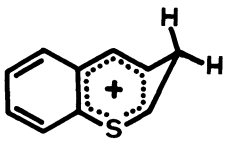
1a



1b

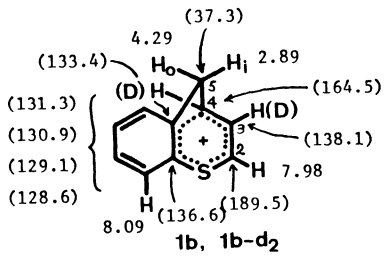


2a



2b

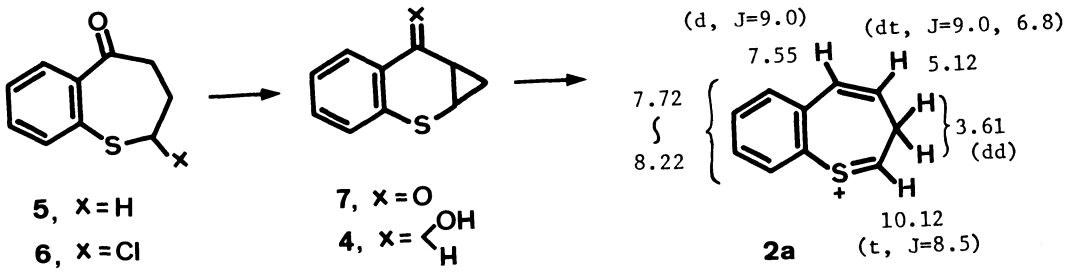
The ion **1** could be generated in a manner similar to that for the 4*H*-2,7-di-*t*-butylthiepinium ion.[1] Addition of a solution of benzo[*b*]thiepin (**3**)[2] in CD_2Cl_2 into a mixture of FSO_3H/SO_2 at -78 °C gave a single protonated species, the structure of which was assigned as benzohomothiopyrylium ion (**1b**) based on the following NMR findings. The same ion was also generated from **3** in concentrated sulfuric acid at room temperature. The ^{1}H-NMR spectrum of **1b** in $FSO_3H/SO_2/CD_2Cl_2$ at -70 °C consisted of a multiplet at δ 7.58-7.88 (4H, H-4, -6, -7, and -8), a multiplet at δ 7.96-8.14 (3H, H-2, -3,and -9) together with two broad signals at δ 4.29 (1H, H-5_o) and 2.89 (1H, H-5_i) due to the frozen conformation. The spectrum of the same solution at room temperature displayed essentially the same signals except methylene protons which appeared as doublet at δ 3.56 (J_{vic}=7.0 Hz). In order to simplify the spectrum, 3,4-dideuteriobenzo[*b*]thiepin (**3**-d_2)[2] was subjected to protonation in concentrated sulfuric acid. The simplified spectrum of **1b**-d_2 thus obtained allows assignments of H-2 and H-9 to be δ 7.98 (s) and 8.09 (dd, J=8.5 and 1.5 Hz), respectively. These assignments are summarized alongside the following structure where the values in parentheses denote carbon shifts. The formation of **1b** bears a close parallel to the observation that the benzohomotropylium ion was produced from



1b, 1b-d_2

benzocyclooctatetraene on protonation.[3]

In addition to confirming the benzohomothiopyrylium ion **1b**, a second goal of this work was to extend to the generation of an alternative ion **2**. The most reasonable precursor for **2** would be a known alcohol **4**,[4] however, extremely low yield of **4** reported in the literature forced to examine alternative synthesis. The chloro ketone **6**, prepared from the ketone **5**[5] (NCS/CCl_4, 6 h at r.t.), was converted to the cyclopropyl ketone **7**($Et_3N/CHCl_3$, at r.t., 11% from **5**). Reduction of **7** (LAH/ether, 67%) gave the desired alcohol **4**.[6]



Treatment of **4** with $FSO_3H/SO_2/CD_2Cl_2$ at -78 °C gave a single cationic species whose ^{1}H-NMR spectrum recorded at -40 °C (see formula) is in accord with the localized structure **2a** rather than the homothiopyrylium ion structure **2b**. Taken together these low and high field chemical shifts of H-2 and H-4, respectively, clearly indicate that cation, 3*H*-benzothiepinium ion, produced from **4** can be regarded as being a localized sulfonium ion **2a**.[7] The skeletal structure of **2a** is evidenced by the formation of 2-methoxy-2,3-dihydrobenzo[*b*]thiepin[8] in 38% yield upon quenching the solution of **2a** with methanol in the presence of sodium hydrogencarbonate. Further study directed toward generation and characterization of the parent homothiopyrylium ion is in progress and will be reported in due course.

References

1) K. Yamamoto, S. Yamazaki, A. Matsukawa, and I. Murata, *J. Chem. Soc., Chem. Commun.*, in press.
2) I. Murata, T. Tatsuoka, and Y. Sugihara, *Angew. Chem., Int. Ed. Engl.*, 13, 142 (1974); V. J. Traynelis, Y. Yoshikawa, J. C. Sih, and L. J. Miller, *J. Org. Chem.*, 38, 3978 (1973).
3) W. Merk and R. Pettit, *J. Am. Chem. Soc.*, 90, 814 (1968).
4) P. M. Wintraub and A. D. Sill, *J. Chem. Soc., Chem. Commun.*, 1975, 784.
5) V. J. Traynelis and R. F. Love, *J. Org. Chem.*, 26, 2728 (1961).
6) Although these two compounds, **4** and **7**, have been fully characterized by elemental analyses, MS, IR, and NMR spectra, the observed data did not coincide with those reported (Ref. 4): Compound **4**: mp 104-107 °C; IR (KBr) ν (OH) 3280 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.59-1.18 (m, 2H), 1.69-2.42 (m, 3H), 5.00 (bs, 1H), 7.10-7.73 (m, 4H). Compound **7**: mp 40-41 °C; IR (KBr) ν (C=O) 1650 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.02-1.40 (m, 1H), 1.51-1.88 (m, 1H), 2.17-2.84 (m, 2H), 6.85-7.48 (m, 3H), 7.61-7.76 (m, 1H).
7) The same sulfonium ion structure has been postulated as a reaction intermediate during the synthesis of 4-chloro-5-phenyl-1-benzothiepin. V. J. Traynelis, J. A. Schield, W. A. Lindley, and D. W. H. McDowell, *J. Org. Chem.*, 43, 3379 (1978).
8) T. Tatsuoka, Ph. D. Thesis, Osaka University, 1975.

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