A Novel Rearrangement of Protonated 2-Bromo-5-methylthiophene

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Synopsis. A novel rearrangement of protonated 2-bromo-5-methylthiophene was observed in HSO_3F by means of ^1H NMR spectroscopy.

Recently we reported that well resolved ^1H NMR spectra of the cations formed from chloro- and bromothiophenes were observed in HSO_3F or HCl–$AlCl_3$-Solvent system.[1–4] We extended the observation to protonated 2-bromo-5-methylthiophene, as shown in Scheme 1. The experimental procedures were the same as those described in a previous report.[4]

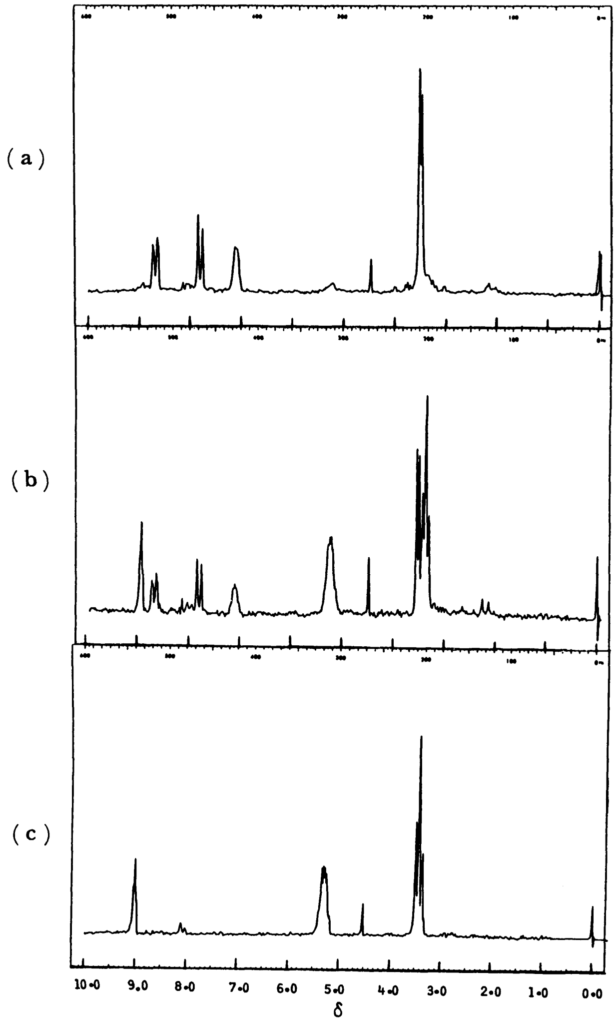
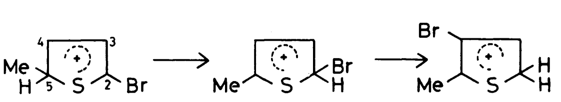


Fig. 1. ^1H NMR spectra of protonated 2-bromo-5-methylthiophene in HSO_3F at 60 MHz; (a) at −50 °C, (b) at −30 °C, and (c) at 10 °C.

Typical examples of ^1H NMR spectra are shown in Fig. 1. The protonation of 2-bromo-5-methylthiophene gave a mixture of the two cations, 5H- and 2*H*-2-bromo-5-methylthiophenium ions at −70 °C. The former ion then underwent an irreversible 2,5-hydrogen shift and changed almost completely to the latter ion at about −50 °C (Fig. 1a), as in the case of 2-chloro-5-methylthiophenium ion.[4] When the temperature was raised to about −30 °C, however, another peculiar rearrangement appeared on the ^1H NMR spectra (Fig. 1b). This rearrangement was accomplished at about 10 °C as shown in Fig. 1c, which showed the presence of only one cation, 2*H*-4-bromo-5-methylthiophenium ion.[5] Evidence of the cation was also obtained from another route. That is, the spectral data of the cation are consistent with those observed for the cation produced from the protonation of 3-bromo-2-methylthiophene in HSO_3F, which was stable and gave an almost unchanged spectrum from −70 to 10 °C. The spectral data were also different from those obtained from the protonation of 4-bromo-2-methylthiophene in HSO_3F, which was stable from −70 to 30 °C. After the ^1H NMR measurement was carried out at 10 °C (Fig. 1c), the sample solution was poured into water and an aqueous solution was extracted by diethyl ether. Then, after the solvent was distilled off, the residue was checked by ^1H NMR. ^1H NMR spectral data were consistent with those of 2-methyl-3-bromothiophene. The spectral data of the ions are given in Table 1.

Two facts must be noted. First, the rearrangement



Scheme 1.

Table 1. ^1H Chemical Shifts of Protonated Bromomethylthiophenes in HSO_3F

Substituents	Temp °C	Chemical shift, ppm			
		2-H	3-H	4-H	5-H
2H, 2-Br, 5-Me	−50	7.11	8.68	7.80	(3.49)[a]
5H, 2-Br, 5-Me	−70	—	8.01	8.87	5.29 (2.11)
2H, 3-Br, 5-Me	−30	5.28	—	8.06	(3.31)
2H, 4-Br, 5-Me	−10	5.26	8.97	—	(3.40)

a) The values in parentheses are the chemical shifts of methyl protons.

proceeded with three clearly separated stages as given in Scheme 1 and only one species of the cation existed in a solution at a specific temperature (Fig. 1a or Fig. 1c). The mechanism of this novel rearrangement is not clear at present. However, this fact strongly suggests that the rearrangement involves an intramolecular process.(6) Second, the 2*H*-2-bromo-5-methylthiophenium ion does not rearrange to a more stable 2*H*-3-bromo-5-methylthiophenium ion, but to a 2*H*-4-bromo-5-methylthiophenium ion.

References

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4) Y. Yokoyama, Y. Yamashita, K. Takahashi, and T. Sone, *Bull. Chem. Soc. Jpn.*, **56**, 2208 (1983).

5) An unknown signal appeared at 4.5 ppm in Fig. 1, but this is not attributed in the cations in problem.

6) In the case of intermolecular proesses, which were observed in the acid-catalyzed reactions of bromothiophenes, several species of the products were obtained in the reaction mixture. For example, R. M. Kelogg, A. P. Schaap, E. T. Harper, and H. Wynberg, *J. Org. Chem.*, **33**, 2902 (1968).