

THE PHOTOCHEMISTRY OF SOME THIOPHENIUM IONS

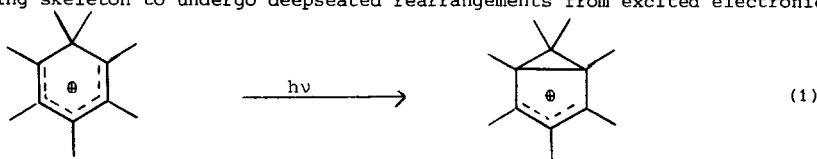
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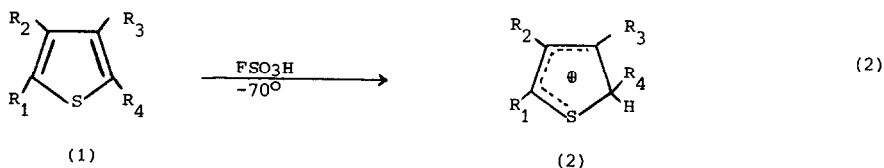
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Our interest in the photochemical reactions of thiophenium ions was aroused both by Childs and Winstein's<sup>1</sup> description of the light induced valence isomerization of polymethylbenzenium ions to their bicyclo[3.1.0]hexenyl valence isomers (eq. 1) and also by the marked proclivity of the neutral thiophene ring skeleton to undergo deepseated rearrangements from excited electronic states.<sup>2</sup>



The thiophenium ions 2a-h were prepared in quantitative yield by protonation of 1a-h in fluorosulfonic acid at low temperature (eq. 2).<sup>3,4</sup> Structural assignments were made readily from the

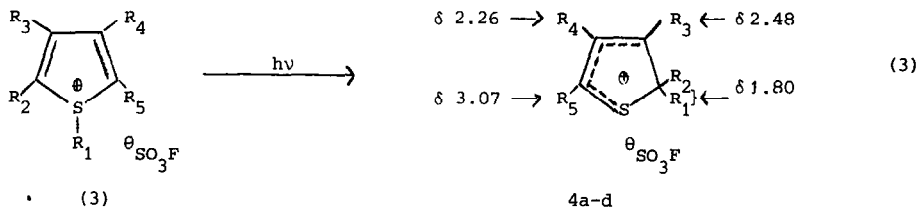


- (1)
- a)  $R_1 = R_2 = R_3 = R_4 = H$   
 b)  $R_1 = R_4 = CH_3$ ;  $R_2 = R_3 = H$   
 c)  $R_1 = CH_3$ ;  $R_2 = R_3 = R_4 = H$   
 d)  $R_1 = R_2 = R_3 = R_4 = CH_3$   
 e)  $R_1 = \text{tert-Bu}$ ;  $R_2 = R_3 = R_4 = H$   
 f)  $R_1 = R_3 = \text{tert-Bu}$ ;  $R_2 = R_4 = H$   
 g)  $R_1 = \text{cyclo-C}_3\text{H}_5$ ;  $R_2 = R_3 = R_4 = H$   
 h)  $R_2 = \text{cyclo-C}_3\text{H}_5$ ;  $R_1 = R_3 = R_4 = H$

$\mu\text{m}$  spectra, several of which have been described previously.<sup>3</sup> In all cases protonation occurred to give exclusively the ion shown. Ultraviolet spectra indicated the presence of a strong absorption

band (for  $2d$ ,  $\lambda_{\max}$  is 293 nm). However when solutions of the ions  $2$  in Pyrex nmr tubes were irradiated (quartz jacketed Hanau TQ 81 lamp) at  $-60^\circ$  no detectable changes occurred even after a number of hours. Control experiments demonstrated that the benzenium ions described by Childs and Winstein<sup>1</sup> rearranged completely under these conditions.

In view of the unanticipated stability of the ions  $2$ , attention was turned to the S-methylated ions  $3a-d$  (eq. 3).<sup>5</sup> These are readily prepared from  $1d$  (or a deuterated derivative) in a solu-



- a)  $R_1 = R_2 = R_3 = R_4 = R_5 = CH_3$   
 b)  $R_1 = CD_3$ ;  $R_2 = R_3 = R_4 = R_5 = CH_3$   
 c)  $R_1 = R_2 = R_5 = CH_3$ ;  $R_3 = R_4 = CH_2D$   
 d)  $R_1 = CD_3$ ;  $R_2 = R_5 = CH_3$ ;  $R_3 = R_4 = CH_2D$

tion of methyl (deuteriomethyl) fluorosulfonate. Methylation is complete after several hours at room temperature.<sup>6</sup> The ions  $3a-d$  are indefinitely stable at ambient temperature or higher ( $75^\circ$  for 24 hr) in methylfluorosulfonate solution. Irradiation at room temperature of dark purple solutions (the color apparently arises from an impurity) of  $3a$  [pmr:  $\delta$  3.10 (s, 3, S- $CH_3$ ),  $\delta$  2.32 (broad s, 6, 2,5- $CH_3$ ), and  $\delta$  2.07 (broad s, 6, 3,4- $CH_3$ )]<sup>7</sup> led to slow but clean (> 80% yield) transformation to a new product  $4a$  [pmr:  $\delta$  3.07 (s, 3,  $CH_3$ ),  $\delta$  2.48 (broad s,  $CH_3$ ),  $\delta$  2.26 (broad s, 3,  $CH_3$ ), and  $\delta$  1.80 (s, 6,  $CH_3$ )]. This product was stable to further photochemical transformation and also showed no changes on standing for extended periods. Partial elucidation of the structure of  $4a$  was forthcoming from the spectral data for deuterated derivatives  $4b-d$ . The following facts emerged: (a) the spectrum of  $4b$  was identical to that of  $4a$  save that only one  $CH_3$  was present in the  $\delta$  1.80 absorption, (b) in  $4c$  the monodeuteriomethyl groups were located in the  $\delta$  2.48 and  $\delta$  2.26 resonances,<sup>8</sup> (c) ion  $4d$  had a spectrum identical to that of  $4c$  except that only one methyl group was present in the  $\delta$  1.80 absorption. Assignment of 2,2,3,4,5-pentamethylthiophenium structures to  $4a-d$  provides a consistent interpretation of the spectral observations.

Attempts to quench  $4a$  under a variety of conditions led to no identifiable products. The proposed structure was substantiated, however, from consideration of the  $^{13}C$  nmr spectrum. Some appropriate data are accumulated in the Table. Assignments of the various resonances were made from consideration of the proton coupled spectra.<sup>6</sup> The striking similarity of the  $^{13}C$  chemical shifts of

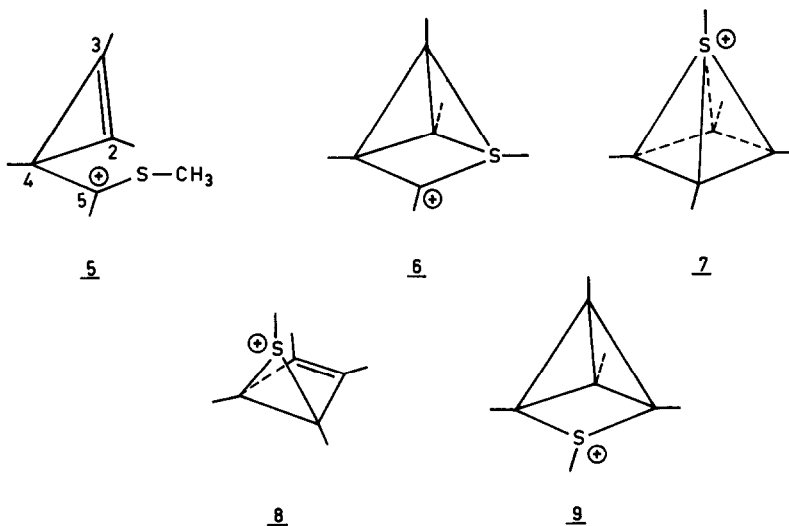
4a and model ion 2d (hydrogen-methyl instead of methyl-methyl at the 2 position) verify the structural assignment for 4.

Table  
 $^{13}\text{C}$  Chemical Shifts<sup>a</sup> of Some Thiophenium Ions<sup>b</sup>

Ion	Ring Carbon Atoms <sup>c</sup>			
	2	3	4	5
<u>3a</u> <sup>d</sup>	128.4	148.5	148.5	128.4
<u>2d</u> <sup>e</sup>	66.4	195.5	145.8	227.9
<u>4a</u> <sup>d</sup>	77.3	199.4	143.9	228.9

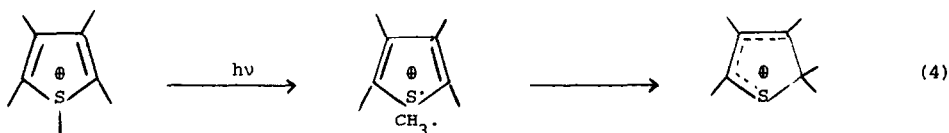
- a) Measured relative to deuterioacetone and converted to  $\delta_{\text{TMS}}$  values by use  $\delta_{\text{TMS}} = -204.1$  ppm.  
 b) Proton decoupled shifts determined on a Varian XL-100 instrument using Fourier transform techniques.  
 c) The  $^{13}\text{C}$  chemical shifts of the methyl groups have been omitted because unambiguous assignment has not yet proved possible.  
 d) Measured at ca  $30^\circ$  in methyl fluorosulfonate as solvent.  
 e) Measured at  $-50^\circ$  in fluorosulfonic acid as solvent.

The selective shift of a S-methyl substituent in 3 from sulfur to an adjacent carbon atom without apparent further effect on the ring substituents excludes valence isomers 5-7 as important



intermediates since intervention of any of these structures predicts degeneracy of the 2,3(4,5) ring carbon positions. Such symmetry considerations fail to allow either rejection or confirmation

of 8 and/or 9 as transitory intermediates; rapid migration of the methyl group from sulfur to carbon would provide observed product 4. One notes that were the excited state geometry to resemble 9 this would be tantamount to the twisting motion about the S-C<sub>2</sub> bond required to permit a Woodward-Hoffmann<sup>9</sup> photochemically allowed [1.5] shift antarafacial on the thiophene skeleton. However an equally valid interpretation of the rearrangement is light induced scission of the carbon-sulfur bond in 3 to a methyl radical and a thiophene radical cation; recombination at carbon affords product 4 (eq.4).



The means by which C-substituted ions 2 and 4 dispose of electronic energy without apparent valence isomerization remain mysterious.<sup>10</sup>

#### References

1. R.F. Childs and S. Winstein, *J. Amer. Chem. Soc.*, 90, 7146 (1968).
2. H. Wynberg, *Acct. Chem. Res.*, 2, 65 (1971).
3. H. Hogeveen, *Rec. Trav. Chim.*, 85, 1072 (1966).
4. Fluorosulfonic acid provides a very tractable medium for preparation of these ions. In this manner a number of furanium ions have also been generated. These ions fail to show any photochemical transformation (unpublished work). See also U.E. Wiersum and H. Wynberg, *Tetrahedron Lett.*, 2951 (1967) and D.M. Brouwer, J.A. van Doorn, and A.A. Kiffen, *Rec. Trav. Chim.*, 91, 1359 (1972).
5. For a discussion of alkylthiophenium ions, see R.M. Acheson and D.R. Hansen, *J. Chem. Soc. (C)*, 1764 (1970).
6. This method of preparation of S-alkylthiophenium salts was developed by R.F. Heldeweg and H. Hogeveen in these laboratories. The complete assignment of proton and <sup>13</sup>C (see further) spectra of these ions has also been performed by R.F. Heldeweg (unpublished work).
7. Measured relative to tetramethylammoniumchloride as internal reference and converted to  $\delta_{\text{TMS}}$  values by using  $\delta_{\text{TMS}} = -3.20$  ppm
8. About 60% exchange of <sup>1</sup>H for deuterium occurs at R<sub>3</sub> in ions 4b,c during the course of irradiation.
9. R. Woodward and R. Hoffmann, *Angew. Chem.*, 81, 797 (1969).
10. For example pyrylium salts apparently provide oxoniabenzvalene intermediates:
  - a) J.W. Pavlik and E.L. Clennan, *J. Amer. Chem. Soc.*, 95, 1697 (1973).
  - b) J.A. Barltrop, K. Dawes, A.C. Day, and A.J.H. Summers, *Chem. Commun.*, 1240 (1972).
  - c) J.A. Barltrop, K. Dawes, A.C. Day, and A.J.H. Summers, *J. Amer. Chem. Soc.*, 95, 2406 (1973).