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THIENO[3,4-b]THIOPHENE. THE THIRD THIOPHTHENE

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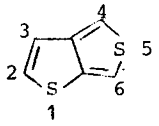
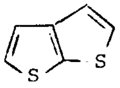
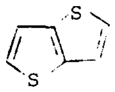
We wish to report the synthesis of thieno[3,4-b]thiophene (I), the only one of the three possible thiophthenes (I-III) (1) which is unknown. Only one derivative of the ring system I, namely 4,6-dimethylthieno[3,4-b]thiophene (2), an unstable colorless oil, has been described previously.



I

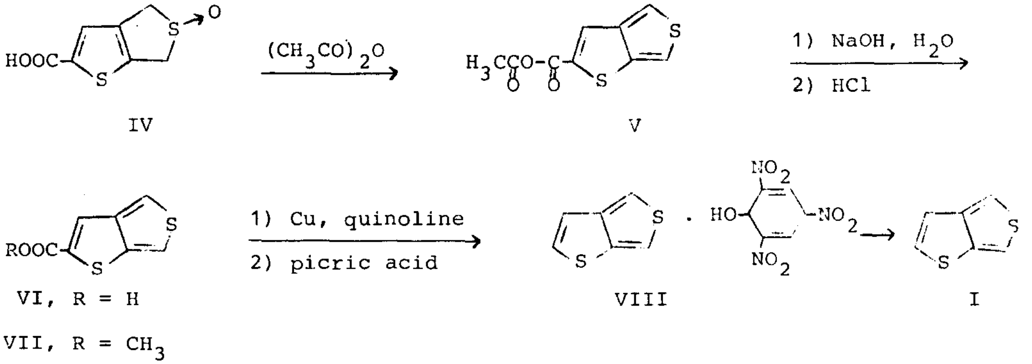


II



III

Using Cava and Pollack's elegant new method for the synthesis of thiophenes from dihydrothiophene sulfoxides (3), we obtained the acetic-thieno[3,4-b]thiophene-2-carboxylic anhydride (V) in 95% yield from the sulfoxide (IV) (4) by refluxing 1.5 hour in acetic anhydride. The mixed anhydride V was hydrolyzed to the free acid VI in 88% yield. Treatment of the latter with diazomethane furnished the methyl ester VII in high yield.



The remarkable stability of V, VI and VII is in noted contrast to the instability of the dimethyl derivative of Dann and Dimmling (2) or to the unsubstituted thiophthene (I).

The acid VI was decarboxylated smoothly by heating for 2-3 minutes with copperpowder in refluxing quinoline. Evaporation of the ether extracts and immediate treatment of the residue with picric acid furnished the picrate of I (VIII) in 71% yield. The free thiophthene I was obtained by decomposition of an ether solution of the picrate with ammonia solution. After evaporation of the ether solution, the residue was dissolved in petroleumether (bp 40-60°). The solution was treated with charcoal and filtered, after which I crystallized from the cooled (-70°) filtrate as colorless plates. The yield of thieno[3,4-b] thiophene (I), a colorless oil, mp 7-7.5°, n_D^{20} 1.6905, was 81%. The thiophthene turned yellow rapidly on standing in air. At -40° as well as in petroleumether solution it appeared to be stable for at least a few days. Anal. (5) calcd for $C_6H_4S_2$ (140.22): C, 51.39; H, 2.88; S, 45.73. Found: C, 51.4, 51.4; H, 3.0, 2.9; S, 45.6, 45.9.

The physical properties (corrected melting points, NMR and ultraviolet spectra) of the five new thiophthenes are reported in table I.

The ultraviolet spectrum of the unsubstituted thiophthene (I), together with those of the two other isomers (6) are drawn in figure 1. The spectrum of I is very similar to that reported for 4,6-dimethylthieno[3,4-b] thiophene (maxima at λ 239; ~258, ~266, ~275; 311 mμ) (2).

The unsymmetrical nature of I, coupled with the lack of theoretical prediction pertaining to its substitution pattern and its aromaticity make a study of the reactivity of this thiophthene eminently worthwhile. Studies in this direction are in progress in our laboratory.

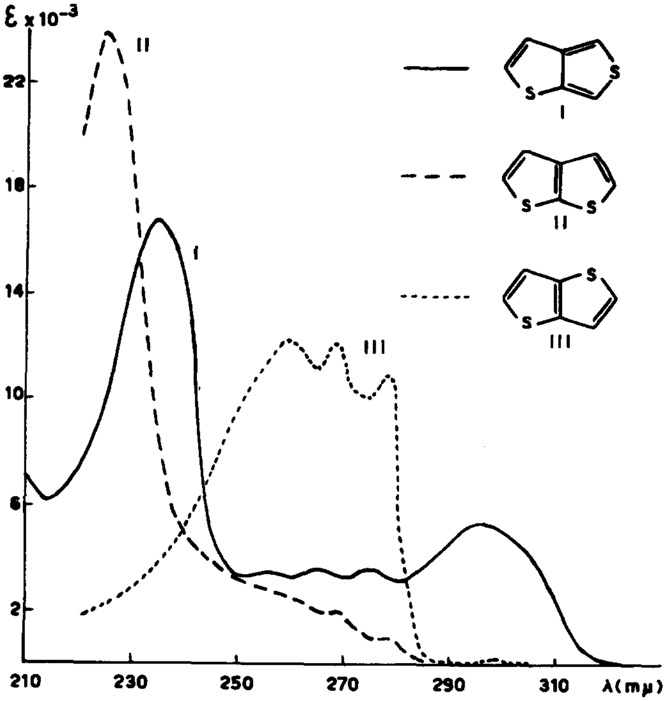
Table I

Melting points (corrected), NMR spectra and UV spectra of the new thiophthenes

Compound	Melting point	NMR spectrum (τ)					UV spectrum (95% ethanol)
		H(2)	H(3)	H(4)	H(6)	Solvent	λ_{max} (ε)
I	7-7.5° n_D^{20} 1.6905	2.78, 2.87 J 5.5	3.21, 3.30 J 5.5	2.93, 2.97 J 2.5	2.83, 2.87 J 2.5	20% in CCl_4	235 (16,800) 257 (3,370) 266 (3,650) 275.5 (3,650) 296.5 (5,330)
V	99-100°	-	2.25	2.70, 2.74 J 2.5	2.32, 2.36 J 2.5	10% in $CDCl_3$	238 sh (4,920) 259.5 (9,480) 284 sh (13,900) 292 (16,600) 343 (3,790)
		-	2.08	2.36, 2.40 J 2.5	2.00, 2.04 J 2.5	10% in CD_3COCD_3	
VI	210 (dec.)	-	2.20	2.28, 2.32 J 2.5	2.01, 2.05 J 2.5	20% in CD_3SOCD_3	225.5 (5,330) 232 (5,480) 255 sh (11,450) 260 (11,860) 283 (15,900) 292 (15,400) 336 (4,360)
VII	65-66.5°	-	2.35	2.44, 2.48 J 2.5	2.76, 2.80 J 2.5	10% in $CDCl_3$	233.5 (4,550) 256 sh (10,030) 261.5 (10,580) 284 (16,580) 293 (17,080) 339.5 (4,170)
VIII	113 (dec.)	2.69, 2.78 J 5.5	3.13, 3.22 J 5.5	2.83, 2.87 J 2.5	2.74, 2.78 J 2.5	7% in $CDCl_3$	224 (30,300) 234.5 (28,200) 275 sh (5,850) 302 (7,600) 359 (16,100)
		2.54, 2.63 J 5.5	3.07, 3.16 J 5.5	?	?	20% in CD_3COCD_3	

Figure I

The UV spectra of the three isomeric thiophthenes



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