Synthesis and Absorption Spectra of Some 2,6-Disubstituted 4-(4-Dimethylaminophenyl)thiopyrylium Perchlorates

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The syntheses of 4-(4-dimethylaminophenyl)thiopyrylium perchlorate and the 2,6-dimethyl derivative are described, and the absorption spectra of these compounds and the 2,6-diphenyl derivative are compared with the corresponding pyrylium salts.

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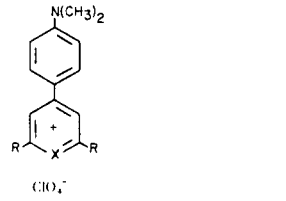
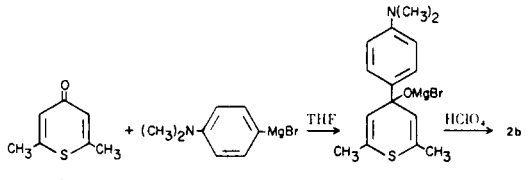
The synthesis and the absorption spectra of the series **1** have been reported (1). We have now completed the synthesis of the corresponding thiopyrylium salts **2**, and the present report describes these syntheses and compares the absorption spectra of the thiopyrylium series with the corresponding pyrylium salts.



1 (X = O): (a) R = C_6H_5 (b) R = CH_3 (c) R = H
2 (X = S): (a) R = C_6H_5 (b) R = CH_3 (c) R = H

The 2,6-diphenyl derivative **2a** was prepared by the published procedure (2) which involves treating **1a** with sodium sulfide in aqueous acetone followed by acidification with perchloric acid. This method was unsuccessful for the preparation of **2b** and **2c**, since in the first case a mixture of **1b** and **2b** was obtained which could not be separated, and in the latter case a mixture of unidentified products was obtained. The scheme outlined below gave a high yield of **2b**. The method which was successful for the preparation of **2c** involves the following reactions.



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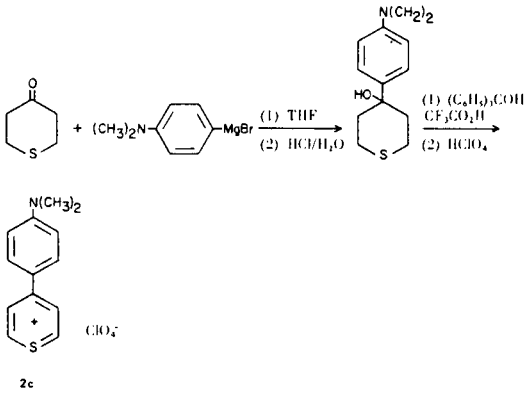
The absorption spectra for the series **2** is given in Table I, and the spectra of the corresponding pyrylium salts (**1**) are listed in Table II. The most striking feature on comparison of the two series is that the order in terms of decreasing wavelength is not the same for the pyrylium and thiopyrylium series. Since this result was completely unexpected, all of the compounds were synthesized again (the m.p.'s, ir spectra and analysis agreed with those previously obtained), and the absorption spectra were redetermined. All of the spectra were identical to the original values reported in Tables I and II except for that obtained for 4-(4-dimethyaminophenyl)pyrylium perchlorate (**1c**) which now showed λ max ($\epsilon \times 10^{-3}$) 500 (54.0), ~280 (5.5) and 258 nm (8.6) in acetonitrile. The order of decreasing absorption in the two series now agrees. The reason for the original value must have been due to a sample mix-up. In order to be certain of the structure **1c** [there is a slight possibility that the Grignard reagent added 1,4 to give the 2-(4-dimethylaminophenyl)-isomer], a C^{13} nmr spectrum was run and showed only four peaks which is consistent with **1c** but not the isomer.



2c

Table I

Absorption Spectra of Thiopyrylium Salts (λ max nm (ε x 10^{-3}))

Compound **2a**		Compound **2b**		Compound **1c**	
in ethanenitrile	in dichloromethane	in ethanenitrile	in dichloromethane	in ethanenitrile	in dichloromethane
577 (59)	592 (58)	525 (51.5)	547 (62.4)	536 (45.0)	558 (58.5)
380 (15.8)	387 (14.2)	288 (7.7)	295 (8.4)	298 (4.2)	302 (5.6)
~285 (13.9)		260 (5.4)	262 (5.6)	276 (4.6)	~275 (6.3)
259 (18.9)	260 (14.3)			265 (4.6)	265 (7.3)
243 (16.4)					

Table II

Absorption Spectra of Pyrylium Salts (λ max nm (ε x 10^{-3})) in Ethanenitrile

Compound **1a**		Compound **1b**		Compound **1c**	
in ethanenitrile	in dichloromethane	in ethanenitrile	in dichloromethane	in ethanenitrile	in dichloromethane
536 (66.2)	550 (98.0)	485 (63.0)	500 (83.0)	430 (31.4)	
377 (22.0)	382 (26.3)	282 (12.3)	285 (13.5)	252 (16.0)	
291 (14.4)	295 (14.5)		~255 (3.6)	New Values	
263 (16.4)	263 (15.8)			500 (54.0)	516 (60.)
				~280 (5.5)	~283 (5.4)
				~258 (8.6)	253 (9.0)

EXPERIMENTAL

The absorption spectra were recorded on Cary 14 and 17 spectrometers.

2,6-Dimethyl-4-(4-dimethylaminophenyl)thiopyrylium Perchlorate (**2b**).

A mixture of 3 g. (0.015 mole) of *p*-bromo-*N*,*N*-dimethylaniline and 0.36 g. (0.015 mole) of magnesium in 25 ml. of dry tetrahydrofuran was refluxed under nitrogen until the magnesium dissolved. The solution was cooled to room temperature and a solution of 1.7 g. (0.012 mole) of 2,6-dimethyl-4*H*-thiopyran-4-one (3) in 20 ml. of dry tetrahydrofuran was added. The mixture was refluxed for 3 hours, cooled to room temperature and poured into a solution of 5 ml. of 70% perchloric acid in 100 ml. of water. The solid was collected and recrystallized from alcohol giving 4 g. of purple needles, m.p. 227-228°.

Anal. Calcd. for $C_{15}H_{18}ClNO_4S$: C, 52.4; H, 5.2; N, 4.1; S, 9.3. Found: C, 52.0; H, 5.3; N, 4.2; S, 9.1.

4-(4-Dimethylaminophenyl)-thiopyrylium Perchlorate (**2c**).

A mixture of 10 g. (0.05 mole) of *p*-bromo-*N*,*N*-dimethylaniline and 1.2 g. (0.05 mole) of magnesium in 75 ml. of dry tetrahydrofuran was refluxed under nitrogen until the magnesium had dissolved. After cooling to room temperature, 5 g. (0.043 mole) of tetrahydro-4*H*-thiopyran-4-one (4) in 50 ml. of dry tetrahydropyran was added, and the mixture was stirred for 2 hours and then poured into aqueous ammonium chloride. The material was extracted into ether, the extract washed twice with water and dried over magnesium sulfate. The ether was removed and 23 g. (0.086 mole) of triphenylcarbinol and 50 ml. of trifluoroacetic acid was added to the residue, and the mixture was refluxed for 1 hour. The trifluoroacetic acid was distilled under vacuum and the residue was dissolved in hot alcohol, cooled to room temperature and filtered to remove some white solid. The filtrate was mixed with 7 ml. of 70% perchloric acid and the solid was collected and washed with alcohol. The solid was boiled with 100 ml. of alcohol and filtered hot. The insoluble material was recrystallized from a small volume of acetonitrile to give 7.5 g. of crystalline product, m.p. 230-231°.

Anal. Calcd. for $C_{13}H_{14}ClNO_4S$: C, 49.4; H, 4.5; N, 4.4. Found: C, 49.5; H, 4.4; N, 4.3.

REFERENCES AND NOTES

(1) G. A. Reynolds and J. A. Van Allan, *J. Heterocyclic Chem.*, **11**, 405 (1974).

(2) R. Wizinger and P. Ulrich, *Helv. Chem. Acta*, **39**, 215 (1956).

(3) A. I. Tolmachev and V. P. Sribnaya, *Khim. Geterotsikl. Soedin.*, **2**, 183 (1966).

(4) Aldrich Chemical Company.