

The Effect of Electron Withdrawing Groups on the Stability of Thiabenzenes

Hooshang Pirelahi, Yahya Abdoh, and Manoochehr Tavassoli

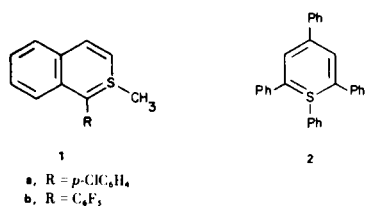
Department of Chemistry, University of Tehran,
P. O. Box 14-1141, Tehran, Iran

Received October 14, 1976

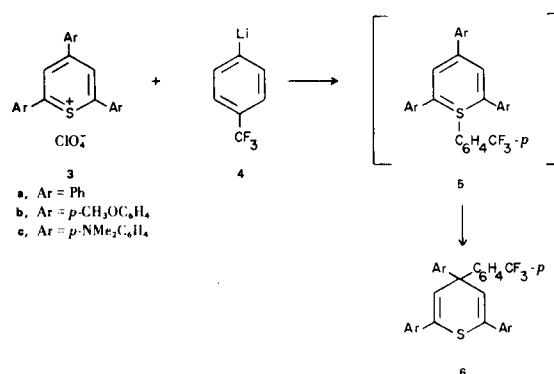
The reactions of *p*-trifluoromethylphenyllithium with 2,4,6-triarylthiopyrylium perchlorates (Ar = Ph, *p*-CH₃OC₆H₄, *p*-NMe₂C₆H₄) have been studied. The initially formed thiabenzenes were not stable enough to be isolated and rearranged readily to their corresponding 4-(*p*-trifluoromethylphenyl)-2,4,6-triarylthiopyrans. The instability of the intermediate thiabenzenes reveals that, in contrast to the stabilization effect of the electron-withdrawing *p*-chloro- and pentafluorophenyl groups attached to carbon atoms in sulfur ring, the electron-withdrawing *p*-trifluoromethyl group on substituents attached to sulfur decreases the stability of thiabenzenes.

J. Heterocyclic Chem., **14**, 199 (1977).

Recently, it has been shown that the substitution of the electron-withdrawing *p*-chloro- or pentafluorophenyl groups on the thianaphthalene α -carbon atom leads to stabilization of thianaphthalenes. Although the resulting 1-*p*-chlorophenyl-2-methyl-2-thianaphthalene (**1a**) could only be generated *in situ*, 1-pentafluorophenyl-2-methyl-2-thianaphthalene (**1b**) was stable enough to permit its isolation as a crystalline compound (1,2). The present investigation was undertaken to determine the effect of electron withdrawing groups on the substituents attached to sulfur atom of thiabenzenes.



There now exists a large body of experimental evidence (2,3) regarding the formation of purple 1,2,4,6-tetraphenylthiabenzene (**2**) through the reaction of phenyllithium with 2,4,6-triphenylthiopyrylium perchlorate (**3a**). For this investigation we have now carried out the reactions of *p*-trifluoromethylphenyllithium (**4**) with different thiopyrylium perchlorates. However, when **3a** was reacted with **4** in ether under nitrogen at -10°, the initially formed thiabenzene **5a** was not stable enough to be isolated and rearranged readily to its isomeric thio-



pyran; the yellowish-white 4-(*p*-trifluoromethylphenyl)-2,4,6-triphenylthiopyran (**6a**) was separated in 61% yield after ten hours. Treatment of 2,4,6-tris(*p*-methoxyphenyl)thiopyrylium perchlorate (**3b**) with **4** in an ethereal solution under nitrogen at -10° also afforded the white crystalline 4-(*p*-trifluoromethylphenyl)-2,4,6-tris(*p*-methoxyphenyl)thiopyran (**6b**) in 56% yield after three hours. Again, the isolation of the intermediate, purple, thiabenzene **5b** was not possible. The reaction of 2,4,6-tris(*p*-dimethylaminophenyl)thiopyrylium perchlorate (**3c**) with **4** in ether under nitrogen at room temperature gave the greenish-white crystalline 4-(*p*-trifluoromethylphenyl)-2,4,6-tris(*p*-dimethylaminophenyl)thiopyran (**6c**) in 31% yield after ten minutes. Here, the purple color of the

intermediate thiabenzene **5c** faded much more faster than **5a** and **5b**. The structural assignments of the products, **6a-c**, were based on their elemental and spectral data. In the mass spectra the molecular ions were the base peak. The nmr spectra showed β -protons of the thiopyran rings at about δ 6 ppm. The uv spectra were also in agreement with those reported for 2,4,4,6-tetrasubstituted thiopyrans (4).

Although the purple solution of **2** also rearranges to its isomeric 2,4,4,6-tetraphenylthiopyran (2,3), the rearrangement is slow enough to permit the isolation of **2**. Comparison of the rearrangement properties of thiabenzene **5a** with thiabenzene **2** indicates that, in contrast to the stabilization effect of the electron-withdrawing *p*-chloro- and pentafluorophenyl groups attached to carbon atoms in sulfur ring (1,2), the electron-withdrawing *p*-trifluoromethyl group on substituents attached to sulfur decreases the stability of thiabenzene. Moreover, the faster rearrangement of **5c**, compared to **5b**, reveals that the electron-donating *p*-dimethylamino group on substituents attached to carbon atoms in sulfur ring is more effective in destabilization of thiabenzene than *p*-methoxy group. The behavior of electron withdrawing groups in stabilization or destabilization of thiabenzene is opposite to the effect of electron donating groups which was reported earlier (5).

EXPERIMENTAL

Melting points were determined on a Gallenkamp apparatus and are uncorrected. Ir spectra were recorded on a Beckman IR-5A spectrophotometer using potassium bromide disks. Uv absorption spectra were recorded on a Varian Techtron uv-visible spectrophotometer Model 635. Nmr spectra were recorded on a Varian T-60 spectrometer relative to internal standard tetramethylsilane. Mass spectra were obtained on a Varian Model CH-5 spectrometer (6). Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

4-(*p*-Trifluoromethylphenyl)-2,4,6-triphenylthiopyran (**6a**).

In a 500-ml. flask equipped with a magnetic stirring bar, a reflux condenser, and a rubber septum were placed 4.24 g. (10 mmoles) of 2,4,6-triphenylthiopyrylium perchlorate (7), **3a**, and 90 ml. of dry ether. The mixture was stirred under nitrogen at -10° for $\frac{1}{2}$ hour, then 6.0 ml. of 0.8 *M* (48 mmoles) ethereal *p*-trifluoromethylphenyllithium (8), **4**, was added through the septum cap. A rapid reaction was indicated by the disappearance of the thiopyrylium salt and the formation of a purple, ether soluble, intermediate (9). After about 15 minutes, the solution was quenched with 70 ml. of aqueous ammonium chloride and allowed to stir for 10 hours. At the end of this period the color had faded to orange. The resulting orange solution was washed with water, dried over sodium carbonate and evaporated to leave a dark orange oily residue. On standing for a few days, the residue gradually changed to solid crystals. Recrystallization from ethanol gave 2.85 g. (61%) of **6a** as yellowish-white crystals, m.p. $107-108^\circ$; ir: 3025, 1600, 1315, 832, 768, 760, 742, 693, 687 cm^{-1} ; uv λ max (methanol): nm (log ϵ) 235 (4.72), 215

(4.65); nmr (carbon tetrachloride): δ 6.1 (s, 2H, β -protons of thiopyran ring), 7.2-7.7 (m, 19H, ArH); mass spectrum: *m/e* (relative intensity) 472 (9.66, P+2), 471 (34.29, P+1), 470 (100, P), 469 (6.76), 395 (8.69), 394 (25.12), 393 (57.97), 327 (6.28), 326 (20.29), 325 (68.60), 316 (5.35), 247 (11.11), 165 (13.04), 121 (22.22), 77 (5.35).

Anal. Calcd. for $\text{C}_{30}\text{H}_{21}\text{F}_3\text{S}$: C, 76.60; H, 4.47; F, 12.12; S, 6.81. Found: C, 76.55; H, 4.51; F, 11.94; S, 6.78.

4-(*p*-Trifluoromethylphenyl)-2,4,6-tris(*p*-methoxyphenyl)thiopyran (**6b**).

The procedure was the same as that described for **6a**, except that the stirring time for changing the purple color to orange was 3 hours. Thus 5.14 g. (10 mmoles) of 2,4,6-tris(*p*-methoxyphenyl)thiopyrylium perchlorate (7), **3b**, gave 3.14 g. (56%) of white crystals of **6b**, m.p. $138-139^\circ$; ir: 3000, 2840, 1600, 1495, 1320, 1235, 825, 807 cm^{-1} ; uv λ max (methanol): nm (log ϵ) 258 (4.73), 212 (4.72); nmr (carbon tetrachloride): δ 3.75 (s, 9H, OCH_3), 5.95 (s, 2H, β -protons of thiopyran ring), 6.64-7.64 (m, 16H, ArH); mass spectrum: *m/e* (relative intensity) 562 (11.88, P+2), 561 (37.76, P+1), 560 (100, P), 559 (6.99), 530 (5.59), 454 (4.19), 453 (11.18), 452 (34.96), 421 (13.07), 416 (4.19), 415 (11.88), 414 (38.46), 409 (6.99), 394 (6.99), 371 (5.59), 264 (9.09), 249 (5.59), 226 (6.99), 152 (4.89), 151 (13.98).

Anal. Calcd. for $\text{C}_{33}\text{H}_{27}\text{F}_3\text{O}_3\text{S}$: C, 70.71; H, 4.82; F, 10.18; S, 5.72. Found: C, 70.62; H, 4.88; F, 10.08; S, 5.80.

4-(*p*-Trifluoromethylphenyl)-2,4,6-tris(*p*-dimethylaminophenyl)thiopyran (**6c**).

The procedure described for **6a** was followed with 5.53 g. (10 mmoles) of 2,4,6-tris(*p*-dimethylaminophenyl)thiopyrylium perchlorate (7), **3c**, and 700 ml. of dry ether at room temperature. The required time for changing the deep purple color of the intermediate was 10 minutes. Since the resulting brown oily residue showed no sign of crystallization, it was subjected to column chromatography on alumina. A diffuse pale yellow band was eluted with ether-petroleum ether (20:80). Evaporation of the solvent and recrystallization from ethanol yielded 1.82 g. (31%) of **6c** as greenish-white crystals, m.p. $147-148^\circ$; ir: 3000, 2835, 1605, 1505, 1320, 1220, 1160, 815, 800 cm^{-1} ; uv λ max (methanol): nm (log ϵ) 292 (4.84), 211 (4.82); nmr (deuteriochloroform): δ 2.94 (s, 18H, NCH_3), 6.07 (s, 2H, β -protons of thiopyran ring), 6.5-7.6 (m, 16H, ArH); mass spectrum: *m/e* (relative intensity) 601 (12.38, P+2), 600 (41.85, P+1), 599 (100, P), 598 (9.52), 567 (4.76), 566 (5.95), 555 (3.57), 479 (7.14), 456 (2.38), 455 (4.76), 454 (9.52), 447 (9.52), 435 (2.38), 416 (3.57), 316 (4.76), 276 (3.57), 275 (7.14), 274 (4.76), 252 (5.95), 181 (5.95), 164 (4.76), 150 (17.85), 137 (15.47), 121 (4.76), 110 (4.78), 108 (4.80), 96 (8.14), 94 (5.95), 91 (8.33), 77 (5.95), 69 (5.60), 67 (9.52), 57 (10.71), 55 (9.54), 45 (11.90), 44 (15.47), 43 (16.66).

Anal. Calcd. for $\text{C}_{36}\text{H}_{36}\text{F}_3\text{N}_3\text{S}$: C, 72.12; H, 6.01; N, 7.01; F, 9.52; S, 5.34. Found: C, 72.14; H, 5.97; N, 6.96; F, 9.38; S, 5.38.

Acknowledgment.

The support of this research by a grant from the research committee of the University of Tehran is gratefully acknowledged.

REFERENCES AND NOTES

- 1) J. Stackhouse, B. E. Maryanoff, G. H. Senkler, Jr., and K. Mislow, *J. Am. Chem. Soc.*, **96**, 5650 (1974); A. G. Hortmann, R. L. Harris, and J. A. Miles, *ibid.*, **96**, 6119 (1974).

- (2) B. E. Maryanoff, J. Stackhouse, G. H. Senkler, Jr., and K. Mislow, *ibid.*, **97**, 2718 (1975).
- (3) G. Suld and C. C. Price, *ibid.*, **83**, 1770 (1961); *ibid.*, **84**, 2094 (1962).
- (4) T. Parasaran and C. C. Price, *J. Org. Chem.*, **29**, 946 (1964); C. C. Price, J. Follweiler, H. Pirelahi, and M. Siskin, *ibid.*, **36**, 791 (1971); C. C. Price and H. Pirelahi, *ibid.*, **37**, 1718 (1972).
- (5) H. Pirelahi, Y. Abdoh, F. Hadjmirsadeghi, and H. Sagheri-chi, *J. Heterocyclic Chem.*, **13**, 237 (1976); F. Ogura, W. D. Hounshell, C. A. Maryanoff, W. J. Richter, and K. Mislow, *J. Am. Chem. Soc.*, **98**, 3615 (1976).
- (6) We are grateful to our colleagues at Aryamehr University for determination of the mass spectra.
- (7) R. Wizinger and P. Ulrich, *Helv. Chim. Acta*, **39**, 207 (1956).
- (8) B. M. Trost and H. C. Arndt, *J. Am. Chem. Soc.*, **95**, 5288 (1973).
- (9) Attempts to isolate a pure sample of **5a** failed.