

The Effect of Electron Donating Groups on the Stability of Thiabenzene

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1-(*p*-Methoxyphenyl)-2,4,6-triphenylthiabenzenes (X) has been synthesized and shown to be more stable than the 1-phenyl analog. 1-Phenyl-2,4,6-tri(*p*-methoxyphenyl)thiabenzenes (XVI) was not stable enough to be isolated in pure form and rearranged readily to the isomeric 2- and 4-thiopyrans. Only the pure 4-phenyl-2,4,6-tri(*p*-methoxyphenyl)thiopyran (XVIII) could be isolated.

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It is clear that the valence electrons of sulfur do participate in conjugation in the thiabenzene ring; however, the extent of conjugation and the exact electronic configuration of the sulfur is still open to debate and, most important, to experiment (1,2).

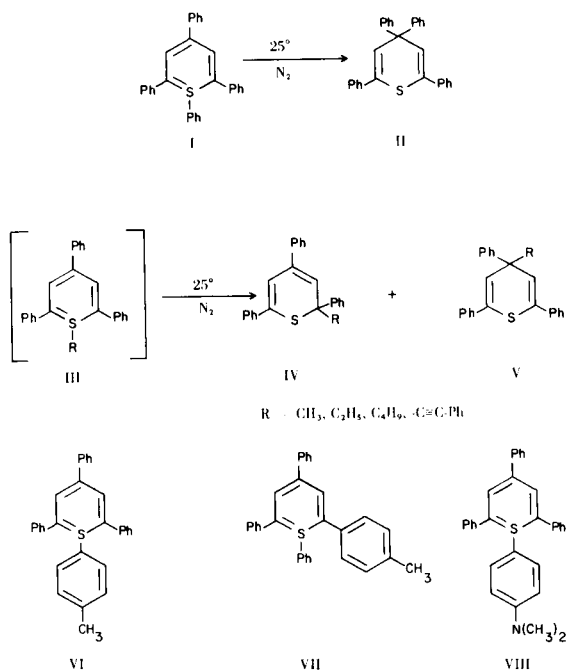
The first thiabenzene prepared, 1,2,4,6-tetraphenyl derivative (I), was an amorphous purple compound, which rearranged to its 4-thiopyran isomer (II) under nitrogen at room temperature and reacted readily with oxygen (3). Attempts to isolate the 1-phenylethynyl- and 1-alkyl-2,4,6-triphenylthiabenzene (III) were unsuccessful and the 2- and 4-isomeric thiopyrans (IV,V) were obtained (1,4).

Although the methyl homologs of 1,2,4,6-tetraphenylthiabenzenes, VI and VII, did not show a significant

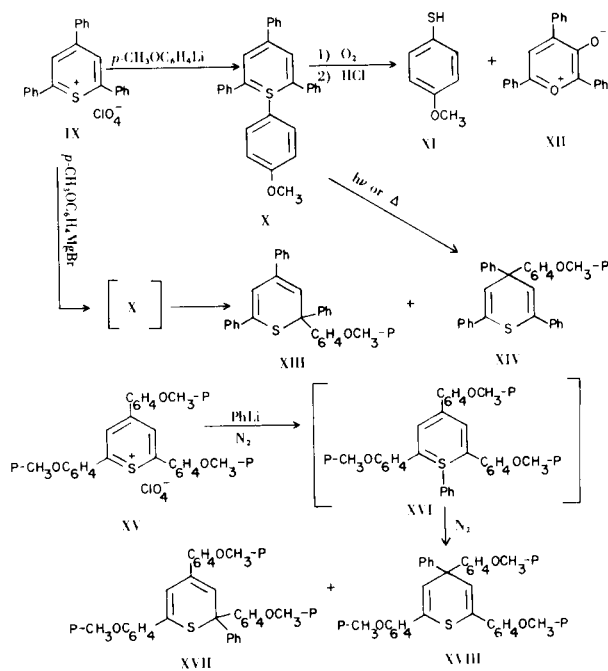
difference in chemical properties, the *p*-dimethylamino analog, VIII, proved to have more stability and was the first thiabenzene to give a crystalline X-ray powder diagram (1,5).

In order to study the effect of electron donating groups further, we have now attempted to prepare two new thiabenzene. Treatment of 2,4,6-triphenylthiopyrylium perchlorate (IX) with 3.8 molar equivalents of *p*-methoxyphenyllithium in dry ether under nitrogen in darkness at -60° afforded a purple solution, from which the 1-(*p*-methoxyphenyl)-2,4,6-triphenylthiabenzenes (X) could be isolated. X-ray powder pattern of X showed an amorphous nature. Unlike thiabenzene VIII which cleaved mainly to give the *p*-dimethylaminophenylmercaptide cation on ionization in the mass spectrometer (1), the fragmentation of X occurred principally at S-phenyl ring, producing the *p*-methoxyphenyl cation as the major peak in the spectrum.

An ethereal solution of X was allowed to react with oxygen for one hour and then with dry hydrogen chloride. The resulting mixture gave *p*-methoxythiophenol (XI) and 2,4,6-triphenyl-3-oxypyrylium zwitterion (XII). In keeping the solid sample of X in a refrigerator, under nitrogen, no change was observed after a few months. On exposing the ethereal solution of X to daylight under nitrogen for one month, the purple color changed to dark-orange and a mixture of 2- and 4-(*p*-methoxyphenyl)-2,4,6-triphenylthiopyran, XIII and XIV, was isolated. A solution of X in benzene was refluxed in an atmosphere of nitrogen. The same 2- and 4-isomeric thiopyrans (XIII and XIV) were afforded. These thiopyrans could also be separated by treatment of an ethereal solution of IX with 3.8 molar equivalents of *p*-methoxyphenylmagnesium bromide under nitrogen at 0° . In this case only a temporary purple color was observed, indicating at least some X may have been formed.



When 2,4,6-tri(*p*-methoxyphenyl)thiopyrylium perchlorate (XV) was treated with 4.8 molar equivalents of phenyllithium in dry ether under nitrogen in darkness at -60° , a purple solution was formed. Attempts to separate any pure sample of 1-phenyl-2,4,6-tri(*p*-methoxyphenyl)thiabenzene (XVI) from the purple solution by the methods used for the other thiabenzene failed. After a few hours the color of the solution turned from purple to dark-orange and afforded a mixture of 2- and 4-phenyl-2,4,6-tri(*p*-methoxyphenyl)thiopyran, XVII and XVIII, from which the 4-isomer XVIII could be isolated.



Comparison of the oxidation and the rearrangement properties of X with those of I (3) and VIII (1,5) reveal that the *p*-methoxy group attached to *S*-phenyl ring stabilizes the thiabenzene, but it is less effective than *p*-dimethylamino group. However, the instability of thiabenzene XVI indicates that the *p*-methoxy group on phenyls attached to sulfur ring decreases the stability of thiabenzene.

EXPERIMENTAL

All melting points were determined using a Gallenkamp melting apparatus and are uncorrected. Uv spectra were recorded on a Varian Techtron uv-visible spectrophotometer Model 635. Ir spectra were obtained in potassium bromide pellets using a Beckman IR-5A spectrophotometer. Nmr spectra were determined on a Varian T-60 spectrometer with tetramethylsilane as internal reference. Mass spectra were measured on a Varian Model CH-5 spectrometer (6).

1-(*p*-Methoxyphenyl)-2,4,6-triphenylthiabenzene (X).

To a yellow suspension of 4.15 g. (10 mmoles) of 2,4,6-tri-

phenylthiopyrylium perchlorate (7) in 80 ml. of dry ether, 60 ml. of 0.63 *M*. (38 mmoles) ethereal *p*-methoxyphenyllithium (8) was added at -60° under a nitrogen atmosphere, in the dark, over a five-minute period. An immediate reaction was indicated by formation of a deeply colored purple product. After five minutes of stirring at -60° , the mixture was warmed to 0° for ten minutes, quenched with 75 ml. of cold saturated aqueous ammonium chloride solution. The organic layer was removed under nitrogen, washed with ice-water, dried over potassium carbonate and evaporated. The purple oily residue was dissolved in 20 ml. of cold ether and poured into 250 ml. of petroleum ether (b.p. $30-60^\circ$) cooled in a dry ice-acetone bath. Filtration removed some purple-brown impurity. The solution was allowed to stand at -60° . The purple solid formed was collected by filtration. Recipitation of the solid gave 1.25 g. (29%) of purple 1-(*p*-methoxyphenyl)-2,4,6-triphenylthiabenzene, m.p. $74-76^\circ$; uv λ max (cyclohexane) nm (log ϵ): 232 (4.5), 305 (4.2), 355 (3.7), 530 (3.7); ir: 3030, 2900, 1575, 1480, 1238, 690-880 cm^{-1} ; nmr (carbon tetrachloride): δ 3.8 (s, 3H, OCH₃), 6.8-7.8 (m, 21H, ArH); mass spectrum (at 90° , 70 eV): *m/e* (relative intensity) 432(1.5), 355(1.2), 325(1.5), 293(1.0), 216(72), 192(16), 191(45), 189(16), 165(9), 139(17), 126(1.5), 125(3.5), 110(4.5), 107(100, C₇H₇O); The observed ratio of parent peak to P+1 and P+2 (100:33.3:10.5) is very close to calculated ratio for C₃₀H₂₄OS (100:33.2:9.9); X-ray powder pattern (vacuum-sealed capillary, copper K α , Ni filter, 40 kV, 5 mA, 8 hours) showed an amorphous nature.

Anal. Calcd. for C₃₀H₂₄OS: C, 83.33; H, 5.56; S, 7.41. Found: C, 83.18; H, 5.52; S, 7.30.

Oxidation of X with Oxygen and Hydrogen Chloride.

The procedure for oxidation of I was utilized (3), using 4.15 g. of 2,4,6-triphenylthiopyrylium perchlorate. When oxygen was bubbled through the purple solution of X, a yellow-orange solution was formed in one hour. Hydrogen chloride was then bubbled in for two minutes, precipitating a yellow-orange solid. A strong odor of thiol was immediately evident. The precipitate was recrystallized from acetone-water to give 0.620 g. (26.8%) of XII as dark red needles with bronze sheen, m.p. $191-193^\circ$, lit. (3) m.p. $193.5-195^\circ$; uv λ max (ethanol) nm (log ϵ): 230 (4.17), 270 (4.14), 309 (4.6), 490 (4.47); nmr (deuteriochloroform): δ 7.5 (m, 9H, ArH), 7.8 (m, 3H, ArH), 8.1-8.4 (m, 2H, ArH), 8.7-9.0 (m, 2H, ArH).

The supernatant ether from which XII precipitated was extracted with 5% sodium hydroxide. The extract was acidified with hydrochloric acid and treated with ether. Evaporation of the ether yielded an oil with a disagreeable thiol odor. Treatment with 2,4-dinitrochlorobenzene gave yellow prisms of 2,4-dinitro-4'-methoxydiphenyl sulfide, m.p. $114-116^\circ$, lit. (9) m.p. 115° .

Rearrangement of X.

A. By Light.

An ethereal solution of X was prepared from 4.15 g. of 2,4,6-triphenylthiopyrylium perchlorate as described above. After quenching and washing, the solution was dried over potassium carbonate and allowed to stand under nitrogen on exposure to daylight. The purple color was retained for five days, and turned dark-orange after four weeks. The solvent was removed and the oily residue was placed on an alumina column in benzene and developed with benzene-ether (80:20). The orange fraction was collected. Removal of the solvent and several recrystallizations from ethanol gave 1.52 g. (35%) of orange solid, m.p. $92-98^\circ$.

B. Thermal.

A solution of 0.9 g. (2.1 mmoles) of X in 100 ml. of degassed benzene was refluxed under nitrogen for eight hours. A red-orange solution was formed. The solvent was evaporated and the oily residue was subjected to column chromatography on alumina as above. After several recrystallizations from ethanol, 0.288 g. (32%) of orange solid was obtained, m.p. 85-92°.

C. Grignard Reaction.

The procedure for preparation of the rearrangement products of VIII (5) was utilized, using 4.15 g. of 2,4,6-triphenylthiopyrylium perchlorate and 3.8 equivalents of *p*-methoxyphenylmagnesium bromide (10) in ether at 0°. The resulting purple color turned orange when stirred overnight. Washing, drying, and evaporation left a dark-orange oily residue which was placed on an alumina column in benzene. A diffuse orange band was eluted with benzene-ether (80:20). Recrystallizations from ethanol yielded 2.6 g. (60%) of orange solid, m.p. 95-102°.

All spectroscopic data are consistent with a mixture of 2- and 4-(*p*-methoxyphenyl)2,4,6-triphenylthiopyran (XIII and XIV); uv λ max (ethanol) nm (log ϵ): (A), 390 (2.7), 260 (4.3) shoulder, 235 (4.4); (B), 390 (2.9), 260 (4.3) shoulder, 235 (4.5); (C), 390 (3.2), 260 (4.5) shoulder, 235 (4.6); the two absorptions at 390 and 260 are characteristic of 2-thiopyrans and the one at 235 nm is characteristic of 4-thiopyrans (11); the difference in intensities could be due to the amount of isomers in the mixture; ir: 3020-3050, 2850, 1570, 1460, 1228, 690-880 cm^{-1} ; the ir spectra of all three samples were compatible. The nmr spectra (deuteriochloroform) of three samples were essentially identical: δ 3.8 (slightly broad singlet, 3H, OCH₃), 6.0, 6.2, 6.6 (s, 2H, β -protons of thiopyran rings), 6.8-7.8 (m, 19H, ArH); the three singlets at δ 6.0, 6.2, and 6.6 are characteristic of 2- and 4-thiopyrans (11). The mass spectra (at 170°, 70 eV) showed: *m/e* (relative intensity) 432(9), 355(10), 325(12), 293(20), 278(22), 231(15), 216(11), 192(5), 191(6), 189(2), 165(9), 139(100), 126(16), 125(18), 122(18), 110(4), 107(3), 105(8); isotopic analyses for all three samples are in good agreement with theoretical values for C₃₀H₂₄O₃S (100:33.3:10; Calcd., 100:33.2:9.9).

Anal. Calcd. for C₃₀H₂₄O₃S: C, 83.33; H, 5.56; S, 7.41. Found: C, 83.25; H, 5.60; S, 7.54.

4-Phenyl-2,4,6-tri(*p*-methoxyphenyl)thiopyran (XVIII).

To a red-orange suspension of 5.125 g. (10 mmoles) of 2,4,6-tri(*p*-methoxyphenyl)thiopyrylium perchlorate (7) in 120 ml. of dry ether was added dropwise, under nitrogen at -20°, 60 ml. of 0.8 M. (48 mmoles) ethereal phenyllithium (12). A rapid reaction was indicated by formation of a purple, ether-soluble intermediate. Stirring was continued for six hours (13). After the end of this period the color of the solution had changed to orange. The reaction mixture was quenched with 200 ml. of aqueous ammonium chloride solution. The ether layer was dried over potassium carbonate. After removal of ether an orange residual oil was obtained which was placed on an alumina column in benzene and developed with benzene-ether (70:30). The first, colorless fraction was collected. Evaporation of the solvent and two recrystallizations from ethanol furnished 1.3 g. (26.5%) of 4-phenyl-2,4,6-tri(*p*-methoxyphenyl)thiopyran (XVIII) as bluish-white needles, m.p. 128-129°; uv λ max (ethanol) nm (log ϵ): 257 (4.62); ir: 3000, 2830, 1590, 1550, 1492, 1238, 830, 780, 755, 692 cm^{-1} ; nmr (carbontetrachloride): δ 3.65 (s, 9H, OCH₃),

6.0 (s, 2H, β -protons of thiopyran ring), 6.7-7.6 (m, 17H, ArH); mass spectrum (at 100°, 70 eV): *m/e* (relative intensity) 494(9.26), 493(30.0), 492(83.33), 416(13), 415(37), 384(11), 383(37), 226(14), 216(11), 201(13), 200(35), 199(11), 186(31), 167(26), 155(35), 154(30), 153(46), 122(17), 108(11), 18(100); isotope abundances is in good agreement with the theoretical one for C₃₂H₂₈O₃S (100:36.0:11.11; Calcd., 100:35.92:10.99).

Anal. Calcd. for C₃₂H₂₈O₃S: C, 78.05; H, 5.69; S, 6.50. Found: C, 78.17; H, 5.61; S, 6.36.

A slower, orange fraction was also collected. Removal of the solvent and three recrystallizations from ethanol yielded 2.0 g. (40.6%) of orange solid, m.p. 159-164°; uv λ max (ethanol) nm (log ϵ): 417 (3.9), 283 (4.42), 257 (4.18); ir: 3000, 2825, 1590, 1555, 1492, 1235, 830, 802, 752, 685 cm^{-1} ; nmr (deuteriochloroform): δ 3.65 (slightly broad singlet, 9H, OCH₃), 5.8, 6.0, 6.6 (s, 2H, β -protons of thiopyran rings), 6.7-7.6 (m, 17H, ArH); mass spectrum was essentially same as pure 4-isomer XVIII. Two additional singlets in the nmr at δ 5.8 and 6.6, and also two additional absorptions in the uv at 283 and 417 nm reveal that the orange solid is a mixture of 2- and 4-phenyl-2,4,6-tri(*p*-methoxyphenyl)thiopyran (XVII and XVIII). Attempts to separate the 2-isomer from the mixture by thin layer chromatography on alumina or silica gel were unsuccessful.

Anal. Calcd. for C₃₂H₂₈O₃S: C, 78.05; H, 5.69; S, 6.50. Found: C, 78.22; H, 5.73; S, 6.61.

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- (13) The reaction was repeated in the dark at -60°. Attempts to separate any pure sample of XVI by the methods used for other thiabenzenes failed. The ultraviolet spectrum of purple solution showed two absorptions at 527 and 232 nm with two shoulders at 350 and 305 nm.