Thiabenzenes. VII. Preparation and Properties of Some Substituted Thiabenzenes[1]

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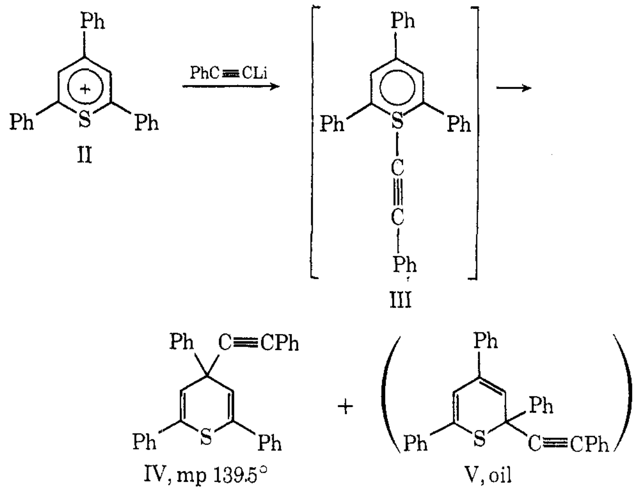
2,4,6-Triphenylthiopyrylium perchlorate coupled with phenylethynyllithium at carbon to give a mixture of 2- and 4-phenylethynyl-2,4,6-triphenylthiopyran rather than at sulfur to give the thiabenzene. 1-*p*-Tolyl-2,4,6-triphenyl- and 2-*p*-tolyl-1,4,6-triphenylthiabenzene have been prepared and shown to be distinct isomeric compounds which do not rapidly exchange the 1- and 2-aryl groups. 1-(*p*-Dimethylaminophenyl)-2,4,6-triphenylthiabenzene is more stable than the 1-phenyl and 1-tolyl analogs and is the first thiabenzene to give a crystalline X-ray powder diagram. Contrary to major fragmentation at the *S*-aryl bond for three other thiabenzenes on ionization in the mass spectrometer, the *p*-dimethylamino analog cleaved mainly to give the *p*-dimethylaminophenylmercaptide cation.

We wish here to report on further experiments to test hypotheses advanced[2] to explain the remarkable properties of the thiabenzenes and the altered color and stability of the hindered thiabenzene, 1,2,4,6-tetraphenylthiabenzene (I).

Efforts to make an ethynyl analog of I were prompted by the hypothesis that hindrance at the 1 position is largely responsible for the thermal, photo, and oxygen sensitivity of I. Furthermore, to date the only stable thiabenzenes isolated and identified have a phenyl group attached to sulfur.[3] We have therefore attempted to prepare an analog of I, introducing an ethynyl group between sulfur and the 1-phenyl with the expectation that this would relieve steric hindrance.[4] The desired thiabenzene III was not isolated although it may have been an intermediate on the path to the two thiopyrans (IV and V) obtained.[5]



II

III

IV, mp 139.5°

V, oil

The structure of IV was confirmed by its uv spectrum, λ_{max} (log ϵ) 240 nm (4.77), and by its nmr spectrum, δ 6.0 (s, 2 H) and 7–8 ppm (20 H), in agreement with values reported for 2,4,4,6-substituted thiopyrans.[5,6] While pure V was not isolated, the content of V in crude product was estimated from the nmr singlets appearing at δ 5.9 and 6.8 ppm[6] in an intensity indicating that the crude product contained an ~7:4 ratio of IV and V. The structure assigned to IV was further supported by its conversion to the sulfone, mp 151°, a characteristic of 2,4,4,6- but *not* 2,2,4,6-tetrasubstituted thiopyrans.[5]

We remain without an adequate explanation of the remarkable difference in coupling of thiopyrylium salts to various metal alkyls, but it does appear that phenylethynyllithium resembles alkyllithiums rather than aryllithiums in this regard.

Observations recorded earlier[7] indicated that the rearrangement of I to a mixture of thiopyrans could be reversible in sunlight. We have now carried out experiments to see whether such a rearrangement was so labile a process that phenyl groups on sulfur and carbon could be rapidly exchanged. This was accomplished by making the isomeric methyl homologs, VI and XI.

Like I, VI and XI are purple amorphous solids, with slightly higher softening points. Like I, they rearrange at room temperature, especially when exposed to light, to give mixtures of thiopyrans from which the crystalline 2,4,4,6 isomers, VII and XII, were isolated and characterized. The nmr and uv spectra are especially useful in identifying their structure. Like I, VI and XI are both rapidly decolorized by oxygen in ether solution. These solutions on treatment with ethereal hydrogen chloride liberate aryl mercaptan (VIII and XIII) and the oxypyrylium zwitterions (IX and XIV). These observations indicate that the tolyl and phenyl groups in VI and XI are not rapidly exchanged (Scheme I).

Coupling of II with *p*-dimethylaminophenyllithium proved successful and, in fact, produced the thiabenzene, 1-(*p*-dimethylaminophenyl)-2,4,6-triphenylthiabenzene (XV), in much better yields than did phenyl- or tolyllithium.

Like the *S*-phenyl analog, XV is a deep purple compound. Unlike any of its analogs, XV proved to have a beautifully sharp X-ray powder diagram with at least 32 readily discernible rings. As yet, we have not succeeded in growing large enough crystals for single

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[1] From the doctoral dissertation of M. Siskin and the master's thesis of J. Follweiler, University of Pennsylvania, 1968; supported in part by National Science Foundation Grant No. GP 5269.

[2] See C. C. Price and D. M. Follweiler, *J. Org. Chem.*, **34**, 3202 (1969).

[3] A. G. Hortmann and R. L. Harris, *J. Amer. Chem. Soc.*, **92**, 1803 (1970), report the preparation of solutions of 1-methyl-3,5-diphenylthiabenzene.

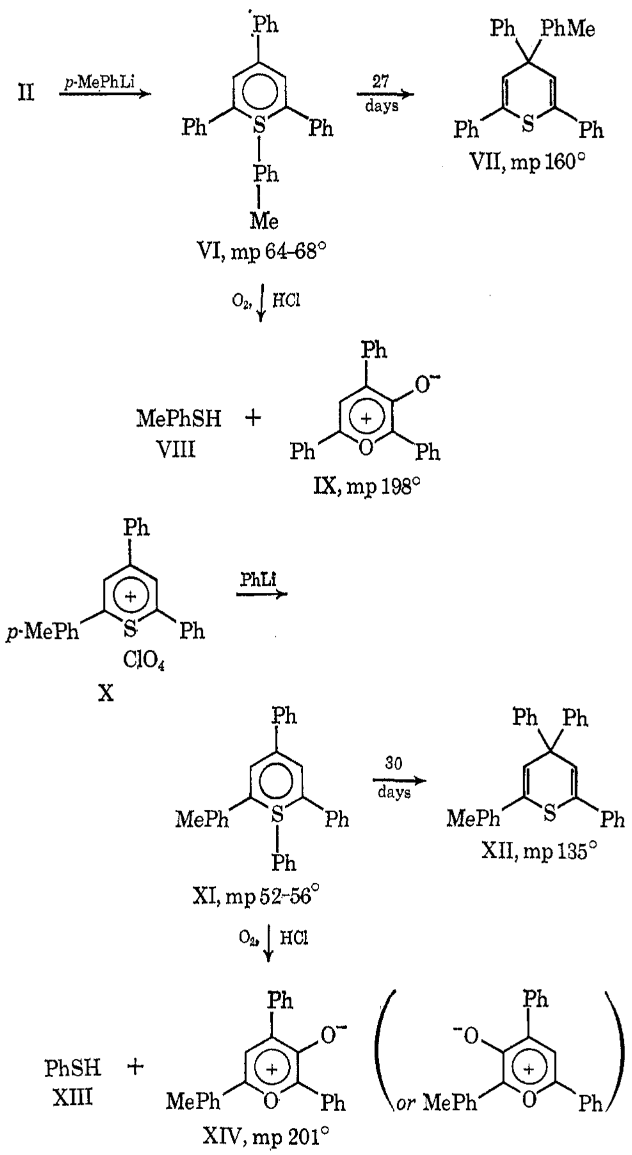
[4] See P. D. Bartlett and L. J. Rosen, *ibid.*, **64**, 543 (1942).

[5] G. Suld and C. C. Price, *ibid.*, **84**, 2090 (1962), have reported that several Grignard reagents and alkyllithiums react with II to give isomeric thiopyrans rather than thiabenzenes, although a transient purple color characteristic of the hindered thiabenzenes suggested that the latter may have been intermediates.

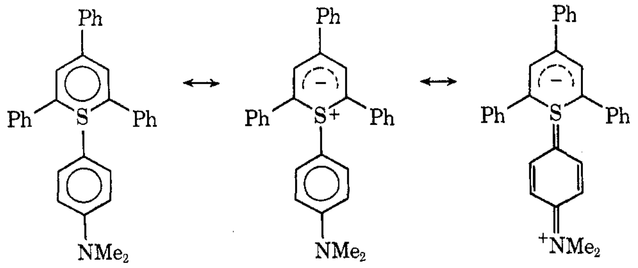
[6] T. Parasaran and C. C. Price, *J. Org. Chem.*, **29**, 946 (1964).

[7] G. Suld, Ph.D. Dissertation, University of Pennsylvania, 1960, reports that solutions of pure crystalline 2,4,4,6-tetraphenylthiopyran, on exposure to sunlight and air, produced 3-oxy-2,4,6-triphenylpyrylium zwitterion and phenyl mercaptan, a characteristic reaction of 1,2,4,6-tetraphenylthiabenzene.

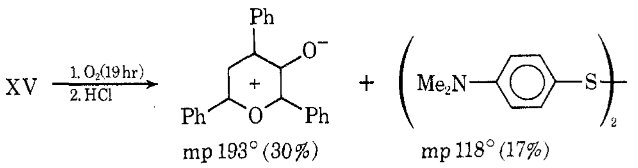
SCHEME I



crystal X-ray structure measurements. The crystallinity is also reflected in a markedly diminished solubility in ether.

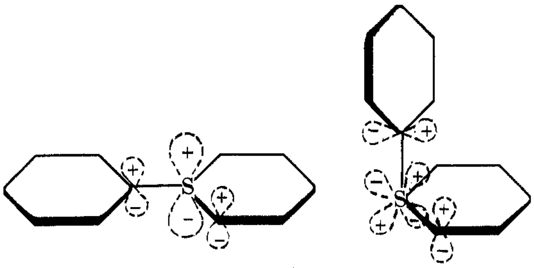

XV, mp 80°(50%) XVa XVb

Enhanced stability for XV, as compared to its S-phenyl analog I, is demonstrated by the much slower rate of reaction of XV with oxygen in ether. Rather than losing its purple color in a few minutes by such treatment, XV requires many hours. When then treated with hydrogen chloride, it did indeed give the same type of decomposition as observed earlier for the simpler analog.



Like the S-phenyl analog, solutions of XV were decolorized on exposure to light. So far, we have not isolated or identified any pure compounds from the gummy mixture of compounds produced. Treatment of XV with HCl in ether also decolorized the solution and addition of aqueous alkali did not regenerate the purple color. These products are being investigated further.

We have earlier proposed that unhindered thiabenzenes have a very low barrier to bending at the S-phenyl bond, with virtually no barrier between conformers XVI and XVII. For each, one can construct a continuous π-molecular orbital, conjugating the aromatic rings through sulfur and permitting a cyclic aromatic ring current in the thiabenzene ring.[8] We suggest that this involves using the $3p_z$ orbital on sulfur for XVI and a single $3d_{xz}$ orbital for XVII. The importance of the through conjugation as represented by XVI and XVII may also be of significance in view of our failure to isolate S-alkylthiabenzenes[5] and the recent report of Hortmann and Harris[3] on the possible nature of an S-methylthiabenzene.


XVI XVII

Since our hypothesis and the higher dipole moment for I than for other thiabenzenes suggest greater ylide character for the bent conformer, and since the positive charge on sulfur in the ylide structure would be stabilized by the p-dimethylamino group in XV, the crystalline nature of XV may indeed be due to a marked preference for the bent conformer, leading to a more rigid geometry. We had also postulated that the characteristic "long tail" absorption out into the visible without a maximum was due to the very low barrier between conformers XVI and XVII.[2] The fact that XV has a strong maximum at 534 nm would also be in accord with a "fixed" conformation and thus a "fixed" excitation energy. The importance of electron donor character for the group attached to sulfur may indeed offer an explanation for our failure to obtain phenylethynylthiabenzene, since the ethynyl group is electrophilic.

The mass spectrum of XV proved to have some significant differences from other analogs. Unfortunately, the thermal instability of I seemed to preclude obtaining mass spectral data for this compound uncomplicated by the isomeric thiopyrans. For comparison, we report the mass spectra of 1-phenylthiabenzene (XVIII),

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[8] This contrasts to the conjugated system proposed by M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969, pp 430–436.

9-phenyl-9-thiaanthracene (XIX), and 9,10-diphenyl-9-thiaanthracene (XX). Fragmentation of the latter three compounds occurs principally at the *S*-phenyl bond, producing the corresponding thiopyrylium ions as major peaks in the spectra.

In contrast, 2,4,6-triphenylthiopyrylium ion was a minor peak in the spectrum of XV. The two major peaks were identified as dimethylaminomercaptide and II less sulfur. Thus both the increased chemical stability and the mass spectral fragmentation indicate a stronger *S*–aryl bond as a result of introducing the *p*-dimethylamino group. This would seem quite reasonable in view of the significant contribution XVb would make to the structure of XV.

One feature of the mass spectra of XVIII, XIX, and XX is the pattern of evidence for ion–molecule reactions. In all three cases, a number of peaks are explicable by reaction of the parent molecule with the major cations observed. For XVIII, three such peaks are diphenyl sulfide, C_5H_5, and biphenyl, all of which could arise from reaction of XVIII with phenyl. For XIX, the peaks at 350, 470, and 546 correspond to reaction of XIX with phenyl, thioxanthyl, and 9-phenylthioxanthyl, respectively. For XX, the peaks at 427, 546, and 623 correspond to reaction of XX with the same three fragments.

Experimental Section

2,4,6-Triphenylthiopyrylium perchlorate (II), mp 121–122°[9] (4.2 g, 9.8 mmol), was stirred in 75 ml of ether under nitrogen while 37 ml of 0.94 *M* phenylethynyllithium[10] was added. The reaction mixture slowly turned a dark brown-green color. After 18 hr the mixture was quenched with 50 ml of saturated aqueous ammonium chloride. The brown ether layer appeared insensitive to oxygen. Washing, drying, and evaporation left a brown oil which was put on an alumina column in hexane. A diffuse green band was eluted with ether–hexane (1:3), which left 2.9 g (69%) of a green oil on evaporation. White crystals of 4-phenylethynyl-2,4,6-triphenylthiopyran (IV) separated from ethanol: mp 139–139.5°; λ_{max} (log ϵ) 240 nm (4.77); nmr ($CDCl_3$) δ 6.1 (s, 2 H), 7.1–7.9 (m, 20 H). Analytical data indicated that some oxidation occurred before combustion.

Anal. Calcd for $C_{31}H_{22}S \cdot {}^1/_4O$: C, 86.46; H, 5.15; S, 7.44; O, 0.93. Found: C, 86.38; H, 4.99; S, 7.53; O, 1.12.

The green oil also showed two additional singlets in the nmr at δ 5.9 and 6.8, characteristic of 2,2,4,6-tetrasubsituted thiopyrans.[6] The ratio of the δ 6.1 to 5.9 and 6.8 peaks was 7:2:2. The same green oil was produced in the same yield when the reaction was carried out in THF.

IV sulfone was prepared from a hot solution of 50 mg of IV in 4 ml of acetic acid to which 6 drops of 70% hydrogen peroxide was added. Addition of 10 ml of water precipitated a white solid which was recrystallized from ethanol to give 30 mg (54.5%) of IV sulfone: mp 150–151°; ir sulfone bands, 1130 and 1295 cm^{-1}.

Anal. Calcd for $C_{31}H_{22}SO_2 \cdot {}^1/_2C_2H_5OH$: C, 79.64; H, 5.43; S, 6.64. Found: C, 79.80; H, 5.31; S, 6.61.

1-*p*-Tolyl-2,4,6-triphenylthiabenzene (VI).—The procedure of Suld[7] was modified by design of a reaction vessel[1] which permitted manipulation with minimum exposure to air. To a stirred suspension of 5.0 g of II under nitrogen was added 35 ml of 1.3 *M* *p*-tolyllithium in ether. An intense purple color developed and the suspended II disappeared. The reaction mixture was quenched with 50 ml of saturated aqueous ammonium chloride, washed with water, and dried over potassium carbonate, all under nitrogen and with minimum exposure to light. The ether solution was added to 50 ml of petroleum ether (bp 30–60°) which had been percolated through alumina and was cooled in a Dry Ice–acetone bath. Filtration removed some white impurity. Evaporation left a purple resin which was redissolved in 30 ml of dry ether which was again added to 150 ml of petroleum ether at −78°. The purple precipitate formed was collected by filtration and vacuum dried to give 1.1 g of VI as a red-violet electrostatic powder: mp 64–68°; λ_{max} (log ϵ) 218 nm (4.49), 296 (4.23) (ether); nmr (CCl_4) δ 2.2 (s, 3 H), 6.6–7.7 (m, 21 H).

When the original ether solution above, after quenching and washing, was allowed to stand under nitrogen for 27 days exposed to daylight, the solution had turned from purple to dark orange. Evaporation and recrystallization from ethanol gave a 35% yield of 4-*p*-tolyl-2,4,6-triphenylthiopyran (VII) as white crystals: mp 158–160°; λ_{max} (log ϵ) 236 nm (4.56); nmr ($CDCl_3$) δ 2.3 (s, 3 H), 6.25 (s, 2 H), 7.2–7.7 (m, 19 H).

Anal. Calcd for $C_{30}H_{24}S$: C, 86.49; H, 5.81; S, 7.70. Found: C, 86.47; H, 5.85; S, 7.53.

When oxygen was bubbled through a purple solution of VI, a clear dark red solution was formed in 12 min. Hydrogen chloride was then bubbled in for 1 min, immediately precipitating an orange solid. Two recrystallizations gave 1 g (31%) of IX as red crystals with a bronze sheen: mp 195–198° (lit.[2] 195°); nmr ($CDCl_3$) δ 7.5 (m, 9 H), 7.8 (m, 3 H), 8.1–8.4 (m, 2 H), 8.7–9.0 (m, 2 H).

The filtrate from the oxidation was washed with 5% NaOH. Acidification of the alkaline extract, extraction with ether, and evaporation left an oil with a disagreeable thiol odor. Treatment with 2,4-dinitrochlorobenzene in ethanol[11] gave yellow crystals of 2,4-dinitro-4′-methyldiphenyl sulfide, mp 99–102° (lit.[11] 103°).

2,4-Diphenyl-6-*p*-tolylthiopyrylium perchlorate (X) was prepared from 2,4-diphenyl-6-*p*-tolylpyrylium perchlorate, mp 224–225° (lit.[12] 224°), by treatment with sodium sulfide in water and then perchloric acid.[9] Three recrystallizations from 2-propanol gave a 50% yield of orange crystals of X: mp 174–175°; λ_{max} (log ϵ) 227 nm (4.20), 243 (4.17) (in CH_3OH); nmr (CF_3COOH) δ 2.5 (s, 3 H), 7.5–8.3 (m, 14 H), 8.9 (s, 2 H).

Anal. Calcd for $C_{23}H_{19}SClO_4$: C, 65.67; H, 4.36; S, 7.30; Cl, 8.07. Found: C, 65.53; H, 4.33; S, 7.14; Cl, 8.08.

2-*p*-Tolyl-1,4,6-triphenylthiabenzene (XI) prepared from X and phenyllithium in ether (as for VI) was a red-violet, electrostatic powder, in 15.7% yield: mp 52–56°; λ_{max} (log ϵ) 233 nm (4.36), 303 (4.10) (ether); nmr (CCl_4) δ 2.25 (s, 3 H), 6.7–7.6 (m, 30 H).

A purple ether solution turned orange after 30 days at room temperature. Recrystallization from ether gave a 19% yield of colorless crystals of XII: mp 134–136°; λ_{max} (log ϵ) 238 nm (4.56) (ethanol); nmr ($CDCl_3$) δ 2.3 (s, 3 H), 6.2 (s, 2 H), 7–7.6 (m, 19 H).

Anal. Calcd for $C_{30}H_{24}S$: C, 86.49; H, 5.81; S, 7.70. Found: C, 86.47; H, 5.93; S, 7.45.

When oxygen and then hydrogen chloride were passed through a purple ethereal solution of XI, a red precipitate formed. It was recrystallized from acetone–water or acetonitrile to give 7.4% of XIV as red crystals with a bronze sheen: mp 198–201°; λ_{max} (log ϵ) 217 nm (4.09), 263 (3.99), 315 (3.85) (ethanol); nmr ($CDCl_3$) δ 2.4 (s, 3 H), 7.2 (d, 1 H), 7.3–7.5 (m, 7 H), 7.7 (s, 1 H), 7.8 (s, 2 H), 8.0–8.3 (m, 2 H), 8.6–8.9 (m, 2 H).

Anal. Calcd for $C_{24}H_{18}O_2 \cdot {}^1/_8H_2O$: C, 84.61; H, 5.41. Found: C, 84.48; H, 5.42.

The filtrate from the oxidation reaction mixture was extracted and treated with 2,4-dinitrochlorobenzene[11] to give yellow crystals of 2,4-dinitrodiphenyl sulfide, mp 117–120° (lit.[11] 121°).

1-(*p*-Dimethylaminophenyl)-2,4,6-triphenylthiabenzene (XV).—A suspension of 6.36 g (15 mmol) of 2,4,6-triphenylthiopyrylium perchlorate[9] in 120 ml of dry ether in the dark under nitrogen at −60° was treated with 57 ml of 1.03 *M* ethereal *p*-dimethylaminophenyllithium[13] (59 mmol) with stirring over a 5-min period. The reaction turned deep purple immediately. After another 5 min of stirring at −60°, the mixture was warmed to 0° for 10 min, quenched with 100 ml of cold saturated aqueous ammonium chloride, and stirred for 2 hr. Filtration gave a deep purple precipitate[14] which was washed thoroughly with distilled water

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[9] R. Wizinger and P. Ulrich, *Helv. Chim. Acta*, **39**, 207 (1956).

[10] H. Gilman and R. Young, *J. Org. Chem.*, **1**, 315 (1936).

[11] S. M. McElvain, "The Characterization of Organic Compounds," MacMillan, New York, N. Y., 1945, pp 277–278.

[12] K. Dimroth, G. Neubauer, and G. Osterloo, *Chem. Ber.*, **90**, 1668 (1957).

[13] R. G. Jones and H. Gilman, "Organic Reactions," Collect. Vol. VI, Wiley, New York, N. Y., 1967, p 353; H, Gilman, E. A. Zoellner, and W. M. Selby, *J. Amer. Chem. Soc.*, **55**, 1252 (1933).

[14] The purple ether layer of the filtrate gave 1.2 g of tan solid when treated with 500 ml of cold petroleum ether. This filtrate, on evaporation and vacuum distillation, gave 2.67 g of *N*,*N*-dimethylaniline, and then vacuum sublimation gave 1.1 g of *p*-bromo-*N*,*N*-dimethylaniline and 650 mg of brown resinous residue.

and dried. Half of this crude product was dissolved in 1.2 l. of dry 0° ether under N_2 in the dark, and 900 ml of −20° petroleum ether (bp 30–60°) was added. After standing 1 hr at −20°, 20 mg of purple-brown solid was removed by filtration. Rotoevaporation of the filtrate at 5–10° in the dark gave, after washing with −30° petroleum ether, 3.35 g (50%) of deep purple shiny microcrystalline 1-(*p*-dimethylaminophenyl)-2,4,6-triphenylthiabenzene: mp 78–80° (changing to orange-brown at 82°); λ_{max} (log ϵ) 231 nm (4.31), 271 (4.40), 311 (4.42), 357 (4.13), and 534 (4.05) (cyclohexane);[15] nmr (CCl_4, 0°) δ 2.9 (s, 6 H), 6.5 (d, J = 8 Hz, 2 H), ~7.3 (m, 19 H); ir (KBr) (% absorbed) 3048 (56), 3020 (56), 2915 (53), 2845 (49), 2800 (45), 1588 (94), 1490 (84), 1440 (88), 1420 (88), 1358 (68), 1249 (81), 1192 (67), 1070 (63), 892 (37), 874 (32), 808 (55), 755 (78), 712 (50), 692 (78), 598 (31), 532 (26), 511 cm^{-1} (27); X-ray powder pattern (vacuum-sealed capillary, chromium K_α, V filter, 40 kV, 20 mA, 16 hr) Å (rel intensity) 10.18 (vs), 9.32 (vs), 7.05 (vw), 6.68 (s), 6.26 (w), 5.72 (m), 5.34 (vs), 5.09 (m), 4.71 (vs), 4.59 (vs), 4.44 (vs), 4.36 (vs), 4.14 (vs), 3.95 (mw), 3.78 (mw), 3.70 (s), 3.56 (w), 3.49 (s), 3.41 (w), 3.23 (mw), 3.14 (m), 3.02 (mw), 2.93 (m), 2.84 (w), 2.77 (mw), 2.68 (w), 2.58 (mw), 2.50 (mw), 2.39 (w), 2.35 (mw), 2.30 (vw), 2.26 (mw).

Anal. Calcd for $C_{31}H_{27}NS$: C, 83.59; H, 6.07; N, 3.15; S, 7.19. Found: C, 83.35; H, 6.17; N, 3.15; S, 7.18.

When oxygen was bubbled through 500 mg of the thiabenzene in 600 ml of ether, the solution was still purple after 3.5 hr, orange after 8.5 hr, and yellow after 19 hr. Hydrogen chloride gave a yellow precipitate which on recrystallization proved to be 2,4,6-triphenyl-3-oxypyrylium zwitterion, 110 mg (30%), mp 191–193° (lit. 193.5–195°), with ir and uv spectra the same as reported earlier. Alkaline extraction of the ethereal mother liquor gave the mercaptan, which oxidized in air[16] to disulfide, recrystallized from ethanol to give bis(*p*-dimethylaminophenyl) disulfide (28 mg, 17%), mp 117–118° (lit.[16] 118°).

The **mass spectra** were carried out on Consolidated Electrodynamics Corp., Model 21-30, or Associated Electrical Industries, Ltd., Model MS-9023, mass spectrometers.

The preparation of the **1-phenylthiabenzene**[17] (**XVIII**) has been described elsewhere: *m/e* (rel intensity) 186 (12), 154 (3), 97 (100) for inlet at 90°; 186 (27), 154 (100), 97 (11) for inlet at 130°, 70 eV.

9-Phenyl-9-thiaanthracene (**XIX**), softening at 123–128°, was prepared from thioxanthylium perchlorate and phenyllithium in 8% yield:[18] *m/e* (rel intensity) 546 (1), 470 (2), 350 (4), 274 (100), 197 (87), 154 (42) for inlet at 150–200°, 70 eV.

9,10-Diphenyl-9-thiaanthracene (**XX**), softening at 142–145°, was obtained in 43% yield from 9-phenylthioxanthylium perchlorate and phenyllithium:[18] *m/e* (rel intensity) 623 (10), 546 (20), 426 (10), 350 (39), 273 (93), 197 (100), 154 (31) for inlet at 150–200°, 70 eV.

XV, obtained as described above, had the following mass spectrum: *m/e* (rel intensity) 445 (14), 368 (10), 325 (4), 294 (24), 153 (52), 152 (100) for inlet at 120°; 445 (9), 368 (7), 325 (4), 294 (20), 153 (16), 152 (32) for inlet at 90°, 50 eV. Using the Hitachi Perkin-Elmer RMH-2 mass spectrometer with biphenyl as internal standard, the 152 peak was shown to consist of 84% of $Me_2NC_6H_4S$ (*m/e* 152.0537; calcd, 152.05340) and 16% of $C_{12}H_8$ (calcd, 152.06260). The major intensity at *m/e* 153 was found due to $Me_2NC_6H_4SH$ (*m/e* 153.06129; calcd, 153.06123).

Registry No.—IV, 28278-42-4; IV sulfone, 28278-43-5; VI, 28278-44-6; VII, 28278-45-7; X, 28278-46-8; XI, 28278-47-9; XII, 28278-48-0; XIV, 28264-15-5; XV, 28278-49-1.

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(15) G. Suld, Ph.D. Dissertation, University of Pennsylvania, 1960, has reported for 1,2,4,6-tetraphenylthiabenzene λ_{max} 244, 265, 273, 524 (isooctane).

(16) C. S. Argyle and G. M. Dyson, *J. Chem. Soc.*, 1629 (1937).

(17) M. Polk, M. Siskin, and C. C. Price, *J. Amer. Chem. Soc.*, **91**, 1206 (1969).

(18) C. C. Price, M. Hori, T. Parasaran, and M. Polk, *ibid.*, **85**, 2278 (1963).

Thiabenzenes. VIII. One-Electron Reductions and Disproportionations of Thioxanthylium and 9-Phenylthioxanthylium Ion and a Bithiabenzene Analog

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In inert media, thioxanthylium perchlorate (I) is converted by a number of reducing agents, such as zinc, cobaltocene, dithionite, and potassium and phosphonium iodide, to bithioxanthyl (II). The reaction evidently proceeds through one-electron reduction to a free radical (Ia) and oxygen and nitric oxide divert Ia to thioxanthone as the main product. Although 9-phenylthioxanthyl (VIa) was once reported to be a stable free radical, one-electron reduction of 9-phenylthioxanthylium perchlorate (VI) gave a nearly quantitative yield of a pale green oily S–S dimer (VII). On heating, this S–S dimer rearranged to the colorless crystalline C–C dimer, 9,9′-diphenylbithioxanthyl (VIII). Both dimers II and VIII are reconverted to I and VI, respectively, by perchloric acid while with hydrogen peroxide in acetic acid they form the dimeric disulfones. Disproportionation reactions involving I, VI, and the corresponding thioxanthenes (III and XI) can be explained by ready hydranion exchange and by condensation of I and III to form the dimer II.

There have been many reports of the one-electron reductions of aromatic cations, such as tropylium,[3] pyrylium,[4] and pyridinium[5] salts. In a few cases, the free radical initially formed could be isolated as a stable entity,[5b] but more frequently the carbon-to-carbon dimer was the product.

We[6] have reported such a dimer (bithioxanthyl, II) as a by-product in the formation of 9-phenyl-9-thiaanthracene from thioxanthylium perchlorate (I) and phenyllithium. Since II may indeed have resulted from a one-electron reduction of I by phenyllithium,[7,8] we have undertaken a more systematic investigation of the one-

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(1) From the Ph.D. Dissertation of M. Siskin, University of Pennsylvania, 1968, which contains details of infrared and mass spectra.

(2) Supported in part by National Science Foundation, Grant No. GP 5269.

(3) W. v. E. Doering and L. H. Knox, *J. Amer. Chem. Soc.*, **76**, 3206 (1954); **79**, 351 (1957).

(4) A. T. Balaban, C. Bratu, and C. N. Rentea, *Tetrahedron Lett.*, No. 20, 265 (1964).

(5) (a) A. W. Hofmann, *Chem. Ber.*, **14**, 1503 (1881); K. Wallenfels and M. Gellrich, *Justus Liebigs Ann. Chem.*, **621**, 198 (1959). (b) E. M. Kosower and E. J. Poziomek, *J. Amer. Chem. Soc.*, **86**, 5515 (1964); M. Itoh and S. Nagakura, *Tetrahedron Lett.*, 417 (1965).

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