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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Received April 15, 1970

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).

[6] C. C. Price, M. Hori, T. Parasaran, and M. Polk, *J. Amer. Chem. Soc.*, **85**, 2280 (1963).

[7] K. Ziegler and C. Ochs, *Chem. Ber.*, **55**, 2257 (1922), have reported the reduction of 9-phenylxanthylium perchlorate to a stable free radical by phenylmagnesium chloride.

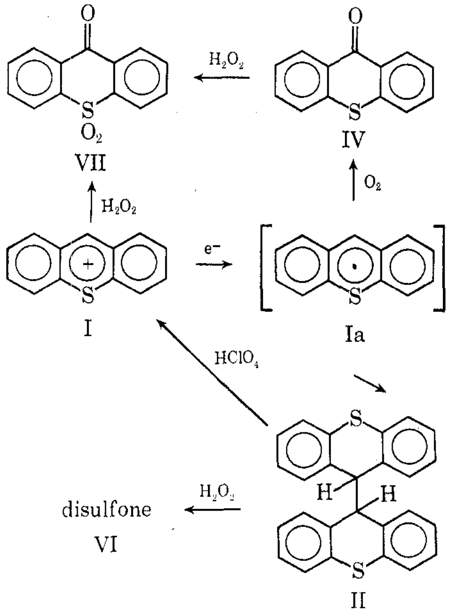
[8] See also C. C. Price and D. M. Follweiler, *J. Org. Chem.*, **34**, 3202 (1969).

electron reduction of thiopyrylium salts. We wish to report here some studies of one-electron reductions of I and its 9-phenyl analog (VI) and some characteristics of the processes and products.

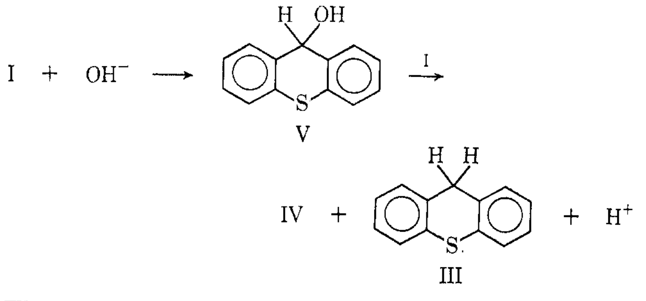
Results

Reductions.—The major conversions observed for thioxanthylium perchlorate (I) are summarized in Scheme I.

SCHEME I



In diglyme solution under nitrogen or *in vacuo*, with zinc dust, sodium dithionite, cobaltocene, or phosphonium iodide, the yields of II were essentially quantitative. With the alkali metals, thioxanthene and thioxanthone were obtained as well, presumably by the following sequence.

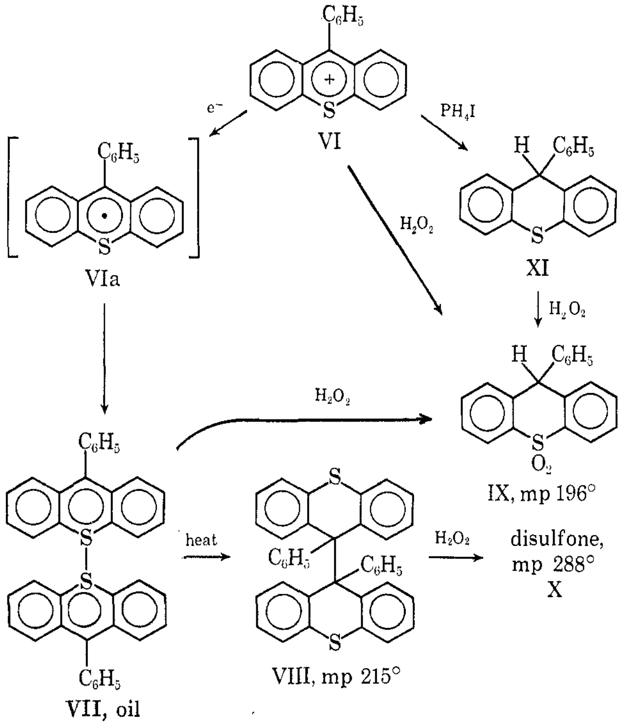


The reaction of I with hydroxyl ion adventitiously present with the alkali metal would give V. Hydranion exchange to I would produce thioxanthene (III) and protonated IV.[9]

Since III was not formed when water was added to a zinc reduction, it may be concluded that the reduction proceeds by one-electron addition to give the radical Ia, rather than by two electrons to form an anion intermediate. Presumably this addition would put an electron in the lowest unfilled anthracene-like orbital of I, a process enhanced in I as compared to anthracene by the formal positive charge in I.

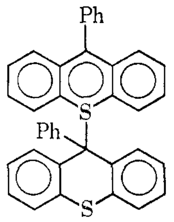
The major conversions observed for 9-phenylthioxanthylium perchlorate (VI) are summarized in Scheme II.

SCHEME II

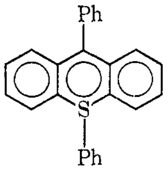


Reduction of VI with sodium dithionite, zinc, or sodium gave a viscous oil, obtained in excellent yield after passing a benzene solution through a neutral alumina column. Molecular weight determination, both by mass spectrometry and cryoscopically, showed the material to be a dimer, rather than the stable triaryl free radical VIa.[10]

The failure of the radical VIa to couple at the 9 position is not so unexpected in view of the added hindrance of the 9-phenyl group as compared to Ia. The sulfur–sulfur coupling would, of course, be much less hindered and indeed the coupling of simple sulfur radicals from oxidation of mercaptans to form disulfide bonds is common. The evidence that the oil is in fact the dimer VII is supported by (1) its molecular weight, (2) its mass spectra, and (3) its failure to give a disulfone (as does IX). We believe the carbon–sulfur dimer XII is excluded since this would be a thiaanthracene analogous to XIII and since XIII and its analogs are deeply colored amorphous solids with softening points above 125°.



XII



XIII

The amorphous nature of thiabenzenes has been ascribed to a very low barrier to bending at the S–C_6H_5

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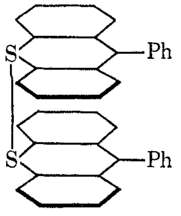
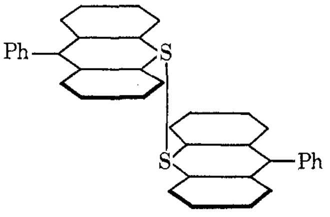
[9] E. K. Fields and S. Meyerson, *J. Org. Chem.*, **30**, 937 (1965), have reported III and IV as the products from treatment of thioxanthylium perbromide with aqueous sodium hydroxide.

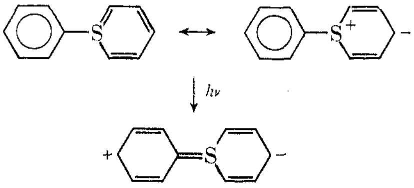
[10] The original claim to have obtained this free radical [W. Schlenk and J. Renning, *Justus Liebigs Ann. Chem.*, **394**, 190 (1912)] was discounted by M. Gomberg and W. Minnis, *J. Amer. Chem. Soc.*, **43**, 1940 (1921).

bond.[6,8] Similar behavior in VII would allow a remarkable degree of flexibility at the S–S bond. We postulated a 180° bending in thiabenzenes, *i.e.*, from orthogonal above to orthogonal below the plane defined by the sulfur ring. In VII this bending may extend another 90° in each direction, permitting a geometry with the two rings parallel, one above the other (VIIa). In addition to freedom of bending at the S–S bond, there is the likely possibility of low barriers to rotation at the S–S bond, as indicated by VIIb.[11] It may be this extreme flexibility which permits this molecule to be an oil at room temperature. Certainly some remarkable and unique structural feature must be invoked to explain how a molecule of this size and structure could exhibit such a property.


VIIa


VIIb

The other surprising feature of this molecule, as compared to *S*-phenylthiabenzenes, is the lack of intense color. One of the possible electronic excitations responsible for the color of thiabenzenes is electron transfer from the phenyl group to a molecular orbital involving increased participation of the vacant orbitals on the sulfur atom. This could be represented as electron transfer from phenyl to the partially positive sulfur atom. In the case of VII, neither ring would serve so readily as an electron donor; so the type of excitation depicted by XIV[12] may not occur in the visible region or may be forbidden.



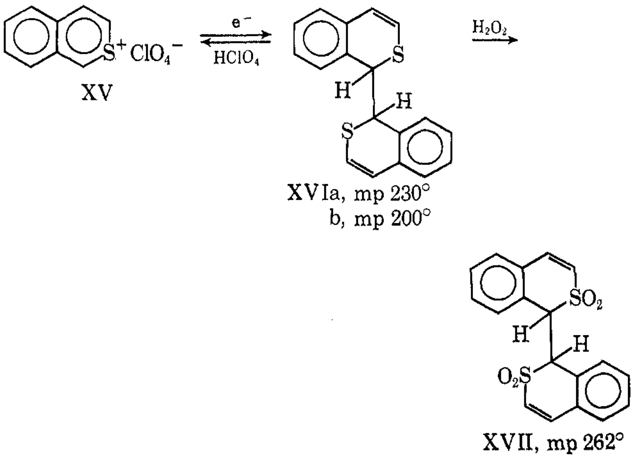
XIV

Although the reduction of I and VI by zinc and dithionite are very similar, there is a remarkable contrast with phosphonium iodide. While this reagent gave II, the one-electron reduction product in 1 min from I, with VI, the reduction to a colorless state required 50 min of reflux in 1-butanol and the product was XI, the result of two-electron reduction. Actually the bright red color of VI rapidly turned to bright yellow, which only slowly faded to colorless. This suggests the possibility that the bright yellow color was due to VIa, which couples only slowly to VI but can be reduced by phosphonium iodide to XI.

The mass spectrum fragmentation patterns of VII and VIII deserve brief comment. Cleavage back to the stable 9-phenylthioxanthylium ion (VI, *m/e* 273) represents the most intense peak for either compound, but the sulfur–sulfur dimer obviously undergoes this cleavage more readily since the parent peak (*m/e* 546) is observed readily at 19.9 eV but not at 70 eV. While the spectra of VII at 19.9 eV and VIII at 70 eV are generally similar, a major difference is the presence of peaks from VII at *m/e* 350 (4.6%), 349 (11.6%), and 348 (25.6%) entirely absent from VIII. These three peaks could be cations related to 9,9-diphenylthioxanthene. One could envision a ready cleavage of conformation VIIa by simultaneous breaking of the S–S bond and phenyl transfer to give thioxanthylium ion (*m/e* 197, 44.5%) and the ions of *m/e* 350 to 348 (total abundance, 41.8%). Another major difference is the peaks at *m/e* 288 (32.1%) and 287 (30.7%) from VII, absent from VIII. These two peaks formally correspond to I plus CH_2 and CH_3. A third difference is the formation of *m/e* 239 (9.3%, 9-phenylfluorenyl cation?) from VIII but not from VII. Both give substantial peaks at *m/e* 165 (fluorenyl cation).

The mass spectrum fragmentation of the disulfone X gave a much more complex pattern perhaps partly due to the fact that simple cleavage of one or two bonds could not produce stable thioxanthylium cations. Symmetrical cleavage to *m/e* 305 (100%) does represent the most prominent ion formed except for *m/e* 44 (384%, CO_2), although this ion less one oxygen (*m/e* 289, 57.4%) and two oxygens (*m/e* 273, 15.4%) is also observed, as well as *m/e* 321 (29.7%) which represents addition of one oxygen. The thioxanthylium ion [*m/e* 197 (17.4%), 196 (26.7%)] is prominent as are a series of small ions which appear to represent analogs of thiopyrylium ion ($C_5H_5S^+$, *m/e* 97, 93%) appearing at *m/e* 111 (54%, $C_6H_5S^+$), 99 (49.7%, $C_5H_7S^+$), 85 (98.2%, $C_4H_5S^+$), 73 (93.4%, $C_3H_5S^+$), 71 (96.5%, $C_3H_3S^+$). There is also a strong peak at *m/e* 64 (94.8%, SO_2) and at 57 (215%) which is the correct mass for the *tert*-butyl cation.

We have also reduced 2-thianaphthalenium perchlorate (XV) by zinc dust, cobaltocene, sodium dithionite, and, coincidentally, *tert*-butylmagnesium chloride.[8] From the first three reducing agents the product isolated was the dimer XVIa (mp 230°), while the Grignard reagent also gave about an equal amount of the diastereoisomer XVIb (mp 200°). We have not determined which isomer is *dl* and which is *meso;* that coupling oc-



XV

XVIa, mp 230°
b, mp 200°

XVII, mp 262°

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[11] As compared to conventional disulfides, RSSR, which have a strongly preferred 90° dihedral angle at the S–S bond, there are in VII no unshared electrons on sulfur in p orbitals, believed to be the major source of the fixed conformation for disulfides and peroxides.

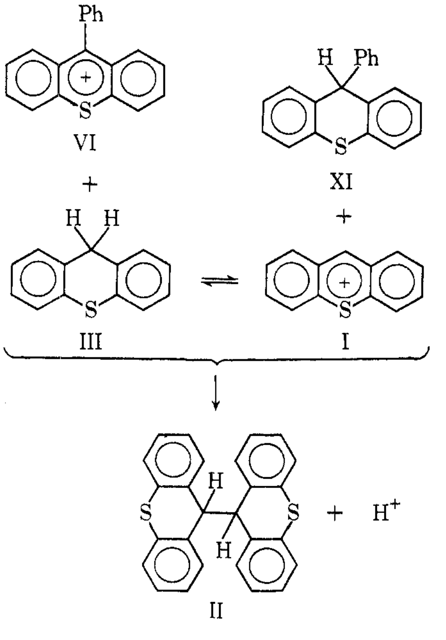
[12] We have found that a methyl or especially a dimethylamino group in the para position of the phenyl ring enhances the stability of 1,2,4,6-tetraphenylthiabenzene: J. Follweiler, M.S. Thesis, Department of Chemistry, University of Pennsylvania, 1968; C. C. Price, J. Follweiler, H. Pirelahi, and M. Siskin, *J. Org. Chem.*, **36**, 791 (1971).

curs at the 1 position is supported by the 2-thiochromene-like uv, ir, and nmr spectra of XVIa and XVIb.

Oxidation of XVIa occurs in good yield by perchloric acid to regenerate XV. With hydrogen peroxide in acetic acid, the product is the disulfone XVII.

Disproportionations.—The ready one-electron[8] and two-electron[6,13] reduction of thiopyrylium salts, as well as extensive studies of reversible one- and two-electron reductions of analogous pyridinium systems,[5,14] has suggested to us the possibility of redox disproportionations between thioxanthenes and thioxanthylium salts. We have therefore studied reactions of the four possible combinations of thioxanthylium (I) and 9-phenylthioxanthylium (IV) ions with thioxanthene (III) and 9-phenylthioxanthene (XI).

The reactions observed in dry diglyme can be summarized in the following reaction scheme.



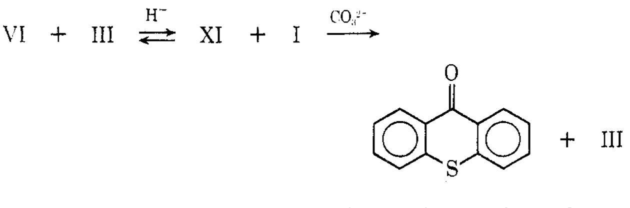
Reactions between I and III, I and XI, or VI and III all produced the bithioxanthyl II and titratable acid was liberated.

For I and III, the disproportionation gave a 27% conversion to II with 80% of III recovered unchanged. When this reaction was not carried out in the dark, the reaction mixture turned black and the yield of II decreased but more III was recovered than added.[15]

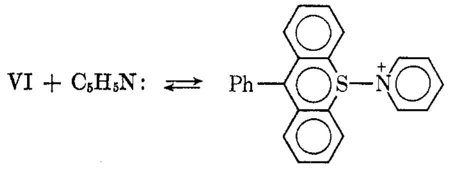
In every case above, the product II crystallized from the reaction mixture and its low solubility may indeed by a major factor pushing the disproportionations. When VI and XI were mixed, no reaction occurred. In this case, one-electron disproportionation would produce a radical (VIa) which undergoes S–S coupling nearly quantitatively to give a soluble, oily dimer. The failure to obtain the dimer of VIa argues against radical intermediates for the generation of II.

The addition of pyridine (to react with perchloric acid produced) did not seem to substantially alter the course of the reaction between I and III although a good yield of pyridinium perchlorate was isolated. However, for the reaction of VI and III, addition of 1 equiv of pyridine blocked disproportionation and led to recovery of reactants.

The use of magnesium carbonate as a base diverted the reaction to a new course, producing from I and III thioxanthone IV and more III than initially added, presumably through the same intermediate thioxanthol as mentioned above for the alkali metal reduction of I. Of somewhat more interest is the formation of thioxanthone from VI and III in the presence of magnesium carbonate. This must involve a prior hydranion transfer.

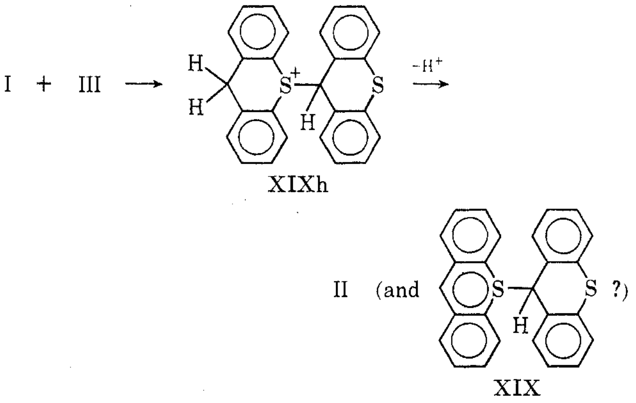


The disproportionation products observed can be accounted for by two types of reaction. One is simply a hydranion exchange such as that between VI and III giving XI and I, or its reverse. The second is the reaction of I with III to give dimer II. The presence of pyridine may block hydranion exchange to VI, by reversibly coupling with II to form the thiaanthracene analog XVIII. It is reasonable to assume that phenyllithium coupling to form thiabenzenes proceeds through analogous coupling of the electronically similar phenyl anion at sulfur of a thiopyrylium salt. Phenyl anion couples to sulfur in VI in much better yield than to I.



XVIII

The failure to isolate any dimer of VIa leads us to propose a nonradical mechanism for the formation of II from I and III. Structures XIX and XIXh are an *S*-alkylthiabenzene and its protonated form, analogous to the *S*-alkylthiabenzene recently reported by Hortmann and Harris[16] to be reversibly protonated. We had earlier evidence[13] that ortho-unsubstituted *S*-alkylthiabenzenes rearranged to isomeric thiopyrans which in this instance would be II. The species XIXh could represent part of the titratable acid observed.



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[13] G. Suld and C. C. Price, *J. Amer. Chem. Soc.*, **84**, 2093 (1962).

[14] See, *e.g.*, N. O. Kaplan, "The Enzymes," Vol. III, Academic Press, New York, N. Y., 1960.

[15] We have not carried out independent tests to see whether, in fact, II is photoreducible to III.

[16] A. G. Hortmann and R. L. Harris, *J. Amer. Chem. Soc.*, **92**, 1803 (1970).

The failure to observe dimeric coupling products from VI and XI or VI and III could be due to enhanced resonance stabilization of the cationic center of VI as well as increased steric hindrance to coupling at the 9 carbon of VI. The failure to observe dimeric coupling products from I and XI could be due to steric restrictions arising from the p^3 geometry at a sulfonium center and an adverse inductive effect from the 9-phenyl group in XI.

The poor yields of dimer II obtained may be due in part to oxidation of II by the perchloric acid formed, since 70% aqueous perchloric acid has been shown to produce an 80% yield of I from II.[8] This cannot be the sole reason for the poor yield of II, however, since the yield of acid formed was consistently greater than that of II. In the reaction mixture of I and III containing pyridine, a quantitative yield of "crude" dimer was obtained, which yielded only 30% of the dimer II. The large loss on recrystallization may be due to our failure to recover the dimer XIX.

Experimental Section

Reduction of I[6] was carried out in diglyme dried by vacuum distillation from calcium hydride or lithium aluminum hydride, either in a vacuum system or under nitrogen. On stirring 1 g of I with 4 equiv of zinc dust for 1 hr, the red color faded and a white precipitate of II formed in quantitative yield. On recrystallization from xylene, it melted at 330-332° (lit.[17] 325°). Addition of 0.2 ml of water gave 91% of II in 45 min. When oxygen was bubbled through the diglyme, no precipitate of II formed. The solvent was removed by vacuum distillation and the yellow residue recrystallized from benzene yielding 207 mg (30%) of thioxanthone (IV), mp 216–218° (lit.[18] 209°). A similar experiment with nitrogen dioxide in place of oxygen gave 53% of IV and no II. With sulfur dioxide, 87% of II and 6% of IV were isolated.

Reduction of 1 g of I with 1 equiv of sodium dithionite in diglyme gave 90% of II in 6 hr; at 60° with 4 equiv, the yield was 96% in 30 min. When 500 mg (1.68 mmol) of I in dry 1-butanol was treated with 550 mg (3.40 mmol) of phosphonium iodide, shiny white crystals of II separated in quantitative yield in 1 min. A 10% solution of cobaltocene in benzene (2 equiv, Aldrich Chemical Co.) was added to 1 g of I in 50 ml of diglyme and stirred for 48 hr giving II in quantitative yield.

Reduction with 1 equiv of alkali metal in diglyme for 4–7 days gave the following yields of II: Li, 9%, Na, 22%; K, 66%.

Oxidation of II (250 mg) was accomplished by heating to 100° in 10 ml of 70% perchloric acid. The dark red solution was rapidly chilled to 0° and poured into 150 ml of ether at 0°, precipitating 277 mg (80%) of I, mp 226–229°.

When 250 mg of II was suspended in 3 ml of acetic acid, heated under reflux, and treated dropwise with 4 ml of 50% H_2O_2, a vigorous reaction occurred. After addition and 30 min of further reflux, cooling, filtration, and recrystallization from acetic acid, II gave 235 mg (82%) of 9,9′-bithioxanthyl disulfone (VI): white plates; mp 416–417°; ir sulfone bands at 1285 and 1155 cm^{-1}; uv (CH_3OH) λ_{max}, nm (log ϵ), 271.5 (4.01), 278.5 (3.95); nmr (CF_3CO_2H) δ 8.2 (d, 2 H), 7.7 (t, 2 H), 7.6 (t, 2 H), 6.7 (d, 2 H, J = 7 Hz), and 5.0 (s, 1 H). *Anal.* Calcd for $C_{26}H_{18}S_2O_4$: C, 68.10; H, 3.96; S, 13.99. Found: C, 68.17; H, 3.89; S, 13.94.

Oxidation of I (500 mg) by hydrogen peroxide in acetic acid in a similar manner gave an immediate change from red to colorless. Addition of water and ether, followed by evaporation of the ether layer and recrystallization from acetic acid, gave 289 mg (81%) of thioxanthone sulfone (VII), white needles, mp 190.5–191.5° (lit.[19] 187°). The same product was obtained by a similar oxidation of thioxanthone (IV, Aldrich).

Oxidation of III in the same manner gave white needles of thioxanthene sulfone (85%) on cooling: mp 169° (lit.[20] 170°); uv (CH_3OH) λ_{max}, nm (log ϵ), 232.5 (3.39), 268 (2.70), 276.5 (2.78).

Reduction of VI[6] (2.00 g) by 1 equiv of sodium dithionite (or zinc dust or sodium) in 100 ml of stirred diglyme was carried out under vacuum. The bright red solution turned dark red in 30 min. After 48 hr the solvent was removed by vacuum, leaving an oily red residue. The organic material was extracted therefrom with benzene and evaporation left a red oil, which was placed neat on a neutral alumina column and eluted with benzene. A green band was washed through the column and evaporation left 1.69 g of pale green oil.[21] This material was homogeneous on silica gel and alumina tlc plates: λ_{max}, nm (log ϵ), 254 (3.98), 267 (4.12), and 370 (2.97) (in acetonitrile and dioxane), 255 (4.04), 270 (4.21), 359 (2.92), and 377 (2.99) (in cyclohexane); nmr broad aromatic multiplet at δ 6.7–7.5 ppm; mol wt, 544 (cryoscopic in benzene). The mass spectrum at 70 eV gave a "parent" peak at 273.0719 (calcd 273.0738).[22] By reducing the ionizing potential to 19.9 eV, the true parent peak of m/e 546 appeared at nearly the same intensity as the 273 peak: mass spectrum (19.9 eV) m/e (rel intensity), 547 (42), 546 (98), 545 (54), 469 (45), 348 (25), 288 (32), 287 (31), 274 (54), 273 (100), 197 (45), 78 (293), 77 (261), 52 (84), 51 (84), 50 (61); mass spectrum (70 eV) 274 (95), 273 (100), 198 (44), 197 (68), 165 (35), 78 (52), 77 (84), 51 (21).

When 1.4 g of VII was heated to 200° (0.04 mm), a violet solid, mp *ca.* 65°, was formed. A benzene eluate from neutral alumina was recrystallized several times slowly from petroleum ether–ethanol to give 61.2 mg of white powder, mp 212–215° and analyzing correctly for VIII: mol wt, 528 (cryoscopic in benzene); uv (CCl_4) λ_{max}, nm (log ϵ), 276 (4.30); mass spectrum (70 eV) m/e (rel intensity) 547 (21) 546 (86), 469 (53), 274 (92), 273 (100), 271 (52), 197 (65), 97 (17), 91 (21), 83 (23), 77 (16), 71 (31), 69 (38), 58 (41), 57 (43), 56 (31), 55 (45). *Anal.* Calcd for $C_{38}H_{26}S_2$: C, 83.48; H, 4.79; S, 11.73. Found: C, 83.22; H, 4.74; S, 11.70.

Reduction of VI (500 mg) in 50 ml of dry 1-butanol by 919 mg of phosphonium iodide turned from red to bright yellow as it was heated to reflux. After refluxing for 50 min, the solution turned colorless. After cooling, the 1-butanol was removed *in vacuo*, leaving white crystals which were dissolved in benzene, washed with water, dried, and evaporated. The residue was recrystallized from methanol to give 9-phenylthioxanthene (XI), white needles, mp 99° (lit.[6] 99°).

Oxidation of VII (195 mg) in 2 ml of acetic acid (wine red on heating) by dropwise addition of 2 ml of 50% H_2O_2 gave a white precipitate which redissolved on refluxing. On cooling to 0°, white crystals separated and were recrystallized from acetic acid to give 123 mg of 9-phenylthioxanthene sulfone (IX): mp 194–196° (lit.[23] 193–194°); uv (CH_3OH) λ_{max}, nm (log ϵ), 270 (3.40) and 277 (3.35); nmr (CF_3CO_2H) δ 8.2 (m, 3 H), 7.4 (m, 10 H), 5.4 (s, 1 H).

Oxidation of VI or XI similarly gave IX in 68 and 55% yields, respectively.

Oxidation of VIII (6.2 mg) suspended in 0.5 ml of boiling acetic acid by dropwise addition of 1 ml of 50% H_2O_2 gave 1.6 mg of disulfone (X): mp 285–288°; ir sulfone bands at 1300 and 1155 cm^{-1}; mass spectrum m/e (at 70 eV) 610.1251 (calcd for $C_{38}H_{26}O_4S_2$, 610.1272),[22] other peaks m/e (rel intensity) 610 (14), 484 (17), 471 (16), 455 (39), 355 (22), 321 (30), 305 (100), 289 (57), 281 (34), 273 (15), 267 (16), 257 (49), 241 (86), 239 (49), 226 (15), 207 (52), 196 (27), 181 (21), 165 (27), 151 (33), 125 (26), 111 (54), 105 (57), 99 (50), 97 (93), 85 (98), 77 (43), 73 (93), 64 (95), 57 (215), 44 (384).

1,1′-Dihydro-2,2′-dithia-1,1′-binaphthyl (XVIa) was prepared by reducing 1.00 g (40 mmol) of 2-thianaphthalenium perchlorate in 75 ml of benzene with 20 ml of 10% cobaltocene (80 mmol, Aldrich Chemical Co.) with stirring under reflux for 4 hr. After cooling the benzene was washed and dried. Evaporation gave colorless needles which, after recrystallization from benzene, weighed 300 mg (50%): mp 230–231°; uv λ_{max} (log ϵ) 241 (4.84), 253 (4.61), and 330 (4.44) nm; nmr δ 7.2–7.4 (m 8 H), 6.9 and 6.3 (d, 2 H each, J = 10 Hz), and 3.8 (s, 2 H).

Anal. Calcd for $C_{18}H_{14}S_2$: C, 73.47; H, 4.76; S, 21.77. Found: C, 73.62; H, 4.90; S, 21.67.

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[17] A. Schonberg and A. Mustafa, *J. Chem. Soc.*, 657 (1945).

[18] E. G. Davis and S. Smiles, *ibid.*, **97**, 1296 (1910).

[19] E. T. Kaiser and D. H. Eargle, Jr., *J. Amer. Chem. Soc.*, **85**, 1821 (1963).

[20] C. Graebe and O. Schultess, *Justus Liebigs Ann. Chem.*, **263**, 8 (1891).

[21] Since the theoretical yield is 1.47 g, this material evidently was not free of residual benzene, also indicated by the relatively strong m/e 78 peaks in the mass spectra at both 19.9 and 70 eV.

[22] Using an Associated Electrical Industries, Ltd., Model MS9023, high resolution mass spectrometer, matching the m/e 273 peak with perfluoro-*n*-butylamine.

[23] M. Gomberg and E. C. Britton, *J. Amer. Chem. Soc.*, **43**, 1946 (1921).

The same isomer (XVIa) was obtained in 50% yield by reduction with 4 equiv of sodium dithionite in acetonitrile at room temperature for 1 hr. In diglyme, the yield was 64% after 3 hr. Stirring with zinc dust (4 equiv) in benzene under nitrogen for 12 hr gave 51% while in diglyme the yield was 68%.

Reaction of XV with *tert*-butylmagnesium chloride has been reported[8] not only to give XVIa in 12% yield, but also the stereoisomer XVIb, mp 199–200°, in 10% yield, with the same uv and nmr spectra.

Anal. Found: C, 73.12; H, 4.60; S, 21.95.

Oxidation of XVIa (100 mg) in 6 ml of 2:1 70% perchloric acid–acetic acid by heating to boiling gave a dark red-green solution which was quickly cooled to 0° and then 20 ml of ether, precooled to −78°, was added slowly to give 136 mg (72%) of dark green crystals of XV, mp 192–195°.

Oxidation of XVIa[8] (339 mg) in 4 ml of boiling acetic acid by dropwise addition of 1 ml of 50% H_2O_2 gave, on cooling, pale yellow crystals. Recrystallization from acetic acid yielded 317 mg (77%) of the disulfone XVII: mp 261–262°; sulfone bands at 1290 and 1112 cm^{-1}; uv λ_{max} (log ϵ) 284 (4.06) nm.

Anal. Calcd for $C_{15}H_{14}S_2O_4$: C, 60.32; H, 3.94; S, 17.86. Found: C, 60.57; H, 4.13; S, 17.90.

Disproportionations.—All disproportionation reactions were carried out under vacuum at 40–50° in diglyme first dried over calcium hydride and then distilled from a 5:1 potassium–sodium alloy into an evacuated flask containing the reactants and a Teflon-coated magnetic stirring bar. Some reactions involving thioxanthene were carried out in the dark to avoid its possible photodimerization.[24]

A solution of 1.00 g of I and 655 mg of III (protected from light) turned red-violet after 5 days. Filtration yielded 355 mg (27%) of II, mp 330–332°, after recrystallization from xylene.[2] Evaporation of the diglyme, benzene extraction of the black residue, benzene elution from a neutral alumina column, and recrystallization from $CHCl_3$–ethanol recovered 534 mg of III, mp 126–128°. Duplicate reactions not protected from light turned black within 3 days and yielded 181 mg (126 mg) of II and 674 mg (818 mg) of III. An aliquot of this reaction mixture (0.500 g, 1.68 mequiv of I, 0.333 g, 1 mequiv of III) was added to distilled water and titrated with 0.01 *N* NaOH, indicating the formation of 1.33 mequiv (79%) of free perchloric acid.

A similar reaction of 500 mg of I and 333 mg of III carried out in the presence of 1 equiv of pyridine (to neutralize perchloric acid formed) gave a pale pink reaction mixture in 4 hr. The white precipitate (670 mg) was collected. The acetone-soluble fraction gave, after addition of benzene, 233 mg (75%) of pyridinium perchlorate: mp 299–300°; uv (MeOH) λ_{max}, nm (log ϵ), 250 (4.69), 255 (4.73), 262 (4.56).

Anal. Calcd for $C_5H_6ClNO_4$: C, 33.42; H, 3.37; N, 7.79. Found: C, 33.66; H, 3.40; N, 7.66.

The acetone-insoluble solid gave 204 mg (30%) of II on recrystallization from xylene.

A solution of 378 mg of I and 600 mg of XI was red-violet after 5 days. Filtration gave 110 mg (45%) of II. Evaporation of the diglyme solvent, extraction with chloroform, charcoal treatment, filtration, evaporation, and recrystallization recovered 230 mg of XI.

A solution of 500 mg of VI and 531 mg of III gave a red-violet solution in 4 days, either in the light or dark. Filtration gave 184–190 mg (69–71%) of II. Vacuum evaporation of solvent, benzene extraction, benzene elution from neutral alumina, evaporation, and recrystallization from methanol gave 307–328 mg (86–93%) of XI, mp 99°. A similar reaction mixture containing 1 equiv of pyridine to neutralize perchloric acid formed gave no reaction; both starting materials were recovered unchanged.

Reaction of 500 mg of I, 330 mg of III, and 71 mg of $MgCO_3$ in diglyme gave a red reaction mixture which faded to a clear pale yellow overnight. After vacuum distillation of the solvent, the residue was placed on a neutral alumina column and eluted with CCl_4 to give 436 mg of III after recrystallization from ethanol, mp 126–128°. Methanol elution gave 250 mg (71%) of thioxanthone after recrystallization from ethanol as pale yellow needles, mp 216–217°.

Reaction of 250 mg of VI, 134 mg of III, and 28.5 mg of $MgCO_3$ turned from red to colorless overnight. Similar work-up gave 293 mg of what appeared to be a mixture of III and XI (by its infrared spectrum) and 59 mg (22%) of thioxanthone, mp 216–218°.

Registry No.—I, 26401-81-0; II, 10496-86-3; VI disulfone, 26430-92-2; VII, 3166-15-2; VIII, 26430-88-6; IX, 26430-89-7; X disulfone, 26430-90-0; XV, 7432-88-4; XVIa, 25548-01-0; XVIb, 26372-65-6; XVII, 26438-45-9; pyridinium perchlorate, 15598-34-2.

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(24) A. Schönberg and A. Mustafa, *J. Chem. Soc.*, 657 (1945).

Chemistry of the Sulfur-Nitrogen Bond. I. Thermal Reactions of Nitrobenzenesulfenanilides[1,2]

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Received July 24, 1970

2-Nitrobenzenesulfenanilides undergo an unusual thermal rearrangement to give *o*- and *p*-amino-2-nitrodiphenyl sulfides, phenothiazines, and 2-aminobenzenesulfonanilides. 3-Nitrobenzenesulfenanilide when heated gave only *o*- and *p*-amino-3-nitrodiphenyl sulfides.

Compounds which contain the sulfur–nitrogen bond are of considerable importance both from a practical as well as theoretical standpoint. Compounds which contain this bond have been reported to be useful as antiradiation drugs, antioxidants, and accelerators in the vulcanization of rubber. Factors which may contribute to the sulfur–nitrogen bond's activity, such as steric interactions, coulombic repulsion between nitrogen and sulfur lone-pair electrons, and p–d π bonding, have only recently been investigated in connection with studies of rotation about the S–N bond.[4]

Moore and Johnson investigated the thermal reactions of arylsulfenanilides.[5] They reported that when 2-nitrobenzenesulfenanilide (**1a**) was heated at 160° in aniline for 6 hr a 70% yield of 4′-amino-2-nitrodiphenylsulfide (**2a**) was obtained.[5a] Similar results were obtained with 2-nitrobenzenesulfen-*p*-toluide (**1b**) which gave 2′-amino-5′-methyl-2-nitrobenzene sulfide (**2b**) on heating in *p*-toluidine.[5a] When **1a** was heated in *p*-to-

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(1) Reported in part at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969.

(2) For a preliminary communication, see F. A. Davis, R. B. Wetzel, T. J. Devon, and J. F. Stackhouse, *Chem. Commun.*, 678 (1970).

(3) National Science Foundation Ungergraduate Research Participant, 1968.

(4) (a) J. M. Lehn and J. Wagner, *Chem. Commun.*, 1298 (1968); (b) M. Raban and F. B. Jones, Jr., *J. Amer. Chem. Soc.*, **91**, 2180 (1969); (c) M. Raban, G. W. J. Kenney, Jr., and F. B. Jones, Jr., *ibid.*, **91**, 6677 (1969).

(5) (a) M. L. Moore and T. B. Johnson, *ibid.*, **57**, 1517 (1935); (b) *ibid.*, **57**, 2234 (1935); (c) *ibid.*, **58**, 1091 (1936); (d) *ibid.*, **58**, 1960 (1936).