We were naturally concerned by the difference in the reported and observed melting points of the *p*-methoxy diphenylacetylene. Hence, we attempted to prepare this material by the method of Orekhoff and Tiffeneau.[33] All attempts resulted in a yellow solid which melted between 60 and 100°, most of it melting at 60°. Attempts to purify this material by recrystallization from a variety of solvents were unsuccessful; g.l.p.c. analysis of the material showed two peaks, one with a retention time identical to the retention time of the product from the reaction of *cis*- and *trans*-IV with potassium *t*-butoxide and the other identical with 1-*p*-methoxyphenyl-2-phenylethylene. Except for a peak at 859 cm.$^{-1}$, every peak in the infrared spectrum could be accounted for by assuming the reaction product was a mixture of the acetylene and 1-*p*-methoxyphenyl-2-phenylethylene.

Product Analysis.—The products from the reaction of potassium *t*-butoxide in *t*-butyl alcohol with all of the starting materials were determined by isolation, spectroscopic analysis and, in some cases, by g.l.p.c. Isolation from each reaction mixture gave between 60 and 70% yields of the pure diarylacetylenes. Spectroscopic analysis indicated that in every case, at least 85% of each of the reactions proceeds by the elimination–rearrangement reaction path. Furthermore, g.l.p.c. analysis of the 1,1-diphenyl-2-bromoethylene reaction mixture showed it to contain no volatile material other than diphenylacetylene and a little unreacted starting material.

Spectra.—Ultraviolet absorption spectra were employed to determine the concentrations of starting materials and products used in the kinetic measurements. All spectra were run in 95% ethanol. Extinction coefficients were determined with a Beckman spectrophotometer, model DU. The extinction coefficients and wave lengths employed were: 1-*p*-methoxyphenyl-2-phenylacetylene, $2.02 \pm 0.007 \times 10^4$ (306 mμ); *trans*-IV, $1.98 \pm 0.015 \times 10^3$ (306 mμ); *cis*-IV, $4.76 \pm 0.03 \times 10^2$ (306 mμ); 1-*p*-chlorophenyl-2-phenylacetylene, $2.58 \pm 0.03 \times 10^4$ (302 mμ); and diphenylacetylene, $2.48 \pm 0.015 \times 10^4$ (296.5 mμ). Neither *cis*- nor *trans*-1-*p*-chlorophenyl-1-phenyl-2-bromoethylene showed any absorption at 302 mμ.

A Varian high-resolution nuclear magnetic resonance spectrometer, model 4300–2, with a field homogeneity control was used to obtain the n.m.r. spectra at a frequency of 60 Mc. Chemical shifts were determined by the side band technique.

The samples were dissolved in carbon tetrachloride containing tetramethylsilane as an internal reference.

The chemical shifts of the vinyl hydrogens are: I, 3.32 τ; *cis*-III, 3.32 τ; *trans*-III, 3.30 τ; *cis*-IV, 3.40 τ; *trans*-IV, 3.43 τ. These are all sharply defined singlets.

Kinetics.—All kinetic studies were run in the presence of a large excess of base (*ca.* 200-fold). All runs of *cis–trans* pairs of olefins were effected with identical base concentrations (approximately 0.20 *M*), thus eliminating differences in the rate constants resulting from the base term inherent in these constants.[6] In all cases a plot of $-\log C_{\text{(ethylene)}}$ *vs.* time gave a straight line representative of a first-order reaction. Values of the specific rate constant were calculated from the slope of the lines by the method of least squares and activation energies were obtained from the data fit of the simple Arrhenius equation, using the method of least squares. Values of ΔH^* and ΔS^* were calculated from the equations $\Delta H^* = E_a - RT$ and $k = \dfrac{RT}{Nh} e^{-\Delta H^*/RT} e^{\Delta S^*/R}$

The temperature used was 119.2°. All the values are included in Table I.

Essentially, the kinetic method described by Pritchard and Bothner-By[6] was used. *t*-Butyl alcohol was purified by refluxing with a small amount of sodium for 1 hr. and then distilling

through a 3-ft. column packed with stainless steel sponge, b.p. 82–82.5°. Standard base was prepared in a nitrogen atmosphere by dissolving potassium metal (cut under white mineral oil and dipped once in dry pentane) in *t*-butyl alcohol. Concentrations of the solutions were determined by titrating aliquots added to water against standard acid. In each run, a weighed amount of 1,1-diaryl-2-bromoethylene was dissolved in 25 ml. of *t*-butyl alcohol. To this was added standard base to give a total volume of 50 ml. Five-ml. samples were then transferred to dry 10-ml. ampoules which had been previously flushed well with nitrogen. The tubes were then sealed, pre-heated for 20 seconds and immediately transferred to a constant temperature silicone oil-bath which was maintained throughout the reactions at temperatures of 95.6, 109.1 and 119.2 $\pm$ 0.05°. Zero time was taken when the tubes were placed in the bath. Ampoules were withdrawn at intervals and the reaction was quenched by placing in an ice-bath. While frozen, the tubes were opened and distilled water was added to convert any remaining potassium *t*-butoxide to the hydroxide. After warming to room temperature, the contents of the tubes were diluted with 95% ethanol to standard volumes. The spectra were run with ethanol as a blank.

Optical densities were measured at wave lengths corresponding to maxima of the acetylenes. These were selected because the starting olefins either absorbed very little or not at all at these wave lengths. In those cases where the starting olefin did show some absorption at these wave lengths (the two *p*-methoxyphenyl-olefins), the following equations were used to calculate the concentration of the acetylene.

$$A_{\text{Total}} = e_{\text{T}} b c_{\text{T}} + e_{\text{EH}} b c_{\text{EH}}$$

$$c_{\text{EH}} + c_{\text{T}} = c_0$$

A_{Total} = total absorbance of the mixture
e_{T} = extinction coefficient of the pure acetylene (tolan)
c_{T} = concentration of the acetylene
e_{EH} = extinction coefficient of the pure olefin
c_{EH} = concentration of the olefin
b = thickness of the cell
c_0 = initial concentration of the olefin

Dipole Moments.—Dielectric constants of *cis*- and *trans*-1-*p*-methoxyphenyl-1-phenyl-2-bromoethylene (*cis*- and *trans*-IV) were measured in pure benzene previously prepared for dielectric studies (n^{23}D 1.4982, d^{25} 0.8736). Dielectric constants were measured with a General Radio type 716-C capacitance bridge containing the measuring cell (unknown capacitor) and a precision capacitor (balancing capacitor).[34] Dipole moments were calculated using the equation

$$\mu = 0.01281 \times 10^{-18}[(P_\infty - R_2)T]^{1/2}$$

where R_2 is the molar refraction of the solute and P_∞ is the polarization of the solute at infinite dilution; P_∞ was determined by the method of Hendestrand.[35] All measurements were made at 25 $\pm$ 0.02°.

(34) For a more detailed discussion of this method see C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, p. 212, and references cited therein.
(35) G. Hendestrand, *Z. physik. Chem.*, **B2**, 428 (1929).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA, PHILADELPHIA 4, PA.]

Thiabenzenes. IV. 1- and 2-Thianaphthalenes and 10-Thiaanthracenes. Evidence for Cyclic Conjugation

By CHARLES C. PRICE, MIKIO HORI, THYAGARAJA PARASARAN AND MALCOLM POLK[1]

By reaction of appropriate thiopyrylium salts with phenyllithium, four new thiabenzene analogs have been prepared. The new compounds are much more stable to heat, light and oxygen than 1,2,4,6-tetraphenylthiabenzene. Covalent conjugated bonding in all five compounds is indicated by the single aromatic band in the proton n.m.r. spectra and by the low dipole moments (1.5–1.9 D.).

The preparation of the first example (I) of a new aromatic heterocyclic ring system, called thiabenzene, was reported earlier.[2] By similar procedures, two

thianaphthalenes and two thiaanthracenes have now been prepared. We wish to report here on their properties, particularly their stability, n.m.r. spectra and dipole moments, which have particular significance to the type of bonding which may exist in this new ring system.

C₆H₅

I

II
R

III
C₆H₅

IV, R = H
V, R = C₆H₅
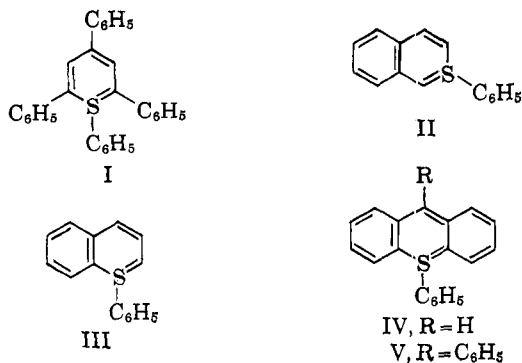
Experimental

1,2,4,6-Tetraphenylthiabenzene (I) was prepared, as before, from 2.5 g. (0.006 mole) of 2,4,6-triphenylthiopyrylium perchlorate by treatment of an ether suspension with excess phenyllithium under nitrogen in a serum-capped centrifuge flask. With cooling at −20°, carbon dioxide was then bubbled in. After centrifuging at −15°, the organic layer was removed, washed twice with ice-water, dried over potassium carbonate and evaporated. The violet, oily solid was dissolved in 20 ml. of cold ether and poured into 200 ml. of petroleum ether cooled in a Dry Ice–acetone-bath. The violet precipitate was collected by centrifugation at −15°, the reprecipitation repeated and the solid dried for 24 hr. in the dark at 1 mm.; yield 1.0 g. (42.3%). On heating, shrinkage occurred at 43–45°, melting at 65°, and the violet color disappeared at 85–90°. The n.m.r. spectrum in carbon tetrachloride showed a single sharp band at 2.66 τ. Infrared bands (KBr disk) occurred at 1610, 1590, 1490, 1440, 1420, 1245, 1120, 1100, 740 and 695 cm.⁻¹. The dipole moment (μ 1.88 D.), molar refractivity (146.41 cc.) and molar polarization (218.00 cc.) were measured in benzene as described below.

2,4,4,6-Tetraphenylthiopyran (Ia),[2] m.p. 159.5°, showed two peaks in its n.m.r. spectrum, 2.87 and 4.00 τ, with an intensity ratio of 10:1.

Isothiochromanone (VI) was prepared from benzylmercaptoacetic acid,[3] except that vacuum distillation rather than steam distillation raised the yield of product from 35% to 50–60%, b.p. 160–165° (12 mm.), m.p. 64°; semicarbazone, m.p. 235° (lit.[3] 64°, 236°[4]). Reduction with sodium borohydride (rather than lithium aluminum hydride[5]) gave **isothiochromanol (VII**, 90%), m.p. 52° (lit.[5] 50°).

Isothiochromene (VIII) was prepared from the above alcohol by heating with potassium pyrosulfate.[4] As much product as possible was removed by vacuum distillation. The inorganic residue was extracted with ether. The combined distillate and extract were distilled, b.p. 105° (5 mm.), m.p. 32°, yield 35 g. (80%) (lit.[4] m.p. 39°, b.p. 124° (13 mm.)). The ultraviolet spectrum in ethanol showed λmax (log ε) 207 (4.08), 235 (3.85) and 315 (3.68) mμ. The n.m.r. spectrum showed a split band for four aromatic hydrogens at 2.87 τ, the expected four bands for two olefin hydrogens between 3.2 and 3.7 τ and a single sharp band at 6.2 τ for the methylene hydrogens.

Anal. Calcd. for C₉H₈S: C, 72.99; H, 5.44; S, 21.63. Found: C, 72.83; H, 5.42; S, 21.78.

2-Thianaphthalenium perchlorate (IX) was prepared from VIII in 60% yield[5] or by treatment of 2 g. of VII with 4.5 g. of trityl perchlorate[6] in 15 ml. of boiling glacial acetic acid for 15 min. On slow cooling and evaporation, green needles separated, 1.5 g. (50%), m.p. 185–190°. Recrystallized from acetic acid with a little acetic anhydride, it melted at 189–190° (lit.[5] 187–190°). The ultraviolet spectrum in 1% perchloric acid in acetic acid showed λmax (log ε) 260 (3.99), 305 (3.60), 315 (3.58) and 384 (3.55) mμ.

Anal. Calcd. for C₉H₇ClO₄S: C, 43.81; H, 2.86; Cl, 14.37; S, 12.99. Found: C, 44.00; H, 3.02; Cl, 14.18; S, 13.23.

2-Phenyl-2-thianaphthalene (II) was prepared by treating 2.5 g. (0.01 mole) of IX suspended in 50 ml. of ether under nitrogen in a separatory funnel capped with a rubber serum cap with 15 ml. of 2 M phenyllithium in ether–benzene (Lithium Corp. of America, N. Y., N. Y.) added by a syringe slowly with shaking. After 15 min. additional shaking, excess ice-cold saturated ammonium chloride was added slowly with external cooling. The aqueous layer was discarded and the red ether–benzene solution washed with water, dried over magnesium sulfate and

evaporated. The dark red-brown concentrate was washed with petroleum ether (30–60°), leaving a yellow-brown precipitate. This washing procedure was repeated, the residue dissolved in benzene and the clear red solution freeze-dried to leave 1.1 g. 50%) of II as a red-brown solid, m.p. 121–125°. It (or a contaminating by-product) was volatile enough to give the product a characteristic aromatic odor.

Anal. Calcd. for C₁₅H₁₂S: C, 80.35; H, 5.39; S, 14.29; mol. wt., 224. Found: C, 80.26; H, 5.56; S, 14.40; mol. wt., 300 (cryosc., benzene).

The n.m.r. spectrum of a sample freeze-dried from benzene showed only a single absorption centered at 3.0 τ. A sample prepared by evaporation of ether showed in addition small bands at 6.8 τ (doublet) and at 8.4–8.9 τ (triplet) characteristic of the ethyl ether group and a sample prepared by evaporation of a petroleum ether solution showed a series of bands near 9 τ, characteristic of parafin hydrocarbon. The ultraviolet spectra (in ethanol) showed λmax (log ε) 207 (4.62) and 300 (4.08) mμ, and major infrared absorption bands (KBr disk) occurred at 3050, 3015, 1585, 1467, 1430, 1095, 1075, 1015, 730 and 680 cm.⁻¹.

The dipole moment and molecular refractivity were measured at 30 ± 0.002° according to methods described in detail elsewhere.[7] A General Radio Co. frequency capacitance bridge, oscillator and null detector were used for measuring the dielectric constants of various concentrations of II in benzene and a Pulfrich refractometer for the corresponding refractive indices. The Halverstadt–Kumler[8] equation was then used to calculate the molar polarization (118.42, 128.18 cc.), molar refractivity (75.50, 74.77 cc.) and dipole moment (1.46, 1.63 D.).

Desulfurization of 3 g. of II with 20 g. of Raney nickel[9] by refluxing for 6 hr. in 100 ml. of sulfur-free benzene followed by filtration and careful removal of most of the benzene through an efficient fractionating column left a residue which was assayed by gas chromatography on 20% Carbowax 20M on Chromosorb at 160° (flow rate, 78 ml./min., 180 mamp.). It showed three peaks at 2.4, 3.35 and 5.8 min., in addition to benzene. These were *not* impurities in the benzene used as solvent. Toluene was found to have a retention time of 2.4 min. and o-ethyltoluene of 5.8 min. The yield of the latter was estimated to be only 3–5% of theoretical. There was a larger amount of toluene but much less of the unidentified material at 3.35 min.

Oxidation of 1 g. of II in 100 ml. of ether and benzene by bubbling in oxygen for 30 min. did not destroy the color (as for I[2]). Addition of hydrogen chloride gas, followed by alkali wash, gave less than 30 mg. (6%) of thiophenol, identified as the 2,4-dinitrophenyl derivative.

1-Phenyl-1-thianaphthalene (III) was prepared by treating 10 g. of 1-thianaphthalenium perchlorate[5,6] with excess phenyllithium as described above. The suspended salt dissolved to give a dark brown solution. Washing with aqueous ammonium chloride and water, drying and evaporation left a red solid. It was reprecipitated from ether by petroleum ether and then freeze-dried from benzene to give a brown solid, 2.0 g. (21.4%), m.p. 106–111°.

Anal. Calcd. for C₁₅H₁₂S: C, 80.35; H, 5.39; S, 14.29. Found: C, 80.15; H, 5.54; S, 14.39.

The n.m.r. spectrum showed a single broad structured peak from 2.4–3.0 τ. Ultraviolet absorption in ethanol occurred at λmax (log ε) 208 (5.46) and 230 (5.15) mμ and infrared (KBr disk) at 3054, 2920, 1578, 1460, 1430, 1062, 1020, 726 and 690 cm.⁻¹. The molar refractivity (in benzene) was 73.64 cc., the molar polarization, 131.04 cc., and the dipole moment, 1.69 D.

Thioxanthen-9-ol (XI) was prepared by reducing 20 g. of thioxanthen-9-one[10] with 13.3 g. of sodium borohydride in 300 ml. of boiling methanol; yield 18.3 g. (95%) of white needles (from petroleum ether (60–110°)), m.p. 104–105° (lit.[11] 105°).

Thioxanthylium perchlorate (XII) was prepared from 10 g. of XI in 100 ml. of ether by treatment with 15 ml. of 70% perchloric acid initially cooled to −70°. After warming to room temperature, the red solid was collected and recrystallized twice from acetic acid to give 8.5 g. (61%) of red plates, m.p. 229° dec. (lit.[6] 217–219°). The ultraviolet spectrum (in 1% perchloric acid in acetic acid) had λmax (log ε) 241 (3.05), 276 (3.76), 377 (3.21), 480 (1.39) and 506 (1.32); and major infrared bands at 1580, 1540, 1485, 1360, 1260, 1115, 1080, 750, 615 and 580 cm.⁻¹.

Anal. Calcd. for C₁₃H₉ClO₄S: C, 52.61; H, 3.06; Cl, 11.61; S, 10.81. Found: C, 52.41; H, 3.11; Cl, 11.85; S, 10.68.

(3) A. K. Kiang and F. G. Mann, *J. Chem. Soc.*, 1913 (1951).

(4) J. von Braun and K. Weissbach, *Ber.*, **62**, 2416 (1929).

(5) A. Lüttringhaus and N. Engelhard, *ibid.*, **93**, 1525 (1960).

(6) W. Bonthrone and D. H. Reid, *J. Chem. Soc.*, 2774 (1959); *Chem. Ind.* (London), 1192 (1960).

(7) R. A. Prosser, Ph.D. Dissertation, Univ. of Pa., 1960; T. Parasaran, 1962; F. Verderame, 1962.

(8) I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, **64**, 2988 (1942).

(9) R. Mozingo, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 181.

(10) M. Gomberg and W. Minnis, *J. Am. Chem. Soc.*, **43**, 1940 (1921).

(11) E. F. Oehlesehager and I. MacGregor, *ibid.*, **72**, 5332 (1950).

10-Phenyl-10-thiaanthracene (IV) was prepared by treating 8 g. of XII with excess phenyllithium in 100 ml. of ether under nitrogen. The deep red solution was washed in the cold with aqueous ammonium chloride and ice-water and filtered to separate an insoluble by-product (A). The filtrate was dried and evaporated. The residue was washed three times with petroleum ether (30–60°), then dissolved in ether, passed through an alumina column and the product was eluted with ether. Evaporation left a stable brown powder; 2.7 g. (37.5%), m.p. 124–129°, giving red-brown solutions in ether, benzene or carbon tetrachloride.

Anal. Calcd. for $C_{19}H_{14}S$: C, 83.27; H, 5.14; S, 11.58; mol. wt., 274. Found: C, 83.14; H, 5.20; S, 11.55; mol. wt., 366 (cryosc., benzene).

The n.m.r. spectrum showed only one major absorption band (with some splitting) at 2.88–3.04 τ. The dipole moment, μ 1.58 D., the molar refraction, 88.64 cc., and the molar polarization, 140.50 cc., were measured in benzene at 30°. The ultraviolet absorption spectrum showed λ_{max} (log ϵ) 265 (3.85) and 420 (2.05) mμ in dioxane, 374 (2.42) and 420 (2.02) mμ in carbon tetrachloride and 211 (4.39) and 260 (4.04) mμ in ethanol. Infrared maxima were noted at 3055, 1575, 1465, 1430, 730 and 690 cm.$^{-1}$.

The insoluble by-product A was recrystallized from acetic acid or xylene as white needles, 1.4 g. (13.2%), m.p. >280°.

Anal. Calcd. for $C_{26}H_{18}S_2$: C, 78.90; H, 4.59; S, 16.25. Found: C, 78.48; H, 4.12; S, 16.19.

The infrared spectrum, which was identical to that for an authentic sample[12] of dithioxanthyl (IVa, lit.[12] m.p. 325°) but quite different from that of dithioxanthylene (lit.[13] m.p. 345°), had maxima at 3050, 3000, 1570, 1450, 1430, 1185, 1170, 1100, 1060, 1048, 1020, 720 and 560 cm.$^{-1}$.

9-Phenylthioxanthene (XIII).—(a) When 2 g. of XII was treated with excess phenylmagnesium bromide in 100 ml. of ether, a white precipitate was formed rapidly. Recrystallization from methanol gave 1.2 g. (68%) of white needles, m.p. 99°. (b) The same compound was obtained by stirring a slurry of 2 g. of 9-phenylthioxanthylium perchlorate (XIVa, see below) and 2 g. of lithium aluminum hydride in 100 ml. of ether for 3 hr. After washing, drying and evaporation, recrystallization from methanol gave 1.4 g. (95%) of white needles, m.p. 99°. (c) Reduction of 2 g. of XIVa with 5 g. of powdered zinc in 30 ml. of acetic acid and 20 ml. of concd. hydrochloric acid by refluxing for 3 hr. gave the same compound in 81% yield, m.p. 99° (lit.[13] 96°). The n.m.r. spectrum showed bands at 2.87, 3.00 and 4.90 τ in the intensity ratio of 8:5:1. Ultraviolet maxima occurred at 274 (log ϵ 3.66) mμ in dioxane and at 209 (4.40) and 267 (4.02) mμ in ethanol; major infrared maxima were observed at 3050, 1575, 1480, 1450, 1430, 730, 680 and 590 cm.$^{-1}$.

Anal. Calcd. for $C_{19}H_{14}S$: C, 83.27; H, 5.14; S, 11.68. Found: C, 82.89; H, 5.18; S, 11.79.

9-Phenylthioxanthylium Perchlorate (XIVa).—(a) A solution of 2 g. of XV in 50 ml. of glacial acetic acid was treated with 2.4 g. of trityl perchlorate. The red precipitate which formed immediately was recrystallized twice from hot acetic acid as red plates, 2.15 g. (83%), m.p. 239° dec. The ultraviolet spectra in 1% perchloric acid in acetic acid had maxima at 249 (3.24), 280 (3.93), 383 (3.24), 490 (1.68) and 515 (1.61) mμ; the infrared at 1585, 1540, 1450, 1375, 1315, 1150, 1085, 790, 732, 700, 620 and 605 cm.$^{-1}$.

Anal. Calcd. for $C_{19}H_{13}ClO_4S$: C, 61.33; H, 3.51; Cl, 9.48; S, 8.62. Found: C, 61.28; H, 3.35; Cl, 9.62; S, 8.76.

(b) Treatment of 19.3 g. of XV in 50 ml. of ether at −70° with 25 ml. of 70% perchloric acid added dropwise gave a red precipitate; recrystallization from acetic acid yielded 24 g. (85%) of red plates, m.p. 239° dec. (c) Treatment of XIVb[14] or XIVc[14] in ether with an equal weight of 70% perchloric acid gave a red precipitate which afforded XIVa on recrystallization in 83 and 89% yield, respectively, m.p. 239° dec. (d) A solution of 2 g. of XIII in 50 ml. of acetic acid, treated with 2.5 g. of trityl perchlorate and boiled for 3 min., gave, after recrystallization, 2.3 g. (85%) of XIVa, m.p. 239° dec.

9,10-Diphenyl-10-thiaanthracene (V) was prepared from 4 g. of XIVa suspended in 100 ml. of ether under nitrogen by adding 21.2 ml. of 2 M phenyllithium by syringe. The deep red solution was washed with cold aqueous ammonium chloride, with ice-water, then dried and evaporated *in vacuo*. The residue was washed three times with petroleum ether, then dissolved in ether and passed through an alumina column. The product was eluted with ether and the eluate evaporated and dried at 1 mm. for 24 hr. to leave 1.7 g. (32%) of stable brown powder, m.p. 143–146°.

Anal. Calcd. for $C_{25}H_{18}S$: C, 85.67; H, 5.18; S, 9.15; mol. wt., 350. Found: C, 85.47; H, 5.36; S, 9.33; mol. wt., 404 (cryosc., benzene).

Solutions in ether, dioxane, benzene or carbon tetrachloride were red-brown. Boiling 3 g. in acetic acid gave none of the isomeric 9,9-diphenylthioxanthene (XVII).

The n.m.r. spectrum showed a single major peak at 2.98 τ with minor side bands up to 3.4 τ. The dipole moment, μ 1.50 D., the molar refractivity, 116.03 cc., and the molar polarization, 161.14 cc., were measured in benzene at 30°. Ultraviolet absorption occurred at λ_{max} (log ϵ) 271 (3.94) mμ in dioxane, 212 (4.48) and 271 (4.07) mμ in ethanol and 376 (2.12) mμ in carbon tetrachloride; major infrared absorption at 3055, 1580, 1455, 1435, 740 and 690 cm.$^{-1}$.

Desulfurization with Raney nickel[9] was first attempted with 3 g. of V and 30 g. of Raney nickel by refluxing for 20 hr. in thiophene-free benzene. Since the organic product still contained much sulfur, it was redissolved in 350 ml. of ethanol and refluxed again with 16 g. of fresh Raney nickel. Filtration and evaporation left an oily residue which, on extraction with hot ethanol and cooling, gave a white solid. Distillation gave 0.4 g. of oily solid which recrystallized from ethanol as colorless prisms, 0.1 g. (4.78%), m.p. 93.5°. The mixture melting point with an authentic sample of triphenylmethane was undepressed and the infrared spectra of both samples were superimposable.

Anal. Calcd. for $C_{19}H_{16}$: C, 93.44; H, 6.56. Found: C, 93.56; H, 6.57.

o-Phenylmercaptophenyldiphenylcarbinol (XVI) was prepared by treating 3 g. of ethyl o-phenylmercaptobenzoate[15] with 2 equiv. of phenylmagnesium bromide in 100 ml. of ether. Washing, drying and evaporation left an oily residue which, on standing under a small volume of petroleum ether (30–60°), crystallized; 3.0 g. (66%). It was recrystallized from methanol as colorless needles, m.p. 145°. The infrared spectrum showed a strong band for hydroxyl at 3510 cm.$^{-1}$ and no carbonyl absorption.

Anal. Calcd. for $C_{25}H_{20}OS$: C, 81.48; H, 5.46; S, 8.70. Found: C, 81.67; H, 5.26; S, 8.53.

9,9-Diphenylthioxanthene (XVII) was prepared from a solution of 2 g. of XVI in 50 ml. of boiling acetic acid by adding 4 drops of concd. sulfuric acid. After boiling for 2 min., cooling gave white crystals which were recrystallized from acetic acid as colorless tiny plates, 1.83 g. (95%), m.p. 218°. The n.m.r. spectrum showed a major band at 2.9 τ and smaller bands at 3.17 and 3.3 τ, all with much greater fine structure than for the isomer V. Ultraviolet absorption in ethanol occurred at λ_{max} (log ϵ) 214 (4.22) and 274 (3.74) mμ; major infrared bands at 3065, 3030, 1580, 1490, 1460, 1455, 1280, 1190, 1160, 1130, 1080, 1040, 750, 700 and 630 cm.$^{-1}$.

Anal. Calcd. for $C_{25}H_{18}S$: C, 85.67; H, 5.18; S, 9.15. Found: C, 85.85; H, 5.02; S, 9.24.

9-Methylthioxanthylium perchlorate (XVIII) was prepared by adding 3 g. of thioxanthen-9-one in 50 ml. of benzene to 2 equiv. of methylmagnesium iodide in 150 ml. of ether. After stirring for 5 hr. under reflux, it was washed, dried and evaporated *in vacuo*. The yellow residual oil in 50 ml. of ether at −70° was treated with 5 ml. of 70% perchloric acid. The red precipitate was recrystallized from acetic acid to give 3.8 g. (87%) of XVIII as red plates, m.p. 213.5° dec. Ultraviolet absorption (in 1% perchloric acid in acetic acid) occurred at λ_{max} (log ϵ) 246 (3.12), 280 (3.95), 375 (3.31), 480 (1.51) and 508 (1.42) mμ; major infrared bands at 1585, 1540, 1455, 1432, 1360, 1292, 1120, 1050, 769, 725, 630, 620 and 590 cm.$^{-1}$.

9-Methylthioxanthene (XIX). (a).—A suspension of 2 g. of XII in ether was treated with excess methylmagnesium iodide in ether. After washing, drying and evaporation, the pale yellow solid was recrystallized from methanol as pale yellow plates, 1.10 g. (80%), m.p. 84.5° (lit.[16] 74°, but no analysis). The n.m.r. spectrum confirmed the structure, showing a major band at 2.93 τ, a quadruplet at 5.92, 6.05, 6.16 and 6.29 τ and a doublet at 8.58 and 8.67 τ, in the ratio of 8:1:3. Ultraviolet absorption occurred at λ_{max} (log ϵ) 208 (4.26) and 266 (4.04) mμ; major bands at 3055, 2965, 2920, 1455, 1440, 1432, 1355, 1260, 1115, 1070, 1020, 750 and 675 cm.$^{-1}$.

Anal. Calcd. for $C_{14}H_{12}S$: C, 79.20; H, 5.69; S, 15.10. Found: C, 79.03; H, 5.58 S, 15.25.

(b).—Further structure proof for XIX was obtained by its preparation from XVIII by reduction with lithium aluminum hydride in ether (95%) or zinc in acetic–hydrochloric acid (80%); m.p. 84.5°.

(12) A. Schönberg and A. Mustafa, *J. Chem. Soc.*; 657 (1945).
(13) A. Schönberg and W. Asker, *ibid.*, 274 (1942).
(14) H. Bünzly and H. Decker, *ibid.*, **37**, 2937 (1904).

(15) C. Graebe and O. Schultess, *Ann.*, **263**, 6 (1891); F. Mayer, *Ber.*, **42**, 1135 (1909).
(16) H. Decker, *ibid.*, **38**, 2511 (1905).

Discussion

The earlier preparation of the first example of the new "aromatic" thiabenzene ring system, 1,2,4,6-tetra-phenylthiabenzene (I), has now been extended by preparation of four new examples from the corresponding thiopyrylium perchlorates: 2-phenyl-2-thianaphthalene (II), 1-phenyl-1-thianaphthalene (III), 10-phenyl-10-thiaanthracene (IV) and 9,10-diphenyl-10-thiaanthracene (V).

The general schemes used for synthesis are
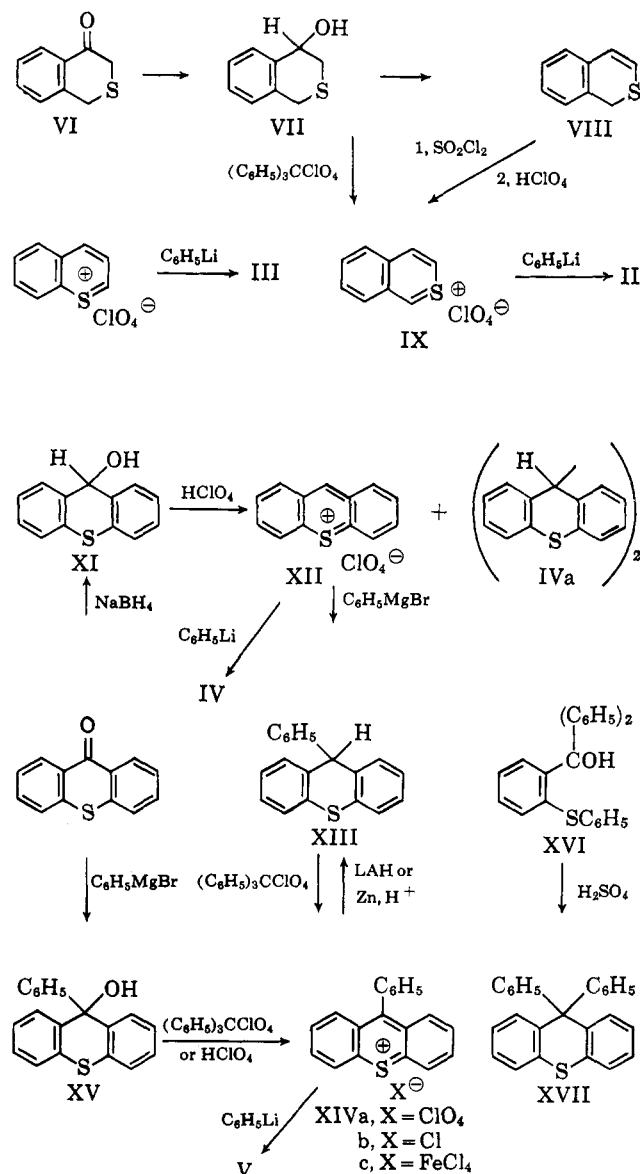
The four new compounds are red-brown (rather than deep purple) and are all much more stable to heat, to light and to oxygen than I. For example, V could be boiled in acetic acid with no loss of color and no conversion to the isomeric thiopyran XVII, whereas compound I must be kept in the cold under nitrogen in the dark and even then is largely isomerized to an isomeric thiopyran (Ia) in a few weeks.


Ia, m.p. 159.5°
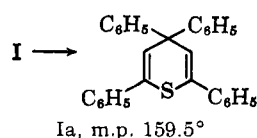
Whereas an ether solution of I was rapidly decolorized by oxygen[2] and converted then by hydrogen chloride

in good yield to phenyl mercaptan and a red oxopyrylium cmpound,[2] II on even more extended treatment with oxygen and then hydrogen chloride gave less than 6% yield of phenyl mercaptan.

Chemical structural proof through oxygen degradation was therefore not suitable, so Raney nickel desulfurization of II and V was attempted. Both proved very resistant to desulfurization (compared to thiopyrans studied earlier[2]) but after extensive reflux, small yields of the expected products were obtained.
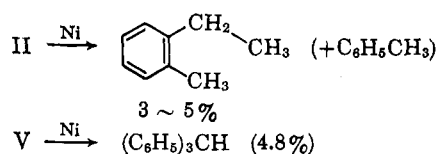

The greater stability and ease of formation of sulfur and phosphorus ylids than of the nitrogen analogs[17,18] has been ascribed to 3d-orbital resonance possibilities for the former which are precluded in the latter.
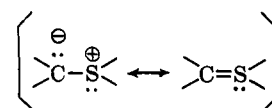
Dipole moment data for 9-dimethylsulfoniofluorenylid,[17] $\mu = 6.2$ D.,[19] and for triphenylphosphoniocyclopentadienylid, $\mu = 7.0$ D.,[20] however, indicate a very substantial ionic character for such compounds.

If the thiabenzenes we have prepared (I–V) can be properly described by the aromatic covalent structures written for them, then they might be expected to have considerably lower dipole moments than open-chain ylids. The dipole moments of the four new compounds are between 1.5 and 1.69 D., while that of I is 1.88 D., as measured in benzene at 30°.

The covalent aromatic structure for the five thiabenzenes is strongly supported by the n.m.r. data. All five show only aromatic-type hydrogen, with absorption shifted downfield from tetramethylsilane to about 3 τ. This seems to argue strongly that the conducting cyclic system of π-electrons responsible for this shift in hydrogen attached to aromatic rings must also be present in the thiabenzene ring. Hydrogen on isomeric thiopyrans, with cyclic conjugation interrupted by a tetracovalent carbon, appears at larger values of τ. For example, that of Ia appears at 4.0 τ, of VIII at 3.2 to 3.7 τ, of XIII at 4.9 τ and of XIX at about 6.0 τ.
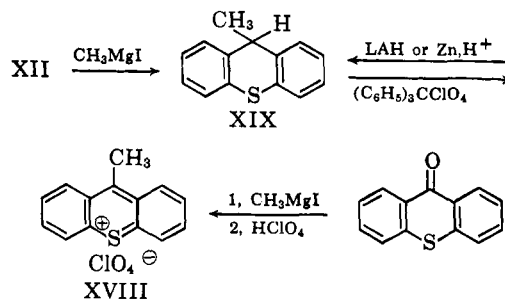
There appears to be a remarkable difference between the aromatic character of the two thianaphthalenes reported here and some compounds recently reported by Breslow and Mohacsi.[21] The open-chain compounds

(17) C. K. Ingold and J. A. Jessop, J. Chem. Soc., 713 (1930); E. D. Hughes and K. I. Kuriyan, ibid., 1609 (1935).
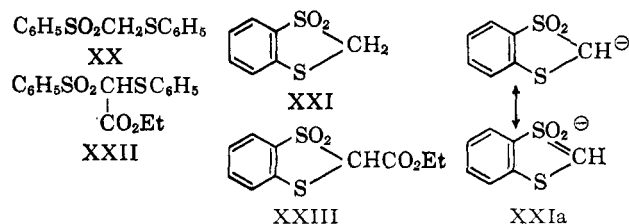
(18) W. E. Doering and A. K. Hoffman, J. Am. Chem. Soc., 77, 521 (1955).

(19) G. M. Phillips, J. S. Hunter and L. E. Sutton, J. Chem. Soc., 146 (1945).

(20) F. Ramirez and S. Levy, J. Am. Chem. Soc., 79, 6167 (1957).

(21) R. Breslow and E. Mohacsi, ibid., 84, 684 (1962).

XX and XXII had very nearly the same dissociation constants as the cyclic analogs XXI and XXIII.

C₆H₅SO₂CH₂SC₆H₅
XX

C₆H₅SO₂CHSC₆H₅
|
CO₂Et
XXII

In the cyclic anion, the resonance indicated in XXIa would suggest a structure analogous to benzothiophene, but actually no enhanced stability is observed for XXIa, as measured by acidity, although the cyclic anions are colored, in contrast to the colorless anions from XX and XXII.

The difference in basicity between open-chain sulfur ylids, which remove protons from water, and the thiabenzene V which can be refluxed unchanged in acetic acid, on the other hand, supports our view of marked stabilization through cyclic conjugation in the thiabenzene ring. The marked stabilization of the latter is also supported by the resistance to desulfurization noted for II and V.

There are some significant differences between the anion XXIa and thiabenzenes, such as II or III. While the sulfonyl sulfur in XXIa and the "sulfonium" sulfur of II or III each have vacant 3d-orbitals to accommodate electrons, only the latter have unshared electrons on the sulfur. We have earlier suggested[22] that the much greater stabilization of a carbon free radical by a sulfide group than by a sulfonyl or silyl group may be due to use of 2p–3p orbitals for π-bonding, with promotion of an unshared electron on sulfide sulfur to a vacant 3d-orbital, and such a possibility was one of those we have already considered for thiabenzene.[2b]

The considerably greater stability of the four new thiabenzenes than of I could also be considered to support this view. Rehybridization of the usual p³-structure of sulfonium salts[22c] to sp² would require that the S-phenyl group become coplanar with the thiabenzene ring. This would be considerably hindered by the bulk of the 2- and 6-phenyl groups in I, in contrast to the lesser hindrance in compounds II–V. It is thus possible that I utilizes p³-orbitals for σ-bonding, retains its unshared pair in a 3s-orbital and uses one (or per-

haps two) 3d-orbitals for cyclic conjugation, whereas compounds II–V utilize sp²-orbitals for σ-bonding, the 3p$_z$-orbital for cyclic conjugation and one (or more) 3d-orbitals for the unshared pair.[23]

The marked color of thiabenzenes, without any marked difference from the normal ultraviolet spectra of related benzenoid analogs, may also be relevant to the state of hybridization of the sulfur atom. If the unshared pair on sulfur is indeed promoted to a 3d-orbital in thiabenzenes, then the color may arise from atomic excitation of one of these electrons to another 3d-orbital of only slightly higher energy, without very great influence on the cyclic conjugated π-electron system. In normal sulfonium salts, with the unshared pair in a 3s-orbital, the excitation energy would be much greater, as indicated by ultraviolet absorption only at very short wave lengths.[22c]

Of many remaining unresolved questions, two are worthy of comment: One is the remarkable difference between coupling of thiopyrylium salts with phenyllithium and with phenylmagnesium bromide. Whereas we find virtually exclusive coupling on sulfur to give thiabenzenes by the former, every case of the latter so far studied couples on carbon to give isomeric thiopyrans. We have reported some examples earlier,[2] several more here, and Lüttringhaus, Engelhard and Kolb[24] report that X couples with the Grignard reagent to introduce a phenyl group at carbon 4. One possible explanation of this marked contrast may be that Grignard reagents coördinate on sulfur through the magnesium atom, blocking direct alkylation of sulfur, although this could not be complete, since we observed fleeting colors characteristic of thiabenzene[2b] during Grignard coupling.

Another preliminary observation, which may or may not be related to the mechanisms of coupling to form thiabenzenes, is that all reaction mixtures for formation of thiabenzenes I–V showed e.s.r. signals, some with remarkable fine structure—if measured before aqueous washing, but not after. The complete destruction of the e.s.r. signals by water suggests they may have arisen from some radical-ion, perhaps formed by electron transfer with phenyl anion. Some such radical-forming process might also be a logical explanation of the appreciable yield of dithioxanthyl (IVa) formed from XII along with the thiabenzene IV.

(23) The puzzling reluctance of the thiabenzenes to crystallize, undoubtedly also related to their ready solubility and affinity for solvents, is, however, hard to reconcile with a planar sp² arrangement at sulfur. Perhaps freedom of motion between sp² and p³ geometry retards crystallization.

(24) A. Lüttringhaus, N. Engelhard and A. Kolb, *Ann.*, **654**, 189 (1962).

(22) (a) C. C. Price and J. Zomlefer, *J. Am. Chem. Soc.*, **72**, 14 (1950); (b) C. E. Scott and C. C. Price, *ibid.*, **81**, 2670 (1959); (c) C. C. Price and S. Oae, "Sulfur Bonding," Ronald Press Co., New York, N. Y., 1962.

The Nature of Camphene Racemization[1,2]

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Camphene-10-C¹⁴ has been prepared by a stereospecific synthesis. It has been diluted with unlabeled optically active camphene and subjected to racemization at 156° in acetonitrile–pyruvic acid for varying lengths of time, after which optical activity and isotope distribution have been measured. With the assistance of a newly developed set of kinetic equations applicable to the unique threefold racemization process, the extents of involvement of the three modes of racemization (*endo*-methyl shift, *exo*-methyl shift and 2,6-hydride shift) have been determined.

In 1953, two independent tracer studies[4,5] of the camphene racemization process demonstrated the

operation of a methyl shift *and* a 2,6-hydride shift process in the course of racemization under a variety

ganic Division of the American Chemical Society, 144th National Meeting, Los Angeles, Calif., March 31–April 5, 1963.

(3) Michigan Memorial Phoenix Project Post-Doctoral Fellow, 1958–1959.

(4) J. D. Roberts and J. A. Yancey, *J. Am. Chem. Soc.*, **75**, 3165 (1953).

(5) W. R. Vaughan and R. Perry, Jr., *ibid.*, **75**, 3168 (1953).