strength, f_i, of a normal electric dipole transition between states k and o with wave functions ϕ_k and ϕ_o. The oscillator strength is given by

$$f_i = \frac{8\pi^2 \nu_{ko} m_e |\vec{M}_{ko}|^2}{3he^2} \qquad (1)$$

where

$$|\vec{M}_{ko}|^2 = |\int \phi_k^* M \phi_o dt|^2 \qquad (2)$$

where M_{ko} is a Hermitian dipole operator between states, ϕ_k and ϕ_o.

The value of f_i is a function of the refractive index of the medium (n). The equation

$$f_i = \frac{2303\ m_e c}{\pi\ Ne^2} \frac{9n}{(n^2+2)^2} \int \epsilon\ d\nu \qquad (3)$$

can be derived from theory and includes a small internal electric field correction $(9n/(n^2 + 2)^2)$ due to the application of an Lorentz–Lorenz field.[31,32]

The extinction coefficient, ϵ_i can be expressed as

$$\epsilon_i = \frac{Ne^2}{2303\ cm_e} f_i \phi(\nu) \qquad (4)$$

where $\phi(\nu)$ determines the shape of the absorption band. Using the Lorentz formula for the line shape with a half-band width of δ cm.$^{-1}$ and the normalization of $\phi(\nu)$

$$\int \phi(\nu)\ d\nu = 1 \qquad (5)$$

the equation

$$\epsilon = \frac{f_i \pi N e^2}{9\delta 2303\ m_e c}\left(n^3 + 4n + \frac{4}{n}\right) \qquad (6)$$

can be derived which expresses the functional dependence of ϵ upon n. The first term will remain constant to a good degree of approximation for sulfur which has an allowed band ($f_i \rightarrow 1$) and a zero dipole moment such that

$$\int \phi_0^* m \phi_0 dt = 0$$

The restrictions on eq. 6 are discussed in detail in another paper.[27] Thus

$$\epsilon \propto n^3 + 4n + \frac{4}{n} \qquad (7)$$

To a higher approximation

$$\epsilon \propto n \quad (n \approx 1) \qquad (8)$$

Friedman and Kerker[10] suggested a linear relationship between ϵ and n for sulfur in inert solvents with n between 1.3 and 1.5. The more exact relationship is the cubic equation 7.

---

[31] N. Chako, *J. Chem. Phys.*, **2**, 644 (1934).

[32] R. S. Mulliken and C. A. Rieke, *Rep. Prog. Phys.*, **8**, 231 (1941).

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

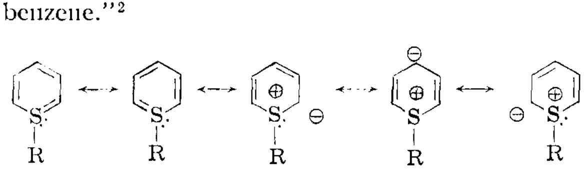
Thiabenzene. II. Rearrangement of 1-Alkyl-2,4,6-triphenylthiabenzenes to 2- and 4-Alkyltriphenylthiopyrans

BY GEORGE SULD[1] AND CHARLES C. PRICE

RECEIVED JANUARY 20, 1962

Whereas phenyllithium reacted with 2,4,6-triphenylthiopyrylium ion (I) to give deep purple 1,2,4,6-triphenylthiabenzene,[2] reaction with methyl, ethyl and butyl Grignard reagents gave only transiently deep red or purple solutions from which the colorless 2- or 4-alkyltriphenylthiopyrans were isolated. The structures of the 2- and 4-methyl homologs were established by desulfurization to 1,3,5-triphenylhexane and 3-methyl-1,3,5-triphenylpentane, respectively. Reaction of I with cyclopentadienyllithium gave the 2-cyclopentadienylthiopyran, while reaction with lithium aluminum hydride formed the 4H-triphenylthiopyran, which was reconverted to I on attempted S-alkylation with methyl iodide, methyl sulfate or triethyloxonium fluoroborate.

The possibility of double bond character for sulfur ylids[3] has interested us in the possible benzenoid conjugation which might be observed in a heterocyclic ring system we have called "thiabenzene."[2]



While there seems to be ample support for the view that sulfur can stabilize an adjacent unshared electron pair by resonance involving the 3d-orbitals on sulfur in some way, there have been arguments advanced against such resonance permitting through conjugation at sulfur or phosphorus.[4] The argument against through conjugation is based on the non-interaction between orthogonal 3d-orbitals. This non-interaction, however, is dependent on the symmetrical nature of the 3d-orbitals. Since two 3d-orbitals involved in overlap with adjacent 2p-orbitals become distorted in the process of 2p–3d π-bonding, their interaction no longer vanishes. Thus, the hybrid $3d_{xz}$ and $3d_{yz}$ orbitals involved in such π-bonding to adjacent $2p_z$-orbitals can be viewed as "pseudo-π" rather than normal 3d-orbitals for the purpose of constructing a cyclic conjugated aromatic system.

There is an alternative scheme which might also provide through conjugation in thiabenzene. This would involve rehybridization of the sulfur bonding electrons so that the σ-bonds become sp^2 rather than p^3, the unshared electrons are promoted to 3d-orbitals and the $3p_z$-orbital is left open for conjugation with the electrons from the adjacent $2p_z$-orbitals on carbon.[5]

---

[1] Abstracted from the doctoral dissertation of George Suld, 1960. Supported in part by National Science Foundation Grant No. G-6270.

[2] G. Suld and C. C. Price, *J. Am. Chem. Soc.*, **83**, 1770 (1961).

[3] See, *e.g.*, W. v. E. Doering and A. K. Hoffman, *ibid.*, **77**, 521 1955).

[4] See, *e.g.*, M. J. S. Dewar, E. A. C. Lucken and M. A. Whitehead, *J. Chem. Soc.*, 2423 (1960).

In an earlier communication[2] and the following paper,[6] we have reported the isolation and partial characterization of 1,2,4,6-tetraphenylthiabenzene (R = C_6H_5). In work reported herein we have found that the rearrangement of the phenyl group from sulfur to carbon, which occurred slowly, occurs very rapidly at room temperature when R = Me, Et or *n*-Bu.

Experimental

2,4,6-Triphenylthiopyrylium perchlorate (Ia), m.p. 211–212°, was prepared from the chloroferrate of the oxygen analog[7,8] in 70–90% yields.

The fluoborate Ib was obtained in 75% yield when a mixture of 70 g. of sodium sulfide nonahydrate in 150 ml. of water and 40 g. of 2,4,6-triphenylpyrylium chloroferrate[7] in 2 l. of acetone was filtered after 30 min. into 2 l. of aqueous 10% fluoboric acid. After 3 hr. the fluocculent yellow precipitate was collected and recrystallized from acetone-ethanol as canary-yellow needles, m.p. 196.5–197.5°.

Anal. Calcd. for $C_{23}H_{17}BF_4S$: C, 67.00; H, 4.16; S, 7.77. Found: C, 66.67; H, 4.45; S, 7.95.

The iodide Ic and the triiodide Id were obtained from reaction of 31 g. of Ib in 250 ml. of acetone and 50 ml. of water with 56.2 g. of sodium iodide in 100 ml. of water. The immediate precipitation of the violet-brown iodide was completed by addition of 1 l. of water. Recrystallization from dilute acetic acid gave 27.3 g. (80.5%) of dark violet iodide, which was recrystallized from acetone as long needles, m.p. 205–206.5° (sealed tube).

Anal. Calcd. for $C_{23}H_{17}IS$: C, 61.08; H, 3.79; I, 28.06; S, 7.08. Found: C, 60.79; H, 3.84; I, 28.75; S, 7.01.

Two less-soluble materials were obtained from the acetic acid. One recrystallized from acetone as black-gray prisms, 2.3 g., m.p. 201–202°, the second as long needles, 0.6 g., m.p. 203.5–204.5°. The latter analyzed properly for the triiodide Id.

Anal. Calcd. for $C_{23}H_{17}I_3S$: C, 39.10; H, 2.43; I, 53.94; S, 4.54. Found: C, 38.64; H, 2.61; I, 53.81; S, 4.63.

The former is evidently a 1:1 mixture of Ic and Id.

Anal. Calcd. for $C_{23}H_{17}I_2S$: C, 47.68; H, 2.96; I, 43.54; S, 5.53. Found: C, 47.18; H, 3.20; I, 43.79; S, 4.59.

2- and 4-Methyl-2,4,6-triphenylthiopyrans (II and III).—A stirred suspension of 5 g. of finely powdered Ic in 80 ml. of ether under dry nitrogen was treated with 35 ml. of 1.15 *M* methylmagnesium bromide in ether. The iodide Ic rapidly dissolved to give a magenta-colored solution. After 1 hour, the color had faded to yellow. The ether was washed with 200 ml. of aqueous ammonium chloride, dried and evaporated to leave a tan viscous oil. Crystallization from acetone-methanol gave two crops of colorless crystals, 2.5 g. (72%), m.p. 93–99°. After several recrystallizations, the 4-methyl isomer III melted at 96–97°; λ_{max} 235 mμ, log ε 4.45.

Anal. Calcd. for $C_{24}H_{20}S$: C, 84.67; H, 5.92; S, 9.40. Found: C, 84.61; H, 5.99; S, 9.38, 9.67.

The combined mother liquors gave 1.2 g. of tan oil which was placed on an alumina column in benzene and developed with benzene–petroleum ether (95:5). A faster moving fraction proved to be additional amounts of III, but from slower moving fractions, the 2-methyl isomer II was obtained, crystallizing from methanol as pale yellow needles, m.p. 118–119°; λ_{max} 257, 347 mμ, log ε, 4.32, 3.75.

Anal. Found: C, 84.33; H, 5.86; S, 9.14.

From several larger scale separations, the ratio of II to III was about one to three.

2-Methyl-2,4,6-triphenylthiopyran 1-Oxide (II-O).—A solution of 310 mg. of II in 20 ml. of glacial acetic acid was treated with 1 ml. of 30% hydrogen peroxide at room temperature for 4 hr. The gummy precipitate resulting from pouring into 100 ml. of water was triturated with methanol, leaving 160 mg. of pale yellow crystals, m.p. 134–136°. Recrystallization raised the melting point to 136–137°. There was a strong sulfoxide band at 9.65 μ and ultraviolet absorption at 230, 253, 297, 340 mμ, log ε 4.28, 4.36, 3.89, 3.57.

Anal. Calcd. for $C_{24}H_{20}OS$: C, 80.86; H, 5.66; S, 9.00. Found: C, 80.80; H, 5.86; S, 8.52.

Attempts to prepare the **sulfone** were unsuccessful. Either the sulfoxide was obtained or, under more vigorous conditions, no water-insoluble products could be isolated.

4-Methyl-2,4,6-triphenylthiopyran 1-oxide (III-O) was prepared from III by a similar procedure. It was recrystallized from hexane containing a little benzene; m.p. 156–157°. There was a strong sulfoxide band at 9.38 μ and ultraviolet absorption at 245 mμ, log ε 4.35.

Anal. Found: C, 80.78; H, 5.71; S, 8.74.

The 1,1-dioxide (III-O_2) was prepared from 300 mg. of III by using 5 ml. of 30% hydrogen peroxide and heating on a steam-bath for 10 min. The precipitate from water was recrystallized from ethanol to give 300 mg. of colorless needles, m.p. 198–198.5°. There were characteristic strong sulfone bands at 7.80 and 8.86 μ and ultraviolet absorption at 233 mμ, log ε 4.32.

Anal. Calcd. for $C_{24}H_{20}O_2S$: C, 77.40; H, 5.41; S, 8.60. Found: C, 77.77; H, 5.81; S, 8.66.

2- and 4-Ethyl-2,4,6-triphenylthiopyran.—To a vigorously stirred suspension of 2.5 g. (0.0059 mole) of finely powdered Ib in 50 ml. of anhydrous ether was added dropwise, under nitrogen, 25 ml. of 0.54 molar ethylmagnesium bromide in ether (2.3 equivalents). A rapid reaction was indicated by the disappearance of the thiopyrylium salt and the formation of a deeply colored (red), ether-soluble intermediate. Stirring was continued for 1 hr. At the end of this period the reaction mixture had assumed a deep yellow color. The ether solution was treated with 100 ml. of aqueous ammonium chloride solution. The aqueous layer was separated and extracted with two 30-ml. portions of ether. The combined organic extracts were washed with water and dried over anhydrous potassium carbonate. The solvent was removed *in vacuo*, leaving a yellowish, crude solid, weighing 1.65 g. (79%). After several recrystallizations from ethanol the light yellow needles melted at 90–91°.

Anal. Calcd. for $C_{25}H_{22}S$: C, 84.70; H, 6.25; S, 9.05. Found: C, 84.60, 84.65; H, 6.50, 6.45; S, 8.72, 8.89.

An inspection of the ultraviolet absorption curve for this material (λ 236, 255, 345 mμ, log ε 4.39, 4.34, 3.66) suggested it was a mixture of the 2- and 4-ethyl isomers. Assuming these two compounds have the same molar extinction coefficients as the 2- and 4-methyl homologs, it was estimated that the compound contained the two isomers in a 3:1 ratio.

4-Ethyl-2,4,6-triphenylthiopyran 1,1-Dioxide.—The mixed ethyl-2,4,6-triphenylthiopyrans (0.50 g., 0.0014 mole) were dissolved in 12 ml. of glacial acetic acid and 1 ml. of 30% hydrogen peroxide was added to the solution. The reaction mixture was heated on the steam-bath for 10 min. and then poured into 50 ml. of ice-water. A yellowish oil that separated from the solution solidified on scratching. After three recrystallizations from ethanol the colorless needles melted at 176–177°. The characteristic strong sulfone bands appeared at 7.75 and 8.88 μ and ultraviolet absorption at 236 mμ, log ε 4.26.

Anal. Calcd. for $C_{25}H_{22}O_2S$: C, 77.68; H, 5.74; S, 8.30. Found: C, 77.67, 77.72; H, 5.90, 5.96; S, 7.74, 7.62.

4-Butyl-2,4,6-triphenylthiopyran. (a) **From Butyllithium.**—Butyllithium solution in light petroleum ether (b.p. 32–37°) was prepared according to the procedure of Gilman, Moore and Baine,[9] cooled and filtered with nitrogen pressure through a glass wool plug. To a well-stirred suspension of 2.5 g. (0.0059 mole) of Ia in 40 ml. of light petroleum ether was added, in an atmosphere of nitrogen, 40 ml. (0.0076 mole) of butyllithium in petroleum ether over a 15-min. period. An immediate reaction was manifested by the disappearance of the thiopyrylium salt and the formation of a deep red, ether-soluble intermediate. Stirring was continued for 25 min. At the end of this period, the color of

---

(5) This scheme would not be available for the corresponding phosphorus analogs since the unshared electron pair of sulfur is now involved in σ-bonding. This may account for our failures (T. Parasaran) to date to prepare phosphopyrylium salts or "phosphabenzenes."

(6) G. Suld and C. C. Price, *J. Am. Chem. Soc.*, **84**, 2094 (1962).

(7) R. Wizinger, S. Losinger and P. Ulrich, *Helv. Chim. Acta*, **39**, 5 (1956).

(8) R. Wizinger and P. Ulrich, *ibid.*, **39**, 207 (1956).

(9) H. Gilman, F. W. Moore and O. Baine, *J. Am. Chem. Soc.*, **63**, 2479 (1941).

the solution had changed to yellow. The reaction mixture was treated with aqueous ammonium chloride solution, the aqueous layer was extracted with ether and the combined organic layers were dried over anhydrous potassium carbonate. After the removal of the solvents under reduced pressure, a yellowish-white, crude solid weighing 1.30 g. (57.5%) was obtained. Three recrystallizations from ethanol afforded colorless needles, m.p. 102–103°; λ_{max} 236 mμ, log ϵ 4.48.

Anal. Calcd. for $C_{27}H_{26}S$: C, 84.77; H, 6.85; S, 8.38. Found: C, 84.72, 84.70; H, 6.99, 7.00; S, 8.30, 8.56.

(b) **From Butylmagnesium Bromide.**—A stirred suspension of 2.5 g. (0.0059 mole) of finely powdered Ia in 40 ml. of anhydrous ether was treated dropwise, in an atmosphere of nitrogen, with 8 ml. of 1.7 molar ethereal butylmagnesium bromide solution in the course of 10 min. A vermilion colored, ether-soluble intermediate was formed with the concurrent disappearance of the thiopyrylium salt. The reaction mixture was stirred for 1 hr. At the end of this period, the color of the solution had changed from red to deep yellow. The ether solution was treated with 100 ml. of aqueous ammonium chloride solution, the aqueous layer was extracted with two 50-ml. portions of ether and the combined organic layers were dried over anhydrous potassium carbonate. After removal of ether a yellow residual oil was obtained which upon crystallization from ethanol yielded colorless needles, weighing 0.80 g. (35.5%), m.p. 101.5–103°. A mixture melting point with a sample of the product from the reaction of butyllithium with 2,4,6-triphenylthiopyrylium perchlorate showed no depression.

4-Butyl-2,4,6-triphenylthiopyran 1,1-Dioxide.—To a solution of 0.40 g. (0.0015 mole) of 4-butyl-2,4,6-triphenylthiopyran in 8 ml. of glacial acetic acid was added 1 ml. of 30% hydrogen peroxide and the mixture was heated on the steam-bath for 10 min. Upon cooling, a crop of colorless needles weighing 0.40 g. was obtained. After recrystallization from ethanol the product melted at 169.5–170.5°. The characteristic sulfone bands appeared at 7.77 and 8.88 μ and the ultraviolet absorption at 234 mμ, log ϵ 4.30.

Anal. Calcd. for $C_{27}H_{26}O_2S$: C, 78.23; H, 6.32; S, 7.72. Found: C, 77.84, 77.78; H, 6.50, 6.33; S, 8.11, 8.10.

2-Cyclopentadienyl-2,4,6-triphenylthiopyran.—Cyclopentadienyllithium was prepared by the method of Doering and DePuy.[10] The ethereal suspension of cyclopentadienyllithium (60 ml., *ca.* 4 equivalents) was added dropwise, under nitrogen atmosphere, in the course of 20 min., to a stirred suspension of 5.0 g. (0.012 mole) of finely powdered Ia in 80 ml. of dry ether. The reaction mixture gradually turned brownish-red. However, after stirring for 30 min. most of the thiopyrylium salt remained unreacted. Heat was then applied and the mixture was stirred under reflux for an additional 40 min. Work-up of the homogeneous, deep yellow ether solution was accomplished by treatment with 200 ml. of aqueous ammonium chloride solution, extraction of the aqueous layer with ether and drying of the combined organic layers over anhydrous potassium carbonate. Ether was removed on the water-pump and the yellowish-gray residual solid was recrystallized from an acetone–ethanol mixture to give 3.4 g. (72.8%) of light yellow platelets, m.p. 137–138°. Ultraviolet absorption was observed at 239, 255 and 348 mμ, log ϵ 4.30, 4.46 and 3.67.

Anal. Calcd. for $C_{28}H_{22}S$: C, 86.12; H, 5.68; S, 8.20. Found: C, 85.82; H, 5.61; S, 8.15.

4H-2,4,6-Triphenylthiopyran.—Finely powdered Ia (5.0 g. 0.012 mole) was added with stirring, in an atmosphere of nitrogen, over a 15-min. period, to a slurry of 2.0 g. of lithium aluminum hydride in 60 ml. of dry ether. When the addition was complete, the mixture was stirred for another 10 min. and the yellow ethereal solution was decanted from the unreacted reducing agent. After treatment with moist ether to decompose the excess lithium aluminum hydride the reaction mixture was shaken with 150 ml. of aqueous ammonium chloride solution, the aqueous layer was extracted with three 50-ml. portions of ether, the combined organic layers were washed with water and dried over anhydrous potassium carbonate. Ether was distilled and the residual oil, after trituration with a small volume of ethanol, solidified to a grayish-yellow solid. Since solutions of the compound in organic solvents were found to be sensitive to air oxidation, especially at elevated temperatures, recrystallization of the compound from ethanol was carried out in an atmosphere of carbon dioxide. The first crop furnished colorless needles, m.p. 100.5–102.5°. Upon concentration of the ethanolic mother liquor another crop of slightly yellowish crystals was obtained, m.p. 92–96°. The total yield of the product was 2.10 g. (53.8%).

Anal. Calcd. for $C_{23}H_{18}S$: C, 84.63; H, 5.56; S, 9.80. Found: C, 84.89, 84.66; H, 5.66, 5.73; S, 10.07, 10.16.

For this compound the 4H-2,4,6-triphenylthiopyran structure was indicated by the infrared and the ultraviolet spectra, λ_{max} 235 and 350 mμ, log ϵ 4.46 and 3.20.

An attempt to chromatograph the compound on an alumina column was unsuccessful. A deep-seated degradation of the thiopyran was indicated by the brownish-red coloration of the column and a yellow, malodorous eluate.

Reaction of 4H-2,4,6-Triphenylthiopyran with Alkylating Agents. A. With Methyl Iodide.—Methyl iodide (5 ml.), was added to a solution of 3.0 g. (0.0092 mole) of 4H-2,4,6-triphenylthiopyran in 20 ml. of nitromethane contained in a Carius tube, in an atmosphere of nitrogen. The tube was sealed and allowed to stand in the dark at 37° for 14 days. At the end of this period the contents of the tube had become a rather viscous solution, assuming a greenish-brown color. The tube was opened and a small quantity of colorless crystals (*ca.* 50 mg.) was removed by filtration. Upon recrystallization from ethanol the colorless crystalline compound melted at 203–206° (lit.[11] melting point for trimethylsulfonium iodide, 203–207°).

The filtrate was concentrated to dryness *in vacuo* and the dark-green, viscous residue was triturated with 30 ml. of benzene. A dark, deep violet solid that separated from the solution was collected by filtration; it weighed 2.10 g. and melted at 196–201°. After two recrystallizations from dilute acetic acid the deep-violet needles melted at 206–207° (sealed tube).

A mixed melting point with an authentic sample of Ib prepared by the methathesis of 2,4,6-triphenylthiopyrylium fluoborate with sodium iodide showed no depression.

The benzene filtrate yielded, after removal of the solvent on the water-pump, 1.8 g. of a dark oil which failed to crystallize. Attempts to purify this material by column chromatography were unsuccessful. Qualitatively analogous results were obtained on varying the length of time or the solvent of the methylation reaction.

B. **With Dimethyl Sulfate.**—To a solution of 3.0 g. (0.0092 mole) of 4H-2,4,6-triphenylthiopyran in 30 ml. of acetone was added 1.80 g. (0.0134 mole) of purified dimethyl sulfate and 2.8 g. of anhydrous potassium carbonate. The reaction mixture was then heated under reflux in an atmosphere of nitrogen for 12 hr. Acetone was removed at the water-pump, the solid residue was extracted with two 20-ml. portions of ether and then shaken with 20 ml. of water. A bright yellow crystalline, water-insoluble solid was collected by filtration, washed several times with water and recrystallized from ethanol. It weighed 1.20 g. and melted at 212–214°. Another recrystallization from ethanol raised the melting point to 213–214.5°. Its analysis agreed with that expected for **2,4,6-triphenylthiopyrylium methosulfate**.

Anal. Calcd. for $C_{24}H_{26}O_4S_2$: C, 66.09; H, 4.59; S, 14.68. Found: C, 66.25; H, 5.02; S, 14.08, 14.19.

C. **With Triethyloxonium Fluoborate.**—Triethyloxonium fluoborate was prepared by the method of Meerwein, Hinz, Hoffmann, Kroning and Pfeil,[12] and a solution of 3.0 g. (0.0158 mole) in 5 ml. of methylene chloride was added to a solution of 2.2 g. (0.0068 mole) of 4*H*-triphenylthiopyran in 6 ml. of methylene chloride, sealed in a Carius tube in an atmosphere of nitrogen. After 40 hr. at room temperature the tube was opened and a small amount (*ca.* 50 mg.) of a colorless, hygroscopic solid was removed by filtration. The reddish-brown filtrate was concentrated to dryness *in vacuo* and a greenish-brown viscous residue was triturated with a small volume of ethanol. A yellow, crystalline solid obtained from the treatment with ethanol was collected by filtration and washed with ether. It weighed 1.10 g. and after recrystallization from ethanol melted at 193–194.5°. A mixture melting point with an authentic sample of 2,4,6-triphenylthiopyrylium fluoborate was not depressed.

---

[10] W. v. E. Doering and C. H. DePuy, *J. Am. Chem. Soc.*, **75**, 5955 (1953).

[11] W. Steinkopf and S. Müller, *Ber.*, **56B**, 1926 (1923).

[12] H. Meerwein, G. Hinz, P. Hoffmann, E. Kroning and E. Pfeil *J. prakt. Chem.*, **147**, 257 (1937).

Desulfurization of III.—Raney nickel W-2 catalyst (20 g.) was added to a solution of 3.0 g. (0.0088 mole) of III in 200 ml. of warm ethanol and the resulting mixture was heated under reflux with stirring for 4 hr. After cooling and removal of the catalyst by filtration, the combined filtrates were concentrated to dryness *in vacuo*. Almost colorless, viscous residual oil was dissolved in 20 ml. of ether and the solution was treated with charcoal and filtered. Upon evaporation of ether, the colorless residual oil weighed 2.50 g., $n^{30.3}\mathrm{D}$ 1.5805. A sample of the oil gave a negative test for sulfur (lead acetate) after sodium fusion and a negative test for unsaturation (iodine on filter paper).

This material was further purified by column chromatography and distillation, $n^{30.3}\mathrm{D}$ 1.5804.

Anal. Calcd. for $C_{24}H_{26}$: C, 91.66; H, 8.34. Found: C, 91.71; H, 8.12.

Desulfurization of II.—Raney nickel W-2 catalyst (16 g.) was added to a solution of 2.0 g. (0.0059 mole) of II in 150 ml. of ethanol and the mixture was heated under reflux, with stirring for 6 hr. After cooling and removal of the catalyst by filtration, the filtrate and the washings were combined and concentrated to dryness *in vacuo*. The colorless, viscous residual oil weighed 1.65 g., $n^{30.2}\mathrm{D}$ 1.5679, and gave negative sulfur and unsaturation tests.

The crude oil was further purified by column chromatography; $n^{30.2}\mathrm{D}$ 1.5682.

Anal. Calcd. for $C_{24}H_{26}$: C, 91.66; H, 8.34. Found: C, 91.66; H, 8.54.

1-Methyl-1-(2-phenethyl)-indane.—1,5-Diphenyl-3-methyl-3-pentanol, b.p. 144° (0.2 mm.), $n^{30.0}\mathrm{D}$ 1.5529,[13] prepared from 2-phenethylmagnesium bromide and methyl acetate, was treated with ferric chloride in benzene. Instead of alkylating the benzene, the alcohol cyclyzed to give **1-methyl-1-(2-phenethyl)-indane**, b.p. 112° (0.2 mm.), $n^{20}\mathrm{D}$ 1.5701, d^{20} 1.0221.

Anal. Calcd. for $C_{18}H_{20}$: C, 91.48; H, 8.52; mol. wt. 236; $M^{20}\mathrm{D}$, 75.9. Found: C, 91.92; H, 8.44; mol. wt. (cryosc.), 238; $M^{20}\mathrm{D}$ 75.8.

1,3,5-Triphenyl-3-pentanol was prepared from 2-phenethylmagnesium bromide and ethyl benzoate. On distillation, material was obtained, b.p. 160–170° (0.05 mm.), $n^{27}\mathrm{D}$ 1.5913.

Anal. Calcd. for $C_{23}H_{24}O$: C, 87.48; H, 7.65. Found: C, 88.66; H, 7.31.

Apparently some dehydration occurred on distillation. The pot residue solidified on standing, and trituration with a small amount of methanol gave a waxy solid, m.p. 53.5–54.5°.

Anal. Found: C, 87.32; H, 7.68.

The 3,5-dinitrobenzoate formed colorless needles from methanol; m.p. 123.5–125°.

Anal. Calcd. for $C_{30}H_{27}N_2O_6$: C, 70.57; H, 5.33; N, 5.49. Found: C, 70.28; H, 5.25; N, 5.36.

Efforts to convert this to the chloride were unsuccessful because of the ease of dehydrochlorination.

3-Methyl-1,3,5-triphenylpentane. (V).—Acetophenone was condensed with 2-phenethylmagnesium bromide and the resulting alcohol, m.p. 47–48°,[14] converted to the chloride by shaking with concentrated hydrochloric acid. The crude chloride (16 g.) was immediately condensed with 2-phenethylmagnesium bromide in ether to give 11.2 g. of viscous oil, b.p. 186° (0.05 mm.), $n^{30.2}\mathrm{D}$ 1.5770; after two redistillations, $n^{20}\mathrm{D}$ 1.5780. The infrared spectrum of this compound was identical to that of the hydrocarbon obtained from the desulfurization of III.

Anal. Calcd. for $C_{24}H_{26}$: C, 91.66; H, 8.34. Found: C, 91.51; H, 8.35.

1,3,5-Triphenylhexane (IV).—1,3-Diphenyl-1-butanone, m.p. 71–72°,[15] from hydrogenation of dypone, was treated with 2-phenethylmagnesium bromide in ether to yield 1,3,5-triphenyl-3-hexanol, b.p. 185–187° (0.11–0.15 mm.), $n^{27}\mathrm{D}$ 1.5845. Analysis indicated partial dehydration had occurred so the process was completed by refluxing with 1% sulfuric acid in glacial acetic acid to yield the unsaturated compound, b.p. 164–168° (0.04–0.05 mm.), $n^{30}\mathrm{D}$ 1.5900.

Anal. Calcd. for $C_{24}H_{24}$: C, 92.26; H, 7.74. Found: C, 91.93; H, 7.75.

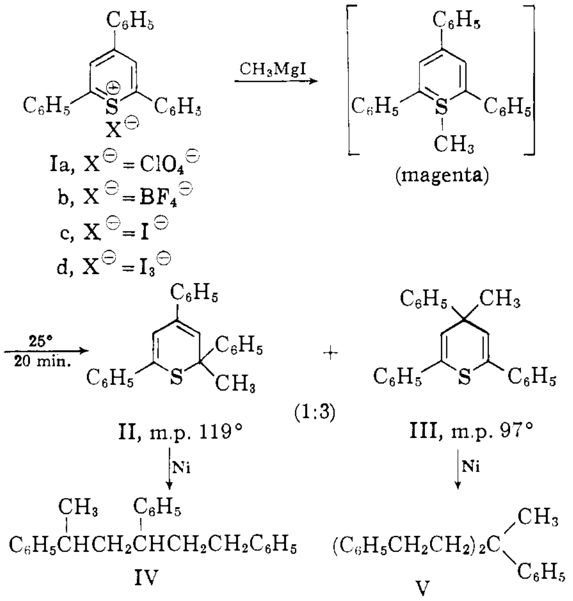
An 11.8-g. sample in 100 ml. of ethanol was hydrogenated at room temperature at 50 p.s.i. hydrogen pressure with Raney nickel catalyst. Hydrogen uptake ceased in 3.5 hr. The product was a colorless oil, 9.9 g. (83%), b.p. 147–153° (0.05–0.07 mm.), $n^{30.1}\mathrm{D}$ 1.5700.

Anal. Calcd. for $C_{24}H_{26}$: C, 91.66; H, 8.33. Found: C, 91.89; H, 8.28.

The infrared spectrum in carbon disulfide was identical to that of the desulfurization product of II. The spectra of IV and V had similar bands at 3.22(m), 3.26(s), 3.38(s), 3.46(m), 5.12(mw), 5.34(w), 5.55(w), 5.74(w), 6.24(s), 7.25(m), 8.49(w), 8.66(w), 9.70(s), 11.04(m), 11.95(w), 13.35(vs) and 14.35(vs). Compound IV had characteristic bands at 6.01(w), 9.05(w), 9.25(m), 9.38(w) and 13.15(vs), while V showed characteristic bands at 7.50(w), 7.85(w), 8.05(w), 9.30(m), 12.95(s) and 14.10(s).

Discussion

The immediate dissolution of the ether-insoluble thiopyrylium salts on addition of methyl, ethyl- or butylmagnesium halide, or of butyllithium, indicates that a rapid reaction occurs. The initially intensely colored (red or purple) ether solution then fades during 20–30 minutes to yellow and the products isolated are the 2- and 4-alkyl-thiopyrans. Since for phenyllithium reaction[6] the deep purple thiabenzene could be isolated, but then slowly rearranged to tetraphenylthiopyran, the above observations would seem to suggest the same chemistry for the alkyl reagents, although the 1-alkylthiabenzenes must rearrange more rapidly.



The structure of the thiopyrans II and III was established by Raney nickel desulfurization to the hydrocarbons IV and V, which were synthesized by the routes shown.

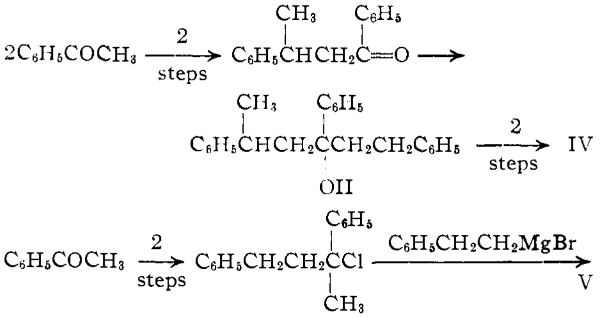
The structures account adequately for the ultraviolet spectra since III, with a simpler conjugated system, has a single maximum at 235 mμ, while II, with a more extended conjugated system, has two maxima at 257 and 347 mμ. Both II and III were readily converted to sulfoxides, but only III gave a sulfone This observation would also

---

[13] J. S. Salkind, *J. Russ. Phys. Chem. Soc.*, **50**, 25 (1917), reported that this alcohol dehydrated during distillation and gave no analytical data. *Anal.* Calcd. for $C_{18}H_{22}O$: C, 84.99; H, 8.72. Found: C, 84.50, 84.77; H, 8.89, 8.81.

[14] R. Stoermer and H. Kootz, *Ber.*, **61**, 2333 (1928).

[15] F. Gollnitz, *Ann.*, **330**, 232 (1904).



$$2C_6H_5COCH_3 \xrightarrow[\text{steps}]{2} C_6H_5\underset{}{\overset{CH_3}{\overset{|}{C}}}HCH_2\overset{C_6H_5}{\overset{|}{C}}{=}O \longrightarrow$$

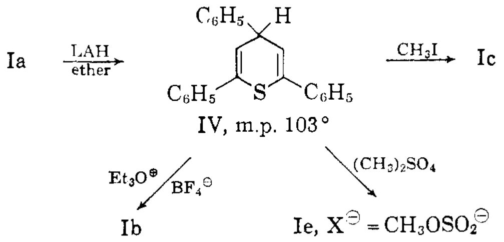
$$C_6H_5\overset{CH_3}{\overset{|}{C}}HCH_2\underset{OH}{\overset{C_6H_5}{\overset{|}{C}}}CH_2CH_2C_6H_5 \xrightarrow[\text{steps}]{2} IV$$

$$C_6H_5COCH_3 \xrightarrow[\text{steps}]{2} C_6H_5CH_2CH_2\underset{\underset{CH_3}{|}}{\overset{C_6H_5}{\overset{|}{C}}}Cl \xrightarrow[V]{C_6H_5CH_2CH_2MgBr}$$

agree with the assigned structures, since the sulfur atom would be less sterically hindered in III than in II.

The factors affecting the ratio of 2-alkyl- to 4-alkylthiopyran are obscure. Under apparently similar conditions, ethylmagnesium bromide gave a mixture favoring the 2-isomer by 3:1, butylmagnesium bromide (or butyllithium) gave the 4-butyl compound while cyclopentadienyllithium gave the 2-isomer. The structure assignment for these compounds was made on the basis of the ultraviolet and infrared adsorption spectra. Only in the latter case did any complication occur; a shoulder at 239 mμ was assumed to be due to the cyclopentadienyl ring chromophore.

Reaction of the thiopyrylium salt I with lithium aluminum hydride produced a thiopyran which, on the basis of its spectrum, was assigned the structure of 4*H*-2,4,6-triphenylthiopyran. The major band at 235 mμ corresponds to this assignment. There is no band at 255–260 mμ.



The band at 348 mμ is only about one-quarter the intensity of the corresponding band in II.

We had hoped to alkylate the sulfur atom of VI and then proton abstraction by base might have produced the 1-alkylthiabenzene. Alkylation with methyl iodide, methyl sulfate and triethyloxonium fluoborate, however, led to the recovery of 2,4,6-triphenylthiopyrylium ion. The nature of the intermediates and the course of this "oxidation" of VI to I is not clear.

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

Thiabenzene. III. 1,2,4,6-Tetraphenylthiabenzene, its Rearrangement and Oxidation[1]

BY GEORGE SULD[2] AND CHARLES C. PRICE

RECEIVED JANUARY 20, 1962

The reaction of phenyllithium with 2,4,6-triphenylthiopyrylium perchlorate gives an intensely purple colored amorphous solid. On the basis of its rapid decolorization by oxygen to a "peroxide" cleaved by acid to thiophenol and 2,4,6-triphenylpyryl-3-oxide (IC), this purple solid is assigned the structure of 1,2,4,6-tetraphenylthiabenzene (III). At room temperature, III rearranges to the isomeric colorless crystalline 2,4,4,6-tetraphenylthiopyran (II).

The observation that the intense color formed by reaction of phenyllithium with I in ether faded much more slowly than those colors from alkyl reagents[3] has encouraged us to undertake the isolation of the colored intermediate, which has been shown to be an etherate complex of 1,2,4,6-tetraphenylthiabenzene (III).

Experimental

2,4,4,6-Tetraphenylthiopyran (II).—To a finely powdered suspension of 2.5 g. (0.0059 mole) of 2,4,6-triphenylthiopyrylium perchlorate in 20 ml. of anhydrous ether was added 7.6 ml. (1 equiv.) of phenyllithium solution in ether and the reaction mixture was then shaken mechanically, in an atmosphere of nitrogen, for 7 days. The suspended thiopyrylium salt dissolved, forming initially a violet-red solution which lightened gradually to give a brownish-yellow ether solution. The ethereal solution was treated with aqueous ammonium chloride solution, the organic layer was washed with water and dried with anhydrous potassium carbonate. The solvent was removed under reduced pressure and the residual brown oil was dissolved in a small volume of ethanol. Since the oil showed no sign of crystallization, the solution was left standing for 3 months. After this period the oil had become a semi-solid mass (the solvent had evaporated). The oil was suspended in a small volume of ethanol and the suspension was shaken mechanically for 24 hr. A solid colorless crystalline product that was obtained was collected by filtration. It weighed 0.82 g. and melted, after two recrystallizations from ethanol, at 157–157.5°. The ultraviolet spectrum showed a single major peak at 235 mμ, log ε 4.29, and the principle infrared absorption bands were at 6.25, 6.70, 6.91, 9.25, 9.69, 10.90, 11.05, 11.25, 12.22, 12.98, 13.27, 14.25 and 14.47 μ (KBr disk).

Anal. Calcd. for $C_{29}H_{22}S$: C, 86.52; H, 5.51; Si, 7.97. Found: C, 86.34, 86.83; H, 6.03, 5.86; S, 8.25.

2,4,4,6-Tetraphenylthiopyran 1,1-Dioxide.—To a hot solution of 50 mg. of the tetraphenylthiopyran in 4 ml. of glacial acetic acid was added 6 drops of 30% hydrogen peroxide and the reaction mixture was heated on a steam-bath for 10 min. Upon dilution of the mixture with 10 ml. of ice-water, a colorless, crystalline solid separated. Twice recrystallized from ethanol, it melted at 192–193°. This sulfone had strong characteristic bands at 7.70 and 8.82 μ, and at 235 and 355 mμ, log ε 4.42 and 3.07.

Anal. Calcd. for $C_{29}H_{22}O_2S$: C, 80.15; H, 5.10. Found: C, 80.04; H, 5.18.

1,2,4,6-Tetraphenylthiabenzene (III).—Reaction of 35 ml. (3.5 equiv.) of phenyllithium in ether with a stirred suspension of 2.5 g. of I in 100 ml. of ether under nitrogen led to

---

[1] Presented in part at the 136th Meeting, Am. Chem. Soc., Atlantic City, N. J., September 15, 1959; see also G. Suld and C. C. Price, *J. Am. Chem. Soc.*, **83**, 1770 (1961).

[2] Supported in part by National Science Foundation Grant No. G-6270.

[3] G. Suld and C. C. Price, *J. Am. Chem. Soc.*, **84**, 2090 (1962).