

Efforts to Synthesize the Trithietanylium Ion (1)

E. Campaine, M. Pragnell and F. Haaf

The Chemistry Laboratories of Indiana University

Recent research on heterocyclic compounds has been focused on nonbenzenoid cyclic conjugated systems. The tropylium cation has served as the parent structure for a variety of heterocyclic aromatic systems. The ability of sulfur to participate in conjugated systems, acting either as an electron donor or acceptor, is well established (2). In conjugated systems, the sulfur atom can be compared formally to a carbon-carbon bond. By replacing a formal ethylenic pair of carbon atoms in the tropylium cation by a sulfur atom, one obtains the thiapyrylium ion, I, and replacement of two such pairs of carbon atoms leads to the 1,2-dithiolium (II) and 1,3-dithiolium (III) cations. Examples of these sulfur heterocyclic cationic systems are well-known (3,4). The ultimate example of such formal structural analogy would be a ring system of three sulfur atoms and a carbon atom, in which all of the doubly-bonded carbon atoms of the tropylium ion are replaced by sulfur atoms. This is the trithietanylium ion, IV. Zahradnik has reviewed the electronic structure of heterocyclic sulfur compounds (5), based on molecular orbital calculations, and concludes that the steric strain and unfavorable energy characteristics of IV offer little hope that it will be a stable compound.

We have attempted to prepare the phenyl derivative of IV by treating dithiobenzoic acid with sulfur dichloride in carbon tetrachloride under nitrogen. Two products were obtained, a yellow crystalline solid which precipitated immediately from solution, and a red oil which could be recovered by concentration of the solution. The yellow solid was insoluble in organic solvents, decomposed in nucleophilic solvents (alcohol or water) and on exposure to air also gradually converted to a red oil. It could, however, be washed well with carbon tetrachloride or dry ether, melted sharply in the range of 90-92° to 105-107°, depending on preparation, gave an excellent elemental analysis for $C_7H_5S_3Cl$ considering the product to be a non-recrystallized washed salt, and showed the presence of chloride ion in alcoholic silver nitrate. The infrared spectrum showed no functional group characteristics, and the fingerprint region was consistent with an electro-positive atom joined to a benzene ring, *i.e.*, it was similar to benzoyl trichloride (6). The red oil showed an I.R. spectrum resembling thiobenzoic acid in the fingerprint range (7-12 μ) and a carbonyl peak at 5.85 μ , indicating that it probably contains C_6H_5COS- .



I



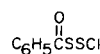
II



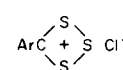
III



IV



V



VIa, Ar = C_6H_5
 VIb, Ar = $p-CH_3OC_6H_4$
 VIc, Ar = $\alpha-C_{10}H_7$

Mass spectral data were inconclusive due to difficulties of sample handling. However, a mass spectrum was carried out on a sample of the yellow solid, sealed under nitrogen in our laboratories (7), using a "Time of Flight" mass spectrometer at several temperatures, voltages and degrees of sensitivity. This spectrum shows peaks at atomic mass units 32 (S) 36 (HCl?) and strong peaks at 105 ($C_6H_5C^+$?) 122 ($C_7H_6S^+$?) 135, 149 and 161. At higher temperatures, peaks at 64 (S_2), 77 (C_6H_5) and at 121 ($C_7H_5S^+$?) begin to appear, and at higher voltages the peak at 161 is greatly reduced while fragmentation of benzene is apparent. The peaks at 135 ($C_3H_3S_3^+$?) 149 ($C_4H_5S_3^+$?) and 161 ± 1 ($C_5H_5S_3^+$?) seem inconsistent with expected fragmentation of $C_7H_5S_3Cl$.

The ready reaction of the yellow crystalline salt with nucleophilic solvents and moist air suggests a highly electrophilic character. Addition to morpholine produced thiobenzmorpholide in 90% yield. Sulfur was also produced in this reaction. Similarly aniline reacts readily with the salt to produce sulfur and thiobenzanilide. However, warming the salt in dimethylaniline or resorcinol have not produced any thioketones; intractable tars

containing free sulfur were the only products obtained. Bohme and Clement (8) prepared benzoyl disulfur chloride (V) by chlorination of dibenzoyl disulfide. This was an oil-soluble material which reacted with β -naphthalenethiol to form benzoyl β -naphthyl trisulfide. However, treatment of the yellow salt with β -naphthalenethiol led to the isolation of only bis β -naphthyl trisulfide in low yield. It is not surprising that reaction of monothiobenzoic acid with sulfur dichloride in carbon tetrachloride under nitrogen produced dibenzoyl trisulfide, as stable recrystallizable colorless needles.

On the basis of available evidence, the most reasonable structure for the yellow salt is that of 4-phenyltrithietanylium chloride (VIa) and the red oils to which it is converted and which are formed with it are probably mixtures of benzoyl and thiobenzoyl disulfur chlorides and polysulfides. The possibility of dimeric or polymeric forms of VI cannot be ruled out at this time.

Two other aryldithiobenzoic acids, *p*-methoxydithiobenzoic acid and α -dithionaphthoic acid, on similar treatment with sulfur dichloride, also produced yellow unstable salts in 10 and 40% yields, respectively. We believe these compounds to be VIb and VIc, or polymers thereof. The *p*-methoxyphenyl derivative (VIb) reacted with morpholine to produce sulfur and *p*-methoxythiobenzoylmorpholide in 93% yield.

EXPERIMENTAL (9)

Reactions of Dithiobenzoic Acid with Sulfur Dichloride.

(A)

A mixture of 3.09 g. (0.03 mole) sulfur dichloride and 100 ml. dry carbon tetrachloride were kept under a nitrogen atmosphere by bubbling in a weak stream of nitrogen. While stirring, 100 ml. of the dithiobenzoic acid solution (10) in ether (containing 0.03 mole dithiobenzoic acid) were added dropwise. Ten minutes after starting the reaction a yellow solid precipitated, which disappeared after 1 hour. The reaction mixture was stirred overnight, then warmed for 1 hour on the steam bath. The solvent was removed under reduced pressure to give 7.5 g. of a red, viscous oil.

The red oil was insoluble in alcohol, ethyl acetate, ether and petroleum ether. An attempt to dissolve 0.9 g. of the red oil in 5 ml. perchloric acid (70%) caused an explosion. The infrared spectrum of the red oil (thin film) showed peaks at 3.25, 3.35, 5.12, 5.32, 5.80, 5.95, 6.35, 6.85, 7.0, 7.35, 7.65 and 7.85 μ .

(B)

To the solution of 3.6 g. (0.035 mole) sulfur dichloride in 100 ml. dry carbon tetrachloride, 100 ml. dithiobenzoic acid solution in ether (0.03 mole) were added dropwise, while the mixture was stirred and kept under nitrogen. After some minutes a yellow solid precipitated. The yellow solid was collected by filtration, after about half of the dithiobenzoic acid solution had been added. After washing several times with dry ether and drying under reduced pressure at room temperature, the yellow solid (0.95 g., 14.3%) melted at 90-92° dec. The infrared spectrum (potassium bromide mull) 4.3, 6.4, 7.0, 7.5, 7.7, 7.8, 8.5 μ .

Anal. Calcd. for $C_7H_5S_3Cl$: C, 38.08; H, 2.29; S, 43.57; Cl, 16.06. Found: C, 38.37; H, 2.54; S, 43.57; Cl, 15.36.

To the filtrate of the yellow solid, the rest of the dithiobenzoic acid solution was added. The solvent was removed under reduced pressure to give a red viscous oil.

(C)

To the solution of 3.4 g. (0.033 mole) sulfur dichloride in 50 ml. carbon tetrachloride, 50 ml. of the dithiobenzoic acid solution in ether (0.015 mole) was added within 10 minutes, while the mixture was stirred and kept under nitrogen. The yellow solid, which immediately precipitated, was collected by filtration under nitrogen and dried under reduced pressure; 0.84 g. (25.5%), m.p. 105-107° dec. The I.R. spectrum was identical to that of the previous preparation.

Reaction of the Yellow Salt with Morpholine.

In 10 ml. of morpholine, 0.30 g. (0.00136 mole) of $C_7H_5S_3Cl$ (yellow solid, VIa) was dissolved by warming to 40-50°. The solution was poured into water and extracted with ether. The ether layer was washed with water and dried (magnesium sulfate). After evaporation of the solvent 0.33 g. of a yellow solid was obtained. The solid was suspended in 30 ml. of acetone and the insoluble part was collected by filtration to give 0.055 g. of yellow crystals (62.5%), m.p. 120°, mixed m.p. with sulfur 119-120°.

The acetone was removed from the filtrate to give 0.255 g. of pale yellow crystals (90%), m.p. 130-134°. They were recrystallized from cyclohexane to give 0.200 g. of pale yellow needles (70%), m.p. 137-138.5°, mixed m.p. 137-138.5° with 1-thiobenzoylmorpholine, prepared from benzaldehyde, sulfur and morpholine. The I.R. spectrum of the yellow needles was also identical to the spectrum of 1-thiobenzoylmorpholine.

Reaction of the Yellow Solid with Aniline.

When 0.2 g. (1 mmole) of VIa was mixed with 0.17 g. (2 mmoles) of aniline, the reaction was exothermic. After warming for 10 minutes on a water bath, the red solution was cooled and triturated with ether, and 0.1 g. (85%) of aniline hydrochloride, melting at 198° on recrystallization from ethanol was recovered. The melting point of this sample was undepressed by mixture with an authentic sample and the I.R. spectrum was identical. The ether filtrate was washed with dilute hydrochloric acid, water, and dried over anhydrous magnesium sulfate. Removal of ether and recrystallization of the residual oil from methanol gave 0.12 g. (65%) of thiobenzanilide, m.p. 97-99°, identical with an authentic sample by mixture melting point and I.R. spectra.

Reaction of *p*-Methoxydithiobenzoic Acid with Sulfur Dichloride.

p-Methoxydithiobenzoic acid was prepared from *p*-anisaldehyde and ammonium polysulfide as a red oily solid in 40% yield, as described by Houben (11). A solution of this acid in ether (50 ml. of 0.3 *M.* solution) was added slowly to a solution of 2 ml. (3 mmoles) of sulfur dichloride in 50 ml. of dry carbon tetrachloride. The yellow solid which precipitated was collected on a sintered glass funnel in a nitrogen-filled glove bag, washed with dry ether, and dried in a vacuum desiccator. The product (0.4 g., 10%) melted at 95-96°, and slowly turned to a red oil on exposure to moist air.

Anal. Calcd. for $C_8H_7ClOS_3$: C, 38.32; H, 2.82; S, 38.36; Cl, 14.14. Found: C, 39.04; H, 3.20; S, 38.52; Cl, 14.41.

When 0.17 g. of the above salt was dissolved in 5 ml. of morpholine, the mixture warmed to 50° and then poured into water, a yellow oil was obtained. The mixture was extracted with ether, and the dried ether extract evaporated, leaving a yellow solid. Extraction of this solid with acetone left a residue of 25 mg. (58%) of sulfur, and evaporation of the acetone solution gave 0.15 g. (93%) of *p*-methoxythiobenzoylmorpholide, m.p. 102-103°

after recrystallization from ethanol. *p*-Methoxythiobenzoylmorpholide is reported to melt at 105° (12).

Anal. Calcd. for C₁₂H₁₅NO₂S: N, 5.90. Found: N, 5.81.

Reaction of α -Dithionaphthoic Acid with Sulfur Dichloride.

α -Dithionaphthoic acid was obtained as a red oil in 52% yield via the Grignard reagent and carbon disulfide (13). A solution of 15 mmoles of this acid in 50 ml. of ether was added dropwise with stirring to 50 ml. of carbon tetrachloride containing 2.06 ml. (30 mmole) of sulfur dichloride. The orange solid which precipitated was collected under nitrogen, washed with dry ether and dried in a vacuum desiccator, (1.45 g., 41%) melted at 91-92°.

Anal. Calcd. for C₁₁H₇S₃Cl: C, 48.79; H, 2.61; S, 35.52; Cl, 13.09. Found: C, 48.87; H, 2.66; S, 35.30; Cl, 12.19.

Reaction of Thiobenzoic Acid with Sulfur Dichloride.

To the solution of 5.8 g. (0.056 mole) sulfur dichloride in 50 ml. carbon tetrachloride, 6.9 g. (0.05 mole) thiobenzoic acid (14), dissolved in 100 ml. ether, were added dropwise, while the mixture was stirred and kept under nitrogen. After some minutes colorless crystals precipitated. After all the thiobenzoic acid solution was added, 3.39 g. of colorless crystals were collected by filtration, m.p. 159-162°. The solvent was partially removed and a second crop was obtained; 0.9 g., m.p. 158-161°. When the solvent was completely removed, 4.0 g. of an oily product was obtained as residue. The crystalline product was recrystallized from chloroform and *n*-hexane to give 3.44 g. well formed colorless needles, m.p. 140-144°. The reported melting point (15) for dibenzoyl trisulfide, recrystallized from chloroform and ligroin in the presence of a little sulfur dichloride, is 167-168°. When the dibenzoyl trisulfide was recrystallized without sulfur dichloride a sample was obtained which melted much lower and over a wide range (15). The crystals, m.p. 140-144°, were analyzed.

Anal. Calcd. for C₁₄H₁₀S₃O₂: C, 54.87; H, 3.29; S, 31.39. Found: C, 54.97; H, 3.46; S, 31.08.

The oily residue of the reaction product was extracted with hot *n*-hexane to give on cooling 0.43 g. of colorless crystals, m.p. 118-119°, mixed m.p. with benzoic acid 119-120°.

Reaction of the Yellow Solid with β -Naphthalenethiol.

To a suspension of 3.85 g. of yellow salt (VIa) in 25 ml. chloroform, 2.4 g. (0.015 mole) β -naphthalenethiol, dissolved in 50 ml. ether, were added. The mixture was stirred and kept under nitrogen for 2 hours. Then the solvent was removed to give 5.34 g. of a red oil, which partially solidified after some time. The oily solid was pressed on filter paper and recrystallized from cyclohexane to give 0.120 g. of a colorless solid, m.p. 98-101°. Two

further recrystallizations yielded 0.05 g. colorless crystals, m.p. 117-118°.

Anal. Calcd. for C₂₀H₁₄S₃: C, 68.53; H, 4.03; S, 27.44. Found: C, 68.67; H, 4.14; S, 27.11.

The I.R. spectrum of the crystals was identical to the I.R. spectrum of β,β -dinaphthyl trisulfide, prepared by the method of Troeger and Hornung (16).

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Bloomington, Indiana 47401