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Thermal Rearrangement of O-(2,4,6-Trihalophenyl) N,N-Dimethylthiocarbamates. An Abnormal Pathway[1]

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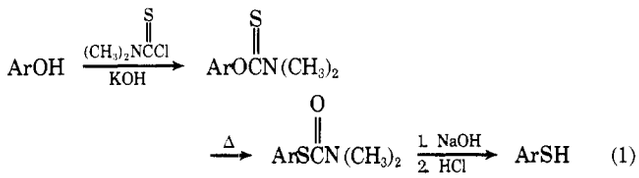
Received March 29, 1976

The conversion of phenols to benzenethiols via the N,N-dimethylthiocarbamates has been applied to the 2,4,6-trihalophenols. Results were highly dependent on whether the halogen was Cl, Br, or I. The pyrolysis of O-(2,4,6-trichlorophenyl) N,N-dimethylthiocarbamate (1) yielded S-(2,4,6-trichlorophenyl) N,N-dimethylthiocarbamate (2) which on hydrolysis gave 2,4,6-trichlorobenzenethiol (3). The pyrolysis of O-(2,4,6-tribromophenyl) N,N-dimethylthiocarbamate (4) gave 78% of S-(2,4,6-tribromophenyl) N,N-dimethylthiocarbamate (5) and 22% of N-(5,7-dibromo-1,3-benzoxathiol-2-ylidene)methanamine (6). Hydrolysis of this reaction mixture gave 2,4,6-tribromobenzenethiol (7) and bis(3,5-dibromo-2-hydroxyphenyl) disulfide (8). Compound 6 was shown to arise from N-(5,7-dibromo-1,3-benzoxathiol-2-ylidene)-N-methylmethanaminium bromide (9), which was isolated as an intermediate. The pyrolysis of O-(2,4,6-triiodophenyl) N,N-dimethylthiocarbamate (13) gave 80% of N-(5,7-diiodo-1,3-benzoxathiol-2-ylidene)-N-methylmethanaminium iodide (14). A mechanism is described.

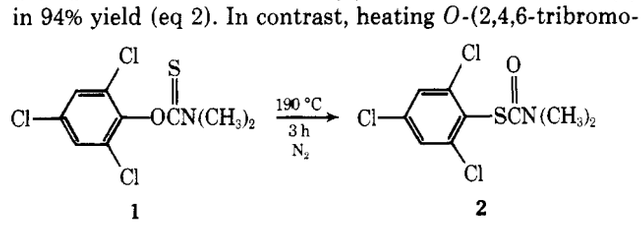
In 1966, Newman and Karnes[2] described a general method for the conversion of a phenol to the corresponding thiophenol which involved (a) reaction of the phenol with potassium hydroxide and dimethylthiocarbamoyl chloride to give the O-(aryl) N,N-dimethylthiocarbamate, (b) thermal rearrangement of the O-(aryl) N,N-dimethylthiocarbamate to the S-(aryl) N,N-dimethylthiocarbamate, and (c) hydrolysis of the S-(aryl) N,N-dimethylthiocarbamate to the thiophenol (eq 1).[3] More recently, this reaction sequence was applied to



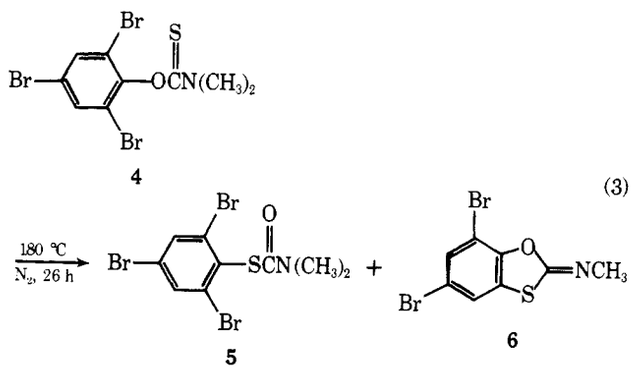
(1)

the preparation of the three isomeric tetrachlorobenzenethiols by Goralski and Burk[4] and to the synthesis of 2-mercaptophenol by Dodson and Hanson.[5] In this paper we discuss the thermal rearrangement of O-(2,4,6-trihalophenyl) N,N-dimethylthiocarbamates.

Pyrolysis of O-(2,4,6-trichlorophenyl) N,N-dimethylthiocarbamate (1) at 190 °C in a nitrogen atmosphere for 3 h afforded an 82% yield of S-(2,4,6-trichlorophenyl) N,N-dimethylthiocarbamate (2).[6] Hydrolysis of 2 with sodium hydroxide in methanol afforded 2,4,6-trichlorobenzenethiol (3) in 94% yield (eq 2). In contrast, heating O-(2,4,6-tribromophenyl) N,N-dimethylthiocarbamate (4) at 180 °C in a nitrogen atmosphere for 26 h afforded 78% S-(2,4,6-tribromophenyl) N,N-dimethylthiocarbamate (5) and 22% N-(5,7-dibromo-1,3-benzoxathiol-2-ylidene)methanamine (6, eq 3).



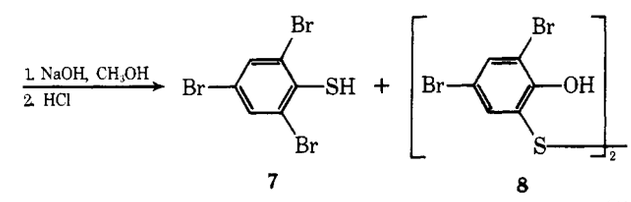
(2)



(3)

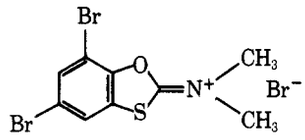
Subsequent hydrolysis of this product mixture with sodium hydroxide in methanol and fractional recrystallization of the acidified product gave 2,4,6-tribromobenzenethiol (7) in 69% yield, and bis(3,5-dibromo-2-hydroxyphenyl) disulfide (8) in 8% yield (eq 4). The structure of 8 was proven by reduction to

5 + 6



(4)

2,4-dibromophenol with Raney nickel. When the rearrangement of 4 was run at 170 °C, an insoluble material, isomeric with 4, was isolated and shown to be N-(5,7-dibromo-1,3-benzoxathiol-2-ylidene)-N-methylmethanaminium bromide (9). The structure of 9 was confirmed by hydrolysis with 1 N sulfuric acid to give 5,7-dibromo-1,3-benzoxathiol-2-one (10a), and by hydrolysis in basic solution to give 2,4-dibromo-6-



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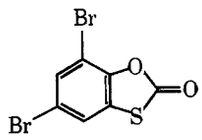
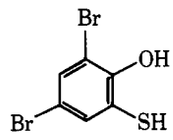
mercaptophenol (**10b**). Mercaptophenol **10b** was shown to readily oxidize to the disulfide **8**. A reasonable mechanistic

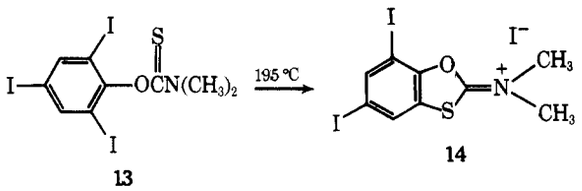


10a



10b

pathway, which adequately explains the above observation, is outlined in Scheme I. The desired *S*-(2,4,6-tribromophenyl) *N,N*-dimethylthiocarbamate (**5**) is proposed to arise via the four-membered-ring intermediate **11** originally postulated by Newman and Karnes.[2] The dimethylimmonium bromide **9** is believed to arise via the five-membered-ring intermediate **12**, which undergoes rearomatization by loss of a bromide ion. Rearrangement via an intermediate such as **12** should be favored by increased steric size of the halogen atoms and increased leaving group character of the halide ion. This hypothesis was substantiated by the fact that heating *O*-(2,4,6-triiodophenyl) *N,N*-dimethylthiocarbamate (**13**) at 195 °C for 30 min afforded an 80% yield of *N*-(5,7-diiodo-1,3-benzoxathiol-2-ylidene)-*N*-methylmethanaminium iodide (**14**, eq 5). The structure of **14** was confirmed by hydrolysis



13 14

(5)

with 1 N sulfuric acid to give 5,7-diiodo-1,3-benzoxathiol-2-one (**15**), and hydrolysis with sodium hydroxide to give 2,4-diiodo-6-mercaptophenol (**16**). Thus, the observed rearrangement of *O*-(2,4,6-trihalophenyl) *N,N*-dimethylthiocarbamates via the abnormal pathway is in the predicted order **13** > **4** ≫ **1**.[7]

The thermal conversion of **9** to **6** was verified by analysis of the thermal decomposition products of **9** in a mass spectrometer by the direct probe method. The mass spectra of **9** were recorded at temperatures varying from 204 to 504 °C, and the molecular ions of both **6** and methyl bromide were observed. The intensities of the molecular ions of both **6** and methyl bromide were found to increase with temperature.

Experimental Section[8]

***O*-(2,4,6-Trichlorophenyl) *N,N*-Dimethylthiocarbamate (1).** The procedure of Newman and Hetzel was employed.[9] A solution of 59.25 g (0.3 mol) of 2,4,6-trichlorophenol and 16.83 (0.3 mol) of potassium hydroxide in 200 ml of water was cooled to 10 °C while a solution of 49.44 g (0.4 mol) of *N,N*-dimethylthiocarbamoyl chloride in 80 ml of tetrahydrofuran was added dropwise with stirring. The addition was made at such a rate that the reaction temperature was maintained below 13 °C. After the addition was complete, the reaction mixture was made basic (ca. pH 9) and extracted with benzene. The benzene extract was dried over anhydrous magnesium sulfate and condensed in vacuo to give a light yellow solid. Recrystallization from methanol gave 61.24 g (71.7%) of **1**, mp 108–110 °C (lit.[10] mp 109–110 °C).

Rearrangement of 1. *S*-(2,4,6-Trichlorophenyl) *N,N*-Dimethylthiocarbamate (2). A sample of 39.8 g (0.14 mol) of **1** was heated at 210–215 °C for 2 h. The NMR spectrum showed the rearrangement to be about 95% complete.[11] After cooling, the solid product was recrystallized from methanol to give 32.5 g (82%) of **2**, mp 129–131 °C.

Anal. Calcd for $C_9H_8Cl_3NOS$: C, 37.98; N, 2.83; Cl, 37.38; N, 4.92. Found: C, 38.10; H, 3.02; Cl, 37.20; N, 4.95.

2,4,6-Trichlorobenzenethiol (3). Carbamate **2** was hydrolyzed by the previously reported[2,3] procedure to give **3**, mp 57–60 °C.

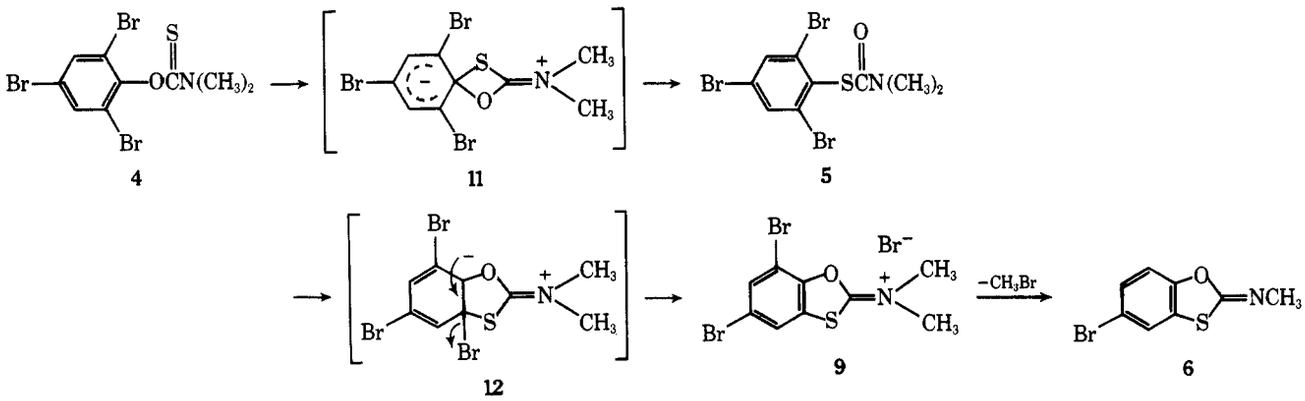
Anal. Calcd for $C_6H_3Cl_3S$: C, 33.75; H, 1.41; Cl, 49.82; S, 15.02. Found: C, 33.60; H, 1.46; Cl, 49.20; S, 15.05.

***O*-(2,4,6-Tribromophenyl) *N,N*-Dimethylthiocarbamate (4).** Two hundred grams (0.6 mol) of 2,4,6-tribromophenol was reacted by the procedure described for **1** to give, after recrystallization from ethanol, 227 g (90%) of **4**: mp 125–126 °C; ν CCl_4/max 3.37 (w), 6.51 (s), 6.95 (s), 7.16 (s), 7.29 (w), 7.76 (s), 8.13 (s), 8.52 (m), 8.90 (m, sh), 9.03 (s, sh), 9.13 (s), 9.34 (w), 11.58 (m), and 13.77 μ (m); NMR ($CDCl_3$) δ 7.74 (singlet, 2 H), 3.49 (singlet, 3 H), and 3.41 (singlet, 3 H).

Anal. Calcd for $C_9H_8Br_3NOS$: C, 25.86; H, 1.92; Br, 57.30; N, 3.34. Found: C, 25.9; H, 1.93; Br, 57.4 ± 0.5; N, 3.35.

Rearrangement of 4. *S*-(2,4,6-Tribromophenyl) *N,N*-Dimethylthiocarbamate (5) and *N*-(5,7-Dibromo-1,3-benzoxathiol-2-ylidene)methanamine (6). Fifty grams (0.12 mol) of **4** was heated at 180 °C while stirring under a nitrogen atmosphere. Progress of the reaction was followed by NMR.[11] Rearrangement was 97% complete after 26 h. The crude product showed two major rearrangement products as evidenced by an aromatic singlet at δ 7.84 and a pair of doublets at δ 7.35 and 7.48, integrating in a ratio of 3.54:1 in the NMR spectrum. Fractional recrystallization of a portion of the rearrangement product mixture from hexane gave a pure sample of

Scheme I



4 11 5

12 9 6

5: mp 129–130 °C; ν CCl_4/max 3.44 (w), 5.56 (s), 6.47 (s), 6.55 (m, sh), 7.12 (w), 7.20 (w, sh), 7.34 (s), 7.38 (s, sh), 7.94 (m), 8.48 (m), 9.10 (s), 9.65 (m), 10.97 (m), 11.56 (m), 14.14 (m), and 14.71 μ (m); NMR ($CDCl_3$) δ 7.84 (singlet, 2 H) and 3.06 (singlet, 6 H).

Anal. Calcd for $C_9H_8Br_3NOS$: C, 25.86; H, 1.92; Br, 57.30; N, 3.34. Found: C, 26.0; H, 2.00; Br, 58.4 ± 0.6; N, 3.38.

Later fractions gave a sample of **6:** mp 133–135 °C; ν CCl_4/max 3.28 (vw), 3.43 (vw), 3.52 (vw), 5.88 (s), 6.33 (w), 6.41 (m), 6.95 (s), 7.13 (m), 7.24 (m), 8.01 (s), 8.60 (w), 8.87 (w), 9.25 (m), 9.75 (s), 11.68 (m), 13.68 (m), and 14.13 μ (m); NMR ($CDCl_3$) a pair of doublets centered at δ 7.55 (J = 2.0 Hz) and 7.42 (J = 2.0 Hz), 3.22 (singlet), and 3.11 (singlet), integrating in a ratio of 3.5:1:4, respectively. The δ 3.22 singlet was assigned to an unknown impurity, but this signal may be indicative of syn and anti isomerism.

Some minor unidentified products were shown to be present by the NMR spectrum of the residues from the above recrystallization.

Rearrangement of 4 Followed by Hydrolysis. 2,4,6-Tribromobenzenethiol (7) and Bis(3,5-dibromo-2-hydroxyphenyl) Disulfide (8). Two hundred grams (0.48 mol) of **4** was heated at 170–175 °C under nitrogen with stirring. The rearrangement was completed after 63 h. An insoluble solid formed in the melt within the first 4 h and remained present during the first 45 h. The solid was absent at the end of the reaction period. The crude product was hydrolyzed[2,3] in methanolic sodium hydroxide to give 170 g of product. Fractional recrystallization from ethanol gave fractions totaling 115 g (69.1%) of **7:** mp 113.5–115.5 °C (lit.[12] mp 115.5–115.9 °C); NMR spectrum (CCl_4) δ 7.69 (singlet, 2 H) and 4.90 (singlet, 1 H).

Isolated as the second major product in later fractions was 11 g (8.1%) of **8:** mp 122.5–124 °C; ν CCl_4/max 2.84 (m), 6.53 (w), 6.94 (s), 7.26 (m), 7.65 (s), 7.97 (w), 8.18 (s), 8.66 (s), 9.14 (w), 9.34 (w), 11.50 (w), and 11.70 μ (w, sh); NMR ($CDCl_3$) δ 7.79 (doublet, 1 H), 7.62 (doublet, 1 H, J = 2.4 Hz), and 6.27 (broad singlet, 2 H).

Anal. Calcd for $C_{12}H_6Br_4O_2S_2$: C, 25.5; H, 1.07; Br, 56.3; S, 11.3. Found: C, 25.6; H, 1.28; Br, 55.9 ± 0.3; S, 11.6.

Reduction of 8 with Raney Nickel. In a 250-ml, single-neck flask equipped with a magnetic stirrer and a reflux condenser fitted with a calcium chloride drying tube were placed 1.42 g (0.0025 mol) of **8**, 4.0 g of active Raney nickel (W. R. Grace, No. 28), and 100 ml of absolute ethanol. This mixture was heated, with stirring, at reflux for 12 h. The reaction mixture was allowed to cool, and was then filtered through a fine glass frit to remove the catalyst. The ethanol was removed in vacuo from the filtrate, leaving 0.8 g of dark oil. The NMR spectrum of the oil in carbon tetrachloride was identical with that of an authentic sample of 2,4-dibromophenol.

Isolation of 9. Fifteen grams (24 mmol) of **4** was heated at 170 °C in a sealed tube under nitrogen for 24 h, during which time a solid formed in the melt. The tube was cooled and opened, and the contents were washed with 75 ml of carbon tetrachloride. The solid which remained insoluble was collected by filtration, washed several times on the filter with fresh solvent, and dried in vacuo to give 2.05 g (13%) of **9**, mp 248–249 °C dec.

Anal. Calcd for $C_9H_8Br_3NOS$: C, 25.86; H, 1.92; Br, 57.30; N, 3.34; S, 7.66. Found: C, 26.01; H, 2.00; Br, 57.2; N, 3.70; S, 8.10.

Analysis of the carbon tetrachloride filtrate from which **9** was isolated showed a 50% conversion of **4** to **5**. Much less **6** was present than found in uninterrupted reactions, suggesting decomposition of **9** under reaction conditions to give **6**.

To confirm this, a sample of **9** was heated in a mass spectrometer by a direct probe method.[13] Mass spectra were recorded at various temperatures. At 204 °C, methyl bromide (m/e 96, M^+) and **6** (m/e 323, $M^+ + 1$) were detected. The intensity of mass peaks of **6** and methyl bromide increased up to 232 °C.

Acid Hydrolysis of 9. 5,7-Dibromo-1,3-benzoxathiol-2-one (10a). Five grams (12 mmol) of **9** in 50 ml of 1 N aqueous sulfuric acid was heated on a steam bath for 30 min. The mixture was extracted with methylene chloride, the organic layer separated and dried, and the mixture condensed in vacuo to give 3.2 g of crude product. Recrystallization from hexane gave 2 g (65%) of **10a:** mp 104–106 °C; ν CCl_4/max 5.58 (s, sh), 5.63 (s), 6.40 (w), 6.96 (m), 7.12 (w), 7.25 (w), 8.03 (m), 9.96 (s), 11.2 (w), 11.69 (m), and 14.11 μ (w); NMR (CCl_4) δ 7.79 (doublet) and 7.63 (doublet, J = 2.08 Hz).

Anal. Calcd for $C_7H_2Br_2O_2S$: C, 27.1; H, 0.65; Br, 51.6; S, 10.4. Found: C, 27.3; H, 0.86; Br, 52.4 ± 0.5; S, 10.5.

Basic Hydrolysis of 9. 2,4-Dibromo-6-mercaptophenol (10b). A sample of 2 g (4.79 mmol) of **9** and 1.15 g (28.8 mmol) of sodium hydroxide were dissolved in a mixture of 30 ml of methanol and 5 ml of water and stirred at room temperature under a nitrogen atmosphere for 4.5 h. The reaction mixture was poured into 50 ml of dilute hydrochloric acid and the precipitated solid was collected by filtration. After drying, there was obtained 0.77 g (57%) of **10b,** mp 77.5–81 °C. Recrystallization from hexane gave a sample mp 82–85 °C; ν CCl_4/max 2.81 (s), 3.38 (w), 3.86 (w), 6.42 (m), 6.90 (s), 7.24 (s), 7.62 (s), 7.89 (m), 8.03 (m), 8.13 (s), 8.31 (m), 8.59 (s), 9.06 (w), 9.82 (w), 11.51 (s), and 11.71 μ (s); NMR (CCl_4) δ 7.38 (doublet), 7.30 (doublet, J = 2.2 Hz), 5.90 (broad singlet, OH), and 3.73 (broad singlet, SH).

Anal. Calcd for $C_6H_4Br_2OS$: C, 25.4; H, 1.42; Br, 56.3; S, 11.3. Found: C, 25.6; H, 1.54; Br, 56.4; S, 11.6.

A sample of **10b** in carbon tetrachloride solution was allowed to stand in an NMR tube under an oxygen atmosphere for several days. The NMR spectrum was periodically recorded and the oxidative conversion of **10b** to **8** observed. The disulfide **8** was less soluble than **10b** in carbon tetrachloride and crystallized at high conversion. A sample of the crystalline product was isolated and its IR and NMR spectra were found identical with those of **8**.

***O*-(2,4,6-Triiodophenyl) *N,N*-Dimethylthiocarbamate (13).** According to the procedure for **1**, a 98% yield was obtained of **13:** mp 182–184 °C dec; NMR ($CDCl_3$) δ 3.48 (singlet, 3 H), 3.43 (singlet, 3 H), and 8.08 (singlet, 2 H).

Anal. Calcd for $C_9H_8I_3NOS$: C, 19.34, H, 1.44; I, 68.12; N, 2.50; S, 5.74. Found: C, 19.40; H, 1.51; I, 68.2 ± 0.2; N, 2.78; S, 5.90.

Rearrangement of 13. *N*-(5,7-Diiodo-1,3-benzoxathiol-2-ylidene)-*N*-methylmethanaminium Iodide (14). A small pressure tube containing 5 g of **13** was sealed under nitrogen and heated in an oil bath at 195 °C for 0.5 h. The contents gradually melted and then resolidified. The tube was cooled and opened and the contents removed by washing with methylene chloride. The insoluble solid was collected by filtration and dried to give 4.0 g (80%) of a tan solid. The solid was washed with methylene chloride and finally with ether. After drying under vacuum there was obtained 2.53 g of **14:** mp 280–282 °C dec: ν KBr/max 2.91 (m, broad), 5.96 (s), 6.32 (w), 6.42 (w), 6.96 (s), 7.02 (m, sh), 7.28 (w), 7.59 (m), 7.71 (w), 8.01 (s), 8.20 (w), 9.20 (w), 9.36 (w), 11.8 (w), and 14.1 μ (m).

Anal. Calcd for $C_9H_8I_3NOS$: C, 19.34; H, 1.44; I, 68.12; N, 2.50; S, 5.74. Found: C, 19.10; H, 1.45; I, 68.8 ± 0.7; N, 2.54; S, 5.89.

Acid Hydrolysis of 14. 5,7-Diiodo-1,3-benzoxathiol-2-one (15). In an Erlenmeyer flask were placed 1 g (1.8 mmol) of **14** and 250 ml of 1 N sulfuric acid. The flask was warmed on a steam bath for 1.5 h with occassional stirring. The reaction mixture, which contained a fluffy solid, was extracted with chloroform. The chloroform extracts were combined, washed with water, and dried over anhydrous magnesium sulfate. After filtration, the chloroform solution was condensed in vacuo to yield a solid. Recrystallization from methanol gave 0.16 g (22%) of **15:** mp 155–157 °C; ν Nujol/max 5.73 (s), 8.08 (m), 9.84 (m), 9.99 (m), 11.30 (w), 11.71 (m), 13.55 (m), and 14.18 μ (w); NMR δ 7.93 (doublet) and 7.58 (doublet, J = 1.8 Hz).

Anal. Calcd for $C_7H_2I_2O_2S$: C, 20.81; H, 0.50; I, 62.83; S, 7.94. Found: C, 21.20; H, 0.68; I, 63.1 ± 0.3; S, 8.10.

Basic Hydrolysis of 14. 2,4-Diiodo-6-mercaptophenol (16). A sample of 13 g (23.3 mmol) of **14** was heated at reflux for 4 h in 200 ml of methanol and 50 ml of 10% aqueous sodium hydroxide. The reaction mixture was filtered, added to 400 ml of water, and acidified with hydrochloric acid. The mixture was extracted with methylene chloride. After drying over anhydrous sodium sulfate the methylene chloride extract was condensed in vacuo to give 6.1 g (69.4% yield) of **16:** mp 177.5–179.5 °C; NMR (Me_2SO-d_6) δ 7.96 (doublet), 7.57 (doublet), and 3.42 (broad singlet).

Anal. Calcd for $C_6H_4I_2OS$: C, 19.06; H, 1.07; S, 8.48. Found: C, 18.80; H, 1.02; S, 8.20.

Registry No.—**1,** 19387-15-6; **2,** 61268-34-6; **3,** 24207-66-7; **4,** 61268-35-7; **5,** 61268-36-8; ***E*-6,** 61288-81-1; ***Z*-6,** 61268-37-9; **7,** 57730-98-0; **8,** 61268-38-0; **9,** 61268-39-1; **10a,** 61268-40-4; **10b,** 61268-41-5; **13,** 61268-42-6; **14,** 61268-43-7; **15,** 61268-44-8; **16,** 61268-45-9; 2,4,6-tribromophenol, 118-79-6.

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(6) The NMR spectrum of the crude rearrangement product showed only the presence of the normal rearrangement product **2**.
(7) This order is opposite to that which would be found if a direct nucleophilic displacement of the aromatic halide by the sulfur atom were taking place.
(8) Melting points were determined using a capillary apparatus and are un-

corrected. The IR spectra were recorded on a Perkin-Elmer Infracord spectrophotometer; the NMR spectra were obtained on a Varian Associates Model T-60 spectrometer.

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(13) We are indebted to Mira Smolarek for the mass spectra determinations.

Mechanism of Thiophene Formation upon Photolysis of Enethiol Esters

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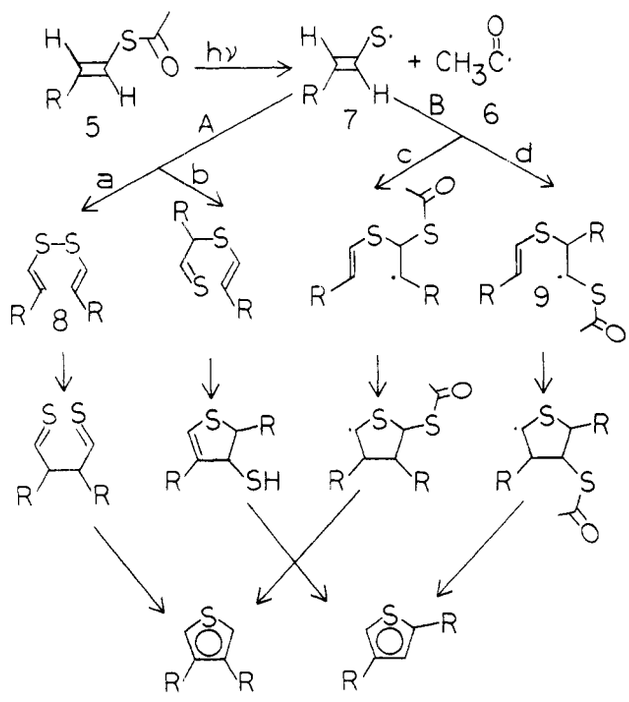
Received June 2, 1976

Evidence for the mechanism of thiophene formation from the photolysis of enethiol esters was obtained by studying β-monosubstituted vinylthiol acetates. Styrylthiol acetate gave exclusively 3,4-diphenylthiophene while β-*tert*-butylvinylthiol acetate yielded β-*tert*-butylvinyl disulfide and no thiophenes. These results suggest that the photolysis involves homolytic cleavage of the *S*-acyl bond followed by dimerization of the enethiyl radical at sulfur to form a vinyl disulfide which undergoes a Cope rearrangement and subsequent loss of hydrogen sulfide to give the thiophenes.

The photolysis of 1-cyclohexene thiolacetate (**1a**) to octahydrodibenzothiophene (**2a**) and *cis*- and *trans*-2-acetylcyclohexane thiolacetate (**3**) was reported in a previous communication.[1] The object of this research was to provide evidence for the mechanism of thiophene production. As shown in Scheme I, there are two basic routes leading to the formation of thiophenes from the photolysis of enethiol esters **5** assuming that following absorption of light by **5** the sulfur–carbonyl carbon bond cleaves homolytically to form an acyl radical **6** and an enethiyl radical **7** in analogy with arylthiol esters.[2] In the first mechanism, **7** can dimerize either by head to head coupling (path Aa) or by head to tail coupling (path Ab) with path Aa being greatly preferred since the spin density is highest at sulfur for **7**.[3] The resultant divinyl disulfides **8** are known to rearrange, ring close, and lose hydrogen sulfide to form thiophenes,[4] which would be 3,4-disubstituted if **5** were β-monosubstituted. In the second mechanism, **7** reacts with starting **5** at either the α position (path Bc) or the β position (path Bd). β-Addition is favored in most cases to form the radical **9**[5] which ring closes and loses thiolacetic acid and hydrogen to give the thiophene, which would be 2,4-disubstituted if **5** were β-monosubstituted.

Scheme I



Therefore, to distinguish between pathways Aa and Bd, we wish to report the photolysis of two β-monosubstituted enethiol esters, styryl thioacetate (**10**) and *tert*-butylvinylthiol acetate (**11**), and additionally to report the experimental details for the photolysis of 1-cyclohexene thiolacetate (**1a**) and 1-cyclopentene thiolacetate (**1b**).

Results and Discussion

Irradiation at 254 nm of **1a** dissolved in cyclohexane gave the thiophene **2a** and the *cis*- and *trans*-2-acetylcyclohexane thiolacetates **3**. Similarly, **1b** photolyzed to the homologous products **2b** and **4**, and in addition formed a substantial amount of the dihydrothiophene **12**. The identities of **2a** and **2b** were established by independent synthesis and comparison of spectral properties. Reduction of **2b** with lithium dissolved in liquid ammonia and *tert*-butyl alcohol gave **12**. Despite a report that thiophene is reduced by sodium dissolved in liquid ammonia and methanol to a 2:1 mixture of 2,5- and 2,3-dihydrothiophene,[6a,b] we have assigned the reduction product structure **12** in which sulfur is conjugated with the double

Scheme II