

REACTIONS OF 2-PHENYL- AND 2-METHYLBENZO-1,3-DITHOLIUM PERCHLORATES WITH WATER

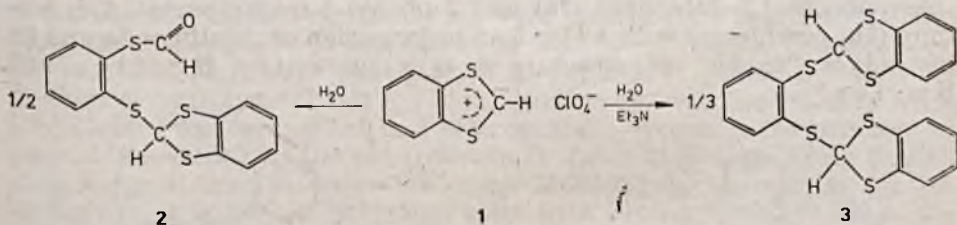
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Zbadano reakcję hydrolizy nadchloranów 2-fenylobenzo-1,3-ditioliowych (7a—b) oraz nadchloranu 2-metylobenzo-1,3-ditiolowego (5). Stwierdzono, że w reakcji soli 7a—b uzyskuje się disulfidy 8a—b, zaś w przypadku soli 5 powstaje tioloctan 10 oraz/lub związek nienasycony 12. Przedyskutowano przebieg badanej reakcji.

Hydrolysis of 2-phenylbenzo-1,3-dithiolium perchlorates (7a—b) and 2-methylbenzo-1,3-dithiolium perchlorate (5) has been investigated. It was stated that salts 7a—b yield disulfides 8a—b and salt 5 produces thioloacetate 10 and/or unsaturated compound 12. The course of the reaction was discussed.

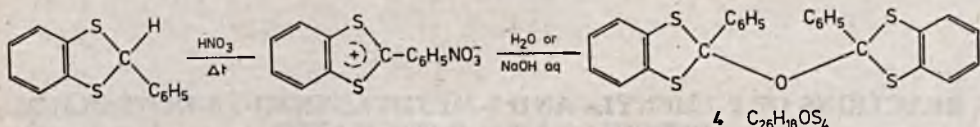
As we have reported previously¹⁻³⁾ the reaction of benzo-1,3-dithiolium perchlorate (1) with water results in formation of compounds 2 or 3 (depending on the reaction conditions) which contain two or three benzo-1,3-dithiol units, respectively.



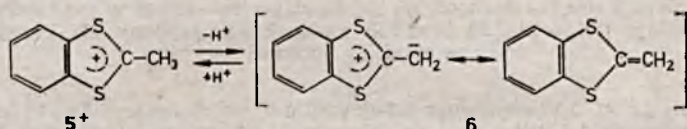
Compounds 2 and 3 are products of a further reaction of 2-hydroxy-1,3-dithiol, the transient formation of which has been confirmed by spectral investigations on the reaction mixtures³⁾. In the present paper we wish to report the results of hydrolysis of benzo-1,3-dithiolium salts with a phenyl ring or a methyl group instead of a proton at C-2.

The only reference concerning the behavior of 2-phenylbenzo-1,3-dithiolium salts towards water could be found in the papers by Hurtle and Smiles⁴⁾ published as far back as in 1924—1926. These authors believed the reaction product to have the formula C₂₆H₁₈OS₄ and the

"oxide" structure **4** consisting of two 2-phenylbenzo-1,3-dithiolyli units. This conclusion was based solely on elemental analysis and determination of molecular weight.



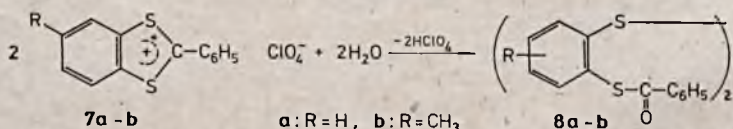
The hydrolysis of 2-methylbenzo-1,3-dithiolium salts has not been studied as yet. The only reported property of these salts is the unusually great mobility of the methyl protons at C-2. Taking advantage of this property Soder and Wizinger⁵⁾ have obtained a series of cyanine dyes containing the benzo-1,3-dithiolium system. The enhanced acidity of the methyl protons at C-2 of the 2-methylbenzo-1,3-dithiolium cation (**5⁺**) is caused by electron deficiency of 1,3-dithiolium ring as well as by the resonance stabilization of the so-called "anhydrobase" **6** formed upon deprotonation of cation **5⁺**.



RESULTS AND DISCUSSION

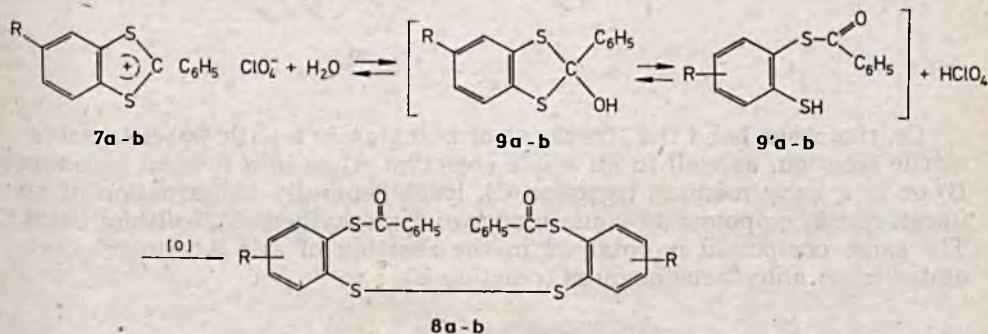
Reactions of 2-phenylbenzo-1,3-dithiolium salts

Our investigations enabled us to establish that the reactions of 2-phenylbenzo-1,3-dithiolium (**7a**) and 2-phenyl-5-methylbenzo-1,3-dithiolium (**7b**) perchlorate with water lead to formation of disulfides **8a** and **8b** instead of "oxides" of structure **4** as suggested by Hurtle and Smiles⁴⁾.



Disulfides **8a** and **8b**, the only isolated reaction products, are obtained in a good yield independently of the reaction medium (acidic, basic or neutral) and of the fact whether the reaction is carried out in a homogeneous or heterogeneous system. The results and the conditions of the reactions are listed in Table 1. Disulfides **8a—b** obtained in these reactions are not the primary products of the hydrolysis of salts **7a—b**. The first step of the reaction involves almost surely the formation of the corresponding "carbinol bases" **9a—b**, as in the case of hydrolysis of benzo-1,3-

-dithiolium salts with a hydrogen at C-2³). Carbinols **9** are in equilibrium with their tautomeric forms **9'a—b** which undergo oxidation to corresponding disulfides **8a—b**. The oxidation may be performed by perchloric acid or by its salt.

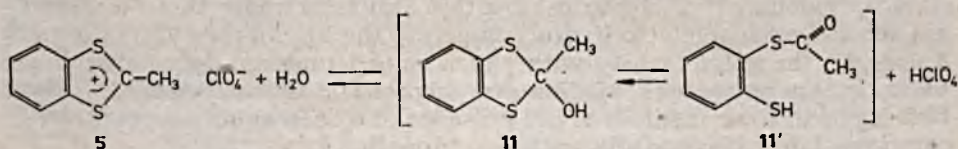


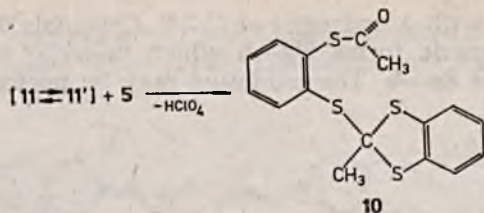
Thus in the course of hydrolysis of 2-phenylbenzo-1,3-dithiolium salts the attack of carbinol **9** (or of the mercapto-ester **9'**) on C-2 of salt **7** does not occur. Such an attack is usually observed in the case of hydrolysis of benzo-1,3-dithiolium salts with a hydrogen at C-2 (**1**) and leads to formation of compounds **2** or **3**. It should be believed that the difference observed in the course of hydrolysis of salts **7** and **1** result from the steric factors, as well as from the decrease in electrophilicity at C-2 due to the presence of phenyl group in this position.

The behavior of 2-phenylbenzo-1,3-dithiolium perchlorates towards water is to some extent analogous to the hydrolysis of 2-phenylbenzo-1,3-oxathiolium perchlorate which has been reported in the literature⁶).

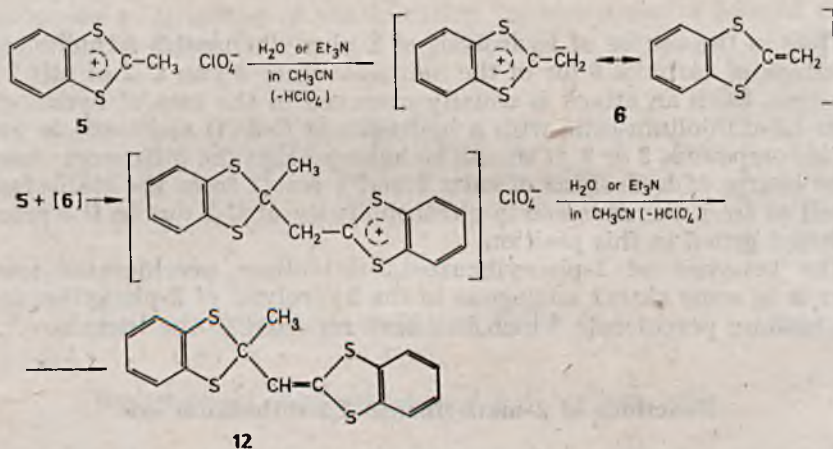
Reactions of 2-methylbenzo-1,3-dithiolium salt

Treating 2-methylbenzo-1,3-dithiolium perchlorate (**5**) with water under various reaction conditions we were able to state that this salt was much more susceptible to deprotonation than to hydrolysis. The results of the reactions performed are collected in Table 2. It turned out that the product of hydrolysis of salt **5**, i.e. thiolacetate **10**, was formed only when the reaction was carried out in a heterogeneous system in the presence of an acid liberated from the salt (reaction D, Table 2). It is probably formed in a range of reaction steps analogous to that proposed earlier for the hydrolysis of benzo-1,3-dithiolium salts with proton at C-2³). Thus, the reaction consists in the attack of water molecule on the electrophilic center of cation **5**⁺, i.e. on C-2, leading to formation of "carbinol base" **11**, and the subsequent reaction of this carbinol (or its tautomeric form **11'**) with salt **5**.





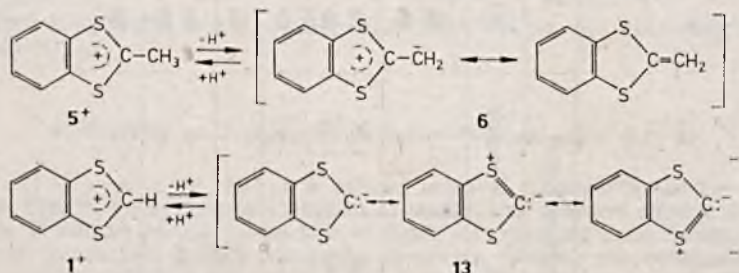
On the other hand the treatment of perchlorate **5** with water in acetonitrile solution, as well in an acidic (reaction A) as in a neutral (reaction B) or in a basic medium (reaction C), leads generally to formation of an unsaturated compound **12** containing two 2-methylbenzo-1,3-dithiol units. The same compound is obtained in the reaction of salt **5** with triethylamine in an anhydrous medium (reaction E).



In our opinion compound **12** is formed from salt **5** in a reaction involving deprotonation of the methyl group by water or an amine molecule, this reaction competing effectively with the attack of water on C-2, i.e. with hydrolysis of the salt. The "anhydrobase" **6** formed by deprotonation reacts thereafter with the dithiolium cation 6^+ resulting in compound **12**.

It must be emphasized that 2-methylbenzo-1,3-dithiolium salt (**5**) loses a proton far more easily than the 2-H-benzo-1,3-dithiolium salt (e.g. salt **1**). Deprotonation of salt **5** in a homogeneous medium occurs so easily that even in acidic medium and in the presence of a great excess of water (reaction A, Table 2) the hydrolysis product (i.e. thioacetate **10**) is not obtained, compound **12** being the only reaction product. As was stated previously^{2,3)} 2-H-benzo-1,3-dithiolium salts under these conditions are subject exclusively to hydrolysis giving the appropriate thioacetate **2**. Despite the great facility with which salts **1** undergo deprotonation by bases in an anhydrous medium (giving bis(1,3-dithiolilidenes-2)) their hydrolysis in basic medium in the presence of a reasonable excess of water competes fairly successfully with deprotonation¹⁾.

It seems that the observed difference in facility of deprotonation of 2-methyl- and 2-H-benzo-1,3-dithiolium salts (5 and 1) is connected with the relative stability of the conjugated bases derived from the cations of those salts.



The lone electron pair on the carbene \leftrightarrow ylide 13 is to a considerable degree localized on C-2 of the heterocycle, whereas in "anhydrobase" 6 its electron pair is localized on a carbon in position α to the ring. This renders possible the formation of a π bond among C-2 and C $_{\alpha}$. Thus "anhydrobase" 6 is much more stable than the carbene \leftrightarrow ylide 13 and, moreover, owing to lesser contribution of dipolar structures, 6 is a less nucleophilic agent than 13. Both factors account for the greater C-H acidity of cation 5⁺ than of 1⁺.

EXPERIMENTAL

IR, ¹H NMR and mass spectra as well as elemental analyses were performed at the Laboratory of Instrumental Analyses of Polytechnical University, Warszawa. ¹H NMR spectra were recorded on a JNM-C-60-H or a JNM-MN-1000 (Jeol) spectrometers (TMS as internal reference), IR spectra—on a UR-10 or a Specord 71 IR spectrometers (Zeiss) and mass spectra—on a LKB 900 spectrometer (at 70 eV). The melting points are uncorrected.

Starting materials

2-Methylbenzo-1,3-dithiolium perchlorate (5) was prepared according to 5³; it was recrystallized by dissolution in slightly warmed glacial acetic acid containing a few drops of 70% HClO₄ and followed, after cooling, by addition of dry ether. The yield was 50.8%; yellow crystals, m.p. 140–143°C (Lit.⁵): m.p. 128°C). ¹H NMR (CF₃CO₂H), δ : 3.6 (s, 3H, CH₃), 7.8–8.5 (m, AA'BB', 3H, aromatic); IR (Nujol), cm⁻¹: 1090 (ClO₄).

2-Phenylbenzo-1,3-dithiolium perchlorate (7a). A mixture of o-benzenedithiol (2.86 g, 0.02 mole), benzoic acid (4.9 g, 0.4 mole) and POCl₃ (50 ccm) was refluxed for 10 min with stirring. The ice-cooled and stirred solution was then treated dropwise with glacial acetic acid (50 ccm), water (50 ccm) and 72% HClO₄ (20 ccm) successively. After stirring for a further 15 min the reaction mixture was slowly poured into 350 ccm of cooled, dry ether. The precipitated crystalline product was filtered off, washed with ether and dried *in vacuo* over KOH. The yield of 2-phenylbenzo-1,3-dithiolium perchlorate (7a, yellow; m.p. 226–229°C) is 5.9 g (89%). The product obtained was sufficiently pure for further purposes. A sample for analysis (0.6 g) was purified by dissolving in warm CH₃CN (5 ccm) containing 2 drops of 72% HClO₄, cooling and addition of ether (8 ccm); pure compound (0.56 g, m.p. 228–231°C) was obtained.

¹H NMR (CF₃CO₂H), δ : 7.70–8.53 (m, aromatic); IR (KBr), cm⁻¹: 1090 (ClO₄).

Table 1
Results and conditions of hydrolysis of salts 7a and 7b

| Reaction | Dithiolium salt mmole | CH ₃ CN or CCl ₄ ccm | H ₂ O | | Et ₃ N or NaOH | | Products | | |
|----------|-----------------------|--|--------------------------|-------|---------------------------|-------|----------|------|----|
| | | | ccm | mmole | ccm | mmole | No | % | |
| A | 7a 1.2 | 15 | 0.45 | 24 | — | — | 8a | 79 | |
| | 7b 1.2 | 15 | 0.45 | 24 | — | — | 8b | 92 | |
| B | 7a 1.2 | 12 | 0.33 | 18 | 0.18 | 1.26 | 8a | 82 | |
| | 7b 1.2 | 12 | 0.33 | 18 | 0.18 | 1.26 | 8b | 85 | |
| C | 7a 1.24 | 15 | 20 | ∞ | — | — | 8a | 95 | |
| D | 7a 1.2 | 15 | 13 ccm of 0.5 N NaOH aq. | | | | | 8a | 92 |
| E | 7a 1.2 | 2×15 | 20 | ∞ | — | — | 8a | 62.5 | |
| | 7b 1.2 | 2×15 | 20 | ∞ | — | — | 8b | 66 | |
| F | 7a 1.2 | 30 | 20 ccm of 5% aq. NaOH | | | | | 8a | 79 |

Analysis:

For $C_{13}H_9S_2ClO_4$ — Calcd.: 47.5% C, 2.7% H, 19.5% S;
found: 47.3% C, 2.7% H, 19.3% S.

2-Phenyl-5-methylbenzo-1,3-dithiolium perchlorate (**7b**) was prepared according to ⁷⁾ with 55.2% yield; orange crystals, m.p. 154–156°C (Lit.⁵⁾: m.p. 150°C).

¹H NMR (CF_3CO_2H), δ : 2.68 (s, 3H, CH_3), 7.76–8.50 (m, 8H, aromatic); IR (KBr), cm^{-1} : 1090 (ClO_4).

Hydrolysis of 2-phenylbenzo-1,3-dithiolium salts (**7a–b**)

Reactions A and B. To a stirred solution of perchlorate **7a** or **7b** (1.2 mmole) in CH_3CN an appropriate portion of water was dropped slowly; in reaction A after ca. 10 min an additional portion of water was dropped until a slight turbidity is produced; in reaction B Et_3N was added dropwise. Stirring was continued for 1 hr and the reaction mixture was poured into water, the precipitate was filtered off, washed with water and dried.

Reactions C and D. A solution of **7a** in CH_3CN was dropped slowly to water or to aqueous 0.5 N NaOH with stirring. After 40 min the precipitate was filtered off, washed with water and dried.

Reactions E and F. A suspension of perchlorate **7a** or **7b** in water or in 5% aq. NaOH was shaken in a separatory funnel with CCl_4 for 0.5 hr. The organic extracts were washed three times with water, dried over $MgSO_4$ and the solvent was removed on rotatory evaporator to give the crude product.

The quantities of reagents and solvents used in the reactions A–F as well as the yields of reaction products are enumerated in Table 1.

Purification of products **8a–b**

Disulfide **8a** was purified by crystallization from light petroleum (b.p. 40–60°C) or from light petroleum—benzene mixture; m.p. 135–137°C.

¹H NMR (CS_2), δ : 6.9–7.8 (m, aromatic); IR (KBr), cm^{-1} : 1660 (ν_{C-O}), in CCl_4 : 1687 (ν_{C-O}); MS: $m/e = 490 [M^+]$, 385 [$M-C_6H_5CO^+$], 280 [$385-C_6H_5CO^+$], 245 [$M/2^+$].

Analysis:

For $C_{26}H_{18}O_2S_4$ — Calcd.: 63.6% C, 3.7% H, 26.1% S;
found: 63.5% C, 4.0% H, 26.3% S.

Disulfide **8b** was purified by crystallization from benzene—light petroleum (b.p. 40–60°C) mixture; m.p. 165–169°C.

¹H NMR (CS_2), δ : 2.16, 2.25 and 2.37 (three singlets*, 6H, CH_3) and 6.8–7.9 (m, 16H, aromatic); IR (KBr); cm^{-1} : 1675 (ν_{C-O}).

Analysis:

For $C_{28}H_{22}O_2S_4$ — Calcd.: 64.9% C, 4.3% H, 24.7% S;
found: 65.1% C, 4.3% H, 24.3% S.

Reactions of 2-methylbenzo-1,3-dithiolium perchlorate (**5**)

A–C. Homogeneous hydrolysis. To a stirred solution of **5** in CH_3CN water was dropped slowly; in reaction A the mixture was stirred for 15 min and in reactions B and C Et_3N was added dropwise after 5 min and stirring was continued for 1 hr. The reaction mixture was then poured into water and extracted with CCl_4 . The organic layers were washed with water, dried over $MgSO_4$ and most of solvent was removed on rotatory evaporator. The ¹H NMR spectra were measured in order to estimate the composition of crude reaction mixtures.

* The product is probably a mixture of three isomeric disulfides differing in the position of CH_3 group in the benzene ring.

Table 2
Results and conditions of reactions of 2-methylbenzo-1,3-dithiolium (5) with water and/or Et₃N

| Reaction | Salt 5 mmole | CH ₃ CH or CCl ₄ ccm | H ₂ O | | Et ₃ N | | Products | |
|----------|-----------------|---|------------------|-------|-------------------|-------|----------|------------|
| | | | ccm | mmole | ccm | mmole | main | secondary |
| A | 2 | 10 | 0.75 | 20 | — | — | 12 | others* |
| B | 3 | 15 | 0.80 | 45 | 0.45 | 3.15 | 12 | — |
| C | 3 | 15 | 0.80 | 45 | 0.84 | 6 | 12 | — |
| D | 3 | 30+15 | 40 | ∞ | — | — | 10 | 12+others* |
| E | 3 | 15 | — | — | 0.84 | 6 | 12 | — |

* Not isolated and not identified.

Table 3

¹H NMR spectra (in CCl₄) of products isolated in reactions of 2-methylbenzo-1,3-dithiolium perchlorate (5) and of crude reaction mixtures (reactions A—E)

| | Signals of the protons (δ, ppm) | | | | | | Unidentified compounds |
|-----------------------------|--|---|--|--------------|-------------|---------------|-----------------------------|
| | $\begin{array}{c} \text{S} \\ \\ \text{C} \\ \\ \text{S} \end{array} \begin{array}{c} \text{CH}_3 \\ \\ \text{C} \\ \\ \text{S} \end{array}$ 10 | $\begin{array}{c} \text{O} \\ \\ \text{C} \end{array} \text{CH}_3$ 10 | $\begin{array}{c} \text{C} \\ \\ \text{S} \end{array} \begin{array}{c} \text{C} \\ \\ \text{S} \end{array} \begin{array}{c} \text{CH}_3 \\ \\ \text{C} \\ \\ \text{S} \end{array}$ 12 | —CH=C< 12 | H aromatic | | |
| | | | | | 10 | 12 | |
| Compound 10 (pure) | 2.10 (s) | 2.25 (s) | — | — | 6.8—7.2 (m) | — | — |
| Compound 12 (pure) | — | — | 2.03 (s) | 5.50 (s) | — | 6.8—7.2 (m) | — |
| Crude product of reaction A | — | — | 2.05 (s) | 5.60 (s) | — | 6.85—7.3 (m) | 2.0, 3.25, 5.77 (s) (s) (s) |
| Crude product of reaction B | — | — | 2.1 (s) | 5.68 (s) | — | 7.0—7.4 (m) | — |
| Crude product of reaction C | — | — | 2.05 (s) | 5.58 (s) | — | 6.85—7.25 (m) | — |
| Crude product of reaction D | 2.12 (s) | 2.12 (s) | 2.0 (s) | 5.47 (s) | 6.8—7.8 (m) | — | 2.38, 3.75 (s) (s) |
| Crude product of reaction E | — | — | 2.05 (s) | 5.65 (s) | — | 7.0—7.5 (m) | — |

D. Heterogeneous hydrolysis. A suspension of 5 in water was shaken in a separatory funnel for ca. 0.5 hr with CCl_4 . The aqueous layer was extracted with CCl_4 and the combined organic layers were treated as described for A—C.

E. Treatment with Et_3N in anhydrous CH_3CN . Et_3N was added dropwise to a stirred solution of salt 5 in anhydrous CH_3CN . After stirring for 1 hr the solution was poured into water and extracted with CCl_4 . The organic layer was treated as in reactions A—C.

The quantities of reagents and solvents used together with the products formed in above reactions of salt 5 are shown in Table 2; ^1H NMR spectral data, which have been employed for identification of products in crude reaction mixtures, are contained in Table 3.

By crystallization of crude product formed in reaction C from light petroleum (b.p. 40—60°C), with a slight quantity of benzene added, a small quantity (ca. 0.1 g) of crystalline, yellow compound 12 was obtained; m.p. 75—79°C.

^1H NMR (CCl_4), δ : 2.03 (s, 3H, CH_3), 5.50 (s, 1H, =C-H), 6.8—7.2 (m, 8H, aromatic); MS: $m/e = 332$ (100%, M^+).

Analysis:

For $\text{C}_{16}\text{H}_{12}\text{S}_4$ — Calcd.: 57.8% C, 3.6% H;
found: 57.2% C, 3.6% H.

By crystallization of crude product formed in reaction D from light petroleum (b.p. 40—60°C) some crystalline thiolacetate 10 (ca. 0.18 g, 35%; m.p. 84—90°C) was isolated.

^1H NMR (CCl_4), δ : 2.10 (s, 3H, >C-CH_3), 2.25 (s, 3H, O=C-CH_3), 6.80—7.80 (m, 8H, aromatic); IR (CCl_4), cm^{-1} : 1710 ($\nu_{\text{C=O}}$); MS: $m/e = 332$ (100%, $[\text{M} - \text{H}_2\text{O}]^+$).

Analysis:

For $\text{C}_{16}\text{H}_{14}\text{OS}_4$ — Calcd.: 54.8% C, 4.1% H;
found: 55.1% C, 4.3% H.

No crystalline products are isolated in other reactions (i.e. A, B and E).

Received April 29th, 1981
(revised manuscript March 17th, 1982).

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