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Thiocarbonyl Ylide Intermediates Generated by Deprotonation of 2-Phenacylthio- and 2-(*p*-Bromophenacylthio)-1,3-dithiolylium and 2-(*p*-Bromophenacylthio)-1,3-dithiolanylium Bromides

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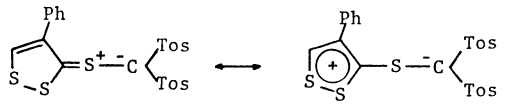
2-(*p*-Bromophenacylthio)-1,3-dithiolylium bromide, when treated with triethylamine, gave 2-(*p*-bromophenacylidene)-1,3-dithiole (17%) and bis[(*p*-bromobenzoyl)(1,3-dithiol-2-ylidene)methyl] disulfide (72%). Treatment of 2-phenacylthio-1,3-dithiolylium bromide with triethylamine also gave similar results. On the other hand, 2-(*p*-bromophenacylthio)-1,3-dithiolanylium bromide yielded 1-(*p*-bromophenyl)-2-(1,3-dithiolan-2-yl)-2-thioxoethanone (12%) in addition to 2-(*p*-bromophenacylidene)-1,3-dithiolane (49%) contrary to the reported results. These results can best be rationalized by 1,3-cyclization of thiocarbonyl ylide intermediates to the valence tautomeric episulfides.

Thiocarbonyl ylides are generally unstable transient intermediates and can not be isolated under normal conditions. One of exceptions is the ylide **1** which is a thermally stable crystalline compound.[1] Unusual stability of **1** must be, at least in part, due to an aromatic sextet retained in the five membered ring. In fact the ylide **2** in which positive charge is delocalized over only a three-atom center is an unstable transient intermediate.[2] Recent ^{13}C NMR study has shown that 1,3-dithiolylium ion belongs to a typical heteroaromatic cation whose positive charge is delocalized over the entire ring.[3] Keeping this background in mind we investigated the reactions of 2-phenacylthio- and 2-(*p*-bromophenacylthio)-1,3-dithiolylium bromides (**4a** and **4b**) with base with expectation of obtaining a new class of stable thiocarbonyl ylides **3**.



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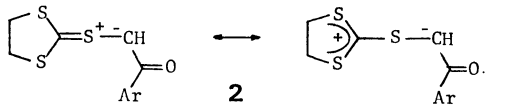

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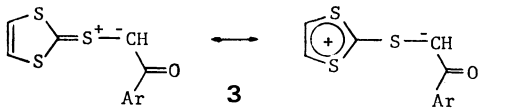
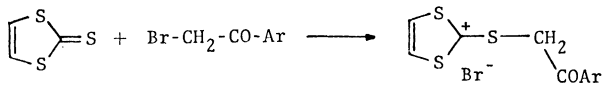


3

Dithiolylium salts **4a** and **4b** were conveniently prepared in good yields by treatment of 1,3-dithiole-2-thione (**5**) with phenacyl and *p*-bromophenacyl bromides, respectively.

An acetonitrile solution of **4b** was treated with a large excess of triethylamine at room temperature. Purification of products by column chromatography gave 2-(*p*-bromophenacylidene)-1,3-dithiole (**6b**) (18%),



5

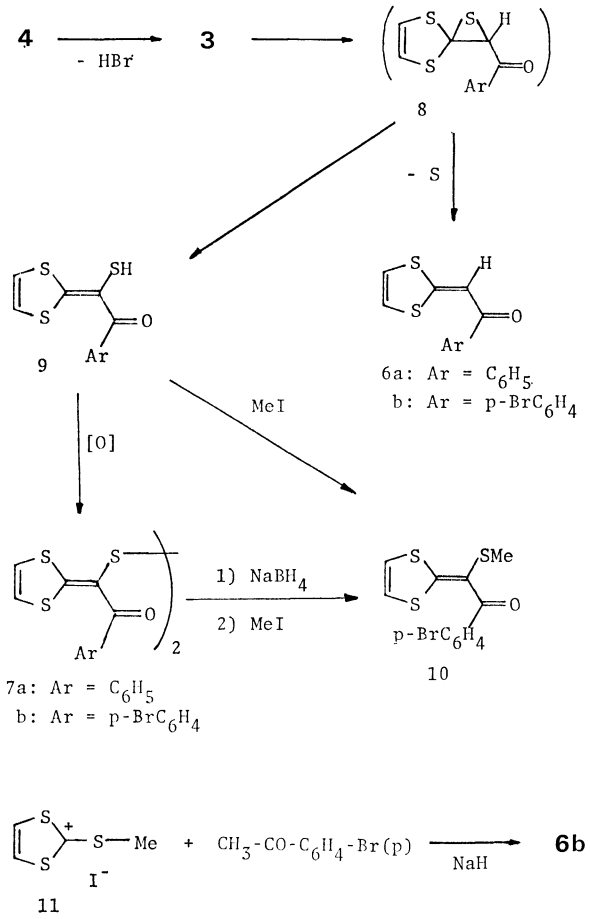
4a: Ar = C_6H_5

b: Ar = p-BrC_6H_4

bis[(*p*-bromobenzoyl)(1,3-dithiol-2-ylidene)methyl] disulfide (**7b**) (72%), and **5** (7%). The mass spectrum of **6b** has an M+2 peak which is almost equal in intensity to the molecular peak at *m/e* 298 because of the presence of the ^{81}Br isotope. The NMR spectrum showed a singlet of the exocyclic vinyl proton at δ 7.43 ppm, a singlet (with fine line structure) of dithiole ring protons at 6.89, and a multiplet of benzene ring protons at 7.5—8.0. The carbonyl stretching absorption appears abnormally low at 1585 cm^{-1} suggesting strong conjugation between carbonyl and 1,3-dithiol-2-ylidene groups. Campaigne and Haaf reported that the carbonyl absorptions of this type of compounds occur at 1590—1610 cm^{-1}.[4] Furthermore the structure of **6b** was confirmed by an independent synthesis; the condensation of the sodium salt of *p*-bromoacetophenone with the dithiolylium salt **11** gave **6b** in a 32% yield. The mass spectrum of **7b** has its molecular peak at *m/e* 658, M+2 peak at 660, and M+4 peak at 662 in intensity ratio of *ca.* 1:2:1 suggesting the presence of two bromine atoms. The base peak appears at *m/e* 329 which is exactly the half of the molecular peak. The NMR spectrum shows a singlet at δ 7.28 ppm and an $A'_2X'_2$ multiplet at 7.0—7.5. The UV spectrum closely resembles that of **6b** and the IR spectrum has a carbonyl absorption at 1565 cm^{-1}. These data are indicative of the symmetrical structure of **7b** with the same structural unit as **6b** and are in harmony with the presented structure. Further support for the structure of **7b** comes from its conversion to compound **10**; reduction of **7b** by sodium borohydride and methylation of the resulting product with methyl iodide gave **10** in a 61% yield.

Treatment of the dithiolylium salt **5a** with triethylamine gave results similar to those obtained with **5b**. Compounds **6a**, **7a**, and **5** were obtained in 17, 71, and 6% yields, respectively.

These results can best be explained in terms of thiocarbonyl ylide intermediate **3** produced by dehydrobromination of **4**. The ylide **3** is not so stable as was expected and cyclizes immediately to episulfide **8**, which either gives **6** with spontaneous extrusion of sulfur or isomerizes to **9**. The latter gives rise to disulfide **7** as the final product by air oxidation. Evidence for the intermediacy of **9** comes from the fact that treatment of **4b** with triethylamine in the presence of methyl iodide gives **10**, the product of methylation of **9**, in an 83% yield along with a 6% yield of **6b**.

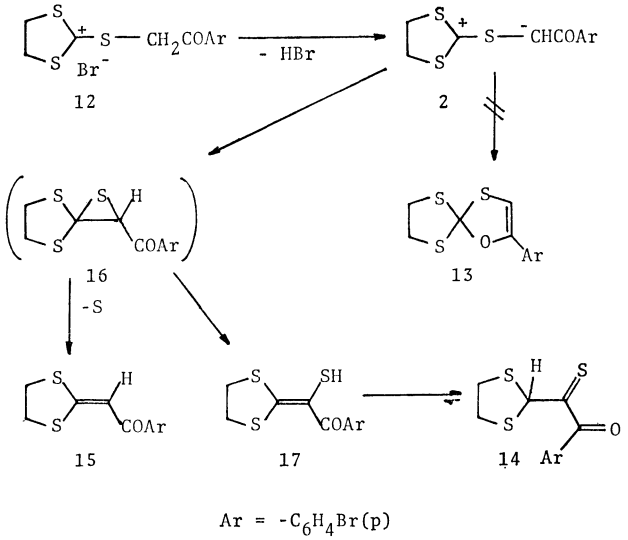


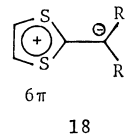
Ueno and Okawara reported that the ylide **2**, generated by deprotonation of the salt **12** with sodium hydride in acetonitrile, gives compound **13** in an excellent yield. The formation of **13** was explained as a result of 1,5-cyclization of **2**.[2] We now investigated the reaction of **12** with triethylamine in order to compare the properties of **2** and **3** under normalized conditions. Results were rather surprising. Treatment of **12** with excess triethylamine gave 1-(*p*-bromophenyl)-2-(1,3-dithiolan-2-yl)-2-thioxoethanone (**14**) (12%), 2-(*p*-bromophenacylidene)-1,3-dithiolane (**15**) (49%), and ethylene trithiocarbonate (27%). Compound **13** was not detected at all.[5] Compound **14** has its carbonyl absorption at 1560 cm^{-1}. The mass spectrum shows molecular and M+2 peaks of about equal intensity at *m/e* 332 and 334. The juncture of 1,3-dithiolan-2-yl group to thiocarbonyl group is supported by the occurence of an intense peak at *m/e* 149 (S–CH_2CH_2–S–CH–C=S).

The presence of *p*-bromobenzoyl group is evident from two peaks at *m/e* 183 and 185. The methylene protons signal appears at δ 3.38 ppm as singlet in harmony with the presented structure. The carbonyl absorption of compound **15** occurs at 1615 cm^{-1}. Reported carbonyl frequencies of this type of compounds are in the range of 1595—1630 cm^{-1}.[4] The NMR spectrum shows a multiplet of methylene protons at δ 3.36—3.62 ppm, a singlet of vinyl proton at 7.30, and a multiplet of benzene ring protons at 7.5—8.0.

The result can be explained as follows: The ylide **2** undergoes 1,3-cyclization to episulfide **16**, which either gives **15** with loss of sulfur or isomerizes to **17**. The latter further isomerizes to the final product **14**. The enol form of compound **9** may be stabilized by the contribution of the canonical structure like **18** as would be expected from unusually low carbonyl absorptions observed with compounds **6**, **7**, and **10**. As a result, compound **9** is easily methylated to give **10** or oxidized to disulfide **7**. However, such stabilization is not expected for the enol form of compound **14** and this accounts for the fact that **14** can be isolated as stable compound in the thiocarbonyl form.

We must thus conclude that (1) the ylides **3** can not be stabilized by the aromatic sextet retained in the five membered ring so that they can be isolated under usual conditions, (2) the ylides **3** undergo 1,3-cyclization to give the valence tautomeric episulfides, which is one of the characteristic reactions of thiocarbonyl ylides,[6] and (3) as far as judging from present evidence, the ylide **2** preferentially undergoes 1,3-cyclization rather than 1,5-cyclization contrary to the reported results.[2]





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Experimental

General. All melting points were measured on a Mel-

temp capillary melting point apparatus and are uncorrected. NMR spectra were recorded on a Varian A-60 spectrometer or a Hitachi R 24B spectrometer with tetramethylsilane as internal reference. IR and UV spectra were determined with a JASCO IRA-2 spectrometer and a Hitachi EPS-3T spectrometer, respectively. Mass spectra were taken on a Japan Electron Optics Lab. Model JMS-OISJ instrument operating at 40 eV. Acetonitrile and tetrahydrofuran were refluxed over and distilled from calcium hydride and stored over molecular sieves. Merck Art 7734 (E. Merck, Darmstadt) was used for silica gel chromatography.

2-Phenacylthio- and 2-(p-Bromophenacylthio)-1,3-dithiolylium Bromides (4a and 4b). A mixture of 1.0 g (7.5 mmol) of 1,3-dithiole-2-thione[7] (**5**) and 7.2 g (36.3 mmol) of phenacyl bromide in 45 ml of anhydrous acetonitrile was stirred at room temperature. After 1.5 h of stirring, **4a** began to separate as yellowish brown crystals. The mixture was stirred for 2 d and diluted with 45 ml of anhydrous ether to complete the precipitation of **4a**. The resulting precipitate was collected and washed with ether to give **4a** in 66—71% yield. **4a**, on attempted recrystallization from hot acetonitrile or ethanol, suffered extensive decomposition to **5** and phenacyl bromide. It was therefore purified by reprecipitating it from an acetonitrile solution with ether as diluent. **4a**, thus obtained, melted at 114—115 °C.

NMR (CF_3CO_2H) δ 5.32 (2H, s, $-CH_2-$), 7.39—8.02 (5H, m, phenyl), and 8.33 (2H, s, dithiole ring); IR (KBr) $\nu_{C=O}$ 1676 cm^{-1}. Found: C, 39.52; H, 2.73; S, 28.85% Calcd for $C_{11}H_9OS_3Br$: C, 39.64; H, 2.72; S. 28.86%.

4b was prepared from **5** and *p*-bromophenacyl bromide in 65—70% yield as above; mp 138 °C (decomp), yellowish brown crystals. Although, judging from the NMR spectrum, the compound thus obtained was sufficiently pure, satisfactory elemental analysis could not be obtained (Found: C, 32.78; H, 2.18; S, 22.32%. Calcd for $C_{11}H_8OS_3Br$: C, 32.05; H, 1.96; S, 23.34%). NMR (CF_3CO_2H) δ 5.52 (2H, s, $-CH_2-$), 7.7—8.2 (4H, $A'_2X'_2m$, benzene ring), and 8.71 (2H, s, dithiole ring); IR (KBr) $\nu_{C=O}$ 1652 cm^{-1}; UV (EtOH) λ_{max} (log ε) 229 (4.02) (sh), 260.5 (4.00), and 465 nm (4.19).

Reaction of 4a with Triethylamine. Over a period of 10 min, 3 ml of triethylamine was added dropwise to a stirred suspension of 932 mg (2.8 mmol) of **4a** in 50 ml of anhydrous acetonitrile cooled at -10 °C. The mixture was warmed to room temperature and stirred for additional 2 h. The resulting red mixture was diluted with ice-water (150 ml) and extracted with 150 ml of chloroform. The extract was washed with water, dried (Na_2SO_4), and evaporated to give 813 mg of a red oil, which was subjected to column chromatography on silica gel (50 g). Elution with benzene gave 42 mg (6%) of **5**, 105 mg (17%) of 2-phenacylidene-1,3-dithiole (**6a**), and 503 mg (71%) of bis[benzoyl(1,3-dithiol-2-ylidene)methyl] disulfide (**7a**).

In a separate reaction carried out under similar conditions, **5**, **6a**, and **7a** were obtained in 7, 14, and 55% yields, respectively.

6a: Yellow needles (from hexane); mp 80—81 °C; NMR ($CDCl_3$) δ 6.82 (2H, s with fine structure, dithiole ring), 7.30—8.13 (5H, m, phenyl), and 7.47 (1H, s, vinyl); IR (KBr) $\nu_{C=O}$ 1587 and 1560 cm^{-1}. Found: C, 59.91; H, 3.69; S, 29.07%. Calcd for $C_{11}H_8OS_2$: C, 59.97; H, 3.66; S, 29.11%.

7a: Orange needles (from benzene); mp 115—116 °C. Compound recrystallized from benzene contained one molecule of benzene as solvent of crystallization. Found: C, 57.89; H, 3.45; S, 33.06%. Calcd for $C_{22}H_{14}O_2S_6 \cdot C_6H_6$: 57.94; H, 3.47; 33.08%. NMR ($CDCl_3$) δ 6.80—7.52 (14H, m); IR (KBr) $\nu_{C=O}$ 1580 and 1555 cm^{-1}.

Reaction of 4b with Triethylamine. Triethylamine (3 ml) was added dropwise during 10 min to a stirred suspension of 1.0 g 2.4 mmol) of **4b** in 40 ml of anhydrous acetonitrile cooled at -12 °C with an ice-salt bath. The bath was removed and stirring was continued for 2 h. During this period, crystals of the starting material disappered and orange crystals of product began to precipitate instead. The mixture was left overnight at room temperature and the resulting orange crystals were collected to give 485 mg of bis[(*p*-bromobenzoyl)(1,3-dithiol-2-ylidene)methyl] disulfide (**7b**). The filtrate was diluted with water and extracted with chloroform. The extract was washed with water, dried, and evaporated to leave 272 mg of a dark red oil, which was chromatographed on a column of silica gel (30 g). Elution with benzene gave 20 mg (7%) of **5**, 133 mg (18%) of 2-(*p*-bromophenacylidene)-1,3-dithiole (**6b**), and 87 mg (total yield; 72%) of **7b**.

The reaction was repeated three times. The yield of **6b** varied in the range of 18—20% and that of **7b** in the range of 65—72%.

6b: Yellowish brown crystals (from acetonitrile); mp 168 °C (decomp); NMR ($CDCl_3$) δ 6.89 (2H, s with fine line structure, dithiole ring), 7.43 (1H, s, vinyl), and 7.47—7.97 (4H, $A'_2X'_2m$, benzene ring); IR (KBr) $\nu_{C=O}$ 1585 cm^{-1}; UV (EtOH) λ_{max} (log ε) 226 (4.05), 234 (3.99) (sh), 270.5 (4.06) and 412 nm (4.49); MS *m/e* (%) 300 (M^++2, 98), 298 (M^+, 95), 185 ($^{81}BrC_6H_4CO$, 22), 183 ($^{79}BrC_6H_4CO$, 25), 157 ($^{81}BrC_6H_4$, 41), 155 ($^{79}BrC_6H_4$, 44), 149 (48), 143 (S–CH=CH–S–C=CH–C=O, 100), and 115 (S–CH=CH–S–C=CH, 18). Found: C, 44.13; H, 2.39; S, 21.41; Br, 26.79%. Calcd for $C_{11}H_7OS_2Br$: C, 44.15; H, 2.36; S, 21.43; Br, 26.71%.

7b: Orange prisms (from chloroform–hexane); mp 198—198.5 °C; NMR ($CDCl_3$) δ 7.28 (4H, s, dithiole ring) and 7.03—7.40 (8H, m, benzene ring); IR (KBr) $\nu_{C=O}$ 1565 cm^{-1}; UV (EtOH) λ_{max} (log ε) 225 4.26) (sh), 270 (3.98), 339.5 (3.78), and 425 nm (4.37); MS *m/e* 662 (M^++4), 660 (M^++2), 658 (M^+), 331, and 329. Found: C, 39.93; H, 1.84; S, 29.12%. Calcd for $C_{22}H_{12}O_2S_6Br_2$: C, 40.00; H, 1.83; S, 29.12%.

6b from 11 and p-Bromoacetophenone. A solution of 1.55 g (7.8 mmol) of *p*-bromoacetophenone in 20 ml of anhydrous tetrahydrofuran was added to a suspension of 0.52 g (10.9 mmol) of 50% sodium hydride dispersion in oil in 20 ml of anhydrous acetonitrile. The mixture was stirred for 1 h, and then 1.07 g (3.9 mmol) of **11**[7] was added all at once. The mixture was stirred for 1 h, poured into ice-water, and extracted with chloroform. The extract was washed with water, dried, and evaporated, The brown oily residue was purified by chromatography on a column of silica gel (40 g) with benzene as eluent to give 0.37 g (32%) of **6b**, mp 168 °C (decomp) (from acetonitrile). **6b**, thus obtained, agreed with a specimen obtained from **4b** and triethylamine in all respects.

Conversion of 7b to (p-Bromobenzoyl)(1,3-dithiol-2-ylidene)-methyl Methyl Sulfide (10). A solution of 0.50 g (0.75 mmol) of **7b** in 35 ml of tetrahydrofuran was added during 1 h to a stirred suspension of 104 mg (2.7 mmol) of sodium borohydride in 20 ml of tetrahydrofuran. After 2 h of stirring at room temperature, 0.37 g (2.6 mmol) of methyl iodide in 20 ml of tetrahydrofuran was added. The mixture was stirred for 1 h, poured into ice-water, and extracted with chloroform. The extract was washed with water, dried and evaporated to leave an orange oil. The crude product was separated by chromatography on silica gel (35 g) with chloroform as eluent to give 208 mg (61%) of **10** and 170 mg (34%) of the starting material.

10: Yellowish orange needles (from cyclohexane); mp 125—126 °C; NMR ($CDCl_3$) δ 2.09 (3H, s, Me), 6.94—7.24 (2H, m, dithiole ring), and 7.40—7.80 (4H, m, benzene ring); IR (KBr) $\nu_{C=O}$ 1564 cm^{-1}. Found: C, 41.77; H, 2.65; S, 27.77%. Calcd for $C_{12}H_9OS_3Br$; C, 41.74; H, 2.63; S, 27.86%.

*Reaction of **4b** with Triethylamine in the Presence of Methyl Iodide.* Over a period of 10 min, 3.3 ml of triethylamine was added to a stirred mixture of 1.19 g (2.9 mmol) of **4b** and 2.05 g (14.4 mmol) of methyl iodide in 30 ml of acetonitrile at −10 °C under nitrogen. The mixture was warmed to room temperature and stirred overnight. The resulting yellow crystalline precipitate was collected to give 224 mg of **10**. The filtrate was diluted with water and extracted with chloroform. The extract was washed, dried, and evaporated to leave an orange oil, which was chromatographed on silica gel (30 g). Elution with chloroform afforded 37 mg (10%) of **5**, 332 mg (total yield; 83%) of **10**, and 55 mg (6%) of **6b**. **10**, thus obtained and recrystallized from cyclohexane, melted at 128—128.5 °C and agreed in all respects with a specimen derived from **7b**.

*Reaction of 2-(p-Bromophenacylthio)-1,3-dithiolanylium Bromide[8] (**12**) with Triethylamine.* Triethylamine (4 ml) was added to a stirred solution of 828 mg (2 mmol) of **12** in 35 ml of anhydrous acetonitrile at 0 °C. The mixture was warmed to room temperature and stirred for 8 h, and then poured into ice–water and extracted with ether. The extract was washed with water, dried, and evaporated. The residue was chromatographed on silica gel (40 g). Elution with chloroform afforded 82 mg (12%) of 1-(*p*-bromophenyl)-2-(1,3-dithiolan-2-yl-)-2-thioxoethanone (**14**), 74 mg (27%) of ethylene trithiocarbonate, and 296 mg (49%) of 2-(*p*-bromophenacylidene)-1,3-dithiolane (**15**).

The reaction was repeated several times. The yield of **14** changed in the range of 7—24%, that of ethylene trithiocarbonate in the range of 20—40%, and that of **15** in the range of 49—57%.

14: Yellow prisms (from cyclohexane); mp 84.5—85 °C; NMR ($CDCl_3$) δ 3.38 (4H, s, dithiolane ring), 6.48 (1H, s, methine), and 7.52—8.00 (4H, $A'_2X'_2m$, benzene ring); IR (KBr) $\nu_{C=O}$ 1660 cm^{-1}; UV (EtOH) λ_{max} (log ε) 260 (4.31) and 350 nm (3.76); MS *m/e* (%) 334 ($M^+ + 2$, 58), 332 (M^+, 53), 185 ($^{81}BrC_6H_4CO$, 96), 183 ($^{79}BrC_6H_4CO$, 95), 156 ($^{81}BrC_6H_4$, 91), 154 ($^{79}BrC_6H_4$, 100), 149 (S–CH_2CH_2–S–CH–C=S, 88), and 105 (S–CH_2CH_2–S–CH, 61). Found: C, 39.63; H, 2.75; S, 28.87%. Calcd for $C_{11}H_9OS_3Br$: C, 39.64; H, 2.72; S, 28.86%.

15: Yellow needles (from acetonitrile); mp 145 °C (decomp); NMR ($CDCl_3$) δ 3.36—3.62 (4H, m, dithiolane ring), 7.30 (1H, s, methine), and 7.49—7.99 (4H, $A'_2X'_2m$, benzene ring); (CF_3CO_2H) δ 3.90 (4H, s), 7.15 (1H, s), and 7.70 (4H, broad s); UV (EtOH) λ_{max} (log ε) 220 (3.89) (sh), 269 (4.00), and 349 nm (4.30). Found: C, 43.73; H, 2.99%. Calcd for $C_{11}H_9OS_2Br$: C, 43.86; H, 3.01%.

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