16d, 85369-80-8; 17, 762-72-1; 18a, 92763-99-0; 18b, 92764-00-6; 18c, 92764-02-8; 18d, 92764-03-9; 20, 33542-53-9; 22a, 92764-04-0; 22b, 92764-05-1; 22c, 92764-06-2; 22d, 92764-08-4; 23a, 92764-09-5; 23a (dihydroxy deriv), 92764-19-7; 23b, 92764-11-9; 23c, 92764-13-1; 23d, 92764-15-3; 24a, 2158-04-5; 24b, 25017-47-4; 24c, 25017-27-0; 24d, 92764-07-3; 25, 95-92-1; 26a, 92764-10-8; 26b, 92764-12-0; 26c, 92764-14-2; 26d, 92764-16-4; 27, 54608-40-1; 28, 92764-17-5; 32, 92764-18-6.

Reactions of Monothiobenzil and Its Dimer

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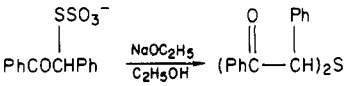
In contrast to the usual formation of monothiobenzil from desyl thiosulfate in a two-phase system involving aqueous sodium hydroxide and methylene chloride, the dimer, 2,4-dibenzoyl-2,4-diphenyl-1,3-dithietane, is obtained in the absence of methylene chloride; and didesyl sulfide is obtained in ethanolic sodium hydroxide–methylene chloride. Thermolysis of monothiobenzil or monothioanisil gives 1,2,3,4-tetraaryl-2-butene-1,4-diones which may be accompanied by benzil or anisil. Monothiobenzil forms an unstable adduct with cyclopentadiene which can be converted to a stable dibromo derivative; it is converted to benzil by treatment with peracids or nitric acid. Dibenzoylstilbene is obtained by thermolysis of the dimer of monothiobenzil or by treatment of the dimer with triphenylphosphine. Treatment of the dimer with Cleland's reagent (2,3-dihydroxy-1,4-butanedithiol) gives didesyl sulfide, and treatment with cyanide ion gives 2-benzoyl-2,4,5-triphenyl-1,3-oxathiole.

Monothiobenzil was first obtained[1] by photolysis of the *S*-oxide of 2-benzoyl-2,4,5-triphenyl-1,3-oxathiole, which was originally incorrectly identified as the episulfoxide of 2,3-dibenzoyl-2,3-diphenylthiirane largely because the parent sulfide gave dibenzoylstilbene on desulfurization with triphenylphosphine.[2] Norin and co-workers revised this thiirane structure[2,3] to that of an oxathiole.[4a,b] A convenient preparation of monothiobenzil is the elimination of sulfite ion from desyl thiosulfate in aqueous sodium hydroxide–methylene chloride,[5] which is related to early investigations of the elimination of hydrogen cyanide from desyl thiocyanate (1,2-diphenyl-2-thiocyanatoethanone) which gave oxathiole instead of monothiobenzil.[2a] Treatment of desyl thiocyanate with excess sodium hydride in dimethoxyethane gives 2,4,5-triphenyl-2*H*-1,3-oxathiole,[4c] and monothiobenzil is converted to 2-benzoyl-2,4,5-triphenyl-1,3-oxathiole by azibenzil.[6] A dimer of monothiobenzil, 2,4-dibenzoyl-2,4-diphenyl-1,3-dithietane, undergoes photochemical cycloreversion to monothiobenzil.[7] This paper reports some new relationships between monothiobenzil, the dimer, and the oxathiole.

Results and Discussion

Monothiobenzil and Monothioanisil. These two monothio-1,2-diketones are prepared from the appropriate desyl thiosulfate as described previously.[5] The two-phase system of aqueous sodium hydroxide and methylene chloride is essential because if the monothiobenzil is not efficiently removed from the aqueous medium by methylene chloride, other reactions intervene. In ethanolic sodium hydroxide–methylene chloride, didesyl sulfide, **1**, is obtained, possibly by hydrolysis of the thiosulfate to the mercaptan, the latter then displacing a thiosulfate ion from a second molecule of desyl thiosulfate. Alternatively, the mercaptan might be formed by a Meerwein–Ponndorf–Verley reduction of the thiocarbonyl group of monothiobenzil. Although the dimer, **2**, of monothiobenzil is a side



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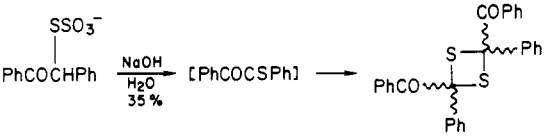
product in the preparation of the latter, a better yield of dimer is obtained by treatment of desyl thiosulfate with aqueous sodium hydroxide in the absence of methylene chloride.



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Thermolysis of monothiobenzil or monothioanisil gives mainly the 1,2-diaroyl-1,2-diarylethylene analogous to other reactions, especially those involving thiones.[8,9] The reaction may proceed via a 1,2-dithietane intermediate of the kind previously proposed to account for alkene formation from thiocarbonyl compounds,[9c,10] or it may proceed via the 1,3-dithietane, **2**. The predominance of cis alkene may be due to secondary orbital or electrostatic interactions which favor a cis configuration in the transition state. If the 1,3-dithietane is the precursor and if it is puckered, the bulkier phenyl groups would prefer the

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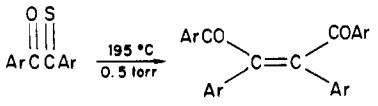
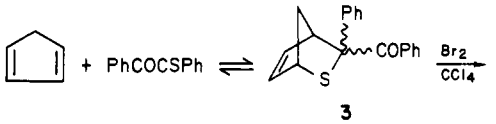
equatorial positions leaving the benzoyl groups to occupy the axial positions.[11] A $\pi^2s + \pi^2a$ dimerization of monothiobenzil that occurs by a transition state in which the more bulky phenyl groups are furthest apart also would give the *cis*-1,3-dithietane. Perhaps this cis arrangement in the dithietane is translated into the cis configuration of the alkene.

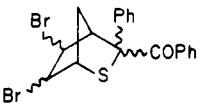


59% (Ar = Ph)
65% (Ar = *p*-$CH_3OC_6H_4$)

Monothiobenzil forms an unstable adduct, **3**, with cyclopentadiene; a stable dibromo derivative is obtained by treatment with bromine.

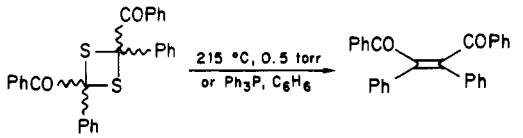


3



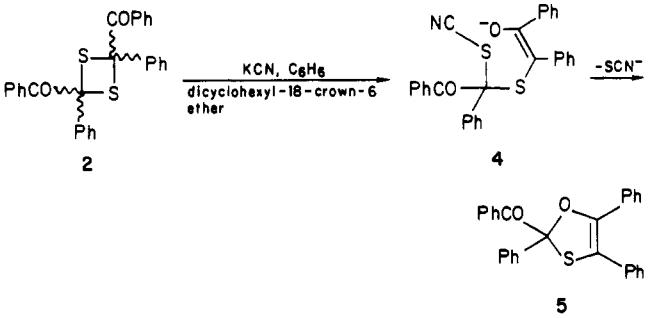
Oxidation of monothiobenzil by *m*-chloroperbenzoic acid, monoperphthalic acid, or concentrated nitric acid yields benzil. No sulfine could be detected in the reaction with the peracids although other sulfines have been obtained by oxidation of thiocarbonyl compounds.[12] A sulfine intermediate is possible since sulfines can be oxidized further to carbonyl compounds.[13]

2,4-Dibenzoyl-2,4-diphenyl-1,3-dithietane; 2-Benzoyl-2,4,5-triphenyl-1,3-oxathiole. Thermolysis of the dimer, **2**, or treatment of it with triphenylphosphine gives dibenzoylstilbene. The results of the thermolysis reaction can be explained in terms of the cycloreversion to monothiobenzil,[7a] whose behavior has been discussed above. The reaction with triphenylphosphine probably involves an initial thiophilic attack, after which several possible pathways may be taken.



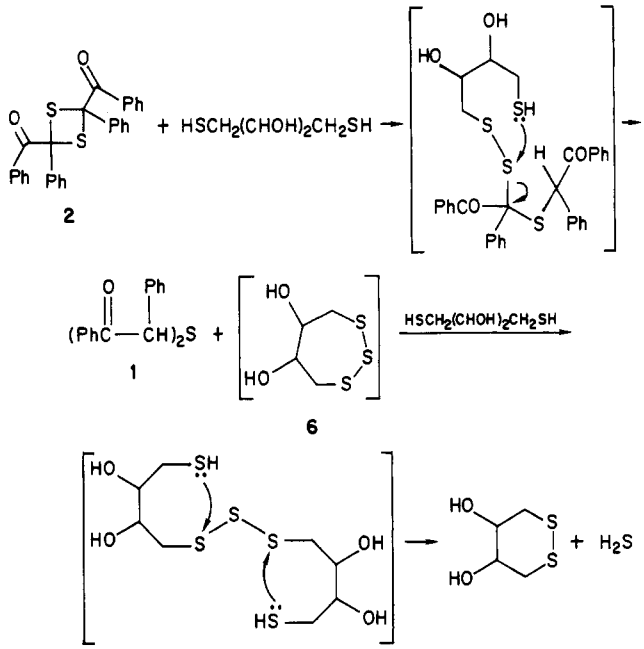
Monothiobenzil dimer, **2**, gives oxathiole **5** on treatment with potassium cyanide in the presence of dicyclohexyl-18-crown-6 ether in benzene solvent. No dibenzoylstilbene was detected. A possible mechanism involves attack of cyanide ion on sulfur to give enolate ion, **4**. The thiophilic reactions of **2** with triphenylphosphine and with cyanide ion no doubt are facilitated by the formation of stabilized phenacyl carbanions and by relief of ring strain.

Cleland's reagent, 2,3-dihydroxy-1,4-butanedithiol, is used principally to reduce 1,2-disulfides under mild conditions.[14] Since its mechanism of action probably involves



2 **4** **5**

a thiophilic attack of a thiol group on a sulfur atom of a 1,2-disulfide,[14] a comparison of its action on monothiobenzil dimer, **2**, with that of triphenylphosphine or cyanide ion might show similarities. Treatment of dimer **2** with Cleland's reagent gave didesyl sulfide, **1**. A possible mechanism is shown. Hydrogen sulfide was detected by odor and may be formed by the reaction of hypothetical intermediate **6** with Cleland's reagent.



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1 **6**

Experimental Section[15]

Didesyl Sulfide (1). Sodium desyl thiosulfate[5a] (4.13 g, 0.0125 mol) in water (125 mL) was added with vigorous stirring to sodium hydroxide (5 g) dissolved in 95% ethanol (125 mL) and to which methylene chloride (200 mL) was added. After 15 min the organic layer was separated, washed with water (3 × 100 mL), and dried (sodium sulfate). Concentration yielded a yellow powder, mp 143 °C (2.28 g, 0.019 mol, 86%). Recrystallization from benzene gave colorless needles (1.07 g, 0.0025 mol, 20%): mp 151–152 °C;[16] IR (KBr) 1670 (C=O) cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 5.43 (s, 2 H), 7.10–7.83 (m, 20 H); ^{13}C NMR (20 MHz, $CDCl_3$) δ 194.4, 136.0, 135.3, 133.2, 129.3, 129.1, 128.7, 128.4, 128.2, 54.6. Anal. Calcd for $C_{28}H_{22}O_2S$: C, 79.58; H, 5.25; S, 7.59. Found: C, 79.35; H, 5.27; S, 7.82. The infrared and proton NMR spectra were identical with those of a sample of didesyl sulfide prepared from desyl

(11) The Taft steric parameter, E_s, for the phenyl group is −2.55; it is not known for the benzoyl group. However, the benzyl group (E_s = −0.38) is an approximation. Charton has determined that a phenyl group has a larger steric effect than benzoyl in ortho-substituted benzene derivatives: Charton, M. *J. Org. Chem.* **1983**, *48*, 1016 and supplementary material.

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(15) Infrared spectra were taken on either a Perkin-Elmer Model 137 or Model 521 spectrometer. NMR spectra were obtained on a Varian A-60, a Varian CFT-20, or a Bruker WM-360 spectrometer. Mass spectra were obtained on a Perkin-Elmer Hitachi Model RMU-6E spectrometer. Microanalyses were done by Micro-Analysis Inc., Wilmington, DE. Monothiobenzil and monothioanisil were prepared as previously described (ref 5).

(16) Didesyl sulfide exists as a pair of enantiomers and a meso form. Melting ranges have been reported that involve mixtures of the diastereomers of individual mp 128–129 and 168–169 °C (ref 17). The 168 °C isomer is converted in part to the 128 °C isomer at its melting point as observed on a hot-stage microscope melting point apparatus.

chloride and sodium hydrosulfide according to the procedure of Schönberg and Iskander.[17]

2,4-Dibenzoyl-2,4-diphenyl-1,3-dithietane (2). Sodium desyl thiosulfate[5a] (0.83 g, 0.0025 mol) in water (50 mL) was rapidly added dropwise with vigorous stirring to sodium hydroxide (0.5 N, 10 mL). As the salt was added, a faint blue-green color was observed which disappeared quickly to leave a milky emulsion. Stirring was continued for 30 min after the addition of the salt was complete. The emulsion was neutralized with 5% hydrochloric acid and was continuously extracted with methylene chloride (190 mL) for 36 h. The organic layer was separated, washed with water (50 mL) and dried (sodium sulfate). Removal of the solvent gave the dithietane as a white solid (0.20 g, 0.00044 mol, 35%): mp 215 °C (blue melt) (lit.[7a] mp 215 °C); M_r (rast, β-naphthol) calcd 452, found 451 (average of three determinations); UV (CH_2Cl_2) 245 (ε 24 900), 350 (ε 1000) nm. The IR and mass spectra and the elemental analysis are comparable with those described previously.[7a]

Thermolysis of Monothiobenzil and Monothioanisil. Monothiobenzil (3.00 g, 0.0133 mol) was heated at 195 °C, 0.5 torr, for 2 h in a 25-mL flask fitted with a short-pass distillation head. Ether (1.5 mL) was added to the brown residue leaving the yellow-brown product which was recrystallized from 95% ethanol to give *cis*-dibenzoylstilbene (1.52 g, 0.0039 mol, 59%): mp 208–210 °C (lit.[18] mp 210–210.8 °C). Infrared and ultraviolet spectra were identical with those of an authentic sample.[19] Refluxing monothiobenzil (3.65 g, 0.016 mol) for 24 h in *m*-xylene (50 mL) gave *cis*-dibenzoylstilbene (1.00 g, 0.00259 mol, 32%) and benzil (0.65 g, 0.0031 mol, 19%) whose melting points and infrared spectra were identical with those of authentic samples.

Monothioansil (1.51 g, 0.00528 mol) was heated at 220 °C, 4 torr, for 3 h as described for monothiobenzil. Ether was added to the residue, insoluble material was removed by filtration, and the ether was removed to give a brown oil which was chromatographed on silica gel. Elution with benzene gave anisil (0.36 g, 0.0013 mol, 25%), identified by its melting point and infrared and ^1H NMR spectra, and 1,2,3,4-tetrakis(*p*-methoxyphenyl)-2-butene-1,4-dione (0.88 g, 0.0017 mol, 65%): mp 183–184 °C; IR (KBr) 1670 (C=O), 1580, 1515, 1255, 1025 cm^{-1}; UV (95% C_2H_5OH) 220 (ε 26 400); 291 (ε 41 900) nm; ^1H NMR (60 MHz, $CDCl_3$) δ 3.67 (s, 6 H), 3.78 (s, 6 H), 6.81 (dd, 8 H), 7.35 (d, 4 H) 8.01 (d, 4 H). Anal. Calcd for $C_{32}H_{28}O_6$: C, 75.59; H, 5.51. Found: C, 75.62; H, 5.53.

Adduct of Monothiobenzil and Cyclopentadiene. Monothiobenzil (4.4 g, 0.019 mol) in ether (50 mL) was added dropwise with stirring during 15 min to freshly distilled cyclopentadiene (1.50 g, 0.0227 mol) cooled to −78 °C in a nitrogen atmosphere. Stirring was continued for 30 min at −20 °C until the green color disappeared. If the reaction mixture is allowed to warm to room temperature, it becomes blue-green. Before cycloreversion could proceed further, bromine (3.0 g, 0.019 mol) in carbon tetrachloride (35 mL) was added; the mixture was stirred for 15 min. Removal of solvent gave a pale yellow solid which was recrystallized from chloroform-ligroin to give colorless needles (1.22 g, 0.0029 mol, 15%): mp 196–197 °C dec; IR (KBr) 1670 (C=O) cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 1.92 (dd, 1 H), 2.57 (dt, 1 H), 3.68 (d, 1 H), 3.73 (s, 1 H), 4.60–4.77 (m, 2 H), 7.20–7.64 (m, 10 H); ^{13}C NMR (90 MHz, $CDCl_3$) δ 194.1, 136.9, 132.7, 129.7, 129.5, 128.4, 128.2, 126.7, 66.3, 55.9, 55.8, 47.1, 35.3. Anal. Calcd for $C_{19}H_{16}Br_2OS$: C, 50.44; H, 3.54; S, 7.08. Found: C, 50.70; H, 3.45; S, 6.86.

Oxidation of Monothiobenzil. *m*-Chloroperbenzoic acid (85%, 1.51 g, 0.0074 mol) and monothiobenzil (1.77 g, 0.0078 mol) were dissolved in ether (50 mL) at 0 °C. The reaction mixture was protected from light and was stirred for 1 h. It was washed with saturated sodium bicarbonate solution (3 × 50 mL), dried over sodium sulfate, and concentrated to give benzil in essentially quantitative yield. Recrystallization from ethanol gave pale yellow needles, mp 95 °C, whose infrared spectrum was identical with that of an authentic sample. A similar result was obtained with monoperphthalic acid and with concentrated nitric acid.

Thermolysis of Monothiobenzil Dimer. The dithietane, **2** (1.25 g, 0.0027 mol), was heated at 215 °C at 0.5 torr for 2 h. The white dithietane melted to a blue-green liquid which ultimately became brown. After the reaction mixture was cooled, ether (15 mL) was added and *cis*-dibenzoylstilbene (0.62 g, 0.0016 mol, 59%) was collected by filtration and recrystallized from ethanol: mp 209–210 °C (lit.[18] mp 210–210.8 °C). A small amount of *trans*-dibenzoylstilbene was formed according to thin-layer chromatography.

Reaction of Monothiobenzil Dimer with Triphenylphosphine. A mixture of the dithietane, **2** (0.50 g, 0.0011 mol), and triphenylphosphine (0.58 g, 0.0022 mol) was refluxed in benzene (15 mL) for 48 h. The solution was cooled and the solvent removed to give a yellow semisolid. Addition of ether precipitated *cis*-dibenzoylstilbene (0.26 g, 0.00068 mol, 61%). Additional product was obtained (0.062 g, 0.00016 mol, 14%) from the filtrate by chromatography on alumina: mp 207–209 °C. Triphenylphosphine sulfide (0.53 g, 0.0018 mol, 80%) was isolated by column chromatography, mp 159–160 °C (lit.[20] mp 160–161 °C). Its infrared spectrum was identical with that of an authentic sample.

Reaction of Monothiobenzil Dimer with Cyanide Ion. A complex of potassium cyanide and dicyclohexyl-18-crown-6 ether was prepared by refluxing the cyanide salt (0.087 g, 0.0013 mol) and the crown ether (0.50 g, 0.0013 mol) in methanol (25 mL) for 30 min. The methanol was removed, and the dithietane, **2** (0.90 g, 0.00020 mol), and benzene (25 mL) were added to the complex and refluxed 18 h. The reaction mixture was filtered and the filtrate concentrated to yield 2-benzoyl-2,4,5-triphenyl-1,3-oxathiole, **5** (0.068 g, 0.00016 mol, 81%) whose infrared, ultraviolet, and proton NMR spectra were identical with those of an authentic sample.[2a] Potassium thiocyanate was identified in the solid residue by its infrared spectrum and by the formation of a deep red color on treatment with ferric chloride.

Reaction of Monothiobenzil Dimer with Cleland's Reagent. The dithietane, **2** (0.090 g, 0.00020 mol), and Cleland's reagent (2,3-dihydroxy-1,4-butanedithiol) (0.034 g, 0.00022 mol) were sealed under argon in a glass tube which was heated to 135 °C to melt the mixture, after which the temperature was reduced to 120 °C. After 2 h, the tube was cooled and opened; the odor of hydrogen sulfide was noticed. The contents of the tube were removed with methylene chloride (2 mL) and filtered to give oxidized Cleland's reagent, 1,2-dithiane-4,5-diol (0.018 g, 0.00012 mol, 59%): mp 130.5–131.5 °C (lit.[14] mp 132 °C). The remaining oil was chromatographed on silica gel with elution by methylene chloride to give a mixture of diastereomers of didesyl sulfide (0.068 g, 0.00016 mol, 80%), mp 153 °C.[16] Its infrared and proton magnetic resonance spectra were identical with those of an authentic sample prepared by the method of Schönberg and Iskander.[17] An additional amount (11.5 mg, 0.0755 mmol, 38%) of 1,2-dithiane-4,5-diol was eluted from the column.

Registry No. **1**, 6540-70-1; **2**, 74950-05-3; **5**, 51911-53-6; PhC(O)C(S)Ph, 16939-18-7; PhC(O)C(O)Ph, 134-81-6; MeO-*p*-$C_6H_4C(O)C(S)C_6H_4$-*p*-OMe, 71193-34-5; Ph_3P, 603-35-0; KCN, 151-50-8; $HSCH_2CH(OH)CH(OH)CH_2SH$, 7634-42-6; $PhC(O)CH(Ph)SSO_2O^-Na^+$, 92844-65-0; 5,6-dibromo-3-phenyl-3-(phenylcarbonyl)-2-thiabicyclo[2.2.1]heptane, 92844-64-9; *cis*-dibenzoylstilbene, 6313-26-4; *trans*-dibenzoylstilbene, 10496-80-7; 1,2-dithiane-4,5-diol, 74185-01-6; 1,2,3,4-tetrakis(*p*-methoxyphenyl)-2-butene-1,4-dione, 92844-66-1; cyclopentadiene, 542-92-7; triphenylphosphine sulfide, 3878-45-3.

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