

The solvent and residual 3-chloroindene (1.1 g) were then removed by distillation; the residue was triturated with ether and recrystallized from ether-cyclohexane to give 490 mg (21%) of white crystalline dimer.

Further purification was achieved by vacuum sublimation [150° (1 mm)] and subsequent recrystallization from cyclohexane. Two crystalline modifications of the dichlorotruxane [(a) (mp 169–170°, and (b) (180–181°)] deposited from cyclohexane which were separated mechanically. The infrared spectra determined in potassium bromide were very similar, while in solution they are identical as are the nmr spectra (deuteriochloroform) τ 2.19 and 2.65 (m, s, aromatic) and 6.40–7.60 (m, 6, aliphatic).

Anal. Calcd for $C_{18}H_{14}Cl_2$: C, 71.77; H, 4.68; Cl, 23.43. Found: C, 71.82; H, 4.80; Cl, 23.16 (determined on lower melting isomer).

Dehalogenation of *syn,trans*-3,3'-Dichlorotruxane (6).—To a solution of 0.20 g (0.67 mmol) of the dichlorotruxane 6 dissolved in a mixture of 10 ml of tetrahydrofuran and 3 ml of *tert*-butyl alcohol at 0° was added in small portions (1.0 g, 43.5 mg-atoms) of finely divided sodium metal under nitrogen. After 72 hr the solution was warmed to 25° and the excess sodium metal collected on a filter. The filtrate was then quenched by pouring onto ice, the organic material extracted repeatedly with ether, and the combined ethereal extracts were dried over anhydrous magnesium sulfate. Upon concentration of the ethereal solution, a white crystalline material (mp 110–111°) separated which was shown to be identical with *syn,trans*-truxane 2a by infrared and nmr spectroscopy.

Attempted Photocycloaddition of 3-Chloroindene (5) to Indene (1a).—A mixture of 7.5 g (50 mmol) of 3-chloroindene and 5.8 g (50 mmol) of indene dissolved in 25 ml of benzene containing 1.0 g of benzophenone was irradiated^{15a} for 10 hr at 10°. The oil remaining after removal of solvent and unreacted indenenes from the brown irradiation mixture was chromatographed over silica gel using mixtures of *n*-hexane and ether as the eluting solvent. *syn,trans*-3,3'-Dichlorotruxane (6) (2.2 g, 29%) and *syn,trans*-truxane (2a) (40 mg, 0.7%) were isolated. No crossed dimer was detected in this case or under a variety of different reaction conditions in which the solvent, light source, and temperature were changed (–30–40°). Acetophenone also was employed as a solvent in an attempt to sensitize the reaction without success.

Dimerization of 2-Chloroindene (7).—A modification of the method described by Metzner⁷ was employed for the dimerization of 2-chloroindene (7). A benzene solution (100 ml) of 7.5 g (55 mmol) of freshly distilled 2-chloroindene [bp 95–98° (11 mm), n_D^{20} (1.5824)¹¹ containing 2 g of benzophenone were irradiated^{15c} in a Pyrex vessel for 25 hr. After removal of the solvent and excess 2-chloroindene under vacuum the residue was chromatographed on silica gel using hexane ether (20:1) as the eluent mixture. The two crystalline fractions were isolated and recrystallized from methanol to give two dimers, mp 115° (1.1 g, 14.5%) and 173° (1.0 g, 13.5%) (lit.⁷ 115 and 173–174°).

Dehalogenation of the Isomeric Dichlorotruxanes Obtained from 2-Chloroindene (7).—To a solution of 200 mg (0.67 mmol) of each of the 2-chloroindene dimers in 12 ml of tetrahydrofuran containing 3 ml of *tert*-butyl alcohol at 0° was added 0.8 g of sodium metal. The mixture was stirred for 50 hr at 0–5° under nitrogen. An additional 0.1 g of sodium metal and 1 ml of *tert*-butyl alcohol were then added; the resulting mixture was allowed to warm to room temperature over a period of 2–3 hr. The reaction mixture after removal of excess sodium by filtration was poured onto ice, the aqueous phase extracted repeatedly with ether, and the combined organic phases dried over anhydrous magnesium sulfate. The residues obtained after removal of solvent were purified by elution chromatography on silica gel.

The 2-chloroindene dimer 8 (mp 172°) upon dechlorination afforded 130 mg (84.5%) of a crude product which was purified by recrystallization from methanol to give a hydrocarbon (mp 141°) shown to be identical with *anti,trans*-truxane (3a) by mixture melting point and infrared and nmr spectroscopy.

The reduction of the 2-chloroindene dimer 9 (mp 115°) gave a more complex mixture of reduction products. The absence of *syn,trans*-truxane (2a) among the products was demonstrated by tlc; however, insufficient material was available to achieve separation and unambiguous structural characterization of any product.

Photocycloaddition of 3-Chloroindene (5) to 2-Chloroindene (7).—An equimolar mixture of 3-chloroindene (1.2 g, 8.0 mmol) and 2-chloroindene (1.2 g, 8.0 mmol) dissolved in *n*-hexane (~30 ml) containing 0.16 g of benzophenone was irradiated for 12 hr.^{15a} Upon work-up according to procedures previously described a dimer (mp 190°) was isolated (100 mg): nmr (deuteriochloroform) τ 2.69 (m, s, aromatic), 5.80, 6.41, and 6.6 (s, br, 6, aliphatic).

Registry No.—1a, 95-13-6; 5, 25894-22-8; 6, 25894-23-9; 7, 18427-72-0; 8, 25894-25-1; 9, 25957-54-4.

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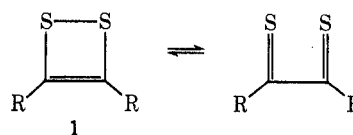
Monothiobenzil^{1,2}

DONALD C. DITTMER* AND GEORGE E. KUHLMANN

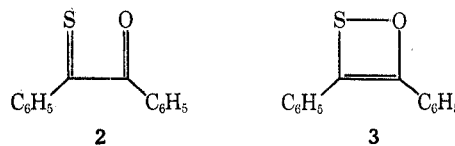
Department of Chemistry, Bowne Hall,
Syracuse University, Syracuse, New York 13210

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Considerable interest has been shown recently in the interaction of two sulfur atoms or a sulfur and an oxygen atom when they are situated near each other.³ The interaction of two sulfur atoms on adjacent carbon atoms has been considered theoretically,^{4a} and 1,2-



dithietes (1) appear to have some relative stability.^{4b} Several molecules with very short S–O intramolecular distances have been investigated.⁵ In monothiobenzil,⁶ (2), a possibility exists for interaction of sulfur and oxygen, leading in the extreme case to an oxathiete structure, 3.



* To whom correspondence should be addressed.

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(5) P. L. Johnson and I. C. Paul, *ibid.*, 91, 781 (1969); J. A. Kapecki and J. E. Baldwin, *ibid.*, 1120 (1969).

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The wavelength of the thiocarbonyl $n \rightarrow \pi^*$ absorption of monothiobenzil [λ_{\max} (CHCl_3) 606 nm (ϵ 32.5), (95% $\text{C}_2\text{H}_5\text{OH}$) 610, (C_6H_6) 617 (40.4)] compares favorably with that of thiobenzophenone [λ_{\max} (CHCl_3) 598 nm, (95% $\text{C}_2\text{H}_5\text{OH}$) 602 (ϵ 181),⁷ (C_6H_6) 606]. The infrared spectrum of **2** in carbon disulfide clearly shows the carbonyl band at 1670 cm^{-1} and the thiocarbonyl band at 1230 cm^{-1} which compares with the carbonyl band at 1665 cm^{-1} for benzil and the thiocarbonyl band⁸ at 1223 cm^{-1} for thiobenzophenone. In the mass spectrum of monothiobenzil, the parent ion at m/e 226 is relatively less intense than the parent ion of thiobenzophenone but more than ten times as intense as that of benzil. The *stepwise* loss of a sulfur atom and an oxygen atom is not observed. In the mass spectrum of thiobenzophenone, an important ion fragment corresponds to the parent ion minus a sulfur atom. A rather weak peak at m/e 178 in the mass spectrum of monothiobenzil corresponds to the loss of sulfur monoxide. Consequently, an oxathiete configuration may be of some importance in the molecular ion derived from monothiobenzil. The comparisons of mass spectra are shown in Table I. A benzoxa-

TABLE I
MASS SPECTRA OF MONOTHIOBENZIL,
BENZIL, AND THIOBENZOPHENONE^a

m/e	% of base peak Monothiobenzil	Possible ion
226	43.5	$\text{C}_6\text{H}_5\text{CSCOC}_6\text{H}_5$
198 (P - CO)	2.34	$(\text{C}_6\text{H}_5)_2\text{CS}$
178 (P - SO)	0.59	$\text{C}_6\text{H}_5\text{C}\equiv\text{CC}_6\text{H}_5$
121 (P - $\text{C}_6\text{H}_5\text{CO}$)	42.0	$\text{C}_6\text{H}_5\text{CS}$
105 (P - $\text{C}_6\text{H}_5\text{CS}$)	100	$\text{C}_6\text{H}_5\text{CO}$
Benzil		
210	3.48	$\text{C}_6\text{H}_5\text{COCOC}_6\text{H}_5$
105	100	$\text{C}_6\text{H}_5\text{CO}$
Thiobenzophenone		
198	80.4	$(\text{C}_6\text{H}_5)_2\text{CS}$
166 (P - S)	14.6	$(\text{C}_6\text{H}_5)_2\text{C}$
165 (P - HS)	100	$\text{C}_6\text{H}_5\text{S}^b$
121 (P - C_6H_5)	99.4	$\text{C}_6\text{H}_5\text{CS}$

^a 110°, indirect inlet, 70 eV. ^b Fluorenyl cation?

thiete was suggested as an ion in the mass spectrum of a trithiatiazine.⁹

Unless there is some unusual coincidence of ultraviolet and infrared absorption frequencies between the monothiobenzil (**2**) and oxathiete (**3**) structures, the structure must be best represented as monothiobenzil (**2**). Stabilization of the carbonyl and thiocarbonyl groups by conjugation with the phenyl groups may outweigh any stabilization caused by interaction of the oxygen and sulfur atoms.

Experimental Section

Infrared spectra were taken on a Perkin-Elmer Model 521 grating spectrophotometer. Ultraviolet spectra were obtained

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on a Perkin-Elmer Model 202 spectrophotometer. Proton nmr spectra were obtained on a Varian Model A-60 spectrometer. Mass spectra were obtained using a Perkin-Elmer Hitachi Model RMU 6E single focusing spectrometer. All chemicals were either "Chromatoquality" or reagent grade.

Monothiobenzil.—Cooled solutions of 0.3–2.0 g of dibenzoylstilbene episulfoxides⁸ in 500 ml of benzene were irradiated at 5–11° with an internal mercury arc lamp (Hanovia Type L, 450 W) in a water-cooled quartz immersion well.¹⁰ Irradiations lasted for 30–120 min and were conducted with or without a Pyrex filter. Purified nitrogen was passed through the solution and reaction vessel for at least 30 min before irradiation and a positive pressure of nitrogen was maintained during the reaction. The benzene solvent (Baker and Adamson) was dried with sodium ribbon and distilled. All solvents and glassware used with monothiobenzil were flushed with purified nitrogen and the glassware was wrapped in aluminum foil to keep out light.

The deep blue solutions were concentrated to ca. 20 ml by flash evaporation below 25°. Separation of the blue monothiobenzil from the yellow benzil was effected easily by column chromatography on 100 g of silicic acid (Baker and Adamson) with 1500 ml of chloroform. Cyclohexane (about 20 ml) was added to the column before and after application of the benzene solution of the reaction products to the column.

The blue oil obtained from chromatography of a reaction mixture of dibenzoylstilbene episulfoxides (0.474 g, 1.08 mmol) after irradiation through a Pyrex filter for 90 min weighed 0.0968 g (0.428 mmol, 40%). Monothiobenzil is rapidly oxidized by oxygen and obtaining an analysis was difficult. If monothiobenzil was kept under nitrogen in a sealed vial, a rough analysis could be obtained.¹¹ Monothiobenzil is stable for at least several days under nitrogen at –20° when protected from light. Its long term stability was not investigated but it should be able to be kept indefinitely if protected from oxygen, light, and nucleophilic reagents.

Anal. Calcd for $\text{C}_{14}\text{H}_{10}\text{OS}$: C, 74.33; H, 4.42; S, 14.17. Found: C, 75.92; H, 4.64; S, 15.23.

The blue monothiobenzil had the following properties: ir (CS_2) 3050 (w), 1670 (C=O) (s), 1310 (w), 1270 (m), 1230 (C=S) (s), 1210 (m), 1175 (s), 1155 (w), 1115 (w), 1095 (m), 1070 (w), 1020 (m), 1005 (m), 975 (w), 935 (w), 920 (w), 900 (w), 840 (s), 785 (s), 765 (s), 755 (s), 740 (m), 703 (s), and 691 cm^{-1} (s); nmr (CDCl_3) 430, 450, 480 Hz (complex); uv max (95% $\text{C}_2\text{H}_5\text{OH}$) 325, 247, 231 nm; uv max (CHCl_3) 325, 247 nm.

The mass spectrum of the blue oil was used in an attempt to check its empirical formula by a comparison of the relative intensities of the peaks due to isotopes. *Anal.* Calcd¹² for $\text{C}_{14}\text{H}_{10}\text{OS}$: 100 (P + 1)/P, 16.11; 100 (P + 2)/P, 5.7. Found: 100 (P + 1)/P, 13.90; 100 (P + 2)/P, 5.9.

Dioxime of Monothiobenzil.—Treatment of 0.124 g (0.000549 mol) of blue oil, obtained by irradiation of 0.436 g (1.00 mmol) of a mixture of episulfoxides for 120 min through a Pyrex filter, with 1.5 ml of 95% ethanol, 1 ml of pyridine, and 0.097 g (1.40 mmol) of hydroxylamine hydrochloride resulted in the same dioxime, mp 238° dec (lit.¹³ mp 237–238° dec), obtained from benzil. The dioxime has the same infrared spectrum as that of the anti isomer of benzil oxime.¹⁴

Over several days, a blue-green ethanolic solution obtained by irradiation of an episulfoxide mixture (2.0 g, 4.6 mmol) faded in color on exposure to room light and air; hydrogen sulfide was evolved as determined by darkening of lead acetate paper. Thin layer chromatography on silica gel with chloroform showed that with time the concentration of monothiobenzil, which gives a blue spot, decreased while that of benzil increased. A mono-2,4-dinitrophenylhydrazone of the residual benzil was prepared, mp 188–190° (lit.¹⁵ mp 189°).

Registry No.—2, 16939-18-7.

(10) Data about the lamp and immersion well may be obtained from the Hanovia Lamp Division of Englehard Hanovia Inc., Newark, N. J.

(11) We wish to thank Mr. Al Vulcano for obtaining the analysis.

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