with 80 mg. of lithium aluminum hydride in 25 ml. of dry ether just until disappearance of the yellow color.[42] (Note: The large excess of the hydride can probably be reduced.) Excess hydride was then immediately destroyed, and the reaction mixture processed, in a manner similar to that used for the m.p. 103° tetroldithiol diketal (see above).

The oil obtained upon evaporation of the ethereal extract was crystallized from 6.0 ml. of petroleum ether, giving 180 mg. of colorless crystals, m.p. 150–152°. This material was again recrystallized, giving 140 mg. (57%) of colorless, fine needles, m.p. 151–152°.

The n.m.r. spectrum (see below) indicated that incomplete reduction had caused formation of mercaptodithiolane instead of tetroldithiol diketal. A sample was recrystallized again for analysis, which confirmed the mercaptodithiolane structure.

Anal. Calcd. for $C_{12}H_{20}O_4S_2$: C, 49.29; H, 6.89; S, 21.93. Calcd. for $C_{13}H_{20}O_4S_3$: C, 46.40; H, 5.99; S, 28.60. Found: C, 46.68; H, 6.01; S, 29.19.

The n.m.r. spectrum of the mercaptodithiolane diketal showed signals for isopropylidene methyl groups at $\delta = 1.37$ (6 protons), 1.48 (3 protons), and 1.55 (3 protons). A doublet for the $-SH$ proton appeared at $\delta = 2.98$, 3.08, and a doublet for the HCS_3 proton at 5.70, 5.80. The signals for the two ring protons on C-5 and C-6 appeared in a series of peaks centered near $\delta = 3.6$. The signals for the four ring protons on C-1, C-2, C-3, C-4 appeared in a narrower pattern near $\delta = 4.5$. Prior treatment of the sample with deuterium oxide almost eliminated the signals due to the $-SH$ group, and greatly weakened and broadened the signals due to the HCS_3 proton (isotopic exchange was not entirely complete under the conditions employed).

D(125/346) Stereoisomer of 5,6-Dimercapto-1,2,3,4-cyclohexanetetrol 5,6-Trithioörthoformate Pentaacetate[46] [Mercaptodithiolane Pentaacetate, M.p. 132°, XIIIa].—The starting material was an oil which had been obtained by successive reduction and hydrolysis (see above) of the trithiocarbonate diketal (m.p. 191°). This oil was believed to consist of impure (125/346) tetroldithiol, but due to incomplete reduction, actually consisted mainly of the mercaptodithiolanetetrol (not the diketal).

To 100 mg. of this oil was added 40 mg. of fused sodium acetate and 3.0 ml. of redistilled acetic anhydride. The mixture was boiled under reflux 3 hr., evaporated, and the residue distributed between chloroform and water. The washed (5% sodium bicarbonate) and dried chloroform phase was evaporated. The residue was taken up in 3.0 ml. of hot 2-propanol (decolorizing charcoal used). On cooling, the solution deposited 150 mg. of colorless needles, m.p. 126–129°. This material was recrystallized thrice more, giving 50 mg. of product of constant m.p. 131–132°, $[\alpha]^{26}\text{D}$ $-44°$ (chloroform, *c* 2.7), MR $-204°$.

Anal. Calcd. for $C_{16}H_{24}O_{10}S_2$: C, 46.54; H, 5.21; S, 13.80. Calcd. for $C_{17}H_{22}O_9S_3$: C, 43.76; H, 4.35; S, 20.62. Found: C, 44.37; H, 4.52; S, 20.05.

L(125/346) Stereoisomer of 5,6-Di-*O*-(*S*-methylthiolcarbonyl)-1,2:3,4-di-*O*-isopropylidene-1,2,3,4-cyclohexanetetrol (IV).—A solution of 0.26 g. of (−)-inositol diketal[14b] (m.p. 151°) and 0.50 g. of methanethiol chloroformate[33] in 5 ml. of dry pyridine was kept at 25° for 4 days. The solution was poured into 25 g. of mixed ice and water with stirring. After 30 min. the precipitate was collected, washed with ice-cold water, and dried. The product was recrystallized from absolute ethanol, giving 175 mg. of colorless needles, m.p. 160–163°. This material was again recrystallized from the same solvent, giving 100 mg. of needles, m.p. 166–167°, $[\alpha]\text{D}$ $-115°$ (chloroform, *c* 1), MR $-470°$. A sample was again recrystallized for analysis.

Anal. Calcd. for $C_{16}H_{24}O_8S_2$: C, 47.04; H, 5.92; S, 15.70. Found: C, 47.21; H, 6.04; S, 15.78.

With the spectropolarimeter, this compound showed a negative plain dispersion curve, RD in dioxane (*c* 0.103), 26°; $[\alpha]_{650}$ $-60°$, $[\alpha]_{589}$ $-74°$, $[\alpha]_{255}$ $-546°$.

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(46) The preferred *Chemical Abstracts* name for XIIIa would be hexahydro-2-mercapto-1,3-benzodithiole-4,5,6,7-tetrol pentaacetate.

Further Studies of Schoenberg's Reagent and Sulfur[1]

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The reaction of Schoenberg's reagent with sulfur leads to the formation of a mixture of products, one of which is the previously unreported bis(*p*-methoxyphenyl)methyleneimine. The infrared spectrum of this imine shows ten bands characteristic of one or more aspects of the $>C=N-H$ grouping. Bis(*p*-methoxyphenyl)methyleneimine was observed to react with carbon disulfide and hydrogen sulfide; implications of the latter reaction in analytical applications of Schoenberg's reaction are discussed.

The production of the deep blue *p,p'*-dimethoxythiobenzophenone from a mixture of sulfur and *N*-(4,4'-dimethoxybenzohydrilidene)benzylamine (Schoenberg's reagent) was reported by Schoenberg and Urban[4] in 1934. Ory, Warren, and Williams[1a] utilized this reaction as the basis for a direct quantitative colorimetric determination of free sulfur and cited the first evidence that products other than the thioketone were also formed in the reaction. Attempts by Huddleston[5] to isolate and characterize these products led to the observation of an acid-soluble fraction in the reaction mixture. This paper reports the purification and identification of the acid-soluble product together with some related observations.

Huddleston[5] reported that the acid-soluble compound, which he obtained in crystalline form from the acid extract of the reaction mixture, was stable in 5% hydrochloric acid at room temperature, but that at reflux temperature hydrolysis took place with the formation of *p,p'*-dimethoxybenzophenone. Subsequent elemental analysis indicated that the acid-soluble component might be bis(*p*-methoxyphenyl)methyleneimine. Independent synthesis of this imine confirmed this identification.

Neely[6] had noted the appearance of five bands in the infrared spectra of samples taken during the course

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(1) Previous papers in this series: (a) H. A. Ory, V. L. Warren, and H. B. Williams, *Analyst* **82**, 189 (1957); (b) W. C. Neely and H. B. Williams, *Anal. Chim. Acta*, **24**, 575 (1961).

(2) National Science Foundation Undergraduate Research Participant, Summer, 1961.

(3) National Science Foundation College Teacher Research Participant, Summer, 1961.

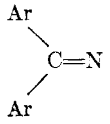
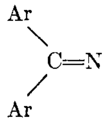
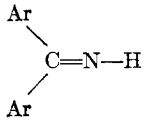
(4) A. Schoenberg and W. Urban, *Ber.*, **67**, 1999 (1934).

(5) G. Huddleston, Ph.D. dissertation, Louisiana State University, 1960.

(6) C. Neely, M.S. thesis, Louisiana State University, 1960.

of the reaction and observed that none of these bands were present in the spectrum of Schoenberg's reagent or of any of the then known products of the reaction. Huddleston[5] established the fact that all five of these bands were present in the spectrum of the acid-soluble material. Comparison of the infrared spectrum of the acid-soluble fraction with that of Schoenberg's reagent (both in potassium bromide disks) shows that there are at least ten such bands. These absorption bands and their probable assignments are given in Table I.

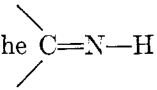
TABLE I

Frequency of absorption maximum, cm.$^{-1}$		Assignment
3257	ms	N—H stretch[a]
1646	w	C=N[b]
1558	s	N—H in-plane bend[b]
1367	m (sh)	 $\mathrm{Ar_2C{=}N}$
1355	s	 $\mathrm{Ar_2C{=}N}$
1195	s	Ar—C=N[c]
896	s (sh)	C=N—H bend
890	vs	C=N—H bend
773	s	N—H out-of-plane bend
674	m	 $\mathrm{Ar_2C{=}N{-}H}$

[a] See ref. 7. [b] See ref. 8. [c] See ref. 9.

The relatively weak absorption observed at 1646 cm.$^{-1}$ was assigned to C=N, consistent with observations by others, and in particular by Picard and Polly[7] who noted that the C=N stretching vibration of bis(*p*-chlorophenyl)methyleneimine occurred at 1653 cm.$^{-1}$. In Schoenberg's reagent this vibration occurs at 1626 cm.$^{-1}$.[1b]

Assignment for the 674-cm.$^{-1}$ absorption is based on the spectra of twenty-two imines or substituted imines as reported in the Sadtler Index. Only diphenylmethyleneimine also showed this absorption. On the basis of the available evidence at this time, we can only conclude that the 674 cm.$^{-1}$ band is correctly assigned.

When bis(*p*-methoxyphenyl)methyleneimine was dissolved in carbon disulfide, a relatively slow reaction occurred which apparently formed 4,4'-dimethoxythiobenzophenone and thiocyanic acid. The characteristic thioketone absorption at 590 cm.$^{-1}$ was observed for the resulting intensely blue carbon disulfide solution and an acid wash of this solution gave a strong positive test for thiocyanate ion. All ten of the above listed absorption bands disappeared during the course of this reaction, which seems to be conclusive evidence that they are associated with some aspect of the  $\mathrm{>C{=}N{-}H}$ grouping and that whatever molecular form thiocyanic acid assumes in carbon disulfide solution it does not absorb measurably at these frequencies.

Experimental

Bis(*p*-methoxyphenyl)methyleneimine.—A 10-g. (0.03 mole) quantity of *N*-(4,4'-dimethoxybenzohydrilidene)benzylamine as obtained from the Distillation Products Industries was carefully blended in the solid state with 0.3 g. (0.009 mole) of powdered sulfur. The mixture was placed in a 200-ml. round-bottom flask and heated in an oil bath for 30 min. at 200°. The flask was open to allow the escape of volatile products. The reaction mixture was then permitted to cool, dissolved in 100 ml. of benzene which solution was then extracted twice with 75-ml. portions of 5% aqueous hydrochloric acid. A red-brown, acetone-soluble oil invariably formed during the first extraction. If hydrolysis of unconsumed reagent occurred (as indicated by a white milky precipitate of dimethoxybenzophenone in the aqueous acid phase), the ketone was removed readily by extraction with ether. On occasion when the acid solution was very yellow at this point, the impurity was effectively removed by a single wash with benzene.

Aqueous sodium hydroxide (20%) was added to the aqueous acid phase until the precipitation of the white crystalline imine was complete. Purification of the imine was obtained by dissolving the crude product in ether, re-extracting with acid (5% hydrochloric acid) and treating the aqueous phase with 20% sodium hydroxide. The imine precipitated as a fine white powder which could again be extracted directly with ether from the aqueous phase. This process could be repeated as many times as necessary to obtain the imine in the form of very white flakes.

After two recrystallizations from ether, there was obtained 0.72 g. (10% yield based on starting reagent) of bis(*p*-methoxyphenyl)methyleneimine, melting at 129.5–130°.

Anal. Calcd. for $C_{15}H_{15}NO_2$: C, 74.63; H, 6.31; N, 5.80. Found: C, 74.51; H, 6.04; N, 5.59.

Analytical results obtained by Galbraith Laboratories, Inc., were the average of two determinations in each case.

Independent synthesis of this imine by reaction of *p*-methoxyphenylmagnesium bromide with anisonitrile, followed by hydrolysis with 5% hydrochloric acid, gave a product, the melting point and infrared spectrum of which were identical with those of the acid-soluble material obtained from Schoenberg's reagent and sulfur.

Results

In benzene or carbon tetrachloride solution, the imine reacted readily with hydrogen sulfide at room temperature to produce the dimethoxythiobenzophenone and, presumably, ammonia. However, in the presence of hydrogen sulfide the ammonia was not detected.

In the original Schoenberg reaction hydrogen sulfide was formed along with the blue thioketone, and the amount of the latter produced became the basis for a quantitative determination for free sulfur.[1a] We now have shown that hydrogen sulfide reacts with another product of the reaction—the imine—also to form the thioketone. The analytical chemical implications are immediately apparent. In order to obtain reproducible results for sulfur analysis by this method, one must standardize procedures with care. The experimental conditions of temperature and reaction time as well as the practice of using open or closed reaction vessels must be rigidly duplicated.

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(7) P. L. Pickard and G. W. Polly, *J. Am. Chem. Soc.*, **76**, 5169 (1954).

(8) R. Jones and C. Sandorfy, "Technique of Organic Chemistry, IX," Interscience, New York, N. Y., 1956.

(9) "Sadtler Standard Spectra Midget Edition," Sadtler Research Laboratories, Philadelphia, Pa., 1961.