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Catalysis by Molybdenum Complexes. The Reaction of Diazenes and Acetylenes with Thiophenol

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The reaction of diethyl azodicarboxylate with thiophenol to give the appropriate hydrazine and disulfide is catalyzed by various oxomolybdenum compounds, Vaska's compound, and triethylamine. Of these same compounds, only $OMo(S_2CNR_2)_2$ catalyzed the similar reduction of azobenzene. In contrast, dimethyl acetylenedicarboxylate gave the 1:1 and 2:1 adducts with thiophenol. The ratio of the isomers of both adducts was dependent upon the reaction conditions and the catalyst used. The stereochemistry of these additions was determined by NMR for the 1:1 adducts and by resolution (brucine salt) for the 2:1 adducts. The probable reaction sequences are discussed. Relevance to the action of molybdenum- and sulfhydryl-containing enzymes is noted.

Studies[1-3] of the reactions of diazenes, acetylenes and related compounds with complexes of molybdenum in its higher oxidation states may aid the understanding of the possible modes of reaction of redox-active molybdoenzymes, particularly nitrogenase. The possibility that coordinated diimide is a significant intermediate in the nitrogen fixation process and the knowledge that acetylenes are reduced by this enzyme under very mild conditions prompted this study.

We showed previously[1] that oxobis(*N,N*-dialkyldithiocarbamato)molybdenum(IV) reacts with unsaturated organic molecules, such as diazenes and activated acetylenes, to yield 1:1 adducts. Those formed with diazenes hydrolyze to produce the appropriate *cis*-dioxobis(*N,N*-dialkyldithiocarbamato)-molybdenum(VI) and a substituted hydrazine and are probably best described as substituted hydrazido complexes of molybdenum(VI) (eq 1).

$$OMo(S_2CNR_2)_2 + R'N{=}NR' \rightarrow OMo(S_2CNR_2)_2(R'N_2R') \xrightarrow{+H_2O} MoO_2(S_2CNR_2)_2 + R'NHNHR' \quad (1)$$

These reactions therefore involve the formal transfer of an electron pair from molybdenum to diazene and we have suggested[1,2] this oxidative addition reaction as a model for nitrogenase activity. If the *cis*-dioxomolybdenum(VI) moiety formed in reaction I could be reduced to oxomolybdenum(IV) again, then these reactions would be individual steps in a catalytic cycle. We set out to determine whether thiols could function as both the electron and proton donor in these systems. Herein we report the reaction of thiophenol with diethyl azodicarboxylate (DEAZ), azobenzene, and dimethyl acetylenedicarboxylate (DMAC) using various metal complexes and some organic bases as catalysts.

Experimental Section

Materials and Physical Measurements. Azobenzene, hydrazobenzene, diethyl azodicarboxylate, dimethyl acetylenedicarboxylate, monopotassium acetylenedicarboxylate, and thiophenol were obtained from Aldrich Chemical Co. Oxobis(*N,N*-diethyldithiocarbamato)molybdenum(IV)[4] and *cis*-dioxobis(*N,N*-diethyldithiocarbamato)molybdenum(VI)[5] were prepared by literature methods. The 1-piperidino, 4-morpholino, and *N,N*-dimethyl analogues were prepared similarly. The adducts $OMoL_2X$ (X = DMAC or DEAZ)[1] and $Ir(CO)Cl(PPh_3)_2X$ (X = DEAZ[6] or DMAC[7]) were prepared by published methods. The preparation and properties of the other molybdenum complexes used will be reported separately.

Infrared (ir) spectra were recorded on a Beckman IR20A spectrophotometer (KBr disks); NMR spectra were obtained with a Varian A60 spectrometer ($CDCl_3$ solutions); microanalyses for carbon, hydrogen, and nitrogen were measured with a Hewlett-Packard 185 CHN Analyzer; and optical rotation data were obtained on a Cary 60 instrument.

Reaction of $MoO_2(S_2CNR_2)_2$ (R = CH_3, C_2H_5) with Thiophenol. $MoO_2[S_2CN(CH_3)_2]_2$ (0.5 g, 1.5 mmol) was suspended in degassed benzene (50 ml) under argon and thiophenol (4 ml, 4.29 g, 39 mmol) was added. The mixture was stirred for 3 days and the pink precipitate of oxobis(*N,N*-dimethyldithiocarbamato)molybdenum(IV), $OMo[S_2CN(CH_3)_2]_2$ (0.41 g, 86% yield), was isolated by filtration, washed with benzene and Et_2O, and dried in vacuo. Anal. Calcd for $C_6H_{12}MoN_2OS_4$: C, 20.5; H, 3.4; N, 7.7. Found: C, 20.4; H, 3.4; N, 7.7. A similar reaction using $MoO_2[S_2CN(C_2H_5)_2]_2$ gave $OMo[S_2CN(C_2H_5)_2]_2$.

Reaction of $OMo[S_2CN(C_2H_5)_2]_2$(DEAZ) with Thiophenol. The adduct (0.41 g, 0.70 mmol) and thiophenol (0.18 g, 1.6 mmol) in dichloromethane (20 ml) were stirred for 20 h. The red solution was evaporated in vacuo and the resultant solid was extracted with diethyl ether (2 × 25 ml) to leave a red residue of $OMo[S_2CN(C_2H_5)_2]_2$ (0.23 g, 0.56 mmol; identified by ir). The ether extracts were evaporated to dryness and the residue extracted with hexane to leave 1,2-bis(ethoxycarbonyl)hydrazine (0.10 g, 0.57 mmol; identified by ir). Diphenyl disulfide (0.11 g, 0.51 mmol; mp 58–59 °C (from CH_3OH), lit. mp 61 °C) was obtained from the hexane extracts.

Reaction of $Ir(CO)Cl(PPh_3)_2$(DEAZ) with Thiophenol. The adduct (0.15 g, 0.19 mmol) was dissolved in $CDCl_3$ (1 ml). Its NMR spectrum was monitored before and after addition of thiophenol (0.02 g, 0.18 mmol). No spectral changes were observed after 6 h. A trace of 1,2-bis(ethoxycarbonyl)hydrazine was observed after 30 h.

Reaction of DEAZ with Thiophenol. (a) In the Absence of Solvent. Mixtures of DEAZ (0.2 g, 1.15 mmol) and thiophenol (0.6 g, 5.45 mmol) were monitored by NMR spectroscopy which indicated mainly the 1:1 adduct with varying amounts (0–15%) of 1,2-bis(ethoxycarbonyl)hydrazine. Previously,[8] such mixtures had been reported to yield 90% of the hydrazine.

(b) In Chloroform. DEAZ (0.1 g, 0.58 mmol) was dissolved in $CDCl_3$ in an NMR tube and the spectrum was monitored as small amounts of thiophenol were added. The CH_3 resonances of the ethyl groups at 1.45 ppm (t) gradually disappeared while new CH_3 triplets at 1.32 and 1.25 ppm grew in. When more than 1 equiv of thiophenol was added, a third triplet (assignable to the hydrazine) at 1.28 ppm appeared with up to 15% of the intensity of the others.

A 1:1 mixture of DEAZ (2.01 g, 11.6 mmol) and thiophenol (1.27 g, 11.6 mmol) was prepared in chloroform (to minimize any hydrazine formation). The chloroform was evaporated and the yellow oil pumped in vacuo to constant weight (3.6 g; 1:1 adduct requires 3.3 g). The ir spectrum of this yellow oil showed ν(NH) at 3320 cm^{-1} and its NMR consisted of two quartets for the methylene resonances and two triplets for the methyl resonances of the ethyl groups. These data are consistent with this oil being the 1:1 adduct. Attempted distillation of the oil resulted in vigorous decomposition to 1,2-bis(ethoxycarbonyl)hydrazine.

NMR Studies of the Catalyzed Reaction of DEAZ with Thiophenol. A mixture of DEAZ (2.2 g, 12.6 mmol) and thiophenol (3.2 g, 29.1 mmol) was dissolved in $CDCl_3$ and aliquots were placed in NMR tubes. Various reagents (ca. 10 mg) were added directly to the tubes and the succeeding reactions were monitored at 34 °C by NMR spectroscopy. Results are summarized below [catalyst, and time taken to achieve complete conversion to 1,2-bis(ethoxycarbonyl)hydrazine]: (1) $MoO_2[S_2CNR_2]_2$ and $OMo[S_2CNR_2]_2$, 60–100 min, depending on R; (2) $Mo_2O_3(S_2COC_2H_5)_4$, 3 days; (3) $OMo[S_2PR_2]$ and $Mo_2O_3[S_2PR_2]_4$ (R = OC_6H_5, OCH_3, C_6H_5), 2.5–5 days, depending on R; (4) $Ir(CO)Cl(PPh_3)_2$, 1–2 min; (5) $(C_2H_5)_3N$, 1–2 min.

Reaction of DEAZ with Thiophenol Catalyzed by $MoO_2[S_2C(1\text{-pip})]_2$. DEAZ (2.0 g, 11.5 mmol) and thiophenol (6.0 ml, 6.4 g, 58.5

Table I. NMR Data for the Thiol Adducts[a]

Compd	CH_3-O	=CH	-CH
7a	3.34, 3.79	6.39	
7b	3.67, 3.72	5.53	
8a	3.70		3.95
8b	3.61		3.80
9		6.48[b]	
10a			3.75,[b] 3.83[c]
10b			3.83,[b] 3.67[c]

[a] Ppm from TMS; $CDCl_3$ solution unless otherwise specified. [b] $NaHCO_3/D_2O$ solution. [c] DMSO-d_6 solution.

mmol) were dissolved in degassed chloroform (20 ml) under argon. $MoO_2[S_2C(1\text{-pip})]_2$ (0.04 g, 0.09 mmol) was added and the mixture was stirred for 18 h. Hexane (100 ml) was added and the colorless precipitate of 1,2-bis(ethoxycarbonyl)hydrazine [1.8 g, 89% yield; mp 131 °C (from diethyl ether), lit. mp 135 °C; confirmed by ir] was filtered off. The filtrate was evaporated in vacuo to an oil which was dissolved in hexane (25 ml) and filtered. After extraction with 5% aqueous sodium carbonate solution (to remove residual thiophenol) and then with water, the filtrate was evaporated to dryness to give diphenyl disulfide [2.4 g, 95% yield; mp 58–59 °C (from CH_3OH), lit. mp 61 °C].

Attempted Reactions of Thiophenol with Pyridazine and 2,2′-Azobis(2-methylpropionitrile). Mixtures of the diazene and thiophenol in 1:6 molar ratios, with added $MoO_2[S_2CNR_2]_2$ as catalyst, were monitored over 4 days by NMR spectroscopy. No spectral change was observed in either case.

Reaction of Azobenzene with Thiophenol Catalyzed by $MoO_2[S_2C(1\text{-pip})]_2$. Azobenzene (3.0 g, 16.5 mmol), thiophenol (15 ml, 16.1 g, 146.3 mmol), and $MoO_2[S_2C(1\text{-pip})]_2$ (0.1 g, 0.22 mmol) were dissolved in dichloromethane (50 ml) and stirred for 48 h. The solvent was removed in vacuo, hexane (75 ml) was added, and the orange precipitate of hydrazobenzene (2.0 g, 66% yield; identified by ir and NMR) was removed by filtration and dried in vacuo. After extraction of the filtrate with 5% aqueous sodium carbonate, the hexane was removed in vacuo to yield diphenyl disulfide [2.3 g, 64% yield; mp 56–58 °C (from CH_3OH)].

NMR Studies of the Catalyzed Reaction of Azobenzene with Thiophenol. A mixture of azobenzene (1.6 g, 8.8 mmol) and thiophenol (3.0 g, 27.3 mmol) was dissolved in $CDCl_3$ and divided among several NMR tubes. Various reagents (10–20 mg) were added directly to the mixture in the tubes and the reactions were monitored at 34 °C by NMR spectroscopy. The results (catalyst used and time taken for complete conversion to hydrazobenzene) were: (1) $MoO_2[S_2CNR_2]_2$, 2–5 h depending on R; (2) $OMo[S_2P(i\text{-}C_3H_7)_2]_2$ and $MoO_2[S_2P(C_6H_5)_2]_2$, no conversion in 24 h; (3) $Ir(CO)Cl(PPh_3)_2$, no conversion in 48 h; (4) $(C_2H_5)_3N$, no conversion within 65 h.

Reaction of DMAC with Thiophenol Catalyzed by $MoO_2[S_2C(1\text{-pip})]_2$. A mixture of DMAC (7.5 g, 52.8 mmol), thiophenol (20 ml, 21.46 g, 195.1 mmol), and $MoO_2[S_2C(1\text{-pip})]_2$ (0.15 g, 0.33 mmol) in degassed chloroform (20 ml) was stirred until NMR showed no free DMAC (16 h). Extraction with 0.2 M aqueous K_2CO_3 (3 × 50 ml) (to remove excess thiophenol), followed by evaporation and molecular distillation (at 100 °C (0.05 mm)), gave a 2:1 trans to cis mixture (NMR, see Table I) of monoadducts $CH_3O_2CHC{=}C(SPh)CO_2CH_3$ (**7**) as a golden oil (5.9 g). Anal. Calcd for $C_{12}H_{12}O_4S$: C, 57.13, H, 4.80. Found: C, 57.01; H, 5.16. Before the distillation, the monoadduct was essentially all trans isomer (NMR). The nonvolatile gum was dissolved in ether (25 ml), filtered, evaporated, and recrystallized from methanol to give a mixture of the diastereoisomeric diadducts, $CH_3O_2CH(SPh)CH(SPh)CO_2CH_3$, **8a** and **8b** (5.0 g) in a 2:1 molar ratio (NMR). Anal. Calcd for $C_{18}H_{18}O_4S_2$: C, 59.65; H, 5.00. Found: C, 59.81; H, 5.15.

NMR Studies of the Catalyzed Reaction of DMAC with Thiophenol. DMAC (1.1 g, 7.75 mmol) and thiophenol (3.1 g, 27.3 mmol) were dissolved in $CDCl_3$ and aliquots were transferred to NMR tubes. Various compounds (~10 mg) were then added and the NMR spectra were monitored. Results are listed below (catalyst and time taken to produce the indicated ratio of monoadducts): (1) $MoO_2[S_2CNR_2]_2$ and $OMo[S_2CNR_2]_2$, 0.25–8 h depending on R, >9:1 trans; (2) $OMo[S_2P(OC_6H_5)_2]_2$, no reaction in 24 h; (3) $Ir(CO)Cl(PPh_3)_2$, <6 h, 4:1 trans (see text about other products formed); (4) $(C_2H_5)_3N$, 0.25 h, >4:1 trans; (5) $CH_3(C_6H_5)_2P$, 0.25 h, 4:1 trans (isomerizing within 4 h to a 1:1 mixture).

Table II. Requirements for Production of **7a** from Dimethyl Acetylenedicarboxylate and Thiophenol

Tube No.	$OMoL_2$-(DMAC),[a] equiv	Thiophenol, equiv	DMAC,[b] equiv	Approx rel[c] yield of **7a**
1(a)	1	1.05	0	0
1(b)	1	2.10	1	3
2	1	10.50	10	25
3	1	10.50	0	0
4	1	1.05	10	1
5	1	0	10	0

[a] $OMo[S_2CN(CH_3)_2]_2(CH_3O_2CC_2CO_2CH_3)$. [b] Dimethyl acetylenedicarboxylate. [c] **7a** is dimethyl 2-(phenylthio)fumarate, *trans*-$CH_3O_2CC(SPh){=}CHCO_2CH_3$, and approximate yield was determined from =CH resonance in NMR spectrum.

Reactions of $OMo[S_2CN(C_2H_5)_2]_2$(DMAC) and $Ir(CO)Cl(PPh_3)_2$(DMAC) with Thiophenol. Saturated solutions of the adducts in $CDCl_3$ were separately treated with excess thiophenol in NMR tubes and the spectral changes were monitored. No mono- or diadducts of thiophenol and DMAC were observed.

Reactions of $OMo[S_2CN(CH_3)_2]_2$(DMAC) with DMAC and Thiophenol. A stock solution of $OMo[S_2CN(CH_3)_2]_2(CH_3O_2CC_2CO_2CH_3)$ (299.5 mg in 6.5 ml of $CDCl_3$) was distributed in 0.8-ml aliquots (0.075 mmol) among five NMR tubes. The following additions were then made (see Table II): tube 1, 0.079 mmol of thiophenol; tube 2, 0.79 mmol of thiophenol and 0.75 mmol of DMAC; tube 3, 0.79 mmol of thiophenol; tube 4, 0.079 mmol of thiophenol and 0.75 mmol of DMAC; and tube 5, 0.75 mmol of DMAC. Their NMR spectra were monitored for 4 days. Only tubes 2 and 4 contained the DMAC–thiophenol adducts; in the former, no free acetylene was observed at 20 h and ~25 times as much of the 1:1 trans adduct (**7a**) was present as compared to tube 4. After 4 days, 0.079 mmol of thiophenol and 0.075 mmol of DMAC were added to tube 1 to produce some 1:1 trans adduct within 0.25 h and ~3 times the amount of tube 4 within 3 h when free acetylene was no longer observable.

Preparation of Dimethyl 2-(Phenylthio)fumarate (7). A solution of thiophenol (50 mmol) in dry, ethanol-free chloroform (25 ml) was added (40 min) to a stirred solution of DMAC (50.2 mmol) in chloroform (50 ml) containing Et_3N (1 drop) as a catalyst at 0 °C. After stirring for 2.5 h, the solution was washed with 1 M Na_2CO_3 and H_2O and dried over Na_2SO_4. Removal of the solvent left a yellow oil which would not crystallize, and NMR indicated an 85:15 ratio of trans/cis isomers. Distillation (134 °C (0.09 mm)) led to isomerization and an increase in the amount of cis isomer. The presence of thiophenol hastened this isomerization and led to a 1:1 ratio.

A sample of the pure trans isomer (**7a**) was obtained by esterification of the diacid **9** with diazomethane. This pure material also resisted attempts at crystallization and remained as a yellow oil. Anal. Calcd for $C_{12}H_{12}O_4S$: C, 57.13; H, 4.80. Found: C, 57.14; H, 4.84.

Preparation of 2-(Phenylthio)fumarate (9). The above crude diester mixture containing ca. 85% **7a** (10 mmol) was heated under reflux (1 h) with 1 M NaOH (40 ml), and the cooled reaction mixture was extracted with CH_2Cl_2. The aqueous phase was acidified (2 ml concentrated HCl) and the crude product was filtered off (64% yield). Recrystallization from 1:10 methanol–water gave 1.24 g of pure (NMR) **9**, decomposing at 172–174 °C. An analytical sample was vacuum dried 1 h (55 °C). Anal. Calcd for $C_{10}H_8O_4S$: C, 53.57; H, 3.60. Found: C, 53.62; H, 3.66.

Preparation of *meso*-Dimethyl 2,3-Bis(phenylthio)succinate (8a). DMAC (50 mmol) was added over ca. 30 min to a stirred solution (<5 °C) of thiophenol (100 mmol) in dry, ethanol-free chloroform (100 ml) containing 2 drops of triethylamine. After stirring an additional 2 h in ice, the solvent was removed. The residue was recrystallized from methanol (80 ml), washed with cold methanol, and vacuum dried to yield colorless **8a** (16.23 g, 89.7%; mp 104–105.5 °C). Anal. Calcd for $C_{18}H_{18}O_4S_2$: C, 59.65; H, 5.00. Found: C, 59.74; H, 5.16.

With a reaction temperature of ~50 °C, the crude product contained ca. 25% **8b** (NMR), while the 0–5 °C reaction showed only 5% **8b**.

Preparation of 2,3-Bis(phenylthio)succinic Acids (10a,b). A mixture of monopotassium acetylenedicarboxylate (100 mmol), thiophenol (218 mmol), triethylamine (120 mmol), methanol (100 ml), and water (15 ml) was heated under reflux 4 h (becoming homogeneous in ca. 2 h). The cooled reaction mixture was treated with concentrated HCl (19 ml) and water (200 ml), and the crude solid product was filtered off and washed with water. Residual thiophenol was removed by dissolving the crude product in 1.6 M $NaHCO_3$ (125 ml) and extracting with dichloromethane (2 × 50 ml). Acidification of the aqueous phase (HCl) gave 31.4 g (94% yield) of an off-white solid containing ca. equal amounts (NMR, DMSO-d_6) of **10a** and **10b**.

Separation of *meso*-10a. The above mixture of isomers (11 g) was dissolved in boiling methanol (35 ml) and hot water (35 ml) was added slowly. After standing overnight at ambient temperature, the colorless crystals of **10a** were filtered off and washed with a small amount of cold solvent. [The filtrate from this crystallization was used (see below) for separation of **10b**.] Recrystallization from the same solvent gave 5.50 g (50.0% yield); mp near 210 °C dec, dependent on the rate of heating. Anal. Calcd for $C_{16}H_{14}O_4S_2$: C, 57.47; H, 4.22; mol wt 334. Found: C, 57.30; H, 4.15; mol wt 343 (osmometry, ethyl acetate).

Treatment of a small sample of **10a** in methanol with ethereal diazomethane gave a nearly quantitative yield of the diester **8a** (NMR, mmp).

Attempted resolution of **10a** via its crystalline dibrucine salt (methanol) gave an optically inactive product.

Separation and Resolution of *dl*-10b. The filtrate from the separation above of **10a** was evaporated to give **10b** as a gum (4.40 g), which finally crystallized (6% meso isomer by NMR). This material was used for the resolution. Anal. Calcd for $C_{16}H_{14}O_4S_2$: C, 57.47; H, 4.22; mol wt 334. Found: C, 57.53; H, 4.30; mol wt 344 (osmometry, ethyl acetate).

A methanol solution (10 ml) of **10b** (5.95 mmol) was added to a warm solution of brucine (12.4 mmol) in methanol (50 ml), and crystallization was induced by scratching. Cooling overnight (5 °C) gave 3.86 g of the colorless dibrucine salt, which was recrystallized from methanol (3×). An analytical sample was vacuum dried 1.5 h at 55 °C (hygroscopic). Anal. Calcd for $C_{62}H_{66}O_{12}S_2 \cdot H_2O$: C, 65.24; H, 6.00; N, 4.91. Found: C, 65.41; H, 6.29; N, 4.97.

The salt (400 mg) was converted to the free acid by stirring with 0.1 M HCl (10 ml) and ethyl acetate (10 ml) until no solid remained. The organic layer was washed with 0.1 M HCl and water and dried (Na_2SO_4), and the solvent was removed. The residue was recrystallized from hexane–ethyl acetate to give (−)**10b** as colorless plates [mp 155–160 °C dec; $[\alpha]^{25}_D$ −243° (concentration of 4 × 10^{-3} g/ml in methanol); RD in methanol (concentration of 4 × 10^{-5} g/ml) at 25 °C; $[\alpha]_{296}$ −2750° (trough), $[\alpha]_{261}$ +460° (peak), ca. $[\alpha]_{230}$ −6600° (trough)]. Anal. Calcd for $C_{16}H_{14}O_4S_2$: C, 57.47; H, 4.22. Found: C, 57.64; H, 4.49. Acid derived from the once-recrystallized dibrucine salt already possessed a specific rotation of −240° and NMR indicated none of the meso acid present.

Results

Addition to Diazenes. Mixtures of DEAZ and thiophenol in a 1:1 molar ratio produce solutions containing species having a nitrogen–hydrogen stretching frequency at 3320 cm^{-1} (ir) and two triplets centered at 1.28 ppm for the methyl protons and two quartets for the methylene protons at ~4.17 ppm (NMR) of the ethyl groups originating in DEAZ. These observations are consistent with the presence of the 1:1 adduct, diethyl *N*-(phenylthio)hydrazodicarboxylate (**1**). Sometimes a minor set of NMR signals (one methyl triplet and one methylene quartet) is observed due to the presence of up to 15% of **2** (reaction 2).

$$\underset{\text{(DEAZ)}}{EtO_2CN{=}NCO_2Et} + PhSH \rightarrow \underset{\mathbf{1}}{EtO_2CN(SPh)\text{-}NHCO_2Et} + \underset{\mathbf{2}}{EtO_2CNH\text{-}NHCO_2Et} \quad (2)$$

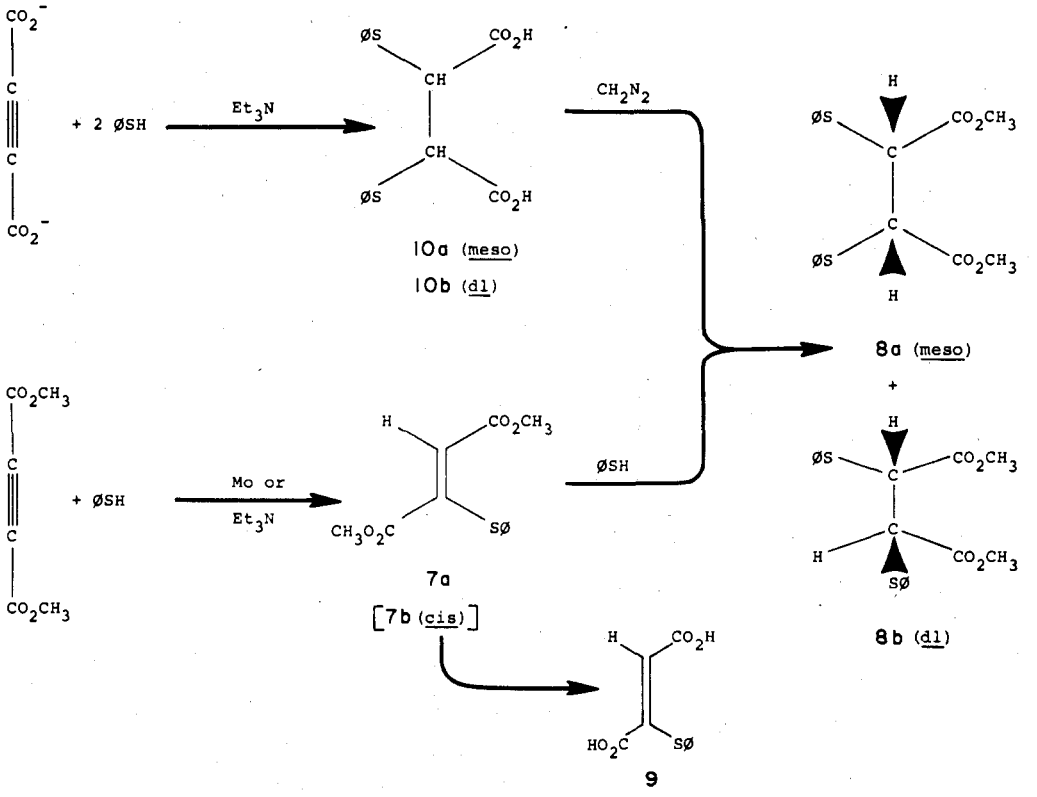
The heat liberated when DEAZ and thiophenol are mixed probably accounts for the formation of some **2**. The NMR spectrum of these mixtures did not change further over 48 h at 34 °C ($CDCl_3$ solution), indicating that **1** is a stable entity toward decomposition to **2** under these conditions. The same observations were made with neat mixtures and with solutions containing a fivefold excess of thiophenol. **1** was not isolated, as it decomposed to **2** on attempted distillation.

On addition of a catalytic amount of either *cis*-dioxobis(*N*,*N*-diethyldithiocarbamato)molybdenum(VI), MoO_2L_2, or oxobis(*N*,*N*-diethyldithiocarbamato)molybdenum(IV), $OMoL_2$, to a 1:2 molar ratio (or greater) mixture of DEAZ and thiophenol, 1,2-bis(ethoxycarbonyl)hydrazine (**2**) and diphenyl disulfide were formed quantitatively within 2 h (34 °C, NMR probe temperature). Vaska's compound [Ir(PPh$_3$)$_2$COCl] catalyzed this reaction more quickly, with completion after 2 min under the same conditions. Triethylamine also produced complete conversion in less than 2 min. The related molybdenum compounds, μ-oxo-bis[oxobis(ligand)molybdenum(V)] [$Mo_2O_3L_4$; L = $S_2COC_2H_5$, S_2PR_2 (R = OCH_3, OC_6H_5, C_6H_5)] and oxobis(diphenylphosphorodithioato)molybdenum(IV), $OMo[S_2P(OC_6H_5)_2]_2$, produced **2** only very slowly, about 30–35% conversion in 16 h, total conversion to **2** in ~4 days. It was also found that although $OMoL_2$(DEAZ) (L = S_2CNR_2) reacted with thiophenol to produce $OMoL_2$, diphenyl disulfide, and **2**, Ir(CO)Cl(PPh$_3$)$_2$(DEAZ) was effectively inert to reaction with thiophenol.

Similar reaction mixtures containing pyridazine or 2,2′-azobis(2-methylpropionitrile) [$(CH_3)_2(CN)C{-}N{=}N{-}C(CN)(CH_3)_2$] exhibited no reaction either alone or with catalyst under similar conditions, but those containing azobenzene (**3**), thiophenol, and certain molybdenum catalysts did. Mixtures of 1:2 (or greater) molar ratio of **3** and thiophenol in chloroform were monitored by NMR. No 1:1 adduct was observed. On addition of $MoO_2(S_2CNR_2)_2$ as catalyst, quantitative conversion to hydrazobenzene occurred in 2–5 h, depending on the dithiocarbamate used. In contrast, no hydrazobenzene was formed on addition of $OMo[S_2P(i\text{-}C_3H_7)_2]_2$, $Mo_2O_3[S_2P(i\text{-}C_3H_7)_2]_4$, $MoO_2[S_2P(C_6H_5)_2]_2$, $Mo_2O_4[S_2P(C_6H_5)_2]_2$, or $Mo_2O_3[S_2P(C_6H_5)_2]_4$ to such mixtures. Neither Ir(CO)Cl(PPh$_3$)$_2$ nor Et$_3$N catalyzed this reaction.

Addition to Dimethyl Acetylenedicarboxylate (DMAC). Reaction mixtures in $CDCl_3$ solution, containing the substituted acetylene and thiophenol in a 1:1 molar ratio with small quantities of various reagents added as catalyst, were monitored by NMR spectroscopy. Without added catalyst, no spectral change was observed. However, with triethylamine, methyldiphenylphosphine, Vaska's compound, or $OMoL_2$ (or MoO_2L_2; L = a dithiocarbamate), reaction was observed. All four catalysts gave the monoaddition reaction products, dimethyl 2-(phenylthio)fumarate and dimethyl 2-(phenylthio)maleate (*trans*- and *cis*-$CH_3O_2CC(SPh){=}CHCO_2CH_3$, **7a** and **7b**, respectively), whose geometries were readily assigned from NMR data (Table I) by comparison with appropriate fumarate and maleate derivatives.[9,10] These products were, however, formed in widely varying ratios. Triethylamine and methyldiphenylphosphine gave an 85:15 ratio of trans to cis within 1 h. This ratio remained unchanged over at least 7 h for the triethylamine catalyst, but with the phosphine, isomerization to a 50:50 mixture occurred within that same time period. The molybdenum catalyst was much more stereospecific producing ~95% trans adduct. The preferred stereochemistry is consistent with the "trans rule" of nucleophilic addition to triple bonds.[11] Vaska's compound, in addition to giving ~40% conversion to trans and cis monoadducts (in a 4:1 ratio), produced ~30% of the two diastereoisomers of the diadduct, **8** [$CH_3O_2CCH(SPh)\text{-}CH(SPh)CO_2CH_3$], with ~30% of the free acetylene remaining. A pure sample of **7a** was obtained from the triethylamine-catalyzed addition of thiophenol to DMAC.[12] The crude product again contained ca. 15% of **7b**. Hydrolysis of this mixture afforded the pure crystalline trans diacid (**9**), which

Scheme I. Stereochemistry and Interrelationships of the 1:1 and 2:1 Adducts of Thiophenol and Dimethyl Acetylenedicarboxylate and Acetylenedicarboxylic Acid



upon treatment with diazomethane yielded pure **7a** as an oil which resisted attempts at crystallization. Attempted distillation of the mixture of isomeric esters led to extensive thermal isomerization, a characteristic noted[9,14] for similar compounds, especially in the presence of traces of thiol.

The two diadducts, **8a** and **8b**, were also produced by the other catalysts when a twofold (or greater) excess of thiophenol was present. One of the isomers was predominant and this same one (accounting for 80% of the diaddition product at a reaction temperature of 0 °C) was readily synthesized by the triethylamine-catalyzed addition of 2 mol[12] of thiophenol to DMAC and easily purified by crystallization.

The stereochemistry of the addition of the second mole of thiol could be determined (the first mole adding mainly trans) because of this diastereoisomerism; e.g., cis addition to **7a** would yield **8a** (meso, and not resolvable), while trans addition would give **8b** (a *dl* pair, and thus resolvable). The free acid was necessary to attempt resolution via an optically active base, but attempts to hydrolyze the ester led to much decomposition by loss of thiol. However, this problem was circumvented by reacting the thiol directly with acetylenedicarboxylic acid to get **10a** and **10b**. The reaction required heating under reflux for several hours but resulted in an apparently clean mixture of isomers (ca. 1:1 ratio). One of these (least soluble in methanol) was separated by crystallization and gave a diester (diazomethane) identical with the predominant one isolated above. However, attempts to resolve this diacid via its crystalline brucine salt failed, suggesting it to be the meso form (**10a**). Final proof was obtained when the more soluble diacid, after isolation from the reaction mixture and treatment with brucine, gave active (−)**10b**. Thus, the dominant product in these catalyzed diaddition reactions can be assigned structure **8a** (meso) and results from cis addition of the second mole of thiol (see Scheme I).

To investigate the nature of the catalytic entity, solutions of $OMo[S_2CN(CH_3)_2]_2$(DMAC), containing 1, 10, or 0 equiv of thiophenol and DMAC, were monitored by NMR for 4 days (see Table II). The spectrum of tube 5 was that of a combination of $OMoL_2$(DMAC) and free DMAC and was stable. The spectra for tubes 1(a) and 3 showed a collapse of the normal spectrum of $OMoL_2$(DMAC). These spectra then remained constant over 4 days, with no observable adduct. In addition, tube 3 showed free thiophenol. In contrast, those tubes (2 and 4) containing all three species produced the 1:1 trans adduct **7a**, as did tube 1(b), which consisted of tube 1(a) to which 1 more equiv of thiophenol and 1 equiv of DMAC were added after 4 days. Free DMAC was still observable in tube 4 after 4 days, but none was observed in tubes 2 and 1(b) after a similar time period.

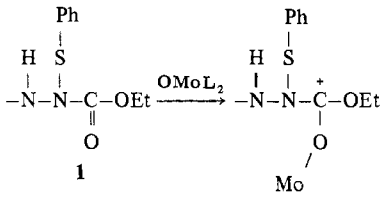
Discussion

DEAZ has been shown to undergo hydrogen-abstracting reactions with a variety of compounds[15] and also to form 1:1 adducts with mercaptans.[16,17] We therefore followed its reaction with thiophenol at or near ambient temperature by NMR and ir spectroscopy. The major product (~85%) was indeed the 1:1 adduct (**1**), which remained unchanged under the conditions of the experiment (34 °C in $CDCl_3$) until a catalytic amount of triethylamine, Vaska's compound, oxo-bis(*N*,*N*-diethyldithiocarbamato)molybdenum(IV), $OMoL_2$, or *cis*-dioxobis(*N*,*N*-diethyldithiocarbamato)molybdenum(VI), MoO_2L_2, was added. Complete conversion to **2** then occurred. The catalyzed reaction is represented by:

$$\underset{\mathbf{1}}{EtO_2CN(SPh)\text{-}NHCO_2Et} + PhSH \xrightarrow{\text{catalyst}} \underset{\mathbf{2}}{EtO_2CNHNHCO_2Et} + PhS\text{-}SPh \qquad (3)$$

Although the three catalyst types give the same products, it is unlikely that their mechanisms are the same. For the molybdenum system, *cis*-dioxomolybdenum(VI) is reduced to oxomolybdenum(IV) by thiophenol, as was found for the μ-oxo-bis[oxomolybdenum(V)] species,[4] but is then inert to further reaction with thiophenol. These observations suggest that the catalytic species is derived from oxomolybdenum(IV).

Although $OMoL_2(DEAZ)$ reacts with thiophenol to liberate **2**, $OMoL_2$, and diphenyl disulfide, the intermediacy of $OMoL_2(DEAZ)$ in the catalytic system is unlikely as all DEAZ should be in the form of **1**. More attractive is the activation of **1** via a carbonyl function (reaction 4), so po-

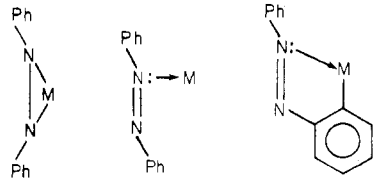


(4)

1

larizing the C=O bond and facilitating attack by thiophenol. The initial polarizing interaction could occur between Mo and an azo nitrogen on **1**, but this is unlikely as their amide nature should lead to greatly decreased basicity. The carbonyl interaction gains support from a recent x-ray crystallographic study[18] of $(PPh_3)_2Pt(PhCON_2COPh)$, showing that the diazene is bound asymmetrically through one azo and one carbonyl oxygen function, not symmetrically to the azo bond.[6,19] That work suggests that all such compounds[1,6,18-20] are bound similarly. A carbonyl interaction is suggested to be responsible for activation of **1** by Vaska's compound also. The likelihood of $Ir(CO)Cl(PPh_3)_2(DEAZ)$ being an intermediate in this system is even less, as it does not react with thiophenol under these conditions at any appreciable rate. Triethylamine reacts with thiophenol (to produce thiophenolate), but not with DEAZ. Therefore, the catalysis by triethylamine probably involves attack by thiophenolate on a carbonyl carbon atom of **1**.

Of the attempts to utilize pyridazine, 2,2′-azobis(2-methylpropionitrile), and azobenzene (**3**), i.e., diazenes without a carbonyl function, in these systems, only the last of these substrates exhibited reactivity. Mixtures of **3** and thiophenol were catalytically converted to hydrazobenzene by $OMo(S_2CNR_2)_2$. Neither $Ir(CO)Cl(PPh_3)_2$ nor Et_3N catalyzed this reaction, indicating that activation of the diazene is a most important step that only $OMo(S_2CNR_2)_2$ can accomplish in this case. Complexes of **3** with metals are well known and either involve a π-bonded azo linkage (**4**)[21-27] or nitrogen-to-metal σ bonding (**5** and **6**).[28-34] However, **3** does not form



4 **5** **6**

an isolable complex with $OMoL_2$ nor with $Ir(CO)Cl(PPh_3)_2$, again indicating that catalysis may occur without easily detectable (or isolable) intermediates.

Other systems have been reported to produce hydrazobenzene from **3** either: (i) stoichiometrically, e.g., treatment of $(R_3P)_2Ni(PhN_2Ph)$ with aqueous ethanol or dimethylglyoxime (with concomitant loss of phosphine from nickel)[22] and in the synthesis[21] of $(C_5H_5)Mo(PhN_2Ph)$ from $(C_5H_5)_2MoH_2$ and **3**; or (ii) catalytically, e.g., by lithium aluminum hydride[35] with various metal halides and with $[Rh(CO)_2Cl]_2$. None of these catalyzed reactions appear to be as facile as our thiophenol system, either more forcing conditions or much stronger reducing agents being required.

Of the molybdenum compounds studied, only those containing dithiocarbamate ligands demonstrated reasonable catalytic activity in these diazene systems. We have found[36] that $OMoL_2$ (L = S_2PR_2) does not form isolable 1:1 adducts with DEAZ, DMAC, or tetracyanoethylene. It does, however, form 1,2-bis(ethoxycarbonyl)hydrazine with DEAZ, producing either $Mo_2O_3L_4$ (R = OC_2H_5, OC_6H_5) or $Mo_2O_4L_2$ (R = i-C_3H_7) in the process via a self-destroying, internal redox reaction resulting in loss of both complexed Mo and L as the disulfide.[3c] Although $Mo_2O_3L_4$ (but not $Mo_2O_4L_2$) may be reduced to $OMoL_2$ again by thiophenol, it is obvious that these intermediate reactions are detrimental to any catalytic capability. The complex $OMo(S_2COR)_2$ has not yet been isolated by any means, although spectral evidence for its existence has been presented.[3d] It certainly is not produced from $Mo_2O_3(S_2COR)_4$ with thiophenol. It would appear then that the dithiocarbamate ligands confer on $OMoL_2$ the necessary properties for adduct formation,[1] stabilization of the appropriate oxidation states (viz. IV–VI) and thus the capability to operate catalytically in these reaction systems. The lack of reactivity of $Ir(CO)Cl(PPh_3)_2$ with **3** suggests that although it is more efficient in activating **1**, it is more demanding in its requiements for interaction with substrate than is $OMoL_2$.

To determine the generality of this reaction of thiophenol with multiple bonds, similar reactions were attempted with dimethyl acetylenedicarboxylate (DMAC). In contrast to the diazene systems, no 1:1 adduct is formed without catalyst. The products formed with any of the four catalysts used (i.e., $OMoL_2$, Vaska's compound, Et_3N, and $PMePh_2$) were the mono- and diadducts *trans*- and *cis*-$CH_3O_2CC(SPh)=CHCO_2CH_3$ (**7**) and *meso*- and *dl*-$CH_3O_2CCH(SPh)CH(SPh)CO_2CH_3$ (**8**). In no case was diphenyl disulfide formed. All four systems gave initially ~4:1 trans to cis monoadduct and ~4:1 meso to *dl* diadduct.

The mechanism by which the addition occurs with triethylamine probably involves attack by thiophenolate at an acetylenic carbon atom followed by protonation.[13] The oxomolybdenum catalysts and $Ir(CO)Cl(PPh_3)_2$ do not function by simply complexing the acetylene thus activating the triple bond for addition, because neither $OMoL_2(DMAC)$ nor $Ir(CO)Cl(PPh_3)_2(DMAC)$ alone produces **7** with thiophenol. Activation may occur via complexation of the metal [or a modified acetylene adduct (see below)] to the carbonyl function of DMAC (as in the DEAZ reaction) so polarizing the acetylenic triple bond and allowing attack by thiophenol to occur.

These observations led to attempts to detect the species responsible for the catalysis (see Table II). In a series of NMR experiments, reaction mixtures containing $OMoL_2(DMAC)$ with or without varying amounts of thiophenol and DMAC were monitored. An interaction was observed between mixtures of $OMoL_2(DMAC)$ and thiophenol, but not between $OMoL_2(DMAC)$ and DMAC. Significant amounts of the 1:1 trans adduct **7a** were detected only when all three components were present. These data suggest that the catalyst consists of "$OMoL_2$ + DMAC + thiophenol". We have also found[36] that $OMoL_2(DMAC)$ is prone to loss of L (dithiocarbamate) in the presence of proton donors. It may be therefore that the catalyst contains a molybdenum species which has lost a ligand L (or had it modified), thus becoming coordinatively unsaturated and catalytically active. At present, all attempts to isolate and characterize the active entity have been thwarted.

Relevance to Molybdenum Sulfhydryl Enzymes. All molybdenum-containing redox enzymes have the amino acid cysteine present in varying amounts. In certain other metalloproteins, cysteine has been shown to be in close association with the metal(s).[37] The reactions observed between thiophenol and analogues of enzyme substrates open up an interesting alternative to the reduction–hydrolysis sequence postulated previously.[1-3] Although not models in the strict sense, these reactions do suggest the possibility that a protein-bound mercaptan might be involved in proton and electron

transfer to (or from) substrate during reductase (oxidase) activity, particularly if the active site is hydrophobic. A related hypothesis has been proposed previously[38] for proton transfer alone from nitrogen and/or oxygen donor atoms in redox-active molybdoenzymes. The implication of this present work is in line with the suggestions of Massey[39] and Bray[40] concerning the involvement of a sulfhydryl or persulfhydryl group in xanthine oxidase action. It does, though, contrast with certain nitrogenase models[41] containing both a metal (molybdenum) and a mercaptan (cysteine), where the cysteine mercaptide is postulated to remain bound throughout the reaction with reduction of substrate being effected by borohydride mediated by the molybdenum complex. However, the involvement of molybdenum with thiols in a variety of reactions, both as catalysts (as above) and directly with one another,[2-4,42-44] suggests a peculiar relationship that may be very important in the various reactions involving molybdenum that occur in nature.

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Registry No. $MoO_2[S_2CN(CH_3)_2]_2$, 18078-68-7; thiophenol, 108-98-5; $OMo[S_2CN(CH_3)_2]_2$, 39587-09-2; $MoO_2[S_2CN(C_2H_5)_2]_2$, 18078-69-8; $OMo[S_2CN(C_2H_5)_2]_2$, 25395-92-0; $OMo[S_2CN(C_2H_5)_2]_2$(DEAZ), 39584-75-3; 1,2-bis(ethoxycarbonyl)hydrazine, 4114-28-7; diphenyl disulfide, 882-33-7; $Ir(CO)Cl(PPh_3)_2$(DEAZ), 15380-65-1; DEAZ, 1972-28-7; **1**, 40986-21-8; $Mo_2O_3(S_2COC_2H_5)_4$, 18078-56-3; $OMo[S_2P(OC_6H_5)_2]$, 25395-93-1; $OMo[S_2P(OCH_3)_2]$, 59796-75-7; $OMo[S_2P(C_6H_5)_2]$, 59796-76-8; $Mo_2O_3[S_2P(OC_6H_5)_2]_4$, 32210-08-5; $Mo_2O_3[S_2P(OCH_3)_2]_4$, 59796-77-9; $Mo_2O_3[S_2P(C_6H_5)_2]_4$, 59796-78-0; $Ir(CO)Cl(PPh_3)_2$, 14871-41-1; $(C_2H_5)_3N$, 121-44-8; azobenzene, 103-33-3; hydrazobenzene, 122-66-7; DMAC, 762-42-5; $CH_3(C_6H_5)_2P$, 1486-28-8; $OMo[S_2CN(CH_3)_2]_2$(DMAC), 39584-77-5; **7a**, 59790-38-4; **7b**, 59790-39-5; **9**, 59790-40-8; **8a**, 53256-00-1; **8b**, 53256-05-6; **10a**, 53255-99-5; **10b**, 53256-04-5; (−)**10b**·2brucine, 59790-42-0; (−)**10b**, 59790-41-9; $MoO_2[S_2C(1\text{-pip})]_2$, 59796-74-6.

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