to the formation of the N-acylated derivatives **3a** (84%) and **3b** (51%), which were debenzylated ($H_2$, Pd/C) to give **4a** and **4b**, respectively. Bromination of **4a** with NBS (2 equiv) in a refluxing solution of $CHCl_3$–$CF_3CO_2H$ (10:1) gave **5a** (43%). The structure of **5a** was confirmed by spectroscopic means, and its stereochemistry was established by X-ray analysis, fortunately for our purposes, to have the cis configuration at the C–N and C–O bonds. The reaction of **4b** with NBS (2 equiv) in boiling solution of $CH_2Cl_2$–$CF_3CO_2H$ (10:1) gave **5b** (29%), which was converted to **5c** (AcOH–Zn).[8]

With the imidazoindole spirolactone moiety corresponding to **1** in hand, we turned to the construction of the quinazolinone moiety. The reaction of L-tryptophan methyl ester (**6a**) and ethyl orthoformate with isatoic anhydride (**7**) in refluxing xylene for 3 h afforded quinazolinone derivative **9a** (25%).[9] An increase in the yield of **9a** was obtained when **6a** and **7** were converted to the amide **8a** (95%) by heating in benzene, which in turn was refluxed in benzene (3 h) with $(EtO)_3CH$ in the presence of a catalytic amount of TsOH to give **9a** (83%). Likewise, **9b** (79%) was obtained via **8b**.[2] Subsequent condensation of **10b** with **2b** in MeCN (KF, 18-crown-6, $EtN(i\text{-}Pr)_2$, 1 h) provided **10a** (42%).[10] Debenzylation of **10a** in $MeCO_2Et$ gave the key compound **10b** (94%). The stage was now set for the construction of **1** by oxidative double cyclization.

Addition of 3 mol of NBS[11] to a boiling solution of **10b** in $CF_3CO_2H$ gave, presumably via intermediate **11**, a mixture of cyclization products of **12** and **13**. Upon reduction of the reaction mixture with Zn in AcOH, there were obtained **14** [21% from **10b**; mp 246–247 °C, $[\alpha]^{18}_D$ −183° (*c* 0.20)][12] and **15** (14%). The melting point and NMR spectrum of **14** were identical with those published by Buchi.[2] The total synthesis of **1** was now completed as follows. Oxidation of **14** with *m*-CPBA[2] in $CH_2Cl_2$ afforded the hydroxylamine **16** [mp 263–264 °C; $[\alpha]^{16}_D$ −217° (*c* 0.115)], which was identical (mp, NMR, IR, $[\alpha]_D$) with (−)-tryptoquivaline L (**16**) derived from natural tryptoquivaline G. Epimerization of **16** with *t*-BuLi in THF at −70 °C followed by addition of AcOH gave (+)-tryptoquivaline G (**1**). *m*-CPBA oxidation of **15** afforded (−)-tryptoquivaline G [**17**: mp 241–242.5 °C; $[\alpha]^{17}_D$ −148° (*c* 0.11)], whose IR and NMR spectra were superimposable with those of **1**. On the other hand, analogous series of reactions starting from D-tryptophan provided (+)-tryptoquivaline G [**1**: mp 241–242 °C; $[\alpha]^{15}_D$ +156° (*c* 0.21)][13] without the elaborate epimerization step the via 3′-epimer of **14** [mp 241–242 °C; $[\alpha]^{12}_D$ +100° (*c* 0.20)]. Chromatographic mobility and IR, mass, and NMR spectra of the synthetic **1** were indistinguishable from those of natural specimen.

These results implicate biosynthesis of tryptoquivalines by fungus.

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**Supplementary Material Available:** Spectral and physical data for compounds **4a**, **4b**, **5a**, **5b**, **5c**, **8a**, **8b**, **9a**, **9b**, and **10b** and the X-ray structure and crystal data along with various bond parameters of **5a** (14 pages). Ordering information is given on any current masthead page.

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(8) Treatment of **5c** with $ClCO_2Me$ and $K_2CO_3$ in acetone provided **5a**, indicating that the stereochemistry of **5b** is also of cis configuration.

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(10) Prolonged reaction for the conversion of **8b** to **10a**, under these conditions, was accompanied with a partial racemization; about 25% racemization of **10a** occurred after 24 h.

(11) One equivalent of NBS was added three times in every 30 min (total 3 mol of NBS). When 3 equiv of NBS were added to a boiling solution of **10b** all at once, **15** (27.5%) was obtained as major product together with **14** (11%).

(12) All the $[\alpha]_D$ values were determined in acetone.

(13) The $[\alpha]^{12}_D$ value of natural tryptoquivaline G obtained by our hand is +154° (*c* 0.14, acetone).

## Homogeneous Hydrogenolysis of Carbon Disulfide Catalyzed by a Molybdenum Dimer with Sulfido Ligands

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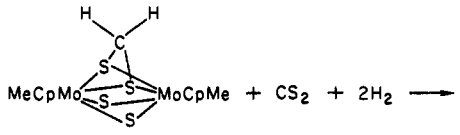
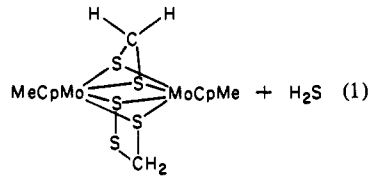
We have recently reported that molecular hydrogen reacts with bridging sulfido ligands in cyclopentadienylmolybdenum complexes to form hydrosulfido bridges.[2] The activation of hydrogen by the sulfido ligands in heterogeneous metal sulfide surfaces has been considered as a possible step in the mechanism of the commercially important hydrodesulfurization catalysts.[3,4] In order to determine whether the synthetic molybdenum complexes have value as potential models for the commercial catalysts, we have begun an investigation of the homogeneous hydrodesulfurization activity of these complexes. We report here a hydrogenolysis of carbon–sulfur bonds that is catalyzed by the Mo(IV) dimer $(CH_3C_5H_4MoS)_2S_2CH_2$ (I).[5] The reaction, which proceeds under the mild conditions of 75 °C and 2–3 atm of hydrogen, involves the initial conversion of carbon disulfide to hydrogen sulfide and thioformaldehyde. Although carbon disulfide has been reduced previously in homogeneous systems by its insertion into transition metal–hydride bonds,[6,7] no previous accounts of homogeneously catalyzed desulfurizations of this molecule have appeared.

The initial products of the hydrodesulfurization reaction are shown in eq 1. Hydrogen sulfide has been readily identified by




I




II

GC,[8] mass spectral, and NMR analysis. The reactive thioformaldehyde molecule is stabilized by its interaction with the bridging sulfur atoms in molybdenum complex II, an orange microcrystalline product that has been isolated and characterized.[9] NMR data are particularly relevant in the characterization of this complex. Resonances assigned to the two types of methylene groups in II are observed at 2.5 and 6.1 ppm in the $^1H$ spectrum

(1) Alfred P. Sloan Fellow, 1981–1983; Camille and Henry Dreyfus Teacher-Scholar, 1981–1986.

(2) Rakowski DuBois, M.; VanDerveer, M. C.; DuBois, D. L.; Haltiwanger, R. C.; Miller, W. K. *J. Am. Chem. Soc.* 1980, *102*, 7456.

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(8) Gas chromatographic identification of $H_2S$ was achieved by using a 6-m Porapak N column from Varian in a Varian 920 instrument equipped with a thermal conductivity detector.

(9) Anal. Calcd for $C_{14}H_{18}S_5Mo_2$: C 31.23; H, 3.37; S, 29.77. Found: C, 31.32; H, 3.25; S, 29.90. $^1H$ NMR ($CDCl_3$) $\delta$ 1.94 (s, 6, $CH_3$), 2.50 (s, 2, $S_3CH_2$), 5.32 (m, 8, $C_5H_4$), 6.09 (s, 2, $S_2CH_2$); $^{13}C$ NMR ($CDCl_3$; results of off resonance decoupling included in parentheses) $\delta$ 15.70 ($CH_3$, q), 38.38 ($S_3CH_2$, t), 90.92 ($S_2CH_2$, t), 89.43, 94.37, 94.81 (Cp, d), 112.05 (Cp, s); IR (Nujol) 424 $cm^{-1}$ (m, $\nu_{S\text{-}S}$); mass spectrum, 506 (P − S), 492 (P − $CH_2$S), 446 ($Cp_2Mo_2S_3$). Cyclic voltammetry in $CH_3CN$ (0.1 M $n$-$Bu_4NBF_4$), scan rate = 100 mv/s: $E_{p/2}$ = +0.275 V vs. SCE, $\Delta E_p$ = 60 mV, $i_{pc}/i_{pa} \simeq 1$; $E_{p/2}$ = +0.835 V; $\Delta E_p$ = 70 mv, $i_{pc}/i_{pa} \simeq 1$. No reductions observed.

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and at 38 and 91 ppm in the $^{13}C$ spectrum. When the latter spectrum is off-resonance decoupled, each of these two resonances is observed as a triplet. Previous spectral studies have shown that when alkenes or alkynes form adducts with the sulfido ligands in I, the resonance assigned to the methanedithiolate ligand, originally observed at 2.53 ppm, undergoes a large downfield shift.[5] The resonances near 6 ($^1H$) and 90 ppm ($^{13}C$) in the spectra of II have chemical shifts similar to those observed for other adducts of I and are therefore assigned to the methylene group of the methanedithiolate ligand.

The synthesis of II by an alternate route provides additional support for its proposed formulation. The reaction of formaldehyde with hydrogen sulfide in the presence of an acid catalyst has been previously reported to yield the transient thioformaldehyde molecule, which rapidly trimerizes to form trithiane.[10] A similar reaction in the presence of I (eq 2) takes advantage of

$$I + H_2CO/H_2O + H_2S \xrightarrow[THF]{25\ ^\circ C} II \qquad (2)$$

the high affinity of the sulfido ligands in the complex for the thioaldehyde and forms complex II in 75% yield. Additional studies of II are described below.

The ability of I to promote the reductions of other cumulenes has been established previously. For example, allenes and ketenes react with I to form stable adducts in which an olefinic bond has interacted with the sulfido ligands to produce new 1,2-dithiolate ligands.[5] Each of the allene or ketene adducts reacts with hydrogen under mild conditions (60 °C, 1–2 atm) to form the free alkene or aldehyde, respectively, and to regenerate I.[5] The presence of excess cumulene inhibits the reactions with hydrogen, and the systems are not catalytic. In contrast, carbon disulfide does not form a stable adduct with I, but under hydrogen pressures it is reduced catalytically. The NMR spectrum of I in carbon disulfide is identical with its spectrum in $CDCl_3$; however, in a tube sealed under hydrogen pressure (1–2 atm) the former spectrum shows significant shifts in the resonances of I.[11] After a period of 2–3 weeks at 70 °C, the spectrum in carbon disulfide shows the presence of an approximately equal molar ratio of I and II, ~5 mol of $H_2S$/mol of I, and other organosulfur products (vida infra). Even when reaction 1 is carried out under much higher hydrogen pressures (16.5 atm), it does not go to completion after 2–3 weeks at 75 °C; significant amounts (>50%) of I are recovered. Additional experiments, which are discussed below, have confirmed that under hydrogen pressure, II undergoes a further reaction that regenerates I and results in a catalytic cycle.

The interaction of thioformaldehyde with the sulfur bridges in the molybdenum dimer II can be reversed under a variety of mild conditions. Although II is stable in the presence of air and moisture at 25 °C, it reacts with ethylene at this temperature to form the known ethylene adduct $(CH_3C_5H_4Mo)_2(S_2CH_2)(SC_2H_4S)$.[5] In a sealed NMR tube at 75 °C under nitrogen pressure, II dissociates in $CDCl_3$ to form I and trithiane. No other products are detected by NMR. The reaction is very slow under these conditions; after a period of 14 days, the ratio of I:II is approximately 0.4. Under similar conditions II reacts with hydrogen (1–2 atm) in $CDCl_3$ to regenerate I. The organosulfur products that are produced in the latter reaction result in a complex set of resonances in the $^1H$ NMR spectrum between 3 and 4.2 ppm. Methanethiol, dimethyl disulfide, and hydrogen sulfide, which would be possible products in this reaction, are not detected. In a separate experiment we have established that methanethiol also reacts with II to produce I. Organosulfur products that are characterized by NMR resonances between 3 and 4 ppm are again observed. Further studies will be necessary to completely identify these products. Relatively few reactions of thioaldehydes, either generated in solution[12-14] or stabilized by coordination to one or more metal ions,[15-17] have been characterized. We anticipate that the ability of II to function as a source of free thioformaldehyde or of the unusual sulfur-coordinated species will play a useful role in establishing the reaction chemistry of this molecule. Further studies of the ability of I to mediate the hydrogenolyses of related heterocumulenes and of aromatic organosulfur compounds are in progress.

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**Registry No.** I, 85565-70-4; II, 85565-71-5; $H_2CS$, 865-36-1; $CS_2$, 75-15-0.

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## Isotopic Multiplets in the Proton-Decoupled Carbon-13 NMR Spectra of Carbohydrates with Partially Deuterated Hydroxyls

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The effect of deuterium substitution on carbon-13 chemical shifts is well-known in the art. Specific deuterium labeling is often used for spectral assignments. Partial deuteration of hydroxyl groups of carbohydrates dissolved in $Me_2SO$ leads to isotope shifts and splitting of the resonances of the carbon atoms bearing such groups.[1] In alcohols and phenols in $Me_2SO$ solutions, the resonances of carbon atoms vicinal to hydroxylated carbons are also shifted, but to a lesser extent.[2] Individual spectra of protonated and deuterated sugars in $Me_2SO$ have been compared.[3] More extensive measurements of isotope effects on carbon-13 chemical shifts of carbohydrates have been carried out in concentric sample tubes, one containing $H_2O$ and the other $D_2O$ solutions.[3,4] Analysis of the data resulted in separation of the $\beta$-effect (due to deuteration of a directly bonded hydroxyl), in the range 0.11–0.15 ppm, and the $\gamma$-effect (due to deuteration of a hydroxyl on a vicinal carbon), in the range 0.03–0.06 ppm.[4] The hydrogen-exchange rate of hydroxyl groups in $Me_2SO$ solutions is usually sufficienty slow to allow the direct observation of shifts of such magnitude.[2] Direct observation of new peaks slightly displaced from those observed for the protio forms in the spectra of carbohydrates with partially deuterated hydroxyls should permit the assignment of the affected carbons with respect to hydroxyls on vicinal carbons as well as relative to directly bonded hydroxyls.

This communication presents a demonstration of multiplet structures in the proton-decoupled carbon-13 NMR spectra of

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