

equilibrium thermal systems.¹⁴ These effects are strongly pressure dependent and become normal near the high pressure limit. This might contribute to the observed inverse effect of dimethylmercury. Effects of this type are known not to occur in solution.

The explanation for anomalous α -effects in the cleavage of the carbon-mercury bond¹⁵ is not obvious at present.

The demonstrated normal behavior of the methyl radical strengthens the usefulness and unambiguity of the secondary α -deuterium effect as a criterion for "unimolecular" cleavage.

(14) F. W. Schneider and B. S. Rabinovitch, *J. Am. Chem. Soc.*, **85**, 2365 (1963).

(15) See also M. M. Kreevoy and B. M. Eisen, *J. Org. Chem.*, **28**, 2104 (1963).

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RECEIVED DECEMBER 27, 1963

New Types of Organosulfur Derivatives of Metal Carbonyls¹

Sir:

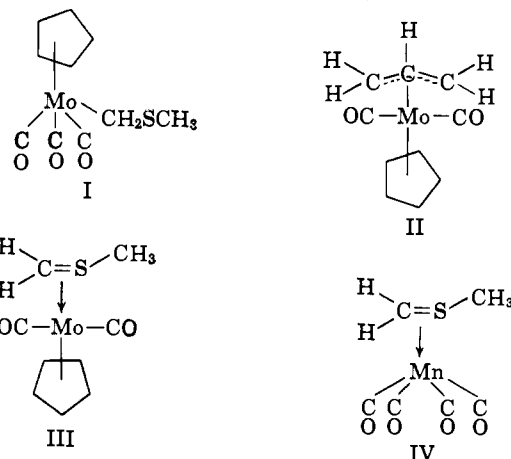
Numerous unusual organosulfur transition metal compounds have been obtained by reactions of various metal carbonyls and cyclopentadienylmetal carbonyls with certain mercaptans, sulfides, disulfides, and dithietenes.^{2,3} Other types of organosulfur transition metal compounds have been obtained from metal sulfides and certain acetylene derivatives.⁴ This communication describes a new and entirely different synthesis of new types of organosulfur derivatives of metal carbonyls with metal-sulfur bonds. These new compounds have been obtained by thermal or photochemical decarbonylation of compounds of general formula $\text{CH}_3\text{S}(\text{CH}_2)_n\text{M}(\text{CO})_x(\text{C}_5\text{H}_5)_y$ ($n = 1, 2$, or 3 ; $\text{M} = \text{Fe}$ [$x = 2, y = 1$], Mo [$x = 3, y = 1$], or Mn [$x = 5, y = 0$]) without metal-sulfur bonds. These sulfur-containing transition metal alkyl derivatives, none of which has been previously reported, may in turn be obtained from metal carbonyl anions and the chloroalkyl methyl sulfides $\text{CH}_3\text{S}(\text{CH}_2)_n\text{Cl}$.

Thus, the sodium salt $\text{NaMo}(\text{CO})_3\text{C}_5\text{H}_5$ ⁵ reacts with chloromethyl methyl sulfide in tetrahydrofuran solution at 25° to give the yellow crystalline alkyl tricarbonyl derivative $\text{CH}_3\text{SCH}_2\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$ (I), m.p. 66–67°.⁶ On heating to ~70° or ultraviolet irradiation this tricarbonyl derivative forms the likewise yellow crystalline dicarbonyl derivative $\text{CH}_3\text{SCH}_2\text{Mo}(\text{CO})_2\text{C}_5\text{H}_5$ in up to 60% yield, m.p. 66–67°.^{6,7}

The infrared⁸ and proton n.m.r. spectra⁸ and close analogies in stoichiometry, physical properties, and general method of preparation to π -cyclopentadienyl- π -allylmolybdenum dicarbonyl (II)⁹ lead us to propose structure III for the dicarbonyl derivative CH_3SCH_2 -

$\text{Mo}(\text{CO})_2\text{C}_5\text{H}_5$. In structure III a carbon-sulfur double bond is π -bonded to the molybdenum atom and the neutral CH_3SCH_2 group donates three electrons¹⁰ to the molybdenum atom in a similar manner to the π -allyl ligand. The relationship between the metal-ligand bonding in $\text{CH}_3\text{SCH}_2\text{Mo}(\text{CO})_2\text{C}_5\text{H}_5$ (III) and the π -allyl derivative (II) is very similar to the relationship between the metal-ligand bonding in benzene-chromium tricarbonyl and thiophene-chromium tricarbonyl¹¹ and is a further demonstration of the well-known analogy between the groupings $>\text{C}=\text{C}<$ and $>\ddot{\text{S}}:$.

A similar yellow liquid manganese derivative $\text{CH}_3\text{SCH}_2\text{Mn}(\text{CO})_4$ (IV) has been obtained from $\text{NaMn}(\text{CO})_5$ and chloromethyl methyl sulfide at ~65°.⁶



Analogous experiments with 2-chloroethyl methyl sulfide¹² and various metal carbonyl anions led to some surprising results. Thus, treatment of $\text{NaMn}(\text{CO})_5$ with 2-chloroethyl methyl sulfide in boiling tetrahydrofuran gave a 26% yield of pale yellow diamagnetic¹³ crystalline volatile $\text{CH}_3\text{SCH}_2\text{CH}_2\text{Mn}(\text{CO})_5$, m.p. 56.5–58.5°.⁶ The infrared spectrum of this new organomanganese compound besides very strong bands at 2071, 1996, and 1972 cm^{-1} due to the terminal metal carbonyl groups exhibits a very strong band at 1622 cm^{-1} , which may be assigned to an acyl carbonyl group suggesting structure VI rather than structure V.

Reaction between $\text{NaFe}(\text{CO})_2\text{C}_5\text{H}_5$ ⁵ and 2-chloroethyl methyl sulfide in tetrahydrofuran solution at room temperature yields a rather unstable orange liquid indicated by analysis and other properties to be $\text{CH}_3\text{SCH}_2\text{CH}_2\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5$ (VII). Ultraviolet irradiation of this material in benzene solution gives a complex mixture from which the following compounds can be isolated by chromatography on alumina in benzene solution followed by crystallization from pentane or ethanol of the fractions thus obtained: (1) unchanged $\text{CH}_3\text{SCH}_2\text{CH}_2\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5$; (2) brown crystalline $[\text{CH}_3\text{SFeCOC}_5\text{H}_5]_2$ ⁶ (VIII) identical with the compound of this composition previously isolated in low yield¹⁴ from the reaction between $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$

(1) This work was supported in part by Grant AF-AFOSR-580-64 from the Air Force Office of Scientific Research.

(2) R. B. King, *J. Am. Chem. Soc.*, **85**, 1587 (1963), and references to previous work from various research groups cited therein.

(3) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, in press.

(4) G. N. Schrauzer and V. Mayweg, *J. Am. Chem. Soc.*, **84**, 3221 (1962).

(5) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1955).

(6) These compounds gave satisfactory analyses for three to six elements. Detailed analytical data will be given in the full paper.

(7) A mixture of ~25% $\text{CH}_3\text{SCH}_2\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$ and ~75% $\text{CH}_3\text{SCH}_2\text{Mo}(\text{CO})_2\text{C}_5\text{H}_5$ exhibited a melting point of 55–60° indicating the melting point depression to be small but detectable.

(8) Details of these spectra will be given in the full paper.

(9) M. Cousins and M. L. H. Green, *J. Chem. Soc.*, 889 (1963).

(10) Complexes III and IV may possibly be regarded as derivatives of the unsaturated sulfonium ion $\text{H}_2\text{C}=\text{S}-\text{CH}_3$ where the carbon-sulfur double bond is π -bonded to the transition metal like a carbon-carbon double bond.

(11) E. O. Fischer and K. Öfele, *Ber.*, **91**, 2395 (1958).

(12) Although we have experienced no difficulties in handling 2-chloroethyl methyl sulfide apart from the usual obnoxious odor of divalent sulfur compounds, we advise caution in handling this compound due to its probable high toxicity based on its close chemical relationship to bis(2-chloroethyl) sulfide, highly toxic "mustard gas."

(13) From the proton n.m.r. spectrum.

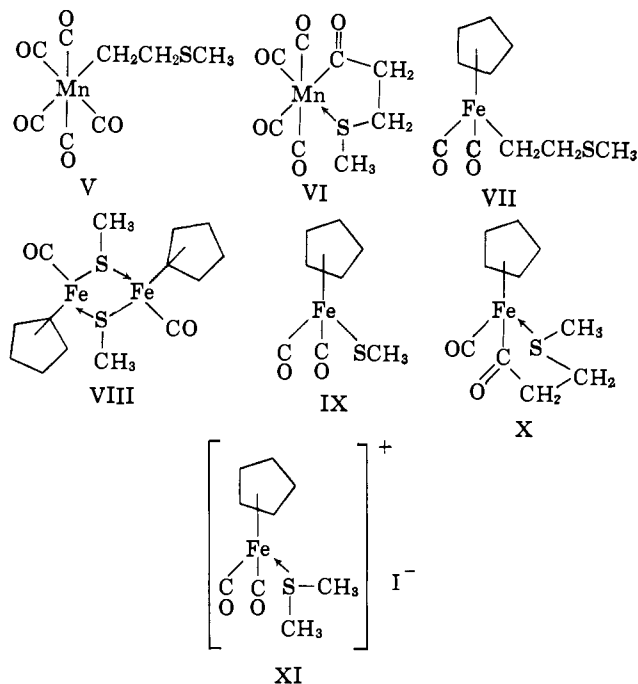
(14) An improved preparation of $[\text{C}_5\text{H}_5\text{FeCOC}_5\text{H}_5]_2$ from $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ and dimethyl disulfide giving a 37% yield rather than a 9% yield has been developed and will be described in the full paper.

and dimethyl disulfide¹⁵; (3) $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$; (4) brown crystalline $\text{CH}_3\text{SFe}(\text{CO})_2\text{C}_5\text{H}_5$ (IX), m.p. 67–69°⁶; and (5) red crystalline $\text{CH}_3\text{SCH}_2\text{CH}_2\text{COFeCO}\text{C}_5\text{H}_5$, m.p. 70°⁶, exhibiting a single strong terminal metal carbonyl band at 1934 cm^{-1} and a single strong acyl carbonyl band at 1618 cm^{-1} in its infrared spectrum clearly indicating structure X analogous to the structure VI proposed for $\text{CH}_3\text{SCH}_2\text{CH}_2\text{COMn}(\text{CO})_4$.

The monomeric product $\text{CH}_3\text{SFe}(\text{CO})_2\text{C}_5\text{H}_5$ (IX) is the first example of a methylthio derivative of a transition metal where the sulfur atom does not bridge between two metal atoms. This organosulfur derivative may also be obtained in 13% yield from $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{H}$ ¹⁶ and dimethyl disulfide.⁶ Similar reactions of dimethyl disulfide with $\text{HMn}(\text{CO})_5$ and $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{H}$ have previously been shown to give the dimeric derivatives $[\text{CH}_3\text{SMn}(\text{CO})_4]_2$ and $[\text{CH}_3\text{SMo}(\text{CO})_2\text{C}_5\text{H}_5]_2$.¹⁸

The chemical properties of $\text{CH}_3\text{SFe}(\text{CO})_2\text{C}_5\text{H}_5$ are consistent with its formulation as IX. Thus, on heating to 70° at atmospheric pressure, gas is evolved and the dimeric derivative $[\text{CH}_3\text{SFeCO}\text{C}_5\text{H}_5]_2$ (VIII) may be isolated in 26% yield. Treatment of $\text{CH}_3\text{SFe}(\text{CO})_2\text{C}_5\text{H}_5$ with excess methyl iodide forms an exothermic reaction yellow solid $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{S}(\text{CH}_3)_2]\text{I}$ (XI), m.p. 104° dec.⁶

Detailed aspects of the chemistry outlined in this communication will be presented in future papers.



(15) R. B. King, P. M. Treichel, and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 3600 (1961).

(16) Prepared *in situ* from $\text{NaFe}(\text{CO})_2\text{C}_5\text{H}_5$ and $(\text{CH}_3)_2\text{CS}$ in tetrahydrofuran solution.¹⁷

(17) M. L. H. Green and P. L. I. Nagy, *J. Organometal. Chem.*, **1**, 58 (1963).

(18) P. M. Treichel, J. H. Morris, and F. G. A. Stone, *J. Chem. Soc.*, 720 (1963).

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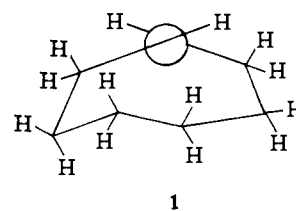
The Absolute Configuration of *trans*-Cyclooctene

Sir:

The complete resolution of *trans*-cyclooctene was reported recently.¹ The absolute configuration of

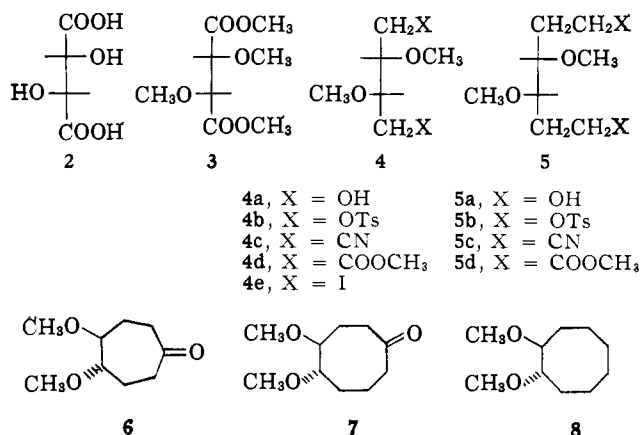
(1) A. C. Cope, C. R. Ganellin, H. W. Johnson, Jr., T. V. Van Auken, and H. J. S. Winkler, *J. Am. Chem. Soc.*, **85**, 3276 (1963).

trans-cyclooctene has now been determined and the levorotatory enantiomer is assigned the (*R*)-configuration² as shown in the Newman projection formula (1).



(1*S*:2*S*)-1,2-Dimethoxycyclooctane (8) was synthesized from the dextrorotatory (2*R*:3*R*)-tartaric acid (2) and its sign of rotation was shown to be identical with that of the same diether obtained from (–)-*trans*-cyclooctene.

(+)-Tartaric acid (2) was esterified³ with methanolic hydrogen chloride and the resulting dimethyl (2*R*:3*R*)-tartrate was methylated⁴ with methyl iodide and silver oxide to give 3. Lithium aluminum hydride reduction of the dicarboxylic ester (3) afforded the



glycol (4a) in 62% yield. The distilled glycol crystallized on cooling and was recrystallized from chloroform-ether (1:1) at 0°, m.p. 37–38°.⁵ The reaction of 4a with *p*-toluenesulfonyl chloride and pyridine yielded the ditosylate (4b, 94%). The corresponding diiodide (4e) was prepared⁶ from the ditosylate (4b) with sodium iodide and anhydrous acetone. Alkylation of either the ditosylate (4b) or the diiodide (4e) with acetonitrile did not give a satisfactory yield of the dinitrile (5c). An alternative sequence of reactions was therefore utilized.

The ditosylate (4b) was converted to (3*S*:4*S*)-3,4-dimethoxy-1,6-hexanedinitrile (4c)⁷ with sodium cyanide in dimethyl sulfoxide. Optimum yields (65–78%) were obtained with a reaction time of 6 days and careful control of the temperature at $20 \pm 3^\circ$. The dinitrile (4c) was converted to dimethyl (3*S*:4*S*)-3,4-dimethoxyadipate (4d) by treatment with methanolic hydrogen chloride followed by hydrolysis of the bis-

(2) The nomenclature for absolute configuration used throughout is that of R. S. Cahn, C. K. Ingold, and V. Prelog, *Experientia*, **12**, 81 (1956).

(3) A. Skrabal and L. Herman, *Montash.*, **48**, 633 (1922).

(4) T. Purdie and J. C. Irvine, *J. Chem. Soc.*, **79**, 957 (1901).

(5) Posternak and Susz⁸ had prepared the same glycol as an oil by its isolation from reduction as the diacetate followed by saponification of the purified diacetate with methanolic barium hydroxide. We isolated the glycol by treating the aluminate salt with a minimum of aqueous base and repeated washing of the filter cake with acetone as the glycol is sparingly soluble in ether.

(6) Th. Posternak and J. Ph. Susz, *Helv. Chim. Acta*, **39**, 2032 (1956).

(7) Satisfactory analytical data were obtained for all major intermediates in this synthesis. The assigned structures are supported by spectral data.