TABLE I

SULFINIC ESTERS PREPARED

No.	RS(O)OCH₃	Pro-cedure	Total product — Yield, %	Total product — Conversion, %	Total product — $n^{25}D$ (m.p., °C.)	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Sulfur, % Calcd.	Sulfur, % Found
II	Phenyl	A	79	47	1.5434-7	53.82	53.57	5.16	5.37	20.53	20.74
		A'	62	38	1.5428-30						
III	Phenyl[a]	A[a]	87	61	1.5246-8	58.67	58.44	6.57	6.62	17.40	17.20
IV	Phenyl[b]	A[b]	80	38	1.5214-22	58.67	58.23	6.57	6.69	17.40	17.36
V	p-Tolyl	B[c]	73	73	1.5405-8	56.45	56.36	5.92	5.92	18.84	18.56
VI	o-Tolyl	B'	72	72	1.5421-5	56.45	56.62	5.92	5.66	18.84	18.52
VII	o-Methoxycarbonylphenyl	B[d]	30	11[d]	1.5511-55	50.46	49.18[d]	4.71	4.91	14.97	15.38
VIII	2-Naphthyl	B[e]	33	33	(43-44)	64.05	64.13	4.89	4.95	15.55	15.65
IX	2-Benzothiazolyl	A	61	61	(72-74.5)	45.05	45.13	3.31	3.58	30.07	30.26
X	Pentyl	C	35	35	1.4450-2	47.97	48.21	9.39	9.51	21.34	21.62

[a] 1-Propyl ester; an equimolar amount of 1-propanol was substituted for methanol. [b] 2-Propyl ester; an equimolar amount of 2-propanol was substituted for methanol. [c] Kept at 25° instead of at reflux between the two additions of I. [d] Crude VII extracted into warm pentane, then methanol, then distilled (the viscous liquid decomposed partly on distillation and evolved SO₂). [e] Crude VIII was extracted into pentane; chilling gave first tar, then VIII.

more readily accessible than syntheses hitherto available.[3]

Nine esters prepared thus far, shown in Table I, include aromatic, heterocyclic and aliphatic types.[4] 1-Propyl and 2-propyl esters (III, IV) were prepared by using the appropriate alcohols instead of methanol (the methyl esters themselves presumably are alternative sources of other esters via transesterification[5]).

That electronegative groups inhibit the oxidation was suggested by the reduced yield with the o-methoxycarbonyl sulfinate VII. This indication was confirmed by recovery of 92 and 78%, respectively, of o- and p-nitrophenyl disulfide when oxidation of these disulfides was attempted.[6] Steric hindrance seems to be less deleterious than electron withdrawal, since results were comparable in the preparation of the p- and o-toluenesulfinic esters (V and VI).

In Procedure A, disulfide (0.075 mole) was stirred under reflux in chloroform–methanol (140 ml. of each), and I (0.30–0.34 mole) in chloroform (600 ml.) was added over 8.5–12 hr. Heating was continued for ca. 12 hr. The mixture was cooled, treated with water (100 ml.) and filtered. The chloroform layer was washed free of lead salts with water and dried (MgSO₄). After removal of solvent, products were purified by recrystallization or distillation (21–47 cm. spinning-band columns). In Procedure B, for improved conversions, the disulfide was used in chloroform (140–440 ml.)–methanol (60–75 ml.) with I (0.33 mole) in chloroform (600 ml.), but after the heating period (10–24 hr.) the addition of I and heating (12 hr.) were repeated. In Procedure A' and B', 0.15 mole of thiol in chloroform (50–100 ml.) first was oxidized to disulfide by addition to I (0.093 mole) in chloroform (500 ml.) during ca. 1 hr. at ca. 25°; Procedure A or B then was followed. Procedure C differs

(3) Cf. "Methoden der Organischen Chemie (Houben–Weyl)," E. Müller, Ed., Vol. 9, 4th ed., G. Thieme Verlag, Stuttgart, 1955, p. 297 (M. Quaedvlieg), 338–340 (F. Muth).

(4) Further work is necessary before the reaction is considered adequately developed for alkanesulfinates such as X. Variations of Procedure C gave products with $n^{25}D$ and infrared spectra similar to those of X, but poor analyses suggested difficultly separable impurities.

(5) Cf. H. Phillips, J. Chem. Soc., 127, 2552 (1925).

(6) Infrared spectra indicated trace formation of methyl p-nitrobenzenesulfinate.

from A in that the I was added during 2 hr. and distillation was from potassium carbonate.

Evidence that the products are sulfinic esters includes: (a) elementary analysis; (b) strong infrared absorption at 1099–1150 cm.$^{-1}$ and 909–991 cm.$^{-1}$; absorption at 1126–1136 cm.$^{-1}$ and 960 cm.$^{-1}$ is reportedly characteristic[7]; (c) identity of the infrared spectra of II, V and VIII with published spectra[8] and agreement for II, V, and VIII in other reported properties; (d) sap. equiv. of 153 for II (calcd. 156) and of 142–158 for X (calcd., 150); the sulfinate salts produced were converted to phenyl and pentyl 2,4-dinitrophenyl sulfone; (e) consumption of 103% of expectation of potassium permanganate by X, assuming that 3 moles of X reacts with 2 of permanganate, and isolation of methyl 1-pentanesulfonate in 53% yield.

(7) S. Detoni and D. Hadži, J. Chem. Soc., 3163 (1955).

(8) Cards 1061–1063, respectively, in the collection published by Butterworths, London, or Verlag Chemie, Weinheim (Dec., 1956). The spectrum of our II lacked bands at 1370 and 1185 cm.$^{-1}$; these evidently resulted in the reported spectrum from methyl benzenesulfonate, which absorbs strongly at these points.

DEPARTMENT OF CHEMISTRY　　　　　L. FIELD
VANDERBILT UNIVERSITY　　　　　C. B. HOELZEL
NASHVILLE 5, TENN.　　　　　J. M. LOCKE
　　　　　J. E. LAWSON

CYCLOPENTADIENYL-3-CYCLOPENTENYLNICKEL(II)

Sir:

Nickel carbonyl and cyclopentadiene react to form the red crystalline diamagnetic complex.[1] C₁₀H₁₂Ni, for which Structure I has been assigned. It has been reported[2] that this same complex can be prepared more conveniently by reducing dicyclopentadienylnickel with sodium amalgam in ethanol. We wish to propose the alternative structure, II, for the C₁₀H₁₂Ni complex which is in better accord with our experimental data. Structure II indicates that during the reduction of dicyclopentadienylnickel only one of the cyclopentadienyl rings is reduced to a cyclopentenyl grouping and the
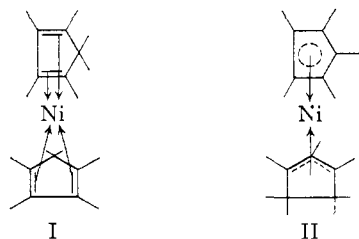
(1) E. O. Fischer and H. Werner, Ber., 92, 1423 (1959).

(2) A. H. Filbey, J. C. Wollensak and K. A. Keblys, Abstracts of Papers Presented at the 138th Meeting of the American Chemical Society, New York, N. Y., September 1960, p. 54-P.

I　　　　　　　II

other ring maintains the highly stable cyclopentadienyl metal bond, thus enabling nickel to attain rare gas electron structure. The formation of $C_{10}H_{10}Ni$ (dicyclopentadienylnickel) together with the $C_{10}H_{12}Ni$ complex in the nickel carbonyl-cyclopentadiene reaction system[1] reveals the existence of hydrogen abstraction, which coupled with a transfer would clearly produce structure II.

Supporting evidence for structure II has been obtained through a study of the n.m.r. spectrum of the $C_{10}H_{12}Ni$ complex coupled with an alternative synthesis. The strongest signal in the spectrum consists of a singlet with a chemical shift of -5.22 p.p.m. relative to tetramethylsilane. This corresponds exactly to the shift displayed by the protons of a cyclopentadienyl group bonded to nickel and has been observed in our laboratory with other similarly bonded complexes.[3] The remaining portion of the spectrum consists of complex unresolved multiplets at -4.07 p.p.m. and between -1.49 to -0.76 p.p.m. which have been assigned to protons on the 3-cyclopentenyl anion bonded to nickel. Because of the complexity of this part of the spectrum a correlation of protons and signals could not be made. Additional evidence for II was obtained by an alternative synthesis of the $C_{10}H_{12}Ni$ complex involving reaction of the cyclopentadienyl and 3-cyclopentenyl anions with nickel bromide. Thus, to a dispersion of 11.0 g. (0.05 mole) of anhydrous nickel bromide in tetrahydrofuran maintained at $-10°$, a solution of cyclopentadienylsodium (0.05 mole) in tetrahydrofuran was added over a period of one hour with rapid stirring under a protective atmosphere of pure nitrogen. This was followed by a tetrahydrofuran solution of 3-cyclopentenylmagnesium chloride (0.05 mole) also added over a period of one hour. The reaction mixture was maintained at room temperature for a period of 15 hours and all solvent then was removed at reduced pressures and room temperature. Sublimation of the residues at 10^{-5} mm. and $40°$ yielded 1.0 g. of a reddish sublimate which was purified by fractional recrystallization from petroleum ether at temperatures of $-10°$. In addition to some dicyclopentadienylnickel, 0.5 g. of a dark red, crystalline solid, m.p. $43°$ was isolated. Calcd. for $C_{10}H_{12}Ni$: C, 62.9; H, 6.35; Ni, 30.75. Found: C, 62.9; H, 6.15, Ni, 30.6. This crystalline solid was analytically identical with the monomeric and diamagnetic $C_{10}H_{12}Ni$ complex, m.p. $43°$, obtained by the reduction of dicyclopentadienylnickel with sodium amalgam in ethanol.[2] The infrared spectra of both materials were superimposable and correspond to the $C_{10}H_{12}Ni$ complex, m.p. $42°$ reported by Fischer.[1]

(3) M. Dubeck, J. Am. Chem. Soc., 82, 6193 (1960).

We believe that the experimental results are good evidence in support of the cyclopentadienyl-3-cyclopentenylnickel(II) structure for the $C_{10}H_{12}Ni$ complex, and suggest that the structural assignment by Fischer is in error. The recently reported 1,3-cyclohexadienecyclopentadienepalladium(0) complex[4] is also under investigation in our laboratory to determine whether the material could better be represented as 3-cyclohexenyl-cyclopentadienylpalladium(II) in analogy with the discussed nickel complex.[5]

(4) E. O. Fischer and H. Werner, Ber., 93, 2075 (1960).

(5) NOTE ADDED IN PROOF.—The possibility of structure II was first reported at the 138th Meeting of the American Chemical Society.[2] Since the submission of the present manuscript some n.m.r. data have been reported in support of II (E. O. Fischer and H. Werner, Tetrahedron Letters, 1, 17 (1961)) and the general existence of transition metal bonded cyclic "en-yl" structures, an example of which we have reported previously.[3]

ETHYL CORPORATION　　　　　　MICHAEL DUBECK
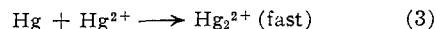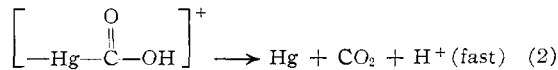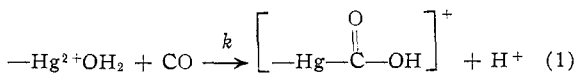RESEARCH LABORATORIES
DETROIT, MICHIGAN　　　　　　ALLEN H. FILBEY

OXIDATION OF CARBON MONOXIDE BY METAL IONS

Sir:

Recent observations[1] that molecular hydrogen, although unreactive toward the majority of common inorganic oxidizing agents, is oxidized under relatively mild conditions in aqueous solution by a few metal ions and complexes, notably Cu^{2+}, Ag^+, Hg^{2+}, Hg_2^{2+} and MnO_4^-, have prompted similar studies on another relatively inert reducing molecule, CO.

At temperatures below $80°$ only Hg^{2+} and MnO_4^-, among the ions listed above, showed measurable reactivity toward CO in aqueous solution; Fe^{3+}, Tl^{3+} and $Cr_2O_7^{2-}$ also were inactive. For the reduction of Hg^{2+}, i.e., $2Hg^{2+} + CO + H_2O \rightarrow Hg_2^{2+} + CO_2 + 2H^+$, kinetic measurements in dilute $HClO_4$ solution over the temperature range 26 to $54°$ yielded the rate law $-d[CO]/dt = k[CO][Hg^{2+}]$ with $\Delta H^* = 14.6$ kcal./mole and $\Delta S^* = -13$ e.u. It is believed that the reaction proceeds by the mechanism (1), (2), (3), in which the first step involves insertion of CO between Hg^{2+} and a coördinated water molecule,

$$-Hg^{2+}OH_2 + CO \xrightarrow{k} \left[-Hg-\overset{\overset{O}{\|}}{C}-OH\right]^+ + H^+ \quad (1)$$

$$\left[-Hg-\overset{\overset{O}{\|}}{C}-OH\right]^+ \longrightarrow Hg + CO_2 + H^+ \text{(fast)} \quad (2)$$

$$Hg + Hg^{2+} \longrightarrow Hg_2^{2+} \text{(fast)} \quad (3)$$

Support for this mechanism is provided by the observation[2,3] that when methanolic solutions of mercuric acetate take up CO under similar conditions, a stable methyl formate derivative, AcO-Hg-CO-OCH$_3$, analogous to the proposed intermediate, is formed and may be isolated.

The reduction of MnO_4^- by CO (to MnO_2 in acid and neutral solutions and to MnO_4^{2-} in basic

(1) J. Halpern, J. Phys. Chem., 63, 398 (1959); Advances in Catalysis, 11, 301 (1959).

(2) W. Schoeller, W. Schrauth and W. Essens, Ber., 46, 2864 (1913).

(3) J. Halpern and S. F. A. Kettle, in press.