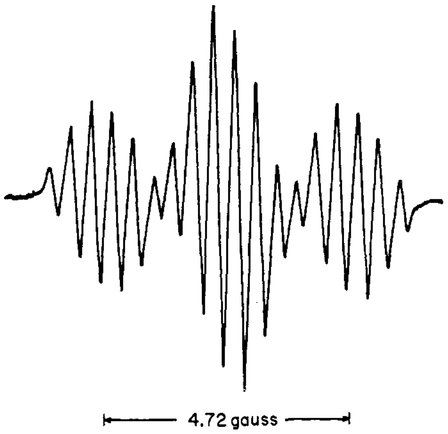
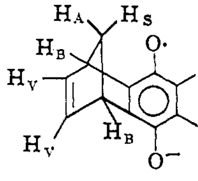


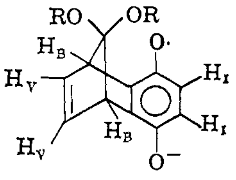
Figure 1. The epr spectrum of Ia in acetonitrile at ambient temperature.

The epr spectrum of the semiquinone (Ia)[5] prepared from 3′,6′-dihydroxybenzobicyclo[2.2.1]heptadiene-2,5 (I) reveals important spin density at the protons of the bicyclic fragment of the molecule.[6] The complexity of the spectrum of Ia, shown in Figure 1, prompted the preparation of group-labeled semiquinones IIa–IVa for a secure assignment of the coupling constants. The large coupling constant (about 2 gauss) for two protons in each radical is assigned to the aryl protons (H_I) on the basis of the many results for other semiquinones. The spectrum of IIa wherein the *syn* and *anti* hydrogen atoms[7] of Ia are replaced by ethoxy substituents is much less complex. Radical anion IIa exhibits a triple resonance (a_H = 0.52 gauss, intensity 1:2:1). The spectrum of IIa indicates selective coupling of either the bridgehead protons (H_B) or the vinyl protons (H_V). The spectrum of semiquinone IIIa with one vinyl proton is much simpler with coupling to only one proton of the bicyclic portion of the radical. Semiquinone IVa with one bridgehead proton and two vinyl protons has an epr spectrum indicative of coupling to two nonequivalent protons. These observations reveal that the vinyl protons (rather than the bridgehead protons) in IIa–IVa are coupled.[8]



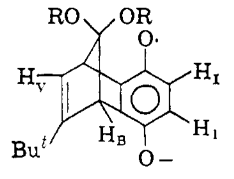
Ia

a_H = 2.36 gauss (2 H); H_I
a_H = 0.80 gauss (1 H); H_A
a_H = 0.40 gauss (3 H); H_S,H_V



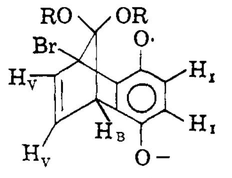
IIa (R = C_2H_5)

a_H = 2.38 gauss (2 H); H_I
a_H = 0.52 gauss (2 H); H_V



IIIa (R = $-CH_2CH_2-$)

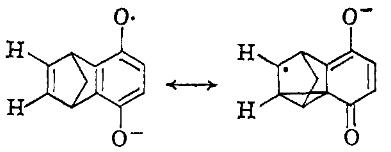
a_H = 2.34 gauss (2 H); H_I
a_H = 0.52 gauss (1 H); H_V



IVa (R = CH_3)

a_H = 2.05 gauss (2 H); H_I
a_H = 0.86 gauss (1 H); H_V
a_H = 0.46 gauss (1 H); H_V

The three-bond coupling constant of the vinyl protons of the bicyclic radical anions is remarkably large when contrasted with other spectroscopic results. For example, a_H for the protons of the *t*-butyl group of 2,5,-di-*t*-butylsemiquinone is about 0.06 gauss.[9] The transfer of spin density to the vinyl protons either by the overlap of the aryl molecular orbital and the carbon–hydrogen bond orbital or by rapid electron transfer cannot be excluded at present. However, it seems more likely that the spin density is transferred *via* the overlap of the aryl molecular orbital with the π-bond orbital, as illustrated in the valence bond structures. Work is in progress to determine the sign of the coupling constant to verify this interpretation.



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[5] The semiquinones were prepared from the corresponding hydroquinones by air oxidation in the presence of base in acetonitrile or dimethyl sulfoxide. A Varian V4500 instrument was used to record the spectra. The synthetic methods and pertinent physical and spectroscopic properties of the hydroquinones confirming the structures will be reported later. However, we wish to acknowledge the sample of the Diels–Alder adduct of benzoquinone and cyclopentadienone diethyl ketal from Eaton and Hudson and the sample of 3-*t*-butylcyclopentadienone dimethylene ketal from Garbish used as starting materials.

[6] The spectroscopic results are summarized under each structure as a_H, the coupling constant, and the number of protons that exhibit the coupling constant. The assignment that follows the experimental observations is based on the differences in the spectra of Ia–IVa.

[7] The assignment of a_{H_A} = 0.80 gauss and a_{H_S} = 0.40 gauss in Ia is based on the observations of Russell and Chang (ref 4). We are now examining the spectrum of hydrocarbon anion radicals, *i.e.*, derivatives of benzonorbornadiene, to confirm these assignments.

[8] Russell and Chang[4] find that the coupling constants for the bridgehead protons in the bicyclo[2.2.1]heptane semidiones are observable and not always small compared to the couplings of the other protons.

[9] G. K. Fraenkel, *Ann. N. Y. Acad. Sci.*, 67, 546 (1957).

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Sulfur Dioxide Insertion. II. S-Sulfinatopentacarbonylmanganese(I) Complexes[1]

Sir:

It was recently demonstrated in these laboratories that cyclopentadienylalkyl- and -aryliron dicarbonyls react readily with liquid sulfur dioxide to give cyclopentadienyliron dicarbonyl S-sulfinato[2] complexes, $C_5H_5Fe(CO)_2(SO_2R)$.[1] Subsequently, the SO_2 insertion was extended to dialkyl- and -arylmercury compounds and to cyclopentadienyl(methyl)molybdenum tricarbonyl.[3] It therefore became of considerable interest to evaluate the scope of this reaction and to show (1) whether the product is invariably a sulfinato-

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[1] For part I of this series, see J. P. Bibler and A. Wojcicki, *J. Am. Chem. Soc.*, 86, 5051 (1964).

[2] To systematize the nomenclature these complexes will be referred to henceforth as sulfinates (S-sulfinates if M–S bonding is present) rather than sulfonyls.

[3] A. Wojcicki and J. P. Bibler, Abstracts, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965, p 36M.

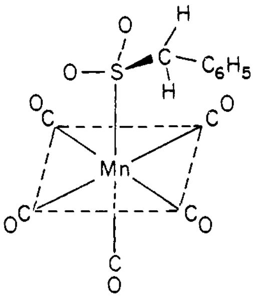

Figure 1. The structure of S-(benzylsulfinato)pentacarbonylmanganese(I).

carbonyl rather than an acyl sulfur dioxide derivative and (2) whether other modes of bonding in the MSO_2R moiety of the products also prevail.

In an attempt to resolve some of the above points we have examined the reaction of liquid sulfur dioxide with $Mn(CO)_5CH_3$, where the methyl group is known to migrate readily onto a carbonyl ligand.[4] Reported now is the synthesis of two sulfinatopentacarbonylmanganese(I) complexes along with some interesting spectral features of these derivatives.

In a typical experiment, sulfur dioxide (*ca.* 20 ml) was condensed onto 1.2 g (5.72 mmoles) of $Mn(CO)_5CH_3$ at about −75°. After 1 hr the sulfur dioxide was allowed to evaporate, the orange residue was extracted with 20 ml of absolute ethanol, and the mixture was filtered. Ether (20 ml) was slowly added to the filtrate and the resultant solution was maintained at *ca.* −20° for 1 hr. Pale yellow needles that formed were collected on a filter and washed with ether (three 5-ml portions). Concentration of the mother liquor, followed by addition of ether and cooling, afforded more product. The total yield was 0.84 g (55%).

Anal. Calcd for $Mn(CO)_5(SO_2CH_3)$: C, 26.29; H, 1.09; S, 11.69; mol wt, 274. Found:[5] C, 26.51; H, 1.33; S, 11.53; mol wt (osmometry in $CHCl_3$), 274.

The compound is readily soluble in chloroform, methanol, and acetonitrile, sparingly soluble in carbon tetrachloride and water, and insoluble in saturated hydrocarbons. It sublimes at 60° (0.01 mm) without decomposition. Its solutions are stable to air.

The proton magnetic resonance spectrum of $Mn(CO)_5(SO_2CH_3)$ shows a sharp signal at τ 6.85; interestingly enough, the same τ value was recorded for the CH_3 protons of $C_5H_5Fe(CO)_2(SO_2CH_3)$.[1] Because of the different possible modes of bonding in the $MnSO_2CH_3$ moiety[3] and the fact that these cannot be differentiated by nmr spectroscopy, we decided to synthesize and examine the corresponding benzyl sulfinate. Here, participation of one oxygen of the SO_2 in bonding to either manganese or the benzyl group is expected to give rise to an AB-type spectrum for the methylene protons.[6]

The preparative method used was analogous to that for the methyl derivative, the reaction time having been extended to 4 hr. The yield of light yellow crystals, which sublime at 85° (0.01 mm), was 65%.

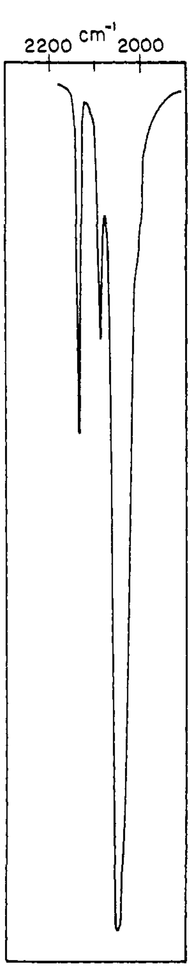

Figure 2. The infrared spectrum of $Mn(CO)_5(SO_2CH_3)$ in $CHCl_3$ in the CO stretching region.

Anal. Calcd for $Mn(CO)_5(SO_2CH_2C_6H_5)$: C, 41.16; H, 1.99; S, 9.15; mol wt, 350. Found:[5] C, 41.03; H, 1.99; S, 9.08; mol wt (osmometry in $CHCl_3$), 358, 340.

The nmr spectrum of $Mn(CO)_5(SO_2CH_2C_6H_5)$ consists of two signals: a singlet at τ 5.61 and a complex multiplet centered at τ 2.40 (relative intensities 2:5). The single sharp resonance for the methylene protons is consistent with magnetic equivalence of the two hydrogens and suggests the structure in which sulfur bonds to both manganese and the benzyl group (Figure 1). On the basis of similarities between the infrared spectra (*vide infra*) and physical properties of the two compounds, the same mode of bonding has been assigned also to the methyl derivative.

The above conclusion derives support from examination of the infrared spectra of the sulfinates in the 1300–1000-cm⁻¹ region. The methyl and benzyl complexes exhibit strong-intensity absorptions at 1200 and 1065 cm⁻¹ and at 1213 and 1057 cm⁻¹ (KBr pellet), respectively. These are in good agreement with the corresponding bands observed in $C_5H_5Fe(CO)_2(SO_2R)$[1] and $C_5H_5Mo(CO)_3(SO_2CH_3)$,[3] and are assigned to the asymmetric and symmetric S–O stretching frequencies. The unusually low wavenumber values reflect considerable manganese–sulfur π interaction.

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(4) See R. J. Mawby, F. Basolo, and R. G. Pearson, *J. Am. Chem. Soc.*, **86**, 5043 (1964), and references therein.

(5) Galbraith Laboratories, Inc., Knoxville, Tenn.

(6) See L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," The Macmillan Co., New York, N. Y., 1959, pp 99–103; also, J. W. Wilt and W. J. Wagner, *Chem. Ind.* (London), 1389 (1964).

Table I. Carbonyl Stretching Frequencies (cm^{-1}) of $Mn(CO)_5(SO_2R)$ Complexes[a]

Complex	Solvent	CO stretches			
		$A_1^{(2)}$	B_1	E	$A_1^{(1)}$
$Mn(CO)_5(SO_2CH_3)$	CCl_4	2139 (m-w)	2090 (w)	2059 (s), 2044 (s)	2027 (m)
	$CHCl_3$	2142 (m-w)	2095 (w)	2055 (s)	2037 (m, sh)
$Mn(CO)_5(SO_2CH_2C_6H_5)$	CCl_4	2137 (m-w)	2089 (w)	2059 (s), 2041 (s)	2024 (m)
	$CHCl_3$	2141 (m-w)	2093 (w)	2061 (s), 2049 (s)	2035 (m, sh)
	CH_3CN	2142 (m-w)	2089 (w)	2057 (s)	2047 (m, sh)

[a] Recorded on a Beckman Model IR-9 spectrophotometer. Abbreviations: s, strong; m, medium; m-w, medium weak; w, weak; sh, shoulder.

The infrared carbonyl stretching frequencies of the derivatives are listed in Table I, and the spectrum of $Mn(CO)_5(SO_2CH_3)$ in $CHCl_3$ in the 2200–1900-cm^{-1} region is given in Figure 2. These data clearly indicate appreciable distortion from regular C_{4v} molecular symmetry, the effect becoming more pronounced as the size of the perturbing sulfinate group increases. Accordingly, the splitting of the E band, not discernible for $Mn(CO)_5(SO_2CH_3)$ in $CHCl_3$, is clearly apparent for $Mn(CO)_5(SO_2CH_2C_6H_5)$ in the same solvent. In both cases, the B_1 absorption is easily detectable.

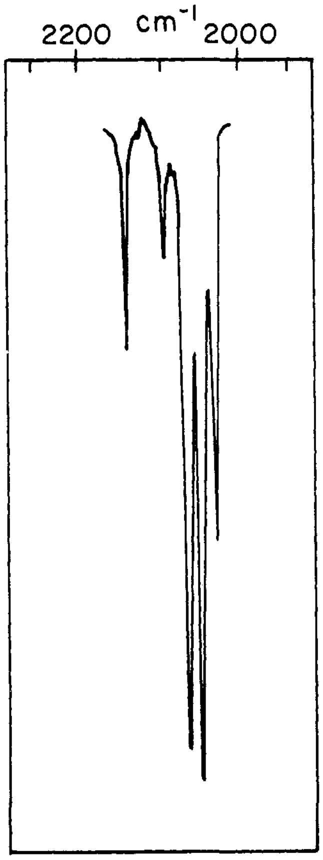

Figure 3. The infrared spectrum of $Mn(CO)_5(SO_2CH_2C_6H_5)$ in CCl_4 in the CO stretching region.

The splitting becomes easier to detect as the polarity of the solvent decreases; this is illustrated by the carbonyl stretching region spectrum of $Mn(CO)_5(SO_2CH_2C_6H_5)$ in CCl_4, given in Figure 3. It may be seen from Table I that the separation of the two components of the E absorption amounts to 18 cm^{-1}, much larger than any of the splittings reported by Wilford and Stone.[7] However, no splitting of the E band is discernible in the polar acetonitrile because of broadening of the peaks.

The absorptions due to the $A_1^{(1)}$ mode occur at much higher wavenumbers (*ca.* 20–35 cm^{-1}) than those reported for the halogeno- and alkylmanganese pentacarbonyls,[8,9] but at frequencies comparable to those found in the acyl and perfluoroacyl derivatives.[7] The values indicate an appreciable π-bonding capacity of the sulfinate ligands, which is consistent with the proposed manganese–sulfur linkage in the complexes.

A study is now in progress on reactions of $Mn(CO)_5(SO_2CH_2C_6H_5)$ with several neutral ligands. Of interest will be to determine whether, as with the thiocyanato complexes,[10] replacement of carbon monoxide by ligands of much lesser π-bonding ability might lead to a linkage rearrangement from $Mn\text{-}SO_2CH_2C_6H_5$ to $Mn\text{-}OS(O)CH_2C_6H_5$. Preliminary results indicate that the reactions with triphenylphosphine and pyridine proceed very slowly.

Acknowledgment. The support of the National Science Foundation is gratefully acknowledged. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the partial support of this research.

(7) J. B. Wilford and F. G. A. Stone, *Inorg. Chem.*, **4**, 389 (1965).

(8) J. C. Hileman, D. K. Huggins, and H. D. Kaesz, *ibid.*, **1**, 933 (1962).

(9) F. A. Cotton, *ibid.*, **3**, 702 (1964).

(10) M. F. Farona and A. Wojcicki, *ibid.*, **4**, 1402 (1965).

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Bicyclo[2.1.0]pent-2-ene

Sir:

We wish to describe the preparation, isolation, and identification of bicyclo[2.1.0]pent-2-ene ("homocyclobutadiene") (I), valence bond isomer of cyclopentadiene

I

and the smallest unsaturated polycycle yet secured in the organic laboratory.[1]

The new hydrocarbon can be generated by ultraviolet irradiation of cyclopentadiene, either in a basic or a neutral ethanolic medium. One of the more satisfactory preparations involves a 1–2 hr photolysis (450-w Hanovia high-pressure mercury arc lamp) of an approx-

(1) For a recent review of small-ring compounds, see D. Seebach, *Angew. Chem. Intern. Ed. Engl.*, **4**, 121 (1965).