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Reactions of Transition Metal-2-Alkynyl Complexes with Sulfur Trioxide. Organometallic Sultone Complexes

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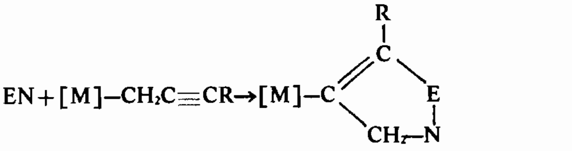
A series of transition metal-vinyl complexes containing a sultone ring have been prepared by the reaction of the corresponding metal-2-alkynyl complexes with SO_3. dioxane or uncomplexed SO_3. The new compounds include h^5-$C_5H_5Fe(CO)_2C{=}C(R)S(O)_2OCH_2$ *($R = CH_3, C_6H_5$),* h^5-$C_5H_5Mo(CO)_3C{=}C(R)S(O)_2OCH_2$ *($R = C_6H_5$), and $Mn(CO)_5C{=}C(R)S(O)_2OCH_2$ ($R = CH_3, C_6H_5$). One member of this class ($Mn(CO)_5$-$C{=}C(C_6H_5)S(O)_2OCH_2$) was also obtained* via *oxidation of the corresponding vinyl-sultine, $Mn(CO)_5$-$C{=}C(C_6H_5)S(O)OCH_2$. These sultone complexes exhibit much greater chemical and thermal stability than their sultine analogs.*

Introduction

The electrophilic molecules SO_2[1-3], $(CN)_2C{=}C(CN)_2$,[4] and C_6H_5NSO[5] (EN) readily participate in cycloaddition reactions with transition metal-2-alkynyl complexes (equation (1)). The resulting metal-vinyl derivatives have been



(1)

([M] = h^5—$C_5H_5Fe(CO)_2$, h^5—$C_5H_5Mo(CO)_3$ or $Mn(CO)_5$; R = H, CH_3, C_6H_5 or $CH_2Fe(CO)_2(h^5$—$C_5H_5)$)

isolated and characterized; in one case (EN = SO_2, [M] = h^5-$C_5H_5Fe(CO)_2$, R = CH_3) the structure was determined crystallographically.[6]

In an effort to ascertain the generality of these reactions we have investigated the interaction of the 2-alkynyl complexes with the powerful electrophile sulfur trioxide. It was of particular interest to compare the behavior of SO_3 with that of SO_2 toward these organometallic compounds and to elucidate the properties of products of the SO_3 reactions.

Reported here in detail are the results of our investigation. A preliminary account of this work appeared earlier[7] and was followed by another communication[8] concerned with these same cycloaddition reactions.

Experimental Section

Materials and Analyses. h^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CR$ (R = CH_3[1] and C_6H_5[9]), $Mn(CO)_5CH_2C{\equiv}CR$ (R = CH_3[1] and C_6H_5[3]), and h^5-$C_5H_5Mo(CO)_3CH_2C{\equiv}CC_6H_5$[3] were prepared by literature methods.

Stabilized liquid sulfur trioxide ("Sulfan") and fuming sulfuric acid (30% SO_3) were obtained from Allied Chemical Co. and were used as received. Si_2Cl_6 was procured from Alfa Inorganics. *p*-Dioxane was distilled from CaH_2 prior to use. Reagent grade benzene was distilled from $LiAlH_4$ whereas tetrachloroethylene was distilled from P_4O_{10} prior to use. All other solvents were reagent grade quality and were used without further purification.

Elemental analyses were performed by Dr. F. Pascher, Mikroanalytisches Laboratorium, Bonn, Germany. Mass spectra were obtained by Mr. C. Weisenberger of The Ohio State University with an A.E.I. Model MS-9 spectrometer.

Preparation of $Mn(CO)_5C{=}C(C_6H_5)S(O)OCH_2$. This metal-sultine complex was prepared by the general method developed for this class of compounds.[1] A solution of $Mn(CO)_5CH_2C{\equiv}CC_6H_5$ (0.22 g, 0.7 mmol) in *ca* 20 ml of liquid SO_2 was allowed to reflux for 1.5 hr. After the excess SO_2 had been removed, the product crystallized from 1:1 CH_2Cl_2-pentane and was air-dried to furnish 0.19 g (72%) of very light yellow crystals, mp 115° dec (uncorr.). Ir (KBr pellet, cm^{-1}): 2125s, 2060sh, 2015vs, br($\nu_{C\equiv O}$), 1122s, 895m (ν_{SO}). Nmr ($CDCl_3$,τ): 2.60 (s, 5H, C_6H_5), 4.32, 4.62 (AB quartet, J_{AB} = 15 Hz, 2H, -CH_2-O).

Anal. Calcd for $C_{14}H_7MnO_7S$: C, 44.94; H, 1.89. Found: C, 44.40; H, 1.84.

Preparation of Metal-Sultone Complexes. Method

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Table I. Analytical Data and Physical Properties of the Metal-Sultones $[M]-\overline{C=C(R)S(O)_2OC}H_2$

Complex		Procedure[a] and Yield,%			Mp(dec),[b]	Color	Analysis, %							
							C		H		S		Mol. wt.	
[M]	R	A	B	C	°C		Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found[c]
h^5–$C_5H_5Fe(CO)_2$	CH_3	2	62		170	Yellow	42.60	42.59	3.25	3.19			310	310
h^5–$C_5H_5Fe(CO)_2$	C_6H_5	36	66		195	Yellow	51.64	51.78	3.25	3.13	8.62	8.31	372	372
$Mn(CO)_5$	CH_3	10	60		145	White	32.94	33.12	1.54	1.53	9.77	9.67	328	328
$Mn(CO)_5$	C_6H_5	57	67	42	150	White	43.09	42.21	1.81	1.68	8.22	8.18	390	390
h^5–$C_5H_5Mo(CO)_3$	C_6H_5	51	54		145	Yellow	46.38	46.35	2.75	2.76	7.28	7.06		

[a] See Methods A,B, and C in the Experimental Section. [b] Measured *in vacuo* and uncorrected. All compounds decompose slowly above the indicated temperature without melting. [c] Molecular ion as observed in the mass spectrum. The mass of only the most common isotopic species is noted.

A: *Using Uncomplexed SO_3*. Sulfur trioxide was vacuum distilled from fuming sulfuric acid and then dissolved in tetrachloroethylene.

In a typical reaction, a portion of this solution (20 ml, containing *ca* 6 mmol of SO_3) was added dropwise over a 15-min period to a solution of h^5-$C_5H_5Fe(CO)_2CH_2C\equiv CC_6H_5$ (0.67 g, 2.3 mmol) in 10 ml of tetrachloroethylene under nitrogen at room temperature. The mixture was stirred for an additional 15 min and the precipitate was collected and dissolved in 60 ml of CH_2Cl_2. This solution was neutralized with saturated aqueous $NaHCO_3$ and the organic layer dried over $MgSO_4$. After filtration, the CH_2Cl_2 solution was concentrated to *ca* 2 ml to afford 0.31 g (36%) of fine yellow wires of h^5-$C_5H_5Fe(CO)_2$-$\overline{C=C(C_6H_5)S(O)_2OC}H_2$. The analytical data for this and other new metal-sultone complexes reported herein are given in Table I.

Method B: *Using SO_3 . Dioxane.* The SO_3 . dioxane complex was prepared by slowly adding SO_3 (0.15 ml, *ca* 3.6 mmol) to a solution of dioxane (0.30 ml, 3.5 mmol) in 5 ml of CH_2Cl_2 at 0° under a nitrogen atmosphere.[10] The resulting suspension was used *in situ.*

A solution of $Mn(CO)_5CH_2C\equiv CCH_3$ (0.88 g, 3.5 mmol) in 20 ml of CH_2Cl_2 at room temperature was added to the ice-cooled, stirred SO_3·dioxane suspension over a 5-min period, and the resultant orange solution was stirred for an additional 5 min while warming to room temperature. After neutralization with saturated aqueous $NaHCO_3$ and drying the organic layer over $MgSO_4$, the solvent was removed to leave a yellow solid. This was washed with pentane and then dissolved in hot benzene. Filtration and evaporation to dryness gave light yellow crystals (0.70 g, 60%). Recrystallization from 20 ml of hot benzene afforded 0.47 g (40%) of analytically pure $Mn(CO)_5\overline{C=C(CH_3)}$-$\overline{S(O)_2OC}H_2$ as white needles.

Method C: *Oxidation of the Corresponding Sultine.* A solution of $KMnO_4$ (0.25 g, 1.6 mmol) in 15 ml of 1:2 (by volume) H_2O-CH_3COOH was slowly added to a solution of $Mn(CO)_5\overline{C=C(C_6H_5)S(O)OC}H_2$ (0.32 g, 0.86 mmol) in 2 ml of glacial acetic acid. After 5 min the stirred solution was treated with a slight excess of $NaHCO_3$ and the resultant precipitate was extracted with 50 ml of CH_2Cl_2. The extract was dried over $MgSO_4$, filtered, and then concentrated to yield a light yellow solid whose ir spectrum (KBr pellet) was identical with that of an analytically pure sample of $Mn(CO)_5\overline{C=C(C_6H_5)S(O)_2OC}H_2$. The yield was 0.14 g (42%).

Attempted Reactions of Metal-Sultone Complexes. (*a*) *With HCl.* Gaseous HCl was passed through a solution of $Mn(CO)_5\overline{C=C(C_6H_5)S(O)_2OC}H_2$ (0.13 g) in 15 ml of CH_2Cl_2 at room temperature. After 70 min the solution was neutralized with aqueous $NaHCO_3$, and the organic layer was dried over $MgSO_4$. The filtered CH_2Cl_2 solution was concentrated to afford white crystals (0.08 g) whose ir spectrum (KBr pellet) was identical with that of the starting material.

Similarly, h^5-$C_5H_5Fe(CO)_2\overline{C=C(C_6H_5)S(O)_2OC}H_2$ was recovered unchanged from an HCl-saturated CH_2Cl_2 solution after 1 hr at room temperature.

(b) *With Si_2Cl_6.* A solution of $Mn(CO)_5\overline{C=C(C_6H_5)}$-$\overline{S(O)_2OC}H_2$ (0.12 g, 0.3 mmol) and Si_2Cl_6 (0.23 g, *ca* 1.3 mmol) in 40 ml of benzene was refluxed under nitrogen for 90 min. After neutralization with aqueous $NaHCO_3$ and drying over $MgSO_4$, the CH_2Cl_2 solution was filtered and concentrated to afford *ca* 0.05 g of the starting sultone, which was identified by its ir spectrum.

Results and Discussion

Transition metal-2-alkynyl compounds react in solution with either uncomplexed sulfur trioxide or SO_3 · dioxane to yield 1:1 adducts as shown in equation (2). The use of SO_3 · dioxane moderates the reactivity of

$$[M]-CH_2C\equiv CR+SO_3\rightarrow[M]-CH_2C_2R\cdot SO_3 \qquad (2)$$

$([M] = h^5–C_5H_5Fe(CO)_2,\ R = CH_3, C_6H_5;$
$[M] = Mn(CO)_5,\ R = CH_3, C_6H_5;$
$[M] = h^5–C_5H_5Mo(CO)_3,\ R = C_6H_5)$

SO_3 and leads to the higher yield of the product with every 2-alkynyl examined. These 1:1 addition compounds are air-stable, crystalline solids which do not dissolve in pentane but are sparingly soluble in benzene and readily soluble in chloroform, acetone, and methanol. Some of their physical properties are listed in Table I.

The structures of the products (I) are formulated as those derived

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Table II. Infrared CO and SO Stretching Frequencies (cm^{-1}) of the Metal-Sultones $[M]-\overline{C=C(R)S(O)_2OC}H_2$.

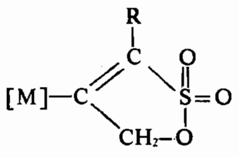
Complex [M]	R	$\nu_{C\equiv O}$ [a]	ν_{SO} [b]
h^5–$C_5H_5Fe(CO)_2$	CH_3	2038 vs, 1989 vs	1301 s, 1181 vs, 913 m
h^5–$C_5H_5Fe(CO)_2$	C_6H_5	2038 vs, 1988 vs	1303 s, 1164 vs, 913 m
$Mn(CO)_5$	CH_3	2127 m, 2069 vw, 2034 vs, br	1316 s, 1186 s, 928 s
$Mn(CO)_5$	C_6H_5	2128 m, 2073 vw, 2036 vs, br	1322 s, 1176 vs, 921 s
h^5–$C_5H_5Mo(CO)_3$	C_6H_5	2041 vs, 1974 vs, 1954 vs	1310 s, 1170 vs, 918 m

[a] $CHCl_3$ solution, Beckman IR-9 spectrophotometer. [b] KBr pellet, Perkin-Elmer Model 337 spectrophotometer. vs, very strong; s, strong; m, medium; vw, very weak; br, broad.

Table III ^{1}H Nmr Spectra of the Metal-Sultones $[M]-\overline{C=C(R)S(O)_2OC}H_2$ [a]

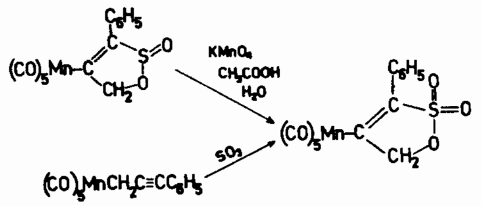
Complex		Chemical Shift (τ)		
[M]	R	–CH_2–O	R	C_5H_5
h^5–$C_5H_5Fe(CO)_2$	CH_3	5.14 q (J=2Hz)	(CH_3) 7.83 t (J=2Hz)	5.02 s
h^5–$C_5H_5Fe(CO)_2$	C_6H_5	4.98 s	(C_6H_5) 2.54 s	5.22 s
$Mn(CO)_5$	CH_3	4.98 q (J=2Hz)	(CH_3) 7.77 t (J=2Hz)	—
$Mn(CO)_5$	C_6H_5	4.84 s	(C_6H_5) 2.54 s	—
h^5–$C_5H_5Mo(CO)_3$	C_6H_5	4.93 s	(C_6H_5) 2.53 s	4.70 s

[a] $CDCl_3$ solution, Varian A60-A spectrometer. s = singlet; t = triplet; q = quartet.



(I)

from (3+2) addition of the 2-alkynyl moiety to sulfur trioxide. This assignment receives strongest support from the conversion of the sultine complex $Mn(CO)_5\overline{C=C(C_6H_5)S(O)OC}H_2$ by means of $KMnO_4$ in aqueous acetic acid to a compound identical with the product of the reaction between $Mn(CO)_5CH_2C\equiv CC_6H_5$ and SO_3 (Scheme 1). Such oxidation has a precedent in the chemistry of organic sultines and sultones.[11-13] There is little doubt about the correctness of the manganese-sultine formulation, since the structure of the complex h^5-$C_5H_5Fe(CO)_2\overline{C=C(CH_3)S(O)OC}H_2$, which exhibits strictly analogous spectroscopic properties, was determined by X-ray diffraction.[6] Further evidence for structure I of the reported products is based on their ir and ^{1}H nmr spectra (*vide infra*). Significantly, addition of SO_3 to the carbon-carbon triple bond was not observed in this work. By comparison, the reaction between acetylene and SO_3 gives a six-membered carbyl sulfate ring.[14]



Scheme 1

The ir spectra of the metal-sultone complexes in the CO and SO stretching regions are summarized in Table II. The carbonyl stretching absorptions average 5 cm^{-1} higher than those of the corresponding metal-sultine complexes under the same conditions.[1,15] This corresponds to a slightly lower electron density at the metal atom in the sultones and is compatible with a higher formal oxidation state of the sulfur therein. The SO stretching frequencies appear at *ca* 1310 and 1175 cm^{-1}. By comparison, the organic sultones exhibit these absorptions at *ca* 1360 and 1180 cm^{-1}.[16]

The ^{1}H nmr spectra of the new sultones are presented in Table III. As expected for this type of structure, the -CH_2-O protons are equivalent. The position of their resonance occurs at *ca* 0.4 ppm upfield from the average of the -CH_2-O signals in the corresponding sultine complex.[1] For the methyl-substituted compounds (I, R=CH_3), the observed CH_2-C=C–CH_3 coupling constant of 2 Hz is identical with that found for the sultine analogs.[1]

As far as chemical properties are concerned, the most striking difference between the sultines and sultones in question is the much greater stability of the latter. Thus, for example, whereas the previously studied sultine complexes are readily decomposed by HCl to yield [M]-Cl,[1] the analogous sultones are remarkably stable to acid. The sultones can be also recovered unchanged after chromatography on Florisil whereas the sultines are known to undergo partial desulfonylation under comparable conditions.[15] Furthermore, the decomposition temperatures of the sultone complexes are considerably higher (25-75°) than those of the sultines. Similar differences may

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Table IV. Major Mass Spectral Peaks for $[M]—CH_2C{\equiv}CC_6H_5$, $[M]—C{=}C(C_6H_5)S(O)OCH_2$, and $[M]—C{=}C(C_6H_5)S(O)_2$-OCH_2 [a]

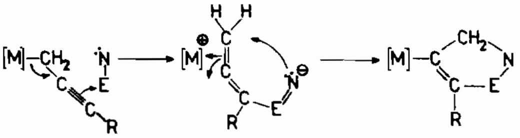
m/e	$[M]C_9H_7$ [b]	$[M]C_9H_7SO_2$ [c]	$[M]C_9H_7SO_3$ [c]	Ion
390	—	—	46 [d]	$[M]C_9H_7SO_3^+$, $[M]_2^+$
374	—	0.1	—	$[M]C_9H_7SO_2^+$
362	—	—	4	$[M]C_9H_7SO_3^+$—CO, $[M]_2^+$—CO
334	—	—	38	$[M]C_9H_7SO_3^+$—2CO, $[M]_2^+$—2CO
310	7	7	—	$[M]C_9H_7^+$
306	—	—	81	$[M]C_9H_7SO_3^+$—3CO, $[M]_2^+$—3CO
298	—	—	5	$[M]C_9H_7O^+$—CO
282	14	12	—	$[M]C_9H_7^+$—CO
278	—	—	36	$[M]C_9H_7SO_3^+$—4CO, $[M]_2^+$—4CO
270	—	—	7	$[M]C_9H_7O^+$—2CO
254	14	13	—	$[M]C_9H_7^+$—2CO
250	—	—	129	$[M]C_9H_7SO_3^+$—5CO, $[M]_2^+$—5CO
242	—	—	17	$[M]C_9H_7O^+$—3CO
226	61	61	7	$[M]C_9H_7^+$—3CO
198	22	26	6	$[M]C_9H_7^+$—4CO
195	4	6	17	$[M]^+$
170	125	139	17	$[M]C_9H_7^+$—5CO
167	6	6	7	$[M]^+$—CO
139	7	6	6	$[M]^+$—2CO
115	202	132	30	$C_9H_7^+$
111	8	5	6	$[M]^+$—3CO
89	19	13	18	$C_7H_5^+$
83	10	7	10	$[M]^+$—4CO
80	5	7	17	$[M]C_2H^+$—5CO, SO_3^+
64	—	62	66	SO_2^+
55	100	100	100	$[M]^+$—5CO

[a] [M] = $Mn(CO)_5$. All intensities relative to $[M]^+$—5CO = 100. [b] Source temp. = 125°. [c] Source temp. = 120°.
[d] High resolution mass spectroscopy shows this m/e feature to be composed of separate peaks at 389.9221 and 389.8233 in an approximate 1:2 ratio. Mass calc. $Mn(CO)_5C_9H_7SO_3$ 389.9242, $Mn_2(CO)_{10}$ 389.8253.

be noted with the organic sultines and sultones. The former are much more easily hydrolyzed and are in some cases stable below room temperature only.[11,13]

The higher thermal and chemical stability of the metal-sultone complexes relative to the metal-sultine analogs is also reflected in their mass spectra. The mass spectra of $Mn(CO)_5CH_2C{\equiv}CC_6H_5$, $Mn(CO)_5$-$C{=}C(C_5H_5)S(O)OCH_2$, and $Mn(CO)_5C{=}C(C_6H_5)S$-$(O)_2OCH_2$, presented in Table IV, are representative of these types of transition metal complexes. It is to be noted that, except for a weak molecular ion peak and a strong peak assignable to SO_2^+, the spectrum of $Mn(CO)_5C{=}C(C_6H_5)S(O)OCH_2$ is nearly identical with that of $Mn(CO)_5CH_2C{\equiv}CC_6H_5$. This clearly underscores a facile loss of SO_2 from the sultine complex. By way of contrast, the mass spectrum of $Mn(CO)_5C{=}C(C_5H_5)S(O)_2OCH_2$ contains a strong molecular ion peak (P^+) and other strong peaks due to P^+-nCO (n = 1 to 5). The simple loss of SO_3 is not observed, but relatively weak peaks corresponding to P^+-nCO-SO_2 (n = 1 to 3) are present. The loss of SO_2 is also a typical feature in the mass spectra of organic sultones.[11]

Considerable information is now available which permits a rational mechanistic proposal for the metal-promoted cycloaddition reactions of, *inter alia*, SO_3. The observation that h^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CR$ (R = CH_3, C_6H_5) undergo protonation to yield h^5-C_5H_5Fe-$(CO)_2(h^2$-$CH_2{=}C{=}CHR)^+$,[7,17] which then react with nucleophiles (N) to afford vinyl complexes of the type h^5-$C_5H_5Fe(CO)_2C(CH_2N){=}CHR$,[18] implicates the following general scheme (Scheme 2) for these 1,3-cycloadditions:



Scheme 2

In further support of this pathway is the recent detection[19] of the corresponding zwitterionic olefin intermediates in the reaction of h^5-$C_5H_5M(CO)_nCH_2CH{=}CH_2$ (M = Fe, n = 2; M = Mo, n = 3) with SO_2.

Acknowledgments. We wish to acknowledge support of this research by the National Science Foundation (GP-35647X and preceding grants).

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