Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

Preliminary communication

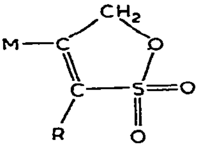
Transition metal-sultone complexes

DALE W. LICHTENBERG and ANDREW WOJCICKI

The McPherson and Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210 (U.S.A.)

(Received October 26th, 1971)

The reactions of electrophiles with complexes containing a transition metal–carbon σ-bond have afforded a variety of novel insertion and addition products[1]. However, only one example of a sulfur trioxide reaction has been reported among them: insertion of SO_3 into the Re–C (alkyl or aryl) bond of $RRe(CO)_5$[2]. The interaction of transition metal-2-alkynyl complexes with sulfur dioxide[3-6], *N*-thionylaniline[7], and tetracyanoethylene[8] has been shown to yield vinyl complexes containing a five-membered ring. In our studies to determine the generality of this reaction with electrophiles, we have found that transition metal-2-alkynyls react with sulfur trioxide to yield vinyl–sultone complexes (I: M = $\pi\text{-}C_5H_5Fe(CO)_2$, R = CH_3 and C_6H_5; M = $\pi\text{-}C_5H_5Mo(CO)_3$, R = C_6H_5; M = $Mn(CO)_5$, R = CH_3 and C_6H_5).



(I)

In a typical reaction, equimolar amounts of dioxane·SO_3 and $Mn(CO)_5CH_2C\equiv CCH_3$ were stirred in CH_2Cl_2 at 0° for 10 min. The resulting solution was neutralized with aqueous $NaHCO_3$, dried over $MgSO_4$, filtered, and evaporated to dryness. The light yellow residue was recrystallized from hot benzene to yield (40%) white needles of the vinyl–sultone complex, $(CO)_5Mn\text{-}\overline{C{=}C(CH_3)\text{-}S(O)_2\text{-}O\text{-}C}H_2$.

In a similar manner, the other sultone complexes have been isolated (40–70% yield) as crystalline solids which are soluble in acetone and chloroform, sparingly soluble in benzene, and insoluble in saturated hydrocarbons and water. They all decompose slowly above ca. 145° *in vacuo* without melting. Elemental analyses for these complexes agree with the calculated values.

The infrared spectra of the vinyl-sultones are presented in Table 1. It is notable that their CO stretching frequencies are, within experimental error, identical with those of the corresponding vinyl–sultine complexes. The SO stretching modes in the former compounds give rise to strong bands at ca. 1310 and 1175 cm^{-1}. Organic sultones, for comparison, show strong absorptions[9] at ca. 1360 and 1180 cm^{-1}.

TABLE 1

IR SPECTRA OF THE VINYL-SULTONE COMPLEXES (I) IN THE ν(CO) AND ν(SO) REGIONS[a]

Compound		Absorption maxima (cm^{-1})	
M	R	ν(CO)	ν(SO) region
π-$C_5H_5Fe(CO)_2$	CH_3	2040 vs, 1975 vs	1301 s, 1181 vs, 1136 m, 913 m
π-$C_5H_5Fe(CO)_2$	C_6H_5	2035 vs, 1985 vs	1303 s, 1222 w, 1164 vs, 913 m
π-$C_5H_5Mo(CO)_3$	C_6H_5	2030 vs, 1975 vs, 1930 vs	1310 s, 1221 w, 1170 vs, 935 m, 918 m
$Mn(CO)_5$	CH_3	2140 s, 2030 vs, br	1316 s, 1186 s, 1135 m, 1066 m, 928 s
$Mn(CO)_5$	C_6H_5	2135 s, 2030, 2015 vs (br)	1322 s, 1226 m, 1176 vs, 938 m, 921 m

[a]KBr pellet, Perkin–Elmer Model 337 spectrophotometer.

The ^1H NMR spectra of the sultone complexes are listed in Table 2. As expected for a sultone structure, the $-CH_2-O$ protons, absorbing at τ4.84—5.14, are equivalent. The positions of these signals are ca. 0.4 ppm upfield from the average of the $-CH_2-O$ resonances in the corresponding sultine complexes. The CH_2/CH_3 proton coupling constant for the methyl sultone complexes ($R = CH_3$) is 2 Hz, identical with that for the sultine analogs[3].

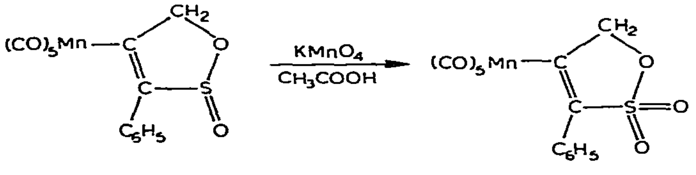
TABLE 2

^1H NMR SPECTRA OF THE VINYL-SULTONE COMPLEXES (I)[a]

Compound		Chemical shift (τ)		
M	R	$-CH_2-O$	R	$M(C_5H_5)$
π-$C_5H_5Fe(CO)_2$	CH_3	5.14 q (J = 2 Hz)	(CH_3), 7.83 t (J = 2 Hz)	5.02 s
π-$C_5H_5Fe(CO)_2$	C_6H_5	4.98 s	(C_6H_5), 2.54 s	5.22 s
π-$C_5H_5Mo(CO)_3$	C_6H_5	4.93 s	(C_6H_5), 2.53 s	4.70 s
$Mn(CO)_5$	CH_3	4.98 q (J = 2 Hz)	(CH_3), 7.77 t (J = 2 Hz)	—
$Mn(CO)_5$	C_6H_5	4.84 s	(C_6H_5), 2.54 s	—

[a]$CDCl_3$ solution, Varian A60-A spectrometer.

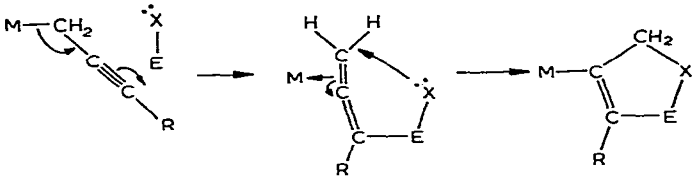
The vinyl-sultine complex $(CO)_5Mn-C=C(C_6H_5)-S(O)-O-CH_2$, prepared from $Mn(CO)_5CH_2C{\equiv}CC_6H_5$ and SO_2, has been oxidized to the analogous vinyl-sultone (42% yield) with $KMnO_4$ in aqueous acetic acid:



thus providing further support for the assigned structure. Organic sultines are also readily oxidized to the corresponding sultones[10-12].

A series of electrophiles (EX:) have now been shown to react with transition metal-2-alkynyl complexes to form vinyl derivatives of the type

$M\text{-}\overline{C{=}C(R)\text{-}E\text{-}X\text{-}C}H_2$. Our recent isolation and characterization of the π-allene complex $[\pi\text{-}C_5H_5Fe(CO)_2(CH_2{=}C{=}CHC_6H_5)]BF_4$ from the reaction of $\pi\text{-}C_5H_5Fe(CO)_2CH_2C{\equiv}CC_6H_5$ with HBF_4[13] implicates the following general scheme in the formation of these 1,3-cycloaddition products:



ACKNOWLEDGMENT

We are grateful to the National Science Foundation for support.

REFERENCES

1 A. Wojcicki, *Accounts Chem. Res.*, 4 (1971) 344.
2 E. Lindner and R. Grimmer, *Chem. Ber.*, 104 (1971) 544.
3 J.E. Thomasson, P.W. Robinson, D.A. Ross and A. Wojcicki, *Inorg. Chem.*, 10 (1971) 2130.
4 M.R. Churchill and J. Wormald, *J. Amer. Chem. Soc.*, 93 (1971) 354.
5 J. -L. Roustan and C. Charrier, *C.R. Acad. Sci. Paris*, 268 (1969) 2113.
6 W.D. Bannister, B.L. Booth, R.N. Haszeldine and P.L. Loader, *J. Chem. Soc. A*, (1971) 930.
7 P.W. Robinson and A. Wojcicki, *Chem. Commun.*, (1970) 951.
8 S.R. Su and A. Wojcicki, *J. Organometal. Chem.*, 31 (1971) C34.
9 R.B. Scott and M.S. Heller, *J. Org. Chem.*, 31 (1966) 1999.
10 E.N. Givens and L.A. Hamilton, *J. Org. Chem.*, 32 (1967) 2857.
11 J.F. King, K. Piers, D.J.H. Smith, C.L. McIntosh and P. DeMayo, *Chem. Commun.*, (1969) 31.
12 R.S. Henion, *Eastman Organic Chemical Bulletin*, Vol. 41, No. 3, Eastman Kodak Co., Rochester, N.Y.,1969.
13 D.W. Lichtenberg and A. Wojcicki, unpublished results.