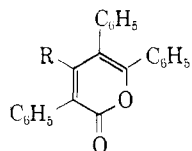


sensitizer behavior suggests that this reaction pathway is not available.<sup>12</sup>

In summary, these data suggest that electronically excited states of the pyrylium oxide II are not intermediates in the photochemical reaction  $I \rightarrow II$ , nor are electronically excited states of the indenone oxide I intermediates in the reverse process.<sup>13</sup> Thus by elimination, *both reactions probably proceed by way of vibrationally excited ground electronic states formed by isoenergetic crossing from  $T_1$ ,  $T_{II}$ , and possibly also  $S_1$  and  $S_{II}$ .*<sup>14</sup>

Similar though less complete data have been obtained for the photointerconversions  $III \rightleftharpoons IV$ . The effects of sensitizers are parallel to those described above, while direct irradiation of III but not IV causes rearrangement to the pyrone VIII.<sup>1b,c,15</sup> Arguments similar to those given again point to reaction by way of a vibrationally excited ground state.



VIII (R = H or C<sub>6</sub>H<sub>5</sub>)

Of particular interest is the observation that lowering the temperature reduces the quantum yields for reactions  $II \rightarrow I$  and  $IV \rightarrow III$ .<sup>1b</sup> An attractive but not unique interpretation of these results may be made in terms of the relative energies of the transition states in the thermal isomerizations and of the vibrationally excited ground states of II and IV formed by isoenergetic crossing from the electronically excited states. Thus the energies of the electronically excited states and transition states are probably sufficiently close to each other that collisional deactivation of the vibrationally excited states may compete with rearrangement to the corresponding epoxides. At increased temperatures more successful competition with collisional deactivation should occur since more energetic vibrationally excited ground states would be produced by internal conversion from thermally populated higher vibrational levels of the electronically excited states.

This reasoning suggests that successful competition with collisional deactivation should also become more likely on lowering the thermal transition state energies. A rough parallel between the quantum yields and thermal rates of reactions  $II \rightarrow I$  and  $IV \rightarrow III$  would be expected, since the energies of at least the singlets of II and IV are very similar. The observed order of quantum yields at 77°K.,  $II \gg IV$  (R = C<sub>6</sub>H<sub>5</sub>) >  $IV$  (R = H), and the thermal fading rates

(12) Additional evidence that nonvertical energy transfer does not play a role in sensitized reaction  $I \rightarrow II$  is found in the absence of energy transfer from sensitizer triplets of energies substantially below the maximum possible triplet energy of I ( $E_{T1} < E_{S1} = 74$  kcal.). By contrast relatively large apparent uphill energy transfers are frequently associated with the nonvertical energy transfer process; cf. ref. 10 and 11.

(13) Rearrangement of  $S_{II}$  or  $T_{II}$  to  $S_1$  or  $T_1$  is energetically forbidden, for  $E_{SII}$  (50 kcal.)<sup>9</sup> is at least 12 kcal. less than  $E_{T1}$  (~68 kcal.) when related to the energy difference of the ground states ( $\Delta F = 6$  kcal.). Thus  $E_{S1} > E_{SII}$  and  $E_{T1} > E_{TII}$ , both by more than 12 kcal.

(14) Since the preparation of this manuscript it has been found that quenching of reaction  $I \rightarrow II$  approaches a limit (quantum yield reduced by 11%) with increasing naphthalene concentrations. This strongly suggests that 89% of II is formed directly from  $S_1$  without the intermediacy of  $T_1$ .

(15) We are indebted to Professor P. Yates for providing a generous supply of III (R = C<sub>6</sub>H<sub>5</sub>).

$k^{25^\circ}_{II} \approx 5 \times 10^{-6}$  sec.<sup>-1</sup>,  $k^{25^\circ}_{IV(R=C_6H_5)} \approx 8 \times 10^{-7}$  sec.<sup>-1</sup>, and  $k^{25^\circ}_{IV(R=H)} \approx 0$ , are in accord with this prediction.

**Acknowledgment.**—We are greatly indebted to Dr. T. F. Ziegler for aid in the preparation and counting of radioactive samples.

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RECEIVED JULY 24, 1964

### A Novel Reaction of Transition Metal Alkyls and Aryls. Sulfur Dioxide Insertion

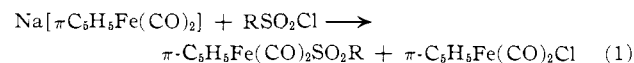
Sir:

Extensive investigations of organic reactions catalyzed by transition metal carbonyls resulted in the discovery of interesting and intriguing carbon monoxide insertion<sup>1</sup> and decarbonylation processes.<sup>2,3</sup> Subsequent experiments by Kebly and Filbey,<sup>4</sup> Booth and Chatt,<sup>5</sup> and Heck and Breslow,<sup>6</sup> as well as mechanistic studies of interconversion of acetyl- and methylmanganese carbonyl complexes by Calderazzo and Cotton,<sup>7</sup> and, more recently, by Mawby, Basolo, and Pearson,<sup>8</sup> point to a facile migration of the methyl group directly bonded to a number of transition metals.

These observations and a general interest in catalysis by complexes prompted us to commence a detailed investigation of the versatility of low-valent metals in effecting insertion and migration processes of small groups or fragments, similar in nature to carbon monoxide. This note describes some preliminary results which indicate that such reactions may be much more general than has been hitherto realized.

A recent report<sup>9</sup> of the synthesis of sulfur dioxide derivatives of iron carbonyls suggested to us an interesting analogy. There is a remarkable structural similarity between the acyl (CO + alkyl) and unknown sulfonyl (SO<sub>2</sub> + alkyl) metal complexes, and therefore it appeared reasonable that the latter might exhibit certain aspects of the chemical behavior characteristic of the former systems.

Investigation of cyclopentadienyliron dicarbonyl complexes has shown that this is indeed the case. Reaction of  $Na[\pi-C_5H_5Fe(CO)_2]$  with alkyl (CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>) and aryl (C<sub>6</sub>H<sub>5</sub>) sulfonyl chlorides affords, in addition to  $\pi-C_5H_5Fe(CO)_2Cl$ , small amounts of iron sulfonyl carbonyls (eq. 1). The sulfonyl complexes,



which may be separated from the carbonyl chloride by alumina chromatography, are yellow, crystalline com-

(1) The word *insertion* is not to be interpreted literally from a mechanistic point of view. In this paper, *insertion* has structural significance only; see R. J. Mawby, F. Basolo, and R. G. Pearson, *J. Am. Chem. Soc.*, **86**, 5043 (1964).

(2) T. H. Coffield, J. Kozikowski, and R. D. Closson, Special Publication No. 13, The Chemical Society, London, 1959, p. 126.

(3) R. D. Closson, T. H. Coffield, and J. Kozikowski, *J. Org. Chem.*, **22**, 598 (1957).

(4) K. A. Kebly and A. H. Filbey, *J. Am. Chem. Soc.*, **82**, 4204 (1960).

(5) G. Booth and J. Chatt, *Proc. Chem. Soc.*, 67 (1961).

(6) R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, **83**, 4023 (1961).

(7) F. Calderazzo and F. A. Cotton, *Inorg. Chem.*, **1**, 32 (1962).

(8) R. J. Mawby, F. Basolo, and R. G. Pearson, *J. Am. Chem. Soc.*, **86**, 3994 (1964).

(9) E. H. Bray and W. Hübel, *Angew. Chem.*, **75**, 345 (1963).

TABLE I  
 PROPERTIES OF SULFONYL COMPLEXES

Complex	Proce- dure <sup>a</sup>	Yield, %	Color	M.p., °C. <sup>b</sup>	Molecular weight		Analyses <sup>d</sup>							
					Calcd.	Found <sup>c</sup>	Carbon, %		Hydrogen, %		Sulfur, %		Iron, %	
							Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
$\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{SO}_2\text{CH}_3$	1	2.0	Yellow	135	256	262	37.60	37.36	3.10	2.99	12.50	12.70	21.87	21.64
	2	95 <sup>e</sup>	Yellow	135				37.80		3.32		12.76		21.80
$\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{SO}_2\text{C}_2\text{H}_5$	1	1.9	Yellow	165	270		40.00	39.94	3.71	3.88	11.83	11.61	20.75	20.86
	2	91 <sup>e</sup>	Yellow	165		306		40.16		3.83		11.68		21.12
$\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{SO}_2\text{C}_6\text{H}_5$	1	2.3	Yellow	137	318	341	49.06	49.02	3.14	3.19	10.05	10.11	17.65	17.76
	2	37 <sup>e</sup>	Yellow	137		348		49.15		3.25		9.86		17.29

<sup>a</sup> Procedure 1,  $\text{Na}[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2] + \text{RSO}_2\text{Cl}$ ; procedure 2,  $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R} + \text{SO}_2$ . <sup>b</sup> Taken with a melting point block and uncorrected. <sup>c</sup> Osmometry,  $1 \times 10^{-2}$ – $2 \times 10^{-2}$  *M* solution in  $\text{CHCl}_3$ . <sup>d</sup> Galbraith Laboratories, Inc. <sup>e</sup> Under conditions described in the note.

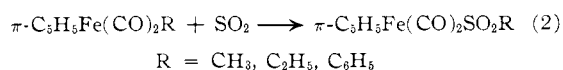
 TABLE II  
 INFRARED AND PROTON MAGNETIC RESONANCE SPECTRA

Complex	Infrared <sup>a</sup>		N.m.r. <sup>b</sup>		
	CO stretching frequencies, cm. <sup>-1</sup>	SO stretching frequencies, cm. <sup>-1</sup>	Chemical shift, $\tau$	Relative intensity	Assignment
$\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{SO}_2\text{CH}_3$	2045 (vs), 1991 (vs)	1191 (vs) <sup>c</sup>	4.75 (singlet) 6.85 (singlet)	5 3	$\pi\text{-C}_5\text{H}_5$ $\text{CH}_3$
$\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{SO}_2\text{C}_2\text{H}_5$	2065 (vs), 2021 (vs)	1188 (vs) <sup>c</sup>	4.58 (singlet) 6.70 (quartet) <sup>d</sup> 8.49 (triplet) <sup>d</sup>	5 2 3	$\pi\text{-C}_5\text{H}_5$ $\text{CH}_2$ $\text{CH}_3$
$\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{SO}_2\text{C}_6\text{H}_5$	2055 (vs), 2003 (vs)	1193 (vs) <sup>c</sup>	2.0–2.5 (complex multiplets) 4.75 (singlet)	5 5	$\text{C}_6\text{H}_5$ $\pi\text{-C}_5\text{H}_5$

<sup>a</sup> Perkin-Elmer Model 337,  $\text{CHCl}_3$  solution. <sup>b</sup>  $\text{CDCl}_3$  solution. <sup>c</sup> Cyclopentadienyl absorption bands preclude complete assignment; see discussion. <sup>d</sup> Separation  $\sim 8$  c.p.s.

pounds with sharp melting points. The solids appear to be indefinitely stable; however, solutions in chloroform show signs of decomposition after several days of exposure to air. The yields, elemental analyses, and other data on the products are summarized in Tables I and II.

When sulfur dioxide is condensed into a trap containing a cyclopentadienyliron carbonyl alkyl or aryl at  $-40$  to  $-60^\circ$ , the latter dissolves to form a red solution. Evaporation of  $\text{SO}_2$  at room temperature, followed by alumina chromatography of the residual solid, affords, in good yields, cyclopentadienyliron carbonyl sulfonate complexes (eq. 2) which are identical with those obtained from  $\text{Na}[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]$  and  $\text{RSO}_2\text{Cl}$  (see Tables I and II).



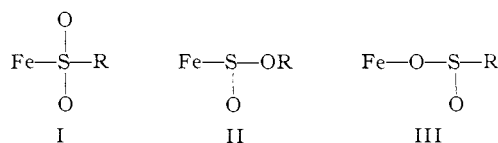
The sulfur dioxide insertion reaction takes place rapidly with the methyl and ethyl derivatives, and more slowly with the phenyl compound. This is evidenced by an instantaneous color change on addition of  $\text{SO}_2$  to a carbonyl alkyl, and also by the absence of the latter in the crude product. However, under similar conditions (evaporation of liquid  $\text{SO}_2$  immediately after the sample of the alkyl had completely dissolved), only about 40% of  $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{C}_6\text{H}_5$  is converted to  $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{SO}_2\text{C}_6\text{H}_5$ .

Nuclear magnetic resonance spectra of the products rule out structures  $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2(\text{SO}_2)\text{R}$ , in which the groups R and  $\text{SO}_2$  are coordinated separately to the metal. The methylsulfonyl complex, for example, shows sharp proton signals at  $\tau$  4.75 and 6.85 (relative intensities 5:3). These are assigned to the cyclopentadienyl and methyl hydrogens, respectively. The proton resonance absorptions in  $\text{CH}_3\text{SO}_2\text{Cl}$  and  $\text{CH}_3\text{-SO}_2\text{F}$  occur at  $\tau$  6.36 and 6.73,<sup>10</sup> respectively, whereas

methyl groups directly bonded to a transition metal give rise to signals at much higher fields (*ca.*  $\tau$  10).<sup>11</sup>

Infrared spectra of the derivatives show two strong metal carbonyl stretching frequencies at 1990–2070  $\text{cm}^{-1}$ ; this feature is consistent with a dicarbonyl structural assignment. Moreover, a notable absence of any bands in the 1450–1800  $\text{cm}^{-1}$  spectral region indicates that the products are not acyl complexes.<sup>5</sup>

The bonding in the  $\text{FeSO}_2\text{R}$  moiety cannot be definitely established at present. Consideration of high affinity of iron for sulfur<sup>12</sup> and assumption that no alkyl group migration takes place in reaction 1 suggest that the most likely structure is I. However,



the attachments II and III cannot be precluded on the basis of the available spectral data. Proton magnetic resonance spectroscopy does not differentiate between S- and O-bonded methyl groups in known sulfur-oxygen compounds; both give rise to absorptions in the region  $\tau$  6.0–7.5.<sup>10</sup> Moreover, each of the three possible structures is expected to exhibit two infrared active SO stretching frequency modes. In the iron sulfonyl derivatives, one SO fundamental is observed at 1188–1193  $\text{cm}^{-1}$ ; the other cannot be unambiguously assigned because of cyclopentadienyl group absorptions. Experiments are now in progress to possibly resolve this aspect of the bonding.

It is of interest to note that reactions of  $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}$  with  $\text{SO}_2$  result in the formation of sulfonyl-

(11) See T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956).

(12) See, for example, R. B. King, *J. Am. Chem. Soc.*, **85**, 1584 (1963), and references therein; also, R. L. Downs, A. Wojcicki, and P. J. Pollick, Abstracts of papers presented at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Aug. 30–Sept. 4, 1964, p. 31-O.

(10) Communication from Dr. G. V. D. Tiers to the Department of Chemistry, The Ohio State University.

rather than acylmetal carbonyls. The latter are to be expected on the basis of mechanistic studies of carbon monoxide insertion and decarbonylation reactions of manganese carbonyl systems.<sup>2,7,8</sup> The attachment of the alkyl group to SO<sub>2</sub> in  $\pi$ -C<sub>5</sub>H<sub>5</sub>Fe(CO)<sub>2</sub>SO<sub>2</sub>R may result from an initial formation of acyl sulfur dioxide complexes,  $\pi$ -C<sub>5</sub>H<sub>5</sub>Fe(CO)(COR)SO<sub>2</sub>, followed by a rapid migration of R onto the SO<sub>2</sub> ligand. However an alternative possibility—direct attack of SO<sub>2</sub> on iron, accompanied by a transfer of R—cannot be ruled out at present. Both of these mechanisms are consistent with a relatively slow insertion reaction of  $\pi$ -C<sub>5</sub>H<sub>5</sub>Fe(CO)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>, since in each case migration of a bulky phenyl group would be involved.

Work continues on the synthesis of the analogous sulfonyl complexes of other transition metals and on the mechanism of sulfur dioxide insertion.

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### Gaseous Alane and Dialane

Sir:

The only trivalent hydride of aluminum that has hitherto been reported in the literature is the crystalline (AlH<sub>3</sub>)<sub>x</sub>.<sup>1</sup> We now wish to describe the conditions under which the gaseous hydrides AlH<sub>3</sub> and Al<sub>2</sub>H<sub>6</sub> can be observed. Because of the electron-deficient character of monomeric AlH<sub>3</sub>, it is predictable that this molecule would readily polymerize at normal pressures, as would also the dimeric Al<sub>2</sub>H<sub>6</sub> in which the aluminum atoms have coordination numbers of four rather than six. Accordingly, the molecules AlH<sub>3</sub> and Al<sub>2</sub>H<sub>6</sub> can only be sought at very low pressures where the polymerization rates are minimized. The technique selected for this study was to follow, in a continuous fashion by time-of-flight mass spectrometry, the gaseous products formed by slow evaporation of aluminum from a hot tungsten filament into hydrogen at low pressure. Siegel<sup>2</sup> had previously shown that the evaporation of aluminum into a hydrogen pressure of about 1 mm. can result in the trapping out of a solid aluminum hydride at -195°. However, the latter study was carried out in a static system, while the present investigation is with a flow system at even lower hydrogen pressures and no cold wall. The present authors<sup>3</sup> have demonstrated previously the utility of time of flight mass spectrometry in studying gaseous hydrides formed at low pressures; Fehlner and Koski<sup>4</sup> have observed the analogous BH<sub>3</sub> molecule directly by mass spectrometry, despite the fact that it is normally present in very small amounts in equilibrium with B<sub>2</sub>H<sub>6</sub>.

Our general method was as follows. In a glass high vacuum system, purified hydrogen was continuously flown past a tungsten wire heating element charged with an aluminum wire which had been melted to a liquid droplet. The pressure at the heating element, as measured by a McLeod gauge, was maintained at 0.3 mm. by a pumping system. During the course of a

run, the temperature of the aluminum charge, as measured by an optical pyrometer, was raised gradually in small increments. It was necessary to have the optical pyrometer at a window offset several inches from the reactor wall since unchanged aluminum deposited rapidly on the wall. Downstream of the aluminum droplet, the flow system divided into paths leading to the pump and to the gold leak of the fast reaction inlet system of a Bendix time-of-flight mass spectrometer. Commencing with the first heating of the aluminum charge, continuous recordings of the mass spectra were obtained as the temperature was increased, a new spectrum being obtained every 3 to 5 min., with an ionizing potential of 70 e.v. The geometry and flow rate were such that the residence time, from introduction of aluminum vapor to mass spectrometer sampling, was 39 msec., with aluminum evaporation rates in the temperature range 1170-1250° of 0.09 to 0.12 mg./sec.

Numerous mass spectra taken at aluminum droplet temperatures up to 1030° gave no evidence of hydride formation. However, a small mass peak at  $m/e = 30$  was observed when the droplet temperature reached approximately 1090°. That this could be attributed to AlH<sub>3</sub><sup>+</sup> was verified by substitution of deuterium for hydrogen, whereupon we observed the expected shift to  $m/e = 33$ . The intensity of the AlH<sub>3</sub><sup>+</sup> peak remained constant over a number of mass spectra. A mass peak for Al<sub>2</sub>H<sub>6</sub><sup>+</sup> was not observed in these spectra. When the temperature of the aluminum droplet was increased to about 1170°, a mass peak at  $m/e = 60$  was noted with hydrogen. That this was due to Al<sub>2</sub>H<sub>6</sub><sup>+</sup> was demonstrated by a shift to  $m/e = 66$  when deuterium was substituted for hydrogen. When Al<sub>2</sub>H<sub>6</sub><sup>+</sup> was first observed, the ratio of ion intensities, Al<sub>2</sub>H<sub>6</sub><sup>+</sup>/AlH<sub>3</sub><sup>+</sup>, was only 0.1 to 0.5. Upon further heating of the aluminum droplet, this ratio progressively increased, ultimately reaching 11 before the aluminum droplet was depleted. The ratio of ion intensities AlH<sub>3</sub><sup>+</sup>/H<sub>2</sub><sup>+</sup> was 0.0017 for most spectra, while the Al<sub>2</sub>H<sub>6</sub><sup>+</sup>/H<sub>2</sub><sup>+</sup> ratio rose to a maximum of 0.019.

Since AlH<sub>3</sub><sup>+</sup> was observed at lower aluminum vapor pressures than was the case for Al<sub>2</sub>H<sub>6</sub><sup>+</sup>, and since the ratio Al<sub>2</sub>H<sub>6</sub><sup>+</sup>/AlH<sub>3</sub><sup>+</sup> progressively increased with temperature, it is clear that these ions are indicative of the neutral species AlH<sub>3</sub> and Al<sub>2</sub>H<sub>6</sub>. From the data, it is also apparent that monomeric AlH<sub>3</sub> is the first hydride to be formed at the lowest pressures of aluminum. However, when the latter become more appreciable, the dimerization 2AlH<sub>3</sub> → Al<sub>2</sub>H<sub>6</sub> becomes predominant. Mass spectra at mass numbers up to 120 were also taken, but higher polymers were not observed under the conditions described.

From equilibrium vapor pressure data on aluminum<sup>5</sup> and the observed aluminum droplet temperatures corresponding to hydride formation, the initial concentrations of Al vapor in H<sub>2</sub> were ~0.43% for AlH<sub>3</sub> formation and ~1.7% for Al<sub>2</sub>H<sub>6</sub> formation at minimum intensity. Without knowledge of the ionization cross section for Al<sub>2</sub>H<sub>6</sub>, its pressure cannot be computed exactly from the relative abundances of Al<sub>2</sub>H<sub>6</sub><sup>+</sup>/H<sub>2</sub><sup>+</sup>. However, by assigning a maximum ratio of 100 to the

(1) A. E. Finholt, A. C. Bond, and H. I. Schlesinger, *J. Am. Chem. Soc.*, **69**, 1199 (1947).

(2) B. Siegel, *ibid.*, **82**, 1535 (1960).

(3) P. Breisacher and B. Siegel, *ibid.*, **85**, 1705 (1963).

(4) T. P. Fehlner and W. C. Koski, *ibid.*, **86**, 2733 (1964).

(5) J. L. Margrave in "Physicochemical Measurements at High Temperatures," J. O'M. Bockris, J. L. White, and J. D. Mackenzie, Eds., Butterworth and Co. (Publishers), Ltd., London, 1959, p. 369.