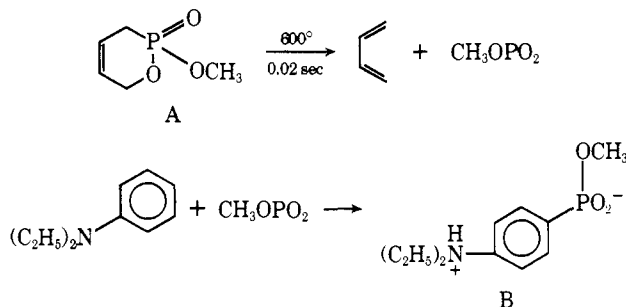


yield (among other products) the monomethyl ester of *p*-diethylaminobenzene phosphonic acid (B). This aromatic electrophilic substitution reaction fully substantiates the claim<sup>1</sup> for monomeric methyl metaphosphate.



The pyrolyses of 0.5–1.0 mmol of phosphonate, A, were conducted as previously described;<sup>1</sup> mixtures of 1.2 g of purified diethylaniline and 3.5 g of purified *n*-butylbenzene were cooled in a dry ice–isopropyl alcohol bath and stirred magnetically in the pyrolysis trap. After the furnace had cooled to 30°, the volatile materials were vacuum distilled from the trap at room temperature. The trap was washed with 8 ml of methylene chloride and 10 ml of 0.1 *N* barium hydroxide. The aqueous layer was extracted with 7 ml of methylene chloride, neutralized with CO<sub>2</sub>, centrifuged, and evaporated; the resulting white residue was extracted with four portions of methanol totaling 7 ml. The extract was then evaporated to 0.1 ml, diluted with 0.1 ml of water, and chromatographed on a 20 × 20 × 0.25 cm precoated silica gel plate with acetonitrile–methanol–water (6:3:1) as developing solvent; the material from the major zone (*R<sub>f</sub>* = 0.35–0.42) was freed of several impurities by high-pressure liquid chromatography, using a 1/8 in. × 2 ft Bondapak C-18/Porasil B column and a Waters Associates ALC 202 high-pressure liquid chromatography apparatus. The product was monitored at 254 nm and appeared after approximately 27 min elution with deionized water at 500 psi.

An authentic sample of phosphonate was prepared by the photochemical analogue<sup>2</sup> of the Arbuzov reaction followed by saponification. *p*-Iododiethylaniline<sup>3</sup> (6.35 g) and trimethyl phosphite (20 g) were photolyzed under nitrogen for 78 hr at 253.7 nm in a Srinivasan–Griffin Rayonet photochemical reactor at 10–15°. Excess trimethyl phosphite and dimethyl methylphosphonate were removed by low pressure distillation at 35°. The viscous yellow residue was extracted with 150 ml of boiling hexanes in four portions, to produce 2.2 g of crystalline product; subsequent sublimation at 100–110° (0.8 mm) and recrystallization from hexanes gave 1.3 g of colorless needles of dimethyl *p*-diethylaminobenzene phosphonate, mp 84–85°. Anal. Calcd for C<sub>12</sub>H<sub>20</sub>NO<sub>3</sub>P: C, 56.03; H, 7.84; N, 5.44; P, 12.04. Found: C, 56.22; H, 7.88; N, 5.41; P, 12.10. NMR (CCl<sub>4</sub>) δ 1.18 (t, *J* = 7 Hz; CH<sub>3</sub>), 3.62 (d, *J* = 11 Hz; OCH<sub>3</sub>), 3.40 (q, *J* = 7 Hz), 6.6, 7.5 (aromatic multiplet).

Dimethyl *p*-diethylaminobenzene phosphonate (223 mg) was hydrolyzed with saturated barium hydroxide solution at 95° for 2.5 hr. The barium salt of methyl *p*-diethylaminobenzene phosphonic acid (227 mg) was isolated from the reaction mixture and purified by high-pressure chromatography as with the salt obtained from the trapping experiment. Anal. Calcd for (C<sub>11</sub>H<sub>17</sub>NO<sub>3</sub>P)<sub>2</sub>Ba·H<sub>2</sub>O: C, 41.30; H, 5.67; N, 4.38; P, 9.68; Ba, 21.47. Found: C, 41.43; H, 5.55; N, 4.30; P, 9.65; Ba, 21.62.

The <sup>1</sup>H NMR spectra of the barium salts from the synthesis and from the trapping experiments, shown in Figure 1, were obtained in D<sub>2</sub>O as solvent, with added K<sub>2</sub>CO<sub>3</sub>, with a Varian Associates XL-100 spectrometer, equipped for Fourier Transform spectra. The spectra demonstrate

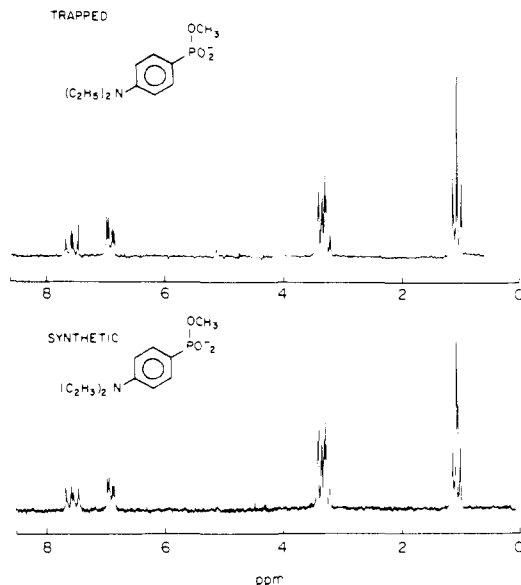


Figure 1. The 100-MHz <sup>1</sup>H NMR spectra of the barium salts of methyl *p*-diethylaminobenzene phosphonate from trapping and synthesis.

that the salts prepared from monomeric methyl metaphosphate and by conventional synthesis are identical; additionally, they confirm the structure. The <sup>31</sup>P spectrum of the crude reaction mixture from the trapping experiment, taken in CDCl<sub>3</sub> with added triethylamine, shows that methyl diethylaminobenzene phosphonate is present; the relevant peak appears at –16.8 ppm, relative to that of 85% phosphoric acid. The best yields of the phosphonate were estimated as only about 3–5%, and were obtained when the 600° zone was less than 0.5 cm from the end of the furnace, and when the butylbenzene–diethylaniline solution was stirred vigorously. In addition to NMR signals from methyl diethylaminobenzene phosphonate and from some unreacted starting material, <sup>31</sup>P spectra associated with pyro, trimeric, and polymeric methyl metaphosphate were observed; these materials constitute the bulk of the pyrolysate.

Despite the low yield, the identification of the aromatic substitution product is definitive; the attack on the ring of diethylaniline at low temperature provides some measure of the electrophilicity of monomeric methyl metaphosphate.

**Acknowledgments.** This research was supported by the National Science Foundation under Grant No. GP-6465X. The NMR spectrometer was purchased under NSF Grant No. GP-32317.

## References and Notes

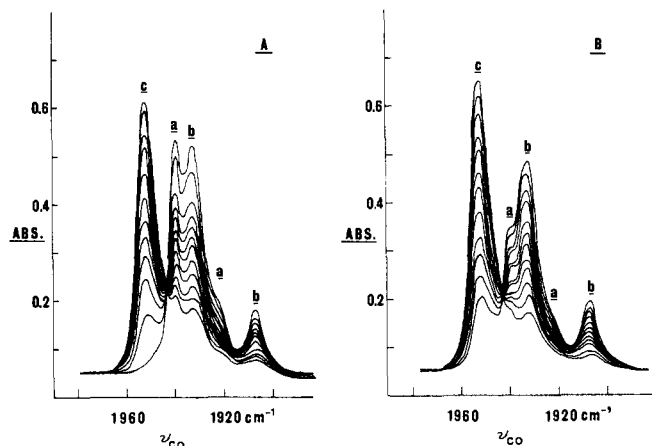
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## Evidence for Hydrogen-Bonded Intermediates in Amine Substitution Reactions Involving Group 6B Metal Pentacarbonyl Amine Derivatives with Phosphines

Sir:

The kinetics of reactions of amine substitution in group 6B metal pentacarbonyl amine derivatives with phosphines

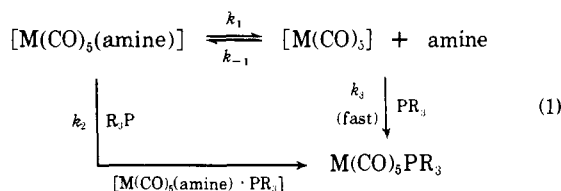


**Figure 1.** Changes in the  $\nu(\text{CO})$  spectra for the reaction of  $\text{Mo}(\text{CO})_5\text{NHC}_5\text{H}_{10}$  with  $(\text{C}_6\text{H}_5)_3\text{P}$  in the presence of tributylphosphine oxide at  $34.5^\circ$  in hexane. Bands labeled a, b, and c correspond to the E +  $A_1$  CO stretching modes in  $\text{Mo}(\text{CO})_5\text{NHC}_5\text{H}_{10}$ ,  $\text{Mo}(\text{CO})_5(\text{NHC}_5\text{H}_{10})\text{OP}(\text{C}_4\text{H}_9)_3$ , and  $\text{Mo}(\text{CO})_5\text{P}(\text{C}_6\text{H}_5)_3$ , respectively: (A)  $[\text{Mo}(\text{CO})_5\text{NHC}_5\text{H}_{10}] = 3.88 \times 10^{-4} \text{ M}$ ,  $[\text{P}(\text{C}_6\text{H}_5)_3] = 0.025 \text{ M}$ , and  $[\text{OP}(\text{C}_4\text{H}_9)_3] = 2.75 \times 10^{-3} \text{ M}$ ; (B)  $[\text{Mo}(\text{CO})_5\text{NHC}_5\text{H}_{10}] = 3.88 \times 10^{-4} \text{ M}$ ,  $[\text{P}(\text{C}_6\text{H}_5)_3] = 0.050 \text{ M}$ , and  $[\text{OP}(\text{C}_4\text{H}_9)_3] = 4.50 \times 10^{-3} \text{ M}$ .

have been shown in several laboratories to obey a rate law of the form<sup>1-4</sup>

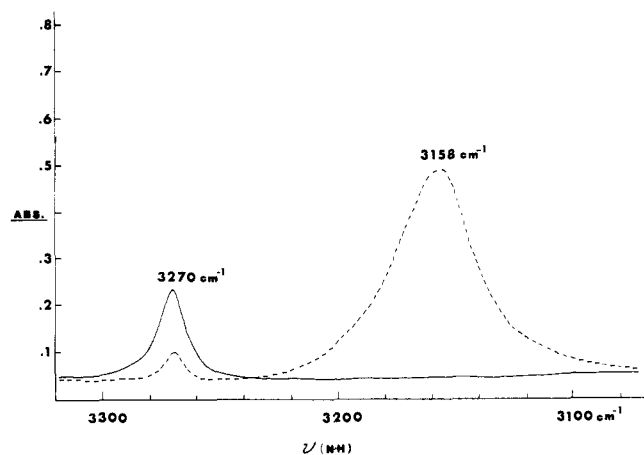
$$\text{rate} = (k_1 + k_2[\text{PR}_3])[\text{M}(\text{CO})_5(\text{amine})]$$

This is interpreted as proceeding by the mechanism below. The associative step ( $k_2$ ) presumably involves an intermediate resulting from interaction of the phosphine at the metal or at a carbonyl carbon.



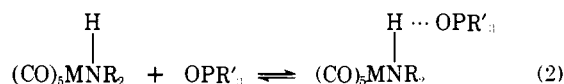
We wish to report in this communication our initial observations in some selected amine substitution processes which involve a spectroscopically identifiable intermediate species. Upon the addition of the phosphine oxides ( $(\text{C}_6\text{H}_5)_3\text{P}=\text{O}$ ,  $(n\text{-C}_4\text{H}_9)_3\text{P}=\text{O}$ , and  $(\text{CH}_3\text{O})_3\text{P}=\text{O}$ ) to a hexane solution of  $\text{M}(\text{CO})_5\text{NHC}_5\text{H}_{10}$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{or W}$ ) a shift in the  $\nu(\text{CO})$  frequencies to lower wave numbers occurs.<sup>5</sup> However, the  $C_{4v}$  structure about the  $\text{M}(\text{CO})_5$  moiety persists when this interaction occurs as indicated by the  $\nu(\text{CO})$  band pattern (Figure 1). For example, the  $\nu(\text{CO})$  frequencies of  $\text{Mo}(\text{CO})_5\text{NHC}_5\text{H}_{10}$  in excess  $(n\text{-C}_4\text{H}_9)_3\text{P}=\text{O}$  are found at 2066, 1930, and  $1906 \text{ cm}^{-1}$  as compared to 2073, 1939, and  $1921 \text{ cm}^{-1}$  in the absence of phosphine oxide (these correspond to the  $A_1^{(2)}$ , E and  $A_1^{(1)}$  vibrational modes, respectively).<sup>3a</sup> In addition, investigation of the infrared spectral properties in the  $\nu(\text{N-H})$  region in  $\text{Mo}(\text{CO})_5\text{NHC}_5\text{H}_{10}$  revealed a shift of this vibration to lower frequency upon addition of the phosphine oxides. As noted in Figure 2 this frequency shift is accompanied by a large enhancement (by a factor of about 8) of the intensity of the shifted  $\nu(\text{N-H})$  vibration. Similarly the deuterated analogue  $\text{Mo}(\text{CO})_5\text{NDC}_5\text{H}_{10}$ , which has a  $\nu(\text{N-D})$  absorption at  $2416 \text{ cm}^{-1}$  ( $\nu(\text{NH})/\nu(\text{ND}) = 1.353$ ), exhibited a shift to lower frequency upon addition of phosphine oxide ( $\nu(\text{NH}\cdots\text{O})/\nu(\text{ND}\cdots\text{O}) = 1.348$ ).<sup>6</sup>

These observations, coupled with the fact that the extent of adduct formation is dependent on the concentration and



**Figure 2.** Infrared spectra in  $\nu(\text{N-H})$  region in  $\text{C}_2\text{Cl}_4$ : (—) spectrum of pure  $\text{Mo}(\text{CO})_5\text{NHC}_5\text{H}_{10}$ ; (---) spectrum of  $\text{Mo}(\text{CO})_5\text{NHC}_5\text{H}_{10}$  with added  $(n\text{-C}_4\text{H}_9)_3\text{PO}$  ( $\nu(\text{CO})$  region as well indicates incomplete adduct formation at this concentration of  $(n\text{-C}_4\text{H}_9)_3\text{PO}$ ).  $\Delta\nu/\nu_0 = 3.4\%$ .

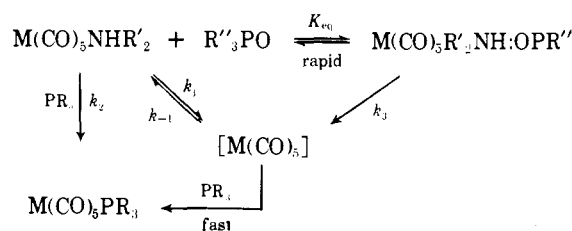
nature of the phosphine oxide (see Figure 1), are taken to be indicative of an equilibrium process involving a hydrogen-bonded species of the type shown below:



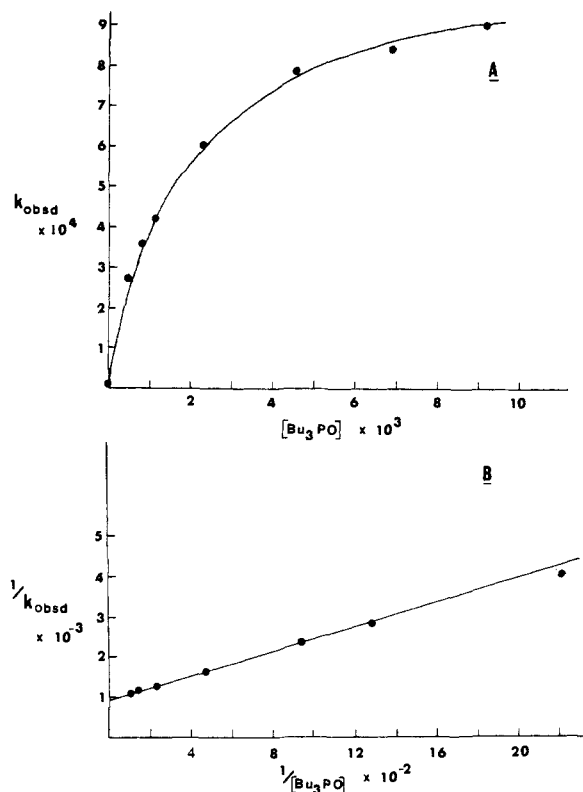
Further evidence for this equilibrium process comes from an analysis of the kinetics associated with subsequent amine replacement reactions to yield  $\text{M}(\text{CO})_5(\text{phosphine})$  derivatives. This substitution process has been studied initially for  $\text{Mo}(\text{CO})_5\text{NHC}_5\text{H}_{10}$  with  $(\text{C}_6\text{H}_5)_3\text{P}$  in the presence of  $(\text{C}_4\text{H}_9)_3\text{P}=\text{O}$ , however, qualitatively similar results have been obtained for other amine group 6B metal derivatives where the bound amine ligand contains a N-H grouping.

Figure 3 illustrates the variation of  $k_{\text{obsd}}$  (obtained from the disappearance of adduct or starting amine complex, see Figure 1)<sup>7</sup> with the concentration of  $(n\text{-C}_4\text{H}_9)_3\text{P}=\text{O}$ . Changes in the concentration (0.0100–0.100 M) of the incoming ligand,  $(\text{C}_6\text{H}_5)_3\text{P}$ , has no effect on the rate of substitution in the presence of hydrogen-bonding ligands. A limiting rate is observed when the amine complex is completely in the adduct form. This same limiting rate is observed whether the incoming ligand is  $(\text{C}_6\text{H}_5)_3\text{P}$  or  $(n\text{-C}_4\text{H}_9)_3\text{P}$ .<sup>8</sup> Dissociation of the amine ligand in the hydrogen-bonded adduct is considerably faster than in the absence of hydrogen bonding, i.e.,  $k_1$  for piperidine dissociation in  $\text{Mo}(\text{CO})_5\text{NHC}_5\text{H}_{10}$  is  $1.36 \times 10^{-5} \text{ sec}^{-1}$  at  $34.5^\circ$  whereas dissociation of piperidine in the  $(n\text{-C}_4\text{H}_9)_3\text{P}=\text{O}$  adduct is  $1.05 \times 10^{-3} \text{ sec}^{-1}$  at  $34.5^\circ$ .

The overall proposed mechanism for substitution of amine ligands in Group 6B metal derivatives,  $\text{M}(\text{CO})_5(\text{amine})$ , is shown below. It is possible that kinetically labile de-



derivatives of the form  $\text{M}(\text{CO})_5(\text{R}''_3\text{PO})$  may be produced from  $[\text{M}(\text{CO})_5]$  and  $\text{R}''_3\text{P}=\text{O}$  as further intermediates which go undetected. However, the  $\text{PR}_3$  concentrations employed in these studies are much greater than that of



**Figure 3.** (A) Observed rate constant vs.  $[(n\text{-C}_4\text{H}_9)_3\text{PO}]$  for the reaction of  $\text{Mo}(\text{CO})_5\text{NHC}_5\text{H}_{10}$  with  $(\text{C}_6\text{H}_5)_3\text{P}$  in the presence of  $(n\text{-C}_4\text{H}_9)_3\text{PO}$ . (B) Reciprocal plot for the reaction of  $\text{Mo}(\text{CO})_5\text{NHC}_5\text{H}_{10}$  with  $(\text{C}_6\text{H}_5)_3\text{P}$  in the presence of  $(n\text{-C}_4\text{H}_9)_3\text{PO}$  (intercept equals  $1/k_3$  and slope equals  $1/k_3K_{\text{eq}}$ ).

$\text{R}'_3\text{P}=\text{O}$  making this fairly unlikely. In any case this would not affect the kinetic analysis given here.<sup>9</sup> For tertiary amines where no hydrogen-bonding can occur or for substitution reactions in the absence of hydrogen-bonding ligands or solvents, the rate law follows the familiar form,<sup>10</sup>

$$\text{rate} = (k_1 + k_2[\text{PR}_3])[\text{M}(\text{CO})_5(\text{amine})]$$

In the presence of hydrogen-bonding ligands or solvents the substitution product  $\text{M}(\text{CO})_5\text{PR}_3$  is obtained in 100% yield which results from the rapid equilibrium ( $K_{\text{eq}}$ ) followed by the rate-determining  $k_3$  term, i.e.,  $\text{rate} = k_3[\text{M}(\text{CO})_5\text{R}'_2\text{NH}\cdot\text{OPR}'_3]$ . For reactions proceeding through the hydrogen-bonded intermediate the observed rate constants obey the expressions

$$k_{\text{obsd}} = \frac{k_3K_{\text{eq}}[\text{OPR}'_3]}{1 + K_{\text{eq}}[\text{OPR}'_3]}$$

or

$$\frac{1}{k_{\text{obsd}}} = \frac{1}{K_{\text{eq}}k_3[\text{OPR}'_3]} + \frac{1}{k_3}$$

as illustrated in Figure 3 for the reaction of  $\text{Mo}(\text{CO})_5\text{NHC}_5\text{H}_{10}$  with  $(\text{C}_6\text{H}_5)_3\text{P}$  in the presence of  $(n\text{-C}_4\text{H}_9)_3\text{P}=\text{O}$ .<sup>11,12</sup> The equilibrium constant,  $K_{\text{eq}}$ , for this reaction was found to be  $600\text{ M}^{-1}$  at  $34.5^\circ$ . Spectroscopic determination of  $K_{\text{eq}}$  for the reaction between  $\text{Mo}(\text{CO})_5\text{NHC}_5\text{H}_{10}$  and  $(n\text{-C}_4\text{H}_9)_3\text{P}=\text{O}$  was in good agreement with that found by kinetic analysis.

This and related systems provide excellent opportunities to carefully investigate the heat of formation of  $\text{M}\text{-NR}_2\text{-H}\cdots\text{OPR}'_3$  bonds since  $K_{\text{eq}}$  for adduct formation (which is measured kinetically) can be obtained quite accurately as a function of temperature. Work along these lines is in progress in our laboratory.

**Acknowledgment.** We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We also thank the Research Corporation for a grant used to purchase the Perkin-Elmer 521 infrared spectrophotometer used in this study.

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- (3) (a) R. J. Dennenberg and D. J. Darensbourg, *Inorg. Chem.*, **11**, 72 (1972); (b) D. J. Darensbourg, M. Y. Darensbourg, and R. J. Dennenberg, *J. Am. Chem. Soc.*, **93**, 2807 (1971).
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- (5) This  $\nu(\text{CO})$  shift has also been observed upon addition of  $(n\text{-C}_4\text{H}_9)_3\text{P}$ ,  $(\text{C}_6\text{H}_5)_3\text{P}$ , and  $(\text{CH}_3\text{O})_3\text{P}$  to  $\text{Mo}(\text{CO})_5\text{NHC}_5\text{H}_{10}$ . However, in these phosphorus ligands it is extremely difficult to eliminate trace quantities of the corresponding oxide species which have been shown to be good hydrogen-bonding ligands. We therefore feel that in these cases the observed shifts are primarily due to the ubiquitous impurities, phosphine oxides, in these phosphorus ligands. This has been verified for the reaction of  $\text{Mo}(\text{CO})_5\text{NHC}_5\text{H}_{10}$  with  $(n\text{-C}_4\text{H}_9)_3\text{P}$ .
- (6) The ratio,  $\nu(\text{NH})/\nu(\text{ND})$ , as calculated by the Teller-Redlich product rule is 1.369.
- (7) Since the two species are related via a rapid equilibrium step, monitoring the disappearance of  $\text{M}(\text{CO})_5\text{NHR}_2$  or  $\text{M}(\text{CO})_5\text{NHR}_2\cdot\text{PR}'_3$  yields the same rate constant.
- (8) Similar rate data were observed for the reaction of  $(n\text{-C}_4\text{H}_9)_3\text{P}$  with  $\text{Mo}(\text{CO})_5\text{NHC}_5\text{H}_{10}$  in the presence of  $(n\text{-C}_4\text{H}_9)_3\text{P}=\text{O}$ .
- (9) There is ir spectral evidence that some  $\text{M}(\text{CO})_5(\text{R}'_3\text{PO})$  forms in solutions where no  $\text{PR}_3$  is added. However, these species are very unstable and therefore difficult to isolate and characterize.
- (10) It should be noted that specific interactions of the type discussed in this communication account for the large deviation in the extrapolated  $k_1$  value for  $(n\text{-C}_4\text{H}_9)_3\text{P}$  substitution reactions of  $\text{W}(\text{CO})_6(\text{amine})$  derivative,<sup>2</sup> as well as some of the solvent effects previously reported.<sup>4</sup> We have also observed similar kinetic and spectral behavior to that reported here for the reaction of  $\text{Mo}(\text{CO})_5\text{NHC}_5\text{H}_{10}$  with  $(\text{C}_6\text{H}_5)_3\text{P}$  in hexane where small quantities of the hydrogen-bonding solvent, THF, has been added.
- (11) It has been brought to our attention by a reviewer that the reaction could be proceeding through the normal rate law,  $\text{rate} = (k_1 + k_2[\text{PR}_3])[\text{M}(\text{CO})_5(\text{amine})]$ , with the hydrogen-bonded adduct being an inert species and not on the reaction coordinate. Kinetically similar behavior would be expected.<sup>12</sup> This should not, however, be the case here since the rates of substitution are much faster than that anticipated on the basis of the normal rate law. In addition, the effect of prior adduct formation on substitution reactions of tungsten is significantly less than that observed for the molybdenum analogue (enhanced by  $<10$  as opposed to 100) which reflects a reduction in steric crowding in the case of tungsten. On the other hand, we would expect an enhanced effect in going from molybdenum to tungsten via the normal mechanism.
- (12) See, for example, J. Halpern, *J. Chem. Educ.*, **45**, 372 (1968), and references therein.

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Received May 16, 1975

## The Epoxidation of Alkenes and the Hydroxylation of Phenols by an Intermediate in the Reaction of Ozone with Alkynes. Possible Model Reactions for Some Flavin-Containing Monooxygenases<sup>1</sup>

Sir:

Although it is now widely believed that the oxygen atom transfer or oxenoid mechanism<sup>2</sup> is involved in many monooxygenase-catalyzed reactions,<sup>3-8</sup> the structures of the various oxenoid reagents have not been elucidated. Recently one of us proposed<sup>4-6</sup> that the oxenoid reagent in flavoenzyme-catalyzed hydroxylations of phenols is a flavin-derived  $\alpha$ -carbonyl carbonyl oxide (or vinylogous ozone), **2**, formed from a flavin hydroperoxide, **1**, as shown in eq 1. By comparison<sup>4-6</sup> with known chemical reactions, including oxidations performed by some unsubstituted carbonyl oxides,<sup>25</sup> it appeared that compounds like **2** should be capable of transferring oxygen atoms to various acceptors but direct evidence for this was not available. In this communication we report experimental results indicating that  $\alpha$ -carbonyl carbonyl oxides, probably in their cyclized trioxide form, are potent oxenoid reagents.