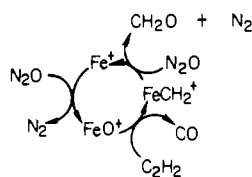
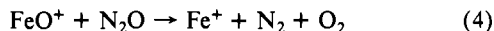


Scheme II



ble-resonance response for  $\text{FeO}^+$  to  $\text{Fe}^+$  reaction which is observed when only  $\text{N}_2\text{O}$  is present may be attributed to reaction 4. This

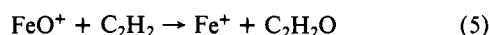


minor process is either very slow or due to a small fraction of excited  $\text{FeO}^+$  molecules.<sup>4</sup> Delayed-ejection double-resonance experiments show that the  $\text{Fe}^+$  produced by reaction 2 reacts again according to reaction 1 and that the complete cycle (Scheme I) occurs repeatedly. No reaction of  $\text{Fe}^+$  is observed in the presence of only CO. With  $\text{N}_2\text{O}$  and CO,  $\text{FeO}^+$  is the only product observed. By assuming that only reactions 1 and 2 are occurring and using the measured rate for reaction 1, the observed variation of ion abundances with time for  $\text{Fe}^+$  and  $\text{FeO}^+$  in mixtures of  $\text{N}_2\text{O}$  and CO can be analyzed to give a rate constant of  $k = 9 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for reaction 2. The same value is obtained by analyzing the delayed-ejection results. Reaction 2 is occurring at its expected Langevin rate,<sup>5</sup> i.e., essentially on every collision. Reaction 1 occurs more slowly, on about every sixth collision.

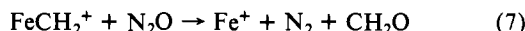
Reactions 1 and 2 involve simple transfer of an oxygen atom from  $\text{N}_2\text{O}$  to  $\text{Fe}^+$  and from  $\text{FeO}^+$  to CO. The homolytic bond dissociation energy for  $\text{FeO}^+$ ,  $D(\text{Fe}^+-\text{O})$ , therefore must lie between  $D(\text{N}_2-\text{O}) = 40 \text{ kcal mol}^{-1}$  and  $D(\text{CO}-\text{O}) = 127 \text{ kcal mol}^{-1}$ .<sup>1b</sup> These limits are consistent with our observations that  $\text{Fe}^+$  will also react with  $\text{O}_3$  to give  $\text{FeO}^+$ ,  $D(\text{O}_2-\text{O}) = 26 \text{ kcal mol}^{-1}$ , but that  $\text{FeO}^+$  is not produced when  $\text{Fe}^+$  is generated in the presence of  $\text{O}_2$ ,  $D(\text{O}-\text{O}) = 119 \text{ kcal mol}^{-1}$ .<sup>1b</sup>

$\text{FeO}^+$  will transfer oxygen atoms to other acceptors in addition to CO. Thus, evidence for catalytic cycles analogous to Scheme I is also seen in mixtures of  $\text{N}_2\text{O}$  with ethylene, propylene, allene, ethane, and propane. In all of these systems other minor ionic products in addition to  $\text{Fe}^+$  are formed when  $\text{FeO}^+$  reacts with the organic neutral. These reactions along with other chemistry of transition-metal oxide cations will be reported in a future paper.<sup>6</sup>

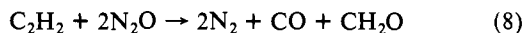
With acetylene an interesting three-step catalytic cycle (Scheme II) is observed to occur.  $\text{FeO}^+$  reacts in part directly to give  $\text{Fe}^+$  (reaction 5), as in Scheme I, but also produces  $\text{FeCH}_2^+$  eliminating



CO (reaction 6).  $\text{FeCH}_2^+$  reacts with  $\text{N}_2\text{O}$  to regenerate  $\text{Fe}^+$  (reaction 7). The net result of this catalytic cycle (reactions 1,



6, and 7) is oxidation of acetylene by two  $\text{N}_2\text{O}$  molecules to give CO and formaldehyde (reaction 8). This overall reaction is



exothermic by 148 kcal/mol.<sup>1b</sup> The branching ratio for reactions 5 and 6 cannot be determined accurately but appears to be approximately 1:1.

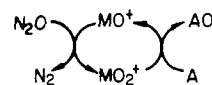
Transition-metal oxide cations can be produced by reaction of  $\text{N}_2\text{O}$  with  $\text{Ti}^+$ ,  $\text{Zr}^+$ ,  $\text{V}^+$ ,  $\text{Nb}^+$ , and  $\text{Cr}^+$  in addition to  $\text{Fe}^+$ . Catalytic cycles involving  $\text{M}^+$  and  $\text{MO}^+$  are not observed for these

(4) Overall, the conversion of two  $\text{N}_2\text{O}$  molecules to an  $\text{O}_2$  and two  $\text{N}_2$  is exothermic by 39.2 kcal mol<sup>-1</sup>.<sup>1b</sup>

(5) Calculation of Langevin rates is discussed in Weston, R. E., Jr.; Schwartz, H. A. "Chemical Kinetics"; Prentice-Hall: Englewood Cliffs, NJ, 1972. Polarizability values for CO of  $\alpha = 1.95 \times 10^{-24} \text{ cm}^3$  and for  $\text{N}_2\text{O}$  of  $\alpha = 3.0 \times 10^{-24} \text{ cm}^3$  were taken from McQuarrie, D. A. "Statistical Thermodynamics"; Harper and Row: New York, 1973. The calculated rates are  $k = 5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for reaction 1 and  $k = 4 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for reaction 2.

(6) Kappes, M. M.; Staley, R. H., in preparation.

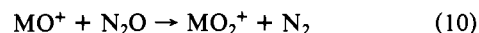
Scheme III



five metals when CO or other simple oxygen acceptors are added. This is because  $D(\text{M}^+-\text{O})$  is too large in these cases. In fact, for Ti, Zr, and Nb,  $\text{CO}_2$  reacts with  $\text{M}^+$  to generate  $\text{MO}^+$  (reaction 9). In other cases neither the forward nor the reverse of reaction



9 is observed, indicating that even in the exothermic direction the reaction is slow. However, further reaction of  $\text{MO}^+$  with  $\text{N}_2\text{O}$  occurs in these five systems to give metal dioxide cations (reaction 10). When simple oxygen acceptors, A, are added, evidence for



a catalytic cycle (Scheme III) involving  $\text{MO}^+$  and  $\text{MO}_2^+$  is observed in each case. With niobium,  $\text{N}_2\text{O}$  can be replaced by  $\text{O}_2$  to give the catalytic cycle. With chromium,  $\text{CrO}_3^+$  is also produced but does not appear to participate in a catalytic cycle. Further details of our observations on the ion chemistry of metal cations with oxidants will be reported separately.<sup>7</sup>

The work presented in this communication is the first example of a new type of ion-molecule reaction. Catalysis in gas phase ion-molecule chemistry has been previously reported for the case of slow proton transfer from toluene to the allyl anion mediated by methanol/methoxy anion.<sup>8</sup> The present work is the first report to our knowledge of catalysis in gas-phase positive ion chemistry. Moreover, it is also the first case of catalysis involving transition-metal species. Other reports of gas-phase transition-metal ion chemistry have recently been appearing with increasing frequency.<sup>2,9</sup> Such studies, including the present work, provide thermochemical data and mechanistic insights which are useful in better understanding the behavior of transition-metal ion species. This promises to continue to be a rapidly advancing field.

**Acknowledgment.** This work was supported by the National Science Foundation by Grant CHE-76-17304.

(7) Kappes, M. M.; Staley, R. H. *J. Phys. Chem.*, submitted for publication.

(8) Brauman, J. I.; Leider, C. A.; White, M. J. *J. Am. Chem. Soc.* **1973**, *95*, 927-928.

(9) For example, see: (a) Cordermann, R. R.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 3998-4000. (b) Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1979**, *101*, 4998-5009. (c) Burnier, R. C.; Carlin, J. J.; Reents, J. J., Jr.; Cody, R. B.; Lengel, R. K.; Freiser, B. S. *J. Am. Chem. Soc.* **1979**, *101*, 7127-7129.

### On the Mechanism of the Fischer-Tropsch Reaction. The Chain Propagation Step

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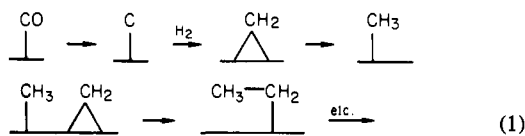
Received November 17, 1980

We wish to report results pertaining to the mechanism of the Fischer-Tropsch reaction, i.e., the conversion of CO and  $\text{H}_2$  to hydrocarbons, principally a mixture of linear alkanes and alkenes, by passage over heterogeneous transition-metal catalysts.

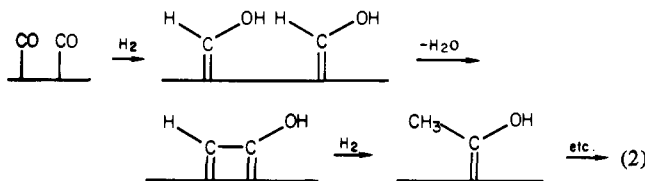
Since the discovery of the reaction, three separate proposals for the mechanism of the reaction have received dominant consideration; the three differ markedly in the manner in which the C-C bonds of the product are purported to be formed. The first, proposed by Fischer and Tropsch in 1926,<sup>1</sup> suggested that the C-C

(1) Fischer, F.; Tropsch, H. *Brennst.-Chem.* **1926**, *7*, 97-116; *Chem. Ber.* **1926**, *59*, 830-836.

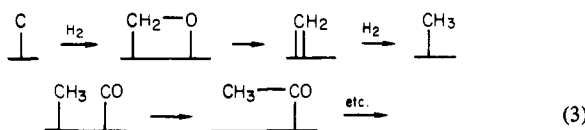
bonds of the product are produced via polymerization of  $\text{CH}_2$  fragments on the metal surface. Through reaction of  $\text{CH}_2\text{N}_2$  under conditions of the reaction, we have recently indicated that in the presence of  $\text{H}_2$  methylene groups do polymerize on such metal surfaces to produce linear hydrocarbons, and the data indicate that the growth occurs via insertion of a surface  $\text{CH}_2$  species into a metal-alkyl bond to generate the next higher homologous alkyl ligand.<sup>2</sup> The essence of the overall scheme is shown in eq 1.



A second mechanism advanced by Anderson and Emmett and their co-workers<sup>3</sup> suggested that the C-C bonds are made through a condensation reaction involving loss of  $\text{H}_2\text{O}$  between hydroxy methylene groups on the surface (eq 2).



The most recent scheme, advanced in 1970 by Pichler and Schultz<sup>4</sup> and subsequently given with minor variations,<sup>5,6</sup> suggested that the C-C bonds arose through insertion of CO into a metal-alkyl bond analogous to the well-known insertion of CO into metal-alkyl bonds in homogeneous systems. The scheme is given in eq 3; of importance to the present work is that the initial

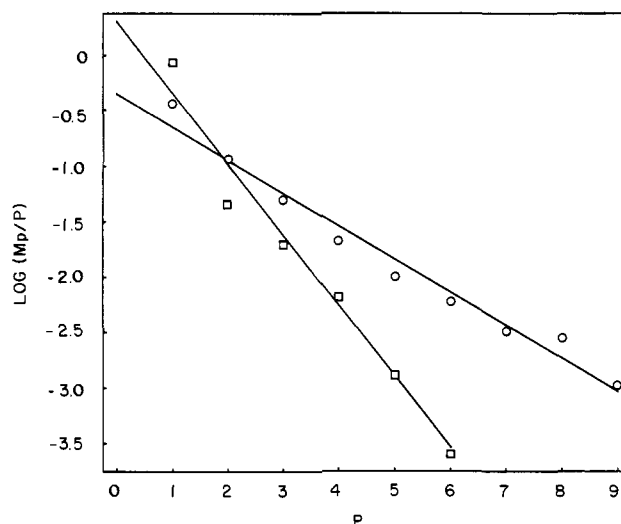


metal-methyl bond is proposed to arise through reduction of a surface-bound  $\text{CH}_2$  species.

Sachtler and Biloen have recently shown that  $^{13}\text{C}$  atoms, pre-deposited on a Fischer-Tropsch catalyst, become incorporated in the product hydrocarbons during reaction of  $^{12}\text{CO}$  and hydrogen in a manner which is consistent with the formation of metal carbide in the Fischer-Tropsch scheme;<sup>7</sup> our studies with  $\text{CH}_2\text{N}_2$  indicate that the polymerization of  $\text{CH}_2$  groups on the surface is also a plausible part of the Fischer-Tropsch scheme. The present work is designed to further distinguish between the three proposals, and the results indicate that only the Fischer-Tropsch scheme is consistent with the experimental observations.

In these studies we take advantage of the different roles alleged to be played by surface  $\text{CH}_2$  species in the three schemes. The Fischer-Tropsch scheme has the  $\text{CH}_2$  species being involved in both the initiation and propagation steps of the hydrocarbon chain growth; the Pichler-Schultz scheme has them being involved only as chain initiators; the Anderson-Emmett scheme says they play no role at all.

In the first test we have noted the effect on product distribution, following the addition of  $\text{CH}_2$  groups to the surface by addition of  $\text{CH}_2\text{N}_2$  gas to feed during an ongoing reaction of  $\text{CO} + \text{H}_2$



**Figure 1.** Plots of  $\log (M_p/P)$  vs.  $P$  for the distribution of oligomers produced when  $\text{CO}$  and  $\text{H}_2$  ( $\square$ ) and  $\text{CO} + \text{H}_2 + \text{CH}_2\text{N}_2$  ( $\circ$ ) are passed over a cobalt catalyst. The lines represent the least-squares fit for the data. The  $\alpha$  values (see text) for the  $\text{CO} + \text{H}_2$  data are 0.23 (ex. slope) and 0.25 (ex. intercept) and for the  $\text{CO} + \text{H}_2 + \text{CH}_2\text{N}_2$  data are 0.51 (ex. slope) and 0.51 (ex. intercept).

producing hydrocarbons.<sup>8</sup> The Pichler-Schultz theory predicts that more chains would be initiated through incorporation of the added  $\text{CH}_2$  but that the relative distribution of the various oligomers should not change. The Fischer-Tropsch mechanism predicts a shift in product distribution leading to higher molecular weight molecules, since surface-bound  $\text{CH}_2$  is involved in chain propagation. The Anderson-Emmett scheme might suggest a bimodal distribution of products, one arising through eq 2 and the other through an independent reaction of  $\text{CH}_2$  and  $\text{H}_2$ .

The results of the effect of adding  $\text{CH}_2$  groups to the catalyst surface of an ongoing Fischer-Tropsch reaction are indicated in Figure 1.<sup>9</sup> The data are presented in the manner of Schultz-Flory distributions of oligomers obtained through polymer chain growth in which  $\log (M_p/P)$  is plotted vs.  $P$ ,  $M_p$  being the weight fraction of that oligomer whose degree of polymerization is  $P$ . A straight line of such a plot indicates a single mode of stepwise chain growth; from both the slope of the plot and also the point of intercept at the ordinate, a quantity  $\alpha$ , equal to (rate of propagation)/(rate of propagation + rate of termination), can be derived.<sup>6</sup> From the two linear plots given in Figure 1 for the distributions before and after the addition of  $\text{CH}_2\text{N}_2$ , it is seen that the addition of  $\text{CH}_2$  groups produces a change in the distribution in favor of formation of higher molecular weight molecules as predicted only by the Fischer-Tropsch scheme. The change in  $\alpha$  from 0.24 to 0.51 indicates that the rate of propagation, relative to termination, has increased by a factor of 3.3 upon addition of this particular amount of  $\text{CH}_2$  to the surface.

In a second test of the three mechanisms we have investigated the nature of the distribution of  $^{13}\text{C}$  atoms in the propene formed when a mixture of  $^{13}\text{CO}$ ,  $\text{H}_2$ , and  $^{12}\text{CH}_2\text{N}_2$  are passed over the catalyst under Fischer-Tropsch reaction conditions. If pure  $^{13}\text{CO}$  were used in this experiment, then the Fischer-Tropsch scheme predicts that the propene should contain every possible combination of  $^{13}\text{C}$  and  $^{12}\text{C}$  atoms; the Pichler-Schultz scheme on the other hand predicts the propene would be a mixture of  $^{13}\text{C}\text{---}^{13}\text{C}\text{---}^{13}\text{C}$  and  $^{12}\text{C}\text{---}^{13}\text{C}\text{---}^{13}\text{C}$  molecules; the Anderson-Emmett scheme says it

(2) Brady, R. C., III; Pettit, R. *J. Am. Chem. Soc.* **1980**, *102*, 6181-6182.

(3) (a) Storch, H. H.; Goulombic, N.; Anderson, R. B. "The Fischer-Tropsch and Related Syntheses"; Wiley: New York, 1951. (b) Kummer, J. F.; Emmett, P. H. *J. Am. Chem. Soc.* **1953**, *75*, 5177-5183.

(4) Pichler, H.; Schultz, H. *Chem. Ing. Tech.* **1970**, *12*, 1160-1174.

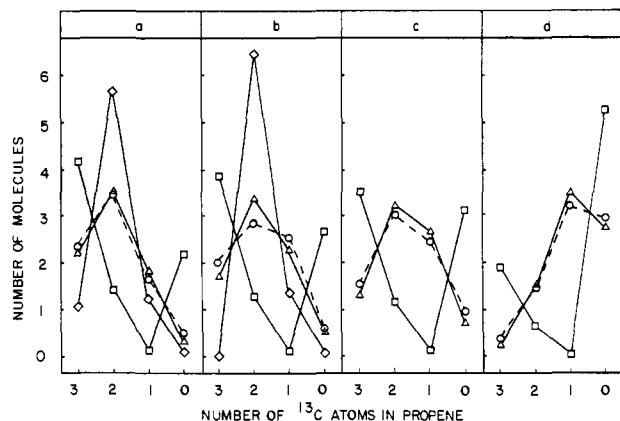
(5) Masters, C. *Adv. Organomet. Chem.* **1979**, *17*, 61-103.

(6) Henrici-Olivé, G.; Olivé, S. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 136-141.

(7) Biloen, P.; Helle, H. N.; Sachtler, W. M. H. *J. Catal.* **1979**, *58*, 95-107.

(8) The assumption is made here that the surface-bound  $\text{CH}_2$  species derived from  $\text{CH}_2\text{N}_2$  would be chemically indistinguishable from that produced upon reduction of  $\text{CO}$ .

(9) A stream of gas (140 mL/min) consisting of 6 parts of  $\text{CO}$ , 24 parts of  $\text{H}_2$ , and 110 parts of  $\text{N}_2$  was passed over 350 mg of catalyst (39% Co on Kieselguhr, 50-60 mesh) previously reduced at 400 °C for 2 h with  $\text{H}_2$ ; the conversion of  $\text{CO}$  at this point was about 1%. Diazomethane was then added to the feedstream (via the  $\text{N}_2$  line) at a rate predetermined to double the amount of hydrocarbons formed in the reaction. After 20 min the product composition appeared to be constant and is reported in Figure 1; an increase in hydrocarbon yield of 90% was observed.



**Figure 2.** Distribution of the isotopically labeled propene molecules produced upon passage of mixtures of 90%  $^{13}\text{C}$ CO + 10%  $^{12}\text{C}$ CO,  $\text{H}_2$ , and  $^{12}\text{CH}_2\text{N}_2$  over a cobalt catalyst. The experimentally observed distribution is given by the points joined via the dotted line. The distributions predicted by the Pichler-Schultz mechanism are given by the symbol  $\diamond$ , that predicted by the Anderson-Emmett mechanism by the symbol  $\square$ , and that predicted by the Fischer-Tropsch scheme are given by the symbol  $\triangle$ .

should be a mixture of  $^{13}\text{C}$ - $^{13}\text{C}$ - $^{13}\text{C}$  and  $^{12}\text{C}$ - $^{12}\text{C}$ - $^{12}\text{C}$  molecules. In each case the relative amount of the various isotopically labeled carbon molecules would depend on the relative amounts of  $^{13}\text{C}$ CO converted and  $^{12}\text{CH}_2\text{N}_2$  added. In actual practice we have used a mixture of 90%  $^{13}\text{C}$ CO and 10%  $^{12}\text{C}$ CO instead of pure  $^{13}\text{C}$ CO; varying amounts of  $^{12}\text{CH}_2\text{N}_2$  were added to the feedstream and the distribution of isotopic molecules in the propene product was determined by mass spectrometric methods.<sup>10</sup> The total percentage of  $^{13}\text{C}$  atoms in the product was determined, and the relative distribution of the various isotopically labeled molecules which would lead to this percentage of  $^{13}\text{C}$ , as predicted by the three mechanisms, then calculated.<sup>11</sup> In Figure 2 we have indicated for four different experiments, with varying amounts of  $\text{CH}_2\text{N}_2$  added, the distribution of molecules leading to the observed percentages of  $^{13}\text{C}$  in the propene as predicted by the three mechanisms, together with the experimentally observed distribution. The total number of molecules have been arbitrarily normalized to eight. It should be noted that in the Pichler-Schultz theory there can be no less than 60% of  $^{13}\text{C}$  in the product no matter how much  $^{12}\text{CH}_2$  is deposited on the surface; the other two schemes allow for less than this if sufficient  $^{12}\text{CH}_2$  is added.<sup>12</sup>

In Figure 2a,b the data are shown for experiments where 65.4% and 60.1%  $^{13}\text{C}$  were found in the propene product and obviously only that distribution as predicted by the Fischer-Tropsch scheme even closely approximates the experimentally observed distribution.<sup>13</sup> Addition of relatively more  $^{12}\text{CH}_2$  produced propene samples containing 54.9% and 30.0%  $^{13}\text{C}$  (Figure 2c,d) and this is incompatible with the Pichler-Schultz scheme; of the two mechanisms still tenable the Fischer-Tropsch scheme again accurately predicts the experimentally observed distribution, while the Anderson-Emmett scheme deviates widely.

Of the three proposed mechanisms being evaluated we conclude that only the sequence of steps outlined in eq 1 remains to be

(10) The reactant gases (8 parts of 90%  $^{13}\text{C}$ CO, 6 parts of  $\text{H}_2$ , and 100 parts of  $\text{N}_2$ , total flow rate 114 mL/min) were passed up an ebullating bed of catalyst consisting of 178 mg of 10% cobalt on 120-140 mesh Cabosil at 250  $^\circ\text{C}$ ; the catalyst had previously been reduced with  $\text{H}_2$  at 400  $^\circ\text{C}$ . Varying amounts of  $\text{CH}_2\text{N}_2$  were introduced to the feedstream, via the  $\text{N}_2$  flow line, and the propene in the product analyzed by GCMS methods.

(11) Dence, J. B. "Mathematical Techniques in Chemistry"; Wiley: New York, 1975, 26-27.

(12) If pure  $^{13}\text{C}$ CO were used this value would be 66%.

(13) The methane component of the product mixture, in that sample in which there was found 60.1%  $^{13}\text{C}$  in the propene component, was found to contain approximately 40%  $^{13}\text{C}$ . The Pichler scheme predicts this value should be less than 1%, while the Anderson-Emmett and Fischer-Tropsch mechanisms predict 50% and 60%, respectively; the discrepancy with either of the latter two schemes is attributed to the presence of  $\text{O}_2$  giving rise to a superficially high value for the mass of 16 (i.e.,  $^{12}\text{CH}_4$ ).

considered as the primary mechanism of the Fischer-Tropsch reaction.

**Acknowledgment.** We thank the Robert A. Welch Foundation, the National Science Foundation, and the Department of Energy for financial assistance.

## A Novel Synthesis of $\beta$ -Lactams<sup>1</sup>

Howard Alper\*<sup>2</sup> and Chulangani P. Perera

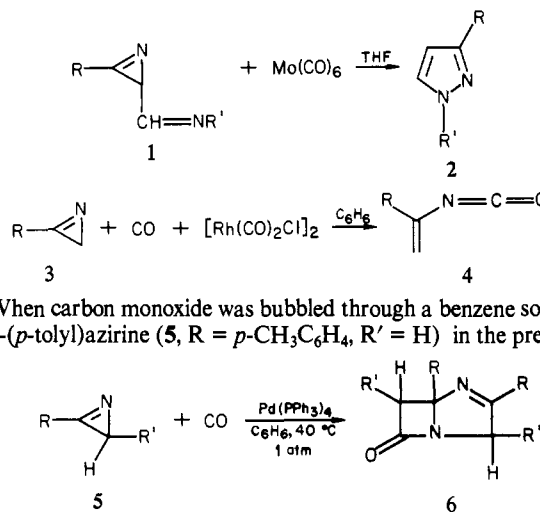
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Received December 1, 1980

Investigations during the past five years have uncovered some fascinating metal complex induced ring-opening reactions of azirines.<sup>3-16</sup> Examples include the intramolecular cycloaddition of azirines in the presence of group 6 metal carbonyls ( $1 \rightarrow 2$ )<sup>8</sup> and the carbonylation of the heterocycles to vinyl isocyanates ( $3 \rightarrow 4$ ) in the presence of chlorodicarbonylrhodium(I) dimer.<sup>16</sup> This communication describes the remarkable palladium(0)-catalyzed carbonylation of azirines.



When carbon monoxide was bubbled through a benzene solution of 2-(*p*-tolyl)azirine (**5**,  $\text{R} = p\text{-CH}_3\text{C}_6\text{H}_4$ ,  $\text{R}' = \text{H}$ ) in the presence

of catalytic amounts of tetrakis(triphenylphosphine)palladium for 1 day at 40  $^\circ\text{C}$ , the bicyclic  $\beta$ -lactam **6** ( $\text{R} = p\text{-CH}_3\text{C}_6\text{H}_4$ ;  $\text{R}' = \text{H}$ ) was obtained in 50% (yields are of analytically pure

(1) Issued as N.R.C.C. No. 19132.

(2) E.W.R. Steacie Fellow, 1980-82.

(3) Hayashi, K.; Isomura, K.; Taniguchi, H. *Chem. Lett.* **1975**, 1011.

(4) Alper, H.; Prickett, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 483.

(5) Alper, H.; Prickett, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 983.

(6) Alper, H.; Prickett, J. E. *Inorg. Chem.* **1977**, *16*, 67.

(7) Komendantov, M. I.; Bekmucharmetov, R. R. *Khim. Geterosikl. Soedin.* **1977**, 1570.

(8) Alper, H.; Prickett, J. E.; Wollowitz, S. *J. Am. Chem. Soc.* **1977**, *99*, 4330.

(9) Schuchardt, U.; Faria dos Santos Filho, P. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 647.

(10) Isomura, K.; Uto, K.; Taniguchi, H. *J. Chem. Soc., Chem. Commun.* **1977**, 664.

(11) Nakamura, Y.; Bachmann, K.; Heimgartner, H.; Schmid, H.; Daly, J. J. *Helv. Chim. Acta* **1978**, *61*, 589.

(12) Bellamy, F. *J. Chem. Soc., Chem. Commun.* **1978**, 998.

(13) Bellamy, F. *Tetrahedron Lett.* **1978**, 4577.

(14) Alper, H.; Sakakibara, T. *Can. J. Chem.* **1979**, *57*, 1541.

(15) Inada, A.; Heimgartner, H.; Schmid, H. *Tetrahedron Lett.* **1979**, 2983.

(16) Sakakibara, T.; Alper, H. *J. Chem. Soc., Chem. Commun.* **1979**, 458.