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Richard H. Fish and Gregg A. Cremer

January 1982

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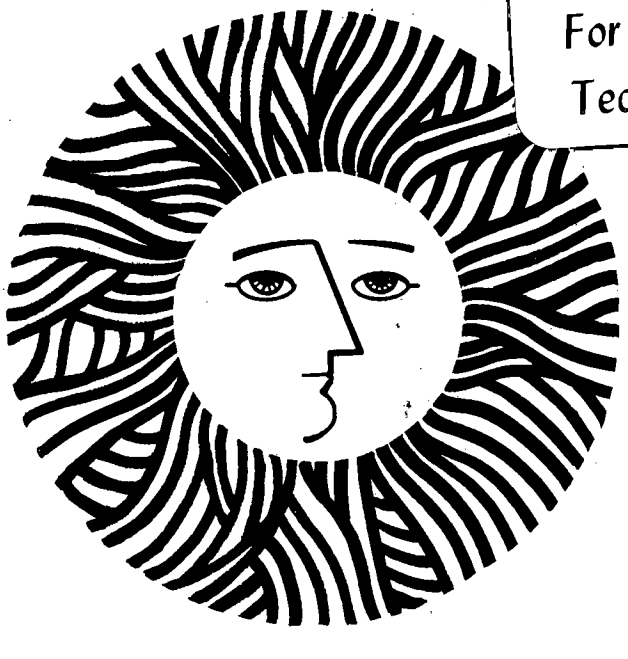

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HOMOGENEOUS CATALYTIC HYDROGENATIONS, 1: Reductions of Polynuclear Aromatic and Polynuclear Heteroaromatic Nitrogen Compounds Utilizing Carbon Monoxide with Water or Hydrogen

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Homogeneous Catalytic Hydrogenations, 1. Reductions of Polynuclear Aromatic and Polynuclear Heteroaromatic Nitrogen Compounds Utilizing Carbon Monoxide with Water or Hydrogen

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Pettit and his co-workers recently demonstrated, in an elegant manner, the use of carbon monoxide and water as a reducing agent for the hydroformylation of olefins and of carbon monoxide, water and hydrogen in the reduction of nitroarenes[1-3]. The compounds responsible for these catalytic reactions, in Pettit's studies, were transition metal carbonyl hydrides that had been generated catalytically under the reaction conditions (eq. 1).

$$M_x(CO)_y + OH^- \longrightarrow M_x(CO)_{y-1}COOH \xrightarrow[+H_2O]{-CO_2} H_2M_x(CO)_{y-1} \qquad (1)$$

These results prompted us to study the utilization of these reagents for the reduction of polynuclear aromatic and polynuclear heteroaromatic nitrogen compounds. The importance of studying these types of polynuclear compounds and reducing agents stems from the need to learn more about the basic aspects of coal liquefaction and the hydroprocessing of coal liquids and shale oils[4]. Additionally, it is well known that homogeneous catalytic reductions proceed at lower temperatures and pressures and give higher regioselectivities when compared to their heterogeneous counterparts[5a,b].

We wish to demonstrate, in this communication, the potential of carbon monoxide and water or carbon monoxide and hydrogen as reducing agents for polynuclear aromatic and polynuclear heteroaromatic nitrogen compounds, 1-8, (Chart 1) using transition metal carbonyl compounds as homogeneous catalysts.

We reacted a wide variety of transition metal carbonyl compounds with anthracene, 1, under water gas shift (wgs) conditions (CO,H_2O, base)[6], and found that only $Mn_2(CO)_8(Bu_3P)_2$, $Fe(CO)_4Bu_3P$ and $Co_2(CO)_6(\phi_3P)_2$ produced the reduction product, 9,10-dihydroanthracene, 9, in yields of 13%, 8% and 3% respectively. The carbonyls of Ru, Rh, W, Os, Re and Mo all produced hydrogen and carbon dioxide (wgs reaction), but no compound 9.

These results can partially be rationalized by the fact that the latter transition metal carbonyl hydrides are unstable under the reactions conditions and undergo reductive elimination of hydrogen rather than hydrogen transfer to the polynuclear aromatic substrate, 1, i.e., $k_2 > k_1$ (eq. 2).

$$M_x(CO)_{y-1} + ArH_2 \underset{k_1}{\overset{+Ar}{\longleftarrow}} H_2M_x(CO)_{y-1} \underset{k_2}{\overset{-H_2}{\longrightarrow}} M_x(CO)_{y-1} \qquad (2)$$

In view of these discoveries, we decided to learn more about the parameters of this reaction using $Mn_2(CO)_8(Bu_3P)_2$ as the catalyst. The reaction of carbon monoxide and deuterium oxide (D_2O) with 1 provided only 9,10-dideutetroanthracene, 10[7], and this result strongly indicates that the hydrogen comes exclusively from water. In addition, the presence of added deuterium gas (D_2) provided no deuterium incorporation; thereby eliminating a mechanism which includes oxidative addition of H_2 to any coordinatively unsaturated manganese species that might be formed[3], and supports the facile reaction (eq. 1) of hydroxide ion on coordinated CO as the major reaction pathway to the carbonyl hydrides[1]. Several control experiments verified that the reduction

product, 9, did not undergo exchange of hydrogen for deuterium under the reaction conditions.

In an experiment to elucidate the stereochemistry of the anthracene reaction, we reacted an analog of 1, 9,10-dimethylanthracene, 11, with $Mn_2(CO)_8(Bu_3P)_2$ under water gas shift conditions (180°, 5 hrs, 350 psi CO, 0.2M KOH in THF, sub/cat = 20), to provide a 30% yield of cis and trans-9,10-dihydro-9,10-dimethylanthracene, 12 and 13, in a ratio of 53%:47% [8]. The mechanistic implication of this result strongly suggests a free radical process for this reaction. A similar result was recently reported by Halpern et al.[9a] for the reaction of 10 and $Mn_2(CO)_{12}$ and Taylor and Orchin[9b] with $Co_2(CO)_8$ under syn gas conditions (CO_2, H_2 1:1,~200°).

We also found that in the absence of aqueous base and in the presence of hydrogen, i.e., synthesis gas (sg) conditions (CO/H_2 = 1), that better yields of reduced polynuclear aromatic products could be obtained using $Mn_2(CO)_8(Bu_3P)_2$ as the catalyst and compounds 1 - 3 as substrates. Thus, under sg conditions[10] reaction of 1 with $Mn_2(CO)_8(Bu_3P)_2$ provided 9 in 30% yield, while reaction with 2 gave no product and 3 produced 4,5-dihydropyrene, 14, in 3% yield.

From these results, it is evident that bent polynuclear aromatic compounds are extremely unreactive under either wgs or sg conditions, when compared to 1, a linear polynuclear aromatic compound[11].

The polynuclear heteroaromatic compounds, specifically with nitrogen as the hereroatom, are important to study, since they are highly prevalent in all coal and oil shale products[12]. We found a dramatic increase in reactivity for the polynuclear heterocyclic nitrogen compounds under either wgs or sg conditions compared to their carbon analogs, e.g., acridine more

reactive than anthracene. Table 1 summarizes our results with polynuclear heteroaromatic nitrogen compounds **4**-**8**.

It is important to note the high regioselectivity observed in these reactions by the ease with which the nitrogen heterocyclic ring gets hydrogenated in preference to a benzene ring. This result might be explained by the lowered aromaticity of the nitrogen heterocyclic ring versus their carbon analog, which would provide a lower activation energy for hydrogenation[13]. The order of reactivity for compounds **4**-**8** either under wgs or sg conditions is:[14] **4** >> **6** > **8** > **5** >> **7**.

The overall observed relative reactivities of compounds **1**-**8**, either under wgs or sg conditions, is as follows:

$$\mathbf{4} \gg \mathbf{1} \gg \mathbf{6} > \mathbf{8} > \mathbf{5} > \mathbf{7} \approx \mathbf{3} \ggg \mathbf{2}$$

This order, while qualitative, is still significant, since these polynuclear compounds are present in coal, coal liquids and shale oil and represents the first logical explanation for compound reactivity under catalytic hydrogenation conditions in these complex matrices.

Finally, the fact that Fe, Mn and Co carbonyls give reduced products, while other transition carbonyls were unreactive imply important mechanistic differences. Pertinently, we found in these studies, in addition to the instability factor for several of the transition carbonyl hydrides, a pronounced carbon monoxide inhibition on the catalytic hydrogenation reactions especially with the ruthenium carbonyls and report these results in the following paper[15].

We are continuing to pursue this important area of fossil energy research and will report further details in forthcoming publications[16].

Acknowledgements

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References and Notes

(1) Kang, H. G.; Mauldin, C. H.; Cole, T.; Slegeir, W.; Cann, K. and Pettit, R.; J. Amer. Chem. Soc., 1977, 99, 8323 and reference therein.

(2) Cann, K.; Cole, T.; Slegeir, W.; Pettit, R.; ibid. 1978, 100, 3969.

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(4) Coal Liquefaction Fundamentals ACS Syn. Series, 139, Whitehurst, D. D., Editor, (1980).

(5a) James, B. J. "Homogeneous Hydrogenations"; John Wiley and Son: New York, N.Y. 1973.

(5b) Parshall, G. W., Science 1980, 208, 1221.

(6) The reaction conditions were as follows for the following carbonyls: $Re(CO)_4Bu_3P$, $Mn_2(CO)_8(Bu_3P)_2$, $CO_2(CO)_6(\phi_3P)_2$, $W(CO)_6$, $Re(CO)_{10}$, $RuCl_2(CO)_2(\phi_3P)_2$, $Rh_6(CO)_{16}$, $Mo(CO)_5Bu_3P$. A 45 ml Parr mini-reactor was used with tetrahydrofuran (12 ml) as solvent, 0.2 M KOH (3 ml), P_{CO} 350 psi, 5 hr reaction time, 1 mmole of 1, 0.1 mmole of transition metal carbonyl catalyst (10:1 substrate to catalyst ratio).

The product percentage was found by area ratio of starting material and product using a HP 5880A capillary gas chromatograph with digital integration (12 m x 0.1 mm OV 101 at 60° to 200 (10°/min) and flame ionization detection. The reduction product, 9, was isolated by column chromatography on florisil (benzene) and identified by GC-EIMS and nmr spectroscopy (^1H, 250 MHz).

(7) GC-EI mass spectral analysis showed m/e 182 (100%) consistent with two deuteriums being incorporated into compound 1 (m/e 178).

(8) The cis and trans isomers of 9,10-dihydro-9,10-dimethylanthracene, 12, 13 could be cleanly separated on a 12 m x 0.1 mm i.d., fused silica capillary column (OV 101) using a HP 5880A instrument with flame ionization detection (temperature programming 60°-200°, 10°/min).

(9a) Sweany, R.; Buttler, S. C; and Halpern, J. Organometal Chem., 1981, 213, 487.

(9b) Taylor, P. D; and Orchin. M. J., Org. Chem., 1972, 37, 3913.

(10) The reactions of 1-3 with $Mn_2(CO)_8(Bu_3P)_2$ as catalyst were run in a 45 ml Parr mini-reactor at 200°C, 350 psi H_2, 350 psi CO in THF for 2 hr with a 10:1 substrate to catalyst ratio. Other carbonyls such as $Fe(CO)_4$ Bu_3P, $Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$, $Re_2(CO)_{10}$ and $Ru_3(CO)_{12}$ produced no reduced product with 1-3 as substrates.

(11) Friedman, S.; Meltin, S.; Svedi, A.; and Wender, I. J., Org. Chem. 1959, 24, 1287.

(12) Larsen, J. W., Editor. Organic Chemistry of Coal, ACS Symposium Series 71, 1978.

(13) Dewar, M.J.S. "The Molecular Orbital Theory of Organic Chemistry" McGraw-Hill, New York, N.Y., 1969.

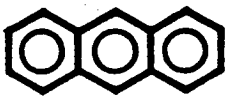
(14) The yields we report in Table 1 were mainly for comparison purposes, i.e., times of 2 hrs used for each reaction. However, longer reaction times provided, in most cases, quantitative conversions and thus the preparative aspects could be of potential interest to synthetic chemists.

(15) See the following paper: Fish, R. H.; and Cremer, G. A., J. Amer. Chem. Soc., 1982, 104, 0000.

(16) Preliminary accounts of this work were presented at the 182nd National ACS Meeting, Aug. 23-28, 181, New York, N.Y., Abstract INOR 49 and the Pacific Conference on Chemistry and Spectroscopy, Anaheim, CA, Oct. 19-21, 1981, Abstract 188.

Chart 1

Polynuclear Aromatic and Polynuclear Heteroaromatic Nitrogen Compounds Reacted under Water Gas Shift or Synthesis Gas Conditions



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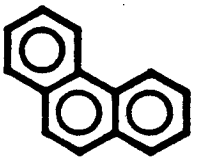

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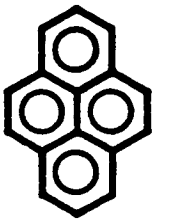

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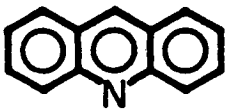

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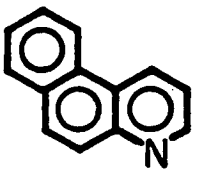

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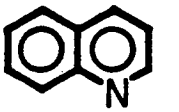

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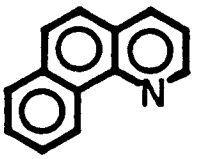

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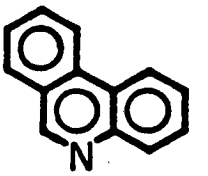

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Table 1

Reductions of Polynuclear Heteroaromatic Nit rogen Compounds under Water Gas Shift [a] (WGS) and Syn Gas (SG) Conditions [b] with Transition Metal Carbonyls as Catalysts.

Substrate	Catalyst [c]	Sub/Cat	Temp.(°C)	Time(hr)	Conditions	Products (%) [d]
4	$Fe(CO)_5$	10	180	2	WGS	9,10-dihydro-acridine (100)
4	$Mn_2(CO)_8(Bu_3P)_2$	10	200	2	WGS	" (38)
4	$Mn_2(CO)_8(Bu_3P)_2$	20	200	2	SG	" (100)
4	$Co_2(CO)_6(\phi_3P)_2$	20	200	2	SG	" (100)
5	$Mn_2(CO)_8(Bu_3P)_2$	20	200	2	SG	1,2,3,4, tetrahydro-5,6-benzo-quinoline (7)
5	$Mn_2(CO)_8(Bu_3P)_2$	20	200	5	WGS	" (4)
5	$Fe(CO)_4(Bu_3P)$	10	180	5	WGS	" (1)
5	$Co_2(CO)_6(\phi_3P)_2$	20	200	2	SG	" (8)
6	$Fe(CO)_5$	10	180	2	WGS	1,2,3,4-Tetrahydro-quinoline (0)
6	$Mn_2(CO)_8(Bu_3P)_2$	20	200	5	WGS	" (4)
6	$Mn_2(CO)_8(Bu_3P)_2$	20	200	5	SG	" (33)
6	$Co_2(CO)_6(\phi_3P)_2$	20	200	1	SG	" (70)
7	$Mn_2(CO)_8(Bu_3P)_2$	20	200	2	SG	1,2,3,4 tetrahydro-7,8-benzo-quinoline (2)
7	$Mn_2(CO)_8(Bu_3P)_2$	20	200	2	WGS	No product
8	$Mn_2(CO)_8(Bu_3P)_2$	20	200	2	WGS	9,10-dihydro-phenanthridine (1)
8	$Mn_2(CO)_8(Bu_3P)_2$	20	200	2	SG	" (11)
8	$Co_2(CO)_6(\phi_3P)_2$	20	200	2	SG	" (21)

a. Reaction run in THF (12 ml) with 0.2 M KOH (3 ml), 350 psi CO.
b. 350 psi H_2 and 350 psi CO in THF (15 ml).
c. 800 psi CO.
d. Determined by capillary GC using a digital integrator (HP 5880A). Isolated by column chromatography (florisil) and identified by GC-MS and nmr spectroscopy (250 mHz, ^1H).

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