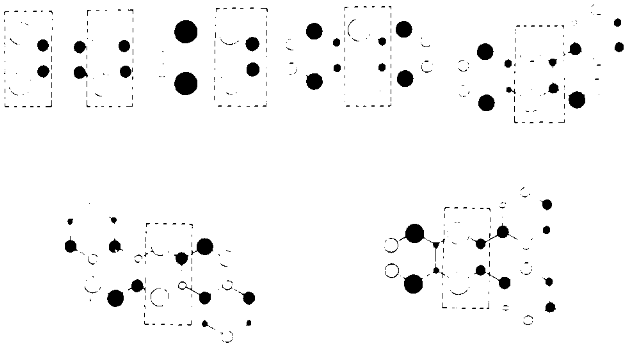
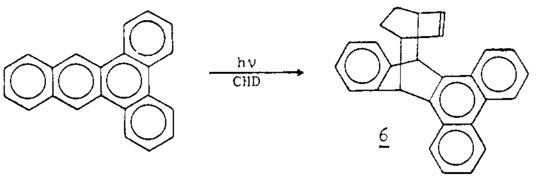


Figure 1. LUMO of 1,3-cyclohexadiene and aromatic hydrocarbons.[25,26]

orbitals undergoing bond formation also is necessarily inadequate in such cases.

As a test of our theory, we irradiated dibenz[*a,c*]anthracene in the presence of CHD; as anticipated, the major product obtained is a $[{}_{4}\pi_{s} + {}_{4}\pi_{s}]$ adduct, **6** (60%, mp 205-206 °C) (eq 4). Furthermore, dibenz[*a,c*]anthracene is known to undergo a thermal reaction with MA with relative facility.[9,27]



(4)

In conclusion, our results suggest that the local symmetry in the frontier orbitals as specified about the reactive positions may determine implicitly the favorable pathway of cycloaddition of unsaturated systems to aromatic compounds. The consideration of this local symmetry rather than the symmetry embracing any other (e.g., more inclusive) assembly of atoms may be used to predict the favorable reaction pathway of these and related reactions.

Acknowledgment. The authors thank the National Science Foundation and the National Institute of General Medical Sciences for the support of this work.

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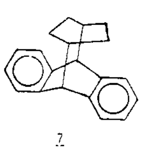

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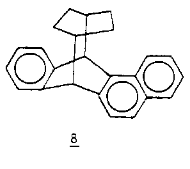

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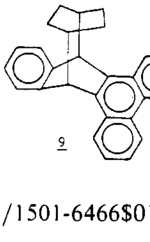

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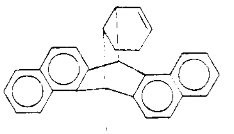
(23) The spectroscopic evidence indicates that the structure of the $[{}_{4}\pi_{s} + {}_{2}\pi_{s}]$ adduct is either **4** or **10**, and the structural assignment of the product as **4** is tentative.



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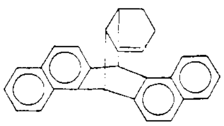

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Nien-chu C. Yang,* John Masnovi, Wei-long Chiang
Department of Chemistry, University of Chicago
Chicago, Illinois 60637

Received March 26, 1979

Facile Hydroxymethylation of an Acyloxymethyl Ligand with Synthesis Gas or Hydrogen. A Model for Catalytic Reactions Yielding Methanol and Ethylene Glycol

Sir:

Conversion of CO and H_2 to organic chemicals by means of transition metal complexes is the goal of much current research, including catalytic applications,[1-3] and stoichiometric or model studies.[4-12] These investigations may lead to improved understanding of the action of metal catalysts and allow development of catalyst systems which are more active or more selective for conversion of synthesis gas to desired products. Homogeneous catalysts and complexes are generally more easily studied than heterogeneous systems, and may serve as models for the heterogeneous catalytic reduction of carbon monoxide.[13]

The probable involvement of the hydroxymethyl ligand, $-CH_2OH$, in Fischer–Tropsch and related reactions has recently been discussed.[4,13,14] However, complexes containing this ligand have been difficult to isolate, and only recently has the first stable hydroxymethyl complex of a low-valent transition metal been reported.[15] Presented herein are some initial results of studies with a metal complex bearing the acyloxymethyl ligand, $-CH_2OC(O)R$, a carboxylate ester of the hydroxymethyl ligand.[16] This ligand is stable to β-elimination (a decomposition pathway perhaps responsible for the general instability of hydroxymethyl complexes), yet should closely resemble the hydroxymethyl ligand in other reactions (e.g., alkyl migration). It therefore appears to be a useful and accurate model. Reported here is the conversion of this hydroxymethyl analogue into methyl and ethylene glycol esters by reaction with H_2 or synthesis gas, and the observation of glycolaldehyde ester, a probable intermediate in glycol ester formation. These findings are summarized in Scheme I.

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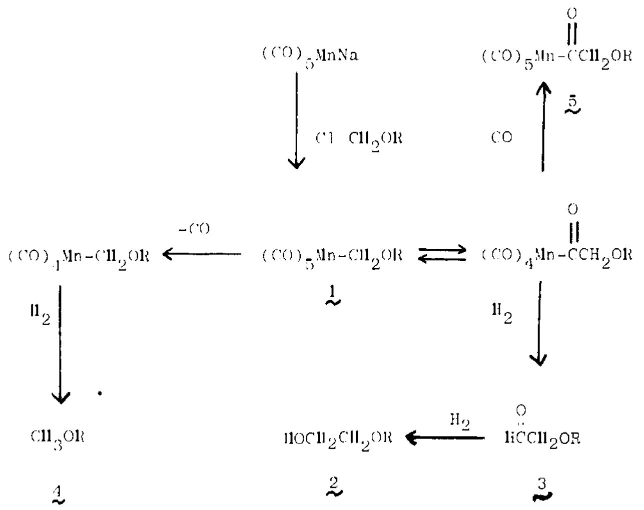
Table I. Reactions of $(CO)_5MnR$ Complexes[a]

reaction	R	mmol	pressure, psi[b]	temp, °C (h)	products	mmol
1	CH_2OPiv[c] (**1**)	4.84	100 (H_2)	75 (1)	$HOCH_2CH_2OPiv$ (**2**)	3.60
2	CH_2OPiv (**1**)	3.22	100 (H_2) + 30 (CO)	100 (2)	$HOCH_2CH_2OPiv$ (**2**) $HC(O)CH_2OPiv$ (**3**)	0.09 0.80
3	CH_2OPiv (**1**)	3.22	3000 (H_2) + 1000 (CO)	100 (2)	$HOCH_2CH_2OPiv$ (**2**) $HC(O)CH_2OPiv$ (**3**)	1.85 0.31
4	CH_2OPiv (**1**)	3.22	15 (H_2)	75 (2)	CH_3OPiv (**4**)	0.82
5	CH_2OPiv (**1**)[d]	4.84	15 (H_2)	75 (2)	CH_3OPiv (**4**)	2.50
6	CH_3	4.76	100 (H_2)	75 (1)	$HOCH_2CH_3$	3.91
7	$CH_2OCH_2CH_3$	3.94	100 (H_2)	75 (1)	$HOCH_2CH_2OCH_2CH_3$	2.22
8	CH_3[e]	4.76	100 (H_2)	75 (1)	$HOCH_2CH_3$	22.8
9	CH_3	4.76	100 (H_2) + 30 (CO)	75 (1)	$HC(O)CH_3$	3.54
10	H[f]	7.69	3000 (H_2)	250 (2)	$HOCH_3$	0.10

[a] All reactions in 30 mL of sulfolane. [b] Pressure in the closed system at 25 °C, before heating. [c] OPiv is pivaloxy, $OC(O)C(CH_3)_3$. [d] Reaction mixture also included 5.13 mmol of $(CH_3)_3NO$. [e] 56.8 mmol of $HC(O)CH_3$ was also added. [f] Charged as $Mn_2(CO)_{10}$.

Scheme I. Preparation and Reactions of $(CO)_5MnCH_2OR$ ($R = C(=O)C(CH_3)_3$). Numbered compounds have been isolated; others are postulated intermediates



Reaction of chloromethyl pivalate with sodium pentacarbonylmanganate in THF at 25 °C yields $(CO)_5MnCH_2OC(O)C(CH_3)_3$ (**1**).[17] This complex was placed in sulfolane[18] (30 mL) under 100 psi of H_2. After the mixture was heated at 75 °C for 1 h and cooled and the pressure released, VPC analysis indicated the presence of a 74% yield of the monopivalate ester of ethylene glycol (**2**)[19] (Table I, reaction 1). Formation of this two-carbon product by coupling of two acyloxymethyl ligands can be ruled out by the high yield of the monoester, and the observation of only small amounts (<0.2 mmol) of the diester. (At 75 °C under N_2, neither **2** nor the diester is obtained from **1**.)

Reactions of **1** performed under mixtures of CO and H_2 yielded another product as well, found to be the pivalate ester of glycolaldehyde (**3**) (Table I, reactions 2 and 3). This compound can also be detected in the early stages of reactions performed under H_2 alone, but it disappears rapidly as alcohol product **2** is produced. This suggests that complexed aldehyde is an intermediate in the conversion into alcohol. (Complexes with coordinated aldehyde have been previously reported.[8,20]) Carbon monoxide inhibits both the total rate of product formation (**2** + **3**), and the rate of hydrogenation of the proposed aldehyde intermediate (as has been previously observed for cobalt carbonyl catalysts[21]).

Small quantities (<0.2 mmol) of methyl pivalate (**4**) were also observed in these reaction mixtures, indicating a second reduction mode not involving alkyl chain extension. Experiments carried out under 1 atm of H_2 yielded this compound as the major product, although relatively slowly (Table I, reaction 4). Reactions performed similarly but with added trimethylamine *N*-oxide (which is expected to decarbonylate **1**) gave much higher yields of **4** (Table I, reaction 5). Thus, one possible route to **4** is that presented in Scheme I. The observation of increasing the ratio of **4** to **2** with decreasing H_2 pressure is consistent with Scheme I if it is assumed that hydrogenation of the coordinatively unsaturated acyl complex becomes rate limiting (for C_2 product formation) under low H_2 pressure. This postulated intermediate can be trapped by reaction with CO (100 psi of CO, 75 °C, THF solvent), to yield complex **5**.[22]

Further support for some of the steps in Scheme I is provided by analogous studies with another hydroxymethyl analogue, $(CO)_5MnCH_2OCH_2CH_3$, and the alkyl complex $(CO)_5MnCH_3$. When these complexes were heated at 75 °C for 1 h in sulfolane under 100 psi of H_2, high yields were obtained of 2-ethoxyethanol and ethanol (Table I, reactions 6 and 7); no aldehydes were observed. Thus hydroxymethylation of the alkyl group in $(CO)_5MnR$ complexes upon reaction with H_2 under pressure is apparently a general process, and the α-oxygen atom does not seem to have a great influence on the course of reaction. However, the finding that α-oxy substitution does not prevent alkyl migration under mild conditions is significant; this had not been previously observed.[23]

Studies relating to aldehyde hydrogenation in this system were carried out with $(CO)_5MnCH_3$ and CH_3CHO. The aldehyde was catalytically hydrogenated at 75 °C, 100 psi of initial H_2 pressure (Table I, reaction 8), although it was found to be stable under these conditions when $Mn_2(CO)_{10}$ was added instead of $(CO)_5MnCH_3$.[27] Unreduced acetaldehyde was obtained from $(CO)_5MnCH_3$, however, when the reaction was carried out with added CO (Table I, reaction 9).[28]

These experiments, along with those of King et al.,[29] suggest that a coordinatively unsaturated manganese acyl complex can be effectively converted into observable organic products under H_2 pressure. Since there is not yet a well-established example in the literature of CO migratory insertion into a metal-hydrogen bond, several experiments were carried out with $(CO)_5MnH$ under H_2 pressure. If, as has been proposed,[30] this complex is in equilibrium with a coordinatively unsaturated formyl complex, $(CO)_4MnC(O)H$, the latter might be expected to yield formaldehyde or methanol upon hydrogenation. Experiments at temperatures up to 250 °C and H_2 pressures up to 5000 psi yielded traces of methanol, but only at the higher temperature and pressure levels (Table I, reaction 10). (Similar conditions were required for catalytic methanol formation from CO/H_2 with $(CO)_5MnH$.[2])

The results summarized in Scheme I show that a transition metal complex bearing a ligand analogous to the hydroxymethyl group can yield ethylene glycol upon reaction with synthesis gas under unusually mild conditions, compared with those needed for homogeneous catalytic CO hydrogenation.[2] This conversion presumably requires operation of two steps which might not have been anticipated to proceed this easily: migratory insertion of CO into an oxy-substituted methyl-metal bond, and hydrogenation of an aldehyde intermediate to alcohol. A second reductive elimination pathway yielding the one-carbon product has also been demonstrated. Mechanistic details of hydrogen activation and transfer in these reactions are not yet clear. Radical species have been shown to be involved in hydrogen activation by $Re_2(CO)_{10}$ and $Mn_2(CO)_{10}$[31] and may be important in this system also. The possibility that a bimolecular process[32] is involved in product-forming steps is being investigated. Nevertheless, the major features of Scheme I appear to provide a mechanistic model for more complex catalytic systems, especially Fischer-Tropsch-type catalysts for production of alcohols from synthesis gas[2] and hydroformylation catalysts which convert formaldehyde to glycoaldehyde and glycol.[26,33] Studies dealing with other mechanistic aspects of these reactions are also in progress.

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(17) Calcd for $C_{11}H_{11}O_7Mn$: C, 42.58; H, 3.55. Found: C, 42.16; H, 3.44. NMR ($CDCl_3$): δ 1.15 (s, 9 H), 4.70 ppm (s, 2 H). IR (*n*-hexane): 2119 (w), 2052 (w), 2018 (vs), 2001 (s), 1726 cm^{-1} (m).

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(22) Calcd for $C_{12}H_{11}O_8Mn$: C, 42.60; H, 3.25. Found: C, 42.05; H, 3.25. NMR ($CDCl_3$): δ 1.20 (s, 9 H), 4.70 ppm (s, 2 H). IR (*n*-hexane): 2118 (w), 2059 (w), 2019 (vs), 2007 (s), 1751 (m), 1674 cm^{-1} (m).

(23) The electron-withdrawing effect of a hydroxy or acyloxy substituent is expected to decrease substantially the ability of an alkyl group to undergo CO insertion, based on observations[24] and calculations[25] on migration rate as a function of alkyl group electronegativity. Facile insertion of CO into a metal–α-silyloxybenzyl bond has been reported,[4] but this ligand is electronically and sterically very different from hydroxymethyl. Insertion of CO into a cobalt–hydroxymethyl bond under mild conditions has been postulated as a step in the stoichiometric hydroformylation of formaldehyde.[26]

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(28) Although these results might appear to be inconsistent with those of King and co-workers,[29] who report the observation under somewhat more severe conditions of unreduced acetaldehyde from $(CO)_5MnC(O)CH_3$ and H_2 alone, it should be noted that the acetyl complex may release CO upon reaction with H_2. Small amounts of CO may also have remained in solution from formation in situ of the acetyl complex from $(CO)_5MnCH_3$ and CO.

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B. Duane Dombek
Union Carbide Corporation
South Charleston, West Virginia 25303
Received June 11, 1979

Reactions of Vinylcyclopropane Induced by Multiphoton Absorption of Infrared Radiation

Sir:

Over the past few years, the activation of chemical reactions via multiphoton absorption of infrared radiation has been shown to be a fairly general phenomenon in polyatomic molecules.[1] As part of an investigation of applications of this technique to problems in organic reaction dynamics, we report here our work on the CO_2 laser-induced unimolecular reactions of vinylcyclopropane (VCP). From changes in the product distribution as a function of photolysis conditions, we make inferences about the influence of bath gas pressure and structure and laser frequency on the energy distribution in laser-activated reactants. There have been several previous studies of the unimolecular reactions of VCP initiated both thermally[2] and via chemical activation.[3] The product distributions from these studies make an interesting comparison with our work.

Our experiments have been carried out using a grating-tuned Lumonics TEA 101 CO_2 laser tuned to the P(24) line of the 001–100 transition (940.6 cm^{-1}). The beam was focused with a 15-in. ZnSe lens, and the cell was centered 5 cm beyond the focal point. In all cases reported, the laser fluence at the front window of the cell was 5.0 ± 1 J/cm^2.[4] Typically, 250 pulses were delivered to a given sample prior to chemical analysis by gas chromatography or gas chromatography-mass spectrometry (GC-MS), in both cases by direct gas injection. The cell was a Pyrex cylinder 5 cm × 2.5 cm (i.d.) fitted with KCl windows. It was filled to known pressures of materials ranging from 0.02–10 Torr on a vacuum line equipped with an MKS Baratron capacitance manometer. Vinylcyclopropane is prepared by the procedure of Kirmse et al.,[5] and purified by preparative GC prior to use.

When 0.2 Torr of vinylcyclopropane is irradiated under these conditions, the product distribution shown in Table I is obtained. Mass balance is good. The sum of the product yields equals 100 ± 2% of the VCP disappearance. It is interesting to compare this distribution with those obtained in the thermal and chemical activation experiments (Table I). The high cyclopentadiene yields distinguish the laser-activated results from thermal distributions at 362 °C. Although at higher temperatures cyclopentene (**4**) will decompose to cyclopentadiene (**5**) and H_2,[6] the laser results cannot be rationalized by simple

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