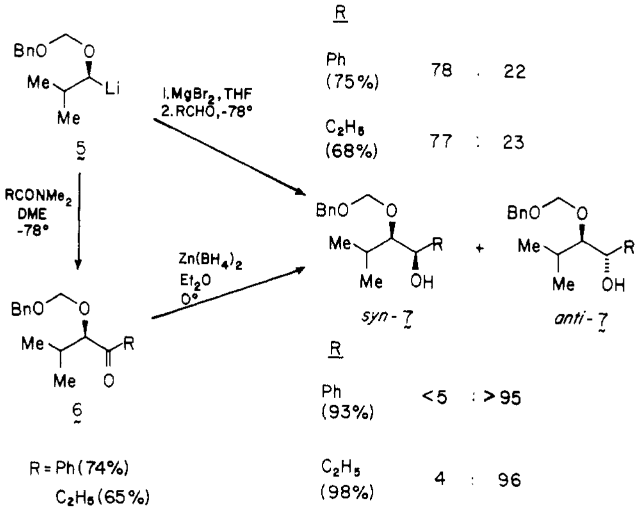
Scheme II



stitution shows no improvement (entries F and G). The nature of the metal is also an important factor. In every case examined, syn selection increases with the replacement of the organolithium compound with the corresponding organomagnesium derivative. Addition of catalytic amounts of copper salts gives modest improvement (entry K), while attempts to further enhance diastereoselectivity through other organometallic species was, unfortunately, precluded by their unreactive nature.[11]

This data lends itself to a rational of kinetic stereoselection as presented in Scheme I. Diastereotopic transition states **4a** and **4b** seem reasonable through extrapolation of the mechanism proposed for the addition of simple organolithium and organomagnesium reagents to carbonyl compounds.[12] Enantiofacial discrimination results from the unfavorable R_1/R_2 interaction present in **4b** (minor) but absent in **4a** (major). The stereoregulating effect of the metal center is still unclear, though adjustment in the ground-state energy of **1** and geometrical preference in transition states **4a**/**4b** remain as possibilities.[13] In all cases, internal coordination of the type **3** apparently imparts a directing effect upon the interaction of the reaction partners.

Along more practical lines, these asymmetric carbanions should allow convenient, stereoselective access to 1,2-diol derivatives. The utility of these intermediates is illustrated in Scheme II.[14,15] Direct condensation of organomagnesium derivative **5** with either benzaldehyde or propionaldehyde leads to an approximately 3.5:1 mixture of diol derivatives **7** favoring the syn isomer. Alternatively, these carbanions may be acylated to give carbonyl compounds **6**,[16] which are cleanly reduced to the anti isomers **7** with zinc borohydride.[17] It is noteworthy that this scheme allows convergent synthesis of diols of either stereochemical series through formation of the same carbon-carbon bond.

In conclusion, these studies demonstrate the enantiofacial discrimination of some asymmetric carbanions in their condensation with prochiral carbonyl compounds. While this preliminary work already offers a synthetically useful, convergent approach to some 1,2-diols, improved syn selection can now be expected on the basis of the emergence of a model for the transition state in these condensations. Furthermore, these results underscore the importance in considering the reaction parameters described at the outset in the design of stereoselective transformations. Finally, the present observations may shed light on the factors governing the stereoselectivity exhibited by related asymmetric carbanionic species.[18] Further refinement of the stereoregulating features, as well as exploitation of the synthetic potential of these condensations, will be reported in due course.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Institutes of Health (AI 17595-02) for support of this work.

Registry No. **1A**, 83879-83-9; **1B**, 83876-84-0; **1C**, 83876-85-1; **1D**, 83876-86-2; **1E**, 83876-87-3; **1F**, 83876-88-4; **1G**, 83876-89-5; **1H**, 83876-90-8; **1I**, 83876-91-9; **1J**, 83876-92-0; **1L**, 83876-93-1; **1M**, 83897-16-9; *anti*-**2A**, 83876-94-2; *syn*-2A, 83877-00-3; *anti*-**2C**, 83876-95-3; *syn*-**2C**, 83877-01-4; *anti*-**2D**, 83876-96-4; *syn*-**2D**, 83877-02-5; **2E**, 83877-03-6; *anti*-**2F**, 83876-97-5; *syn*-**2F**, 83877-04-7; *anti*-**2G**, 83876-98-6; *syn*-**2G**, 83877-05-8; *anti*-**2L**, 83876-99-7; *syn*-**2L**, 83877-06-9; **6** (R = Ph), 83877-07-0; **6** (R = C_2H_5), 83877-08-1; *anti*-**7**(R = C_2H_5), 83897-17-0; *syn*-**7** (R = C_2H_5), 83877-09-1; benzaldehyde, 100-52-7; propanal, 123-38-6; *trans*-4-ethyl-2,2-dimethyl-5-phenyl-1,3-dioxolane, 83877-10-5; *cis*-4-ethyl-2,2-dimethyl-5-phenyl-1,3-dioxolane, 83877-11-6; *trans*-4-isopropyl-2,2-dimethyl-5-phenyl-1,3-dioxolane, 83877-12-7; *cis*-4-isopropyl-2,2-dimethyl-5-phenyl-1,3-dioxolane, 83877-13-8; *trans*-4-*tert*-butyl-2,2-dimethyl-5-phenyl-1,3-dioxolane, 83877-14-9; *cis*-4-*tert*-butyl-2,2-dimethyl-5-phenyl-1,3-dioxolane, 83877-15-0.

Supplementary Material Available: A listing of the NMR data for the cyclic derivatives used for stereochemical analysis is available (2 pages). Ordering information is given on any current masthead page.

Glenn J. McGarvey,* Masayuki Kimura
Department of Chemistry
University of Virginia
Charlottesville, Virginia 22901

Received September 8, 1982

---

[11] No reaction was observed when the organolithium species was treated with boron, aluminum, and zinc compounds as well as stoichiometric quantities of copper salts, prior to condensation with the aldehyde.

[12] (a) Ashby, E. C.; Laemmle, J. T. *Chem. Rev.* **1975**, *75*, 521. (b) Ashby, E. C. *Pure Appl. Chem.* **1980**, *52*, 545.

[13] For an example of steric preferences exhibited by different metals, see: Still, W. C.; Schneider, J. A. *Tetrahedron Lett* **1980**, 1035.

[14] All yields (in parentheses) reported after flash chromatography.[9]

[15] The analysis of the stereoisomeric mixture was carried by gas chromatographic resolution of the dimethyl acetals corresponding to *syn*-7/*anti*-7 (prepared from *syn*-7/*anti*-7 by (i) H_2, Pd-C, MeOH, (ii) $Me_2C(OMe)_2$, Me_2CO, TsOH). The isomer corresponding to *syn*-7 eluted first on a 10-ft column of 5% SE-30 on Chromosorb W with a carrier gas flow rate of 30 mL/min.

[16] Further information on this useful transformation will be reported shortly.

[17] (a) Nakata, T.; Tanaka, T.; Oishi, T. *Tetrahedron Lett.* **1981**, 4723. (b) *Ibid.* **1980**, 1641.

[18] These results are consistent with the erythro selectivity shown by α-metallo carbonyl compounds.[3b]

HI-Induced Reductive Coupling of Carbon Monoxide and Homologation of a Carboxylic Acid

Summary: Carbon monoxide reacts with aqueous HI to give acetic acid. Acetic acid reacts with carbon monoxide and aqueous HI to give propionic acid.

Sir: We report that HI can effect the remarkable transformations

$$CO \xrightarrow{HI,\ H_2O} CH_3CO_2H, \tag{1}$$

and

$$CH_3CO_2H + CO \xrightarrow{HI,\ H_2O} CH_3CH_2CO_2H \tag{2}$$

Table I. Reaction of CO with HI[a]

solvent[b]	pressure, psi		product[f] in solution, g	
	CO	H_2	CH_3CO_2H	HCO_2H
65% aq HI	2500	2500	0.04	0.5
65% aq HI	3750	1250	0.07	0.6
65% aq HI	4000		0.05	0.6
65% aq HI	2100		~0.02	0.2
56% aq HI	3750	1250	0.024	0.6
43% aq HI[c]	3750	1250	~0.014	0.6
aq HI/HBr[d]	3750	1250	~0.01-0.02	0.5
water/HI/LiI[e]	3750	1250	~0.01	0.4

[a] In virgin glass for 2 h at 250 °C; 40 mL of solvent, unless noted otherwise. [b] No acetic acid was produced in water, 59% aq H_3PO_4, 30% aq HCl, or 48% aq HBr. [c] 43% HI is 65% HI that has been diluted with an equal volume of water. [d] 40 mL of 48% aq HBr + 4 mL of 65% aq HI. The amount of hydrogen ion in this reaction solution is almost the same as in 40 mL of 65% aq HI. [e] 25 mL of water, 4 mL of 65% aq HI, 50 g of LiI. This mixture contains the same amount of water and I^- as does 40 mL of 65% aq HI. [f] Identified and determined by use of VPC and ^1H and ^{13}C NMR spectroscopy.

Acetic acid has been produced from CO and H_2 by reaction on supported heterogeneous transition-metal catalysts[13] and by reaction with solutions containing compounds of rhodium,[1ab] platinum,[1a] iridium,[1a] palladium,[1a] and ruthenium.[1cde] We have found that reaction of aqueous HI with CO leads to the formation of acetic acid (reaction 1). Results are in Table I. Substantial amounts of both hydrogen and iodide ions are necessary to obtain highest yields; the yield of acetic acid was less than stoichiometric.

Some of our observations and some reports in the literature are relevant to a consideration of pathway: (1) Protonation of CO would give a species that could react (a) with water to give HCO_2H (Table I), (b) with CO,[2] followed by reaction with water, to give HO_2CCHO,[3a] possibly reversibly, or (c) with iodide to give HCOI.[4] (1a.1) Protonation of HCO_2H at the carbonyl oxygen would give a species that could react with CO, followed by reaction with water, to give the hydrate of HO_2CCHO.[3a] (1c.1) The reaction, $HCOI + HI \rightarrow CH_2O + I_2$, would be analogous to the known reaction,[5] $CH_3COI + HI \rightarrow CH_3CHO + I_2$. (2) The conversion of HO_2CCHO by acid to CH_2O has been reported.[6] (3) We have found that the reaction of formaldehyde (α-polyoxymethylene) with 65% aqueous HI and 500 psi of CO at 100 °C results in its quantitative conversion to CH_3CO_2H.[7a] The reaction of HO_2CCHO with 65% aqueous HI results in the formation of HO_2CCH_2OH in high yield at room temperature[3b] and in the formation of CH_3CO_2H and $CH_3CH_2CO_2H$ (see below) under the conditions of Table I. In contrast, introduction of CH_3OH in an amount that resulted in the conversion at room temperature to an amount of CH_3I equivalent to 0.4 g of CH_3OH did not result in the formation of CH_3CO_2H in an amount greater than is formed when CH_3OH is not introduced. (4) The conversion of HO_2CCH_2OH (from CH_2O[3a] or HO_2CCHO) by HI to CH_3CO_2H would be precedented.[7bc] (5) The conversion of HO_2CCHO to CH_3CO_2H by HI would be analogous to that of CH_3COCO_2H to $CH_3CH_2CO_2H$ (see below).

We have also found that reaction of acetic acid (88 mmol) in 65% aqueous HI (40 mL) in virgin glass for 2 h at 250 °C with 5000 psi of CO or 3/1 CO/H_2 led to conversions to propionic acid of 17% and 10%, respectively (reaction 2); reaction in 12% aqueous HI led to no propionic acid and to quantitative recovery of the acetic acid.

Some of our observations and some reports in the literature are relevant to a consideration of pathway: (1) A reaction of CH_3COOH analogous to that described in 1a.1 above would give the hydrate of CH_3COCO_2H. (2) The product of the reaction[8] of CH_3CO_2H with HI could give a species that could react with CO, followed by reaction with water, to give CH_3COCO_2H. (3) The reaction, $CH_3COCO_2H + HI \rightarrow CH_3CH_2CO_2H$ has been reported.[9] (4) We have found that CH_3COCO_2H and $CH_3CHOHCO_2H$ react at room temperature with 65% aqueous HI to give a species that has characteristics of CH_3CHICO_2H and that reacts under conditions of the homologation reaction (see above) to give $CH_3CH_2CO_2H$; in contrast, ethanol did not give $CH_3CH_2CO_2H$ under those conditions.

Our observation of reaction 2 is relevant to the mechanism of the homologation of carboxylic acids effected in the presence of compounds of iodine plus compounds of transition metals.[10]

Acknowledgment. We are grateful to Wilbur L. Berry and Jack W. Fitzwater for expert technical assistance.

---

(1) (a) Kaplan, L., following communication in this issue. (b) Kaplan, L. U.S. Patent Application 1980, 201713. (c) G. Jenner, A. Kiennemann, E. Bagherzadah, and A. Deluzarche (*React. Kinet. Catal. Lett.* **1980**, *15*, 103) reported the $RuCl_3 \cdot 3H_2O$- and RuO_2-catalyzed conversion of 1-propanol to *n*-propyl acetate by 1100 atm of 1/1 CO/H_2. (d) D. W. Smith (British Patent Publication **1981**, 2074164A) reported the formation of CH_3CO_2H and $CH_3CO_2CH_3$ in unreported amounts as minor products of the reaction of CO/H_2 with halogen-containing ruthenium catalysts in *N-methyl*pyrrolidone as solvent at ~500 atm. (e) J. F. Knifton has reported the $RuO_2/[Mn_2(CO)_{10}$, $Mn(acac)_3$, $MnCO_3$, or $Re_2(CO)_{10})]$-, $[RuO_2$, $Ru(acac)_3$, or $Ru_3(CO)_{12}]/[Co(acac)_3$ or $Co_2(CO)_8]$- and $[RuO_2$ or $Ru(acac)_3]/[Ti(acac)_2(OBu)_2$, $Ti(OMe)_4$, or $Ti(acac)_3]$-catalyzed conversion of CO/H_2 to acetate esters in molten R_4PX at 4000–6000 psi and 220 °C in U.S. Patents **1982**, 4332914, 4332915, and 4339545, respectively.

(2) The gas phase reaction, $HCO^+ + CO \rightarrow H(CO)_2^+$, has been reported but the structure of the product is unknown: (a) Hiraoka, K.; Kebarle, P. *J. Am. Chem. Soc.* **1977**, *99*, 366. (b) Meot-Ner, M.; Field, F. H. *J. Chem. Phys.* **1974**, *61*, 3742. (c) Sieck, L. W. *Int. J. Chem. Kinet.* **1978**, *10*, 335. (d) Hiraoka, K.; Saluja, P. P. S.; Kebarle, P. *Can. J. Chem.* **1979**, *57*, 2159. (e) Hiraoka, K. *Int. J. Mass Spectrom. Ion Phys.* **1980**, *33*, 73.

(3) (a) The acid-catalyzed hydrocarboxylations of CO and HCO_2H to HO_2CCHO and $HO_2CCH(OH)_2$, respectively, would be analogous to the well-known acid-catalyzed hydrocarboxylation of H_2CO to HO_2CCH_2OH. (b) The autoconversion of HO_2CCHO to HO_2CCH_2OH upon heating is well-known.

(4) HCOCl and its formation from HCl and CO are well-known.[13]

(5) O'Neal, H. E.; Benson, S. W. *J. Chem. Phys.* **1962**, *37*, 540.

(6) Voisenet, E. *Bull. Soc. Chim. Fr.* **1918**, *23*, 361.

(7) (a) S. J. Lapporte and V. P. Kurkov (in "Organotransition-Metal Chemistry"; Ishii, Y., Tsutsui, M., Eds.; Plenum Press: New York, 1975; p 199) reported the conversion of trioxane to CH_3CO_2H in 2% yield by reaction with ~11% aqueous HI at 1000–1500 psi of CO and 150 °C. (b) The reactions, $ROH + HI \rightarrow RI$ and $RI + HI \rightarrow RH + I_2$, are well-known. (c) W. W. Paudler and T. E. Walton (*J. Org. Chem.* **1981**, *46*, 4306) have reported the reaction, $ROH + (I_2 \text{ or } HI)/H_2 \rightarrow RH$.

(8) The gas-phase reaction of acetic acid with HBr has been studied: Daly, N. J.; Gilligan, M. F. *Aust. J. Chem.* **1969**, *22*, 713; **1971**, *24*, 765, 1081.

(9) Wislicenus, W. *Justus Liebigs Ann. Chem.* **1863**, *126*, 229.

(10) (a) Knifton, J. F. *Abstr Pap.—Am. Chem. Soc.* **1980**, 179th, INOR 209; *ACS Symp. Ser.* **1981**, *152*, 225; British Patent Publication 1981, 2058749; Prepr. ACS Div. Petrol. Chem. 1981, Atlanta, 35; *J. Mol. Catal.* **1981**, *11*, 91; *Chem. Commun.* **1981**, 41; *Hydrocarbon Process.* **1981**, *60*, Dec, 113; *ChemTech* **1981**, 609; U.S. Patents 1982, 4334092, 4334093, 4334094. (b) Possibly,[11] there are other examples.[12] (c) See also ref 1 of the accompanying communication.

(11) When $CH_3CH_2CO_2^-$ is produced from reactants that contain also a methoxy group, it is unclear as to which pathway, $CH_3CO_2\text{-} \rightarrow CH_3CH_2CO_2\text{-}$ or $CH_3O\text{-} \rightarrow CH_3CH_2O\text{-} \rightarrow CH_3CH_2CO_2\text{-}$, is being followed.

(12) (a) Hohenschutz, H.; v. Kutepow, N.; Himmele, W. *Hydrocarbon Process.* **1966**, *45*, Nov, 141. (b) Braca, G.; Sbrana, G.; Gregorio, G. French Patent Application 1977, 22876. (c) Braca, G.; Sbrana, G.; Valentini, G.; Andrich, G.; Gregorio, G. In "Fundamental Research in Homogeneous Catalysis"; Tsutsui, M., Ed.; Plenum Press: New York, 1979; Vol. 3, p 221. (d) Braca, G.; Busni, S.; Sbrana, G.; Valentini, G. *Chim. Ind.* 1981, *63*, 516. (e) Drent, E. European Patent Application 1981, 31606.

(13) See paragraph at the end of the paper about supplementary material.

Registry No. CO, 630-08-0; HI, 10034-85-2; CH_3CO_2H, 64-19-7; $CH_3CH_2CO_2H$, 79-09-4.

Supplementary Material Available: References (2 pages). Ordering information is given on any current masthead page.

Leonard Kaplan
Union Carbide Corp.
P.O. Box 8361
S. Charleston, West Virginia 25303

Received July 1, 1982

Transition Metal/Acid Induced Reductive Coupling of Carbon Monoxide

Summary: Carbon monoxide is converted to acetic acid and to glycolic acid by solutions containing acid and compounds of palladium, rhodium, platinum, and iridium; glycolic and acetic acids are produced in the presence of HCl or H_3PO_4 but, in the presence of iodide, acetic acid alone is produced.

Sir: We report reductive coupling of carbon monoxide to acetic acid and to glycolic acid.

The conversions were effected by solutions containing acid, either introduced as such or formed in situ, and compounds of transition metals.[1-3]

$$CO + H_2 \xrightarrow[\text{acid}]{\text{compound of Pd, Rh, Pt, or Ir}} CH_3CO_2H,\ HOCH_2CO_2H$$

Acetic acid has been produced from CO and H_2 by reaction on supported heterogeneous transition-metal catalysts and by reaction with solutions containing ruthenium[4a]; we have recently described its formation from CO and aqueous HI in the absence of a metal.[4b]

Representative results obtained by use of compounds of palladium in the presence of acids containing halide or phosphate are in Tables I and II.[5] Glycolic acid was produced by palladium in combination with HCl or H_3PO_4 (Table I); both palladium and acid are necessary (Table I, note *b*). In the presence of iodide, acetic acid alone was produced by reaction of CO or CO/H_2 (Table II). Palladium is used in an amount greater than the molal amounts of products.

On the basis of reports in the literature and our own observations, we believe that a body of indirect evidence exists that is consistent with a pathway resembling $CO \rightarrow (HC(=O)CO_2H, CH_2O) \rightarrow HOCH_2CO_2H \rightarrow CH_3CO_2H$ for the formation of products: (1) See ref 4b for a discussion of the transformations $CO + H_2O \rightarrow HCO_2H$; $2CO + H_2O \rightarrow HO_2CCHO$; $CO + HX \rightarrow HCOX$; $HCO_2H + CO + H_2O \rightarrow HO_2CCHO$; $HCOI + HI \rightarrow CH_2O + I_2$; $HO_2CCHO \rightarrow CH_2O$; $HO_2CCHO \rightarrow HOCH_2CO_2H$; $CH_2O + CO + H_2O \rightarrow CH_3CO_2H, HOCH_2CO_2H$; $HO_2CCHO \rightarrow HO_2CCH_2OH$; $HOCH_2CO_2H \rightarrow CH_3CO_2H$ in the absence of a metal. (2) The palladium-catalyzed reduction of acyl halides is well-known. (3) The acid-catalyzed conversion of a glycoloyl–metal compound to an acetyl compound, $ROCH_2C(=O) \rightarrow CH_3C(=O)$, is known.[6] (4) It was reported that trioxane (formaldehyde trimer), water, and HI reacted with 1000 psi of CO at 150 °C in the presence of $PdCl_2$ to give $HOCH_2CO_2H$, CH_3CO_2H, and HCO_2H;[7] we made similar observations upon addition of formaldehyde (20 mmol) to the $PdCl_2$/water system of Table I. (5) In contrast, addition of CH_3OH (21, 18, and 11 mmol) to the $PdCl_2$ system in water, 30% aqueous HCl, and 65% aqueous HI, respectively, resulted in the formation of products in amounts very similar to those given in Tables I and II, respectively.[8,9] (6) Addition of $HOCH_2CO_2H$ (18 mmol) to the $PdCl_2$/30% aqueous HCl and $PdCl_2$/water systems gave a yield of CH_3CO_2H that was 55% and 18%, respectively, after exclusion of any amount produced (Table I) in the absence of added $HOCH_2CO_2H$. (7) The $CH_3CO_2H/HOCH_2CO_2H$ ratio increased and the amount of $HOCH_2CO_2H$ decreased with increases in time and in [HCl] (Table I). (8) In the presence of I^-, anticipated to be better than Cl^- at effecting a metal/acid catalyzed conversion of ROH to RH, only CH_3CO_2H was observed (Table II vs. Table I).

Other metals also effected these reactions: (a) $Rh(CO)_2acac$ (1.5 mmol), in sulfolane[10] at 250 °C and 12500 psi of 1/1 CO/H_2, combined with HI (3 mmol), I_2 (1.5 mmol), or ZnI_2 (150 mmoles)[11] gave 2–5 g of CH_3CO_2H in 4 h. (b) Under conditions similar to those used for palladium (Table I), $Ir_4(CO)_{12}$ (1.2 mmol) in 30% aqueous HCl and $IrCl_3$ (10 mmol) in water each produced ~0.05 g of CH_3CO_2H; Ir powder produced none. Under 5000 psi of CO and otherwise similar (Table I) conditions, Na_3IrCl_6 (4 mmol) in 30% aqueous HCl and in water produced 0.08 and 0.03 g, respectively, of CH_3CO_2H. (c) Under conditions similar to those used for palladium (Table I), $PtCl_2$ (10

---

(1) A unified discussion of "acid catalysis" and "transition metal catalysis" is provided as Supplementary Material.

(2) For a review of proton-induced reduction of CO, see Shriver, D. F. in "Catalytic Activation of Carbon Monoxide"; Ford, P. C., Ed.; American Chemical Society: Washington, DC, 1981; ACS Symp. Ser. No. 152, p 1.

(3) References to the use of compounds of Pd, Ir, Pt, Ru, and Rh in the presence of acid as ionic hydrogenation catalysts, e.g., as "hydride-transfer agents" to electrophilic centers, are provided as Supplementary Material.

(4) (a) J. F. Knifton has reported the $RuO_2/[Mn_2(CO)_{10}$, $Mn(acac)_3$, $MnCO_3$, or $Re_2(CO)_{10}]$-, $[RuO_2$, $Ru(acac)_3$, or $Ru_3(CO)_{12}]/[Co(acac)_3$ or $Co_2(CO)_8]$-, and $[RuO_2$ or $Ru(acac)_3]/[Ti(acac)_2(OBu)_2$, $Ti(OMe)_4$, or $Ti(acac)_3]$-catalyzed conversion of CO/H_2 to acetate esters in molten R_4PX at 4000–6000 psi and 220 °C in U.S. Patents 4 332 914, 4 332 915, and 4 339 545, 1982, respectively. G. Jenner, A. Kiennemann, E. Bagherzadah, and A. Deluzarche (*React. Kinet. Catal. Lett.* **1980**, *15*, 103) reported the $RuCl_3 \cdot 3H_2O$- and RuO_2-catalyzed conversion of 1-propanol to *n*-propyl acetate by 1100 atm of 1/1 CO/H_2. D. W. Smith (British Patent Publication 2074164A, 1981) reported the formation of CH_3CO_2H and $CH_3CO_2CH_3$ in unreported amounts as products of the reaction of CO/H_2 with halogen-containing ruthenium catalysts in *N-methyl*-pyrrolidone as solvent at ~500 atm. (b) Kaplan, L., preceding communication in this issue.

(5) A discussion of the chemistry of palladium in the presence of CO, anions, and/or acids and of the chemistry of palladium carbonyl halide anions is provided as Supplementary Material.

(6) For example, see Cutler, A.; Bodnar, T.; Coman, G.; LaCroce, S.; Lambert, C.; Menard, K. In "Catalytic Activation of Carbon Monoxide"; Ford, P. C., Ed.; American Chemical Society: Washington, DC, 1981; ACS Symp. Ser. No 152, p 283.

(7) Lapporte, S. J.; Toland, W. G. U.S. Patent 3 754 028, 1973.

(8) However, if it is the reaction of compounds other than the material added or its progeny that limits the formation of product, the absence of an increase in amount of the product upon addiiton of that material is not necessarily citable as evidence against the intermediacy of that material. We did observe in the two experiments, however, the formation of products, not normally formed, tentatively identified as $CH_3Cl + CH_3OCH_3$ and two-carbon hydrocarbons, respectively. The significance of these observations also is ambiguous since those products may have been consolation fates of the added CH_3OH, i.e., a limiting reagent may not have been available to the CH_3OH in adequate quantity.

(9) The same results were obtained upon addition of HCO_2CH_3 to the $PdCl_2$/65% aqueous HI system. Cf., e.g., Wada, K.; Baba, A.; Wada, N. Japan Patent Application 22 745, 1981.

(10) Kaplan, L. U.S. Patent 4 224 237, 1980.

(11) Some other iodides produced smaller amounts of CH_3CO_2H. ZnF_2, $Zn(CN)_2$, and $Zn(stearate)_2$ were ineffective.

(12) Vauquelin *Ann. Phil.* 1814, *4*, 216.