Vapor-Phase Olefin Isomerization with Cobalt Hydrocarbonyl and the Mechanism of the Hydroformylation Reaction

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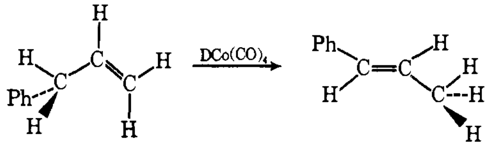
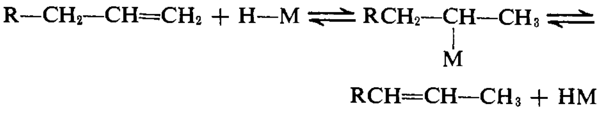
Abstract: Experiments on the isomerization of propene-d_6 catalyzed by $HCo(CO)_4$ show appreciable incorporation of H onto the central carbon atom. These experiments demonstrate that isomerization occurs, at least in part, by the 1,2 addition–elimination of $HCo(CO)_4$. Analysis of the reaction mixture also shows that approximately 70% of the addition of $HCo(CO)_4$ to propylene, in the absence of carbon monoxide, proceeds by Markovnikov addition.

Although it is well known that extensive olefin isomerization competes with the hydroformylation of an olefin, especially under stoichiometric conditions,[1] the mechanism of this isomerization has not been clearly demonstrated. In the $DCo(CO)_4$-catalyzed rearrangement of allyl alcohol to propionaldehyde there is evidence for a 1,3 intermolecular allylic exchange.[2] With allylbenzene there is some evidence[3] for a catalyzed intramolecular 1,3 shift.



(1)

A concerted [1,3] sigmatropic shift *via* a suprafacial pathway is forbidden, but the presence of the cobalt catalyst may remove the symmetry restrictions.[4] Perhaps the simplest mechanism for the isomerization is the 1,2 addition–elimination[5] of the metal hydride.



$$R{-}CH_2{-}CH{=}CH_2 + H{-}M \rightleftharpoons RCH_2{-}\underset{\displaystyle M}{\underset{|}{C}H}{-}CH_3 \rightleftharpoons RCH{=}CH{-}CH_3 + HM \quad (2)$$

The extent of this isomerization is very sensitive to the carbon monoxide partial pressure.

In order to avoid solvent effects and to more closely control the concentration of carbon monoxide, we have developed simple techniques for conducting the hydroformylation in the vapor phase. Operation in the vapor phase is fortunately made possible by the unusually low boiling point of $HCo(CO)_4$. We now wish to report a series of experiments on the isomerization of $CD_3CD{=}CD_2$ with $HCo(CO)_4$ which show that the isomerization must proceed, at least in part, by the 1,2 addition–elimination mechanism, and that the addition is predominantly Markovnikov under these conditions.

Experimental Section

(1) **Procedure.** The vapor-phase isomerization experiments were conducted in a Pyrex bulb, having a capacity of 1130 cm^3, attached to a glass manifold as shown in Figure 1. The reaction bulb L was cleansed by washing with hot alcoholic KOH and rinsing with water, then washing with aqua regia and rinsing with distilled water before drying and attaching it to the manifold. The entire system was evacuated and heated with a low flame under a dynamic vacuum for 1 hr. Stopcock A was closed and carbon monoxide was admitted into the entire glass system to 1 atm and stopcock I was closed. A standardized solution of cobalt hydrocarbonyl in pentane, 1 ml, was injected through serum stopper J into side-arm tube K, and simultaneously a small dewar of liquid nitrogen was placed around it. Stopcock I was opened and the entire system was evacuated and kept under a dynamic vacuum for 10–15 min before again closing stopcock I and warming the cobalt hydrocarbonyl solution to −78° with a Dry Ice–acetone bath until it melted. The solution in the side arm was again cooled with a liquid nitrogen bath and stopcock I was opened to the dynamic vacuum for 10–15 minutes. This procedure of thawing, freezing, and pumping was repeated two more times to completely degas the cobalt hydrocarbonyl solution. The entire bulb L was immersed in a liquid nitrogen dewar, stopcocks D and A were closed, and 1-butene (or propene) was admitted into the manifold B, 300 ml at 26 ± 1°, to the desired pressure. Stopcock C was then closed and stopcock D opened to condense the 1-butene on the walls of the flask L. This procedure was repeated for experiments which involved propene-d_6. After the reactants were in flask L, the liquid nitrogen dewar was removed and a small dewar again placed around the side-arm tube K. With stopcock I closed, flask L was warmed as rapidly as possible with a stream of compressed air and immersed in a beaker of water at 26° for 2–3 min. The cobalt hydrocarbonyl solution in the side-arm tube K was warmed to −78° and then quickly flashed (30–40 sec) by warming it with hot water (60–70°) into the reaction bulb L. The reaction time was recorded at the point when the $HCo(CO)_4$ solution completely evaporated. A gas sample was taken by replacing the glass cap F with a small sampling bulb for mass spectra analysis.

(2) **Deuterium Exchange Reactions. Propene-d_6 and Propene Catalyzed by Cobalt Hydrocarbonyl (11:11:1).** Propene-d_6 (4.6 mmol) and propene (4.6 mmol) were condensed in the reaction flask and mixed at 26° with cobalt hydrocarbonyl (4.17×10^{-1} mmol) by flashing a solution of pentane–cobalt hydrocarbonyl into the flask. After 240 min the gases were condensed in a small flask attached to the line and the reaction flask was removed, cleaned, dried, and replaced on the manifold. The gases were transferred back into the reaction vessel and a small sample was taken for mass spectral analysis, with the results shown in Table I. The remaining gases were treated with bromine, 1 ml, with shaking in the dark. After 40 min a solution of water–sodium thiosulfate was added slowly with constant agitation until the bromine color disappeared. Pentane, 5 ml, was added to the flask and used to extract the dibromo compounds. After two more pentane extractions the organic layer was dried over sodium sulfate and evaporated on a Rotavapor at 25°. Mass spectra of the dibromopropanes showed no further deuterium scrambling.

(3) **Propene-d_6 and 1-Butene Catalyzed by Cobalt Hydrocarbonyl (11:11:1).** The preceding experiment was repeated, except 1-butene was used in place of propene. After 240 min of

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(1) M. Orchin, *Advan. Catal.*, **16**, 1 (1966).

(2) R. W. Goetz and M. Orchin, *J. Amer. Chem. Soc.*, **85**, 1549 (1963).

(3) L. Roos and M. Orchin, *ibid.*, **87** 5502 (1965).

(4) F. Mango and J. D. Schachtschneider, *ibid.*, **89**, 2484 (1967); F. Mango, *Advan. Catal.*, **20**, 291 (1969).

(5) B. Fell, P. Krings, and F. Asinger, *Chem. Ber.*, **99**, 3688 (1966); R. Cramer and R. V. Lindsey, Jr., *J. Amer. Chem. Soc.*, **88**, 3524 (1966), suggest that the small quantity of D incorporation in the allylbenzene isomerization reaction is consistent with a 1,2 addition–elimination mechanism.

Table I. Mass Spectral Analysis of Deuterated Propenes from the $HCo(CO)_4$-Catalyzed Exchange between C_3D_6 and $1\text{-}C_4H_8$ or C_3H_6

Deuteriopropenes	Propene, %[a] 1-Butene	Propene
C_3D_6	53.5	62.7
C_3D_5H	33.5	27.8
$C_3D_4H_2$	9.0	7.7
$C_3D_3H_3$	4.0	1.8

[a] Per cent propene in mixture after exchange with the compound in question.

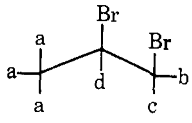
reaction time, the analysis of a gas sample by vpc showed that isomerization had occurred: 1-butene, 15%; *trans*-2-butene 50%; and *cis*-2-butene, 35%. Again, a gas sample was taken and analyzed by mass spectroscopy, with the results shown in Table I. The remaining gases were treated with bromine in the dark and worked up as in the above experiment, and the 1,2-dibromopropanes were collected from preparative gas chromatography and analyzed by mass spectra. The analysis indicated that virtually no exchange had occurred during the bromination.

A sample of the 1,2-dibromopropane was collected from the gas chromatograph and analyzed by proton nmr to determine the positions of deuterium exchange. The pmr spectra assignments, chemical shifts, and percentages of exchange are in Table II. The assignments were based on the published[6] spectrum of 1,2-dibromopropane.

Table II. Pmr Data from Exchange of C_3D_6 with $HCo(CO)_4$

Proton chemical shift[a]	Rel % exchange[b]
(a) 1.90	44.3
(b) 3.55	17.0
(c) 3.87	17.9
(d) 4.27	20.8

[a] Parts per million from TMS. Letters refer to structure I. [b] From integration.



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(4) Propene-d_6 and Isobutylene Catalyzed by Cobalt Hydrocarbonyl. The preceding experiment was repeated except that 2-methylpropene was used instead of 1-butene. After 300 min a gas sample was taken and analyzed by mass spectroscopy with the following results: C_3D_9, 77.7%; C_3D_5H, 15.7%; and $C_3D_4H_2$, 4.7%.

(5) Hydroformylation and Attempt to Disproportionate Propene Using Cobalt Hydrocarbonyl as Catalyst. Propene (9.2 mmol) was mixed at 26° with cobalt hydrocarbonyl (4.17×10^{-1} mmol) by flashing a solution of pentane–cobalt hydrocarbonyl into the reaction flask. After 12 hr, analysis of a gas sample by vpc showed 99.5% propene. Thus, no dismutation into ethylene and butene occurred.

Toluene (2 ml) was added to the reaction flask and the solution analyzed by vpc. The analysis showed the formation of aldehydes of which 41.5% was butanal and 58.5% 2-methylpropanal.

(6) Analysis. Gas chromatography analyses were carried out on an F and M 700 equipped with thermal conductivity detectors and matched 13 ft × 0.25 in. copper columns packed with Ucon 50-HB-5100, 23 wt %, and silver nitrate, 1.5 wt %, supported on Chromosorb-R. Helium was used as a carrier gas with a flow rate of 50 cm^3/min. Separation of 1-butene, *trans*-2-butene, and *cis*-2-butene was accomplished by cooling the columns to 0°, and the butenes were eluted in the above order, respectively. Aldehydes were analyzed by heating the columns to 140°, whereupon the branched aldehyde was eluted first, followed by the straight-chain aldehyde. Percentages of the compounds were determined from the areas under the respective traces from the vpc and reported as mole per cent.

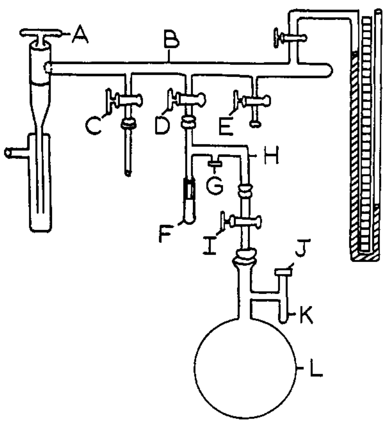


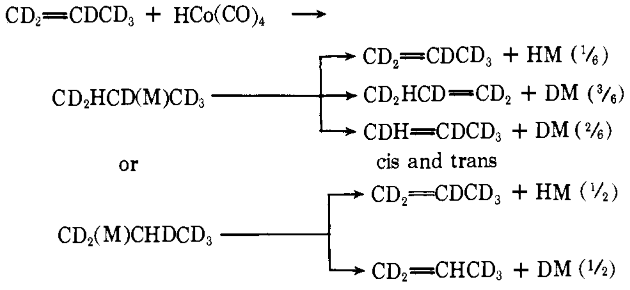
Figure 1. Apparatus for vapor-phase reactions with $HCo(CO_4)$.

All mass spectral analyses were performed on a Hitachi Perkin-Elmer RMU-7 mass spectrometer.

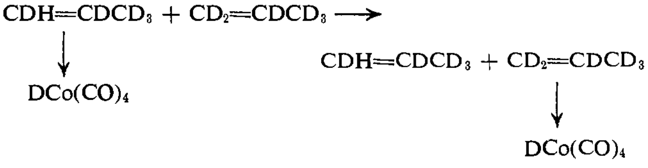
The nmr spectra were obtained on a Varian T-60 instrument at about 30°.

Results and Discussion

The addition of $HCo(CO)_4$ to $CD_2{=}CDCD_3$ can lead to either of two σ complexes, one corresponding to Markovnikov and the other to anti-Markovnikov addition of HM.



Each of these, on elimination, can lead to some incorporation of hydrogen, the one arising from Markovnikov addition having a probability of 5:6 for H incorporation, while the σ complex arising from anti-Markovnikov addition can collapse to the protio olefin with a probability of 0.5, neglecting kinetic deuterium effects. When reaction leading to hydrogen incorporation is achieved, $DCo(CO)_4$ is liberated. It is conceivable that this $DCo(CO)_4$ would be catalytically effective for a large number of consecutive isomerization cycles, especially if collision of the π complex with olefin is required for the isomerization, *e.g.*



The isomerization was conducted in the presence of 1-butene (and propene). In the presence of a competing protio olefin, a substantial concentration of $HCo(CO)_4$

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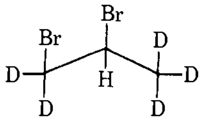
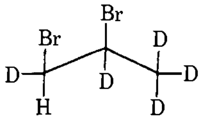
[6] N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "High Resolution NMR Spectra Catalog," Varian Associates, 1962, Spectra No. 30.

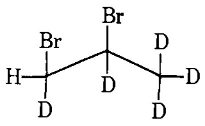
relative to $DCo(CO)_4$ is assured. Furthermore, the isomerization of 1-butene to its isomers provides an additional monitor for the isomerization reaction.

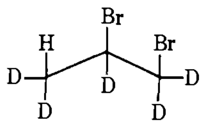
When propene-d_6, 1-butene, and $HCo(CO)_4$ were placed together in the vapor phase in a molar ratio of approximately 11:11:1 and allowed to react, the butenes were found to consist of 1-butene (15%), *cis*-2-butene (35%), and *trans*-2-butene (50). Deuterium incorporation into the butenes was not determined, but the various deuterated propylenes were analyzed by mass spectra with the results shown in Table I. The distribution of the various deuterated propylenes when propylene was used in place of 1-butene are also shown in this table. The presence of appreciable protiopropylene derived from C_3D_6 confirms the fact that intermolecular exchange of hydrogen between olefins readily occurs in the presence of $HCo(CO)_4$. Such exchange has been shown previously by tritium experiments.[5]

The position of the proton in C_3D_5H is of particular importance because, were it found on the middle carbon atom, the 1,2 addition–elimination must be operative. The total product resulting from the gas-phase reaction between $HCo(CO)_4$, C_3D_6, and C_4H_8 was treated with bromine, and the dibromopropanes were separated by gas chromatography. In separate experiments it was ascertained that the bromine treatment did not cause an H, D exchange. The dibromopropanes were analyzed by proton nmr. The composition of the mixture determined from the integration of the areas for the various protons gave the results


1, 20.8 %


2, 17.0 %


3, 17.9%


4, 44.3%

The presence of **1** in appreciable quantity confirms the 1,2 addition–elimination mechanism.

It should be noted that the rate at which catalytic olefin isomerization occurs is remarkably fast when one considers that in these experiments the total molar ratio of olefin:$HCo(CO)_4$ is 22:1 and that during the catalysis the $HCo(CO)_4$ is disappearing irreversibly by hydroformylation, decomposition, and hydrogenation of both olefin and aldehyde. Each of these competing reactions requires the consumption of 2 mol of $HCo(CO)_4$.

Direction of Addition. The analysis of the mixture of the monoprotiodibromopropanes permits important conclusions to be drawn relative to the proportion of Markovnikov and anti-Markovnikov addition of $HCo(CO)_4$. Of the six possible propylenes that can be formed in one cycle by addition of HM to C_3D_6 and elimination of either HM or DM, only four lead to monoprotiopropylene. Hence, the relative concentrations of the four dibromo derivatives as determined by pmr and given above need to be normalized to take account of this fact. When the appropriate statistical factors are taken into account, and a calculation is made on the basis of 70% of the addition proceeding by way of the Markovnikov route, the composition of the four dibromopropanes would be: **1**, 20.7%; **2** + **3**, 31.7%; and **4**, 47.5%. As can be seen, this is in reasonably good agreement with experimental results. Accordingly, it may be concluded that vapor-phase addition of $HCo(CO)_4$ to propylene in the absence of a carbon monoxide atmosphere leads to approximately 70% addition of the metal atom to the central carbon atom.

Analysis (vpc) of the aldehydic products from the above reaction shows about 70% branched and 30% straight-chain aldehyde. This distribution is consistent with 70% Markovnikov addition, and hence under these conditions it is likely that the direction of initial addition controls the product distribution.[7] It is, of course, possible that relative rates of subsequent reactions such as carbonyl insertion to the known acylcobalt[8] complexes may control aldehyde distribution under other conditions, but the detailed steps of the hydroformylation reaction remain to be elucidated.

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(7) For a review of the oxo reaction, see I. Wender, H. Sternberg, and M. Orchin, *Catalysis*, **5**, 73 (1957); I. Wender and P. Pino, "Organic Synthesis Via Metal Carbonyls," Vol. I, Wiley, New York, N. Y., 1968; R. F. Heck, *Advan. Chem. Ser.*, **No. 49**, 181 (1965); J. Falbe, "Carbon Monoxide in Organic Synthesis," Academic Press, New York, N. Y., 1967, p 117; A. J. Chalk and J. F. Harrod, *Advan. Organometal. Chem.*, **6**, 119 (1968).

(8) R. F. Heck and D. S. Breslow, *J. Amer. Chem. Soc.*, **83**, 4023 (1961).