Mechanism of the Hydrogenation of Butadiene with Cobalt Hydrocarbonyl

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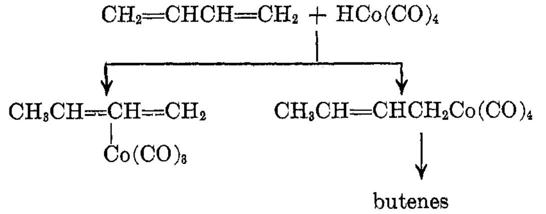
The isomeric *syn*- and *anti*-1-methyl-π-allylcobalt tricarbonyl complexes 1 and 2, respectively, are readily prepared from butadiene and $HCo(CO)_4$. Both of these isolable complexes react with $HCo(CO)_4$ to give, from 1, principally *trans*-2-butene and, from 2, 1-butene and *cis*-2-butene. However, the distribution of butenes obtained directly from butadiene and $HCo(CO)_4$ cannot be rationalized on the basis of exclusive intermediacy of these complexes. It is proposed that a σ-allyl complex also is an intermediate in the hydrogenation and that it is converted to 1-butene by hydride attack.

Since the time nearly 30 years ago when the hydroformylation reaction was first discovered[1] and recognized as a commercially important process until the present time when more than five billion pounds of oxo products are produced worldwide annually, much effort has been devoted to the possibility of using butadiene as a substrate. The introduction of carbonyl functions at both double bonds by this reaction is of great interest as an inexpensive route to adipic acid and its derivatives. To date the dihydroformylation of butadiene, using the cobalt catalyst system, has not been achieved, although substantial yields can be realized with a rhodium catalyst.[2] The difficulty is that under oxo conditions the diene is hydrogenated to butenes, which then undergo further reaction in a normal hydroformylation to the C-5 products which characterize the reaction. The present paper deals with the mechanism of the reaction between butadiene and stoichiometric quantities of $HCo(CO)_4$, the catalytic intermediate in the conventional high-pressure oxo synthesis.[3]

The stoichiometric reaction between conjugated diolefins and $HCo(CO)_4$ has been studied previously by several groups of workers.[4-12] These studies have been concerned primarily with the formation, isolation, and characterization of the resulting π-methallyl complexes. Only recently has attention been directed to the hydrogenation of butadiene to butenes and a mechanism proposed.[13] It was suggested that the butenes arise from a σ complex derived from 1,4 addition of $HCo(CO)_4$ to C_4H_6 and that the π-methallyl complex was a by-product rather than an intermediate. Our work shows that the cis σ complex is probably the principal intermediate to 1-butene but also that the π-methallyl complexes are indeed precursors to 1-butene and other butenes as well.



Experimental Section

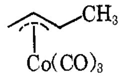
The vapor-phase reactions between C_4H_6 and $HCo(CO)_4$ were carried out at 24–25° in a 2.27-l. reactor and by a technique described elsewhere.[14] The reaction was very rapid and was accompanied by the formation of a brownish liquid on the walls of the reactor. This liquid disappeared during the course of the reaction and is apparently an intermediate. Its structure was not investigated. In liquid-phase reactions a 50-ml flask fitted with a magnetic stirrer and a serum stopper and side arm was first evacuated and 5 ml of decane was introduced by syringe. After introducing carbon monoxide to 1 atm, the flask was cooled, and the desired quantities of 1-pentene, liquid butadiene, and $HCo(CO)_4$ in pentane were introduced. Samples were taken either directly from the gas phase or in an alternate procedure, the volatile material was separated first and then vaporized and sampled for analysis. The reactions of $HCo(CO)_4$ with the π-methallyl complexes were carried out in essentially the same way as described for the liquid-phase hydrogenation of butadiene.

Pure (95%) *syn*-1-methyl-π-allylcobalt tricarbonyl was prepared by treating $Co_2(CO)_8$ with butadiene under oxo conditions at 120°.[15] After several distillations, the purified material was analyzed by nmr and stored at Dry Ice temperature. Yields of 20–30% based on $Co_2(CO)_8$ were obtained.

The preparation of a mixture of *anti*- and *syn*-1-methyl-π-allylcobalt tricarbonyl was achieved by introducing a cold pentane solution of $HCo(CO)_4$ (~9 g) into a cold (Dry Ice) autoclave. A 10 molar excess of liquid C_4H_6 was then added and the autoclave was pressured to 600 psi with carbon monoxide. After standing at room temperature overnight, the gases were vented through a cold trap. Analysis (vpc) showed recovered C_4H_6 and mixed butenes. On cooling the autoclave contents, 6 g of $Co_2(CO)_8$ was precipitated. Vacuum distillation of the mother liquor at room temperature gave about 2.5 g of π complex consisting of 30–35% of 1 and 65–70% of 2. The mixed complexes were stored at Dry Ice temperature. Yields of 20–30% of π complex based on $HCo(CO)_4$ were obtained.

Results and Discussion

The reaction of $HCo(CO)_4$ with C_4H_6 is reported[6] to lead to a mixture of two 1-methyl-π-allyl complexes, 1 and 2. The syn (when CH_3 and H on carbons 1 and 2, respectively, are in the cis configuration) isomer 1 is much more thermally stable than the anti isomer 2; indeed 2 is converted to 1 by heating the former at 120°.[6]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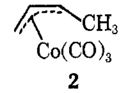
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TABLE I[a]

REACTIONS OF π-METHALLYL COMPLEXES WITH $HCo(CO)_4$ IN THE PRESENCE OF 1-PENTENE[a]

π-Allyl complex	Increment of $HCo(CO)_4$, mmol	Composition of butenes, % 1-	cis-2-	trans-2-	Recovered pentenes, % 1-	2-
Syn 1 (95%)	0.58	9.3	8.7	82.0	99	
	0.29	9.7	7.1	83.2	98	2
	0.29	9.8	8.2	82.1	94	6
1 (31%) + 2 (69%)	0.58	25.0	47.2	27.8	99	
	0.29	23.4	47.7	28.9	99	
	0.29	23.5	45.3	31.2	97	3

[a] Reaction conditions: 5 ml of decane, 1.9 mmol of complex, 0.58 mmol of HCo $(CO)_4$ per ml of solution, 2 mmol of 1-pentene, temperature 24–25°, 1 atm of CO.

TABLE II

HYDROGENATION OF BUTADIENE WITH $HCo(CO)_4$ IN THE PRESENCE OF 1-PENTENE

Partial pressure, CO, mm	Temp, °C	Composition of butenes, % 1-	cis-2-	trans-2-	Recovered pentenes, % 1-	2-
0[a]	25	44.7	29.7	25.6	95.5	4.5
150[a]	25	49.5	24.3	26.2	99+	
300[a]	25	48.2	21.0	30.8	99+	
300[a]	25	49.7	22.1	28.1	99+	
740[b]	−10	43.4	39.1	17.5	99+	
740[b]	0	44.1	35.5	20.6	99+	

[a] Reaction conditions: 2 mmol of $HCo(CO)_4$ in pentane (0.83 mmol per ml); 5 mmol of C_4H_6; 1.6 mmol of 1-pentene. [b] Reaction conditions: 2.5 mmol of $HCo(CO)_4$ in 10 ml of decane, 5 mmol of C_4H_6, 2 mmol of 1-pentene.

The two isomers can be identified readily by their nmr spectra[6,11] and the composition of mixtures of them can be determined from such spectra. In our work, the reaction of $HCo(CO)_4$ with C_4H_6 led to a mixture, which after purification to remove traces of paramagnetic species was analyzed by nmr. The spectrum showed that the mixture consisted of about 30–35% of **1** and 65–70% of **2**. When butadiene is treated with $Co_2(CO)_8$ under oxo conditions, analysis (nmr) of the π-methallyl complexes shows that almost pure (95% or more) syn isomer is present.

The hydrogenolysis of the complexes **1** and **2** with $HCo(CO)_4$ was investigated. It is well known that $HCo(CO)_4$ readily isomerizes 1 olefins to 2 olefins.[16] One must therefore exercise extreme caution when deducing initial butene distribution from analysis of the final product. In order to minimize isomerization, it is desirable to have excess butadiene present at all times. In addition, the simultaneous presence of a monitoring olefin such as 1-pentene permits evaluation of the extent of isomerization caused by free $HCo(CO)_4$.

The reaction of pure (95%) syn isomer **1** with C_4H_6 was carried out by adding a total of 1.16 mmol of $HCo(CO)_4$ in pentane in three portions to 1.9 mmol of **1** in 5 ml of decane in the presence of 1-pentene (2.0 mmol) and 1 atm of carbon monoxide. The reaction mixture was sampled from the gas phase after the reaction with each incremental portion of $HCo(CO)_4$ was complete. The results of these experiments and analogous experiments with a mixture of **1** (31%) and **2** (69%) are shown in Table I. In order to make certain that no error was introduced by sampling from the gas phase, in one experiment, the total liquid product was subjected to distillation. The distillate was vaporized, collected, and analyzed (vpc). This analysis of the butene fraction showed a composition essentially identical with that from the vapor-phase sample.

Because of the very rapid reaction between the π complexes and $HCo(CO)_4$ to give butenes, the standard procedures reported for the preparation of such complexes should also produce butenes. As a matter of fact, the yield of complexes is generally low. In order to demonstrate that conditions that usually are employed for the formation of the π-allyl complexes also produce butenes, 14 g of $Co_2(CO)_8$ was transformed to $HCo(CO)_4$ by the standard procedure[17] and treated with 30 g of C_4H_6 as described in the Experimental Section. In addition to recovered C_4H_6, substantial quantities of butenes were found. The mixed butenes consisted of 41.2% 1-butene, 31.0% *cis*-2-butene, and 27.8% *trans*-2-butene. Approximately 6 g of $Co_2(CO)_8$ and 2.5 g of mixed 1-methyl-π-allyl complexes were formed.

Since we know the isomer distribution obtained from treating pure (95%) **1** with $HCo(CO)_4$ and the isomer distribution resulting from similar treatment of mixed **1** and **2** of known composition, we may estimate the isomer distribution expected from pure **2**

$$\mathbf{1} \longrightarrow \begin{array}{ll} \text{trans} & C{-}C{=}C{-}C\ 86\% \\ \text{cis} & C{-}C{=}C{-}C\ \ 6\% \\ & C{=}C{-}C{-}C\ \ 8\% \end{array}$$

$$\mathbf{2} \xrightarrow{\text{(calcd)}} \begin{array}{ll} \text{cis} & C{-}C{=}C{-}C\ 65\% \\ & C{=}C{-}C{-}C\ 35\% \end{array}$$

With the knowledge of the behavior of 1-methyl-π-allyl complexes toward $HCo(CO)_4$, the hydrogenation of C_4H_6 with $HCo(CO)_4$ was now carried out. The results of the gas-phase studies are shown in Table II. The principal advantage of the gas-phase technique is control of the partial pressure of carbon monoxide and elimination of solvation effects. The data in Table II show that the carbon monoxide partial pressure has relatively little effect on product distribution. The liquid-phase reaction gave somewhat similar results (last two lines of Table II).

The hydrogenation of butadiene with $HCo(CO)_4$ in the gas phase and in the presence of carbon monoxide yields a mixture of butenes consisting of approximately

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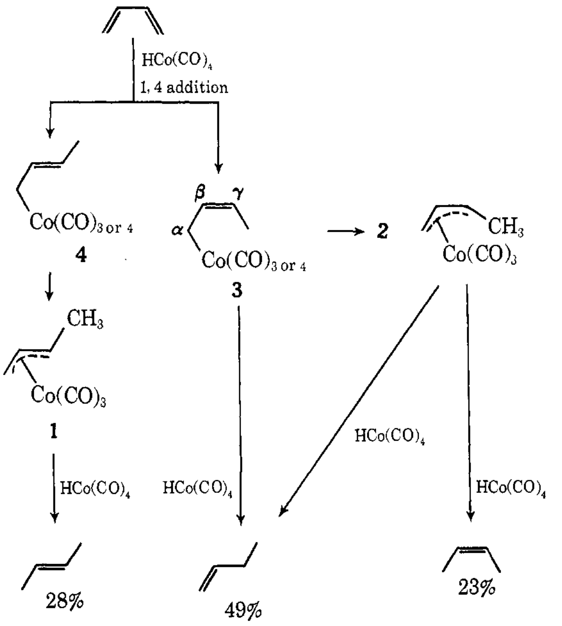
CHART I
A SCHEME FOR THE HYDROGENATION OF BUTADIENE WITH $HCo(CO)_4$



49% 1-butene, 23% *cis*-2-butene, and 28% *trans*-2-butene. Although we have shown that the π-allyl complexes **1** and **2** are both directly converted to butenes, the distribution of products from the butadiene reaction cannot be explained by the intermediacy of only these two complexes; another complex leading directly to 1-butene is required. This may very well be the σ complex **3** (Chart I), a precursor to **2**. The various reactions of importance which best explain the results are shown in Chart I. We believe that hydride attack at the γ carbon atom of intermediate **3**, accompanied by bond migration and elimination of cobalt, produces 1-butene almost exclusively. An analogous reaction with the complex **4** probably is repressed by steric factors, and hence **4** is rapidly converted to **1**, which yields *trans*-2-butene almost exclusively. Because attack of $HCo(CO)_4$ on **1** provides little 1-butene, it is also reasonable to assume that such attack on **4** is similarly ineffective in giving 1-butene while **3** is much more exposed to a γ attack. Analogous explanations have been used to explain product distribution from butadiene in the $[Co(CN)_5H]^{3-}$ system.[18] A σ complex arising from 1,2 Markovnikov addition is also a possible intermediate leading to 1-butene.

Although Chart I outlines what we consider to be the principal reactions, it must be kept in mind that equilibria probably exist between many of the species and that the number of coordinated carbon monoxides is variable.

Registry No.—**1**, 31627-44-8; **2**, 31627-45-9; butadiene, 106-99-0; cobalt hydrocarbonyl, 17186-02-6; 1-pentene, 109-67-1.

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Peroxyacetic Acid Oxidation of 4-Methylphenols and Their Methyl Ethers[1]

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The peroxyacetic acid oxidations of 4-methylpyrocatechol, 4-methylveratrole, *p*-cresol, *p*-methylanisole, 2-methoxy-*p*-cresol, and 4-methyl-*o*-benzoquinone were investigated in aqueous acetic acid at 25°. In all cases, *cis,trans*-β-methylmuconic acid and the related lactones γ-carboxymethyl-β-methyl-$\Delta^{\alpha,\beta}$-butyrolactone and γ-carboxymethyl-γ-methyl-$\Delta^{\alpha,\beta}$-butyrolactone were produced. With the exception of 4-methyl-*o*-benzoquinone, the substrates all produced γ-carboxymethyl-γ-hydroxy-β-methyl-$\Delta^{\alpha,\beta}$-butyrolactone. This product was suggested to arise from electrophilic hydroxylation ortho to the methyl substituent and para to an oxygen-bearing substituent followed by aromatic ring cleavage and lactonization. Similar hydroxylation was evident in the formation of 4-hydroxy-4-methyl-2,5-cyclohexadienone from *p*-cresol and *p*-methylanisole. 4-Methylveratrole and *p*-methylanisole each gave 2-methoxy-5-methyl-*p*-benzoquinone as a major product. This product was slowly oxidized in the presence of excess peroxyacetic acid. Although the combined yields of identified products were low, stoichiometry data on oxidant and substrate consumption for the unmethylated compounds agreed with that predicted on the basis of the products formed. Higher than predicted ratios of oxidant consumed/substrate consumed were found for the methylated substrates. The results can be accounted for on the basis of competitive pathways involving hydroxylation at activated ring positions, demethoxylation, ortho and para quinone formation, and aromatic ring cleavage.

Hydroxylation appears to be an important result of reactions between peroxy acids and many aromatic compounds. Thus, oxidation of *m*-xylene by trifluoroperoxyacetic acid gave 2,4- and 2,6-xylenol along with the corresponding *p*-quinone.[2] Oxidation of phenol by peroxyacetic acid is known to produce *p*-benzoquinone and muconic acid;[3-5] apparently, initial para and ortho hydroxylation are followed by further oxidation to the para quinone and the muconic acid, respectively. Peroxyacetic acid was reported to convert *p*-cresol to *cis,trans*-β-methylmuconic acid and a related lactone.[3,6] The muconic acid derivatives have also been reported

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