

## The Reaction between Hydrogen Tetracarbonylcobaltate(-I) and 1,4-Pentadiene at Various Temperatures and Carbon Monoxide Pressures

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Hydrogen tetracarbonylcobaltate(-I) and 1,4-pentadiene were allowed to react in an autoclave at various carbon monoxide pressures. The yield of oxygenated products was found to reach a maximum near 10 atm of carbon monoxide pressure. The yield of the complex 1-ethyl- $\pi$ -allyltricarboxylcobaltate decreased with increasing pressure.

At high temperature, cyclohexene-1-aldehyde was formed which probably results from an internal aldol condensation of a dialdehyde formed by insertion of CHO groups at both double bonds of the olefin.

Reaction of hydrogen tetracarbonylcobaltate(-I) with 1,4-pentadiene yields the *syn* and *anti* forms of 1-ethyl- $\pi$ -allyltricarboxylcobaltate and several oxygenated compounds of which 5-hexenal and 2-methyl-cyclopentanone are the major products.<sup>1</sup>

This reaction has now been repeated at room temperature at various carbon monoxide pressures.

The complex and the oxygenated products were extracted with pentane under nitrogen and separated by distillation. Components in the products obtained at room temperature were identified by means of comparison of their gas chromatograms with those of the known compounds. Mass spectrographic and infrared data confirmed the results of the gas chromatograms.

The yields of products from these reactions are listed in Table 1.

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Table 1. Products from room temperature reactions at various CO pressures.

CO added in p.s.i.	Relative percentages of oxygenated products				Weight of com- plex fraction in grams
	Minor products	5-Hexenal	2-Methyl- cyclopentanone	Weight of organic fraction in grams	
0	5.2	33.3	61.5	3.194	1.696
50	6.1	34.3	59.6	3.403	1.374
134	4.7	32.8	62.5	3.518	0.956
210	3.0	34.2	62.8	3.432	1.018
1220	8.1	36.3	55.6	1.069	0.0

In another experiment the reaction mixture was heated to above 120°C (no additional CO pressure) to decompose the  $\pi$ -allyl complex.

In the reactions at 210 and 1220 p.s.i. of added carbon monoxide pressure, IR spectra of the pentane extract showed strong bridging carbonyl absorptions near 1850  $\text{cm}^{-1}$ . Upon cooling, large amounts of orange dicobalt octacarbonyl crystals were formed. Below 210 p.s.i. only traces of bridging carbonyl absorptions were present and no dicobalt octacarbonyl precipitated.

In the high temperature reaction, the reaction mixture was heated to between 120 and 130°C for 3 h and then analyzed. The gas chromatogram revealed a new major component with a somewhat higher retention time. The major components were separated on a Beckman Megchrom preparative scale gas chromatograph and infrared spectra, a mass spectrogram and elemental analyses were obtained. The mass spectral and NMR data of the higher boiling major component are found in Tables 2 and 3, respectively.

Table 2. Mass spectrogram of cyclohexene-1-aldehyde (parent mass italicized).

Mass	Relative intensity
<i>110</i>	1320
95	548
81	2139
53	1098
41	1314
39	1383

Table 3. N.M.R. data of cyclohexene-1-aldehyde.

Peak No.	Chem. shifts in p.p.m. (T.M.S. = 0)
1	1.68
2	2.25
3	6.70
4	9.35

## DISCUSSION

It can be seen from Table 1 that a maximum yield of oxo products was obtained around 150 p.s.i. of carbon monoxide. This is in agreement with earlier work by Natta<sup>2</sup> on the hydroformylation reaction at varying low carbon monoxide pressure at constant hydrogen pressure where a reaction rate maximum was observed near a carbon monoxide pressure of 150 p.s.i. The relative yields of the major organic products surprisingly changed very little, indicating a common intermediate step involving carbon monoxide. The amount of complex formed seems to be reduced as the carbon monoxide pressure is increased; at high pressures (1220 p.s.i.) no complex could be isolated.

The major products obtained in the high temperature reaction were 5-hexenal, 2-methyl-cyclopentanone and a cyclic unsaturated aldehyde. Relative yields of these products were 14.8 %, 54.9 %, and 19.1 %, respectively, while minor products counted for the last 11.2 %. The presence of 2-methyl-4-pentenal and cyclohexanone in small amounts was indicated by mass spectrographic and gas chromatographic studies.

The cyclic unsaturated aldehyde showed an infrared absorption near  $1690\text{ cm}^{-1}$  indicating an aldehyde group.

Mass spectrographic data (Table 2) indicated a parent mass of 110 and a large mass of 81 indicating the loss of a  $-\text{CHO}$  group. The large 53 mass peak

indicates the group:  $\begin{array}{c} \text{H} \\ | \\ \text{C}=\text{C} \\ / \quad \backslash \\ \text{CH}_2 \quad \text{CH}_2 \end{array}$  A somewhat smaller mass peak at 95 seems to

indicate the loss of a  $\text{CH}_3$  group. This might indicate the presence of a branched  $\text{CH}_3$  group.

Four major peaks were observed in the NMR spectra as shown in Table 3. Long range coupling effects are evident from this spectrum. Peak 4 indicates a conjugated, aldehydic hydrogen atom. Unconjugated hydrogen atoms of this type normally absorb at 9.8 p.p.m. relative to T.M.S. Peak 3 shows ole-

finic hydrogen located terminal to a conjugated system, or  $\begin{array}{c} \text{H} \quad \quad \text{O} \\ \diagdown \quad \quad \parallel \\ \text{C}=\text{C}-\text{CH} \end{array}$ .

If this would be situated internally it would have resonated at 6.1–6.2 p.p.m. and peak 4 would also have been a doublet. Peak 2 arises from hydrogen atoms alpha to the conjugated system and peak 1 from hydrogen atoms beta to it. Proton counting, using the aldehydic hydrogen atom as a reference indicates 10 hydrogen atoms. Integration of peaks 1 and 2, however, was a little high. This was probably due to about 7 % impurities observed in a separate gas chromatogram of the sample. The absence of a methyl group peak is apparent. This indicates that the methyl group mass found in the mass spectrographic data cannot be due to a branched methyl group.

This was confirmed by preparing cyclohexene-1-aldehyde<sup>3</sup> and obtaining its mass spectrogram and its NMR and IR spectra. All of these are identical with those obtained for the cyclic unsaturated aldehyde prepared in this study. The melting points of the 2,4-dinitrophenylhydrazones also were the same,  $211^\circ\text{C}$ . A detailed interpretation of the NMR spectrum will be reported elsewhere.

The formation of cyclohexene-1-aldehyde can be explained by the following reaction scheme:

(a) 5-Hexenal is hydroformylated to the dialdehyde



(b) The dialdehyde yields the cyclic cyclohexene-1-aldehyde by an acid catalyzed intramolecular aldol condensation. Aldol condensations have been observed under such conditions.<sup>4</sup> Comparison of the yields reveals furthermore that the combined percentage of 5-hexenal and cyclohexene-1-aldehyde above is of the same magnitude as that of 5-hexenal found in Table 1, a further point in favor of this reaction scheme.

### EXPERIMENTAL

I. *Preparation of  $\text{KCo}(\text{CO})_4$ .* Preparation of potassium tetracarbonylcobaltate in aqueous solution was made according to a modification of Gilmont and Blanchard's method.<sup>5,6</sup>

II. *CO pressure variation reactions.* In this reaction series, 225 ml of solution from I containing 0.11 mole of the salt were placed in a 1 l stainless steel autoclave. Concentrated phosphoric acid (70 ml) and 10 g of olefin (0.15 mole) were lowered into the vessel in separate test tubes without mixing. The vessel was closed, pressurized with CO and rocked for 24 h with mixing at room temperature. The dark red organic layer was then separated, washed with oxygen free water, dried over anhydrous sodium sulphate and distilled. The organic products boiled below 32°C (0.5 mm), the complex at *ca.* 32°C (0.5 mm).

III. *High temperature reaction.* In this reaction, the procedure was similar to the above example except that 355 ml potassium tetracarbonylcobaltate solution containing 0.2 mole salt and 110 ml acid and 0.24 mole of 1,4-pentadiene were used. After 24 h of rocking at room temperature, the reaction was heated for 3 h between 120 and 130°C. The yellow, organic layer was then extracted, washed and distilled to yield 7.18 g of organic products distilling below 40°C (1 mm). The major components were separated through a Beckman Megchrom preparative scale gas chromatograph. In addition to the cyclic aldehyde and other identified products about 1 g of an oily black residue was obtained which was not analyzed.

The analyses were performed by Alfred Bernhardt, Mülheim, Germany. The NMR data were obtained on a Varian Associates A 60 Nuclear Magnetic Resonance Spectrometer. The mass spectral results were obtained on a CEC 21-103C Mass Spectrometer. The cyclohexene-1-aldehyde was prepared by Columbia Organic Chemicals Company, Inc.

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