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A facile synthesis of acetals and aldehydes from allylic ethers catalyzed by cobalt compounds

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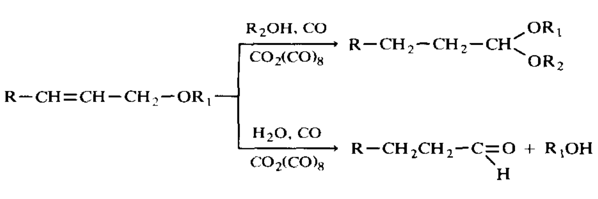
Abstract

Octacarbonyldicobalt has been found to be a very effective catalyst for both converting allylic ethers to their corresponding acetals in the presence of an alcohol and hydrolyzing allylic ethers to aldehydes. High yields (> 95%) were obtained in a very short reaction time under mild carbon monoxide pressure. Iron pentacarbonyl was also found to be an active catalyst but less effective than $Co_2(CO)_8$.

Keywords: Cobalt; Acetal; Aldehyde; Allyl; Carbonylation; Ether

1. Introduction

Allylic ethers usually lack reactivity and, accordingly, are often used as selective protecting groups for alcohols [1]. Their removal usually requires isomerization to the corresponding vinyl ether followed by hydrolysis [2]. Boss and Scheffold [3] reported that allyl ethers can be cleaved to alcohol products in good yield in the presence of catalytic amounts of palladium on activated charcoal and *p*-toluenesulfonic acid or mineral acid. Akiyama et al. [4] reported that benzyl and allyl ethers can also be cleaved readily on treatment with aluminum trichloride and *N,N*-dimethylaniline. The acetal or aldehyde (propionaldehyde) product was usually not determined. Yamahara and Deguchi [5] patented a process for the preparation of acetals by treating allylic ethers with alcohols in the presence of a ruthenium trichloride catalyst. The yield of acetal was low. We now wish to report a high-yield conversion of an allylic ether to its corresponding acetal or aldehyde as shown in Scheme 1:



Scheme 1.

2. Experimental details

2.1. Materials

Carbon monoxide and hydrogen were Matheson purified grade. Reagents and solvents (ACS reagent grade) were obtained from Aldrich Chemical Co. and were used without further purification. $Co_2(CO)_8$ and $Fe(CO)_5$ were obtained from Strem Chemicals.

2.2. Preparation of methyl 9-methoxy-7-nonenoate

After being purged with nitrogen, a 300 ml stirred autoclave reactor was charged with 0.464 mol 8-methoxy-1,6-octadiene, 0.927 mol methanol and 0.418 mol pyridine. These liquids had originally been combined in a bottle prior to being charged into the reactor. Separately, 9.27 mmol $Co_2(CO)_8$ was added to the stirred reactor.

Upon sealing, the reactor was purged three times with carbon monoxide, pressurized to 40 psig with hydrogen and then to 3500 psig with carbon monoxide. After being stirred for a few minutes, the reactor was heated to 150°C and the pressure was adjusted to 4000 psig with carbon monoxide. The reactor was maintained at these conditions for 3 h. Upon reaction completion, the product mixture was analyzed by gas chromatography and found to include methyl 9-

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Table 1
Isomerization/acetalization of allylic ethers

Expt. No.	Substrate	Products	Conversion (%)	Selectivity (%)
1	allyl ethyl ether	1,1-dimethoxypropane (74%) and 1-ethoxy-1-methoxypropane (26%)	98	99
2	allyl phenyl ether	1,1-dimethoxypropane (81%) and 1-methoxy-1-phenoxypropane (19%)	97	98
3	methyl 9-methoxy-7-nonenoate	methyl 9,9-dimethoxynonanoate	97	99

Reaction conditions: A solution consisting of 136 mmol of substrate and 0.59 mmol $Co_2(CO)_8$ in 600 mmol methanol was heated at 170°C under 1000 psig pressure of carbon monoxide containing 4.0 vol.% hydrogen for 30 min.

methoxy-7-nonenoate in a yield of 46.3%. The allylic ether ester was isolated by distillation.

2.3. *Isomerization / acetalization of allylic ethers*

Typically, a glass bottle was charged with 150 mmol of methyl 9-methoxy-7-nonenoate (contains 7.8% methyl 8-methoxy-2-methyl-6-octenoate, a branched isomer derived from the carbomethoxylation of 8-methoxy-1,6-octadiene), 600 mmol of methanol and 23.6 mmol of pentamethylbenzene which was used as an internal gas chromatography standard, and the contents mixed. The mixture was added to a nitrogen gas-purged 300 ml autoclave reactor along with 0.29 mmol of $Co_2(CO)_8$ which was separately charged from a vial. The reactor was sealed, purged three times with carbon monoxide and pressurized to 800 psig (768 psig CO and 32 psig H_2). The reactor was heated to 170°C and the premixed carbon monoxide containing 4% (by volume) of hydrogen was added to bring the total pressure up to 1000 psig. The reactor was maintained at these conditions for 30 min. The reactor was then cooled to room temperature and the product mixture was analyzed by using a Varian gas chromatograph model 3400 with a 4270 integrator and an 8 ft long glass column of 10% Carbowax 1000 on 100–120 mesh chromosorb WAW-DMCS. It was found that 97% of the allylic ether was converted to methyl 9,9-dimethoxynonanoate with a selectivity of 99% (the branched isomer of allylic ether was converted to 8,8-dimethoxy-2-methyloctanoate). The yield of isolated product was 94%.

2.4. *Hydrolysis of allylic ethers*

In a typical experiment, the procedure employed in the above acetalization was repeated except that the glass bottle was charged with 300 mmol water and 68 ml THF instead of 600 mmol methanol. It was found that 96% of the allylic ether was converted to methyl 9-oxononanoate with a selectivity of 99%.

3. Results and discussion

The allylic ether to be converted to acetal or aldehyde was treated with alcohol or water at 150–200°C in the presence of a catalytic amount of a cobalt compound (preferably octacarbonyldicobalt) under carbon monoxide pressure. Among the existing allylic ethers, methyl 9-methoxy-7-nonenoate, prepared by telomerization of butadiene [6] followed by hydrocarbomethoxylation, is particularly interesting because it is an intermediate in the synthesis of industrially important azelaic acid [7]. Therefore, this allylic ether was chosed to be studied extensively.

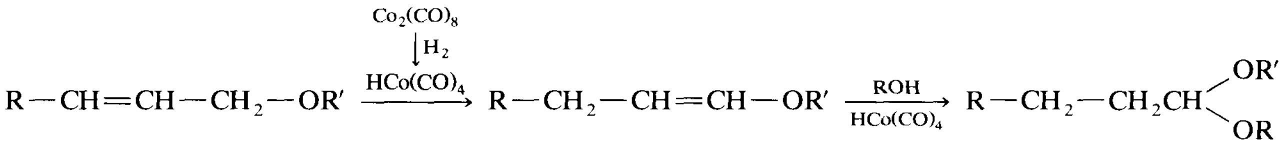
3.1. *Isomerization / acetalization of allylic ethers*

When allyl ethyl ether, allyl phenyl ether or methyl 9-methoxy-7-nonenoate was contacted with methanol at 170°C in the presence of $Co_2(CO)_8$ under 1000 psig pressure of carbon monoxide containing a small amount of hydrogen, the corresponding acetals were obtained in almost quantitative yields in 0.5 h (see Table 1). If the alkyl substituent on the allylic ether is different from that on alcohol, mixed acetal products are formed (Examples 1 and 2 in Table 1). The ratio of mixed acetals depends on the amount of alcohol used in the reaction. In our cases, 1,1-dimethoxypropane was obtained in greater than 70% yield. Table 2 shows some effects on the conversion of methyl 9-methoxy-7-nonenoate to methyl 9,9-dimethoxynonanoate. At constant temperature, both conversion and selectivity increased with increasing pressure from 500–1000 psig (Examples 1 and 6). At a pressure of 1000 psig and temperatures

Table 2
Isomerization/acetalization of methyl 9-methoxy-7-nonenoate

Expt. No.	Partial pressure		Temp. (°C)	Conversion (%)	Selectivity to acetal (%)
	CO (psig)	H_2 (psig)			
1	960	40	170	97	99
2	990	10	170	97	99
3	1000	0	170	22	96
4	960	40	180	97	99 [a]
5	960	40	160	99	99
6	480	20	170	84	86
7	960	40	170	55	93 [b]

Reaction conditions: A solution consisting of 150 mmol of methyl 9-methoxy-7-nonenoate, 600 mmol of methanol and 0.29 mmol of $Co_2(CO)_8$ was heated under the pressure of carbon monoxide and hydrogen for 30 min. [a] Reaction time of 10 min was employed. [b] Pyridine (66 mmol) was added.



$$R{-}CH{=}CH{-}CH_2{-}OR' \xrightarrow[\quad]{HCo(CO)_4} R{-}CH_2{-}CH{=}CH{-}OR' \xrightarrow[HCo(CO)_4]{ROH} R{-}CH_2{-}CH_2CH(OR')(OR)$$

Scheme 2.

Table 3
Isomerization/hydrolysis of allylic ethers

Substrate (mmol)	Water (mmol)	Product	Time (h)	Conversion (%)	Selectivity (%)
allyl ethyl ether (174)	350	propanal	0.5	100	70
allyl phenyl ether (112)	220	propanal	1.0	98	72
methyl 9-methoxy-7-nonenoate (150)	300	methyl 9-oxononanoate	0.5	100	99
8-methoxy-1,6-octadiene (143)	280	octenals	2.0	63	11 [a]

Reaction conditions: A solution of substrate and 0.73 mmol of $Co_2(CO)_8$ in 68 ml of THF was heated at 170°C under 1000 psig pressure of carbon monoxide containing 4.0 vol.% hydrogen for 0.5–2 h.

[a] The reaction was carried out under 2000 psig pressure of carbon monoxide containing 4.0 vol.% hydrogen.

of 160–180°C, the reactions gave nearly quantitative yields (Examples 1, 4 and 5). The presence of a small amount of hydrogen enhanced both conversion and selectivity (Examples 1, 2 and 3). Reactions proceeded very slowly at temperature below 100°C. Catalyst decomposition was observed at temperatures above 160°C and carbon monoxide pressure below 500 psig. Higher carbon monoxide pressure tends to stabilize the cobalt carbonyl catalyst.

Hydridotetracarbonylcobalt has been reported to be readily formed from octacarbonyldicobalt and hydrogen under pressure [8] and is a strong acid and an active olefin isomerization catalyst [9]. Also vinyl ethers are susceptible to alcohol attack in the presence of acids. $HCo(CO)_4$ was detected in the reaction product mixture. Hence, the formation of acetal is believed to involve carbon–carbon double bond isomerization of allylic ethers to give vinyl ethers followed by $HCo(CO)_4$-catalyzed alcohol addition to give the corresponding acetal (Scheme 2). The intermediate, vinyl ether, was not detected under the above reaction conditions, possibly due to its good reactivity towards alcohol in the presence of acidic $HCo(CO)_4$. Since pyridine and methanol were used in the $Co_2(CO)_8$-catalyzed hydrocarbomethoxylation for the preparation of methyl 9-methoxy-7-nonenoate, pyridine was used in the acetalization reaction to determine its effect on acetal formation. It was found that the addition of pyridine tended to lower the conversion and selectivity to acetal (Table 2, Example 7), possibly due to the acid–base interaction of acidic $HCo(CO)_4$ with basic pyridine.

3.2. *Isomerization / hydrolysis of allylic ethers*

Under similar conditions to those used for acetalization, allylic ethers underwent isomerization and hydrolysis reactions to give aldehydes when treated with water in tetrahydrofuran (THF) solvent in the presence of $Co_2(CO)_8$ catalyst (see Table 3). The formation of some aldehyde products was not quantitative because aldol condensation and hydrogenation reactions of aldehydes were observed under these reaction conditions. An attempt to convert an allylic ether containing a terminal carbon–carbon double bond such as 8-methoxy-1,6-octadiene under similar conditions was unsuccessful. Increasing the pressure from 1000–2000 psig resulted in the formation of octenals with low selectivities. Under such conditions some hydrocarboxylation at the terminal double bond was also observed,

Table 4
Effects of solvent on isomerization/hydrolysis of methyl 9-methoxy-7-nonenoate

Expt. No.	Solvent	Conversion (%)	Selectivity (%)
1	THF	98	97
2	1,4-dioxane	56	78
3	1,4-dioxane	99	99 [a]
4	acetone	91	70
5	acetonitrile	56	80
6	toluene	96	99
7	hexane	98	98 [b]
8	none	98	59 [c]
9	none	39	82 [c,d]
10	THF	6	99 [e]
11	THF	42	91 [e,f]

Reaction conditions: A solution consisting of 150 mmol of methyl 9-methoxy-7-nonenoate, 300 mmol of water, 68 ml of solvent and 0.73 mmol of $Co_2(CO)_8$ was heated at 170°C under 1000 psig pressure of carbon monoxide containing 4.0 vol.% hydrogen for 30 min.

[a] 1500 psig pressure of CO containing 4.0 vol.% H_2 was employed.

[b] The aldehyde product was not completely soluble in hexane.

[c] About 24% of methyl 9,9-dimethoxynonanoate was also obtained.

[d] About 600 mmol of water was used.

[e] $Fe(CO)_5$ (5.26 mmol) was used to replace $Co_2(CO)_8$.

[f] Reaction was carried out at 200°C.

Table 5
Isomerization/hydrolysis of methyl 9-methoxy-7-nonenoate

Expt. No.	$Co_2(CO)_8$ (mmol)	Partial pressure		Temp. (°C)	Time (h)	Conversion (%)	Selectivity to acetal (%)
		CO (psig)	H_2 (psig)				
1	0.73	960	40	170	0.5	100	99
2	0.73	990	10	170	0.5	96	99
3	0.73	1000	0	170	0.5	47	90
4	0.29	960	40	170	0.5	96	99
5	0.09	960	40	170	2.0	20	99
6	0.73	960	40	180	0.3	99	99
7	0.73	960	40	160	0.5	98	99

Reaction conditions: A solution consisting of 150 mmol of methyl 9-methoxy-7-nonenoate, 68 ml of THF and 0.09–0.73 mmol of $Co_2(CO)_8$ was heated under the pressure of carbon monoxide and hydrogen for 0.3–2 h.

but the quantities of the products were not determined. These results might indicate that the interaction of cobalt carbonyl complex with the terminal carbon–carbon double bond is stronger than that with the internal double bond in the methoxyoctadiene.

Table 4 lists the solvent effects on the isomerization hydrolysis of methyl 9-methoxy-7-nonenoate. Among the solvents tested, THF, toluene and hexane were the most suitable. The nonpolar hexane solvent is particularly interesting because over 90% of the aldehyde product was not soluble in hexane and over 85% of the cobalt catalyst remained in the hexane layer. This indicates that a simple separation of product from the solvent and catalyst can be achieved. In the absence of solvent, the formation of 9,9-dimethoxynonanoate and aldol condensation products was observed (Examples 8 and 9). Use of iron pentacarbonyl as a catalyst resulted in good selectivities to aldehydes but at low conversions (Examples 10 and 11).

Since THF was one of the most suitable solvents, the hydrolysis of methyl 9-methoxy-7-nonenoate was studied extensively in this solvent as shown in Table 5. Similar to the acetalization reaction, quantitative yields were obtained when the reactions were carried out at 160–180°C and 1000 psig pressure (Examples 1, 6 and 7). Increasing the hydrogen content increased the conversion while the selectivity to the aldehyde remained high (Examples 1, 2 and 3). Increasing the molar ratio of substrate to $Co_2(CO)_8$ from about 200 to 520 gave no change in either conversion or selectivity. Further increasing the molar ratio to 1670 (Example 5) resulted in a decrease of conversion to 20%.

4. Conclusion

Our process provides a simple and efficient method for synthesizing acetals and aldehydes from allylic ethers using an inexpensive cobalt catalyst and mild reaction conditions.

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