CHEMISTRY LETTERS, pp. 1811-1814, 1982. © The Chemical Society of Japan 1982

# $HCo(CO)_4$ AS AN ACID CATALYST IN VINYL ETHER REACTIONS

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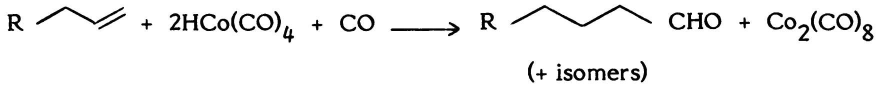
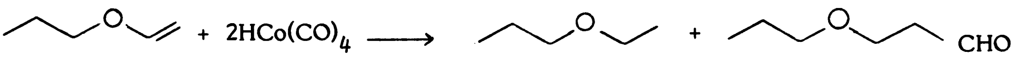
At room conditions in the presence of alcohols, $HCo(CO)_4$ instead of being consumed by vinyl ethers, functions as an acid catalyst for acetal formation.

All 1-alkenes consume approximately two moles of $HCo(CO)_4$ in a stoichiometric hydroformylation reaction, (eq. 1):



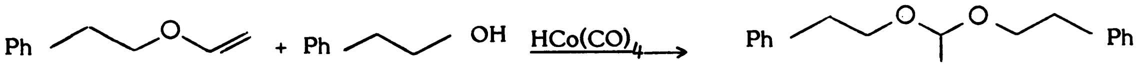
(1)

Vinyl ethers react similarly [1] except that saturated ethers (hydrogenation) as well as aldehydes are formed, eq. (2):



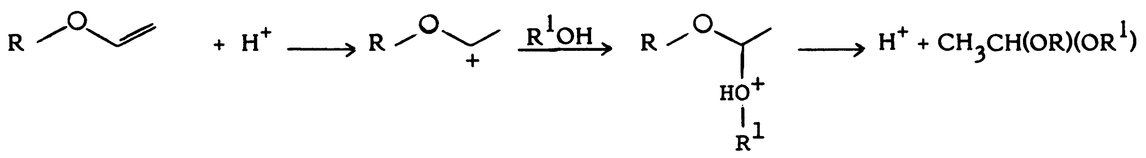
(2)

We have now found that when the stoichiometric reaction with vinyl ethers is conducted in the presence of alcohols, the $HCo(CO)_4$ is not consumed at all but instead functions as a true acid catalyst for acetal formation. Thus when phenethyl vinyl ether in $CH_2Cl_2$ is treated with 2-phenylethanol at room conditions in the presence of a catalytic quantity of $HCo(CO)_4$, the acetal **1** is formed in quantitative yield, eq. (3):



(3)

Ethyl vinyl ether on treatment with $PhCH_2CH_2OH$ gave a quantitative yield of the mixed acetal $CH_3CH_2OCH(CH_3)OCH_2CH_2Ph$. The analagous reactions occur when methanol is used in place of $PhCH_2CH_2OH$. The catalysis appears to involve a typical protonation by the strong acid $HCo(CO)_4$, followed by nucleophilic attack by ROH and release of the proton, the intermediate carbocation being highly stabilized by the adjacent oxygen atom, eq. (4):



(4)

The literature [2] records a small number of reactions occurring under catalytic hydroformylation conditions with cobalt which proceed because of the acidic nature of the $HCo(CO)_4$. Those reactions of $HCo(CO)_4$ that have been reported to occur under stoichiometric conditions and which presumably proceed because of the acidic properties of $HCo(CO)_4$ consume the carbonyl irreversibly, e.g., the conversion of triphenylcarbinol to triphenylmethane [3]. Reaction (3) represents the first room temperature reaction of an olefin in the presence of $HCo(CO)_4$ (other than isomerization) in which the $HCo(CO)_4$ is not consumed in the process.

## Experimental

A 30 ml $CH_2Cl_2$ solution of .296 g (2.00 mmoles) 2-phenylethyl vinyl ether, .366 g (3.00 mmoles) 2-phenylethanol and .256 g (2.00 mmoles) of naphthalene (used as a G.L.C. standard) was deaerated by bubbling CO through it for 10 minutes. 1.0 ml of .10 M $HCo(CO)_4$ in $CH_2Cl_2$ (.10 mmoles) was pipetted into the solution, and the solution was stirred under CO. After two hours a 1 ml. sample was removed, concentrated, and analyzed by gas chromatography (20% SE-30, 15 ft, 152°C). The analysis showed a 1:2 mixture of 2-phenylethanol:naphthalene, and no remaining vinyl ether. The product, the 2-phenylethyl acetal of acetaldehyde, remained in the column under these conditions. To the remainder of the reaction mixture was added with stirring .5 ml of ethylenediamine. After several minutes the solution was washed three times with $H_2O$, dried over $MgSO_4$, filtered, and stripped of solvent. The $^1H$ NMR of the residue revealed a 2:1 ratio of acetal:2-phenylethanol. Pure acetal was isolated by chromatography of the mixture. $^1H$ NMR: $\delta$7.20 (s,10,phenyl), 4.67 (q,1,acetal), 3.63 (m,4,oxy), 2.80(t,4,benzyl), 1.25(d,3,methyl). A similar reaction carried out with ethyl vinyl ether gave a quantitative yield of $CH_3CH_2OCH(CH_3)OCH_2Ph$: $^1H$ NMR: $\delta$7.2 (s,5,phenyl), 4.65 (q,3,methine), 3.90 - 3.20 (m,4,$OCH_2$), 2.85 (t,2,benzyl), 1.25 (d,3,methyl on methine), 1.12 (t,3,methyl).

### Reactions With Methanol

Similar reactions were carried out with methanol and the two vinyl ethers. In both cases the expected mixed acetals of acetaldehyde were secured. Thus 1.2 mmoles 2-phenylethyl vinyl ether and 2.0 ml of methanol in 35 ml $CH_2Cl_2$ gave the mixed acetal. $^1H$ NMR of methyl 2-phenylethyl acetal of acetaldehyde: $\delta$ 7.27 (m,5,phenyl), 4.63 (q,1,acetal), 3.73 (m,2,oxy) 3.23 (s,3,methoxy), 2.88 (t,2,benzyl), 1.27 (d,3,methyl). With ethyl vinyl ether and methanol,

$CH_3CH_2OCH(CH_3)OCH_3$ was obtained. The presence of a large excess of methanol led to some alcohol exchange with the initially formed acetal as might be expected in an acid-catalyzed reaction. The 2-phenylethyl acetal of acetaldehyde was also prepared using sulfuric acid as the catalyst. One drop of conc. $H_2SO_4$ was added to a solution of 1.00 g 2-phenylethanol and 1.22 g 2-phenylethyl vinvyl ether in 10 ml benzene. After allowing the mixture to stir overnight, 100 ml ether was added and the solution washed with saturated aqueous $NaHCO_3$ and then with water. After drying over $MgSO_4$, the solution was stripped of solvent and the residue was chromatographed using a 4 inch silica gel column and 1:3 $CHCl_3$:hexanes as the eluant. The product was collected in the first fractions. Evaporation of the solvent gave 2.05 g of the pure acetal (92.3% yield).

Acknowledgement: We wish to thank the Standard Oil Co. of Ohio for financial assistance.

References

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(Received August 9, 1982)