Tetrahedron Letters, Vol.32, No.4, pp 505-508, 1991
Printed in Great Britain

0040-4039/91 $3.00 + .00
Pergamon Press plc

CATALYTIC PROCEDURE FOR THE SYNTHESIS OF CYCLOALKANEMETHANOLS FROM CYCLOALKENES AND AQUEOUS METHYL FORMATE.

G. JENNER
Laboratoire de Piézochimie Organique (associé au CNRS), EHICS,
Université Louis Pasteur, 1, rue Blaise Pascal 67008 Strasbourg (France)

Summary : Cycloalkanemethanols are synthesized via hydrocarbonylation (hydroformylation) of the corresponding cycloalkenes in the presence of aqueous methyl formate. Methyl formate is the source of carbon monoxide and hydrogen is generated by the water gas shift reaction. The selectivity is affected by the concomitant hydrogenation process.

It has been recently demonstrated that synthesis gas ($CO+H_2$) can be easily generated from methyl formate-water mixtures in the presence of appropriate ruthenium catalysts[1]. The advantage of the process is highlighted by the fact that the decarbonylation occurs without initial gas pressure. Later on, we have been moved to consider potential applications of this finding, for example for hydroformylations, which are important industrial reactions. The hydroformylation reaction usually requires pressures of 50 to 100 bar with phosphine modified rhodium or cobalt catalysts[2]. As pressures of this order or even higher are readily developped during the decarbonylation reaction[1], we have considered the hydroformylation of cycloalkenes starting from methyl formate.

The process is sequential and involves three steps :

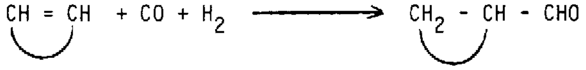
i) decarbonylation of methyl formate

$$HCOOCH_3 \longrightarrow CH_3OH + CO \qquad \text{(Eq. 1)}$$

ii) water gas shift reaction (WGSR)

$$CO + H_2O \rightleftharpoons H_2 + CO_2 \qquad \text{(Eq. 2)}$$

iii) hydroformylation of the cycloalkene



$$CH = CH + CO + H_2 \longrightarrow CH_2 - CH - CHO \qquad \text{(Eq. 3)}$$

The combination of equations 2 and 3 is known[3]. However, to our knowledge, hydroformylations with no initial $CO + H_2$ pressure have never been reported. A number of secondary reactions are obviously possible (hydroesterification[4], aldolisation, hydrogenation[3], isomerization of the alkene, oxidative condensation of alcohols and aldehydes[5]). However, under our conditions, hydroformylation is generally the dominant reaction, together with concomitant hydrogenation of the cycloalkene which can occur to a significant degree. The high temperature employed precludes isolation of the intermediate aldehyde.

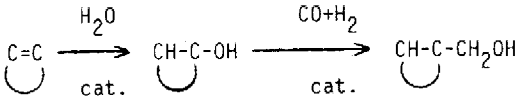
The catalyst system used throughout the work is a combination of $Ru_3(CO)_{12}$ and tricyclohexylphosphine, which was found to be the best promotor for the decarbonylation of methyl formate[6]. The WGS reaction occurs at or above 100°C[7] and temperatures employed for hydroformylation are of the same order or a little higher[8], whereas decarbonylation of methyl formate requires 180°C in order to proceed at a convenient rate. Consequently, the one-pot reaction must be performed at 180°C, since the generation of carbon monoxide conditions the subsequent steps. It is evident that, at this temperature, any aldehyde produced will be readily hydrogenated to the corresponding alcohol in the presence of the active ruthenium catalyst[9].

Cycloalkenes have thus been allowed to react with methyl formate and water in the appropriate concentration in the presence of the ruthenium catalytic system (Table).

In all cases, conversion of the cycloalkene is high. The expected cycloalkanemethanol is produced together with the cycloalkane. The extent of hydrogenation versus hydroformylation is very dependent on the substrate and the mechanical agitation system. Cyclohexene and norbornene are the least sensitive to hydrogenation, whereas cyclooctene is mostly hydrogenated.

As the process involves gas-liquid reactions, the method of agitation is expected to influence the product distribution. Intimate mixing of the gas and liquid phases by shaking (method A) gave better yields of cyclohexanemethanols than static methods. Magnetic stirring (B) does not achieve efficient gas-liquid mixing and favours hydrogenation of the alkene. In this case, the extracted liquid shows two distinct layers with the upper one consisting mostly of the cycloalkane. IR analysis shows the characteristic bands of $[HRu_3(CO)_{11}]^-$ which is the active catalytic species as demonstrated in the former work[1].

The presence of minor quantities of the alcohol corresponding to the hydrated cycloalkene could possibly be due to a hydration reaction followed by hydrocarbonylation of the alcohol produced[10] :



$$C{=}C \xrightarrow[\text{cat.}]{H_2O} CH\text{-}C\text{-}OH \xrightarrow[\text{cat.}]{CO+H_2} CH\text{-}C\text{-}CH_2OH$$

Table

Ruthenium catalyzed cycloalkene-methyl formate reaction[a]

Cycloalkene	Agitation mode[b]	Conversion %	Yield[c] (%)	
			cycloalkane	cycloalkanemethanol(s)
cyclopentene	A	100	47	43
cyclohexene	A	81	9	60
d°	B	60	55	4
cycloheptene	A	86	24	60
d°	B	70	25	30
cyclooctene	A	95	77	15
d°	B	80	45	15
1-methylcyclohexene	A	100	40	33[d]
4-methylcyclohexene	A	90	6	50[d]
norbornene	A	100	9	86[d]

[a] Methyl formate (4 ml), H_2O (0.75 ml), cycloalkene (0.6 ml), $Ru_3(CO)_{12}$(0.045 mmol), Tricyclohexylphosphine (0.28 mmol), 180°C, 10h

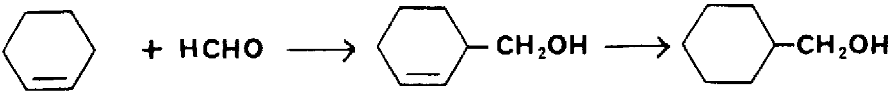
[b] A (shaking autoclave), B (magnetic stirring)

[c] Determined by GC using diglyme as internal standard

[d] Neither regio- nor stereodiscrimination has been made

However, a comparative experiment using cyclohexanol as the starting material does not produce cyclohexanemethanol. The reactions therefore represent true hydroformylations or hydrohydroxymethylation reactions, as the observed product is the alcohol and not the aldehyde. We have also checked whether cyclohexene could be hydroformylated in the usual way with compressed synthesis gas (200b, 180°C, 10h) in methanol solution under the same catalytic conditions. The result was that extensive hydrogenation of cyclohexene occurs and only a low yield of cyclohexanemethanol is produced.

The present method is also largely superior to the former procedure involving thermal ene reactions between cycloalkenes and paraformaldehyde with subsequent hydrogenation of the double bond.



This procedure gave poor yields: cyclohexanemethanol was synthesized from cyclohexene in 9% yield (180°C, 86h)[11].

In conclusion, the ruthenium catalyzed methyl formate-cycloalkene reactions yield fair amounts of the corresponding cycloalkanemethanols.

Acknowledgments. The author gratefully thanks Dr. J. Crane for linguistic co-operation and Dr. G. Teller for MS recordings.

REFERENCES

1 G. Jenner, E.M. Nahmed and S. Libs-Konrath, J. Mol. Catal., in press.
2 B. Cornils, New Syntheses with Carbon Monoxide, J. Falbe Ed., Springer Verlag, Berlin (1980) p. 1.
3 R.M. Laine, J. Am. Chem. Soc., 100, 6451 (1978).
4 E.M. Nahmed and G. Jenner, J. Mol. Catal., 59, L15 (1990).
5 S.I. Murahashi, T. Naota, K. Ito, Y. Maeda and H. Taki, J. Org. Chem., 52, 4319 (1987).
6 G. Jenner and E.M. Nahmed, J. Organomet. Chem., 387, 315 (1990).
7 P.C. Ford, Acc. Chem. Res., 14, 31 (1981).
8 G. Süss-Fink and G.F. Schmidt, J. Mol. Catal., 42, 361 (1987).
9 U. Matteoli, M. Bianchi, G. Menchi, P. Frediani and F. Piacenti, J. Mol. Catal., 22, 353 (1984).
10 G. Jenner and P. Andrianary, J. Mol. Catal., 58, 307 (1990).
11 A.T. Blomquist, J. Verdol, C.L. Adami, J. Wolinsky and D.D. Phillips, J. Am. Chem. Soc., 79, 4976 (1957).

(Received in France 9 October 1990)