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Ruthenium-catalyzed oxidation of primary alcohols with the new oxidation system *N*-methylmorpholine/hydrogen peroxide

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Abstract

Long chain alcohols such as octanol, dodecanol and hexadecanols are oxidized to the corresponding aldehydes and carboxylic acids in the presence of the homogeneous catalyst tris(triphenylphosphine) ruthenium dichloride. The known oxidizing agent *N*-methylmorpholine *N*-oxide (MMO) has been compared with a new system involving *N*-methylmorpholine (MM) and hydrogen peroxide. With the system MM/H_2O_2 simple recycling of the ruthenium catalyst and of the oxygen transmitter MM is possible by a simple phase separation process. A mechanism is proposed in which the oxygen of the MMO formed in situ serves to convert a dihydrido-ruthenium complex into the catalytically active ruthenium species.

Introduction

Homogeneous transition metal catalyzed oxidation of alcohols provides a useful route for the synthesis of aldehydes and carboxylic acids. A variety of oxidizing agents has already been investigated in this reaction; for instance sodium bromate [1–3] and iodosobenzenediacetate [4]. Catalytic oxidations with oxygen [5] or phase transfer reactions with hydrogen peroxide [6] have also been described. An interesting oxidizing agent is *N*-methylmorpholine *N*-oxide (MMO), which permits the oxidation of alcohols in the presence of ruthenium catalysts under mild conditions [7,8]. However, MMO is a very costly reagent, and so the use of MMO in industrial applications is strictly limited. We have thus developed a new oxidizing system consisting of *N*-methylmorpholine (MM) and hydrogen peroxide, which forms the oxidizing agent MMO in situ during the reaction. Hence, *N*-methylmorpholine functions only as oxygen carrier and can be recycled. In this way the costly oxidizing agent MMO is replaced by the cheap hydrogen peroxide and no troublesome by-product is formed.

Results and discussion

The oxidation of alcohols was studied using the homogeneous catalyst tris(triphenylphosphine)ruthenium dichloride. Alcohols such as 1-octanol, 1-dodecanol,

Table 1

Oxidation with *N*-methylmorpholine *N*-oxide [a]

No.	Alcohol	Alcohol/ catalyst	Temperature (°C)	MMO/ alcohol	Conversion (%)	Yield aldehyde (%)	Yield carboxylic acid (%)
1.1	1-Octanol	150/1	30	1/1	40	27	2
1.2		150/1	30	2/1	54	36	3
1.3		150/1	30	3/1	56	34	10
1.4		150/1	70	1/1	46	36	–
1.5		75/1	30	2/1	69	45	4
1.6	1-Dodecanol	150/1	30	2/1	30	20	–
1.7		150/1	70	2/1	50	41	–
1.8	1-Hexadecanol	150/1	70	2/1	63	55	–
1.9	2-Hexyl-1-decanol	150/1	30	2/1	21	17	–
1.10		150/1	70	2/1	50	46	–

[a] Cat.: $RuCl_2(PPh_3)_3$.

1-hexadecanol and 2-hexyl-1-decanol were investigated. For comparison, reactions with *N*-methylmorpholine *N*-oxide (MMO) will first be described, then the results of analogous reactions with the new system *N*-methylmorpholine (MM) and hydrogen peroxide will be discussed.

a. Oxidations with MMO

The oxidations of alcohols with MMO were carried out by dissolving the alcohol, the MMO, and the catalyst $RuCl_2(PPh_3)_3$ in methylene chloride or 1,2-dichloroethane. Reactions were carried out by stirring for 2 h at a temperature of 30 or 70 ° C. Table 1 shows the reaction conditions and the results.

With 1-octanol, a typical reaction was carried out with a molar alcohol/catalyst ratio of 150/1, a molar MMO/alcohol ratio of 1/1 and a temperature of 30 ° C, to give a conversion of 40% and an aldehyde yield of 27% (exp. 1.1). Increasing the molar MMO/alcohol ratio to 3/1 raises the extent of conversion to 56% (exp. 1.3).

Increasing the temperature from 30 to 70 ° C does not change the extent of conversion significantly (exp. 1.4), whereas a change in the alcohol/catalyst ratio to 75/1 (exp. 1.5) leads to optimum conversion (69%) and high yield of aldehyde (45%).

Similar results can be obtained with longer chain alcohols but the reactions seem to be more temperature-dependant. For instance, at 30 ° C 1-dodecanol yields only 20% aldehyde, whereas at 70 ° C the yield is 41%. With 1-hexadecanol and 2-hexyl-1-decanol yields of aldehydes of 55% (exp. 1.8) and 46% (exp. 1.10) were obtained, thus showing that the branched isomer has a somewhat lower reactivity.

b. Oxidation with MM/H_2O_2

The alcohol, and equimolar amount of *N*-methylmorpholine, the solvent, and the catalyst $RuCl_2(PPh_3)_3$) were placed in a glass flask and an excess of hydrogen peroxide was then pumped continuously into the reaction mixture. The results are shown in table 2.

At a molar ratio of octanol/catalyst of 75 : 1 a conversion of 57% was reached (exp. 2.1), a value in the same range as that for similar oxidations with MMO. However, the selectivity of the reaction changes and larger amounts of caprylic acid

Table 2

Oxidation with *N*-methylmorpholine/hydrogen peroxide [a]

No.	Alcohol	Alcohol/ catalyst	Temperature (°C)	Conversion (%)	Yield aldehyde (%)	Yield carboxylic acid (%)
2.1	1-Octanol	75/1	30	57	8	27
2.2		150/1	30	36	8	14
2.3 [b]		75/1	30	46	16	14
2.4 [b]		150/1	30	24	8	4
2.5 [b]		75/1	30	47	21	11
2.6	1-Dodecanol	150/1	30	26	11	–
2.7	1-Hexadecanol	150/1	70	33	25	–
2.8	2-Hexyl-1-decanol	150/1	30	28	17	–

[a] Cat.: $RuCl_2(PPh_3)_3$; $t = 2$ h. [b] Runs with recycled catalyst (see text).

are formed. Halving of the catalyst concentration lowers the extent of conversion of alcohol in a similar way as that for the oxidation with MMO.

The long chain alcohols can also be oxidized with MM/H_2O_2, but the yields are lower than those in the analogous MMO experiments.

It can be seen that the MM/H_2O_2-system has a similar reactivity to the MMO system, although the results are not completely equivalent. It should be noted that the *N*-methylmorpholine is an essential part of the oxidising system; in similar experiments with hydrogen peroxide without MM and in those without the ruthenium catalyst, there was negligible oxidation, and so it can be assumed that MMO formed in situ is the actual oxygen transmitter.

c. Catalyst recycle

After the oxidation with the MM/H_2O_2-system the products are obtained by simple phase separation. The remaining aqueous solution contains both the catalyst and the *N*-methylmorpholine. To investigate the MM-recycle the aqueous phase of run 2.2 was used again in experiment 2.3 (see Table 2), and fresh catalyst was added, generating an alcohol/catalyst ratio of 75/1. The results of run 2.3 show an increase in aldehyde yield and the same extent of formation of carboxylic acid as in run 2.2. Again, the aqueous phase from run 2.3 was recycled: one half was used in run 2.4 without additional catalyst, the other half in run 2.5 with additional catalyst. Experiment 2.4 with an alcohol/catalyst ratio of 150/1 gave similar results to those from the foregoing run 2.2; run 2.5, with an alcohol/catalyst ratio of 75/1, give conversions and yields comparable to those in run 2.3. These results show that in principle recycling of both *N*-methylmorpholine and the catalyst is possible without much effect on the activity and selectivity.

This possibility of recycling the catalyst components is demonstrated in the simplified flow scheme of Fig. 1 which contains three units: reactor, separator, and distillation equipment.

Alcohol, solvent, the aqueous catalyst/MM-solution and H_2O_2 are allowed to interact in the reaction unit, then phase separation is carried out in the separator, thus recycling the catalyst solution [9]. In the multistage distillation unit both of the products are isolated and, solvent as well as unchanged alcohol are recycled into the

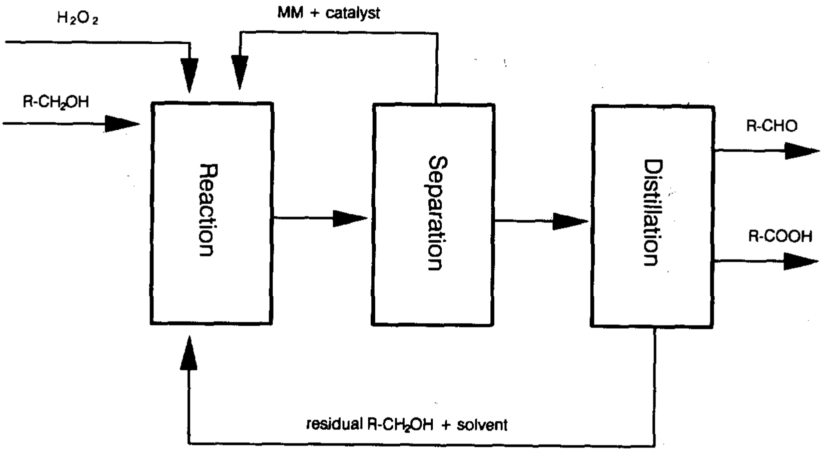

Fig. 1. Oxidation with 4-methylmorpholine (MM) and hydrogen peroxide: flow scheme with catalyst recycle.

reactor. In this way an efficient overall oxidation with MM/H_2O_2 can be achieved, although the extent of conversion and the yield of a single run are rather modest.

d. Mechanistic considerations

The mechanism of the homogeneous transition metal catalyzed oxidation of alcohols has not yet been studied in detail. We offer below some suggestions about possible reaction pathways.

One possible first step may be the oxidation of the ruthenium species by MMO to form a ruthenium-oxo-complex with an increased oxidation state of ruthenium [10–12]. Addition of the alcohol then yields the aldehyde, probably with ruthenium hydridooxo-species as intermediates.

Another possible initial step could be the oxidative addition of the alcohol to the ruthenium catalyst the aldehyde being formed in a subsequent elimination step. Depending on the reaction conditions the aldehyde may be oxidized to the carboxylic acid. The remaining ruthenium-bis-hydridocomplex then reacts with MMO to yield water and the catalytically active ruthenium compound. In Fig. 2 this process

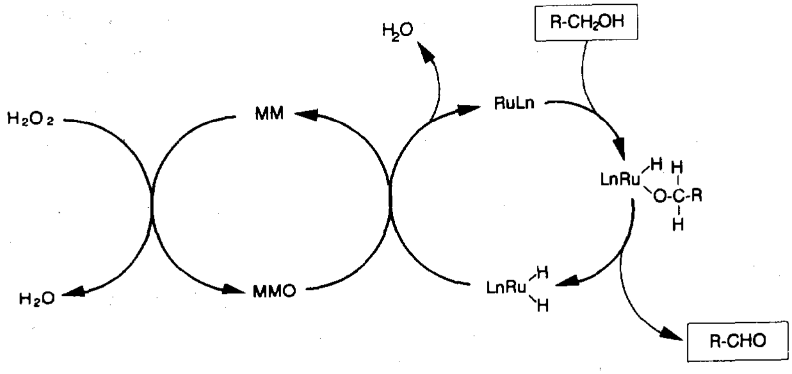

Fig. 2. Oxidation with *N*-methylmorpholine (MM) and hydrogen peroxide: proposed catalytic cycle.

represents the main cycle in the mechanistic scheme, and is incompanied by an additional cycle for the regeneration of MM by hydrogen peroxide.

Experimental

Oxidations with N*-methylmorpholine* N*-oxide*

The experiments were carried out in 100 ml glass flasks fitted with a reflux condenser. $RuCl_2(PPh_3)_3$ (200 mg; 0.21 mmol) was dissolved in 50 ml methylene chloride or 1,2-dichloroethane and *N*-methylmorpholine *N*-oxide (4.22 g; 31 mmol) and 5 ml octanol (31 mmol) were added. Then the mixture was stirred for 2 h at 30 °C and then shaken with 100 ml of distilled water. The phases were separated, the organic phase was dried, and the solvent was evaporated. The residue was analyzed by GLC using a Hewlett Packard apparatus GC 5890A fitted with an OV 101 column (25 m · 0.32 mm).

Oxidations with N*-methylmorpholine and hydrogen peroxide*

The experiments were carried out in the apparatus described above. A solution of $RuCl_2(PPh_3)_3$ (200 mg; 0.21 mmol) in 50 ml of acetone was placed in the flask and 5 ml (31 mmol) of octanol and 3.5 ml (31 mmol) of *N*-methylmorpholine were added. The mixture was stirred for 2 h at the chosen temperature during which 13.5 ml (156 mmol) of an aqueous hydrogen peroxide solution (35 weight%) was pumped continuously into the flask at a feed rate of $v = 6.7$ ml/h. After the reaction was complete 100 ml of methylene chloride was added, the layer were separated, and the organic layer dried and evaporated. The residue was analyzed by GLC.

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