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SELECTIVE REDUCTION OF ALDEHYDES BY A FORMIC ACID- TRIALKYLAMINE- $RuCl_2(PPh_3)_3$ SYSTEM

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Summary- In the presence of trialkylamine and formic acid, $RuCl_2(PPh_3)_3$ selectively reduces aldehydes to the corresponding alcohols at room temperature. Other reducible groups are unaffected.

The selective reduction of an aldehyde in the presence of other reducible groups is a problem of current interest in organic synthesis. In recent reports[1] some borohydride complexes have been used to this purpose, but some reduction of keto groups still occurs.

As part of our investigation of the use of Ruthenium complexes as homogeneous catalysts[2] we have found that, in the presence of trialkylamine and formic acid, $RuCl_2(PPh_3)_3$ is a suitable catalyst for the selective reduction of aldehydes to alcohols at room temperature.

We note that at a ratio of less than 3 mol of formic acid per mol of trialkylamine a catalytic amount of the said Ru complex decomposes formic acid at room temperature into hydrogen and carbon dioxide. If a tenfold molar excess of formic acid is used, a higher temperature is required for the reaction to take place. However even at 75°C, other groups such as ketones and alkenes are reduced, as has already been reported for reductions carried out at 125° with a Ruthenium complex-formic acid system without trialkylamine[3].

We have observed that in the experimental conditions reported beneath, aldehydes may be almost quantitatively reduced, while groups such as nitro, keto, alkene, ester, tertiary amide and acetal are not affected (Table 1 and ref. 4). For example, on reducing an equimolecular mixture of benzaldehyde and acetophenone, benzylalcohol is obtained (95% yield after 30 minutes), while no 1-phenylethanol is determined by GLC. Acetophenone is recovered unchanged.

Other groups may alter the course of the reaction and even inhibit the catalyst; in the presence of benzoic acid, benzaldehyde is reduced to a minor

extent in 30 minutes (33% yield) and is not reduced at all in the presence of nitriles or alkynes[4].

Polar substituents do not seem to influence the reduction rate as revealed by the similarity of the results obtained with 4-methyl, 2-bromo, 4-nitro, and 2-methoxy benzaldehydes which all gave the corresponding alcohols in high yields. Similarly no significant difference in the yield of the reduction product is observed when benzaldehyde and hexanal are reacted toghether. This contrasts with the results reported for the reduction with borohydride complex[1b]. The poor result obtained with salicylaldehyde (15% yield) in comparison with o-methoxybenzaldehyde (97% yield) may be ascribed to a strong coordination of the less reactive substrate.

Steric hindrance seems to play a rather important role. In fact in the contemporaneous reduction of benzaldehyde and mesitaldehyde the former is better reduced (95% yield after 30 minutes) than the latter (just 1% yield). Mesitaldehyde alone is reduced by 27% in the same time (Table 1). Even a more subtle difference in the structure, like that between ethanal and decanal, may give different yields by competitive reduction (64% and 27% of the corresponding alcohols in 30 minutes at 17°C).

In a recent paper[5], we ascribed the selectivity of the synthesis of dialkylmethylamines and of dimethylalkylamines to a competition of methanol and alkylamine with the Ruthenium complex. The results obtained in the competitive reduction of pairs of aldehydes again suggest a competition in their coordination to the catalyst.

Finally we found that in the reduction of benzaldehyde, no differences were observed on varying the solvent from furan to tetrahydrofuran, N,N-dimethylformamide, benzene and toluene. The reaction also showed to be insensitive to variations in the structure of the tertiary amines as shown from experiments using trimethyl-, triethyl-, tributyl-, trihexyl- and trioctylamines. However the solid polyamine Amberlite IRA-93 was not very effective. The reaction was slowed down by ethanol and inhibited by pyridine. The solubility of the substrate and the recovery of the reaction product dictates the choice of the most suitable solvent and amine.

A typical procedure was:
0.05 mol of triethylamine and 25 ml of THF were placed in a flask under argon. 0.075 mol of formic acid were then added and the solution was cooled at room temperature (20 - 25°C). 2×10^{-4} mol (0.4%) of $RuCl_2(PPh_3)_3$ were then introduced into the flask and the mixture was allowed to evolve gas under stirring. About three minutes later 0.05 mol of the aldehyde were added and the agitation was continued until the reaction was over (about 30 minutes by GLC). The solution was then neutralized with 2N HCl, THF was removed under vacuum and the residue was taken up with ether. The ether layer was dried over

Table 1. Reduction of Aldehydes and Ketones by $RuCl_2(PPh_3)_3$, HCOOH, R_3N in THF at room temperature.

Substrate	Product	Yield %[a]	Substrate Recovered %[a]
CH_3CHO	CH_3CH_2OH[b]	94 (89)	5
$CH_3(CH_2)_2CHO$	$CH_3(CH_2)_3OH$	88	10
$CH_3(CH_2)_4CHO$	$CH_3(CH_2)_5OH$	99(95)	trace
$CH_3(CH_2)_6CHO$	$CH_3(CH_2)_7OH$	79	20
$CH_3(CH_2)_8CHO$	$CH_3(CH_2)_9OH$	86	13
C_6H_5CHO	$C_6H_5CH_2OH$	97(92)	trace
$2\text{-}CH_3C_6H_4CHO$	$2\text{-}CH_3C_6H_4CH_2OH$	99	trace
$4\text{-}CH_3C_6H_4CHO$	$4\text{-}CH_3C_6H_4CH_2OH$	98	trace
$2\text{-}BrC_6H_4CHO$	$2\text{-}BrC_6H_4CH_2OH$	89(86)	9
$4\text{-}NO_2C_6H_4CHO$	$4\text{-}NO_2C_6H_4CH_2OH$	91(78)	7
$2\text{-}CH_3OC_6H_4CHO$	$2\text{-}CH_3OC_6H_4CH_2OH$	97	2
$2\text{-}HOC_6H_4CHO$	$2\text{-}HOC_6H_4CH_2OH$	15	84
$2,4,6,(CH_3)_3C_6H_2CHO$	$2,4,6,(CH_3)_3C_6H_2CH_2OH$	27	70
C_6H_5CHO +	$C_6H_5CH_2OH$	95	4
$2,4,6,(CH_3)_3C_6H_2CHO$	$2,4,6,(CH_3)_3C_6H_2CH_2OH$	1	98
$C_6H_5CHO + CH_3(CH_2)_4CHO$	$C_6H_5CH_2OH$	57	41
	$CH_3(CH_2)_5OH$	50	49
citral	geraniol	99	trace
citronellal	citronellol	95(89)	trace
$C_6H_5COCH_3$	$C_6H_5CH(OH)CH_3$	0[c]	100
$CH_3COCH_2CH_3$	$CH_3CHOHCH_2CH_3$	0[c]	100
$C_6H_5CHO + C_6H_5COCH_3$	$C_6H_5CH_2OH$	91	7
	$C_6H_5CH(OH)CH_3$	0	100
$n\text{-}C_7H_{15}CHO + C_5H_{11}COCH_3$	$CH_3(CH_2)_7OH$	73	23
	$CH_3(CH_2)_4CHOHCH_3$	trace	99.5
$C_6H_5CH=CHCHO$	$C_6H_5CH=CHCH_2OH$	99(95)	trace
$C_6H_5COCH_3$ [d]	$C_6H_5CH(OH)CH_3$	66	trace
	$HCOOCH(CH_3)C_6H_5$	27	
$CH_3(CH_2)_5CH=CH_2$ [d]	$CH_3(CH_2)_6CH_3$	44	3.5
	$CH_3(CH_2)_4CH=CHCH_3$	37	

a) Determined by GLC. In parentheses are the yields of the isolated product. b) The reaction was carried out with tributylamine in furan. Ethanol was recovered by fractional distillation of the mixture evaporated at the end of the reaction. c) Even after 24 hour reaction. d) 0.05 mol of substrate, 0.05 mol of Bu_3N, 0.5 mol of HCOOH and 5×10^{-4} mol of catalyst at 75°for an hour.

magnesium sulfate and evaporated. The residue was a rather pure alcohol which after distillation or crystallization from a suitable solvent had boiling or melting point, I.R. and ^{1}H N.M.R. spectra in agreement with those of a pure sample.

In conclusion, we underline the versatility of the method described above for the clean and selective reduction of the aldehyde group in mild conditions. The procedure is very simple and does not present some disadvantages which accompany other methods such as the reduction to hydrocarbon by hydrogenolysis[6a,b] or by decarbonylation[3c] or the esterification with formic acid[6c] or by the Tischenko reaction[6d].

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4.We carried out the reduction of benzaldehyde in the presence of equimolecular quantities of acetophenone, 1-octene, 1-undecene, 1-octyne, ethyl benzoate, N,N-dibutylbenzamide, benzaldehyde dimethylacetal, benzonitrile with three mol of formic acid and two mol of trimethylamine at room temperature for one day.

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