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OXIDATION OF ALCOHOLS BY TRANSITION METAL COMPLEXES

PART II.[1] HYDROGENOLYSIS OF ORGANIC CHLORIDES

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Catalytic hydrogenolysis of organic halides using heterogeneous catalysts is a well known process. Homogeneous catalysts for this process are less common but examples involving both molecular hydrogen[2] and hydrogen transfer from organic compounds[3] are known.

The current interest[2,3] in the homogeneous process prompts us to report our studies on the catalytic reduction of benzylic chlorides and related compounds. Benzylic chlorides, phenacyl chloride, chloroacetamide and ethyl chloroacetate all undergo hydrogenolysis by hydrogen transfer from simple alcohols in the presence of rhodium trichloride, triphenylphosphine and sodium carbonate (Table 1). n-Hexyl chloride and cyclohexyl bromide did not react under these conditions. The hydrogenolysis of phenacyl chloride produced a significant amount of the corresponding alcohol and the amount of alcohol increased with time (Table 1). In most reactions with benzylic chlorides small amounts of the corresponding alkyl benzyl ether were also produced and this was the major product in the absence of rhodium trichloride or when triphenyl- or dimethyl-phosphite was used in place of triphenylphosphine (Tables). The ability of phosphites to catalyse nucleophilic replacement of halogen has been previously observed.[4] Increasing the amount of triphenylphosphine led to a slower reaction and promoted ether formation (Table 2). Variation of the alcohol showed there was little difference between ethanol and isopropanol but methanol was inferior (Table 2). Ruthenium trichloride, iridium trichloride and palladium chloride were found to give less efficient catalysts than rhodium trichloride (Table 2). In all cases phosphine complexes were clearly formed but in the case of palladium chloride the complex decomposed and deposited metallic palladium during the reaction.

Table 1. Transfer Hydrogenolysis of Benzylic Chlorides and Related Compounds (1 mmol) , using $RhCl_3.3H_2O$ (0.05 mmol), Ph_3P (0.25 mmol) and Na_2CO_3 (1.1 mmol) in boiling EtOH (20 ml)[≠]

Halide (R-X)	Time (h)	% Yield (R-H)[a]	Halide (R-X)	Time (h)	% Yield (R-H)[a]
$PhCOCH_2Cl$	6	60.0 [b]	EtO_2OCH_2Cl	6	77.0 [d]
$PhCOCH_2Cl$	22.5	38.5 [c]	*p*-$ClC_6H_4CH_2Cl$	6	50.0
H_2NOOCH_2Cl	12	73.0	*p*-$MeC_6H_4CH_2Cl$	12	44.5 [d,e]

[≠] The reactions were run under a small positive pressure of nitrogen.

a. isolated yields, b. PhCH(OH)Me (18.5%) also isolated, c. PhCH(OH)Me (23.5%) also isolated, d. % yields calculated from glc (see Table 2), e. *p*-$MeC_6H_4CH_2OEt$ (ca. 12%) also formed.

Table 2. Transfer Hydrogenolysis of Benzyl Chloride

Alcohol	Metal Compound (5 mole %)	Ligand (25 mole %)	Reflux time (h)	% Yields[≠]	
				RH	ROR'
MeOH	$RhCl_3.3H_2O$	PPh_3	12	39	21
EtOH	$RhCl_3.3H_2O$	PPh_3	4	64	trace
EtOH	$RhCl_3.3H_2O$	PPh_3 [a]	4	61	trace
EtOH	$RhCl_3.3H_2O$	PPh_3 [b]	7	69.5	8
Me_2CHOH	$RhCl_3.3H_2O$	PPh_3	4	64	
EtOH	$RhCl_3.3H_2O$	-	4 [c]	39.5	11.5
EtOH	$RhCl_3.3H_2O$	$P(OMe)_2(O)H$	23 [d]	3.5	56
EtOH	$RhCl_3.3H_2O$	$P(OPh)_3$	23 [e]	6	79
EtOH	$PdCl_2$	PPh_3	22	61	13.5
Me_2CHOH	$RuCl_3.3H_2O$	PPh_3	15	61	
Me_2CHOH	$IrCl_3.H_2O$	PPh_3	15 [f]	46	23 [g]
EtOH	-	PPh_3	90	13	76

≠ % yields calculated from glc (2m 20% carbowax 20M, 60-150°; xylene as internal standard) unless otherwise stated.

a. 15 mole %, b. 35 mole %, c. conversion 54%, d. conversion 72%, e. conversion 50%, f. conversion 53%, g. uncorrected glc value.

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