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Nickel Mediated Conversion of Acyl Halides in Aldehydes

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Abstract: Aldehydes are obtained from acyl halides employing stoichiometric tri n.butyl tin hydride (TBTH) and catalytic nickeldiphenylphosphinoethane dichloride (NidppeCl$_2$), at room temperature.
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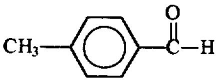
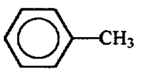
The synthesis of aldehydes from acyl halides represents an important functional group interconversion (FGI) in organic chemistry. However, if we exclude the use of Rosenmund[1] or Brown[2] reagents, few efficient methods are available and those that there are tend to affect other functional groups present in the target molecule.

On the other hand, there are many exotic[3] or expensive catalytic systems based on transition metal catalysts[4]. This paper reports the synthesis of aldehydes, starting from acyl halides and employing a catalytic amount of NidppeCl$_2$ with a stoichiometric amount of the commonly available TBTH as a hydride source.

In a typical run 0.01 mol of the TBTH in 20 ml of freshly distilled glyme or THF was slowly added to a solution containing 0.01 mol of the acyl chloride, $1.9\ 10^{-4}$ mol of NidppeCl$_2$ and, when specified, 0.01 mol of NaI as a co-catalyst in the same solvent. After 15 min. at room temperature the yellow solution was hydrolyzed with water and extracted with diethyl ether. After the usual workup and purification of the product by distillation or alternatively by precipitating the corrisponding 2,4-dinitrophenylhydrazone with the Brady reagent[5], the product was obtained chemically pure (g.c., ^{1}H-NMR and ^{13}C-NMR).

Table 1 reports the various reaction conditions adopted when employing, as a starting material, p.methylbenzaldehyde. In particular the catalyst, the solvent, the temperature and the addition of other ligands are taken into account.

Table 1. Reduction of p.Methylbenzoyl Chloride with TBTH and a Nickel Catalyst

Run	Reaction Conditions		
1	Bu_3SnH, $NidppeCl_2$, THF, 25 ^{0}C	47%	53%
2	Bu_3SnH, $NidppeCl_2$, THF, -20 ^{0}C	0%	10%
3	Bu_3SnH. $NidppeCl_2$, THF, 50 ^{0}C	0%	90%
4	Bu_3SnH, $Ni(CO)_3(PPh_3)_2$, THF, 25 ^{0}C	53%	43%
5	Bu_3SnH, NaI stechiom. $NidppeCl_2$, THF 25 ^{0}C	72%	28%
6	Bu_3SnH, $NidppeCl_2$, THF 25 ^{0}C, 2 atm. CO	0%	0%
7	Bu_3SnH, $NidppeCl_2$, PPh_3 cat., THF 25 ^{0}C	0%	10%

When the reaction is carried out at a low temperature (Run 2, Table 1), the corresponding decarbonylated product (toluene) in low conversion is the sole compound obtained, but when the reaction is performed at 50 ^{0}C, the conversion in toluene rises to 90% (Run 3, Table 1). The best results are obtained when the reaction is carried out at 25 ^{0}C (Run 1, Table 1).

The use of $Ni(PPh_3)_2(CO)_3$ instead of the $NidppeCl_2$, to avoid the known CO extrusion[6] as a side reaction, gave the p.methylbenzaldehyde in 53% yield only (Run 4, Table 1).

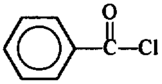
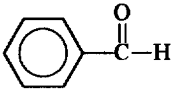
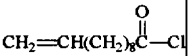
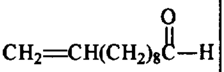
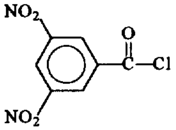
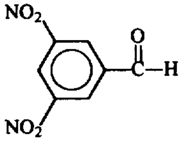
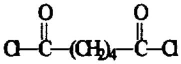
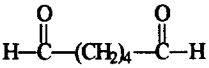
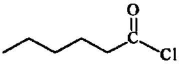
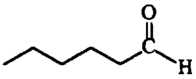
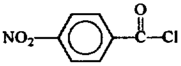
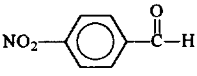
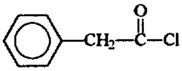
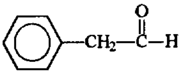
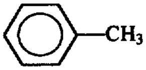
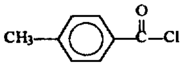
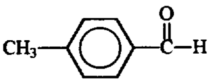
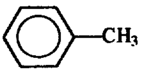
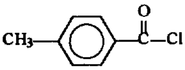
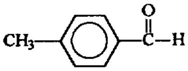
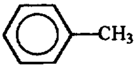
The best results are obtained by carring out the reaction in the presence of a stoichiometric amount of NaI in glyme instead of THF as the solvent. The use of this last solvent is necessary to prevent the THF ring opening reaction caused by the acyl iodide[7] formed in solution.

Table 2 shows the results obtained by reacting different acyl chlorides.

The reaction does not seem to be applicable to sterically hindered substrates and the proposed reaction mechanism shows how the decarbonylated byproduct can be obtained through two different pathways, the first of which, at low (-20 ^{0}C) temperatures (with low yields) and the second at higher temperatures (50 ^{0}C), under thermodynamic conditions (Scheme 1).

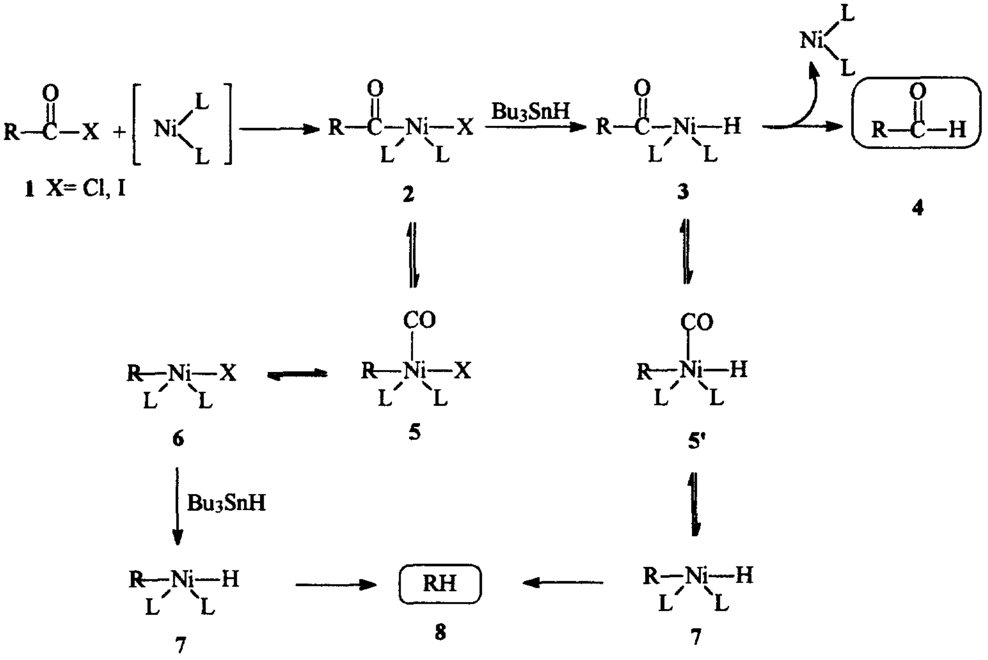
Starting from this point of view, a stoichiometric amount of NaI is needed to convert the acyl halide into the more reactive iodide, which at room temperature, can rapidly give the nickel acyl hydride. The aldehyde formation, in these conditions, occurs faster than the carbonylation reaction (Kinetic conditions).

Table 2. Nickel Mediated Reduction of Acyl Halides in Aldehydes[8].

Run	Acyl Halide	Aldehyde	Byproduct	Reaction Conditions
1		 90%	-----	Bu_3SnH, $NidppeCl_2$, THF, 25 °C
2	 $CH_2{=}CH(CH_2)_8\overset{O}{\overset{\|}{C}}{-}Cl$	 $CH_2{=}CH(CH_2)_8\overset{O}{\overset{\|}{C}}{-}H$ 79%	$CH_3CH{=}CH(CH_2)_6CH_3$ 21%(cis/trans)	Bu_3SnH, $NidppeCl_2$, THF, 25 °C
3		 90%	-----	Bu_3SnH, NaI stoich. $NidppeCl_2$, glyime, 25 °C
4	 $Cl{-}\overset{O}{\overset{\|}{C}}{-}(CH_2)_4{-}\overset{O}{\overset{\|}{C}}{-}Cl$	 $H{-}\overset{O}{\overset{\|}{C}}{-}(CH_2)_4{-}\overset{O}{\overset{\|}{C}}{-}H$ 90%	-----	Bu_3SnH, NaI stoich. $NidppeCl_2$, glyme, 25 °C
5		 80%	-----	Bu_3SnH, $NidppeCl_2$, THF, 25 °C
6		 90%	-----	Bu_3SnH, NaI stoich., $NidppeCl_2$, glyme, 25 °C
7		 44%	 56%	Bu_3SnH, $NidppeCl_2$, THF, 25 °C
8		 72%	 28%	Bu_3SnH, NaI stoich. $NidppeCl_2$, THF, 25 °C
9		 95%	 5%	Bu_3SnH, NaI stoich. $Ni(AsPPh_3)_2Cl_2$, THF, 25 °C

The decarbonylation reaction can be suppressed by employing $Ni(AsPPh_3)_2Cl_2$ as a catalyst (Run 9, Table 2). Substituting of the P-Ni bond (in the $NidppeCl_2$) with the As-Ni one [in the $Ni(AsPPh_3)_2Cl_2$] prevents the decarbonylation of the intermediates **2** and **3** (Scheme 1, $L=AsPh_3$) because a better stabilising overlap of σ^*_{Ni-As} orbital with the corresponding trans σ_{Ni-CO} orbital, take places.

Scheme 1



Further studies are in progress.

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8. All compounds synthesized gave satisfactory ^1H, ^{13}C NMR, IR and Mass spectral data as well as elemental analises.

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