# Palladium-catalysed Reaction of Tributyltin Hydride with Acyl Chlorides. A Selective Route to Aldehydes

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*Summary* In the presence of catalytic amounts of tetrakis(triphenylphosphine)palladium, tributyltin hydride rapidly and selectively reduces acyl chlorides to aldehydes under very mild conditions.

Organotin hydrides are known to reduce, probably by a free radical chain mechanism, acyl chlorides to aldehydes.[1] However, competing[1] and sometimes predominant[2] ester formation (equation 1) is also observed and the reaction is not very useful for the synthesis of aldehydes.

$$\mathrm{RCOCl} \xrightarrow{\mathrm{R_3SnH}} \mathrm{RCHO} + \mathrm{RCH_2OCOR} \qquad (1)$$

We report here that the reaction of acyl chlorides with tributyltin hydride can be made much more rapid and, seemingly, completely selective towards the formation of aldehydes by use of tetrakis(triphenylphosphine)palladium as a catalyst.

Experiments, performed on a $5 \times 10^{-4}$ molar scale in acyl chloride and in tributyltin hydride have been run in solution (0·5 M) in benzene and at room temperature for 2 h in the presence of $2{\cdot}5 \times 10^{-5}$ mol ($5 \times 10^{-2}$ equiv.) or $0{\cdot}5 \times 10^{-5}$ mol ($1 \times 10^{-2}$ equiv.) of catalyst. Yields (see the Table) have been determined by n.m.r. spectroscopy (anisole as the reference). Aldehyde formation has also been monitored by g.l.c. analysis and i.r. spectroscopy. In no cases and by none of these methods could appreciable amounts of ester be detected.

The yields of aldehydes are high with both aliphatic and aromatic acyl chlorides used in this study (see the Table). They are not significantly affected by increasing the reaction time. In the absence of catalyst and under the same conditions of temperature and dilution, the reaction is much slower (see the Table); only *ca.* 10% of aldehyde is formed after 2 h. In the case of benzoyl chloride, when the reaction was brought to completion by heating at 60 °C for 20 h, benzylbenzoate was obtained as the major product.

Table. Reaction between RCOCl and $\mathrm{B^n_3}$ SnH (1 : 1·1 mol ratio) catalysed by $\mathrm{Pd(PPh_3)_4}$.

| Acyl radical in RCOCl | Catalyst/ $10^2$ mol | Yield[a] RCHO/% |
|---|---|---|
| Benzoyl | 1 | 95 |
| 1-Naphthoyl | 1 | 97 |
| 2-Naphthoyl | 1 | 75 |
| | 5 | 85 |
| Cinnamoyl | 5 | 85 |
| n-Heptanoyl | 1 | 81 |
| Palmitoyl | 5 | 75 |
| Benzoyl | | 10[b] (approx.) |
| n-Heptanoyl | | 10[b] (approx.) |

[a] After two hours. [b] Without catalyst.

The palladium–catalysed reaction has also been performed on a preparative scale; thus benzoyl chloride (2·81 g, $2 \times 10^{-2}$ mol) in benzene solution (10 ml) was treated with 6·40 g (1·1 equiv.) of freshly distillated tributyltin hydride in the presence of $\mathrm{Pd(PPh_3)_4}$ (0·231 g, $1 \times 10^{-2}$ equiv.) for 2 h at room temperature. $\mathrm{CCl_4}$ (1 ml) was then added in order to convert all the unreacted tributyltin hydride into the corresponding chloride; after evaporation of the solvents, precipitation of the palladium compounds with pentane, and filtration, the benzaldehyde formed was distilled twice under reduced pressure from the high-boiling tributyltin chloride to give 1·72 g (81%) of pure product. Similar experiments with heptanoyl chloride gave heptanaldehyde in 77% yield. With 2-naphthoyl chloride [$2{\cdot}5 \times 10^{-2}$ equiv. of $\mathrm{Pd(PPh_3)_4}$ used in this case] the corresponding aldehyde was first isolated as the bisulphite addition compound from which tributyltin chloride was eliminated by repeated washings with pentane. Treatment with an aqueous solution of $Na_2CO_3$, followed by recrystallisation from hexane gave pure 2-naphthaldehyde in 65% yield.

The results obtained here in the palladium-catalysed reduction by tributyltin hydride compare well with those of other catalytic reductions of acyl chlorides to aldehydes, such as the Rosenmund reactions[3,4] and the palladium-[5] or platinum-[6] catalysed reduction by organosilicon hydrides.

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