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Palladium-catalyzed reduction of acyl chlorides with tributylgermanium hydride

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Abstract

Tributylgermanium hydride in the presence of $Pd(PPh_3)_4$, can reduce acyl chlorides selectively to aldehydes under mild conditions in good yields.

Introduction

Most of the reactions used to reduce acyl chlorides to aldehydes require complex metal hydrides [1] as the reducing agents. Guibe et al. reported that tributyltin hydride in the presence of a palladium catalyst is an effective reagent for the conversion of acyl chlorides to aldehydes [2]. This reaction is similar to the palladium-, platinum-, or rhodium-catalyzed reduction of acyl chlorides by trialkylsilanes [3,4]. Tributylgermanium hydride, similar to tributyltin hydride and trialkylsilanes, can reduce acyl chlorides to aldehydes at high temperature catalyzed by aluminium halides [5], but the aldehydes produced can be further reduced to alcohols. Furthermore, the selectivity is unsatisfactory. We wish to report here a mild and selective reaction of the palladium(0)-catalyzed reduction of acyl chlorides with tributylgermanium hydride to aldehydes.

Results and discussion

We have found that tributylgermanium hydride can reduce acyl chlorides selectively to aldehydes catalyzed by tetrakis(triphenylphosphine)palladium at 80–100 °C in hexamethylphosphoric triamide (HMPA) in high yields. The results are shown in Table 1:

$$\underset{(1)}{RCOCl} + n\text{-}Bu_3GeH \xrightarrow[\text{HMPA, 80–100 °C}]{Pd(PPh_3)_4} \underset{(2)}{RCHO} + n\text{-}Bu_3GeCl$$

The reductive ability of Bu_3GeH is low compared with Bu_3SnH, and we have found that the solvent effect is important for the reduction of acyl chlorides with

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Table 1

Pd(0)-catalyzed reduction of acyl chlorides with Bu_3GeH [a]

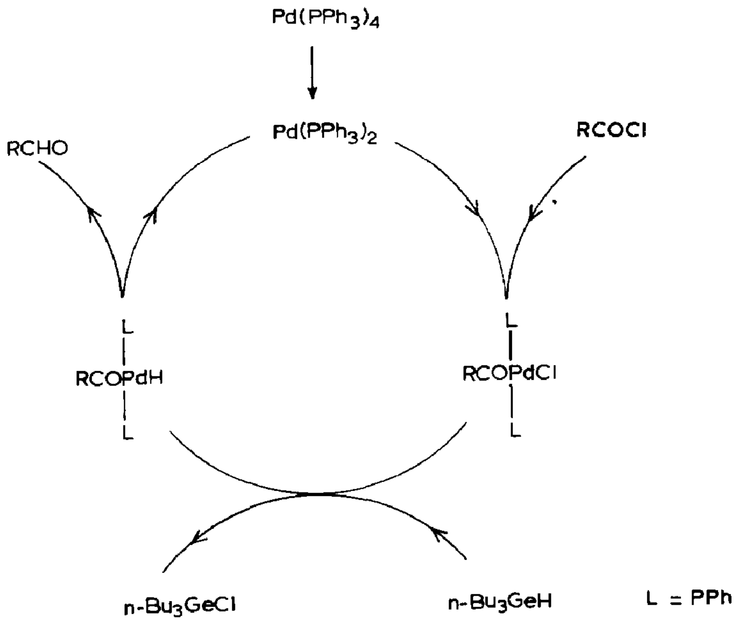
Entry	1	(R =)	Temp. (°C)	Time (h)	Product [b]	Isolated yield (%)
1	**1a**	$(2,4\text{-}Cl_2C_6H_3)$	80	1	**2a**	85
2	**1b**	$(4\text{-}O_2NC_6H_4)$	80	1	**2b**	80
3	**1c**	$(C_6H_5CH{=}CH)$	90	1.5	**2c**	88
4	**1c**	$(C_6H_5CH{=}CH)$	100	2	$C_6H_5(CH_2)_2CHO$	37 [c]
5	**1d**	$(2\text{-}FC_6H_4)$	80	0.5	**2d**	80 [d]
6	**1e**	(C_6H_5)	80	1	**2e**	93 [d]

[a] **1** (1 mmol) was treated with Bu_3GeH (1.3 mmol) in HMPA in the presence of $Pd(PPh_3)_4$ (0.05 mmol) at 80–100 °C. [b] All the products were characterized by ^1H NMR and from their m.p. or b.p.. [c] 3 mmol of Bu_3GeH was used. [d] $(Bu_3Ge)_2O$ (about 5%) was detected in the product by ^1H NMR. Further purification should give the pure product.

n-Bu_3GeH. The reaction scarcely proceeds when THF is the solvent, while the rate of the reaction is negligible in dioxane solution. HMPA was found to be the best solvent for this reaction. From Table 1 it is seen that the nitro group and chlorine atom on the benzene ring remain intact during the reaction (entries 1 and 2). Alcohols were not detected in the reaction (TLC). α,β-Unsaturated acyl chlorides can be reduced selectively to give α,β-unsaturated aldehydes, but the olefinic double bond can also be reduced to give saturated aldehydes if three equivalents of n-Bu_3GeH are used (cf. entries 3 and 4).

This reaction seems to proceed in a manner similar to the palladium-catalyzed reduction of acyl chlorides with Bu_3SnH [2]. The possible mechanism is shown in Scheme 1.

Further applications of the reaction are being investigated in this laboratory.



Scheme 1

Experimental

Melting points and boiling points were uncorrected. ^1H NMR spectra were recorded on a Varian EM 360-A (60 MHz) spectrometer using Me_4Si as the standard.

Materials

Tetrakis(triphenylphosphine)palladium(0) was prepared by a previously published procedure [6]. Tributylgermanium hydride was prepared by the reduction of tributylgermanium chloride [7]. All solvents were freshly distilled and degassed immediately before use.

General procedure for the reduction of acyl chlorides to aldehydes

Reactions were performed under prepurified nitrogen in degassed HMPA by Schlenk techniques. To a solution of acyl chloride (1 mmol) and $Pd(PPh_3)_4$ (0.05 mmol) in HMPA (5 ml) was added n-Bu_3GeH (1.2–1.3 mmol) by syringe. The reaction mixture was heated at 80–100 °C for 1–2 h. The reaction mixture was cooled, aqueous NaCl solution (5 ml) was added, and the mixture was extracted with diethyl ether (3 × 20 ml). The ether layer was dried over $MgSO_4$ and the solvent was removed. For the volatile aldehydes (PhCHO, *o*-FC_6H_4CHO), the products were distilled by short-path distillation (further purification by column chromatography should give the pure products). The nonvolatile aldehydes were purified by column chromatography or by preparative thin-layer chromatography.

Reduction of cinnamoyl chloride to 3-phenylpropionaldehyde. To a solution of cinnamoyl chloride (167 mg, 1 mmol), and $Pd(PPh_3)_4$ (0.05 mmol) in HMPA (2 ml) in a Schlenk tube, was added Bu_3GeH (310 mg, 3 mmol) by syringe under nitrogen. The reaction mixture was heated at 100 °C for 2 h. Aqueous NaCl solution (5 ml) was added, then the mixture was extracted with ether (3 × 20 ml), dried over $MgSO_4$, and the solvent was evaporated. The residue was separated by TLC (ethyl acetate/petroleum ether = 1/10), 3-phenylpropionaldehyde (50 mg) was isolated in 37% yield. B.p. 105–106 °C/13 Torr (literature [8] 211–214 °C/744 Torr), ^1H NMR δ (ppm): 1.24(t, 2H), 2.75(t, 2H), 7.24(m, 5H), 9.26(s, 1H).

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