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SHORT COMMUNICATION

Organic Reactions Using Sodium Hydrogentelluride: Part 4. The Selective Reduction of Aromatic Aldehydes or Ketones with Electron-Withdrawing Groups on the Benzene Ring by Sodium Hydrogentelluride[*]

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Aromatic aldehydes or ketones which have electron-withdrawing groups on the benzene ring were selectively reduced to the corresponding alcohols in good yields by sodium hydrogentelluride; common aldehydes such as benzaldehyde and tolualdehyde were inert.

Keywords: selective reduction; carbonyl compound; sodium hydrogentelluride

INTRODUCTION

In the context of investigations on the reactivity of tellurium compounds towards functional substrates (renewed recently in Refs 1–3), we have studied reduction using sodium hydrogentelluride (**1**) as a stoichiometric reductant.[4] Recently, this reagent has been employed for several chemoselective reductions[5–14]. However, the reduction of a carbonyl group to an alcohol has never been reported.

In this paper, we report the selective reduction by NaTeH (Scheme 1) (**1**) of aromatic aldehydes which have electron-withdrawing groups (EWG) on the benzene ring, to the corresponding alcohols. This reduction is specific to these aldehydes; aldehydes such as benzaldehyde and tolualdehyde are inert.

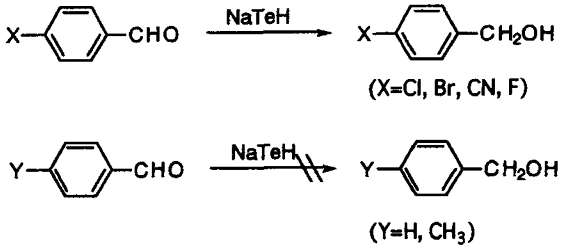
RESULTS AND DISCUSSION

For example, **1** in ethanol generated *in situ* reacted with *p*-chlorobenzaldehyde at room temperature for 24 h under an argon atmosphere to give *p*-chlorobenzyl alcohol in 74.4% yield (Scheme 1). Similar or greater yields were obtained when the reaction was carried out at 60 °C for 5 h.

As shown in Table 1, where other results are summarized, aromatic aldehydes with EWG such as –Cl, –Br, and –CN on the benzene ring were reduced to the corresponding alcohols in good yields, regardless of the location of the substituents. Furfural reacted with **1** to give furfuryl alcohol in low yield.

In addition to aromatic aldehydes, aromatic ketones such as 4-chloro- and 4,4′-dichlorobenzophenone were also reduced to the corresponding secondary alcohols in good yields (Table 2). 4-Chloro- and 2,4-dichloro-acetophenones were also reduced, but the yields were rather low. As expected, acetophenone and benzophenone themselves did not react.

From these results, it is thought that only



SCHEME 1

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[*] For Part III, see Ref. 4.

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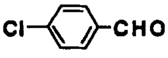
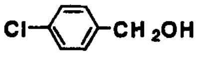
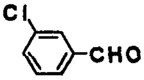
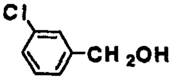
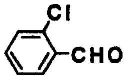
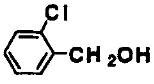
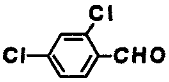
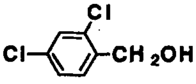
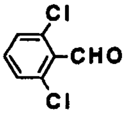
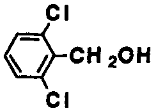
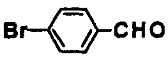
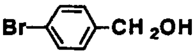
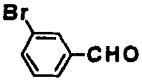
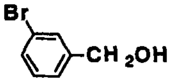
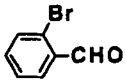
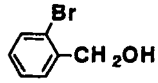
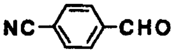
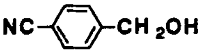
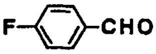
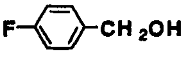
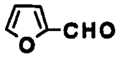
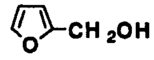
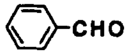
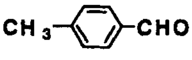
benzaldehydes having EWGs could react with **1** owing to the low electron density on the carbonyl carbon. However, reduction seems to be limited to relatively stable EWGs such as chloro-, bromo, fluoro and cyano groups. Benzaldehydes with relatively reactive EWGs such as *p*-nitrobenzaldehyde were examined, but no expected product was obtained.

This selective reduction is also applicable to the mixture of two aldehydes such as *p*-chlorobenzaldehyde and benzaldehyde, or *m*-bromobenzaldehyde and benzaldehyde. From

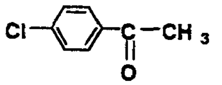
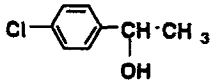
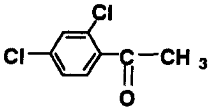
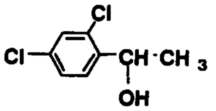
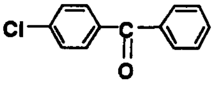
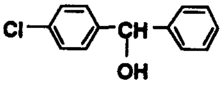
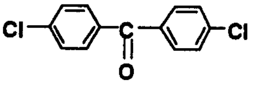
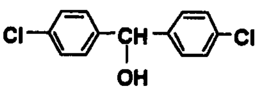
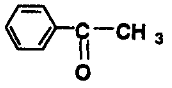
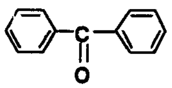
Table 1. Reduction of substituted benzaldehyde by sodium hydrogentelluride

Run	Substrate	Temp.[a] (°C)	Time (h)	Product	Yield[b] (%)
1		r.t. 60	24 5		74.4 74.3
2		r.t.	24		68.6
3		r.t. 60	24 5		661. 73.2
4		r.t.	24		73.6
5		r.t.	24		87.0
6		r.t.	24		69.8
7		r.t.	24		79.8
8		r.t.	24		66.4
9		r.t.	24		48.8
10		r.t.	24		15.2
11		r.t.	24		8.9
12		r.t. 60	24 5	— —	— —
13		r.t. 60	24 5	— —	— —

[a] r.t., room temperature.

[b] Isolated yield.

Table 2. Reduction of ketones with sodium hydrogentelluride

Run	Substrate	Temp. (°C)	time (h)	Product	Yield[a]
1		r.t. 60	24 5		2.1 10.3
2		r.t. 60	24 5		1.6 12.3
3		r.t. 60	24 5		19.9 65.3
4		r.t. 60	24 5		46.6 61.2
5		r.t.	24	—	—
6		r.t.	24	—	—

[a] Isolated yield.

these mixtures, only p-chlorobenzyl alcohol or m-bromobenzyl alcohol was obtained, in 70% or 72% yield, respectively, as a reduction product, and benzaldehyde was recovered in both cases.

EXPERIMENTAL

Ethanol was distilled and stored over 3 Å molecular sieves. Tellurium powder and sodium borohydride were purchased from Nacalai Chemicals, and used without further purification. Sodium hydrogentelluride (**1**) in ethanol was prepared according to a method in the literature, and used for the next reaction *in situ*. The following organic compounds were commercial products of the highest available purity: p-chlorobenzaldehyde, m-chlorobenzaldehyde, o-chlorobenzaldehyde, 2-4-dichlorobenzaldehyde, 2,6-dichlorobenzaldehyde, p-bromobenzaldehyde, m-bromobenzaldehyde, o-bromobenzaldehyde, p-formylbenzonitrile, p-fluorobenzaldehyde, furfural, benzaldehyde, p-tolualdehyde, p-chloroacetophenone, 2,4,-dichloroactophenone, p-chlorobenzophenone, 4,4′-dichlorobenzophenone, benzophenone and acetophenone. All reduction experiments were carried out under an argon atmosphere.

General procedure for the reduction of substituted benzaldehydes by 1

As a representative procedure, the reduction of p-chlorobenzaldehyde is described in detail. To a solution of **1** (10 mmol) in ethanol, an ethanol solution (5 cm^3) of p-chlorobenzaldehyde (5 mmol) was added. This mixture was stirred at room temperature for 24 h, and then filtered through Celite. The filtrate was diluted with ethyl acetate, washed with aqueous $NaHCO_3$ and then brine, dried over $MgSO_4$, filtered and concentrated. The residual liquid was purified by column chromatography to give p-chlorobenzyl alcohol in 74.4% yield. The product was identified by comparison of IR, NMR and mass spectra with those of an authentic sample.

Reductions of the other compounds were conducted in a similar manner.

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