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### Preliminary communication

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## Efficient selective hydrodebromination of aryl bromides by montmorillonitesilylaminepalladium(II) chloride \*

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### Abstract

A new convenient method for selective and quantitative hydrodebromination of aryl bromides by molecular hydrogen catalysed by a heterogenised homogeneous catalyst at room temperature and 1 atmospheric pressure is described.

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Selective hydrodebromination of aryl bromides is of considerable importance in organic chemistry. In general, heterogeneous palladium catalysts or palladium complexes with sodium formate, triethyl ammonium formate and sodium methoxide as hydride source are used for such hydrodehalogenations, but require temperatures (50–100 °C) and high molar equivalents of catalysts or longer times [1–3]. Recently a palladium complex (0.05–0.15 molar equiv. of the catalyst) and molecular hydrogen have been used for hydrodehalogenation of aryl halides at 100 °C [4]. We report here a new convenient method for selective hydrodebromination of aryl bromides by molecular hydrogen catalysed by a heterogenised homogeneous catalyst, montmorillonitesilylaminepalladium(II) chloride complex (0.01 molar equivalents of Pd), the first method to give quantitative yields at room temperature and atmospheric pressure.



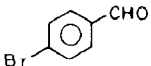

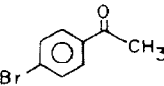
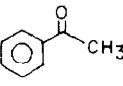
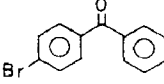
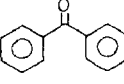
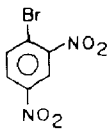
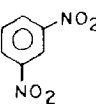
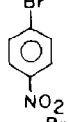
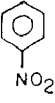






The catalyst complex was synthesised as described previously [5\*]. The hydrogenation was conducted under mild conditions in a 100 ml flask. The catalyst (50 mg, 0.0236 mmol) suspended in ethanol was treated with hydrogen for 30 min and a solution of the substrate (2.360 mmol) in ethanol was then introduced into a classical hydrogenation apparatus. The hydrogenation reaction was continued until the theoretical volume of hydrogen was absorbed. The catalyst was then filtered off and the filtrate was diluted with water and extracted with n-pentane. The products were purified by column chromatography on silica gel. All the products were satisfactorily characterised. The hydrodebromination reaction proceeded rapidly,

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Table 1

Selective hydrodebromination of aryl bromides

Entry No.	Substrate	Product	Time (hrs)	Yields <sup>a</sup> (%)
1.			4.5	98 <sup>b</sup>
2			9.0	92
3			9.0	92
4			0.5	97
5			2.5	95
6			3.0	98
7			4.0	85
8			24.0	95 <sup>b</sup>
9			12.0	96 <sup>b</sup>

a : Isolated yields. b : Yields are based on GC.

with turnover numbers of 12–200 h<sup>-1</sup>. However, the reaction was very slow for chlorobenzene (entry 8) and benzyl bromide (entry 9). The hydrodebromination is selective, and functional groups such as nitro, aldehyde, acetyl, and benzoyl groups are unaffected, as can be seen from Table 1. No other products are observed.

The new method described involves use of a readily available and inexpensive active catalyst [5,6], and molecular hydrogen in stoichiometric quantities for hydrodebromination of aryl bromides. It thus has advantages over other methods, which involve expensive hydride agents without [7] or with [1–3] palladium metals, and required relatively high temperatures. Our catalyst also has better functional group compatibility [1,3] than the other methods.

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