

An efficient synthesis of benzyl bromides from aromatic aldehydes using polymethylhydrosiloxane and (bromodimethyl)sulfonium bromide or *N*-bromosuccinimide[☆]

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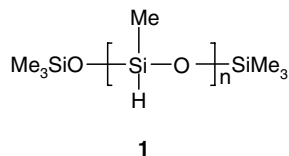
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Abstract—Polymethylhydrosiloxane (PMHS) in combination with (bromodimethyl)sulfonium bromide or NBS has been utilized for the first time for reductive bromination of aromatic aldehydes at room temperature to afford the corresponding benzyl bromides in excellent yields.

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1. Introduction

Polymethylhydrosiloxane (PMHS) (**1**) is an important reducing agent for eco-friendly reductive processes as it is non-toxic and stable to air and moisture.¹ It is a co-product of the silicon industry and is inexpensive. It has recently been utilized to carry out various organic syntheses.¹ However, this reagent was found unsuitable for the synthesis of benzyl bromides starting from benzaldehydes.²

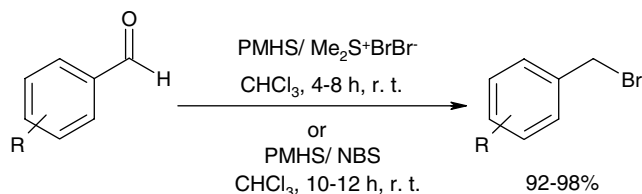


2. Results and discussion

In continuation of our work³ on the application of PMHS for the development of novel synthetic methodologies, we have observed that aromatic aldehydes can easily undergo reductive bromination with PMHS in combination with (bromodimethyl)sulfonium bromide

($\text{Me}_2\text{S}^+\text{Br}^-$) or NBS at room temperature to form the corresponding benzyl bromides in excellent yields (Scheme 1).

A series of benzyl bromides were prepared from various aromatic aldehydes (Table 1). No disubstituted product was obtained. Aromatic aldehydes containing both electron-donating and electron-withdrawing groups underwent the conversion smoothly. However, aldehydes possessing electron-withdrawing groups required longer reaction times (Table 1, entries 4 and 5) though the yields were very high. Alkyl, halogen, ether and nitro groups remained unaffected. Aliphatic aldehydes and ketones (both aliphatic and aromatic) did not show any change under the present reaction conditions. The combination of PMHS and $\text{Me}_2\text{S}^+\text{Br}^-$ was found to be better for reductive bromination of aromatic aldehydes compared to the combination of PMHS and NBS. For example, the conversion of *p*-chlorobenzaldehyde into *p*-chlorobenzyl bromide (entry 2) using PMHS/ $\text{Me}_2\text{S}^+\text{Br}^-$ took 4 h while PMHS/NBS required 11 h. Both



Scheme 1.

Keywords: Polymethylhydrosiloxane (PMHS); (Bromodimethyl)sulfonium bromide; NBS; Aromatic aldehydes; Benzylic bromide.

[☆] Part 147 in the series 'Studies on novel synthetic methodologies'.

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Table 1. Preparation of benzyl bromides from aromatic aldehydes using PMHS/Me₂S⁺BrBr⁻

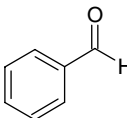
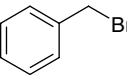
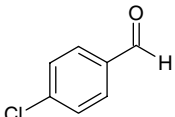
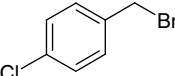
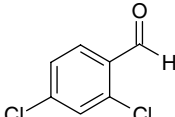
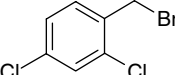
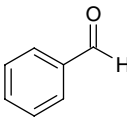
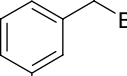
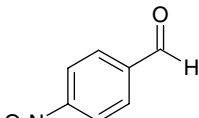
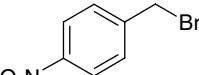
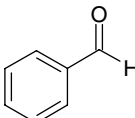
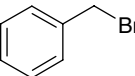
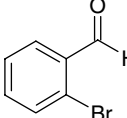
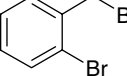
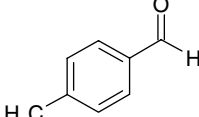
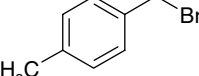
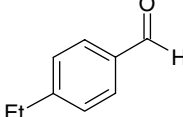
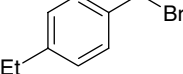
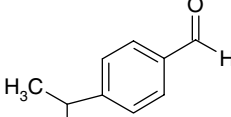
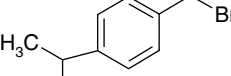
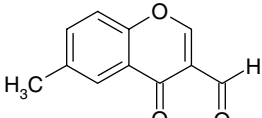
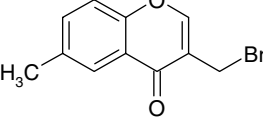
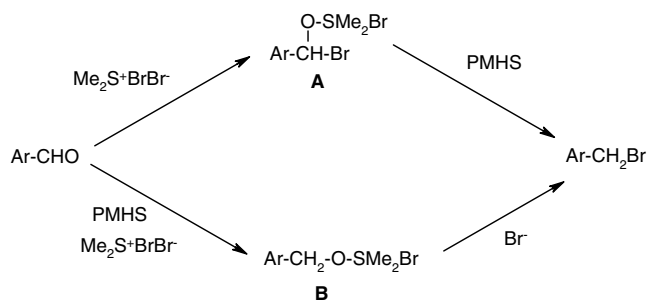
Entry	Substrate	Product ^a	Time (h)	Isolated yield (%)
1			5	96
2			4	98
3			4	98
4			7	94
5			8	92
6			7	94
7			4	95
8			4	96
9			4	96
10			4	95
11			4	96

Table 1 (continued)

Entry	Substrate	Product ^a	Time (h)	Isolated yield (%)
12			6	94
13			5	98

^a The structures of the products were determined from spectral (IR, ¹H NMR and MS) data.



Scheme 2.

combinations converted the aromatic aldehydes into the corresponding benzyl bromides in similar yields. (Bromodimethyl)sulfonium bromide, an inexpensive reagent, has been used mainly as a catalyst but the scope of its reaction has not yet been fully explored.⁴

The formation of benzyl bromides from aromatic aldehydes and PMHS/Me₂S⁺BrBr⁻ may take place by reduction of the intermediate bromohydrin **A** or of the aldehyde into the corresponding alcohol derivative **B** followed by subsequent attack by bromide (Scheme 2).

In conclusion, the combination of PMHS and (bromodimethyl)sulfonium bromide or NBS has been utilized here for the first time for an efficient synthesis of benzyl bromides from aromatic aldehydes under mild reaction conditions.

3. General experimental procedure

An aromatic aldehyde (1 mmol) and PMHS (1.5 mmol) were added to CHCl₃ (5 mL) and the mixture was stirred

at room temperature. (Bromodimethyl)sulfonium bromide or NBS (1 mmol) was added and stirring continued. After a few hours, effervescence appeared. The progress of the reaction was followed by TLC. After completion, the CHCl₃ was evaporated under vacuum and water (10 mL) was added. The mixture was extracted with EtOAc (3 × 10 mL) and the extract was dried and concentrated. The crude mass was subjected to column chromatography (silica gel, hexane–EtOAc) to afford the pure benzyl bromide. (**CAUTION!** The products are hazardous and potent lachrymators.)

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