SHORT PAPER

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Sulfurated borohydride exchange resin: reductive cleavage of aryl acetates under mild conditions[†]

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A variety of aryl acetates are selectively cleaved to the corresponding phenols using sulfurated borohydride exchange resin in methanol at 25°C. Other sensitive groups present elsewhere in the molecule remain unaltered under these reaction conditions.

Keywords: sulfurated borohydride exchange resin, aryl acetates

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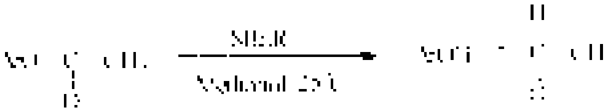
Alcoholic and phenolic hydroxyl groups are present in a number of biological and synthetic interests including nucleosides, carbohydrates, steroids, side chains of some amino acids, hormones and antibiotics.[1] In developing a synthesis of any phenol containing product, protection is mandatory to prevent reaction with oxidizing agents and electrophiles or reaction of the nucleophilic phenoxide ion with even alkylating agents. Aryl acetate, one of the developed protecting group for phenols has long played a key role in organic synthesis because of the ease with which acetates are formed and cleaved. In spite of several efforts the methods available for selective removal of aryl acetates in the presence of other sensitive functional groups are very few,[2] and not general[3] and most involve homogenous conditions. Ytterbium triflate,[4] and hafnium triflate[5] have been recently developed as efficient catalysts for selective deacylation. However, deacylation using hafnium triflate involves Fries migration whereas ytterbium triflate requires long reaction time (64 h), drastic conditions, aqueous work-up and does not discriminate between aryl and alkyl acetates. Sulfurated borohydride obtained from sulfur and sodium borohydride has shown very distinctive properties in its reactions with organic substrate as compared with sodium borohydride itself.[6] In continuation with our ongoing research work on polymer supported reagents in organic synthesis,[7] we wish to report in this communication a preliminary account of the use of sulfurated borohydride exchange resin (SBER) as a novel reducing reagent for selective cleavage of aryl acetates in the presence of other sensitive functional groups under mild conditions (Scheme 1).



Scheme 1

A series of aryl acetates were subjected to the deprotection conditions with SBER in methanol at 25°C to give the corresponding phenols. The results are presented in Table 1. It is important to note that this simple protocol allows chemoselective deprotection of aryl acetates in the presence of other sensitive functional groups like F (entry 2), Cl (entry 3) Br (entry 4), I (entry 5), NO_2 (entry 6), methoxy (entry 8). Note that aryl acetate is chemoselectively deprotected in the presence of alkyl acetate (entries 9, 10) within a period of 10 minutes under neutral and mild conditions whereas alkyl acetates remain intact with SBER even after stirring for a longer time (5 h). Thus tolerance of different reducible groups to these reaction conditions depicts the flexibility and generality of the protocol.

In conclusion, the present results demonstrate the novelty of SBER which shows unique selectivity under mild and neutral conditions and constitutes a useful alternative to the commonly accepted deacylation procedures. Moreover, the superiority and flexibility of the protocol lies in the ease of isolation of products by simple filtration of the reagent that can be reactivated and reused.

Experimental

All solvents were distilled before use. All chemicals were of analytical grade.

General procedure for deacylation of aryl acetates with SBER: Sulfur powder (2 mmol) and borohydride exchange resin (prepared using the reported method,[7a] 2g) was added in methanol (10 ml) and stirred until the color of resin became red (15–20 min), ensuring that BER changed to sulfurated borohydride exchange resin (SBER). Then aryl acetate (2 mmol) was added to the SBER and stirred at 25°C for a specified time (Table 1). A spontaneous reaction took place which was observed by change in colour of the resin from red to faint yellow. After completion of reaction (TLC) the resin was removed by filtration and washed with methanol (2 × 5 ml) and the combined filtrate was concentrated under reduced pressure to yield pure phenols.

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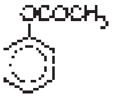
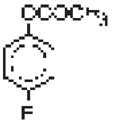
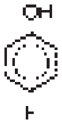
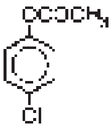
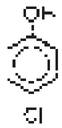
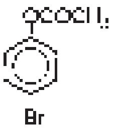
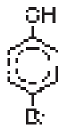
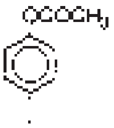
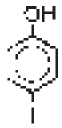
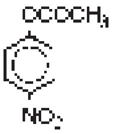
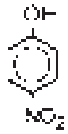
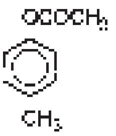
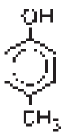
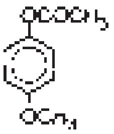
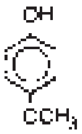
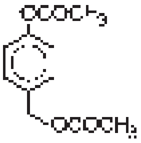
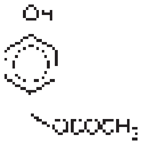
[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Table 1 Reductive cleavage of aryl acetates

Sr. no.	Reactant	Product	Time/min	Yield[a,b]/%
1			10	94
2			11	91
3			10	96
4			12	90
5			12	85
6			05	90
7			15	90
8			08	79
9			10	85
10			10	85
11	$CH_3CH_2CH_2CH_2OCOCH_3$	No reaction	–	–
12		No reaction	–	–

[a] Yields are of isolated products. [b] products are characterised by their physical constants, IR, 1HNMR, elemental analysis and comparison with authentic samples.