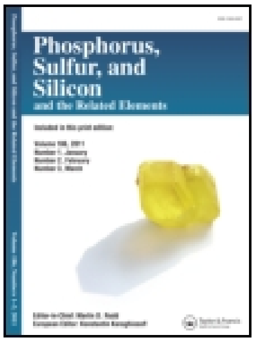

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BENZYLTRIPHENYLPHOSPHONIUM TETRABORATE (BTPPTB) AS A SELECTIVE REDUCING AGENT FOR REDUCTION OF ALDEHYDES AND KETONES TO THE CORRESPONDING ALCOHOLS

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Benzyltriphenylphosphonium tetraborate (BTPPTB) (1) generated as a white solid from benzyltriphenylphosphonium chloride and sodium borohydride has been found to be a selective and versatile reducing agent. The reagent in methanol is very useful for reduction of aldehydes and ketones to the corresponding alcohols

Keywords: Benzyltriphenylphosphonium tetraborate; Reduction; Alcohol; Aldehyde; Ketone; Modification of sodium borohydride

INTRODUCTION

Lithium borohydride and sodium borohydride are two extremes of nucleophilic hydride transfer agent. Lithium borohydride is very powerful reducing agent and is able to reduce most of reducible functional groups. On the other hand sodium borohydride is a mild reagent and is mostly used for the reduction of aldehydes and ketones in protic solvents.[1] In spite of great convenience for using $NaBH_4$, certain limitation may be observed for using this reagent. Polar and protic solvents are needed, this reagent reduces few functional groups, and long reaction time is observed. In order to increase or decrease the reactivity of $NaBH_4$, the modification of

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sodium borohydride has attracted a great deal of attention recently.[2–12] In general, the modification of the usual reducing ability of the sodium borohydride has led to selective reduction of several functional groups that are otherwise inert to sodium borohydride alone. For instance, the reductions of acid chlorides to aldehydes, 3 and alkenes to saturated hydrocarbons 4 can be achieved by use of the combination of sodium borohydride with Cu (I), Co (II) respectively, while such conversions can not be achieved with sodium borohydride alone. Very recently 1-benzyl-4-aza-1-azoniabiyclo[2.2.2]octane tetrahydroborate (2) has been reported for reduction of reducible organic compounds.[12]

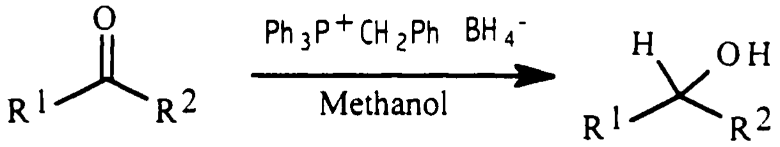
RESULTS AND DISCUSSION

In this paper we wish to report the preparation of benzyltriphenylphosphonium tetraborate (BTPPTB) (1) and reduction of aldehydes and ketones to the corresponding alcohols with this reagent. This reagent is able to reduce aldehydes and ketones to the corresponding alcohols in methanol at room temperature using one mole ratio of this reagent. The reagent is quite soluble in methanol and produces a clear solution, which upon standing at room temperature does not loss its reducing ability. This observation is in contrast to what is reported for tetrabutylammonium tetraborate (Bu_4NBH_4) which decomposes to Bu_3N, BuH, and BH_3 upon standing in solution. [13] The stability of this reagent in compare to tetrabutylammonium tetraborate (Bu_4NBH_4) is the reflection of the presence of the phosphonium cation in the reagent, which is more stable than ammonium cation. Benzyltriphenylphosphonium tetraborate (BTPPTB) (1) is a white powder, which is prepared by the dropwise addition of an aqueous solution of $NaBH_4$, to an aqueous solution of benzyltriphenylphosphonium cloride at room temperature. Filtration and drying of the precipitates resulted in a white powder, which could be stored for months without losing its reduction ability (Scheme 1).

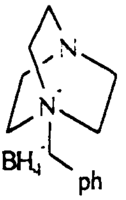
$$Ph_3P^+CH_2Ph\,Cl^- + NaBH_4 \xrightarrow{H_2O} Ph_3P^+CH_2Ph\,BH4^- + NaCl$$

SCHEME 1

This reagent is able to reduce aldehydes and ketones to their corresponding alcohols in high yield (Scheme 2 and Table I). The reagent reduces benzylic and allylic aldehydes almost immediately. Reduction of saturated aldehydes and benzylic ketones with this reagent is much slower than benzylic and allylic aldehydes; α,β-unsaturated carbonyl compounds are selectively reduced via 1,2-reduction.

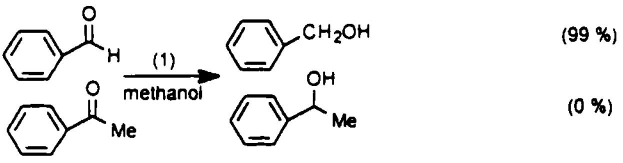


SCHEME 2

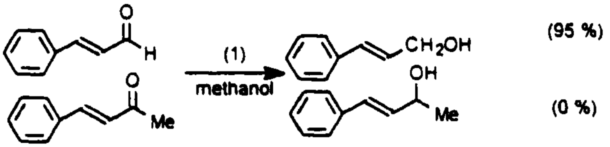


(2)

Another noteworthy advantage of this reaction lies in its ability to selective reduction of aldehydes in the presence of other reducible functions such as ketones and double bonds. When we retreated an equimolar amount of aldehyde with (1) in the presence of ketone, only the aldehyde was selectively reduced (Eq. 1). The C=O groups of α,β-unsaturated aldehydes or α,β-unsaturated ketones were selectively reduced to the corresponding alcohols and the C=C double bonds remained intact (Table I). In order to evaluate the chemo and regioselectivity of reagent (1) an experiment was performed with equimolar amount α,β-unsaturated aldehyde or α,β-unsaturated ketone and the reagent ((Eq. 2).



Eq. 1



Eq. 2

TABLE I Reduction of carbonyl compounds to their corresponding alcohols

Entry	*R¹*	*R²*	*Reaction Time (min.)*	*Yield %*^{ab}	*mp or bp °C/mm Hg*
1	C_6H_5	H	1	94	205
2	2-MeO-C_6H_4	H	1	93	245–246/760
3	3-MeO-C_6H_4	H	1	94	130–132/760
4	4-MeO-C_6H_4	H	1	92	257–259/760
5	2-Br-C_6H_4	H	1	90	78–80
6	4-Br-C_6H_4	H	1	87	77–79
7	2-Me-C_6H_4	H	1	89	35–36
8	4-Me-C_6H_4	H	1	96	59–61
9	2-Cl-C_6H_4	H	1	91	69–71
10	3-Cl-C_6H_4	H	1	88	235
11	4-Cl-C_6H_4	H	1	90	70–71
12	2-$NO_2C_6H_4$	H	1	94	69–71
13	3-$NO_2C_6H_4$	H	1	91	30–32
14	4-$NO_2C_6H_4$	H	1	93	92–94
15	2,5-$(MeO)_2C_6H_4$	H	1	85	99–101/0.2
16	3,4-$(MeO)_2C_6H_4$	H	1	90	135–137/0.2
17	3,5-$(MeO)_2C_6H_4$	H	1	94	43–46
18	(-CH2-)$_5$	–	50	95	22–24
19	(-CH2-)$_4$	–	50	92	139–140/760
20	C_6H_5	CH3	40	88	204/745
21	(-CH2-)$_6$	H	55	90	82–85/10
22	$C_6H_5CH{=}CH$	H	1	90	33–35
23	$C_6H_5CH{=}CH$	Me	45	94	142–144/21
24	2-pyridile	C_6H_5	5	88	60–63
25	3-pyridile	Me	5	90	154–155/28
26	2-pyridile	me	5	93	112–113/760
27	4-pyridile	Me	3	93	63–64

a. All yields refer to pure isolated products.

b. All of the products were fully characterized by comparing with known compounds and by their IR and ^{1}H NMR spectra.

In summary we have discovered a new and useful method for reduction of aldehydes, and ketones to the corresponding alcohols with reducing reagent (1) in high yield. The reaction proceeds in methanol. This reagent is able to reduce selectively aldehydes in the presence of ketones. The reagent is cheap and can be stored at room temperature for month without loosing of its activity.

Experimental Section

All products were identified by comparison with an authentic sample (IR, NMR, and mp). All mps. Were taken on a Gallenkamp melting apparatus and are uncorrected. The Research Institute of Petroleum Industry, Tehran, and I. R. IRAN performed elemental analyses. ^1H NMR spectra were recorded on a Varian EM-390 NMR Spectrometer operating at 90 MHz. ^{13}C NMR spectra were recorded on a Varian Unity 400 Fourier Transform NMR Spectrometer operating at 100 MHz. The spectra were measured in $CDCl_3$ unless otherwise stated using TMS as internal standard. Mass spectra were recorded on a Shimadzu GC-MS-QP 1000PX.

Synthesis of Reducing Agent 1

To a solution of benzyltriphenylphosphonium chloride (19.43 g, 50 mmol) in 50 ml of water was added sodium borohydride (1.89 g, 50 mmol) in one portion. The reaction mixture was stirred at room temperature for 30 min. The resulting white solid product was collected, washed with water (10 ml) and dried in a desiccator under vacuum over calcium chloride, to yield 16.38 g (98 %) of white solid, mp 151–153°C (dec.). ^1H NMR: δ 7.90–7.50 (m, 20 H), 4.6 (d, J = 25.6 Hz, CH_2-P. ^{13}C NMR: δ 148.50, 133.20, 130.20, 129.60, 129.40, 128.10, 127.70, 127.2, 108.30 (d, J = 85.5 Hz, P-CH_2). IR (KBr): 1298, 1269, 1098, 1060, 700, 658, 590, 546 cm^{-1}. MS (CI) m/z 368 (100, M$^+$. Anal Calcd for $C_{25}H_{26}BP$: C, 81.52; H, 7.07 %. Found; C, 81.80; H, 7.20; %.

Reduction of aldehydes, ketones and to the corresponding alcohols with reducing reagent (1)

Aldehydes or ketones (1 mmol) were added to a stirred solution of reducing agent (1) (1 mmol, 0.37 g) in methanol (10 ml). The mixture was stirred at room temperature until TLC showed complete disappearance of starting material, which required 1–60 min depending on the substrate. The methanol was evaporated and the residue was dissolved in dichloromethane (10 ml) and washed with water (2x15 ml). The dichloromethane layer was dried over $MgSO_4$. Evaporation of the solvent gave the corresponding alcohols. The product was purified by column chromatography on silica gel using mixture of ethyl acetate/n-hexane (10/90) as eluent.

Acknowledgements

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