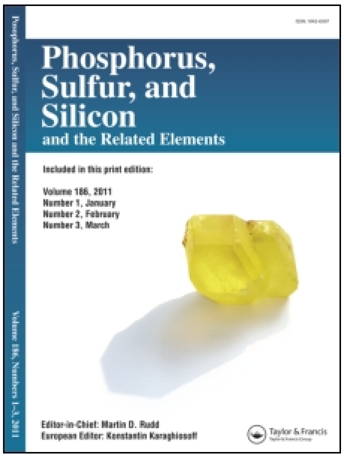

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METHYLTRIPHENYLPHOSPHONIUM TETRAHYDROBORATE ($MePh_3PBH_4$). A STABLE, SELECTIVE AND VERSATILE REDUCING AGENT

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METHYLTRIPHENYLPHOSPHONIUM TETRAHYDROBORATE ($MePh_3PBH_4$). A STABLE, SELECTIVE AND VERSATILE REDUCING AGENT

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Methyltriphenylphosphonium tetrahydroborate as a stable quaternary phosphonium borohydride is introduced. This compound is able to reduce aldehydes, ketones, acyl chlorides, and azides efficiently in CH_2Cl_2. α,β-Unsaturated carbonyl compounds are reduced selectively via 1,2-reduction. The effect of Lewis acids upon the mode and the rate of the reaction of epoxides and acetophenone are also described. This reagent is also able to bring about reductions effectively in the absence of solvent.

Keywords: Borohydride; Methyltriphenylphosphonium; Reducing agent; Tetrahydroborate; Phosphonium borohydride

INTRODUCTION

Lithium aluminum hydride and sodium borohydride are two extremes of nucleophilic hydride transfer agents. Lithium aluminum hydride is a powerful reducing agent and practically attacks most of the 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 and application of $NaBH_4$, certain limitations may be observed by using this reagent. Polar and protic solvents are needed, few functional groups are reduced by the reagent, sometimes slow rate of the reactions are observed, and low selectivity is accompanied with the reactions.[1,2] In order to increase or decrease the

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* Correspondence Author.

reactivity of NaBH4, structural modifications have been made and various derivatives of the reagent are reported in the literature.[3] Recently, we have reviewed modified borohydride agents and their applications in organic synthesis.[4] The modifications are summarized as; (1) the substitution of one or more hydrides with other substituents. (2) the exchange of the alkali-metal cation with other metal cations. (3) A concurrent cation and hydride exchange which has played a key for further structural modifications. (4) The preparation of ligand-metal nucleophilic hydride transfer agents. The use of the ligand can induce considerable stabilities and can effect the hydride transfer properties of the hydride transfer agents. (5) Combination of hydride transfer agents with metals, metal salts, metal hydrides Lewis acids, solid supports, attaching assymetric ligands has effected the properties of the hydride drastically. (6) By using mixed solvent systems specially methanol upon the reducing abilities of $NaBH_4$. (7) By quaternary ammonium exchanges of the cation of the metal hydride.

The first preparation of quaternary ammonium borohydrides was reported 40 years ago. Some of them show properties similar to alkali metal borohydrides with no advantage as a synthetic reagent. Quaternary ammonium borohydrides with long-chain alkyl groups are suitable for varieties of reductions in nonpolar solvents.[5] A new bulky quaternary ammonium borohydride was recently reported which shows more selectivity than the long-chain analogs for the reduction of functional groups.[6]

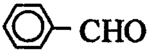
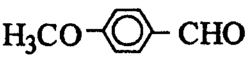
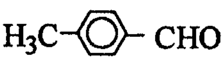
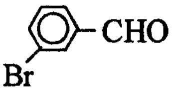
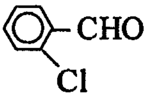
Preparation and the application of poly(vinylbenzenephosphonium) tetrahydroborate for the reduction of carbonyl compounds has been reported a few years ago.[7] To the best of our knowledge, this is the only quaternary phosphonium tetrahydroborate which has been used for the reduction of functional groups. Long reaction times (6–96 h) and low yields of the products could be mentioned as the drawbacks of this polymeric reagent.

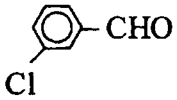
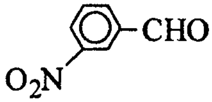
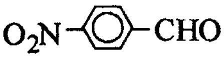
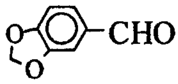
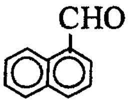
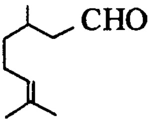
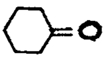
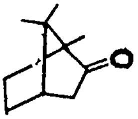
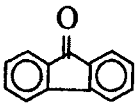
Very recently, in a preliminary report, we have introduced methyltriphenylphosphonium tetrahydroborate ($MePh_3PBH_4$) as a selective and efficient reducing agent.[8] Now in this report, we have extensively studied the application of this reagent for the reductive transformation of varieties of functional groups in aprotic solvents and also under neat conditions. The effect of Lewis acids has also been studied upon the rate and the mode of the reaction of epoxides and acetophenone as a model compound whose reduction encounters difficulties with borohydride agents.

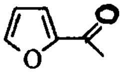
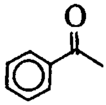
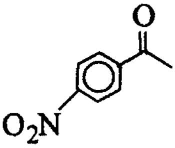
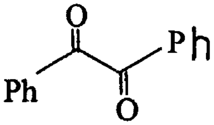
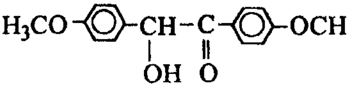
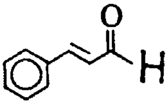
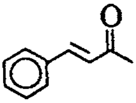
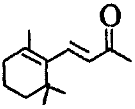
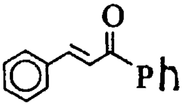
RESULTS AND DISCUSSION

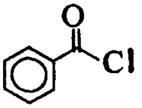
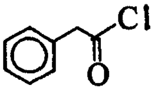
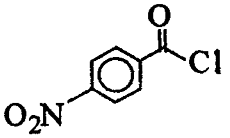
Preparation of methyltriphenylphosphonium tetrahydroborate is reported in the literature.[9] This reagent is able to function as a reducing agent with the molar ratio (1–2) according to the structure of the substrates in CH_2Cl_2 at room temperature. The compound is soluble in CH_2Cl_2 and produces a clear solution which on standing at room temperature does not lose its reducing ability. This observation is in contrast to what is observed with tetrabutylammonium tetrahydroborate (Bu_4NBH_4) which decomposes to Bu_3N, BuH, and BH_3 on standing in solution.[5] $MePh_3PBH_4$ reduces benzylic and allylic aldehydes almost immediately in CH_2Cl_2 at room temperature with high yields. Reduction of saturated aldehydes requires longer reaction times. Reduction of ketones under similar conditions proceeds much slower than aldehydes. This reagent is also able to reduce α-diketones and acyloins to their corresponding diols in high yields (Table I). We have compared the results of the reduction of carbonyl functional groups by this reagent and with $[PhCH_2\text{-}dabco][BH_4]$[6] (Fig 1) and Bu_4NBH_4[5] (Table II) and with poly(vinylbenzylphosphonium) borohydride[7] (Table III).

TABLE I Reduction of carbonyl compounds and carboxylic acid chlorides to their alcohols with $MePh_3PBH_4$ in CH_2Cl_2

Entry	*Substrate*	*Red/Subs*	*Yield%(h)*	*MP or bp (°C)*
1		1	90(-)^a	205
2		1	83(-)^a	23–25
3		1	87(-)^a	59–61
4		1	90(-)	-
5		1	88(-)^a	69–71

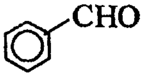
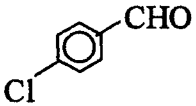
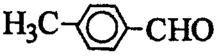
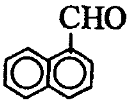
Entry	*Substrate*	*Red/Subs*	*Yield%(h)*	*MP or bp (°C)*
6		1	90(-)^a	235
7		1	86(-)^a	70–72
8		1	80(-)^a	30–32
9		1	92(-)^a	92–94
10		1.2	91(-)^a	53–55
11		1	100(-)^a	60–62
12		1.5	83^b(2.5)	-
13		1	95 (10)^b	161
14		1	77 (24)^b	-
15		1.6	80(18)	153–154

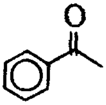
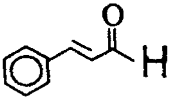
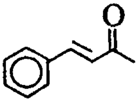
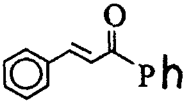
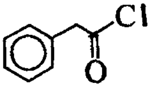
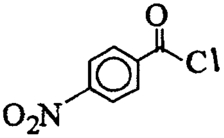
Entry	*Substrate*	*Red/Subs*	*Yield%(h)*	*MP or bp (°C)*
16		1	96(12)	-
17		2	96(12)	204/745 mm Hg
18		1	100(-)[a]	-
19		2	90(0.6)	149–150
20		1	90(1)	-
21		1	95(-)[a]	33–35
22		1	90(3.5)	144/21 mmHg
23		1	71(6)	-
24		1.2	90(6)	-

Entry	*Substrate*	*Red/Subs*	*Yield%(h)*	*MP or bp (°C)*
25		1	76(-)[a]	205
26		1	98(-)[a]	219–221/750 mmHg
27		1	91(-)[a]	92–93

a) Immediate reaction.

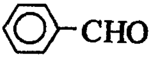
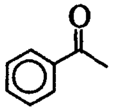
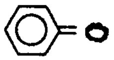
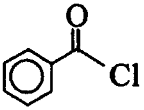
TABLE II Comparisons of the results of some reductions of carbonyl compounds and carboxylic acid chlorides to their alcohols with $MePh_3PBH_4$, $[PhCH_2.dabco][BH_4]$ and BH_4NBH_4

Entry	*Substrate*	*$MePh_3PBH_4$*	*$[PhCH_2.dabco][BH_4]$[6]*	*Bu_4NBH_4[5]*
		Yield%(h)	*Yield%(h)*	*Yield%(h)*
1		90(-)[a]	90(0.25)	91(24)
2		86(-)[a]	90(0.23)	-
3		87(-)[a]	87(0.9)	-
4		100(-)[a]	90(0.25)	90(2)

Entry	Substrate	$MePh_3PBH_4$	$[PhCH_2.dabco][BH_4]$[6]	Bu_4NBH_4[5]
		Yield%(h)	Yield%(h)	Yield%(h)
5		96(12)	95(17)	-
6		95(-)[a]	90(0.33)	90(0.13)
7		90(3.5)	85(0.4)	80(0.4)
8		90(6)	85(3.2)	75(3.3)
9		98(-)[a]	85(2)	85(1.5)
10		91(-)[a]	95(2)	85(1)

a) Immediate reaction.

TABLE III Comparison of the results of reduction of some carbonyl compounds and an acid chloride to their alcohols with [$MePh_3PBH_4$] and poly(vinylbenzylphosphonium) borohydride (PVBPV) in CH_2Cl_2

Entry	*Substrate*	*$MePh_3PBH_4$*	*PVBPB*[7]
		Yield% (h)	*Yield% (h)*
1		90(-)[a]	78(48)
2		96(12)	72(12)
3		95(10)	55(6)
4		76(-)[a]	16(96)

a) Immediatle reaction.

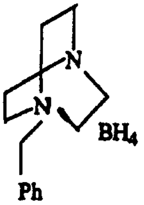
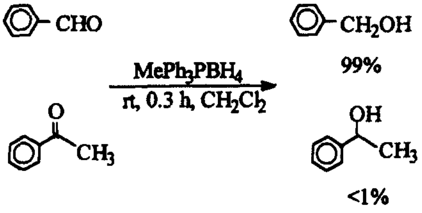


FIGURE 1 1-Benzyl-4-aza-1-azoniabicyclo[2.2.2]octane Tetrahydroborate

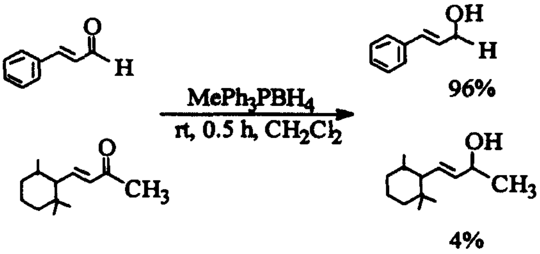
Excellent chemoselectivity for the reduction of aldehydes in the presence of ketones are observed with $MePh_3PBH_4$ in CH_2Cl_2 at room temperature (Scheme 1).



Molar ratio 1:1:1

SCHEME 1

High yield production of allyl alcohols by selective reduction of α,β-unsaturated carbonyl compounds is of synthetic value. This goal is achieved with $MePh_3PBH_4$ in CH_2Cl_2 at room temperature (Table I). In order to show the extent of chemo and regioselectivity of the reagent an experiment was performed with equimolar ratios of an α,β-unsaturated aldehyde, a ketone and the reagent (Scheme 2).



Molar ratio 1:1:1

SCHEME 2

The results of the reduction of α,β-unsaturated carbonyl compounds are compared with those reported for the other modified borohydride agents; $[PhCH_2\text{·}dabco][BH_4]$[6] and Bu_4NBH_4,[5] (Table II).

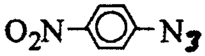
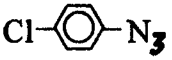
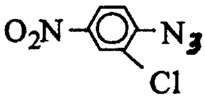
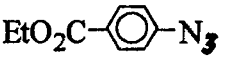
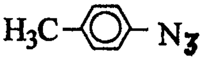
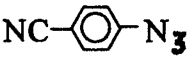
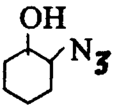
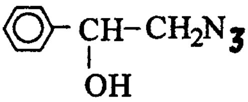
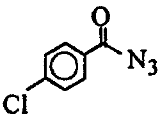
$NaBH_4$ reduction of carboxylic acid chlorides requires vigorous conditions and produces the corresponding alcohols.[10] This type of reduction is performed well in CH_2Cl_2 at room temperature with $MePh_3PBH_4$ in excellent yields (Table I). $MePh_3PBH_4$ reduces acid chlorides much faster and with better yields than $[PhCH_2{\cdot}dabco][BH_4]$ and Bu_4BH_4[5,6] which is the reflection of the effects of the attachment of quaternary phosphonium cation to tetrahydroborate anion (Table II). We have also compared some of the results of reduction of carbonyl compounds and acid chlorides to their corresponding alcohols with $MePh_3PBH_4$ and poly(vinylbenzylphosphonium) borohydride[7] in Table III.

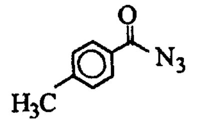
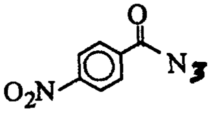
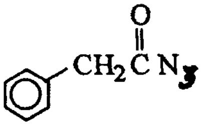
$MePh_3PBH_4$ is a highly selective reagent for the reduction of aryl azides in CH_2Cl_2 at room temperature. Benzyl-, 2-hydroxycyclohexyl-, and 2-phenyl-2-hydroxyethyl azides remain intact with this reagent (Table IV). Quaternary ammoniumm tetrahydroborates do not show such selectivity. e.g. benzyl azide is reduced with $[PhCH_2{\cdot}dabco][BH_4]$ and Bu_4NBH_4 in 10 and 5 h respectively with excellent yields[6] (Table V). This is again the reflection of the presence of the phosphonium cation in the reagent. Aroyl azides are also selectively reduced to their amides in high yields with $MePh_3PBH_4$. Phenylacetyl azide is resistant towards reduction with this reagent (Table IV).

Solvent free reactions have found interest in recent years in organic chemistry.[11] $NaBH_4$ in the absence of solvent has been used for the reduction of various ketones. In this procedure, a tenfold molar ratio of $NaBH_4$ is mixed with ketone and is stored in a dry box for 5 days.[12] The major disadvantage of the heterogeneous reduction with $NaBH_4$ is the long reaction time and the requirement of the large excess of the reducing agent which makes this method of no practical utility. The method also does not show selectivity for the reduction of α,β-unsaturated carbonyl compounds[12].

Very recently, microwave-assisted reduction of carbonyl compounds in solid state using $NaBH_4$-Al_2O_3 was reported.[13] In this report, benzalacetophenone in the presence of 8 molar ratios of $NaBH_4$-Al_2O_3 is radiated with microwave to produce the allyl alcohol in 60% and the corresponding saturated alcohol in 40% yields, respectively. It has also been mentioned that benzophenone reduction with 5 molar ratios of $NaBH_4$-Al_2O_3 in an oil bath at 130°C proceeds in 40% conversion after 4h. We have performed the reduction of benzophenone and benzalacetophenone in the presence of one molar ratio of $NaBH_4$ in the absence of solvent at 60°C for 24h. Diphenylcarbinol and 1,3-diphenylpropen-2-ol were isolated in 60% and 40% yields, respectively plus unreacted starting materials.

TABLE IV Reduction of aryl and alkyl azides to amines and reduction of aroyl and aryl sulfonyl azides to amides with $MePH_3PBH_4$ in CH_2Cl_2

Entry	*Substrate*	*Red./Subs.*	*Yield%(h)*	*MP or bp (°C)*
1		1.5	98(-)[a]	-
2		1.5	99(3)	67–71
3		1	100(-)[a]	107–109
4		1	94(0.16)	88–90
5		1.5	87(5)	42–46
6		1.2	96(0.33)	51–53
7		1	No reaction	
8		1	No reaction	
9		1	No reaction	
10		1.7	98(3)	167–170

Entry	*Substrate*	*Red./Subs.*	*Yield%(h)*	*MP or bp (°C)*
11		1.5	88(0.33)	180
12		1	45.5(0.25)	167–170
13		1.5	No reaction	

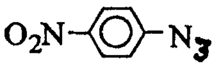
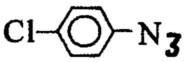
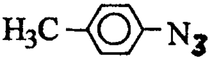
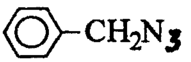
a) Immediate reaction.

Solid state structure of the reagent is important for their chemical reactivities under non-solvent conditions.[11] This prompted us to investigate the reducing ability of $MePH_3PBH_4$ in the absence of solvent. The results show that the reactions are mostly much faster under neat conditions than in solution. Reduction of cyclohexanone, 9-fluorenone, and benzophenone are performed well within 0.08, 0.75, and 3h respectively in 95–100% yields (Table VI). The same reactions in CH_2Cl_2 needed 10, 18, and 20 h and gave lower yields (Table VII). 4-Methylphenyl azide and benzyl azide, as model compounds, are reduced efficiently to their corresponding amines in 80% an 90%, respectively (Table VI). This drastic change in reactivity is also the cause of replacing sodium ion with methyltriphenylphosphonium cation. Comparison of the results of solvent free and in solution reductions of functional groups with $MePh_3PBH_4$ are tabulated in Table VII.

Epoxides are resistant towards ring opening reduction in CH_2Cl_2 with $MePh_3PBH_4$. Solvent free reduction of these compounds with the reagent is not clean and produces several unidentified products.

Lewis acid catalysis of borohydrides is well established in protic solvents.[14] In this study, we have investigated the effect of varieties of Lewis acids; $ZnCl_2$, $ZrCl_4$, $ZrCl_4.SiO_2$, $SnCl_2.2H_2O$, $AlCl_3$, $FeCl_3$, WCl_6, $NbCl_5$, $CeCl_3$, and $CuCl_2$ upon the reactivity of $MePh_3PBH_4$ in CH_2Cl_2. For this purpose, the reduction of acetophenone as a model compound was studied. The rate of the reduction was drastically increased from 12h (in the absence) to an immediate reaction (in the presence) of Lewis acids (Table VIII).

TABLE V Comparison of the reduction of some azides to their amines with $MePh_3PBH_4$, $[PhCH_2.dabco][BH_4]$ and BH_4NBH_4

Entry	*Substrate*	*$MePh_3PBH_4$*	*$[PhCH_2.dabco]$ $[BH_4]$*[6]	*Bu_4NBH_4*[6]
		Yield%(h)	*Yield%(h)*	*Yield%(h)*
1		98(-)[a]	92(2.5)	90(0.25)
2		99(3)	90(2.5)	90(1)
3		87(5)	85(2)	90(3)
4		No reaction	90(10)	90(5)

a) Immediate reaction.

Reduction of unsymmetrically substituted epoxides in the presence of $ZrCl_4$-$NaBH_4$-L-proline was reported very recently.[15]

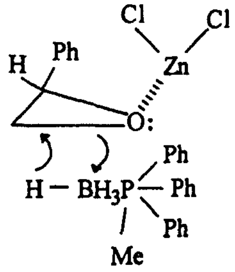
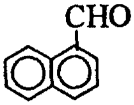
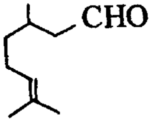
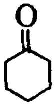
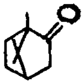
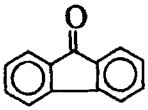
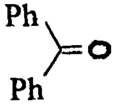
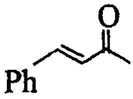
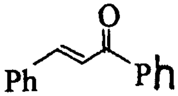
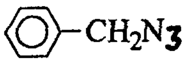


FIGURE 2 Shows the interaction of $ZnCl_2$ with the oxirane molecule and the subsequent hydride transfer from the reagent to the less hindered site of the ring

TABLE VI Solvent free reduction of carbonyl compounds to their alcohols and azides to their amines with $[MePh_3PBH_4]$

Entry	*Substrate*	*Red./Subs.*	*Yield%(RXn Temp)*	*MP or bp (°C)*
1		1	100(-)[a]	60–62
2		1	100(0.08)[b]	-
3		1	100 (0.08)[b]	161
4		1	No reaction (24)	
5		2	95(0.75)	153–154
6		1	98(3)	65–67
7		1.5	80(1)	144/21mg Hg
8		1	75(0.08)	-

Entry	*Substrate*	*Red./Subs.*	*Yield%(RXn Temp)*	*MP or bp (°C)*
9		1	80(0.08)	42–46
10		1	90(1)^b	180–18

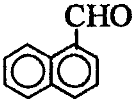
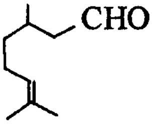
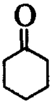
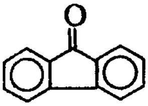
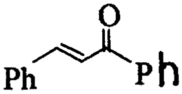
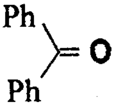
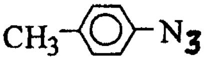
a) Immediate reaction.
b) GC yield.

We have also studied the possibility of the reduction of styrene oxide, as a model compound, with $MePh_3PBH_4$ in the presence of Lewis acids; $ZnCl_2$ and $ZrCl_4$ in CH_2Cl_2 at room temperature. Both catalysts catalyze the reaction but via two different pathways. In the presence of $ZnCl_2$, styrene oxide gives a mixture of 1-phenylethanol and 2-phenylethanol in 75% and 25% respectively with the isolated total yield of 85%. Analysis of the ^{1}HNMR spectrum of the mixture shows clearly the formation of the two alcohols with the indicated yields. This observation indicates that the nucleophilic attack by the bulky hydride transfer agent has occurred mostly from the least hindered part of the oxirane ring probably via a SN_2 reaction to produce 1-phenylethanol. This is in contrast to what is normally expected from the epoxide ring opening reactions by the acid catalysis. Therefore, we may suggest the formation of the intermediate complex (Fig 2) for the reaction. Formation of 2-phenylethanol shows the expected normal ring opening of epoxides under acid catalysis via a SN_1 reaction (Table IX).

Zirconium tetrachloride ($ZrCl_4$) which is quite larger than $ZnCl_2$ does not allow a similar intermediate complex formation (Fig 2) in the presence of the bulky hydride transfer agent. Therefore, the expected alcohols are not formed, instead, 2-chloro-1-phenylethanol is isolated in 80% yield as the sole product of the reaction (Table IX).

However, we may suggest that the large $ZrCl_4$ forms a complex with styrene oxide which makes a close approach of the bulky nucleophile to the complex more difficult. Therefore, the reducing agent transfers its hydride ion to zirconium which is accompanied by the transfer of chloride from zirconium to the less hindered carbon of the oxirane ring to produce the corresponding chlorohydrin (Fig 3). It is noteworthy to mention that styrene oxide has been isolated intact in the presence of $ZrCl_4$ in CH_2Cl_2 at room temperature after several hours in our laboratory.

TABLE VII Comparison of the results of solvent free and in solution reductions of carbonyl compounds to their alcohols and azides to their amines with $MePh_3PBH_4$

Entry	*Substrat*	*In solution*		*Solvent free*	
		React/Sub.	*Yield%(h)*	*React/Sub.*	*Yield%(h)*
1		1	100(-)[a]	1	100(-)[a]
2		1.5	83(2.5)[b]	1	100(0.08)[b]
3		1	95(10)	1	100(0.08)
4		1.6	80(18)	2	95(0.75)
5		1.2	90(6)	1	75(0.08)
6		1	60(20)	1	98(3)
7		1.5	87(5)	1	80(0.08)
8	$PhCH_2N_3$	1	No Reaction	1	90(1)[b]

a) Immediate reaction.
b) GC yield.

TABLE VIII Reduction of acetophenone to 1-phenylethanol with $MePh_3PBH_4$ in the presence of Lewis acids in CH_2Cl_2[a]

Entry	*Lewis Acid*	*Time(h)*	*Temp.*	*Yield%*
1	-	12	Δ	96
2	$ZnCl_2$	3.15	Δ	90
3	$ZnCl_2.SiO_2$	-	-	N.R.
4	$ZrCl_4$	$(-)^b$	rt	94
5	$ZrCl_4.SiO_2$	$(-)^b$	rt	100^c
6	$SnCl_2.2H_2O$	0.25	rt	95
7	$SnCl_2.SiO_2$	-	-	N.R.
8	$AlCl_3$	$(-)^b$	rt	80
9	$AlCl_3.SiO_2$	-	-	N.R.
10	$MnCl_2$	24	Δ	60
11	$CrCl_3$	0.33	Δ	60
12	$FeCl_3$	0.17	rt	89
13	WCl_6	$(-)^b$	rt	88
14	$NbCl_5$	0.17	rt	93
15	$CeCl_3$	0.25	rt	85
16	$NiI_2.6H_2O$	4	rt	40
17	$CuCl_2$	1.5	rt	83

a) The ratio of Lewis Acid/$MePh_3PBH_4$/$PhCOCH_3$ 1:2:1
b) Immediate reaction.
c) GC. yield.

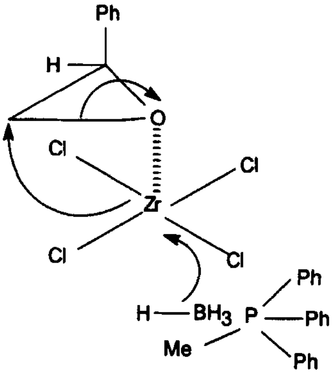
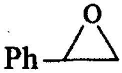
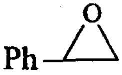
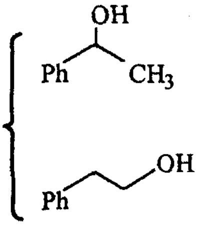
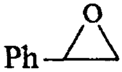
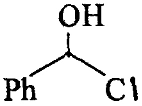
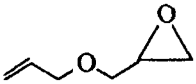
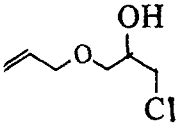
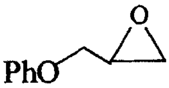
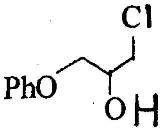


FIGURE 3 Presents the interaction of $ZrCl_4$ with the oxirane ring and the hydride transfer from the reducing agent to zirconium nucleus with the subsequent chloride transfer to the less hindered part of the ring

TABLE IX Reaction of epoxides with $[MePh_3PBH_4]$ in the presence of $ZnCl_2$ and $ZrCl_4$[a]

Entry	*Substrate*	*Product(s)*	*Lewis Acid*	*Time(h), Temp.*	*% Yield*
1			-	(24)Δ	No Reaction
2			$ZnCl_2$	(1)rt	63 b 21 b
3			$ZrCl_4$	(0.17)rt	80
4			$ZrCl_4$	(0.3)0°C	88[c]
5			$ZrCl_4$	(0.25)0° C	82[c]

a) The mole ratio of subs./red../Lewis acid is 1:2:1.

b) NMR yield.

c) The structural assignments are based on mass spectral data and analysis, and $BaMnO_4$[16] oxidation of the products which afford the corresponding ketones.

d) The physical constants are compared with those reported in the literature.[17]

CONCLUSIONS

$MePh_3PBH_4$ is a highly soluble reducing agent in CH_2Cl_2 which is able to effect reductions under aprotic solvents. The reagent is selective for the reduction of aldehydes in the presence of ketones. 1,2-reduction of α-β-unsaturated carbonyl compounds is performed with high selectivity. Aryl and aroyl azides are reduced easily whereas, their alkyl analogues remain intact. High rate enhancement of reduction of ketones in the presence of Lewis acids in CH_2Cl_2 is also observed. In the presence of Lewis acids, the bulky structure of the reducing agent controls the mode of the ring opening reaction of the epoxides. $MePh_3PBH_4$ is an effective reducing agent under solvent free conditions. In general, this reagent shows more reactivity than its nitrogen and phosphorus polymeric analogues. Ease of preparation, high yields of the products, high rates of the reactions, selectivity of the reagent, working under aprotic reaction conditions or in the absence of solvent, and mild reaction conditions are the advantages of the presented method. In all the experiments which are performed in this study, the positive effects of the phosphonium cation upon the reactivity, selectivity, and stability of the reagent are observed.

EXPERIMENTAL

General: All products were characterized by comparison with authentic samples (IR TLC, GLC, ^{1}HNMR, and mp). Yields refer to isolated products unless otherwise indicated. The reactions proceeded in CH_2Cl_2 and also under solvent free conditions.

Preparation of methyltriphenylphosphonium chloride ($MePh_3Cl$)[8]

Methyltriphenylphosphonium chloride was prepared by the addition of triphenylphosphine (30 g, 0.11 mol) to an excess amount of methyliodide (20 g, 0.14 mol) under neat condition.The reaction was extremely exothermic and the mixture was cooled in an ice bath. To the resulting mixture Et_2O (50 ml) was added and was magnetically stirred for 0.5 h which on filtration afforded $MePh_3PI$ as a white precipitate (46 g, 100% yield). The resulting phosphonium salt in absolute C_2H_5OH (100 ml) was passed through a Dowex 1-X8 anion exchange column to afford $MePh_3PCl$ as white crystals (mp 133.2°C) in a quantitative yield after evaporation of the solvent.

Preparation of $MePh_3PBH_4$[8]

A solution of $NaBH_4$ (11.4 g, 0.3 mol) in absolute EtOH (200 ml) was added with stirring to a solution of $MePh_3PCl$ (37 g, 0.12 mol) in absolute EtOH (300 ml). After stirring for 2h, the mixture was filtered to remove precipitated NaCl. To the resulting filtrate, CH_2Cl_2 (150 ml) was added and by the removal of solvent it was concentrated to 50 ml. Addition of Et_2O (120 ml) to the resulting concentrated solution afforded $MePh_3PBH_4$ as a white precipitate (33g, 96%).

A typical procedure for the reduction of aldehydes to alcohols with $MePh_3PBH_4$

To the solution of 4-nitrobenzaldehyde (0.40 g, 2.65 mmol) in CH_2Cl_2 (10 ml) the reducing agent (0.77 g, 2.65 mmol) was added. As the reaction proceeded, several fast color changes from yellow to deep violet and then to dark red were observed. The reaction was completed within a minute (TLC, eluent CCl_4/Et_2O: 5/1). CH_3OH (3 ml) was added to the reaction mixture and was magnetically stirred for lh. The resulting mixture was evaporated and the crude material was purified by silica gel column chromatography (Hexane/ EtOAc: 4/1) to afford pure 4-nitrobenzyl alcohol (0.38 g, 92% yield, Table I).

A typical procedure for the selective 1,2-reduction of α,β-unsaturated carbonyl compounds with $MePh_3PBH_4$

To the stirring solution of 4-phenyl-3-buten-2-one (0.20 g, 1.37 mmol) in CH_2Cl_2(15 ml) the reducing agent (0.4 g, 1.37 mmol) was added and the resulting mixture was refluxed for 6h. The progress of the reaction was monitored by GLC. CH_3OH (3 ml) was added to the resulting mixture and was magnetically stirred for 2h. Evaporation of the solvent and purification of the crude material by thick layer chromatography (CCl_4/Et_2O, 5/2) afforded 4-phenyl-3-buten-2-ol (0.18 g, 90% yield, Table I).

A typical procedure for the reduction of acyl chlorides to alcohols with $MePh_3PBH_4$

To the stirring solution of 4-nitrobenzoyl chloride (0.15 g, 0.8 mmol) in dry CH_2Cl_2 (10 ml) the reducing agent (0.3 g, 0.8 mmol) was added. The reaction was completed immediately. CH_3OH (3 ml) was added to the reaction mixture and was stirred magnetically for 1.5 h. Evaporation of solvent and purification of crude product by preparative layer chromatography (CCl_4/Et_2O, 5/2) afforded pure 4-nitrobenzyl alcohol (0.15 g, 91%, Table I).

A typical procedure for the reduction of aryl azides to aryl amines with $MePh_3PBH_4$

To a solution of 4-cyanophenyl azide (0.1 g, 0.69 mmol) in CH_2Cl_2 (8 ml), the reducing agent (0.24 g, 0.83 mmol) was added and the resulting mixture was stirred magnetically under reflux conditions for 20 min. CH_3OH (3 ml) was added to the reaction mixture and was magnetically stirred for 1 h. The solvent was evaporated and the resulting crude material was purified by thick layer chromatography (CCl_4/Et_2O, 2/1) to produce 4-cyanoaniline (0.08 g, 96%, Table IV).

A typical procedure for the reduction of aroyl azides to amides with $MePh_3PBH_4$

4-Chlorobenzoyl azide (0.1 g, 0.55 mmol) in CH_2Cl_2 (7 ml) was treated with $MePh_3PBH_4$ (0.24 g, 0.825 mmol) and the reaction mixture was magnetically stirred for 20 min. CH_3OH (3 ml) was added to the reaction mixture and was stirred for 0.5 h. The solvent was removed and the crude product was purified by thick layer chromatography by an appropriate solvent. 4-chlorobenzamide was obtained (0.075 g, 88% yield, Table IV).

A typical procedure for the reduction of ketones to alcohols with $MePh_3PBH_4$ in the presence of $ZrCl_4$

Acetophenone (0.1 g, 0.83 mmol) in CH_2Cl_2 (8 ml) was treated with $ZrCl_4$ (0.19 g, 0.83 mmol) and was magnetically stirred for 0.5 h at room temperature. Immediate reaction was observed upon addition of $MePh_3PBH_4$

(0.48 g, 1.66 mmol). CH_3OH (3 ml) was added to the resulting mixture and was stirred for 1 h. The solvent was evaporated and the crude material was purified by thick layer chromatography in an appropriate solvent. 1-phenylethanol was obtained (0.093 g, 94% Table VIII).

A typical procedure for the reduction of epoxides to chlorohydrin with $MePh_3PBH_4$ in the presence of $ZrCl_4$

To the solution of styrene oxide (0.1 g, 0.83 mmol) in CH_2Cl_2 (8 ml), $ZrCl_4$ (0.19 g, 0.83 mmol) was added and stirred for 0.5 h. $MePh_3PBH_4$ (0.48 g, 1.66 mmol) was added to the resulting mixture and it was magnetically stirred for 10 min. CH_3OH (3 ml) was added to the reaction mixture and was stirred for a few minutes. Solvent was evaporated and the crude material was purified by preparative layer chromatography (eluent; CCl_4/Et_2O: 5/3) to afford 2-chloro-1-phenyl ethanol (0.1 g, 80% yield, Table IX), ^1H NMR ($CDCl_3$), δ 2.4 1H(s), δ 3.6 2H(d), δ 4.7 1H(t), δ 7.1 5H(s).

A typical procedure for the reduction of epoxides to alcohols with $MePh_3PBH_4$ in the presence of $ZnCl_2$

To a solution of styrene oxide (0.1 g, 0.93 mmol) in CH_2Cl_2 (8 ml), $ZnCl_2$ (0.11 g, 0.83 mmol) was added and stirred magnetically for 1 h at room temperature. The progress of the reaction was monitored by TLC. After completion of the reaction, CH_3OH (3 ml) was added and stirred for 1 h. Evaporation of solvent and purification by thick layer chromatography by an appropriate solvent afforded 1-phenylethanol (0.06 g, 63% yield) and 2-phenylethanol (0.02g, 21% yield) Table IX.

A typical procedure for the reduction of ketones to alcohols with $MePh_3PBH_4$ under neat conditions

A mixture of benzophenone (0.1 g, 0.55 mmol) and $MePh_3PBH_4$ (0.16 g, 0.55 mmol) was prepared and was magnetically agitated for 3 h in an oil-bath at 60°C. CH_3OH (3 ml) was added to the mixture and was magnetically stirred for 0.5 h. CH_2Cl_2 (5 ml) was added to the mixture and was filtered. The filtrate was concentrated and purified by thick layer chromatography in an appropriate solvent to afford pure benzhydrol (0.1 g, 98%, Table VI).

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