Bull. Chem. Soc. Jpn., 68, 2595—2602(1995)

Modified Borohydride Agents,[1a,1b] 1-Benzyl-4-aza-1-azoniabicyclo[2.2.2]octane Tetrahydroborate (BAAOTB) versus Tetrabutylammonium Tetrahydroborate (TBATB). Efficient, Selective, and Versatile Reducing Agents

Habib Firouzabadi* and **Gholam Reza Afsharifar**

Department of Chemistry, Shiraz University, Shiraz 71454, Iran

(Received January 9, 1995)

1-Benzyl-4-aza-1-azoniabicyclo[2.2.2]octane tetrahydroborate (BAAOTB) and tetrabutylammonium tetrahydroborate (TBATB) are used for the selective reductions of aldehydes, ketones, α,β-unsaturated carbonyl compounds, acid chlorides, azides, epoxides, and disulfides in *t*-BuOH and hexane/chloroform. ABBOAB with its rigid and bulky structure reacts more selectively than its analogue TBATB.

Sodium borohydride is a relatively mild reducing agent which is practically specific for the reduction of carbonyl groups in aldehydes and ketones, but lithium aluminum hydride is an exceedingly powerful reagent which attacks almost all reducible groups. Both reagents are uncleophilic reducing agents which reduce polar multiple bonds.[2,3] Reduction capacities somewhere between these two extremes and also with electrophilic properties are of practical importance. Possible means of achieving these goals would be to increase the reducing properties of borohydride, another, to diminish the reducing power of aluminum hydride. So many different modifications have been made to modulate the scope, regio, and stereoselectivity of metal hydride reductions. Literally, hundreds of substituted boron and aluminum hydrides have been described in the chemical literature and dozens are now commercially available.[2—5] The most common modifications have been made on $NaBH_4$ are summarized as; (1) by hydride exchange to produce e.g. sodium triacetoxy,[6] sodium trimethoxy,[7] sodium (dimethylamino), and (*t*-butylamino),[8] sodium monoacetoxy,[9] sodium trifluoroacetoxy[10] borohydrides, and sodium cyanoborohydride[11] which all show their own reducing properties, (2) by cation exchange which produces e.g. lithium,[12] potassium,[13] calcium,[14] copper,[15] and zinc borohydrides with different reducing properties, (3) by cation and hydride exchange to produce e.g. lithium triethyl (super hydride),[17] lithium butyl,[18] lithium tris(*s*-butyl) (L-selectride),[19] potassium tris (*s*-butyl) (K-selectride),[20] potassium triisopropoxy,[21] and potassium triphenyl[22] borohydrides, (4) by combining borohydrides with metals, metal salts, metal halides,[23] Lewis acids,[24] solid supports[16,25] attaching assymetric ligands,[26] and (5) by using mixed solvents containing MeOH[27] many different hydride transfer agents are introduced.

Quaternary ammonium borohydrides are another category of modified borohydride agents. The preparations of tetramethyl, tetraethyl, and benzyltrimethyl ammonium borohydrides were reported 40 years ago.[28] The tetramethyl derivative exhibits solubility and reactivity properties similar to those of alkali metal borohydrides and therefore, offers no advantage as a synthetic reagent.[29] Tetrabutylammonium,[29b] cetyltrimethylammonium and tricaprylmethylammonium[30] tetrahydroborates are reported as reducing agents. The reports are very concise and nothing except more than the reduction of only a few carbonyl compounds are reported by these reagents.

Recently we have reported the preparation of 1-benzyl-4-aza-1-azoniabicyclo[2.2.2]octane tetrahydroborate (BAAOTB)[1a] (Fig. 1) as a highly selective reducing agent. We have observed high chemoselectivity for the reduction of aldehydes in the presence of ketones in *t*-BuOH with this reagent. Therefore, the observation sounded and encouraged us to extend our investigation for the reduction of other functional groups. We have also investigated the synthetic utility of the previously reported reducing agent; tetrabutylammonium tetrahydroborate (TBATB) for the reduction of different functional groups.

In this paper we have shown the limitations and advantages of the new reagent in comparison with TBATB

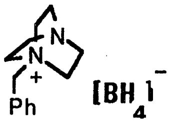


Fig. 1.

and have compared some of the results with other modified tetrahydroborates.

Results and Discussion

1-Benzyl-4-aza-1-azoniabicyclo[2.2.2]octane tetrahydroborate (BAAOTB) is a white powder and a stable compound which is produced quantitatively from alkali solution of the corresponding bromide and sodium borohydride at room temperature. This reagent reduces different functional groups in CH_2Cl_2, $CHCl_3$, and *t*-BuOH. Rate of the reactions are faster in *t*-BuOH. Therefore, most of the reductions are proceeded in this solvent in which sodium borohydride is a sluggish reducing agent.

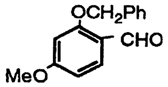
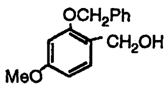
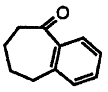
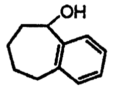
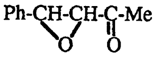
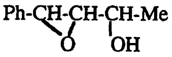
We have accomplished a series of reductions with BAAOTB, as a new reducing agent, and TBATB a formerly reported[28a)] reagent and have compared their reactivities, selectivities, and the yields of the reactions.

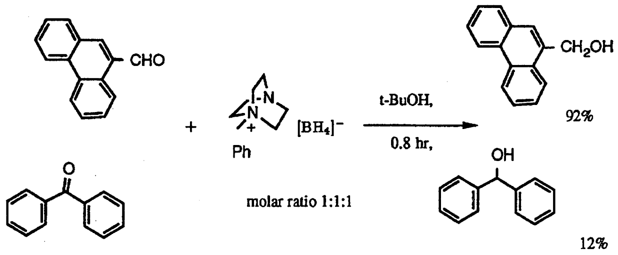
Our observations show that BAAOTB reacts slower with higher molar ratios than are required for the reductions by TBATB. However, in several reactions under our investigation, BAAOTB is much more selective and its use for synthetic purposes is more advantageous than its analogue TBATB. e.g. Reduction of acid chlorides to their aldehydes, reduction of aldehydes in the presence of ketones, and the reduction of carbonyl groups in the presence of epoxide rings. This difference in selectivity may be due to the structural differences of the two borohydrides, their solubilities or both of them.

1. Reduction of Aldehydes and Ketones. Reduction of aldehydes and ketones to their alcohols is a useful transformation in organic synthesis. BAAOTB and TBATB can reduce aldehydes and ketones in $CHCl_3$ or *t*-BuOH under reflux conditions in high yields (Table 1). We have performed most of the reactions in *t*-BuOH in which the rate of the reduction is high and the work-up of the reaction does not need the hydrolysis of the borate. Chemoselective reduction of aldehydes in the presence of ketones is a useful reaction in organic synthesis and continues to attract considerable interest in recent years.[16,31)] Therefore, we have studied the chemoselectivity of this transformation by BAAOTB for the reduction of an aldehyde in the presence of ketone. This investigation is performed by the reduction of phenanthrene-9-carbaldehyde in the presence of benzophenone in an equimolar ratios. The selectivity ratio for the reaction of aldehyde with respect to ketone is 7.6 (Scheme 1). The same reaction is performed with TBATB under the same reaction condition. The ratio of the two products was 4, which means the reagent is less selective than BAAOTB. Reduction of a carbonyl group in the presence of epoxide ring is also investigated. BAAOTB reduces carbonyl group with very high chemoselectivity and produces only one product, whereas TBATB produces many fractions in the reaction mixture (Table 1, Entry 15).

2. Reduction of α,β-Unsaturated Aldehydes and Ketones. Regioselective reduction of α,β-unsat-

Table 1. Reductions of Adehydes and Ketones by BAATOB and TBATB

Entry	Substrate	Product	mp or bp	BAAOTB		TBATB	
			°C[43,44)]	Molar ratio	Yield % (h)	Molar ratio	Yield % (h)
1	Benzaldehyde	Benzyl alcohol	203	1	90 (1)	—	91 (24)
2	3-Nitrobenzaldehyde	3-Nitrobenzyl alcohol	31	1	90 (1)	—	—
3	4-Chlorobenzaldehyde	4-Chlorobenzyl alcohol	71—72	1	90 (0.2)	—	—
4	Anisaldehyde	Anisyl alcohol	92—93	2	85 (0.8)	—	—
5			—	2	90 (0.5)		
6	1-Naphthaldehyde	1-Naphthylmethanol	60—62	1	90 (0.25)	—	—
7	Phenanthrene-9-carbaldehyde	9-Phenanthrene-methanol	—	1	90 (0.5)	—	—
8	Pyridine-3-carbaldehyde	3-Pyridinemethanol	155/28 mmHg	1	80 (0.4)	—	—
9	Furaldehyde	Furfuryl alcohol	172	1.5	90 (0.5)	—	—
10	1,2-Naphthalene-dicarbaldehyde	1,2-naphthalene-dimethanol	—	2	80 (0.7)	—	—
11	Phenylacetaldehyde	2-Phenylethanol	219—221/28 mmHg	1	90 (0.25)	—	—
12	Acetophenone	1-Phenylethanol	94—96	2	80 (17)	—	—
13	Benzophenone	Diphenylmethanol	66—67	2	90 (21.5)	—	—
14			—	4	70 (76)	—	—
15	 $\mathrm{Ph{-}\underset{\diagdown O \diagup}{CH{-}CH}{-}\underset{\overset{\Vert}{O}}{C}{-}Me}$	 $\mathrm{Ph{-}\underset{\diagdown O \diagup}{CH{-}CH}{-}\underset{\overset{\vert}{OH}}{CH}{-}Me}$	—	1	92 (0.25)	1	Mixed products



Scheme 1.

urated aldehydes and ketones is important for the synthesis of structurally different allyl alcohols. Reduction of α,β-unsaturated carbonyl compounds with sodium borohydride is highly solvent dependent and generally does not result in useful regioselectivity.[9] Selective reduction of these systems has stimulated considerable interests, leading to the development of new reagents and new methods for selective 1,2-reductions of α,β-unsaturated aldehydes and ketones.[2,9,32]

Selective 1,2-reduction is usually achieved by the use of modified hydride reagents which are formed by the replacement of hydride with sterically bulky substituents or electron-withdrawing groups in order to discriminate between the structural or electronic environments of the carbonyl groups. Cinnamaldehyde is the only α,β-unsaturated carbonyl compound which has been reported to be reduced by TBATB to its corresponding allyl alcohol.[29a] Nothing more seems to be available for the reduction of these systems with quaternary ammonium tetrahydroborate agents. Therefore, we have investigated 1,2-reduction of several structurally different α,β-unsaturated carbonyl compounds during this study with TBATB and BAAOTB with success and in high yields in *t*-BuOH (Table 2).

It is recently reported that $NaBH_4$ in the presence of $CaCl_2$ reduces selectively α,β-unsaturated carbonyl compounds by a 1,2-addition reaction.[32b] Retardation of this type of reaction is observed by our reagents in the presence of $CaCl_2$, e.g.; only 5% of cinnamaldehyde is reduced to cinnamyl alcohol.

3. Reduction of Acid Chlorides. Primary studies of reduction of acid chlorides with sodium borohydride involves vigorous conditions and only alcohols are obtained.[33] However, this method is less effective for polyfunctional and conjugated acid chlorides and produces different reduced products.[29] To surmount these difficulties, several modified procedures are introduced in the literature.[30,34]

BAAOTB and TBATB reduce acid chlorides to their corresponding alcohols in high yields in acetonitrile at reflux condition (Table 3). We have compared the results with some of those reported by the reductions with $Zn(BH_4)_2/N,N,N',N'$-tetramethylethylene diamine.[34a] Conversion of acid chlorides to their aldehydes is an important transformation in organic synthesis. This goal has been achieved with methods such as lithium tri(*t*-butoxy)aluminum hydride or catalytic hydrogenation (the Rosenmund reduction) with some difficulties. In recent years, several novel reducting agents, have been developed and introduced for this purpose.[15,35] In order to show the synthetic utility of our newly developed methods, we have compared our results with some of those reported with other modified borohydrides.[15a,15b,15c,15e]

Reduction of acid chlorides with TBATB even with less than 0.5 molar ratio of the reductant and different ratios of hexane/chloroform, gives only the corresponding alcohols. This observation shows that BAAOTB could be considered as an effective and a chemoselective reagent for the conversion of acid chlorides to the aldehydes. The structure of the cation in BAAOTB has controlled the reducing potential of the BH_4^- in such a way that it will only reduce carboxylic acid chlorides, specially aroyl chlorides, to their corresponding aldehydes in high yields in hexane/$CHCl_3$=3/1 (Table 4).

4. Reduction of Epoxides. The reductive cleavage of epoxides to alcohols is one of the most useful reactions in organic synthesis. In principle, an unsymmetrical alkyl-substituted epoxides can produce the more substituted alcohols or the less substituted alcohols depending on the type of cleavage of the C–O bond, which may be performed by the electrophilic and nucleophilic

Table 2. 1,2-Addition Reductions of α,β-Unsaturated Aldehydes and Ketones with BAAOTB and TBATB

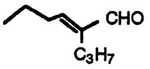
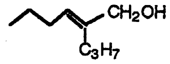
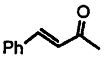
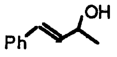
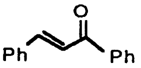
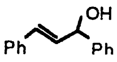
Entry	Substrate	Product	mp or bp	BAAOTB		TBATB	
			°C[43,44]	Molar ratio	Yield % (h)	Molar ratio	Yield % (h)
1	Cinnamaldehyde	Cinnamyl alcohol	32.5	1	90 (0.33)	1	90 (0.13)
2			225	1	85 (0.1)	0.4	85 (0.1)
3	2-Hexenal	2-Hexen-1-ol	159—161	1	80 (0.1)	0.4	85 (0.1)
4			144/21 mmHg	2	85 (0.4)	0.4	80 (0.4)
5			—	2	85 (3.2)	1	75 (3.3)

Table 3. Reduction of Carboxylic Acid Chlorides to the Corresponding Alcohols with ABBOAB and TBATB and Comparisons with $Zn(BH_4)_2/N,N,N',N'$- Tetramethylethylenediamine[34a]

Entry	Substrate	Product	mp or bp	BAAOTB		TBATB		$Zn(BH_4)_4$/TMEDA[34a]
			°C[43,44]	Molar ratio	Yield % (h)	Molar ratio	Yield % (h)	Yield % (h)
1	2-Chlorobenzoyl chloride	2-Chlorobenzyl alcohol	70—71	3	95 (0.25)	1	95 (0.5)	—
2	2-Methoxybenzoyl chloride	2-Methoxybenzyl alcohol	247—250	3	95 (1.6)	1	92 (1)	—
3	4-Nitrobenzoyl chloride	4-Nitrobenzyl alcohol	91—92	3	95 (2)	1	85 (1)	93 (0.25)
4	4-Methylbenzoyl chloride	4-Methylbenzyl alcohol	59—61	3	85 (2.5)	1	95 (1)	—
5	Phenylacetyl chloride	2-Phenylethanol	219/750 mmHg	3	85 (2)	1	85 (1.5)	98 (0.5)
6	Cinnamoyl chloride	Cinnamyl alcohol	32.5	3	80 (3)	1	85 (1)	86 (0.5)

Table 4. Reduction of Carboxylic Acid Chlorides to the Corresponding Aldehydes with BAAOTB and Comparison with Some Other Methods

Entry	Substrate	Product	mp or bp	BAAOTB		Yield% by the other methods[a]	
			°C[43,44]	Molar ratio	Yield % (h)	A[15e]	B[15a]
1	2-Chlorobenzoyl chloride	2-Chlorobenz aldehyde	208—212	2	95 (1.5)	75	—
2	2-Methoxybenzoyl chloride	2-Methoxybenz aldehyde	38—40	2	85 (9)	—	—
3	4-Nitrobenzoyl chloride	4-Ntrobenzal dehyde	104—107	2	75 (1.5)	48	25
4	4-Methylbenzoyl chloride	4-Methylbenzal dehyde	205—207	2	95 (10)	—	—
5	Phenylacetyl chloride	2-Phenylethanol	196	2	70 (1)	55	—
6	Cinnamoyl chloride	Cinnamaldehyde	249	2	60 (4)	61	77

a) $([Ph_3P]_2CuBH_3CN)_2$, B: $(Ph_3P)_2CuBH_4$.

hydride transfer agents.[2,5,26b,36]

BAAOTB and TBATB are efficient reagents for regioselective ring-opening reduction of epoxides from the less-hindered site, in high yields (Table 5).

5. Reduction of Azides. The transformation of azides into amines is a synthetically important process, especially in carbohydrate and nucleoside chemistry,[37] and its value has been well established. A wide variety of methods have been reported to effect this conversion[38] and have been reviewed.[39] Reagents such as lithium aluminum hydride, catalytic hydrogenation, triphenylphosphine, triethyl phosphite,[40a] sodium borohydride/phase transfer catalyst, transfer hydrogenation,[40b] and sodium hydrogen telluride[41] have been used for this transformation. However, some of these methods are not chemoselective and/or require drastic reaction conditions. Reduction of azides with sodium borohydride usually gives poor yields. Sodium borohydride in the presence of phase-transfer catalysts[38] or copper(II) sulfate[38d] reduces azides to amines in high yields.

BAAOTB reduces azides effectively to the corresponding primary amines in *t*-BuOH under reflux condition in high yields (Table 6). TBATB also converts azides efficiently to the corresponding primary amines faster than BAAOTB under the same reaction conditions in high yields and we have compared the results with some other methods[37,38a,38c] (Table 6).

6. Reductive Cleavage of S–S Bonds. The S–S bond in disulfides plays an important role in biological activities. Hence the conversion of the sulfur–sulfur bond in disulfides to thiols has been the subject of considerable studies. This conversion can be achieved most easily by reduction. The reagents utilized include; lithium aluminum hydride, sodium borohydride in mixed solvents, sodium borohydride/aluminum chloride, zinc/acetic acid, triphenylphosphine, as well as other miscelleneous reagents.[21,42] Although $NaBH_4$ in EtOH is not an effective reagent for the reduction of S–S bonds in mixed solvents.[42]

Table 5. Reductive Ring Openings of Epoxides by BAAOTB and TBATB

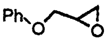
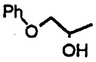
Entry	Substrate	Product	mp or bp	BAAOTB		TBATB	
			°C[43,44]	Molar ratio	Yield % (h)	Molar ratio	Yield % (h)
1	Styrene oxide	1-Phenylethanol	21	1	90 (6.5)	1	90 (6)
2			—	1	85 (1.1)	1	80 (1)
3	Cyclohexene oxide	Cyclohexanol	20—22	2	95 (2)	2	90 (2)
4	Propylene oxide	2-Propanol	83	1	95 (3)	1	90 (2.6)

Table 6. Reduction of Azides with BAAOTB and TBATB and Comparison with Other Methods[37,38a,38c]

Entry No.	Substrate	Product	mp or bp	BAAOTB		TBATB		Yield%(Rxn time (h) by other methods)[a]		
			°C[43,44]	Molar ratio	Yield % (h)	Molar ratio	Yield % (h)	A[38a]	B[37]	C[38c]
1	4-Methylphenyl azide	*p*-Toluidine	42—45.5	2	85 (2)	2	90 (3)	96 (18)	—	—
2	4-Chlorophenyl azide	4-Chloroaniline	69—72	2	90 (2.5)	1	90 (1)	94 (4)	98 (1)	—
3	4-Bromophenyl azide	4-Bromoaniline	62—64	2	90 (2.5)	1	85 (1)	96 (4)	—	—
4	4-Nitrophenyl azide	4-Nitroaniline	147—149	2	92 (2.5)	2	90 (0.25)	97 (0.5)	—	—
5	2-Nitrophenyl azide	2-Niroaniline	74—76	2	90 (2.5)	1	85 (0.3)	95 (0.7)	94 (1)	—
6	1-Naphthyl azide	1-Naphthylamine	49—51	2	90 (6)	3	92 (2)	94 (6)	94 (1)	86 (6)
7	Benzyl azide	Benzylamine	184—186	2	90 (10)	2	90 (5)	46 (24)	48 (4)	89 (3)

a) A: BH_4 supported on an ion exchange resin. B: $NaBH_4$/THF·MeOH, C: $NaBH_4$/PTC.

TBATB converts disulfides to their thiols efficiently in high yields in refluxing *t*-BuOH (Table 7). BAAOTB also converts, in high yields, disulfides to their thiols but in slower rates than TBATB in *t*-BuOH under reflux condition (Table 7). We have also compared a few results obtained by the other methods[20,41] with those obtained with BAAOTB and TBATB.

Conclusion

Is this paper we have focussed our attention to quaternary ammonium borohydrides as potential reducing agents. The structural modifications of the quaternary moiety can affect the rate, selectivity, and the reaction condition effectively. Stability, ease of work-up, high yields, and their preparation from commercially available starting materials, make them attractive bench top reducing agents in organic synthesis.

Experimental

General: Yields refer to isolated products. Reactions proceeded in *t*-BuOH, CH_3CN, or in the mixture of hex-

Table 7. S–S Bond Reductive Cleavage by BAAOTB and TBATB and Comparisons with Other Methods[21,41]

Entry	Substrate	Product	mp or bp	BAAOTB		TBATB		Yield% by the other methods[a]	
			°C[43,44]	Molar ratio	Yield % (h)	Molar ratio	Yield % (h)	A[21]	B[42]
1	Diphenyl disulfide	Benzenethiol	170	5	95 (4)	3	95 (1.5)	83	100
2	Dibenzyl disulfide	Phenylmethanethiol	194—196	7	80 (6)	5	90 (5)	84	50[b]
3	Di-(2-furfuryl) disulfide	2-Furanthiol	156	7	80 (12)	6	90 (6)	—	73[b]
4	Di-(2-pyrimidinyl) disulfide	2-Pyrimidinethiol	231 (decomp)	5	85 (10)	4	90 (4)	—	—
5	Dicyclohexyl disulfide	Cyclohexanethiol	159—161	6	85 (8)	3	90 (5)	—	45[b]
6	Di-*m*-tolyl disulfide	*m*-Toluene thiol	197	5	85 (10)	3	83 (4)	—	93[b]

a) Potassium triispropoxy borohydride, B: $NaBH_4$/THF·CH_3OH. b) Our observations.

ane–$CHCl_3$. Products were characterized by comparison with authentic samples (IR spectrum, TLC, G.C., NMR spectrum, and melting point). Melting points are not corrected.

Preparation of 1-Benzyl-4-aza-1-azoniabicyclo[2.2.2]octane Tetrahydroborate (BAAOTB). To a solution of 1,4-diazabicyclo[2.2.2]octane (DABCO) (56 g, 0.5 mol) in acetone, benzyl bromide (86 g, 0.5 mol) was added dropwise with stirring. The resulting precipitates were collected by filtration, dried, and used for the next step.

The resulting bromide from the preceeding step (142 g, 0.5 mol) was dissolved in water (100 ml). To the resulting solution sodium hydroxide solution (5 M, 130 ml, M=mol dm^{-3}) was added with stirring. To the resulting mixture, a solution of sodium borohydride (20.9 g, 0.55 mol) in water (50 ml) was added and stirred magnetically for 3 h and then extracted with dichloromethane (500 ml) by a continuous extraction apparatus. Dichloromethane solution was dried over anhydrous K_2CO_3 and concentrated, which upon the addition of dry ether, white powder of the BAAOTB precipitated in a quantitative yield (110 g).

Reduction of 4-Chlorobenzaldehyde to 4-Chlorobenzyl Alcohol with BAAOTB: A Typical Procedure. In a round-bottomed flask (25 ml), equipped with a magnetic stirrer and a condenser, a solution of 4-chlorobenzaldehyde (0.28 g, 2 mmol) in *t*-BuOH (5 ml) was prepared. The reducing agent (0.44 g, 2 mmol) was added. The reaction mixture was stirred magnetically under reflux condition for 0.23 h. Progress of the reaction was monitored by TLC (eluent: $CCl_4/Et_2O=5/1$). The solvent was evaporated and the gummy material was extracted with ether (40 ml) in a continuous extraction apparatus overnight. The solvent was evaporated and the pure crystals of 4-chlorobenzyl alcohol were isolated (0.25 g, 90% yield), (mp 70—71 °C, Lit,[43] 70—72 °C).

Reduction of Benzophenone to Diphenylmethanol with BAAOTB: A Typical Procedure. In a round-bottomed flask (25 ml), equipped with magnetic stirrer and a condenser, a solution of benzophenone (0.18 g, 1 mmol) in *t*-BuOH (6 ml) was prepared. The reducing agent (0.44 g, 2 mmol) was added. The reaction mixture was stirred magnetically under reflux condition for 21.5 h. Progress of the reaction was monitored by TLC (eluent: $CCl_4/Et_2O=5/1$). The solvent was evaporated and the gummy material was extraceted with ether (40 ml) in a continuous extraction apparatus overnight. The solvent was evaporated and the pure crystals of diphenylmethanol were isolated (0.166 g, 90% yield), (mp 66—68 °C, Lit,[43] 65—67 °C).

Reduction of Cinnamaldehyde to Cinnamyl Alcohol with BAAOTB: A Typical Procedure. In a round-bottomed flask (25 ml), equipped with magnetic stirrer and a condenser, a solution of cinnamaldehyde (0.13 g, 1 mmol) in *t*-BuOH (5 ml) was prepared. The reducing agent (0.22 g, 1 mmol) was added. The reaction mixture was stirred magnetically under reflux condition for 0.33 h. The progress of the reaction was monitored by TLC (eluent: $CCl_4/Et_2O=5/2$). The solvent was evaporated and the resulting crude material was purified on a silica gel plate (eluent: $CCl_4/Et_2O=5/2$). Pure cinnamyl alcohol was obtained (0.12 g, 90% yield), (mp 34—36 °C, Lit,[43] 33—35 °C).

Reduction of 4-Phenyl-3-buten-2-one to 4-Phenyl-3-buten-2-ol with BAAOTB: A Typical Procedure. In a round-bottomed flask (25 ml), equipped with magnetic stirrer and a condenser, a solution of 4-phenyl-3-buten-2-one (0.146 g, 1 mmol) in *t*-BuOH (5 ml) was prepared. Reducing agent (0.44 g, 2 mmol) was added. The reaction mixture was stirred magnetically under reflux condition for 0.33 h. The progress of the reaction was monitored by G.C. The solvent was evaporated and the resulting crude material was purified on a silica gel plate (eluent: $CCl_4/Et_2O=5/2$). Pure 4-Phenyl-3-buten-2-ol was obtained (0.126 g, 85% yield), (bp 142—144 °C/21 mmHg (1 mmHg=133.322 Pa), Lit,[44] 144 °C/21 mmHg).

Reduction of 2-Chlorobenzoyl Chloride to 2-Chlorobenzaldehyde with BAAOTB: A Typical Procedure. In a round-bottomed flask (25 ml), equipped with magnetic stirrer and a condenser, a solution of 2-chlorobenzoyl chloride (0.175 g, 1 mmol) in mixture of hexane–chloroform, 3/1, (7 ml) was prepared. The reducing agent (0.44 g, 2 mmol) was added. The reaction mixture was stirred magnetically under reflux condition for 1.5 h. The progress of the reaction was monitored by TLC (eluent: $CCl_4/Et_2O=6/1$). The reaction was quenched by the addition of 10 ml of 3% hydrogen peroxide follwed by 10 ml of 10% sodium hydroxide and the mixtrue was stirred for 2 h. The organic layer was separated and the aqueous phase was extracted with dichloromethane (3×30 ml). The combined organic extracts were dried over anhydrous $MgSO_4$. The solvent was evaporated and the resulting crude material was purified on silica gel plate (eluent: $CCl_4/Et_2O=6/1$). Pure 2-chlorobenzaldehyde was obtained (0.133 g, 95% yield), (bp 208—212 °C, Lit,[43] 209—215 °C).

Reduction of 2-Chlorobenzoyl Chloride to 2-Chlorobenzyl Alcohol with BAAOTB: A Typical Procedure. In a round-bottomed flask (25 ml), equipped with magnetic stirrer and a condenser, a solution of 2-chlorobenzoyl chloride (0.175 g, 1 mmol) in acetonitrile (8 ml) was prepared. The reducing agent (0.66 g, 3 mmol) was added. The reaction mixture was stirred magnetically under reflux condition for 0.25 h. The progress of the reaction was monitored by TLC (eluent: $CCl_4/Et_2O=5/2$). Water was added and the mixture was stirred for 2 h. The resulting mixture was extracted with dichloromethane (3×40 ml). The combined organic extracts were dried over anhydrous $NaSO_4$. Evaporation of the solvent afforded pure 2-chlorobenzyl alcohol (0.135 g, 95% yield), (mp 70—71 °C, Lit,[43] 69—71 °C).

Reduction of Styrene Oxide to 1-Phenylethanol with BAAOTB: A Typical Procedure. In a round-bottomed flask (25 ml), equipped with magnetic stirrer and a condenser, a solution of styrene oxide (0.12 g, 1 mmol) in *t*-BuOH (5 ml) was prepared. The reducing agent (0.22 g, 1 mmol) was added. The reaction mixture was stirred magnetically under reflux condition for 6.5 h. The progress of the reaction was monitored by G.C. The solvent was evaporated and the resulting crude material was purified on a silica gel plate (eluent: $CCl_4/Et_2O=5/2$). 1-Phenyl ethanol was obtained (0.11 g, 90% yield), (bp 93—95 °C, Lit,[43] 94—96 °C).

Reduction of 4-Nitrophenyl Azide to 4-Nitroaniline with BAAOTB: A Typical Procedure. In a round-bottomed flask (25 ml), equipped with magnetic stirrer and a condenser, a solution of 2-nitrophenyl azide (0.33

g, 2 mmol) in *t*-BuOH (8 ml) was prepared. The reducing agent (0.88 g, 4 mmol) was added. The reaction mixture was stirred magnetically under reflux condition for 2.5 h. Progress of the reaction was monitored by TLC (eluent: $CCl_4/Et_2O=3/1$). The solvent was evaporated and the resulting crude material was purified on a silica gel plate (eluent: $CCl_4/Et_2=3/1$). Pure 4-nitroaniline was obtained (0.254 g, 92% yield), (mp 148—149 °C, Lit,[43] 147.5—149 °C).

Reduction of Di-(2-pyrimidinyl) Disulfide to 2-Pyrimidinethiol with BAAOTB: A Typical Procedure. In a round-bottomed flask (25 ml), equipped with magnetic stirrer and a condenser, a solution of di-(2-pyrimidinyl) disulfide (0.22 g, 1 mmol) in *t*-BuOH (6 ml) was prepared. The reducing agent (1.1 g, 5 mmol) was added. The reaction mixture was stirred magnetically under reflux condition for 10 h. Progress of the reaction was monitored by TLC (eluent: CCl_4). The solvent was evaporated to afford crude product. Purification of the product with a silica gel plate (eluent: CCl_4) afforded the pure thiol (0.095 g, 85% yield), (mp 231 °C (decomp), Lit,[43] 230 °C (decomp)).

Reduction of Cinnamaldehyde to Cinnamyl Alcohol with TBATB: A Typical Procedure. In a round-bottomed flack (25 ml), equipped with magnetic stirrer, a solution of cinnamaldehyde (0.132 g, 1 mmol) in *t*-BuOH (5 ml) was prepared. The reducing agent (0.26 g, 1 mmol) was added. The reaction mixture was stirred magnetically under reflux condition for 0.13 h. The progress of the reaction was monitored by TLC (eluent: $CCl_4/Et_2O=5/2$). The solvent was evaporated and the resulting crude material was purified on a silica gel plate (eluent: $CCl_4/Et_2O=5/2$). Pure cinnamyl alcohol was obtained (0.12 g, 90% yield), (mp 34—36 °C, Lit,[43] 33—35 °C).

Reduction of 4-Phenyl-3-buten-2-one to 4-Phenyl-3-buten-2-ol with TBATB: A Typical Procedure. In a round-bottomed flask (25 ml), equipped with magnetic stirrer and a condenser, a solution of 4-Phenyl-3-buten-2-one (0.146 g, 1 mmol) in *t*-BuOH (5 ml) was prepared. Reducing agent (0.086 g, 0.33 mmol) was added. The reaction mixture was stirred magnetically under reflux condition for 0.33 h. The Progress of the reaction was monitored by G.C. The solvent was evaporated and the resulting crude material was purified on a silica gel plate (eluent: $CCl_4/Et_2O=5/2$). Pure 4-Phenyl-3-buten-2-ol was obtained (0.12 g, 80% yield), (bp 143 °C/21 mmHg, Lit,[44] 144 °C/21 mmHg).

Reduction of 4-Chlorobenzoyl Chloride to 4-Chlorobenzyl Alcohol with TBATB: A Typical Procedure. In a round-bottomed flask (25 ml), equipped with magnetic stirrer and a condenser, a solution of 4-chlorobenzoyl chloride (0.175 g, 1 mmol) in mixture of hexane–chloroform, 3/1, (6 ml) was prepared. The reducing agent (0.26 g, 1 mmol) was added. The reaction mixture was stirred magnetically under reflux condition for 0.5 h. The progress of the reaction was monitored aby TLC (eluent: $CCl_4/Et_2O=5/2$). Water was added and the mixture was stirred for 2 h. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3×30 ml). The combined organic solutions were dried over anhydrous sodium sulfate. Evaporation of the solvent afforded the pure 4-chlorobenzyl alcohol (0.135 g, 95% yield), (mp 70—71 °C, Lit,[43] 69—71 °C).

Reduction of Styrene Oxide to 1-Phenylethanol with TBATB: A Typical Procedure. In a round-bottomed flask (25 ml), equipped with magnetic stirrer and a condenser, a solution of styrene oxide (0.12 g, 1 mmol) in *t*-BuOH (5 ml) was prepared. The reducing agent (0.26 g, 1 mmol) was added. The reaction mixture was stirred magnetically under reflux condition for 6 h. The progress of the reaction was monitored by G.C. The solvent was evaporated and the resulting crude material was purified on a silica gel plate (eluent: $CCl_4/Et_2O=5/2$). 1-Phenylethanol was obtained (0.11 g, 90% yield), (bp 94—96 °C, Lit,[43] 94—96 °C).

Reduction of 4-Nitrophenyl Azide to 4-Nitroaniline with TBATB: A Typical Procedure. In a round-bottomed flask (25 ml), equipped with magnetic stirrer and a condenser, a solution of 4-nitrophenyl azide (0.33 g, 2 mmol) in *t*-BuOH (8 ml) was prepared. The reducing agent (1 g, 4 mmol) was added. The reaction mixture was stirred magnetically under reflux condition for 0.25 h. Progress of the reaction was monitored by TLC (eluent: $CCl_4/Et_2O=3/1$). The solvent was evaporated and the resulting crude material was purified on a silica gel plate (eluent: $CCl_4/Et_2O=3/1$). Pure crystals of 4-nitroaniline were obtained (0.227 g, 90% yield), (mp 147—149 °C, Lit,[43] 147—149 °C).

Reduction of Di-(2-pyrimidinyl) Disulfide to Pyrimidine-2-thiol with TBATB: A Typical Procedure. In a round-bottomed flask (25 ml), equipped with magnetic stirrer and a condenser, a solution of di-(2-pyrimidinyl) disulfide (0.22 g, 1 mmol) in *t*-BuOH (6 ml) was prepared. The reducing agent (1 g, 4 mmol) was added. The reaction mixture was stirred magnetically under reflux condition for 4 h. Progress of the reaction was monitored by TLC (eluent: CCl_4). The solvent was evaporated to afford crude product. Purification of the crude material with a silica gel plate (eluent: CCl_4) afforded the pure pyrimidine-2-thiol (0.1 g, 90% yield), (mp 231 °C, (decomp), Lit,[43] 230 °C (decomp).

Partial support of this work by Shiraz University Research Council is gratefuly acknowledged.

References

1) a) H. Firouzabadi and G. R. Afsharifar, *Synth. Commun.*, **22**, 497 (1992), and the references cited therein; b) H. Firouzabadi, B. Tamami, and N. Goudarzian, *Synth. Commun.*, **21**, 2275 (1991).

2) M. Hudlicky, "Reductions in Oragnic Chemistry," Ellis Horwood Ltd., Chichester (1984).

3) a) B. Ganem and J. O. Osbey, *Chem. Rev.*, **86**, 763 (1986); b) H. C. Brown and S. Krishnamurthuy, *Tetrahedron*, **35**, 567 (1979).

4) D. C. Wigfield, *Tetrahedron*, **35**, 449 (1979).

5) H. O. House, "Modern Synthetic Reactions," Benjamine, Menlo Park, CA (1972).

6) G. A. Tolstikov and V. N. Odinokov, *Tetrahedron Lett.*, **1979**, 4851.

7) H. C. Brown and E. J. Mead, *J. Am. Chem. Soc.*, **75**, 6263 (1953).

8) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," John Wiely & Sons, New York (1986), Vol. 12.

9) C. F. Nutaitis and J. E. Bernardo, *J. Org. Chem.*, **54**, 5629 (1989), and references cited therein.

10) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," John Wiley & Sons, New York (1977), Vol. 7.

11) a) C. F. Lane, *Synthesis*, **1975**, 135; b) C. S. Rao, *Tetrahedron*, **46**, 2195 (1990).

12) K. Soai and A. Ookawa, *J. Org. Chem.*, **51**, 4000 (1986), and references cited therein.

13) Y. He, H. Zhao, X. Pan, and S. Wang, *Synth. Commun.*, **19**, 3047 (1989).

14) H. C. Brown, S. Narasinham, and Y. M. Choi, *J. Org. Chem.*, **47**, 4702 (1982).

15) a) T. N. Sorrel and R. J. Spillane, *Tetrahedron Lett.*, **1978**, 2473; b) T. N. Sorrel and P. S. Pearlman, *J. Org. Chem.*, **45**, 3449 (1980); c) G. N. J. Fleet, C. J. Fuller, and P. J. C. Harding, *Tetrahedron Lett.*, **1978**, 1437; d) G. W. J. Fleet and P. J. C. Harding, *Tetrahedron Lett.*, **1981**, 675; e) R. O. Hutchins and M. Markowitz, *Tetrahedron Lett.*, **1980**, 813.

16) B. C. Ranu, *Synlet*, **1993**, 885, and references cited therein.

17) a) H. C. Brown, S. C. Kim, and S. Krishnamurthy, *J. Org. Chem.*, **45**, 1 (1980); b) B. E. Blough and F. I. Corroll, *Tetrahedron Lett.*, **1993**, 7239.

18) S. Kim, Y. C. Moon, and K. K. Ahan, *J. Org. Chem.*, **47**, 3311 (1982).

19) E. J. Corey, K. B. Becker, and R. K. Vorma, *J. Am. Chem. Soc.*, **94**, 8616 (1972).

20) a) B. Ganem, *J. Org. Chem.*, **40**, 146 (1975); b) B. Ganem and J. M. Fortunato, *J. Org. Chem.*, **41**, 2194 (1976).

21) H. C. Brown, B. Nazer, and J. S. Cha, *Synthesis*, **1984**, 498, and references cited therein.

22) S. B. Park, K. E. Kim, and E. Kwan, *Bull. Korean Chem. Soc.*, **9**, 352 (1988).

23) a) Y. Tsude, T. Sane, and H. Watanabe, *Synthesis*, **1977**, 652; b) A. L. Gemal and J. -L. Luche, *J. Am. Chem. Soc.*, **103**, 5454 (1981); c) W. B. Smith, *J. Heterocycl. Chem.*, **24**, 745 (1987); d) A. F. Thomas, W. Thommen, and J. Backer, *Helv. Chim. Acta*, **73**, 161 (1981); e) G. Theodoridis, M. C. Manfredi, and J. D. Krevs, *Tetrahedron Lett.*, **1990**, 6141; f) T. Yamakawa, M. Masaki, and K. Nahiro, *Bull. Chem. Soc. Jpn.*, **64**, 2730 (1991).

24) a) A. Ono, T. Maruyama, and N. N. Suzuki, *Synth. Commun.*, **17**, 1001 (1987); b) A. Giannis and K. Sandhoff, *Angew. Chem., Int. Ed. Engl.*, **28**, 218 (1989); c) V. Suseela and M. Periasamy, *Tetrahedron*, **48**, 371 (1992).

25) a) E. Santaniello, C. Farachi, and A. Manzocchi, *Synthesis*, **1979**, 912; b) N. M. Yoon and J. Choi, *Synlet*, **1993**, 135.

26) a) M. Yatagai and T. Ohnuki, *J. Chem. Soc., Perkin Trans. 1*, **1990**, 1826; b) Y. Hu, M. Uno, and S. Harada, *Bull. Chem. Soc. Jpn.*, **64**, 1884 (1991); c) V. K. Singh, *Synthesis*, **1992**, 605.

27) K. Soai, H. Oyamada, M. Takase, and A. Ookawa, *Bull. Chem. Soc. Jpn.*, **57** 1948 (1984).

28) M. D. Bauns, R. W. Bragdon, and T. R. P. Gibb, Jr., *J. Am. Chem. Soc.*, **74**, 2346 (1952).

29) a) D. J. Raber and W. C. Guida, *J. Org. Chem.*, **41**, 690 (1976); b) T. N. Sorrell and P. S. Pearlman, *Tetrahedron Lett.*, **1980**, 3963.

30) E. A. Sullivan and A. A. Hinckly, *J. Org. Chem.*, **27**, 3731 (1962).

31) a) A. Ono and K. Hayakawa, *Chem. Lett.*, **1987**, 853; b) D. E. Ward and C. K. Rhee, *Synth. Commun.*, **18**, 1927 (1988), and references cited therein.

32) a) S. Kim and K. H. Ahn, *J. Org. Chem.*, **49**, 1717 (1984), and references cited therein; b) H. Fujii, K. Oshima, and K. Utimoto, *Chem. Lett.*, **1991**, 1847; c) J. C. Fuller, E. L. Stangeland, C. T. Goralski, and B. Singaram, *Tetragedron Lett.*, **1993**, 257; d) K. S. Ravikumar, S. Baskaran, and S. Chandrasekaran, *J. Org. Chem.*, **58**, 5981 (1993).

33) S. W. Chaiken and W. G. Brown, *J. Am. Chem. Soc.*, **76**, 122 (1949).

34) a) H. Kosuki, Y. Ushio, N. Yashimura, and M. Ochi, *Bull. Chem. Soc. Jpn.*, **61**, 2684 (1988), and references cited therein; b) J. Das and S. Chandrasekaran, *Synth. Commun.*, **20**, 907 (1990).

35) J. H. Babler and B. J. Invergo, *Tetrahedron Lett.*, **1981**, 11, and references cited therein.

36) a) A. Ookawa, H. Hiratsuka, and K. Soai, *Bull. Chem. Soc. Jpn.*, **60**, 1813 (1987), and references cited therein; b) B. C. Ranu and A. R. Das, *J. Chem. Soc., Chem. Commun.*, **1990**, 1334, and references cited therein.

37) K. Soai, S. Yokoyama, and A. Ookawa, *Synthesis*, **1987**, 48, and references cited therein.

38) a) G. W. Kabalka, P. P. Wadgonkar, and N. Chatla, *Synth. Commun.*, **20**, 293 (1990), and the references cited therein; b) N. M. Yoon, J. Choi, and Y. S. Shan, *Synth. Commun.*, **23**, 3047 (1993), and the references cited therein; c) F. Rolla, *J. Org. Chem.*, **47**, 4327 (1982); d) H. S. Prakash Rao and P. Siva, *Synth. Commun.*, **24**, 549 (1994).

39) E. F. Scriven and K. Turnbull, *Chem. Rev.*, **88**, 297 (1988).

40) a) A. Koziara, K. O. Pacewicka, and S. Zawadzki, *Synthesis*, **1985**, 202; b) T. Gartiser, C. Selve, and J. Delpuech, *Tetrahedron Lett.*, **1983**, 1609.

41) H. Suzuki and K. Takaoka, *Chem. Lett.*, **1984**, 1733, and references cited therein.

42) A. Ookawa, S. Yokoyama, and K. Soai, *Synth. Commun.*, **16**, 819 (1986), and references cited therein.

43) Aldrich Catalog-Handbook of Fine Chemicals, 1993—1994.

44) "Dictionary of Organic Compounds," Eyre and Spottiswoode Publishers Ltd., London (1965).