A fluorine-mediated boron reducing agent – sodium tris(pentafluorophenoxy)borohydride. Preparation and reaction with selected organic compounds containing representative functional groups. Facile diastereoselective reduction of substituted cyclohexanones [1]

Joseph C. Fuller, Matthew L. Karpinski, Stanley M. Williamson* and Bakthan Singaram*
Department of Chemistry and Biochemistry, University of California at Santa Cruz, Santa Cruz, CA 95064 (USA)

Abstract

Addition of 3 equiv. of pentafluorophenol to a tetrahydrofuran (THF) suspension of sodium borohydride at 0 °C resulted in the rapid and quantitative formation of sodium tris(pentafluorophenoxy)borohydride (NaTPFPBH) with concurrent evolution of 3 equiv. of hydrogen gas. The reducing agent NaTPFPBH is stable at 0 °C for an extended period of time without having to remain in equilibrium with an alkali metal hydride. The approximate rate and stoichiometry of the reaction of excess pure NaTPFPBH with 41 selected compounds containing representative functional groups was examined in order to characterize the reducing agent for selective reductions. Primary, secondary and tertiary alcohols evolved 1 equiv. of hydrogen slowly over a period of 24 h at 0 °C. Phenol also liberated hydrogen slowly and the reaction of hexylamine was very slow. Aldehydes and reactive ketones are reduced readily and quantitatively to yield the corresponding alcohols. Carboxylic acids generated hydrogen quantitatively without undergoing any further reduction. Esters, lactones and phthalides are essentially inert towards the reagent. Epoxides are not reduced by NaTPFPBH. Primary aliphatic and aromatic amides evolved hydrogen but no significant reduction occurred. Unlike sodium and potassium borohydrides, NaTPFPBH is very stereo- and regio-selective. 2-Methylcyclohexanone is reduced predominantly to the corresponding less stable isomer, *cis*-2-methylcyclohexanol. Switching the order of addition of sodium borohydride and pentafluorophenol to reduce substituted cyclohexanones gave the thermodynamically more stable alcohols with an equatorial hydroxy group. Cinnamaldehyde and 2-cyclohexen-1-one are reduced readily to cinnamyl alcohol and 2-cyclohexen-1-ol, respectively.

Introduction

Sodium borohydride ($NaBH_4$) and lithium aluminum hydride ($LiAlH_4$) are the two most useful reducing agents available to chemists today. With the discovery of $NaBH_4$ in 1942 and $LiAlH_4$ in 1945, it was found that $NaBH_4$ is a very mild reducing agent, reducing only aldehydes, ketones and acid chlorides [2]. On the other hand, $LiAlH_4$ is very powerful and reduces most of the functional groups known to chemists except for olefins [3]. These two reagents represent the two ends of a spectrum of reducing agents. By increasing the reducing power of $NaBH_4$ or by reducing the power of $LiAlH_4$, one can achieve a wide variety of selective reducing agents. It has been known that placing alkoxy groups onto $NaBH_4$ and $LiAlH_4$ modifies their reducing characteristics [4]. Alkoxy groups on $NaBH_4$ increase the electron density on the central boron atom through resonance effects, thus making it a better reducing agent. When alkoxy groups are substituted onto $LiAlH_4$ inductive effects predominate and make these hydridic species less reactive [4]. The most direct procedure for the synthesis of alkoxyborohydrides is the reaction of the corresponding alcohol with $NaBH_4$. It has been shown that only methanol reacts with $NaBH_4$ at ambient temperature to any significant extent [5]. It is difficult to control the number of alkoxy groups and stopping at the tris-alkoxy derivative is essentially impossible since reaction of $NaBH_4$ with methanol results in the rapid formation of tetramethoxyborate [eqn. (1)] [5].

$$NaBH_4 + 4CH_3OH \xrightarrow[THF]{25\ ^\circ C} NaB(OCH_3)_4 + 4H_2\uparrow \qquad (1)$$

Another way to synthesize alkoxyborohydrides is the reaction of the corresponding metal hydride with a trialkoxyborane [6]. These reactions must be carried

*Author to whom correspondence should be addressed.

SSDI 0022-1139(93)03007-9

out at high temperatures and require extended periods of time for completion. The alkoxyborohydrides thus formed are highly unstable and rapidly disproportionate unless an excess of metal hydride is present [7]. Thus, the reaction of sodium hydride (NaH) with tri-t-butoxyborane gives sodium tri-t-butoxyborohydride [eqn. (2)]. Similarly, the reaction of NaH with trimethoxyborane at reflux temperature in THF yields sodium trimethoxyborohydride as a stable solid [eqn. (3)]. However, in solution, sodium trimethoxyborohydride rapidly disproportionates to $NaBH_4$ and sodium tetramethoxyborate at ambient temperature [eqn. (4)] [8].

$$NaH + B[OC(CH_3)]_3 \xrightarrow[\text{triglyme, 72 h}]{150\ ^\circ C} NaBH[OC(CH_3)_3]_3 \quad (2)$$

$$NaH + B(OCH_3)_3 \xrightarrow[THF]{65\ ^\circ C} NaBH(OCH_3)_3 \quad (3)$$

$$4NaBH(OCH_3)_3 \xrightarrow[THF]{25\ ^\circ C} NaBH_4\downarrow + 3NaB(OCH_3)_4 \quad (4)$$

Recently, whilst working on the reaction of trifluoroethanol and pentafluorophenol with sodium borohydride, we found that sodium borohydride reacted with 4 equiv. of trifluoroethanol to form the corresponding tetraalkoxyborohydride [eqn. (5)] [8]. We also observed that sodium borohydride readily reacted with 3 equiv. of pentafluorophenol to give sodium tris(pentafluorophenoxy)borohydride (NaTPFPBH) cleanly [eqn. (6)] [8]. We also found that NaTPFPBH in solution is stable at 0 °C for an extended period of time without having to have an equilibrium concentration of metal hydride present.

$$NaBH_4 + 4CF_3CH_2OH \xrightarrow[THF]{0\ ^\circ C} NaB(OCH_2CF_3)_4 + 4H_2\uparrow \quad (5)$$

$$NaBH_4 + 3C_6F_5OH \xrightarrow[THF,\ 3\ h]{0\ ^\circ C} NaBH(OC_6F_5)_3 + 3H_2\uparrow \quad (6)$$

Since the reducing agent NaTPFPBH is new, easy to synthesize and stable at 0 °C, we undertook to study the approximate stoichiometry and rate of the reaction of NaTPFPBH with 41 compounds containing representative functional groups. In this paper, we report the results of our study.

Experimental

All operations were carried out under a nitrogen atmosphere unless otherwise specified. All glassware, syringes and needles were oven-dried and cooled under a nitrogen atmosphere. Tetrahydrofuran (THF) was freshly distilled from sodium and benzophenone ketyl. Anhydrous ethyl ether (Et_2O) was purchased from Fisher and used directly. The compounds examined here are available from Aldrich Chemical Company and were used neat or in standardized solution as described below.

^{11}B NMR spectra were recorded with a Bruker ACF 250 MHz spectrometer. Chemical shifts are relative to $Et_2O \cdot BF_3$, with chemical shifts downfield from $Et_2O \cdot BF_3$ assigned positive. ^1H and ^{13}C NMR spectra were recorded with a Bruker ACF 250 MHz spectrometer. Chemical shifts are relative to Me_4Si. Capillary GC analyses were carried out on a Hewlett Packard 5890 chromatograph fitted with a 25 m methyl silicate and a 45 m Carbowax capillary columns. All GC yields were determined by using a suitable internal standard and authentic mixtures.

Synthesis of sodium tris(pentafluorophenoxy)borohydride at 0 °C in tetrahydrofuran

The following procedure is representative. An oven-dried 250 ml round-bottom flask, equipped with a magnetic stirring bar and a septum, was charged with $NaBH_4$ (1.7 g, 45 mmol) and THF (10 ml) and cooled to 0 °C. A 3.0 M THF solution of pentafluorophenol (45 ml) was added dropwise by means of a double-ended needle over a period of 30 min and the mixture was stirred at 0 °C for 12 h to ensure complete reaction. The ^{11}B NMR spectrum of the reaction mixture showed a signal at δ 5.8 ppm (d) due to the quantitative formation of NaTPFPBH. Hydride analysis using a gas burette [9] showed that the reaction mixture was 1.0 M in hydride concentration. The reagent thus prepared was kept in an ampoule under nitrogen at 0 °C and no appreciable disproportionation could be detected even after six months.

General procedure for the determination of rate and stoichiometry

A 25 ml round-bottom flask, fitted with a side arm and a rubber septum, was charged with a THF solution of NaTPFPBH (4 ml, 4 mmol) and cooled to 0 °C. A THF solution of the compound to be reduced in (1 ml, 1 mmol) was then added with stirring. This made the mixture 0.8 M in hydride and 0.2 M in the compound under investigation. At various time intervals, 0.5 ml aliquots were withdrawn and analyzed for residual hydride [9]. From these data, the amount of hydride used for the reduction per mole of a given substrate was calculated (see Tables 1–3).

General procedure for the reactions of NaTPFPBH with α,β-unsaturated aldehydes, ketones and substituted cyclohexanones

The reduction of 2-cyclohexen-1-one is representative. To an oven-dried 15 ml serum vial, fitted with a septum

TABLE 1. Reaction of sodium tris(pentafluorophenoxy)-borohydride with representative 'active hydrogen' compounds in tetrahydrofuran at 0 °C

Compound[a]	Time (h)	Hydrogen evolved[b]	Hydrogen used for reduction[b]
3-hexanol	24	1.11	0.02
hexyl alcohol	24	1.02	0.04
t-butyl alcohol	24	0.97	0.03
benzyl alcohol	24	0.98	0.05
phenol	24	1.05	0.05
hexyl amine	48	1.07	0.01

[a]1.00 mmol of compound to 4.00 mmol of NaTPFPBH. [b]Millimol millimol^{-1} of compound.

TABLE 2. Reaction of sodium tris(pentafluorophenoxy)-borohydride with representative carboxylic acids and acyl derivatives in tetrahydrofuran at 0 °C

Compound[a]	Time (h)	Hydrogen evolved[b]	Hydrogen used for reduction[b]
hexanoic acid	0.5	1.03	0.03
benzoic acid	0.5	1.01	0.01
succinic anhydride	24.0	0.00	0.00
phthalic anhydride	24.0	0.00	0.00
hexanoyl chloride	0.25	0.01	0.00
benzoyl chloride	0.50	0.04	0.00

[a,b]See corresponding footnotes in Table 1.

TABLE 3. Reaction of sodium tris(pentafluorophenoxy)-borohydride with representative aldehydes and ketones in tetrahydrofuran at 0 °C

Compound[a]	Time (h)	Hydrogen evolved[b]	Hydrogen used for reduction[b]
heptanal	0.5	0.00	1.08
benzaldehyde	1.0	0.01	1.05
4-heptanone	3.0	0.07	1.03
cyclopentanone	12.0	0.00	1.03
cyclohexanone	6.0	0.09	1.01
acetophenone	24.0	0.02	1.06

[a,b]See corresponding footnotes in Table 1.

and a stirbar, 2-cyclohexen-1-one (1 mmol) was added and dissolved in THF (1 ml) and cooled to 0 °C. NaTPFPBH in THF (1 ml, 1 mmol) was then added and the mixture stirred for 3 h at 0 °C. It was then quenched sequentially with H_2O (1 ml) and 3 M HCl (2 ml). The reaction products were extracted with Et_2O (5 ml), washed with 3 M NaOH (2 ml) and H_2O (2×2 ml), and dried over anhydrous $MgSO_4$. Capillary GC analysis of the organic fraction on a 25 m methyl silicate column showed the product distribution to be essentially 2-cyclohexen-1-ol with a trace amount of unreacted 2-cyclohexen-1-one (see Table 4).

TABLE 4. Reaction of sodium tris(pentafluorophenoxy)-borohydride with representative α,β-unsaturated aldehydes and ketones in tetrahydrofuran at 0 °C

Compound[a]	1,2-Reduction[c] (%)	Unreacted substrate[c] (%)
trans-cinnamaldehyde	100	0
myrtenal	100	0
trans-hexenal	98	2
β-ionone	66	34
4-carboethoxy-3-methylcyclohex-2-en-1-one	66	34
(*S*)-carvone	52	48
2-cyclohexen-1-one	95	5
2-cyclohexen-1-one[b]	61(1)	38
2-cyclopenten-1-one	23(7)	70
2-cyclopenten-1-one[b]	52(48)	0
2-methylcyclopent-2-en-1-one	31	69
2-methylcyclopent-2-en-1-one[b]	33	65
3-methylcyclopent-2-en-1-one	0	100
3-methylcyclopent-2-en-1-one[b]	12	88

[a]See general procedure for the reactions of NaTPFPBH with α,β-aldehydes and ketones described in the Experimental section of paper.
[b]The α,β-aldehydes and ketones along with $CeCl_3 \cdot 6H_2O$ (1 mmol each) were dissolved in 0.4 M MeOH. $NaBH_4$ (0.038 g, 1 mmol) was added in one portion, with 3–5 min stirring [10].
[c]Ratio of products determined by capillary GC analysis with authentic internal standards. The number in the parentheses indicates the percentage of 1,4-reduction product.

TABLE 5. Reaction of substituted cyclohexanones with sodium borohydride in the presence of pentafluorophenol in tetrahydrofuran at 0 °C

Compound[a]	*Trans* isomer[b] (%)	*Cis* isomer[b] (%)
2-methylcyclohexanone	84	16
3-methylcyclohexanone	11	89
4-methylcyclohexanone	100	0
4-t-butylcyclohexanone	100	0

[a]See footnote in Table 6.
[b]See general procedure for the reductions of substituted cyclohexanones with sodium borohydride in the presence of pentafluorophenol in the Experimental section.

General procedure for the reductions of substituted cyclohexanones with $NaBH_4$ in the presence of pentafluorophenol

The reduction of 2-methylcyclohexanone is representative. To an oven-dried 15 ml serum vial, fitted with a septum and stirbar, 2-methylcyclohexanone (1 mmol) and pentafluorophenol in THF (1 ml, 1 mmol) was added and cooled to 0 °C. Solid sodium borohydride

was added slowly and the reaction mixture was stirred at 0 °C for 5 min. It was then quenched sequentially with H_2O (1 ml) and 3 M HCl (2 ml). The reaction products were extracted with Et_2O (5 ml), washed with 3 M NaOH (2 ml) and H_2O (2×2 ml), and dried over anhydrous $MgSO_4$. Capillary GC analysis of the organic fraction on a 25 m methyl silicate column showed the product distribution to be 84% *trans*-2-methylcyclohexanol and 16% *cis*-2-methylcyclohexanol (see Table 5).

Results and discussion

Reactions of NaTPFPBH with compounds containing reducible functionalities

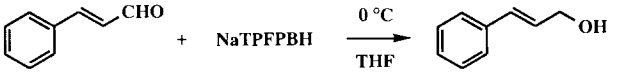
The general procedure involved preparing a reaction mixture of NaTPFPBH (0.2 M, 0.8 M in hydride) and compound (0.2 M) in tetrahydrofuran at 0 °C. The hydrogen evolved on adding the compound to the reagent was measured using a gas burette connected to the reaction vessel. After the desired reaction time, the solution was hydrolyzed and the hydrogen evolved was measured. A blank reaction was performed under identical conditions, but without addition of the compound. From the difference in the volume of hydrogen in the two cases, the hydride utilized by the compound for reduction was calculated [9].

Reactions of NaTPFPBH with compounds containing active hydrogen

All the 'active hydrogen' compounds examined liberated hydrogen upon reaction with NaTPFPBH. Thus, alcohols and phenols liberated 1 equiv. of hydrogen readily. Amines reacted slowly to give off 1 equiv. of hydrogen. Carboxylic acids quantitatively evolved 1 equiv. of hydrogen, without undergoing any further reduction. Acid chlorides react rapidly using 2 equiv. of hydride to afford the corresponding alcohols. Hexanoyl chloride, however, consumed 2 equiv. of hydride to give the ester hexyl hexanoate, as confirmed by ^1H NMR, ^{13}C NMR and MS data. Anhydrides are inert to NaTPFPBH. Succinic anhydride was recovered unchanged after 24 h at 0 °C. These results are summarized in Table 1 and 2.

Reactions of NaTPFPBH with aldehydes and ketones

All the aldehydes and ketones examined took up 1 equiv. of hydride quantitatively over a period of 24 h without any significant evolution of hydrogen. Consequently, in these cases the reduction reaction proceeded cleanly to the alcohol stage. All of the α,β-unsaturated aldehydes and ketones examined underwent 1,2-reduction to yield the corresponding allylic alcohols. The α,β-unsaturated aldehydes *trans*-cinnamaldehyde and *trans*-hexenal upon reaction with NaTPFPBH yielded the allylic alcohols *trans*-cinnamyl alcohol and *trans*-2-hexen-1-ol, respectively [eqns. (7) and (8)].



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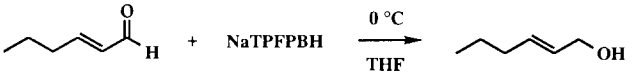

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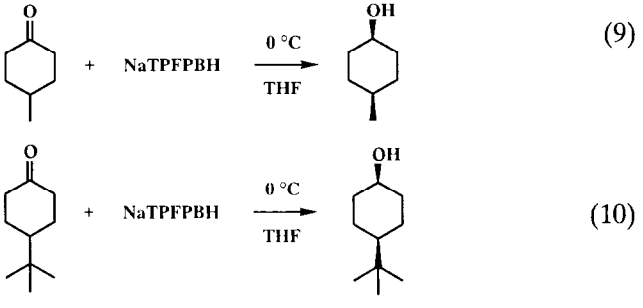
The α,β-unsaturated terpene ketones β-ionone and carvone upon reaction with NaTPFPBH gave the corresponding allylic alcohols. Similarly, reduction of 2-cyclohexen-1-one with NaTPFPBH gave the allylic alcohol 2-cyclohexen-1-ol. Reduction of 4-carbethoxy-3-methylcyclohex-2-en-1-one with NaTPFPBH yielded the allylic alcohol 4-carbethoxy-3-methylcyclohex-2-en-1-ol, with no concomitant reduction of the ester functionality. These results are summarized in Tables 3 and 4.

Reaction of NaTPFPBH with substituted cyclohexanones

Substituted cyclohexanones react with NaTPFPBH at 0 °C to yield the thermodynamically less stable isomers having an axial hydroxy group. Reduction of 4-methylcyclohexanone and 4-t-butylcyclohexanone with NaTPFPBH gave *cis*-4-methylcyclohexanol and *cis*-4-t-butylcyclohexanol, respectively [eqns. (9) and (10)].



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(10)

The ratio of diastereomeric products obtained is similar to that obtained with trialkylborohydride reducing agents [11]. An additional benefit in the case of the NaTPFPBH reduction reaction is that these reactions are carried out at 0 °C, instead of the typical −78 °C needed for the trialkylborohydride reduction reactions. The results for the reductions of substituted cyclohexanones with NaTPFPBH are summarized in Table 6.

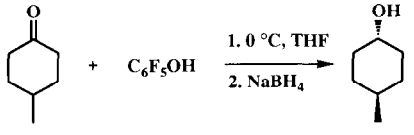
TABLE 6. Reaction of sodium tri(pentafluorophenoxy)-borohydride with substituted cyclohexanones in tetrahydrofuran at 0 °C

Compound[a]	*Trans* isomer[c] (%)	*Cis* isomer[c] (%)
2-methylcyclohexanone	12	88
2-methylcyclohexanone[b]	51	25
3-methylcyclohexanone	94	6
3-methylcyclohexanone[b]	1	99
4-methylcyclohexanone	0	100
4-methylcyclohexanone[b]	95	5
4-t-butylcyclohexanone	0	100
4-t-butylcyclohexanone[b]	76	0

[a]See general procedure for the reactions of NaTPFPBH with substituted cyclohexanones in the Experimental section of this communication.
[b]The substituted cyclohexanones along with $CeCl_3 \cdot 6H_2O$ (1 mmol each) were dissolved in 0.4 M MeOH. $NaBH_4$ (0.038 g, 1 mmol) was added in one portion with 3–5 min stirring [10].
[c]Diastercomeric ratio of alcohols determined by capillary GC analysis with authentic internal standards.

Reduction of substituted cyclohexanones with sodium borohydride in the presence of pentafluorophenol

As pointed out earlier, the reduction of substituted cyclohexanones using NaTPFPBH gave predominantly the axial alcohols as the products. We have found that by a simple modification of the reduction procedure we can control the stereochemical outcome of this reduction. Thus, mixing the substituted cyclohexanones first with pentafluorophenol (an acid source to protonate the carbonyl moiety) followed by the reaction with solid sodium borohydride afforded products containing predominantly the equatorial alcohol group. The combination of 4-methylcyclohexanone and 4-t-butylcyclohexanone with pentafluorophenol and subsequent reduction with sodium borohydride gave *trans*-4-methylcyclohexanone and *trans*-4-t-butylcyclohexanone, respectively [eqns. (11) and (12)].



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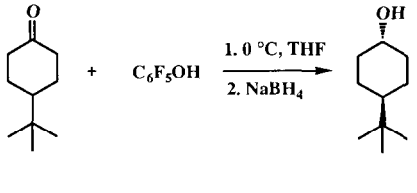

(12)

This makes NaTPFPBH reduction reactions with substituted cyclohexanones unique. Thus, one can selectively synthesize either isomer, axial or equatorial alcohol just by changing the order of addition of sodium borohydride and pentafluorophenol. The results are summarized in Table 5.

Reactions of NaTPFPBH with esters, lactones, epoxides, amides and nitriles

Esters, lactones and epoxides did not react with NaTPFPBH under the set reaction conditions examined. Hexanamide liberated 1 equiv. of hydrogen on reaction with NaTPFPBH with no further reduction. Nitriles were essentially inert towards reduction with NaTPFPBH.

Conclusions

The reducing properties of sodium tris(pentafluorophenoxy)borohydride (NaTPFPBH) are now characterized. The reagent is a very mild reducing agent. With the exception of aldehydes, highly reactive ketones and acid chlorides, all functional groups examined were inert toward NaTPFPBH. NaTPFPBH showed selectivity toward 1,2-reductions in α,β-unsaturated aldehydes and ketones to yield the corresponding allylic alcohols.

Reductions of substituted cyclohexanones with NaTPFPBH yielded the corresponding thermodynamically less stable alcohols with an axial hydroxy group. Unlike the reduction with trialkylborohydrides, the product alcohols are isolated by a non-oxidative work-up [11]. NaTPFPBH's side-product tris(pentafluorophenoxy)borane is easily and rapidly hydrolyzed by simple addition of an inorganic acid. The pentafluorophenol is easily recycled in the work-up process. Switching the order of addition of sodium borohydride and pentafluorophenol to reduce a substituted cyclohexanone gave very interesting results. In this case the corresponding thermodynamically more stable alcohols with an equatorial hydroxy group were predominantly formed.

In comparison with other sodium and potassium borohydrides, which suffer from having four equivalent hydrides per molecule, NaTPFPBH has only one hydride per molecule [12]. Consequently, through the reduction process, different intermediates with different reactivities form for the sodium and potassium borohydrides, while NaTPFPBH's side-product, tris(pentafluorophenoxy)borane, is unreactive under the reaction conditions examined*. Sodium and potassium borohydrides have a very low solubility in common organic solvents such as THF and Et_2O [13]. The use of NaTPFPBH should overcome such problems associated with other alkali metal borohydrides. NaTPFPBH exhibits excellent solubility in common organic solvents such as THF and

*The tris(pentafluorophenoxy)borane byproduct is easily and rapidly hydrolyzed with water and dilute hydrochloric acid.

Et_2O. This reducing agent can be readily prepared. It is stable without having to have an equilibrium concentration of alkali metal hydride present. Since potassium triisopropoxyborohydride is no longer commercially available, NaTPFPBH is an attractive alternative for these selective reductions.

Acknowledgements

This research was supported by faculty research funds granted by the University of California at Santa Cruz.

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