

Reaction of Lithium (2,3-Dimethyl-2-butyl)-*t*-butoxyborohydride with Selected Organic Compounds Containing Representative Functional Groups

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The general reducing characteristics of a newly synthesized reducing agent, lithium (2,3-dimethyl-2-butyl)-*t*-butoxyborohydride (Li Thx'BuOBH₂, **1**), in tetrahydrofuran (THF) toward selected organic compounds containing representative functional groups under practical conditions has been examined. The reagent revealed an interesting and unique reducing characteristics. Especially, the stereoselectivity in the reduction of cyclic ketones was extraordinary. Thus, the introduction of bulky alkyl and alkoxy groups into the parent borohydride affords a high stereoselectivity. In general, the reducing power of the reagent is somewhere between the dialkylborohydride and the parent borohydride. This permits the reagent to be a reagent of choice for selective reduction of organic compounds with an improved selectivity.

Keywords : Li Thx'BuOBH₂, Reduction, Organic compounds.

Introduction

In contrast to the reducing characteristics of lithium borohydride¹, its derivative lithium trialkylborohydride²⁻⁵ and dialkylborohydride⁶ are remarkably powerful and selective reducing agents. The introduction of alkyl groups accelerates the hydride donor activity tremendously. However, situation changes when alkoxy groups are introduced to lithium borohydride. For example, the reducing power of lithium triisopropoxyborohydride⁷ is much milder than that of lithium borohydride¹. Therefore, it appeared of interest to explore a mixed derivative, monoalkylmonoalkoxyborohydride, for its reducing characteristics.

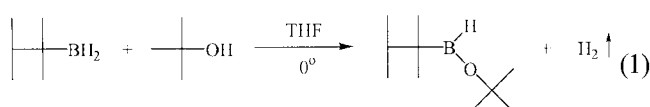
Because of easy preparation of thexyl'butoxyborane (Thx'BuOBH) and its simple conversion into lithium thexyl'butoxyborohydride (Li Thx'BuOBH₂, **1**), this derivative attracted our attention. Being a monoalkylmonoalkoxyborohydride, this reducing agent was anticipated to have different characteristics from those of dialkylborohydride such as lithium 9-boratabicyclo[3.3.1]nonane (Li 9-BBNH).⁶

We undertook a detailed study of the stoichiometry and products of the reaction of Li Thx'BuOBH₂ with selected organic compounds containing representative functional groups under the practical conditions.

Results and Discussion

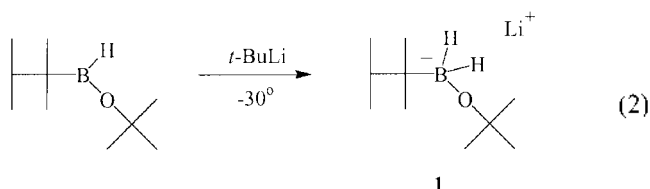
Preparation of Lithium Thexyl'butoxyborohydride (Li Thx'BuOBH₂, **1) Solutions.** Thexylborane (2,3-dimethyl-2-butylborane) has been prepared by the hydroboration of 2,3-dimethyl-2-butene with borane-THF in the ratio of 1 : 1.⁸ The reaction of thexylborane with excess *tert*-butyl alcohol at 0 and 25 °C was examined and the results are summarized in Table 1. As shown in the table, although thexylborane possesses two B-H bonds, it reacts only 1 equiv of *tert*-butyl alcohol even in the presence of excess amount at 0 or 25 °C

(Eq. 1).



The ¹¹B NMR spectrum of a solution of thexyl'butoxyborane in THF showed a doublet (*J*_{B,H} = 390 Hz) centered at δ 48.3 ppm relative to BF₃·OEt₂.

A solution of lithium thexyl'butoxyborohydride (Li Thx'Bu-



OBH₂, **1**) was prepared by adding a solution of *tert*-butyllithium⁹ in pentane to a solution of thexyl'butoxyborane in THF at -30 °C (Eq. 2). The ¹¹B NMR of a solution of **1** in

Table 1. Reaction of Thexylborane with Excess *tert*-Butyl Alcohol in Tetrahydrofuran^a

| Temperature (°C) | Time (min) | Hydrogen evolution ^b |
|------------------|------------|---------------------------------|
| 0 | 1 | 0.56 |
| | 5 | 0.89 |
| | 15 | 0.91 |
| | 30 | 1.00 |
| | 6 | 1.01 |
| 25 | 1 | 0.95 |
| | 5 | 1.00 |
| | 15 | 1.00 |
| | 30 | 1.00 |

^aTwo equiv of alcohol reacted. ^bMmol of per mmol of thexylborane.

Table 2. Reaction of Lithium Thexyl^tbutoxyborohydride with Representative Active Hydrogen Compounds at 0 °C^{a,b}

| Compound | Time (h) | Hydrogen evolved ^c | Hydride used ^c | Hydride used for reduction ^f |
|-----------------------------------|----------|-------------------------------|---------------------------|---|
| 1-hexanol | 0.25 | 0.17 | 0.17 | 0.00 |
| | 6 | 0.36 | 0.36 | 0.00 |
| | 24 | 0.40 | 0.40 | 0.00 |
| benzyl alcohol | 0.25 | 0.36 | 0.36 | 0.00 |
| | 6 | 0.38 | 0.38 | 0.00 |
| | 24 | 0.38 | 0.38 | 0.00 |
| 3-hexanol | 0.25 | 0.12 | 0.12 | 0.00 |
| | 6 | 0.38 | 0.38 | 0.00 |
| | 24 | 0.39 | 0.39 | 0.00 |
| 3-ethyl-3-pentanol | 0.25 | 0.06 | 0.06 | 0.00 |
| | 6 | 0.29 | 0.29 | 0.00 |
| | 24 | 0.30 | 0.30 | 0.00 |
| phenol | 0.25 | 0.98 | 0.98 | 0.00 |
| | 1 | 1.01 | 1.01 | 0.00 |
| | 6 | 1.01 | 1.01 | 0.00 |
| <i>n</i> -hexylamine ^d | 0.25 | 0.02 | 0.02 | 0.00 |
| | 6 | 0.17 | 0.17 | 0.00 |
| | 24 | 0.18 | 0.18 | 0.00 |
| 1-hexanethiol | 0.25 | 0.62 | 0.62 | 0.00 |
| | 1 | 0.73 | 0.73 | 0.00 |
| | 24 | 0.76 | 0.76 | 0.00 |
| benzenethiol | 0.25 | 0.99 | 0.99 | 0.00 |
| | 1 | 1.00 | 1.00 | 0.00 |
| | 6 | 1.00 | 1.00 | 0.00 |

^aIn a mixed solvent of THF and pentane. ^bReagent to compound is 1 : 1. ^cMmol of hydride per mmol of compound. ^dTwo equiv of reagent utilized.

a mixed solvent of THF and pentane showed a triplet ($J_{B,H} = 219$ Hz) centered at δ -7.6 ppm¹⁰ relative to BF₃·OEt₂.

Alcohols, Phenols, Amines, and Thiols (Active Hydrogen

Table 3. Reaction of Lithium Thexyl^tbutoxyborohydride with Representative Aldehydes and Ketones at 0 °C^a

| Compound | Time (h) | Ratio of rgt/cmpd | Product | Yield (%) ^b |
|----------------|----------|-------------------|------------------|------------------------|
| caproaldehyde | 0.5 | 0.5 | 1-hexanol | 99 |
| benzaldehyde | 0.5 | 0.5 | benzyl alcohol | 99.5 |
| | 1.0 | 0.5 | benzyl alcohol | 99.0 |
| 2-heptanone | 0.5 | 0.5 | 2-heptanol | 98.5 |
| norcamphor | 0.5 | 0.5 | norborneol | 99 |
| acetophenone | 3 | 0.5 | 1-phenylethanol | 81 |
| | 0.5 | 1.0 | 1-phenylethanol | 100 |
| benzophenone | 3 | 0.5 | benzhydrol | 38 |
| | 0.5 | 1.0 | benzhydrol | 78 |
| | 0.5 | 2.0 | benzhydrol | 100 |
| cinnamaldehyde | 0.5 | 0.5 | cinnamyl alcohol | 99.5 |

^aSee the corresponding footnote in Table 2. ^bAnalyzed by GC with a suitable internal standard.

Compounds). Among the alcohols examined, only phenol liberated hydrogen relatively fast and quantitatively. All the primary, secondary and tertiary alcohols examined liberated hydrogen very slowly and finally the hydrogen evolution was incomplete within 24 hours under the experimental conditions. The primary amine, *n*-hexylamine, also liberated hydrogen very slowly. The thiols examined appeared to be relatively reactive toward the reagent. Thus, 1-hexanethiol evolved about 70% hydrogen in 1 h and benzenethiol liberated a quantitative hydrogen within 1 h. The results are summarized in Table 2.

Aldehydes and Ketones. Simple aldehydes and ketones listed in Table 3 were cleanly reduced to the corresponding alcohols with the stoichiometric amount (a half equivalent) of 1. However, the reaction of aromatic ketones, such as acetophenone and benzophenone, with the stoichiometric

Table 4. Stereoselectivity in the Reduction of Cyclic Ketones with Lithium Thexyl^tbutoxyborohydride^{a,b}

| Ketone | Temperature (°C) | Time (h) | Conversion yield (%) ^c | Less stable isomer | Selectivity (%) |
|---------------------------------|------------------|----------|-----------------------------------|--------------------|-----------------|
| 2-methylcyclopentanone | 0 | 0.5 | 100 | <i>cis</i> | >99.5 |
| | -20 | 0.5 | 100 | | >99.5 |
| 2-methylcyclohexanone | 0 | 0.5 | 100 | <i>cis</i> | >99.5 |
| | -20 | 0.5 | 100 | | >99.9 |
| 2- <i>t</i> -butylcyclohexanone | 0 | 6 | 100 | <i>cis</i> | >99.5 |
| | -20 | 12 | 100 | | >99.9 |
| 3-methylcyclohexanone | 0 | 0.5 | 100 | <i>trans</i> | 96 |
| | -20 | 0.5 | 100 | | 98 |
| 4-methylcyclohexanone | 0 | 0.5 | 100 | <i>cis</i> | 92 |
| | -20 | 0.5 | 100 | | 94 |
| 4- <i>t</i> -butylcyclohexanone | 0 | 0.5 | 100 | <i>cis</i> | 95 |
| | -20 | 0.5 | 100 | | 97 |
| 3,3,5-trimethylcyclohexanone | 0 | 0.5 | 100 | <i>trans</i> | >99.5 |
| | -20 | 0.5 | 100 | | >99.9 |
| norcamphor | 0 | 0.5 | 100 | <i>endo</i> | 98 |
| | -20 | 0.5 | 100 | | 99.5 |
| camphor | 0 | 48 | 56 | <i>exo</i> | >99.5 |
| | -20 | 72 | 100 | | >99.5 |

^aSee the corresponding footnote in Table 2. ^bA 2 : 1 ratio for reagent to compound was utilized. ^cAnalyzed by GC.

Table 5. Comparison of Stereoselectivity in the Reduction of Cyclic Ketones with Representative Reagents at 0 °C

| Ketone | Selectivity (%) ^f | | | | |
|---------------------------------|--|------------------------------|---|-------------------------------------|----------------------------|
| | Li Thx ^g BuOBH ₂ | K 9-OThx-9-BBNH ^h | Li ⁱ Bu ₃ BH ^c | Li Sia ₃ BH ^h | K 9-Bu-9-BBNH ^d |
| 2-methylcyclohexanone | >99.5 | 98.5 | 99.3 | 99.4 | 99.5 |
| 3-methylcyclohexanone | 96 | 90 | 85 | 98 | 96 |
| 4-methylcyclohexanone | 92 | 85.5 | 80.5 | 93 | 94 |
| 4- <i>t</i> -butylcyclohexanone | 95 | 87 | 87.5 | 96.5 | 98.5 |
| 3,3,5-trimethylcyclohexanone | >99.5 | >99.9 | 99.8 | 99 | 99 |
| norcamphor | 98 | 95 | 99.6 | 99 | 95.5 |
| camphor | >99.5 | 97.5 | 99.6 | >99.9 | 99.9 |

^aAnalyzed by GC. The figures are ratio of the thermodynamically less stable epimers. ^bData taken from ref. 11. ^cData taken from ref. 13. ^dData taken from ref. 12.

amount was relatively slow, requiring a higher concentration of the reagent. In practice, one or two equivalents of reagent was needed to reduce such ketones completely to the corresponding alcohols. In the case of cinnamaldehyde, the reagent in a stoichiometric amount reduced it cleanly in a fashion of 1,2-reduction to provide cinnamyl alcohol in a yield of 99.5%.

Stereoselectivity Study. The stereoselectivity of the reagent **1** in the reduction of cyclic ketones is summarized in Table 4 and the compared data achieved by other representative reagents are listed in Table 5.

The reagent revealed an excellent stereoselectivity in the reduction of representative cyclic ketones both at 0 or -20 °C. Its stereoselectivity is comparable to the results previously achieved with lithium trisiamylborohydride (Li Sia₃BH)¹¹ and potassium 9-*t*-butyl-9-boratabicyclo[3.3.1]nonane (K 9-*t*-Bu-9-BBNH),¹² even higher than the selectivity shown by lithium tri-*n*-butylborohydride (Li ^{*n*}Bu₃BH)¹³ and potassium 9-(2,3-dimethyl-2-butoxy)-9-boratabicyclo[3.3.1]nonane (K 9-OThx-9-BBNH)¹¹ at 0 °C.

Quinones. Two examples for quinones were examined with 2 equiv of the reagent (H⁻/compd = 4) at 0 °C. The reaction of *p*-benzoquinone produced hydroquinone and 1,4-dihydroxycyclohexadiene in a 50 : 50 distribution ratio, along with 0.5 equiv of hydrogen evolution, whereas anthraquinone was reduced completely to give a quantitative yield of 9,10-dihydro-9,10-anthracenediol. The experimental data are summarized in Table 6.

Carboxylic Acids and Derivatives. Carboxylic acids and their derivatives were examined with an excess amount of

Table 6. Reaction of Lithium Thexylbutoxyborohydride with Representative Quinones at 0 °C^{a,b}

| Compound | Time (h) | Product | Yield (%) ^c |
|-------------------------------------|----------|---|------------------------|
| <i>p</i> -benzoquinone ^d | 12 | hydroquinone | 48 |
| | | 1,4-dihydroxycyclohexadiene | 51 |
| Anthraquinone ^e | 12 | 9,10-dihydroxyanthracene | 0 |
| | | 9,10-dihydro-9,10-dihydroxyanthracenediol | 99.9 |

^aSee the corresponding footnote in Table 2. ^bTwo equiv of reagent utilized. ^cAnalyzed by GC. ^dAlong with 0.5 equiv of hydrogen evolution. ^eNo hydrogen evolved.

Table 7. Reaction of Lithium Thexylbutoxyborohydride with Representative Carboxylic Acids and Their Derivatives at 0 °C^a

| Compound | Time (h) | Ratio of rgt/compd | Product | Yield (%) ^b |
|--------------------------------|-----------------|--------------------|----------------|------------------------|
| caproic acid ^c | 60 | 2.0 | none | |
| | 24 ^d | 2.0 | none | |
| benzoic acid ^c | 60 | 2.0 | none | |
| | 24 ^d | 2.0 | none | |
| caproyl chloride | 3 | 1.5 | 1-hexanol | 98 |
| benzoyl chloride | 3 | 1.5 | benzyl alcohol | 99 |
| ethyl caproate | 3 | 2.0 | 1-hexanol | 98 |
| ethyl benzoate | 3 | 2.0 | benzyl alcohol | 98 |
| capronitrile | 3 | 2.0 | 1-hexanol | 98 |
| benzonitrile | 3 | 2.0 | benzyl alcohol | 97 |
| caproamide ^e | 60 | 2.0 | none | |
| | 24 ^d | 2.0 | none | |
| benzamide ^e | 60 | 2.0 | none | |
| | 24 ^d | 2.0 | none | |
| <i>N,N</i> -dimethylcaproamide | 60 | 2.0 | none | |
| | 24 ^d | 2.0 | none | |
| <i>N,N</i> -dimethylbenzamide | 60 | 2.0 | none | |
| | 24 ^d | 2.0 | none | |

^aSee the corresponding footnote in Table 2. ^bAnalyzed by GC. ^cImmediately 1 equiv of hydrogen evolved. ^dAt 25 °C. ^eNo hydrogen evolved.

the reagent at 0 °C. The acids reacted with the reagent to evolve a quantitative amount of hydrogen immediately but the further reduction was not followed at all, whereas the primary and tertiary amides were inert to this reagent without any evolution of hydrogen. However, the acid chlorides, esters and nitriles were reduced readily and cleanly to the corresponding alcohols. The results are summarized in Table 7.

Sulfur Compounds. Among the sulfur compounds listed in Table 8, only the aliphatic disulfide, di-*n*-butyl disulfide, underwent quantitative reduction to *n*-butanethiol, along with 1 equiv of hydrogen evolution. Other sulfur compounds, such as aromatic disulfides, sulfoxides and sulfones, were inert to this reagent. Although methanesulfonic acid evolved 1 equiv of hydrogen immediately, no reduction was followed.

Epoxides. The results of reducing three epoxides are

Table 8. Reaction of Lithium Thexyl^tbutoxyborohydride with Representative Sulfur Compounds at 0 °C^a

| Compound | Time (h) | Ratio of rgt/cmpd | Product | Yield (%) ^b |
|--|----------|-------------------|-----------------------|------------------------|
| di- <i>n</i> -butyl disulfide ^c | 6 | 1.5 | <i>n</i> -butanethiol | 99 |
| diphenyl disulfide | 24 | 1.5 | none | |
| dimethyl sulfoxide | 24 | 1.5 | none | |
| diphenyl sulfone | 24 | 1.5 | none | |
| methanesulfonic acid ^d | 24 | 2.0 | none | |

^aSee the corresponding footnote in Table 2. ^bAnalyzed by GC. ^cAlong with 1 equiv of hydrogen evolution. ^dImmediately 1 equiv of hydrogen evolved.

Table 9. Reaction of Lithium Thexyl^tbutoxyborohydride with Representative Epoxides at 0 °C^a

| Compound | Time (h) | Ratio of rgt/cmpd | Product | Yield (%) ^b |
|-------------------|----------|-------------------|-----------------|------------------------|
| 1,2-epoxyoctane | 0.5 | 0.5 | 1-octanol | 1 |
| | | | 2-octanol | 98 |
| | 0.5 | 1 | 1-octanol | 0.5 |
| | | | 2-octanol | 99.4 |
| styrene oxide | 0.5 | 0.5 | 1-phenylethanol | 96 |
| | | | 2-phenylethanol | 4 |
| | 0.5 | 1 | 1-phenylethanol | 98.5 |
| | | | 2-phenylethanol | 0.5 |
| cyclohexene oxide | 0.5 | 0. | cyclohexanol | 99.9 |

^aSee the corresponding footnote in Table 2. ^bAnalyzed by GC.

summarized in Table 9. The aliphatic epoxides examined were rapidly reduced with a quantitative amount of the reagent to give the S_N2-type of ring-opened products exclusively, whereas the reaction of styrene oxide, an aromatic one, with a theoretical amount of the reagent afforded a mixture of 96% 1-phenylethanol and 4% 2-phenylethanol. However, the reagent in an excess amount (H⁻/compd = 2) reduced styrene oxide to give an almost single product, 1-phenylethanol, in a yield of 98.5%.

Conclusion

The reducing power of a newly synthesized monoalkyl-monoalkoxyborohydride, lithium (2,3-dimethyl-2-butyl)-*t*-butoxyborohydride (lithium thexyl^tbutoxyborohydride, Li Thx^tBuO BH₂, 1), in a mixed solvent of THF and pentane toward organic compounds containing representative functional groups under practical conditions has been investigated. The results reveal that the reducing power of the reagent is somewhere between the dialkylborohydride and the parent borohydride. The reducing power of the lithium borohydride derivatives appears in the order of LiR₃BH > LiR₂BH₂ > LiR(RO)BH₂ > LiBH₄ > Li(RO)₃BH. The introduction of alkyl and alkoxy groups into the parent borohydride affords an interesting and unique reducing characteristics. Consequently, this reagent should find a valuable role as a reagent of choice in organic synthesis.

Experimental Section

All glassware used in the experiments was predried thoroughly in a drying oven and cooled under a dry nitrogen atmosphere. Hypodermic syringes were used to transfer solutions. All reactions were carried out under a static pressure of nitrogen in flasks fitted with septum-covered sidearms with use of standard techniques for handling air-sensitive materials.¹⁴

Materials. Most of the organic compounds utilized in this study were commercial products of the highest purity. They were further purified by distillation or recrystallization when necessary. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl and stored under dry nitrogen. A solution of *tert*-butyllithium was purchased from the Aldrich Chemical Co. A solution of BH₃ in THF was synthesized by the reaction of sodium borohydride and dimethyl sulfate.¹

Instruments. GC analyses were carried out on a Varian 3300 FID with capillary columns of DB-WAX (30 m) and HP-FFAP (25 m). All GC yields were determined with use of a suitable internal standard and authentic mixtures. NMR spectrometer used was a Bruker AMX 300.

Preparation of a Solution of Thx^tBuOBH. An oven-dried, 1-L, round-bottom flask with a sidearm, equipped with a magnetic stirring bar and an adapter, was attached to a mercury bubbler. The flask was flushed with dry nitrogen and then maintained under a static pressure of nitrogen. The flask was charged with 329 mL of a 1.52 M solution of BH₃-THF (500 mmol) and maintained at 0° with the aid of ice-water bath. Into the flask 44.2 g of 2,3-dimethyl-2-butene (525 mmol) was injected slowly and the mixture was stirred for 3 h. The concentration of a solution of thexylborane was estimated gasometrically to indicate 1.25 M. The ¹¹B NMR spectrum showed a triplet (*J*_{B-H} = 359 Hz) centered at δ 24.4 ppm relative to BF₃·OEt₂.

Into the flask was charged with 320 mL of a solution of thexylborane (400 mmol) thus prepared above and the flask was immersed into an ice-water bath. To this 31.4 g of *tert*-butyl alcohol (420 mmol) was injected dropwise. After the complete evolution of hydrogen, the reaction mixture was stirred for additional 1 h. The concentration of the solution was estimated by hydrolysis to indicate 1.07 M. The ¹¹B NMR spectrum exhibited a doublet (*J*_{B-H} = 390 Hz) centered at δ 48.3 ppm.

Preparation of a Solution of Li Thx^tBuOBH₂. 1. Into a 100-mL flask was placed 40 mL of a solution of Thx^tBuOBH (40.3 mmol) thus prepared above and the flask was cooled to -30° by use of a refrigerating bath circulator. To this flask was added 26 mL of a precooled 1.7 M solution of *tert*-butyllithium (44 mmol) in pentane dropwise with vigorous stirring. After the reaction mixture was stirred for additional 1 h at -30°, the flask was brought to 0°. The concentration of the reagent was estimated gasometrically by hydrolyzing an aliquot to give 0.60 M of Li Thx^tBuOBH₂: ¹¹B NMR (THF and pentane) δ 7.6 ppm (*t*, *J*_{B-H} = 219 Hz).¹⁰

General Procedure Used for Reductions. The following

procedure was used for general reductions. The reduction of benzaldehyde is described as an example of the experimental procedure. The reagent **1** solution, 16.7 mL of 0.60 M (10 mmol of the reagent, 20.0 mmol of hydride), was introduced into a dried, 50-mL flask fitted with a rubber syringe cap on an inlet port, a magnetic stirring bar, and a bent adapter connected to a gas burette through a reflux condenser and a dry ice vapor trap. The flask was immersed in an ice-water bath, the stirred solution was maintained at 0°, and 1.07 g of benzaldehyde (10.0 mmol) in 2 mL of THF and tridecane (5 mmol) as an internal standard was injected. After 30 min, a 4.0-mL aliquot of the reaction mixture was removed and injected into a buffer solution (pH 7). After then, the solution was treated with 2 mL of 3 N NaOH and 2 mL of 30% H₂O₂ with stirring at room temperature for 2 h. The aqueous layer was saturated with K₂CO₃. The separated organic layer was washed with saturated NaCl solution and dried over anhydrous MgSO₄. The gas chromatographic analysis showed 99.5% benzyl alcohol. Aliquot was also removed after 1.0 h of the reaction time and worked up for GC analysis. The yield appeared to be 99%. Obviously, the reaction was complete within 0.5 h.

General Procedure for Stereoselectivity Studies. The reduction of 2-methylcyclohexanone is described as representative. To a 50-mL flask was added 8.4 mL of 0.60 M solution of the reagent **1** (5.0 mmol). The flask was cooled to -20° with use of a refrigerating bath circulator and to this was added 1.0 mL of a precooled solution of 2-methylcyclohexanone (0.29 g, 2.5 mmol) in THF. After 30 min, the reaction mixture was quenched with 3 N NaOH and oxidized with 30% H₂O₂ for 2 h at room temperature. The aqueous layer was saturated with K₂CO₃. The separated organic layer was washed with saturated NaCl and dried over anhydrous MgSO₄. The gas chromatographic analysis with use of a 30 m capillary column of DB-WAX showed no presence of the

starting ketone (*i.e.*, 100% conversion) and >99.5% *cis*-2-methylcyclohexanol along with only trace amount of the *trans*-isomer. The results are summarized in Table 4.

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