evaporated in vacuo and the residue was suspended in DMF (500 mL). Then *n*-hexadecyl iodide (11.28 g, 32 mmol) was added and the mixture was stirred for 72 h at 80 °C. The solvent was removed in vacuo and the residue was taken up in chloroform and filtered. The solvent was slowly evaporated and the light yellow precipitate was filtered off and crystallized from anhydrous ethanol. The crystals were dried over $CaCl_2$ in vacuum desiccator: yield 10.49 g (70.1%); mp 52.6–53.3 °C; $^1H$ NMR ($CDCl_3$) $\delta$ 0.9 (t, 3 H), 1.3 (m, 28 H), 4.46 (t, 2 H), 7.3–8.7 (m, 10 H). Anal. Calcd for $C_{32}H_{43}NO_2$: C, 81.14; N, 9.15; N, 2.96. Found: C, 81.22; H, 8.98; N, 3.23.

**Differential Scanning Calorimetry (DSC).** These experiments were carried out by using a Perkin-Elmer DSC-2 apparatus as described previously.[20] The $T_c$ values were reproducible to within 2 °C.

**Vesicle solutions** were prepared using method A[5] or B (see text). Ultrasonic irradiation was carried out by using a Branson Sonifier Cell Disruptor B15 and/or a Bransonic 220 water bath.

**Electron Microscopy.** Micrographs were obtained by using negative staining as well as freeze-fracture techniques. The negative stained samples were prepared as described previously,[5,10] using 1% (by weight) solutions of uranyl acetate or ammonium molybdate as negative stain. The freeze-fracture replicas were obtained as in previous studies.[10] All samples were examined by using a Philips 300 electron microscope at 80 kV and photographed by using Kodak 4463 sheets.

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**Registry No.** 1, 90990-83-3; 2, 91002-39-0; 3, 90990-84-4; 4, 90990-85-5; 5, 90990-86-6; 6, 90990-87-7; 7, 90990-88-8.

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# Selective Reductions. 36. Reaction of Lithium 9-Boratabicyclo[3.3.1]nonane with Selected Organic Compounds Containing Representative Functional Groups

Herbert C. Brown* and C. Poonnoose Mathew

*Richard B. Wetherill Laboratory, Purdue University, West Lafayette, Indiana 47907*

Chongsuh Pyun, Jong Chan Son, and Nung Min Yoon

*Department of Chemistry, Sogang University, Seoul 121, Korea*

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The approximate rates, stoichiometry, and products of the reaction of lithium 9-boratabicyclo[3.3.1]nonane with selected organic compounds containing representative functional groups were examined under standard conditions (tetrahydrofuran, room temperature) in order to explore the reducing characteristics of this reagent and to establish the utility of the reagent as a selective reducing agent. Primary alcohols, phenols, and thiols evolve hydrogen rapidly and quantitatively. However, the reaction of 3-hexanol and 3-ethyl-3-pentanol is very slow. *n*-Hexylamine is inert to this reagent. Aldehydes and ketones are reduced rapidly and quantitatively to the corresponding alcohols. Even the highly hindered ketone, 2,2,4,4-tetramethyl-3-pentanone, is reduced within 30 min. Reduction of camphor gives 91% isoborneol and 9% borneol, respectively. Cinnamaldehyde is rapidly reduced to the cinnamyl alcohol quantitatively without attacking the double bond. Carboxylic acids liberate hydrogen rapidly and quantitatively, but further reduction is very slow. Anhydrides consume 2 equiv of hydride without further hydride uptake, corresponding to reduction to an equimolar mixture of carboxylic acid and alcohol. Acid chlorides, esters, and lactones are rapidly reduced to the corresponding alcohols. Epoxides utilize 1 equiv of hydride at a moderate rate. In the case of unsymmetrical epoxides, the Markovnikov ring opening is predominant. Acetal, ketal, and ortho esters are inert to this reagent. Primary amides liberate hydrogen slowly. Caproamide undergoes slow reduction, but benzamide is not reduced. Tertiary amides consume 2 equiv of hydride slowly, undergoing reduction to the corresponding amines. Benzonitrile is reduced to the amine stage within 12 h; however, an aliphatic nitrile, capronitrile, is reduced only sluggishly. 1-Nitropropane rapidly liberates 1 equiv of hydrogen, but further reduction is very slow. Nitrobenzene utilizes 2.5 equiv of hydride, 1 for hydrogen evolution and 1.5 for reduction. Azobenzene is inert and azoxybenzene is reduced very sluggishly. Cyclohexanone oxime rapidly evolves 1 equiv of hydrogen, but no reduction is observed. Phenyl isocyanate consumes only 1 equiv of hydride to proceed to the formanilide stage. Pyridine is reduced very slowly. However, pyridine *N*-oxide undergoes rapid reduction with this reagent. Disulfides are rapidly reduced to the thiol stage, whereas, sulfoxides, sulfones, sulfonic acids, and sulfides are inert to this reagent. Cyclohexyl tosylate is also inert, but *n*-octyl tosylate undergoes reduction within 3.0 h. This hydride is inert to a typical *n*-alkyl chloride but reacts moderately with an *n*-alkyl bromide and rapidly with an *n*-alkyl iodide. A secondary alkyl bromide is almost inert to this hydride.

In contrast to the mild reducing characteristics of lithium borohydride,[1] its derivative lithium trialkylborohydride[2-5] is a remarkably powerful and selective reducing agent. The introduction of three alkyl groups changes the hydride donor activity tremendously. Therefore, it appeared of interest to explore monoalkyl- and dialkylborohydrides for their reducing characteristics.

Recently preparative procedures for various alkali metal alkylborohydrides have been reported.[6-11] Because of the

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commercial availability of 9-borabicyclo[3.3.1]nonane (9-BBN) and its simple conversion into lithium 9-boratabicyclo[3.3.1]nonane (Li9-BBNH), this derivative attracted our attention.[10] Being a dialkylborohydride, this reducing agent was anticipated to have different characteristics from those of lithium triethylborohydride.[12] Moreover, being a "basic" borohydride, its reducing characteristics should be quite different from those of the "acidic" reducing agent, 9-BBN.[13]

We undertook a detailed study of the rate, stoichiometry, and products of the reaction of Li9-BBNH with our standard list of organic compounds containing representative functional groups. A number of additional derivatives were of interest and they were added, making a total list of 71 compounds. The results of this investigation are reported in the present paper.

## Results and Discussion

**Experimental Approach. A. Preparation of Standard Solutions of Li9-BBNH in THF.**[10] Solutions of Li9-BBNH in THF were conveniently prepared by refluxing 1 equiv of 9-BBN with excess of finely divided lithium hydride (0.5 equiv excess) in THF for 24 h, followed by stirring for another 24 h at room temperature. The excess lithium hydride was removed by filtration through sintered glass filter under a stream of dry nitrogen. The concentration was determined by hydrolyzing a known aliquot of the solution with THF–glycerine–water (1:1:1) at room temperature and measuring the hydrogen evolved. The yields were quantitative. Such solutions are quite stable under a dry nitrogen atmosphere at room temperature.[10].

**B. Procedure for Rate and Stoichiometry Studies.** In order to define the reduction characteristics of Li9-BBNH, we undertook to examine the rates and stoichiometry of the reaction with excess hydride of 71 organic compounds containing representative functional groups. The procedure adopted was to add 5 mmol of organic compound containing a representative functional group to 10 mmol of Li9-BBNH in sufficient THF to give a 20-mL solution.

This made the reaction mixture 0.5 M in Li9-BBNH and 0.25 M in the compound under examination. The mixtures were maintained at room temperature (15 ± 2 °C) and the aliquots were removed at appropriate intervals of time and analyzed for residual hydride by hydrolysis. Simultaneously, a blank was run in which 5 mL of THF was added in place of the 5 mL of THF solution of the compound, all other conditions being the same. In this manner it was possible to establish both the rate at which reduction proceeds and the stoichiometry of the reactions (number of hydrides utilized per mole of the compound) when the reaction proceeds to essential completion under the reaction conditions.

**C. Product Analysis by GC.** Having established the approximate rate and stoichiometry of the reaction, it was desirable to establish the nature of the products wherever they offer the possibility for a useful selective reduction. Accordingly, separate reactions on a 5-mmol scale were carried out by using either a stoichiometric amount of the reagent or an excess amount, depending on the nature of the reaction.

The products were then identified by GC comparison with authentic samples and the yields determined by GC, utilizing internal standards and standard synthetic mixtures.

**Table I. Reaction of Lithium 9-Boratabicyclo[3.3.1]nonane with Representative Alcohols, Phenols, Amines, and Thiols in Tetrahydrofuran at Room Temperature (15 ± 2 °C)**

| compd[a] | time, h | $H_2$ evolved[b] | hydride used[b] | hydride used for reductn[b] |
|---|---|---|---|---|
| 1-hexanol | 0.5 | 0.84 | 0.84 | 0.00 |
| | 1.0 | 0.95 | 0.95 | 0.00 |
| | 1.5 | 1.01 | 1.01 | 0.00 |
| | 3.0 | 1.01 | 1.01 | 0.00 |
| benzyl alcohol | 0.5 | 1.02 | 1.02 | 0.00 |
| | 1.0 | 1.02 | 1.02 | 0.00 |
| 3-hexanol | 1.0 | 0.07 | 0.07 | 0.00 |
| | 3.0 | 0.12 | 0.12 | 0.00 |
| | 6.0 | 0.16 | 0.16 | 0.00 |
| | 24.0 | 0.18 | 0.18 | 0.00 |
| 3-ethyl-3-pentanol | 1.0 | 0.02 | 0.02 | 0.00 |
| | 3.0 | 0.03 | 0.03 | 0.00 |
| | 6.0 | 0.04 | 0.04 | 0.00 |
| | 24.0 | 0.07 | 0.07 | 0.00 |
| phenol | 0.25 | 1.03 | 1.03 | 0.00 |
| | 0.5 | 1.03 | 1.03 | 0.00 |
| 2,6-di-*tert*-butylphenol[c] | 0.25 | 0.81 | 0.81 | 0.00 |
| | 0.5 | 1.02 | 1.02 | 0.00 |
| | 1.0 | 1.02 | 1.02 | 0.00 |
| *n*-hexylamine | 1.0 | 0.02 | 0.02 | 0.00 |
| | 3.0 | 0.04 | 0.04 | 0.00 |
| | 6.0 | 0.05 | 0.05 | 0.00 |
| | 24.0 | 0.06 | 0.06 | 0.00 |
| benzenethiol | 0.25 | 1.00 | 1.00 | 0.00 |
| | 0.5 | 1.00 | 1.00 | 0.00 |
| 1-hexanethiol | 0.25 | 0.98 | 0.98 | 0.00 |
| | 0.5 | 0.98 | 0.98 | 0.00 |

[a] 5 mmol of compound was added to 10 mmol of Li9-BBNH (20 mmol of hydride in 20 mL of solution, 0.25 M in compound and 1.0 M in hydride). [b] mmol/mmol of compound. [c] Immediate color change to light blue, then slowly fades away with formation of white precipitate after 40 min.

**Rate and Stoichiometry. A. Alcohols, Phenols, Amines, and Thiols.** Among the alcohols examined, only primary alcohols liberate hydrogen rapidly and quantitatively. The secondary alcohol, 3-hexanol, liberates hydrogen very slowly, and the tertiary alcohol, 3-ethyl-3-pentanol, is almost inert to the reagent under the experimental conditions. Thus the rate of hydrogen evolution for alcohols decreases in the order: primary ≫ secondary > tertiary. Phenol, 2,6-di-*tert*-butylphenol, and thiols liberate hydrogen instantly and quantitatively. 2,6-Di-*tert*-butylphenol is known to be inert to 9-BBN,[13] the parent compound of Li9-BBNH.

*n*-Hexylamine is inert to the reagent under the experimental conditions. The results are summarized in Table I.

**B. Aldehydes and Ketones.** The aldehydes and ketones examined rapidly utilize 1 equiv of hydride, indicating clean reduction to the corresponding alcohols. Even the hindered ketone, 2,2,4,4-tetramethyl-3-pentanone, is rapidly reduced. This ketone is known to be inert to 9-BBN,[13] the parent compound of Li9-BBNH.

Cinnamaldehyde utilizes 1 equiv of hydride rapidly and shows no further uptake of hydride under the experimental conditions, indicating rapid reduction to the cinnamyl alcohol stage. In fact, cinnamaldehyde gave cinnamyl

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**Table II. Reaction of Lithium 9-Boratabicyclo[3.3.1]nonane with Representative Aldehydes and Ketones in Tetrahydrofuran at Room Temperature (15 ± 2 °C)**

| compd[a] | time, h | $H_2$ evolved[b] | hydride used[b] | hydride used for reductn[b] |
|---|---|---|---|---|
| caproaldehyde | 0.5 | 0.03 | 1.04 | 1.01 |
| | 1.0 | 0.03 | 1.04 | 1.01 |
| benzaldehyde | 0.5 | 0.09 | 1.15 | 1.06 |
| | 1.0 | 0.09 | 1.15 | 1.06 |
| 2-heptanone | 0.5 | 0.04 | 1.09 | 1.05 |
| | 1.0 | 0.04 | 1.09 | 1.05 |
| norcamphor | 0.5 | 0.05 | 1.12 | 1.07 |
| | 1.0 | 0.05 | 1.12 | 1.07 |
| camphor | 0.5 | 0.05 | 1.09 | 1.05 |
| | 1.0 | 0.05 | 1.09 | 1.05 |
| acetophenone | 0.5 | 0.08 | 1.12 | 1.04 |
| | 1.0 | 0.08 | 1.12 | 1.04 |
| benzophenone | 0.5 | 0.02 | 1.04 | 1.02 |
| | 1.0 | 0.02 | 1.04 | 1.02 |
| 2,2,4,4-tetramethyl-3-pentanone | 0.5 | 0.11 | 1.13 | 1.02 |
| | 1.0 | 0.11 | 1.13 | 1.02 |
| cinnamaldehyde | 0.5 | 0.03 | 1.03 | 1.00 |
| | 1.0 | 0.03 | 1.03 | 1.00 |
| | 3.0 | 0.03 | 1.03 | 1.00 |
| | 6.0 | 0.03 | 1.05 | 1.02 |
| | 24.0 | 0.03 | 1.05 | 1.02 |

[a,b] See the corresponding footnotes in Table I.

**Table III. Stereochemistry of the Reduction of Representative Cyclic and Bicyclic Ketones with Lithium 9-Boratabicyclo[3.3.1]nonane in Tetrahydrofuran at Room Temperature (15 ± 2 °C)**

| ketone | $H^-$/compd | time, h | total yield, % | less stable isomer | % |
|---|---|---|---|---|---|
| 2-methylcyclohexanone | 1.0 | 1.0 | 94 | cis | 63 (40)[a] |
| 4-*tert*-butylcyclohexanone | 1.1 | 1.0 | 100 | cis | 24 (8) |
| norcamphor | 1.1 | 1.0 | 100 | endo | 94 (91) |
| camphor | 1.1 | 1.0 | 100 | exo | 91 (75) |

[a] Numbers in the parenthesis are % of the isomers obtained with 9-BBN (ref Brown, H. C.; Krishnamurthy, S.; Yoon, N. M. *J. Org. Chem.* **1975**, *40*, 1864).

alcohol in 97% yield with a slight excess (10%) over the stoichiometric quantity of Li9-BBNH in 1 h at 15 °C.

$$\mathrm{PhCH{=}CHCHO} + \underset{10\%\ \text{excess}}{\text{Li9-BBNH}} \xrightarrow[15\ ^\circ\mathrm{C},\ 1\ \mathrm{h}]{\mathrm{THF}} \underset{97\%}{\mathrm{PhCH{=}CHCH_2OH}}$$

These results are summarized in Table II.

The stereochemistry of cyclic and bicyclic ketones, such as 2-methylcyclohexanone, 4-*tert*-butylcyclohexanone, norcamphor, and camphor, was examined. The results indicate that Li9-BBNH attacked more from the less hindered side of the carbonyl group than 9-BBN.[13] The results are summarized in Table III.

**C. Quinones.** *p*-Benzoquinone rapidly consumes 1.41 equiv of hydride, of which 0.47 is utilized for hydrogen evolution, and the remaining 0.94 for reduction. A blue-black, gelatinous precipitate is observed. The precipitate may have prevented the reduction going to completion since reduction to either hydroquinone or 1,4-dihydroxycyclohexadiene requires 2 equiv of hydride uptake.

Anthraquinone rapidly utilizes 1.95 equiv of hydride, of which 0.29 is used for hydrogen evolution and 1.66 for reduction, suggesting that 9,10-dihydroxyanthracene and 9,10-dihydro-9,10-anthracenediol both were formed in approximately 30% and 70%, respectively. The results are summarized in Table IV.

**Table IV. Reaction of Lithium 9-Boratabicyclo[3.3.1]nonane with Representative Quinones in Tetrahydrofuran at Room Temperature (15 ± 2 °C)**

| compd[a] | time, h | $H_2$ evolved[b] | hydride used[b] | hydride used for reductn[b] |
|---|---|---|---|---|
| *p*-benzoquinone[c,d] | 1.0 | 0.47 | 1.41 | 0.94 |
| | 3.0 | 0.47 | 1.41 | 0.94 |
| anthraquinone[c,e,f] | 1.0 | 0.29 | 1.95 | 1.66 |
| | 3.0 | 0.29 | 1.95 | 1.66 |

[a,b] See the corresponding footnotes in Table I. [c] Each measurement was done separately on a 2-mmol scale and by hydrolyzing the reaction mixture in a reaction flask. [d] Gelatinous blue-black precipitate. [e] Reverse addition (hydride solution was added to suspension of anthraquinone). [f] Immediate reddish-brown precipitate.

**Table V. Reaction of Lithium 9-Boratabicyclo[3.3.1]nonane with Representative Carboxylic Acids and Acyl Derivatives in Tetrahydrofuran at Room Temperature (15 ± 2 °C)**

| compd[a] | time, h | $H_2$ evolved[b] | hydride used[b] | hydride used for reductn[b] |
|---|---|---|---|---|
| caproic acid[c] | 1.0 | 1.08 | 1.23 | 0.15 |
| | 3.0 | 1.08 | 1.27 | 0.19 |
| | 6.0 | 1.08 | 1.29 | 0.21 |
| | 24.0 | 1.08 | 1.33 | 0.25 |
| benzoic acid[d] | 1.0 | 1.03 | 1.08 | 0.05 |
| | 3.0 | 1.03 | 1.08 | 0.05 |
| | 6.0 | 1.03 | 1.08 | 0.05 |
| | 24.0 | 1.03 | 1.18 | 0.15 |
| acetic anhydride[e] | 0.5 | 0.10 | 2.18 | 2.08 |
| | 1.0 | 0.10 | 2.18 | 2.08 |
| | 3.0 | 0.10 | 2.18 | 2.08 |
| | 6.0 | 0.10 | 2.18 | 2.08 |
| succinic anhydride[f] | 0.5 | 0.10 | 2.17 | 2.07 |
| | 1.0 | 0.10 | 2.17 | 2.07 |
| | 3.0 | 0.10 | 2.17 | 2.07 |
| | 6.0 | 0.10 | 2.17 | 2.07 |
| phthalic anhydride[g] | 0.5 | 0.25 | 2.28 | 2.03 |
| | 1.0 | 0.25 | 2.28 | 2.03 |
| | 3.0 | 0.25 | 2.28 | 2.03 |
| | 6.0 | 0.25 | 2.28 | 2.03 |
| caproyl chloride | 0.5 | 0.04 | 2.08 | 2.04 |
| | 1.0 | 0.04 | 2.08 | 2.04 |
| benzoyl chloride | 0.5 | 0.03 | 2.05 | 2.02 |
| | 1.0 | 0.03 | 2.05 | 2.02 |

[a,b] See the corresponding footnotes in Table I. [c] White precipitate within 15 min. [d] White precipitate between 3.0 and 6.0 h. [e] Immediately became turbid. [f] Reverse addition. [g] White precipitate after 6.0 h.

**D. Carboxylic Acids and Acyl Derivatives.** Both caproic acid and benzoic acid liberate hydrogen rapidly and quantitatively. The reaction mixture of caproic acid immediately turned milky when the carboxylic acid is added to the reagent. However, the corresponding reaction mixture of benzoic acid turned milky after 3.0 h. Further reduction of the acids is very sluggish.

Acid anhydride rapidly consumes 2 equiv of hydride without further hydride uptake, corresponding to reduction to the carboxylic acid and alcohol stages. Acid chlorides rapidly utilize 2 equiv of hydride to proceed to the corresponding alcohols.

Such behavior of carboxylic acids and acyl derivatives has already been noted in the reactions with lithium triethylborohydride.[12] The results are summarized in Table V.

**E. Esters and Lactones.** All of the esters and lactones examined rapidly utilized 2 equiv of hydride to proceed to the corresponding alcohol and diol stage, respectively.

**Table VI. Reaction of Lithium 9-Boratabicyclo[3.3.1]nonane with Representative Esters and Lactones in Tetrahydrofuran at Room Temperature (15 ± 2 °C)**

| compd[a] | time, h | $H_2$ evolved[b] | hydride used[b] | hydride used for reductn[b] |
|---|---|---|---|---|
| ethyl caproate | 0.5 | 0.03 | 2.06 | 2.03 |
| | 1.0 | 0.03 | 2.06 | 2.03 |
| ethyl benzoate | 0.5 | 0.03 | 2.08 | 2.05 |
| | 1.0 | 0.03 | 2.08 | 2.05 |
| phenyl acetate | 0.5 | 0.04 | 2.09 | 2.05 |
| | 1.0 | 0.04 | 2.09 | 2.05 |
| γ-butyrolactone[c] | 0.5 | 0.05 | 2.14 | 2.09 |
| | 1.0 | 0.05 | 2.14 | 2.09 |
| phthalide[d] | 0.5 | 0.03 | 2.08 | 2.05 |
| | 1.0 | 0.03 | 2.08 | 2.05 |
| isopropenyl acetate | 0.5 | 0.04 | 2.50 | 2.46 |
| | 1.0 | 0.04 | 2.69 | 2.65 |
| | 3.0 | 0.04 | 2.80 | 2.76 |
| | 24.0 | 0.04 | 2.83 | 2.79 |

[a,b] See the corresponding footnotes in Table I. [c] Immediate white precipitate. [d] Immediate color change to yellow and white precipitate.

Similar observations were realized with lithium triethylborohydride.[12]

Ethyl benzoate and ethyl caprylate are selectively reduced in the presence of an equimolar amount of caproic acid, producing quantitatively benzyl alcohol and 1-octanol, respectively. No trace of 1-hexanol is detected in the above two competitive reactions. Thus it is demonstrated that

$$\underset{5\ \text{mmol}}{\text{PhCOOEt}} + \underset{5\ \text{mmol}}{n\text{-}C_5H_{11}COOH} + \underset{10\ \text{mmol}}{\text{Li9-BBNH}} \xrightarrow[15\ ^\circ\text{C},\ 0.5\ \text{h}]{\text{THF}} \underset{5\ \text{mmol}}{PhCH_2OH} + \underset{\text{not detected}}{n\text{-}C_6H_{13}OH}$$

$$\underset{5\ \text{mmol}}{n\text{-}C_7H_{15}COOEt} + \underset{5\ \text{mmol}}{n\text{-}C_5H_{11}COOH} + \underset{10\ \text{mmol}}{\text{Li9-BBNH}} \xrightarrow[15\ ^\circ\text{C},\ 0.5\ \text{h}]{\text{THF}} \underset{5\ \text{mmol}}{n\text{-}C_8H_{17}OH} + \underset{\text{not detected}}{n\text{-}C_6H_{13}OH}$$

selective reduction of an ester group is possible in the presence of the free carboxylic acid group.

As will be discussed later, a typical *n*-alkyl bromide is reduced at a moderate rate by Li9-BBNH. Yet ethyl acetate could be selectively reduced in the presence of *n*-octyl bromide. Thus a mixture of ethyl acetate (5 mmol) and *n*-octyl bromide (5 mmol) was treated in THF with Li9-BBNH (5 mmol) at 25 °C for 15 min and the product analysis of the resulting reaction mixture revealed that 9.21 mmol of ethanol was formed and 4.9 mmol of *n*-octyl bromide remained intact.

$$\underset{5\ \text{mmol}}{CH_3COOEt} + \underset{5\ \text{mmol}}{n\text{-}C_8H_{17}Br} + \underset{5\ \text{mmol}}{\text{Li9-BBNH}} \xrightarrow[25\ ^\circ\text{C},\ 15\ \text{min}]{\text{THF}} \underset{9.21\ \text{mmol}}{2EtOH} + \underset{4.9\ \text{mmol}}{n\text{-}C_8H_{17}Br}$$

Isopropenyl acetate utilized 3 equiv of hydride, as in the reaction with lithium triethylborohydride,[12] suggesting reduction of the acetate group to the ethanol stage and the isopropenyl group to the 2-propanol stage. The results are summarized in Table VI.

**F. Epoxides, Acetals, Ketals, and Ortho Esters.** 1,2-Butylene oxide, styrene oxide, cyclohexene oxide, and 1-methyl-1,2-cyclohexene oxide consume 1 equiv of hydride within 0.25 h, 1.0 h, 1.5 h, and 24 h, respectively. The reactivity order is well in accordance with the steric requirements of the epoxides examined. The ring opening of the epoxides proceeds at the less hindered sides of the compounds, as was noted in the reactions of lithium triethylborohydride.[12] Thus 1,2-butylene oxide gives 2-butanol in 99% yield (1-butanol, 1%) and styrene oxide gives 1-phenylethanol in 93% yield (2-phenylethanol, 7%), respectively.

**Table VII. Reaction of Lithium 9-Boratabicyclo[3.3.1]nonane with Representative Epoxides, Acetals, Ketals, and Ortho Esters in Tetrahydrofuran at Room Temperature (15 ● 2 °C)**

| compd[a] | time, h | $H_2$ evolved[b] | hydride used[b] | hydride used for reductn[b] |
|---|---|---|---|---|
| 1,2-butylene oxide | 0.25 | 0.03 | 1.05 | 1.02 |
| | 0.5 | 0.03 | 1.05 | 1.02 |
| styrene oxide | 0.5 | 0.04 | 0.93 | 0.89 |
| | 1.0 | 0.04 | 1.10 | 1.06 |
| | 2.0 | 0.04 | 1.10 | 1.06 |
| cyclohexene oxide | 0.5 | 0.02 | 0.67 | 0.65 |
| | 1.0 | 0.02 | 0.90 | 0.88 |
| | 1.5 | 0.02 | 1.02 | 1.00 |
| 1-methyl-1,2-cyclohexene oxide | 1.0 | 0.03 | 0.46 | 0.43 |
| | 3.0 | 0.03 | 0.72 | 0.69 |
| | 6.0 | 0.03 | 0.90 | 0.87 |
| | 24.0 | 0.03 | 1.03 | 1.00 |
| 2-phenyldioxolane | 1.0 | 0.00 | 0.00 | 0.00 |
| | 24.0 | 0.00 | 0.00 | 0.00 |
| 2-methyl-2-ethyldioxolane | 1.0 | 0.00 | 0.00 | 0.00 |
| | 24.0 | 0.00 | 0.00 | 0.00 |
| triethyl orthoformate | 1.0 | 0.00 | 0.00 | 0.00 |
| | 24.0 | 0.00 | 0.00 | 0.00 |

[a,b] See the corresponding footnotes in Table I.

As in the reactions with lithium triethylborohydride,[12] the acetal, ketal, and ortho esters examined proved to be inert toward the reagent under the experimental conditions. Consequently, carbonyl groups can be readily protected from the reagent by converting them to the corresponding acetals or ketals. The results are summarized in Table VII.

**G. Amides and Nitriles.** Caproamide undergoes reduction slowly with a slow evolution of hydrogen. In the case of benzamide, the rate of hydrogen evolution is somewhat increased, but no sign of reduction is noticed.

*N,N*-Dimethylbenzamide takes up 2 equiv of hydride within 24 h to proceed to the corresponding amine stage. A slower rate for the corresponding reduction of *N,N*-dimethylacetamide is noted. When 5 mmol of *N,N*-dimethylcaproamide was treated with 5 mmol of Li9-BBNH in THF at 25 °C for 24 h, *n*-hexyldimethylamine was formed in 94% yield. It is interesting to note that while tertiary amides were reduced by $LiEt_3BH$[12] or 9-BBN[13] to the corresponding alcohols, Li9-BBNH reduced *N,N*-dimethylamides to the corresponding tertiary amines.

Capronitrile undergoes a very sluggish reduction (0.2 equiv of hydride uptake in 24 h). However, benzonitrile consumes 2 equiv of hydride, corresponding to reduction to benzylamine, within 12 h. In the reaction with lithium triethylborohydride, it had been observed that benzonitrile was reduced rapidly to the amine stage, whereas capronitrile took up only 1 equiv of hydride within 5 min without further hydride uptake.[12] The results are summarized in Table VIII.

**H. Nitro Compounds and Their Derivatives.** 1-Nitropropane rapidly evolves 1 equiv of hydrogen, forming a white precipitate with about 0.6 equiv of hydride consumption for reduction and the values do not change significantly with time. The active α-hydrogen seems to be involved in this reaction. Nitrobenzene, however, is reduced at a moderate rate, utilizing 1 equiv of hydride for hydrogen evolution and 1.5 equiv of hydride for reduction in 48 h.

**Table VIII. Reaction of Lithium 9-Boratabicyclo[3.3.1]nonane with Representative Amides and Nitriles in Tetrahydrofuran at Room Temperature (15 ● 2 °C)**

| compd[a] | time, h | $H_2$ evolved[b] | hydride used | hydride used for reductn[b] |
|---|---|---|---|---|
| caproamide[c] | 1.0 | 0.14 | 0.20 | 0.06 |
| | 3.0 | 0.22 | 0.37 | 0.17 |
| | 6.0 | 0.27 | 0.53 | 0.26 |
| | 24.0 | 0.46 | 1.09 | 0.63 |
| | 48.0 | 0.56 | 1.25 | 0.69 |
| benzamide[c] | 1.0 | 0.38 | 0.40 | 0.02 |
| | 3.0 | 0.55 | 0.63 | 0.08 |
| | 6.0 | 0.72 | 0.80 | 0.08 |
| | 24.0 | 0.97 | 1.02 | 0.05 |
| *N,N*-dimethylacetamide | 1.0 | 0.02 | 0.10 | 0.08 |
| | 3.0 | 0.02 | 0.15 | 0.13 |
| | 6.0 | 0.02 | 0.29 | 0.27 |
| | 24.0 | 0.02 | 1.46 | 1.44 |
| | 48.0 | 0.02 | 2.04 | 2.02 |
| *N,N*-dimethylbenzamide | 1.0 | 0.04 | 0.36 | 0.32 |
| | 3.0 | 0.04 | 0.45 | 0.41 |
| | 6.0 | 0.04 | 0.60 | 0.56 |
| | 24.0 | 0.04 | 2.10 | 2.06 |
| capronitrile[d] | 1.0 | 0.02 | 0.14 | 0.12 |
| | 3.0 | 0.02 | 0.18 | 0.16 |
| | 6.0 | 0.02 | 0.21 | 0.19 |
| | 24.0 | 0.02 | 0.23 | 0.21 |
| benzonitrile[d] | 1.0 | 0.02 | 0.54 | 0.52 |
| | 3.0 | 0.02 | 1.15 | 1.13 |
| | 6.0 | 0.02 | 1.68 | 1.66 |
| | 12.0 | 0.02 | 2.03 | 2.01 |
| | 24.0 | 0.02 | 2.04 | 2.02 |

[a,b] See the corresponding footnotes in Table I. [c] Two reactions were done separately, one for hydrogen evolution and one for residual hydride. [d] Color changes to yellow.

**Table IX. Reaction of Lithium 9-Boratabicyclo[3.3.1]nonane with Nitro Compounds and Their Derivatives in Tetrahydrofuran at Room Temperature (15 ± 2 °C)**

| compd[a] | time, h | $H_2$ evolved[b] | hydride used[b] | hydride used for reductn[b] |
|---|---|---|---|---|
| 1-nitropropane[c] | 1.0 | 1.09 | 1.65 | 0.56 |
| | 3.0 | 1.09 | 1.65 | 0.56 |
| | 6.0 | 1.09 | 1.65 | 0.56 |
| | 24.0 | 1.09 | 1.74 | 0.65 |
| nitrobenzene[d,e] | 1.0 | 0.36 | 0.93 | 0.57 |
| | 3.0 | 0.62 | 1.66 | 1.04 |
| | 6.0 | 0.80 | 1.97 | 1.17 |
| | 24.0 | 1.00 | 2.22 | 1.22 |
| | 48.0 | 1.00 | 2.49 | 1.49 |
| azobenzene | 1.0 | 0.03 | 0.05 | 0.02 |
| | 3.0 | 0.03 | 0.05 | 0.02 |
| | 6.0 | 0.03 | 0.05 | 0.02 |
| | 24.0 | 0.03 | 0.05 | 0.02 |
| azoxybenzene | 1.0 | 0.04 | 0.14 | 0.10 |
| | 3.0 | 0.04 | 0.17 | 0.13 |
| | 6.0 | 0.04 | 0.22 | 0.18 |
| | 24.0 | 0.04 | 0.42 | 0.38 |

[a,b] See the corresponding footnotes in Table I. [c] Immediate white precipitate. [d] Color changes to reddish-brown. [e] Two reactions were done separately, one for hydrogen evolution and one for residual hydride.

Azobenzene is inert to the reagent and azoxybenzene undergoes reduction very slowly under experimental conditions. These two compounds are inert to lithium borohydride,[1] whereas, they are reduced rapidly by lithium triethylborohydride.[12] The results are summarized in Table IX.

**I. Other Nitrogen Compounds.** Cyclohexanone oxime is reduced at a moderate rate by $LiBH_4$ at room temperature[1] but is inert to $LiEt_3BH$.[12] When treated with Li9-BBNH, this oxime liberates 1 equiv of hydrogen rapidly, but no reduction is observed, as in the reaction with lithium triethylborohydride. Consequently, the formation of oximes would provide another means for protecting carbonyl groups toward Li9-BBNH.

**Table X. Reaction of Lithium 9-Boratabicyclo[3.3.1]nonane with Other Nitrogen Compounds in Tetrahydrofuran at Room Temperature (15 ± 2 °C)**

| compd[a] | time, h | $H_2$ evolved[b] | hydride used[b] | hydride used for reductn[b] |
|---|---|---|---|---|
| cyclohexanone oxime[c] | 1.0 | 1.03 | 1.11 | 0.08 |
| | 3.0 | 1.03 | 1.11 | 0.08 |
| | 6.0 | 1.03 | 1.12 | 0.09 |
| | 24.0 | 1.03 | 1.12 | 0.09 |
| phenyl isocyanate | 1.0 | 0.07 | 1.07 | 1.00 |
| | 3.0 | 0.07 | 1.07 | 1.00 |
| | 6.0 | 0.07 | 1.07 | 1.00 |
| | 24.0 | 0.07 | 1.14 | 1.07 |
| pyridine[d] | 1.0 | 0.01 | 0.17 | 0.16 |
| | 3.0 | 0.01 | 0.22 | 0.21 |
| | 6.0 | 0.01 | 0.27 | 0.26 |
| | 24.0 | 0.01 | 0.54 | 0.53 |
| | 48.0 | 0.01 | 1.05 | 1.04 |
| | 72.0 | 0.01 | 1.43 | 1.42 |
| pyridine *N*-oxide[e] | 1.0 | 0.04 | 2.58 | 2.54 |
| | 3.0 | 0.04 | 2.68 | 2.64 |
| | 6.0 | 0.04 | 2.75 | 2.71 |
| | 24.0 | 0.04 | 2.77 | 2.74 |

[a,b] See the corresponding footnotes in Table I. [c] Hydrogen evolution ceased within 15 min. [d] Color changes to yellow. [e] Color changes to orange.

Phenyl isocyanate is rapidly reduced, utilizing 1 equiv of hydride, corresponding to reduction to the formanilide stage.

Pyridine undergoes a very slow reduction. However, pyridine *N*-oxide rapidly utilizes almost 3 equiv of hydride totally, without hydrogen evolution. The results are summarized in Table X.

**J. Sulfur Compounds and Alkyl Halides.** Disulfides are rapidly reduced to the thiol stage, utilizing 2 equiv of hydride, one for hydrogen evolution and one for reduction. The rate of reduction of diphenyl disulfide is somewhat faster than that of di-*n*-butyl disulfide.

Methyl phenyl sulfide, dimethyl sulfoxide, tetramethylene sulfone, and diphenyl sulfone are essentially inert to the reagent under experimental conditions.

Sulfonic acids rapidly evolve the theoretical amount of hydrogen, but no conspicuous hydride uptake for reduction is observed.

Cyclohexyl tosylate is also inert to this reagent under experimental conditions. *n*-Octyl tosylate consumes 1 equiv of hydride within 3 h, indicating reduction to the corresponding alkane, *n*-octane. Therefore, this characteristic of the reagent could be utilized for the selective reduction of compounds containing primary and secondary tosylate groups within the same molecule.

*n*-Hexyl iodide consumes 1 equiv of hydride within 1 h and *n*-octyl bromide within 6.0 h, but *n*-octyl chloride is quite inert to the reagent. The reduction of 2-bromopentane is very sluggish. The rates of reduction for alkyl halides decrease in the order: R–I > R–Br ≫ R–Cl and primary alkyl bromide ≫ secondary alkyl bromide. Therefore, it should be possible to reduce alkyl iodide or bromide selectively in the presence of alkyl chloride. It should also be possible to reduce primary alkyl halide in the presence of secondary. These results indicate that this borohydride possesses a weaker hydride donating ability toward alkyl halides than does lithium triethylborohydride,

**Table XI. Reaction of Lithium 9-Boratabicyclo[3.3.1]nonane with Representative Sulfur Compounds and Alkyl Halides in Tetrahydrofuran at Room Temperature (15 ± 2 °C)**

| compd[a] | time, h | $H_2$ evolved[b] | hydride used[b] | hydride used for reductn[b] |
|---|---|---|---|---|
| di-*n*-butyl disulfide | 0.5 | 0.83 | 1.60 | 0.77 |
| | 1.0 | 0.97 | 1.91 | 0.94 |
| | 1.5 | 1.01 | 2.01 | 1.00 |
| diphenyl disulfide | 0.25 | 1.04 | 2.04 | 1.00 |
| | 1.0 | 1.04 | 2.04 | 1.00 |
| methyl phenyl sulfide | 1.0 | 0.03 | 0.03 | 0.00 |
| | 24.0 | 0.03 | 0.03 | 0.00 |
| dimethyl sulfoxide | 1.0 | 0.03 | 0.11 | 0.08 |
| | 3.0 | 0.03 | 0.11 | 0.08 |
| | 6.0 | 0.03 | 0.11 | 0.08 |
| | 24.0 | 0.03 | 0.11 | 0.08 |
| tetramethylene sulfone | 1.0 | 0.05 | 0.10 | 0.05 |
| | 3.0 | 0.05 | 0.10 | 0.05 |
| | 6.0 | 0.05 | 0.11 | 0.06 |
| | 24.0 | 0.05 | 0.06 | 0.01 |
| diphenyl sulfone | 1.0 | 0.02 | 0.05 | 0.03 |
| | 3.0 | 0.02 | 0.05 | 0.03 |
| | 6.0 | 0.02 | 0.05 | 0.03 |
| | 24.0 | 0.02 | 0.05 | 0.03 |
| methanesulfonic acid | 1.0 | 1.09 | 1.09 | 0.00 |
| | 24.0 | 1.09 | 1.09 | 0.00 |
| *p*-toluenesulfonic acid monohydrate | 1.0 | 3.05 | 3.10 | 0.05 |
| | 3.0 | 3.05 | 3.10 | 0.05 |
| | 6.0 | 3.05 | 3.10 | 0.05 |
| | 24.0 | 3.05 | 3.11 | 0.06 |
| *n*-octyl tosylate | 1.0 | 0.03 | 0.77 | 0.74 |
| | 3.0 | 0.03 | 1.04 | 1.01 |
| | 6.0 | 0.03 | 1.04 | 1.01 |
| | 24.0 | 0.03 | 1.04 | 1.01 |
| cyclohexyl tosylate | 1.0 | 0.00 | 0.00 | 0.00 |
| | 24.0 | 0.00 | 0.00 | 0.00 |
| *n*-octyl chloride | 1.0 | 0.03 | 0.03 | 0.00 |
| | 3.0 | 0.03 | 0.04 | 0.01 |
| | 6.0 | 0.03 | 0.09 | 0.06 |
| | 24.0 | 0.03 | 0.23 | 0.20 |
| *n*-octyl bromide | 1.0 | 0.02 | 0.37 | 0.35 |
| | 3.0 | 0.02 | 0.68 | 0.66 |
| | 6.0 | 0.02 | 1.09 | 1.07 |
| 2-bromopentane | 1.0 | 0.02 | 0.02 | 0.00 |
| | 3.0 | 0.02 | 0.04 | 0.02 |
| | 6.0 | 0.02 | 0.07 | 0.05 |
| | 24.0 | 0.02 | 0.10 | 0.08 |
| *n*-hexyl iodide | 1.0 | 0.02 | 1.06 | 1.04 |
| | 3.0 | 0.02 | 1.06 | 1.04 |

[a,b] See the corresponding footnotes in Table I.

but a much stronger hydride donating power than does lithium borohydride,[14] suggesting a hydride donating ability that varies: $LiBH_4 < LiR_2BH_2 < LiR_3BH$. The results of these experiments are summarized in Table XI.

## Conclusion

A systematic exploration of the reaction of representative organic functional groups with Li9-BBNH in tetrahydrofuran has been described. The reactivity of various functional groups toward the reagent can be classified into four broad categories, as follows: (1) rapid or fast reduction—aldehyde, ketone, ester, lactone, acyl chloride, acid anhydride, epoxide, disulfide, *n*-alkyl iodide, and tosylate; (2) slow reduction—tertiary amide, alkyl bromide, and aromatic nitrile; (3) sluggish reduction—carboxylic acid, aliphatic nitrile, primary amide, nitro and azoxy compound, and secondary alkyl bromide and tosylate; (4) inert—olefin, oxime, alkyl chloride, sulfoxide, azo-compound, sulfide, sulfone, and sulfonic acid.

(14) Krishnamurthy, S.; Brown, H. C. *J. Org. Chem.* **1980**, *45*, 849.

Li9-BBNH occupies a unique position in the wide spectrum of reducing agents, exhibiting an intermediate reducing characteristic between mild lithium borohydride and strong lithium triethylborohydride. Li9-BBNH would be a reagent of choice for the selective reduction of esters or lactones in the presence of many other functional groups such as carboxylic acids, amides, nitriles, halides (Br and Cl), azo and azoxy groups, oximes, sulfoxides, and olefins.

It also appears to be especially valuable for the reduction of tertiary amides to amines in the presence of a wide variety of substituents. This application is under investigation.

Its relatively easy availability should make this hydride reagent valuable for a variety of selective reductions.

## Experimental Section

**Materials.** Tetrahydrofuran was distilled over lithium aluminum hydride under nitrogen and stored over 4Å molecular sieves. Lithium hydride (Aldrich) and 9-BBN (Aldrich) were used without further purification. Most of the organic compounds utilized in this study were commercial products of the highest available purity. They were futher purified by distillation or recrystallization when necessary. Some compounds were synthesized by using standard procedures. In all cases physical constants agreed satisfactorily with constants in the literature. All glassware was dried thoroughly in a drying oven. All reduction experiments were carried out under a dry nitrogen atmosphere and hypodermic syringes were used to transfer the solutions.

**Standard Solution of Li9-BBNH.**[10] In a dry, 1-L flask fitted with a side arm, a rubber syringe cap, and a magnetic stirring bar were placed about 400 mL of THF, 48.81 g (400 mmol) of 9-BBN, and 4.77 g (600 mmol, 50% excess) of lithium hydride in this order. A reflux condenser connected to a mercury bubbler was attached. After flushing the system with a stream of dry nitrogen, the reaction mixture was refluxed with stirring for 24 h. After cooling to room temperature and stirring for another 24 h, the reaction mixture was filtered through a sintered-glass filter under a slight positive pressure of nitrogen in order to remove excess lithium hydride. The resulting clear solution was standardized by removing an aliquot, hydrolyzing it with a THF–glycerine–water (1:1:1) mixture, and measuring the hydrogen evolved. With a series of preparations, the concentrations were determined to be in the range of 0.93–1.09 M in Li9-BBNH.

The THF solution of Li9-BBNH was characterized by a many shouldered, strong, broad absorption in the IR at around 2148 $cm^{-1}$ ($\nu$, B–H). Such solutions were observed to be stable at room temperature under a dry nitrogen atmosphere for at least 90 days without any detectable hydride loss, isomerization, or redistribution.[10]

**Procedure for the Study of Rate and Stoichiometry.** The reduction of ethyl benzoate is representative. 9.4 mL of 1.06 M Li9-BBNH solution (20 mmol in hydride) and 5.6 mL of THF were introduced into a dry 50-mL flask fitted with a rubber syringe cap on an inlet port, a magnetic stirring bar, and a reflux condenser connected to a gas buret. The flask was maintained at room temperature with stirring and 5.0 mL (5 mmol) of a 1.0 M solution of ethyl benzoate in THF was injected slowly. Then hydrogen evolution was monitored. In this way, a solution was obtained which was 0.5 M in Li9-BBNH and 0.25 M in ethyl benzoate. Upon addition of the compound, 4.0 mL of hydrogen evolved, corresponding to 0.03 mmol/mmol of compound. No more hydrogen evolution was observed throughout the reaction. After 0.5 h, 4.0 mL of the reaction mixture was removed and injected into a hydrolyzing mixture of THF–glycerine–water (1:1:1). The hydrogen evolved was 1.90 mmol, indicating that 2.08 mmol of hydride had been used per mmol of the ester when compared to 3.98 mmol for blank experiment (in which 5 mL of THF had been substituted for the 5 mL of the ethyl benzoate solution). Therefore, 2.05 mmol (2.08 − 0.93 = 2.05) of hydride was used for reduction per mmol of the ester. Another 4.0 mL of the reaction mixture was also removed and hydrolyzed after 1.0 h of reaction time. The amount of hydride used for reduction in this experiment was also 2.05 mmol, indicating the completion of reduction within 0.5 h.

**Procedure for Product Analysis by GC.** The reduction of 1,2-butylene oxide is representative. In a 50-mL flask fitted with a rubber syringe cap on an inlet port, a magnetic stirring bar, and a reflux condenser connected to a mercury bubbler were placed 4.8 mL (5.09 mmol) of a 1.06 M solution of Li9-BBNH and 0.2 mL of THF. Then 5.0 mL of a 1.0 M solution of 1,2-butylene oxide in THF was introduced while the mixture was vigorously stirred at room temperature. After 3 h, the excess hydride was destroyed with 0.5 mL of water. Then the reaction mixture was oxidized by the addition of 1.6 mL (6.4 mmol) of 4 N aqueous sodium hydroxide, followed by 1.5 mL (13 mmol) of 30% hydrogen peroxide and heating at 50 °C for 1 h. The aqueous layer was saturated with 3 g of potassium carbonate and the dry THF layer was subjected to GC analysis on a 10% Carbowax 20M column, 6 ft × 0.125 in., indicating the presence of 99% 2-butanol and 1% 1-butanol. A similar procedure was employed for examining the stereochemistry of the reduction of cyclic and bicyclic ketones with Li9-BBNH. The other compounds discussed were also examined in this manner by using the appropriate internal standard.

**Procedure for Competitive Reaction.** The reaction of ethyl benzoate in the presence of caproic acid is representative. 9.4 mL of a 1.06 M Li9-BBNH solution (20 mmol in hydride) and 5.6 mL of purified THF were introduced into a dried, 50-mL flask fitted with a rubber syringe cap on an inlet port, a magnetic stirring bar, and a reflux condenser connected to a mercury bubbler. The flask was maintained at room temperature with stirring and 5 mL of THF solution containing 5 mmol of ethyl benzoate and 5 mmol of caproic acid was injected slowly. After 30 min, the remaining hydride was destroyed with water. Then the reaction mixture was oxidized with $NaOH–H_2O_2$, followed by addition of 5 mmol of *n*-octanol in THF (5 mL) as internal standard. GC analysis of the mixture on a 5% Carbowax 20M column, 6 ft × 0.125 in., revealed the presence of 5 mmol of benzyl alcohol and the absence of 1-hexanol.

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**Registry No.** 1-Hexanol, 111-27-3; benzyl alcohol, 100-51-6; 3-hexanol, 623-37-0; 3-ethyl-3-pentanol, 597-49-9; phenol, 108-95-2; 2,6-di-*tert*-butylphenol, 128-39-2; *n*-hexylamine, 111-26-2; benzenethiol, 108-98-5; 1-hexanethiol, 111-31-9; caproaldehyde, 66-25-1; benzaldehyde, 100-52-7; 2-heptanone, 110-43-0; norcamphor, 497-38-1; camphor, 76-22-2; acetophenone, 98-86-2; benzophenone, 119-61-9; 2,2,4,4-tetramethyl-3-pentanone, 815-24-7; cinnamaldehyde, 104-55-2; 2-methylcyclohexanone, 583-60-8; 4-*tert*-butylcyclohexanone, 98-53-3; *p*-benzoquinone, 106-51-4; anthraquinone, 84-65-1; caroic acid, 142-62-1; benzoic acid, 1005-01-2; acetic anhydride, 108-24-7; succinic anhydride, 108-30-5; phthalic anhydride, 85-44-9; caproyl chloride, 142-61-0; benzoyl chloride, 98-88-4; ethyl caproate, 123-66-0; ethyl benzoate, 93-89-0; phenyl acetate, 122-79-2; γ-butyrolactone, 96-48-0; phthalide, 87-41-2; isopropenyl acetate, 108-22-5; 1,2-butylene oxide, 106-88-7; styrene oxide, 96-09-3; cyclohexene oxide, 286-20-4; 1-methyl-1,2-cyclohexene oxide, 1713-33-3; 2-phenyldioxolane, 936-51-6; 2-methyl-2-ethyldioxolane, 126-39-6; triethyl orthoformate, 122-51-0; caproamide, 628-02-4; benzamide, 55-21-0; *N,N*-dimethyl acetamide, 127-19-5; *N,N*-dimethyl benzamide, 611-74-5; capronitrile, 628-73-9; benzonitrile, 100-47-0; 1-nitropropane, 108-03-2; nitrobenzene, 98-95-3; azobenzene, 103-33-3; azoxybenzene, 495-48-7; cyclohexanone oxime, 100-64-1; phenyl isocyanate, 103-71-9; pyridine, 110-86-1; pyridine *N*-oxide, 694-59-7; di-*n*-butyl disulfide, 629-45-8; diphenyl disulfide, 882-33-7; methyl phenyl sulfide, 100-68-5; dimethyl sulfoxide, 67-68-5; tetramethylene sulfone, 126-33-0; diphenyl sulfone, 127-63-9; methanesulfonoic acid, 75-75-2; *p*-toluenesulfonic acid monohydrate, 6192-52-5; *n*-octyl tosylate, 3386-35-4; cyclohexyl tosylate, 953-91-3; *n*-octyl chloride, 111-85-3; *n*-octyl bromide, 111-83-1; 2-bromopentane, 107-81-3; *n*-hexyl iodide, 638-45-9; *cis*-2-methylcyclohexanol, 7443-70-1; *cis*-4-*tert*-butylcyclohexanol, 7214-18-8; *endo*-bicyclo[2.2.1]heptan-2-ol, 497-36-9; *exo*-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol, 124-76-5; lithium 9-boratabicyclo[3.3.1]nonane, 91083-44-2.

# Protonation and Sulfur Trioxide Sulfonation of Some 1,6-Methano[10]annulenes[1]

Hans Cerfontain,* Hans Goossens, Ankie Koeberg-Telder, Cor Kruk, and Hans J. A. Lambrechts

*Laboratory for Organic Chemistry, University of Amsterdam, Nieuwe Achtergracht 129, 1018 WS Amsterdam, The Netherlands*

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The sulfonation of 1,6-methano[10]annulene (1), 2-methoxy-1, 11-fluoro-1, and 11,11-difluoro-1 with $SO_3$ in dioxane at 35 °C and the low temperature protonation of the two fluoro-containing substrates in the $HSO_3F–SO_2ClF$ (1:2 v/v) solvent system has been studied. The sulfonation and protonation of all substrates occur at the α-positions. The subsequent sulfonation of 2-methoxy-5-sulfo-1 occurs at the 3-, 8-, and 9-position. The protonation of 11-fluoro-1,6-methano[10]annulene (3) occurs 36% at the 2-position and 64% at the 7-position, whereas the sulfonation yields 47% of the 2- and 53% of the 7-sulfonic acid. Rate studies have shown that the increase in the free energy of activation on replacing the methylene hydrogens of 1 successively by fluorine is additive.

The bridged monocyclic 10π-electron 1,6-methano[10]-annulene (1)[2] is an intriguing aromatic[3] hydrocarbon in view of the nonplanarity of the annulene perimeter[4,5] and its transannular interaction.[5–7] We now report on the products and reactivities in the sulfonation of the 1,6-methano[10]annulene derivatives **3–5**. In order to obtain

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(7) In 11,11-dimethyl- and 11-cyano-11-methyl-1,6-methano[10]-annulene the distance between C(1) and C(6) is so short (1.83–1.77[8] and 1.85–1.77 Å,[9] respectively) that these compounds are regarded as bis(norcaradiene) derivatives, whereas the C(1)–C(6) of 1, its 2-carboxylic acid, and **5** are relatively large (2.24,[4] 2.26,[10] and 2.27 Å,[11] respectively), illustrating the true [10]annulene nature of these compounds.

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