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# Selective Reductions. 22. Facile Reduction of α,β-Unsaturated Aldehydes and Ketones with 9-Borabicyclo[3.3.1]nonane. A Remarkably Convenient Procedure for the Selective Conversion of Conjugated Aldehydes and Ketones to the Corresponding Allylic Alcohols in the Presence of Other Functional Groups[1]

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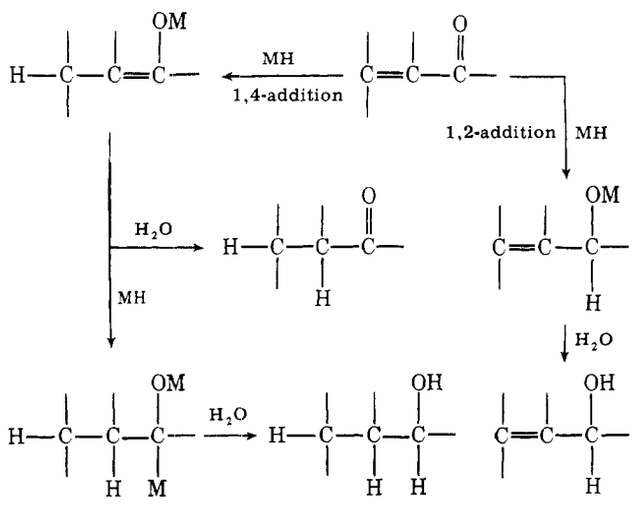
*Received September 24, 1976*

Conjugated aldehydes and ketones are reduced rapidly and quantitatively to the corresponding allylic alcohols by 9-borabicyclo[3.3.1]nonane in tetrahydrofuran in excellent purities. Even cyclic enones, such as 2-cyclohexenone and 2-cyclopentenone, are reduced cleanly to the desired allylic alcohols without concomitant attack at the double bond. The development of a unique workup procedure renders possible the isolation of carbinols in excellent yields. Unlike more conventional reagents, such as aluminum hydride and diisobutylaluminum hydride, the mildness of the reagent, 9-BBN, permits the presence of almost any other functional groups, such as ester, amide, carboxylic acid, nitro, halogen, nitrile, etc. The superior ability of this reagent for the selective reduction of α,β-unsaturated aldehydes and ketones was confirmed by the selective conversion of *o*-nitrocinnamaldehyde to *o*-nitrocinnamyl alcohol and of 4-carbethoxy-3-methyl-2-cyclohexenone to 4-carbethoxy-3-methyl-2-cyclohexenol in yields of 76 and 95%, respectively. The present development provides a highly convenient synthetic procedure for the selective reduction of conjugated aldehydes and ketones in a multifunctional molecule, where this is required in synthetic operations.

Selective reduction of α,β-unsaturated aldehydes and ketones to the corresponding allylic alcohols (1,2-addition) has been examined with a variety of hydride reducing agents.[3] Often this is accompanied with conjugate reduction (1,4-addition) to a varying extent, thereby affording saturated aldehyde or ketone, accompanied by subsequent reduction to yield saturated carbinol (Scheme I). Systematic exploration of the reaction of conjugated aldehydes and ketones with sodium borohydride, a mild reducing agent, clearly indicates that the reaction invariably yields substantial proportions of saturated carbinols[4] (1,4-addition). Comparatively, the results realized with lithium aluminum hydride, a powerful reducing agent, are considerably better. However, this can by no means be adapted as a general procedure; labile systems, such as 2-cyclopentenones, yield considerable amounts of the conjugate reduction products. Application of alkoxy derivatives of lithium aluminum hydride, such as lithium trimethoxyaluminohydride and lithium tri-*tert*-butoxyaluminohydride, do not improve the results. Sodium cyanoborohydride reduces acyclic conjugated aldehydes and ketones cleanly to the allylic alcohols; however, cyclic enones give a mixture of allylic and saturated alcohols.[5]

Scheme I




The failure to achieve clean reduction of α,β-unsaturated aldehydes and ketones with conventional reducing systems led to the exploration of various other new hydride reducing agents. The development of aluminum hydride as a reducing agent in our laboratory and its application to 2-cyclopentenone considerably decreased the unwanted 1,4-reduction products.[6] Recently, diisobutylaluminum hydride has been reported to reduce 2-en-1-ones to the corresponding allylic carbinols in higher yields and cleaner products than observed with aluminum hydride.[7] Unfortunately, its application to acyclic enones appears to give considerable amounts of the undesired saturated products.[3b] Moreover, both aluminum

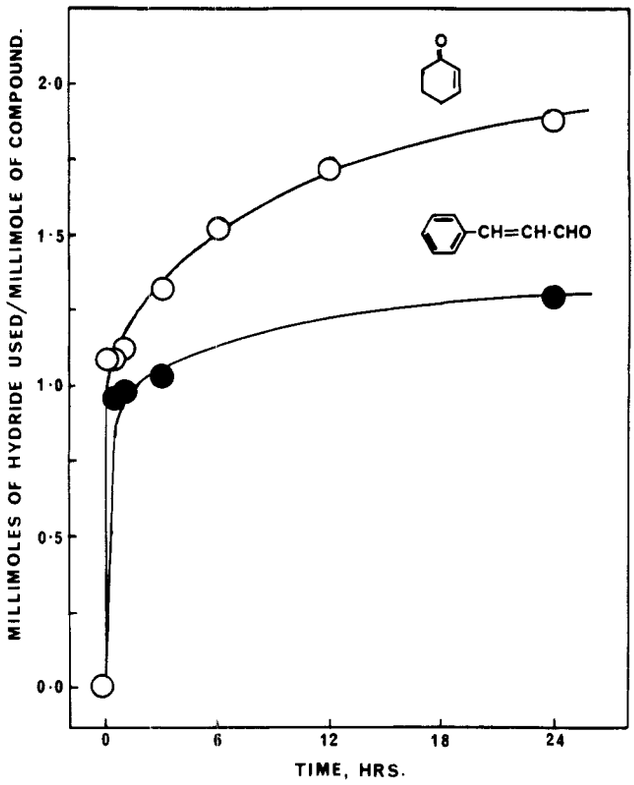



**Figure 1.** Rates of reaction of conjugated aldehydes and ketones (0.125 M) with 9-BBN (0.5 M) in tetrahydrofuran at 25 °C.

hydride and diisobutylaluminum hydride are powerful reducing agents capable of reducing many other functional groups in the same molecule, groups such as esters, acids, nitriles, amides, epoxides, halides, acetals, etc.[8,9] Consequently, this introduces severe limitations in utilizing these reagents for the reduction of a particular group in a multifunctional molecule.

We recently reported an extensive study of the approximate rates, stoichiometry, and products of the reaction of excess 9-borabicyclo[3.3.1]nonane (9-BBN) with organic compounds containing representative functional groups in tetrahydrofuran (THF) at 25 °C. It was observed that conjugated aldehydes and ketones, such as cinnamaldehyde and 2-cyclohexenone, rapidly utilize 1 equiv of 9-BBN (<30 min), with the uptake of a second equivalent being very slow, requiring 3 days or more (Figure 1). In the case of 2-cyclohexenone, analysis by the reaction mixture at the end of 10 min by GLC, following hydrolysis of the intermediate, indicated the presence of 2-cyclohexenol in 100% yield. Consequently, we are achieving a rapid reduction of the carbonyl group followed by a very slow subsequent hydroboration of the double bond. Further, competition experiments involving 9-BBN clearly establish that aldehydes and ketones are rapidly and cleanly reduced to alcohols, much faster than the hydroboration of most olefins ($k_{cyclohexanone}/k_{cyclopentene}$ = 37).

The unique reduction characteristics of 9-BBN revealed in our previous study should permit the selective reduction of the $\alpha,\beta$-unsaturated aldehydes and ketones to the corresponding allylic alcohols in the presence of many other less reactive functional groups. Accordingly, we undertook a systematic study of the scope of the reaction and its applicability for multifunctional molecules. The results of this investigation are reported in the present paper.

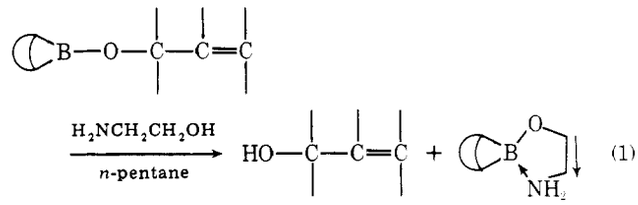
## Results and Discussion

**Reaction Conditions and General Procedure.** The reactions were carried out by the dropwise addition of an essentially stoichiometric quantity of 9-BBN solution in THF (3–5% excess) to the conjugated aldehyde or ketone in THF solution stirred and maintained at 0 °C. The resulting mixture was stirred at 0 °C for 2–4 h, and subsequently at 25 °C for 1 h.

For product analysis by GLC, separate reactions on a 5-mmol scale were carried out. The products were identified by GLC comparison with authentic samples and yields were determined utilizing internal standards and authentic synthetic mixtures.

The preparative reductions were carried out on a 25–100-mmol scale. Two convenient workup procedures have been developed for the isolation of the products. After the reaction is over, the mixture can be treated with alkaline hydrogen peroxide to oxidize the 9-BBN moiety and the carbinol separated from the *cis*-1,5-cyclooctanediol by distillation. Alternatively, the diol can be readily washed out with water from most allylic alcohols (procedure A).

Alternatively and more conveniently, the THF can be removed under vacuum from the reaction mixture and *n*-pentane added. The addition of 1 mol of ethanolamine precipitates the 9-BBN moiety as the adduct, displacing the allylic alcohol to the pentane layer quantitatively. Removal of the pentane and distillation yields the desired carbinol in excellent yields[11] (procedure B) (eq 1).



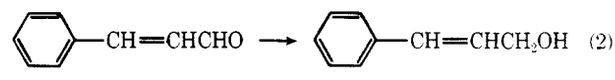

(1)

**Competition Experiments. Relative Reactivity of Enones to Other Organic Functional Groups.** Examination of the reaction of typical organic functional groups with excess 9-BBN gave a rough indication of the relative ease of reduction by this reagent of representative functional groups. We became interested in exploring the possibility of the selective reduction of enones in the presence of other reducible functional groups in a multifunctional molecule. It appeared desirable to establish the reactivity of selected organic functional groups relative to an $\alpha,\beta$-unsaturated ketone by means of competition experiments. Accordingly, equimolar amounts of 2-cyclohexenone and a compound containing the representative functional group were allowed to compete for a limited quantity of 9-BBN solution in THF at 0 °C. After 2 h, the mixture was hydrolyzed, oxidized ($NaOH-H_2O_2$) and analyzed by GLC using an internal standard.

The results summarized in Table I clearly show that the enones can be preferentially reduced in the presence of many other organic functional groups, groups such as ester, nitrile, amide, carboxylic acid, epoxide, halogen, etc.

**Synthetic Utility.** In order to establish the synthetic utility of this synthetic procedure, product studies for the reduction of representative conjugated aldehydes and ketones were carried out.

Simple conjugated aldehydes, such as crotonaldehyde and cinnamaldehyde, are converted into crotyl alcohol and cinnamyl alcohol in yields of 98 and 99%, respectively (eq 2).




(2)

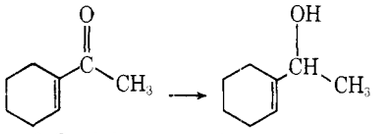
99% (86% isolated)

Acyclic enones, such as 1-acetylcyclohexene and 3-penten-2-one, are selectively reduced to 1-cyclohexene-1-ethanol and 3-penten-2-ol in yields of 90 and 75%, respectively (eq 3).

**Table I. Relative Reactivities of 2-Cyclohexenone to Other Functional Groups toward 9-BBN in THF[a]**

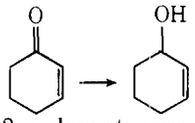
| Compd used | Registry no. | mmol | 9-BBN,[e] mmol | Reaction products | Mol, % |
|---|---|---|---|---|---|
| 2-Cyclohexenone | 930-68-7 | 4.0 | | 2-Cyclohexenol[f] | 50.0 |
| | | | 4.0 | 2-Cyclohexenone | 0.0 |
| Cyclohexene oxide | 286-20-4 | 4.0 | | Cyclohexanol | 0.0 |
| | | | | Cyclohexene oxide | 50.0 |
| 2-Cyclohexenone | | 4.0 | | 2-Cyclohexenol | 50.0 |
| | | | 4.0 | 2-Cyclohexenone | 0.0 |
| *n*-Octyl bromide | 111-83-1 | 4.0 | | *n*-Octane | 0.0 |
| | | | | *n*-Octyl bromide | 50.0 |
| 2-Cyclohexenone | | 4.0 | | 2-Cyclohexenol | 50.0 |
| | | | 4.0 | 2-Cyclohexenone | 0.0 |
| Nitrobenzene | 98-95-3 | 4.0 | | Reduced products | 0.0[b] |
| | | | | Nitrobenzene | 50.0 |
| 2-Cyclohexenone | | 4.0 | | 2-Cyclohexenol | 49.2 |
| | | | 4.0 | 2-Cyclohexenone | 1.0 |
| *n*-Valeronitrile | 110-59-8 | 4.0 | | *n*-Pentylamine | 0.0[b] |
| | | | | *n*-Valeronitrile | 50.0 |
| 2-Cyclohexenone | | 4.0 | | 2-Cyclohexenol | 50.0 |
| | | | 4.0 | 2-Cyclohexenone | 0.0 |
| Ethyl hexanoate | 123-66-0 | 4.0 | | *n*-Hexyl alcohol | 0.0 |
| | | | | Ethyl hexanoate | 49.5 |
| 2-Cyclohexenone | | 4.0 | | 2-Cyclohexenol | 32.5 |
| | | | 4.0 | 2-Cyclohexenone | 17.5 |
| *N,N*-Dimethyl-butyramide[c] | 760-79-2 | 4.0 | | *n*-Butyl alcohol | 1.5 |
| | | | | *N,N*-Dimethylbutyramide | 48.5 |
| 2-Cyclohexenone | | 2.0 | | 2-Cyclohexenol | 41.0 |
| | | | 4.0 | 2-Cyclohexenone | |
| Hexanoic acid[d] | 142-62-1 | 2.0 | | *n*-Hexyl alcohol | 0.0 |
| | | | | Hexanoic acid | 50.0[b] |

[a] 9-BBN solution in THF was added to the THF solution of the compound at 0 °C and stirred at 0 °C for 1 h and at 25 °C for 1 h. [b] Not determined directly; estimated by the difference. [c] It appears that tertiary amide derivatives diminish the reactivity of 9-BBN, presumably by coordination. [d] An extra equivalent of 9-BBN was utilized to correct for the rapid hydrogen evolution from the carboxylic acid. Carboxylic acid destroys some of the 2-cyclohexenone, as indicated by the deep yellow color. [e] Registry no., 280-64-8. [f] Registry no., 822-67-3.



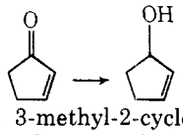
90% (isolated) (3)

2-Cyclohexenone is converted to 2-cyclohexenol in quantitative yield (eq 4).



100% (85% isolated) (4)

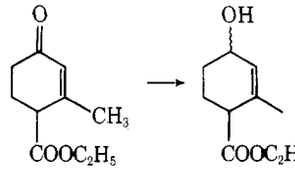
Even 2-cyclopentenone, known for its susceptibility to undergo conjugate reduction, is cleanly converted to the desired 2-cyclopentenol in essentially quantitative yield (eq 5).



99% (85% isolated) (5)

Similarly, 3-methyl-2-cyclopentenone is converted to 3-methyl-2-cyclopentenol in an isolated yield of 75%.

Finally, we examined *o*-nitrocinnamaldehyde and 4-carbethoxy-3-methyl-2-cyclohexenone to test the utility of this procedure for selective reductions. The products, *o*-nitrocinnamyl alcohol and the isomeric (30:70) 4-carbethoxy-3-methyl-2-cyclohexenols, were obtained in excellent yields, confirming the value of this procedure for selective reductions (eq 6).



95% (86% isolated) (6)

The results are summarized in Table II.

**Scope and Applicability.** For the selective reduction of the enones to the corresponding allylic alcohols, 9-BBN offers three major advantages over the conventional reagents, such as lithium aluminum hydride, sodium borohydride, aluminum hydride, and diisobutylaluminum hydride.

First, the reaction is rapid and essentially quantitative, free of side products. The stoichiometric quantity of 9-BBN is adequate to bring about a rapid completion of the reaction.

Second, even enones which are highly susceptible to conjugate reduction, such as 2-cyclopentenones, are cleanly reduced to the allylic alcohols in far superior purity and yields than most of the conventional reagents (Table III) without any observable 1,4-reduction.

Third, the reagent 9-BBN is a very mild reducing agent and can tolerate the presence of many functional groups. Thus, it is evident from our previous rate and stoichiometry studies and the present studies on competition experiments that enones can be selectively reduced completely in the presence of functional groups, such as nitro, halogen, epoxide, carboxylic acid, ester, amide, nitrile, sulfide, disulfide, sulfoxide, sulfone, tosylate, azo, etc. This represents major advantage of 9-BBN over the more conventional reagents for the reduction of enones to allylic alcohols.

## Conclusions

9-Borabicyclo[3.3.1]nonane reduces conjugated aldehydes and ketones, normally highly susceptible to conjugate reduction, cleanly to the allylic alcohols. Moreover, the 9-BBN moiety is readily separated from the product, permitting the isolation of the product in excellent yields utilizing simple procedures.

**Table II. Reduction of α,β-Unsaturated Aldehydes and Ketones with 9-Borabicyclo[3.3.1]nonane in Tetrahydrofuran at 0 °C[a,b]**

| Compd | Registry no. | Time, h | Product | Registry no. | Yield,[c,d] % |
|---|---|---|---|---|---|
| Crotonaldehyde | 4170-30-3 | 2 | Crotyl alcohol | 6117-91-5 | 98 |
| Cinnamaldehyde | 104-55-2 | 2 | Cinnamyl alcohol | 104-54-1 | 99 (86) |
| 3-Penten-2-one | 625-33-2 | 3 | 3-Penten-2-ol | 1569-50-2 | 75 |
| 1-Acetylcyclohexene | 932-66-1 | 2 | 1-Cyclohexene-1-ethanol | 3197-68-0 | (90) |
| 2-Cyclohexenone | | 2 | 2-Cyclohexenol | | 100 (85) |
| 2-Cyclopentenone | 930-30-3 | 4 | 2-Cyclopentenol | 3212-60-0 | 99 (85) |
| 3-Methyl-2-cyclopentenone | 2758-18-1 | 2 | 3-Methyl-2-cyclopentenol | 3718-59-0 | (76) |
| o-Nitrocinnamaldehyde | 1466-88-2 | 2 | o-Nitrocinnamyl alcohol | 1504-65-0 | (76) |
| 4-Carbethoxy-3-methyl-2-cyclohexenone | 487-51-4 | 4 | 4-Carbethoxy-3-methyl-2-cyclohexenol[e] | 61203-59-6[f] 61203-60-9[g] | 95 (86) |

[a] Essentially stoichiometric amount of 9-BBN was utilized (3–5% excess). [b] Reactions were maintained for an additional period of 1–2 h at 25 °C before workup. [c] Yield by GLC. [d] Numbers in parentheses indicate the yield isolated. [e] A 30:70 mixture of cis and trans alcohols, as indicated by GLC examination. [f] Cis. [g] Trans.

**Table III. Reduction of 2-Cyclopentenone with Various Reducing Agents**

| Reagent | Product composition,[a] % O | OH | O[e] | OH[f] |
|---|---|---|---|---|
| $LiAlH_4$, THF, 0 °C[b] | 0.0 | 14.0 | 2.5 | 83.5 |
| $LiAlH(OCH_3)_3$, THF, 0 °C[b] | 0.0 | 90.5 | 0.0 | 9.5 |
| $LiAlH(O\text{-}t\text{-}Bu)_3$, THF, 0 °C[b] | 0.0 | 0.0 | 11.2 | 88.8 |
| $NaBH_4$, EtOH, 78 °C[b] | 0.0 | 0.0 | 0.0 | 100.0 |
| $AlH_3$, THF, 0 °C[b] | 0.0 | 90.0 | 6.1 | 3.9 |
| $i\text{-}Bu_2AlH$, $C_6H_6$, 0 °C[c] | 0.5 | 99.0 | 0.0 | 0.5 |
| 9-BBN, THF, 0 °C[d] | 0.0 | 100.0 | 0.0 | 0.0 |

[a] Analysis by GLC. [b] Reference 6. [c] Reference 7. [d] Present study. [e] Registry no., 120-92-3. [f] Registry no., 96-41-3.

The mildness of the reducing agent permits the selective reduction of the enone grouping in the presence of numerous other organic functional groups. For this reason, 9-BBN appears to be the reagent of choice for the reduction of the enone group, especially in polyfunctional molecules.

Although this feature was not explored in the present study, 9-BBN would appear to have related advantages for the clean reduction of the carbonyl groups of aldehydes and ketones in polyfunctional molecules. It constitutes a valuable addition to the repertoire of the organic chemist interested in the synthesis of complex structures.

## Experimental Section

**Materials.** Tetrahydrofuran was dried with excess lithium aluminum hydride, distilled under nitrogen, and stored over 5-Å molecular sieves. Tetrahydrofuran solution of 9-BBN was prepared by dissolving commercial 9-BBN powder[12] in THF to give a standard solution. Its concentration was determined by hydrolyzing a known aliquot of the solution and measuring the hydrogen evolved (~40 min).

Conjugated aldehydes and ketones were the commercial products of the highest purity. They were further purified by distillation under nitrogen or recrystallization prior to use and kept in the cold room.

All reduction experiments were carried out under a dry nitrogen atmosphere. Hypodermic syringes were used to transfer the solution.

**Procedure for Rate and Stoichiometry. Reaction of 2-Cyclohexenone with Excess 9-BBN.** A 100-ml flask with a side arm was dried in an oven and cooled down to room temperature under a dry stream of nitrogen. The flask was equipped with a rubber syringe cap, a magnetic stirring bar, and a reflux condenser connected to a gas buret through a dry ice trap. The flask was immersed in a water bath (ca. 25 °C) and 4.0 ml of THF was introduced into the reaction flask followed by 31.5 ml (20 mmol) of 0.64 M solution of 9-BBN in THF and 0.57 ml (2.5 mmol) of n-dodecane to serve as the internal standard. Finally, 4 ml (5 mmol) of a 1.25 M solution of 2-cyclohexenone in THF was injected into the reaction flask. Now the reaction mixture was 0.5 M in 9-BBN and 0.125 M in enone. No significant hydrogen evolution was observed (<2%).

At the end of 10 min, a 4-ml aliquot of the reaction mixture (0.5 mmol of the compound) was removed with a hypodermic syringe and injected into a hydrolyzing mixture of THF–MeOH (1:1). The hydrogen evolved was measured. This indicated that 1.08 mmol of hydride had reacted per millimole of the enone. The reaction was monitored at the end of 1 h (1.13 $H^-$), 3 h (1.32 $H^-$), 12 h (1.72 $H^-$), 24 h (1.88 $H^-$) and 72 h (2.05 $H^-$).

At the end of 10 min, a small aliquot of the reaction mixture was hydrolyzed, oxidized, and analyzed by GLC on a 5% Carbowax 20M column, 6 ft × 0.125 in., indicating the presence of 2-cyclohexenol in 100% yield.

**Product Analysis by GLC. Reduction of Crotonaldehyde to Crotyl Alcohol.** A clean oven-dried 25-ml flask equipped with a side arm fitted with a silicone rubber stopple, a magnetic stirring bar, and a reflux condenser connected to a mercury bubbler was cooled down to room temperature with nitrogen. THF (3.1 ml) was injected into the reaction flask followed by 0.42 ml (5 mmol) of crotonaldehyde (freshly distilled) and 0.48 ml (2 mmol) of n-tridecane. The reaction flask was cooled to 0 °C (ice bath) and 8.5 ml (5.1 mmol) of a 0.6 M 9-BBN solution in THF was added dropwise over a period of 5 min. The mixture was stirred at 0 °C for 2 h and at 25 °C for 1 h. Then the reaction mixture was hydrolyzed (MeOH) and oxidized ($NaOH\text{–}H_2O_2$, 60 °C, 1 h). The aqueous layer was saturated with potassium carbonate and the dry THF layer was subjected to GLC analysis on a 5% Carbowax 20M column, 6 ft × 0.125 in., indicating the presence of crotyl alcohol in 98% yield.

**Competitive Experiments. Reaction of 2-Cyclohexenone and Ethyl Hexanoate with Limited Quantity of 9-BBN in THF.** The experimental setup was the same as in the previous experiment. To the reaction flask was added 2 ml of THF followed by 0.4 ml (4 mmol) of 2-cyclohexenone and 0.66 ml (4 mmol) of ethyl hexanoate; n-tridecane (0.49 ml, 2 mmol) was added to serve as the internal standard. The mixture was stirred well and a minute sample was withdrawn and analyzed by GLC. The mixture was cooled to 0 °C in an ice bath. Then 6.7 ml (4 mmol) of a 0.6 M 9-BBN solution in THF was added dropwise over a period of 5 min. The reaction mixture was stirred at 0 °C for 2 h and at 25 °C for 1 h. A small aliquot of the reaction mixture was withdrawn by a syringe hydrolyzed with water and analyzed by GLC on 5% SE-30 column, 6 ft × 0.125 in., for the unreacted ester. There was present 99% of ethyl hexanoate. Now the reaction mixture was hydrolyzed, oxidized ($NaOH\text{–}H_2O_2$, 1 h, 60 °C), and analyzed by GLC on a 5% Carbowax 20M, 6 ft × 0.125 in., indicating the presence of 100% 2-cyclohexenol and 0% n-hexyl alcohol and 2-cyclohexenone.

The results for the other pairs are summarized in Table I.

**General Preparative Procedures for the Reduction of Conjugated Aldehydes and Ketones with 9-BBN.** Representative

α,β-unsaturated aldehydes and ketones were reduced (25–100-mmol scale) with 9-BBN and the allylic alcohols were isolated to establish the synthetic utility of the reaction.

**Reduction of Cinnamaldehyde to Cinnamyl Alcohol (Procedure A).** A 300-ml flask with a side arm capped with silicone rubber stopple, a magnetic stirring bar, and a reflux condenser connected to a mercury bubbler was flame dried and cooled down to room temperature under a dry stream of nitrogen. Tetrahydrofuran (10 ml), was injected into the reaction flask followed by 3.15 ml (25 mmol) of cinnamaldehyde. The contents of the flask were cooled to 0 °C (ice bath). To this well-stirred solution, 42 ml (27 mmol) of a 0.62 M solution of 9-BBN in THF was added dropwise. The resulting mixture was stirred well at 0 °C for 2 h and at 25 °C for 1 h. Then methanol (1 ml) was added to destroy the excess hydride. The boronic acid derivative was oxidized by the addition of 10 ml (30 mmol) of 3 N aqueous sodium hydroxide followed by dropwise addition of 8 ml (70 mmol) of 30% hydrogen peroxide (*Caution*: exothermic reaction). The resulting mixture was stirred at 60 °C for 1 h. The aqueous phase was saturated with anhydrous potassium carbonate. The organic phase was separated. The aqueous phase was extracted with 2 × 20 ml of ether. The combined organic extract was washed four times with 20-ml portions of water to remove 1,5-cyclooctanediol and dried ($MgSO_4$). Removal of the volatile solvents and vacuum distillation yielded 2.87 g (86%) of cinnamyl alcohol as a low-melting white solid, mp 30–32 °C.

**Reduction of 2-Cyclopentenone to 2-Cyclopentenol (Procedure B).** A 500-ml three-necked flask equipped with a side arm fitted with a silicone rubber stopple, egg-shaped stirring bar, and a pressure equalizing dropping funnel connected to a mercury bubbler through a connecting tube was flame dried and cooled to room temperature under a dry stream of nitrogen. The flask was charged with 25 ml of dry THF and 8.35 ml (8.21 g, 100 mmol) of 2-cyclopentenone (distilled under nitrogen, $n^{20}$D 1.4814) and cooled to 0 °C with an ice bath. Then 171.7 ml (103 mmol) of a 0.6 M 9-BBN solution in THF was added dropwise over a period of 2 h with vigorous stirring. After 4 h at 0 °C, the solution was stirred for 2 h at 25 °C. Then 0.5 ml of methanol was added to destroy excess 9-BBN. THF was removed under reduced pressure and dry *n*-pentane (100 ml) was introduced followed by 6.4 ml (6.3 g, 103 mmol) of 2-aminoethanol. Immediately, the ethanolamine derivative of 9-BBN starts to precipitate. The mixture was centrifuged and the clean pentane layer decanted. The precipitate was washed with three 30-ml portions of *n*-pentane and centrifuged, and the decants were added to the main fraction. Pentane was distilled off and the residue on vacuum distillation gave 7.12 g (85%) of 2-cyclopentenol as a colorless liquid, bp 78 °C (59 mm), $n^{20}$D 1.4716, >99% pure by GLC.

**Reduction of 2-Cyclohexenone to 2-Cyclohexenol.** A typical reaction setup was assembled. The flask was charged with 6.5 ml of THF and 2.45 ml (25 mmol) of 2-cyclohexenone. To this solution of the enone stirred and maintained at 0 °C (ice bath), 42.5 ml (25.5 mmol) of a 0.6 M solution of 9-BBN in THF was added dropwise (45 min). The resulting mixture was stirred at 0 °C for 2 h and at 25 °C for 1 h. The reaction mixture was worked up by procedure B. Distillation of pentane and vacuum distillation of the residue gave 2.07 g (85%) of 2-cyclohexenol as a colorless liquid, bp 75 (22 mm), $n^{20}$D 1.4865, >99% pure by GLC.

**Reduction of 3-Methyl-2-cyclopentenone to 3-Methyl-2-cyclopentenol.** 3-Methyl-2-cyclopentenone (2.5 ml, 25 mmol) in 10 ml of THF was reacted with 42.5 ml (27 mmol) of 0.63 M solution of 9-BBN in THF at 0 °C for 2 h and at 25 °C for 1 h and worked up by procedure B. Removal of pentane and distillation of the residue yielded 1.83 g (76%) of 3-methyl-2-cyclopentenol as a colorless liquid, bp 67–68 °C (8 mm), $n^{20}$D 1.4705.

**Reduction of 1-Acetylcyclohexene to 1-Cyclohexene-1-ethanol.** 1-Acetylcyclohexene (3.3 ml, 25 mmol) was reduced with 26 mmol of 9-BBN solution in THF and the product isolated by procedure B. 1-Cyclohexene-1-ethanol (2.84 g, 90%) was isolated as a colorless liquid, bp 78 °C (5 mm), $n^{20}$D 1.4845.

**Selective Reduction of 4-Carbethoxy-3-methyl-2-cyclohexenone to 4-Carbethoxy-3-methyl-2-cyclohexenol.** The reaction setup was the same as in the reduction of 2-cyclopentenone. The flask was charged with 25 ml of dry THF and 17.2 ml (18.2 g, 100 mmol) of 4-carbethoxy-3-methyl-2-cyclohexenone. The flask was immersed in an ice bath and the contents were cooled to 0 °C. Then 191 ml (104 mmol) of a 0.54 M solution of 9-BBN in THF was added dropwise over a period of 1 h through a dropping funnel. After 3 h at 0 °C, the mixture was stirred at 25 °C for 1 h. Methanol (0.5 ml), was added to destroy the excess hydride. THF was removed under reduced pressure and replaced with 120 ml of *n*-pentane. 2-Aminoethanol (6.4 ml, 104 mmol) was added and immediately the ethanolamine derivative of 9-BBN begins to precipitate out. The mixture was centrifuged and the clean pentane layer decanted. The precipitate was washed with 5 × 20 ml of pentane and the decantes were added to the main fraction. Pentane was distilled off and vacuum distillation of the residue gave 15.2 g (83%) of 4-carbethoxy-3-methyl-2-cyclohexenol as a pale yellow liquid: bp 99–100 °C (0.6 mm); $n^{20}$D 1.4812, IR (neat) 3390 (–OH, broad), 1740 $cm^{-1}$ [$OC(=O)CH_2CH_3$]; parent enone has an additional intense absorption at 1675 $cm^{-1}$ (O=CC=C); NMR ($CCl_4$, $Me_4Si$) δ 1.3 (t, 3, $-CH_2CH_3$), 1.4–2.2 (m, 7, $-CH_2CH_2-$, $C=CCH_3$), 2.9 (m, 1, >CHCOOEt), 3.8–4.4 (m, 1, >CHOH), 4.1 (q, 2, $-OCH_2CH_3$), 3.9 (s, 1, –OH, exchange with $D_2O$), 5.6 (m, 1, >C=CH–).

GLC analysis of the product on a 5% Carbowax 20M column, 2 ft × 0.125 in., indicated it to be a mixture of cis and trans isomers in 30:70 proportions and the absence of enone. It is probable that the major isomer is the trans, but the stereochemistry was not investigated at this time.

## References and Notes


(1) (a) Presented at the 169th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1975, Abstracts, No. ORGN-22. (b) For a preliminary communication on this reaction, see S. Krishnamurthy and H. C. Brown, *J. Org. Chem.*, **40**, 1864 (1975).
(2) Postdoctoral Research Associate on Grant DA-ARO-D-31-124-73-G148, supported by the U.S. Army Research Office.
(3) For a recent discussion on this subject, see H. O. House, "Modern Synthetic Reactions", 2d ed, W. A. Benjamin, Menlo Park, Calif., 1972, pp 89–95; (b) C. F. Lane, *Aldrichimica Acta*, **9**, 31 (1976), and references cited therein.
(4) M. R. Johnson and B. Rickborn, *J. Org. Chem.*, **35**, 1041 (1970).
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(8) H. C. Brown and N. M. Yoon, *J. Am. Chem. Soc.*, **88**, 1464 (1966).
(9) (a) "The Use of Aluminum Alkyls in Organic Synthesis", Ethyl Corp., 1970 and 1973; (b) "Speciality Reducing Agents", Texas Alkyls Inc.
(10) H. C. Brown, S. Krishnamurthy, and N. M. Yoon, *J. Org. Chem.*, **41**, 1778 (1976).
(11) This convenient precipitation of the 9-BBN–ethanolamine adduct was developed by Dr. Gary W. Kramer of our laboratory for a related application. In addition to pentane, ether and benzene also work satisfactorily.
(12) 9-BBN is now commercially available from the Aldrich Chemical Co., Milwaukee, Wis., both as the solid and the solutions in tetrahydrofuran and hexane (0.5 M). Use of the hexane solution should avoid the necessity of replacement of THF and thus simplify the procedure.