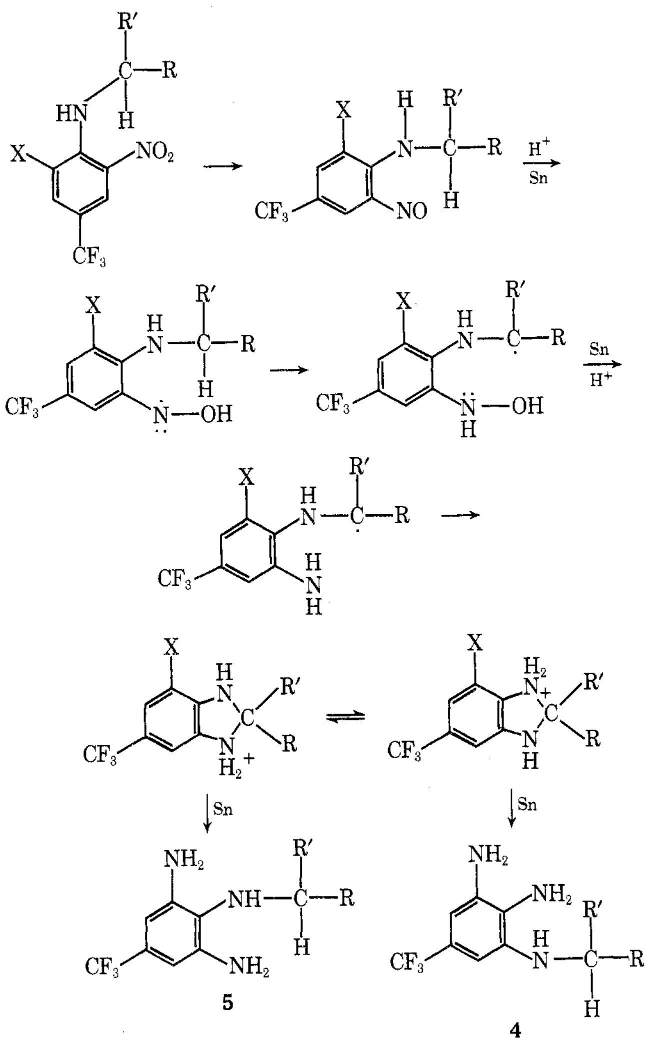
Scheme I



for relative importance of these two pathways). Similar mechanisms have been proposed for the formation of benzimidazoles by the reductive photolysis of dinitroanilines; however, no rearrangement of the alkyl group has been reported. It is probable, however, that such rearrangement products may be formed but not previously detected.

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References and Notes

(1) R. E. Lyle and J. L. LaMattina, *J. Org. Chem.*, **40**, 438 (1975).

(2) (a) E. Leitis and D. Crosby, *J. Agr. Food Chem.*, **22**, 842 (1974); (b) P. C. Kearney, J. Plimmer, and U. Klingebiel, the 166th National Meeting of the American Chemical Society, Chicago, Ill., Aug. 27–31, 1973, PEST-3; (c) C. P. Nilles and M. J. Zabik, *J. Agr. Food Chem.*, **22**, 684 (1974); (d) O-Meth-Cohn and H. Suschitzky, *Adv. Heterocycl. Chem.*, **14**, 211 (1972).

(3) For example see (a) A. J. Boulton and P. B. Ghosh, *Adv. Heterocycl. Chem.*, **10**, 1 (1969); (b) F. Galbraith and S. Smiles, *J. Chem. Soc. (London)*, 1234 (1935).

(4) Since the rearrangement led from a symmetrical to an unsymmetrical product, the reaction is called the "Unsymmetrical Nitrogen Hop" to summarize this process.

(5) H. O. House, "Modern Synthetic Reactions", Second ed, W. A. Benjamin, Inc., Menlo Park, Calif., 1972, pp 148, 211.

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9-Borabicyclo[3.3.1]nonane as A Highly Selective Reducing Agent for the Facile Conversion of α,β-Unsaturated Aldehydes and Ketones to the Corresponding Allylic Alcohols in the Presence of Other Functional Groups[1]

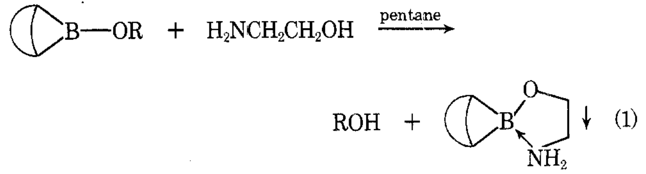
Summary: Reduction of α,β-unsaturated aldehydes and ketones with 9-borabicyclo[3.3.1]nonane proceeds selectively and cleanly to the corresponding allylic alcohols in excellent yield in the presence of many other functional groups.

Sir: 9-Borabicyclo[3.3.1]nonane (9-BBN) is an exceptionally stable bicyclic dialkylborane[2] and hydroborates olefins with very high regio- and stereoselectivity, far greater than those observed with borane and other dialkylboranes.[3] These remarkable characteristics and its commercial availability[4] prompted us to examine the behavior of 9-BBN as a reducing agent toward representative organic functional groups in tetrahydrofuran[5] (THF).

In the course of this investigation we found that 9-BBN reduces aldehydes and ketones rapidly and cleanly (to alcohols) even faster than it hydroborates olefins. For example, $k_{\text{cyclohexanone}}/k_{\text{cyclopentene}}$ was found to be 37 in competition experiments. Thus, the reaction of 2-cyclohexenone with 4 molar equiv of 9-BBN at 25° proceeds rapidly, using 1 equiv of 9-BBN in 10 min, while the uptake of the second equivalent requires 3 days. GLC analysis of the reaction mixture, following hydrolysis at the end of 10 min, indicated the presence of 2-cyclohexenol in 100% yield. Consequently, the reaction involves a rapid initial reduction of the carbonyl group followed by very sluggish subsequent hydroboration. The clean reduction of α,β-unsaturated aldehydes and ketones by hydride reagents has offered considerable difficulty.[6,7] Accordingly, it appeared desirable to examine this reaction in detail.

The reductions were carried out by the dropwise addition of an essentially stoichiometric quantity of 9-BBN solution in THF (3–5% excess) to the ketone in THF solution at 0°. The reaction mixtures were stirred for 2–4 hr at 0° and 1 hr at 25°.

Two procedures can be used to isolate the product. The reaction mixture can be treated with alkaline hydrogen peroxide to oxidize the 9-BBN moiety and the allylic alcohol separated by distillation from the 1,5-cyclooctanediol. More conveniently, the THF can be removed under vacuum from the reaction mixture and then pentane added. Addition of 1 mol of ethanolamine then precipitates 9-BBN as the adduct. Distillation of the pentane solution then provides the products[8] (eq 1). This serves as an excellent neutral work-up procedure for compounds containing acid- and base-sensitive groups.



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).

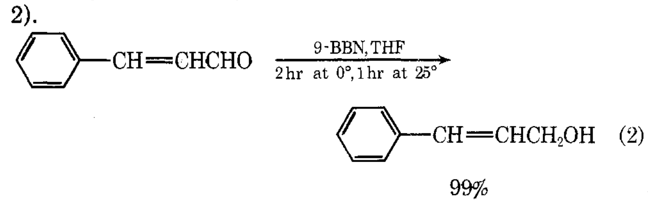
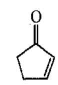
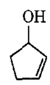
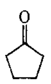
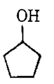
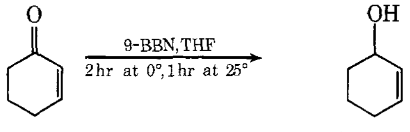


Table I
Reduction of 2-Cyclopentenone with Various Reducing Agents

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

[a] Analysis by GLC. [b] Reference 7. [c] Reference 9a. [d] Present work.

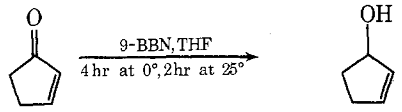
2-Cyclohexenone is converted to 2-cyclohexenol in quantitative yield (eq 3).



(3)

100% (84% isolated)

Even 2-cyclopentenone, known for it's susceptibility to undergo conjugate addition with hydride reducing agents,[7] is cleanly converted to the desired 2-cyclopentenol in essentially quantitative yield (eq 4).

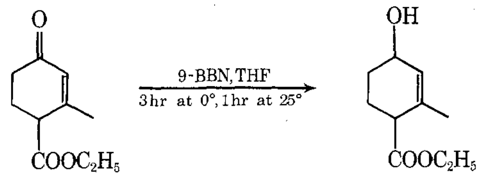


(4)

100% (85% isolated)

Results summarized in Table I clearly reveals the superiority of 9-BBN over previously available reagents, such as lithium aluminum hydride, lithium tri-*tert*-butoxyaluminohydride, sodium borohydride, and aluminum hydride.

Further, the results of the competition experiments involving 2-cyclohexenone and organic compounds containing representative functional groups toward 9-BBN and of other research underway[5] indicate that the present reaction can tolerate the presence of a large variety of functional groups, such as nitro, halogen, epoxide, carboxylic acid, ester, amide, nitrile, sulfide, disulfide, sulfoxide, sulfone, tosylate, azo, etc. This is a major advantage of 9-BBN over other reagents such as diisobutylaluminum hydride.[9] The remarkable utility of 9-BBN for such selective reductions involving polyfunctional substrates is confirmed by the selective conversion of 4-carbethoxy-3-methyl-2-cyclohexenone to 4-carbethoxy-3-methyl-2-cyclohexenol and *o*-nitrocinnamaldehyde to *o*-nitrocinnamyl alcohol in yields of 95 and 76%, respectively (eq 5).



(5)

95% (86% isolated)

The following preparative procedure for the reduction of 2-cyclopentenone to 2-cyclopentenol is representative. An oven-dried 500-ml three-necked flask, equipped with a side arm fitted with a silicone rubber stopple, egg-shaped stirring bar, and 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 (n^{20}D 1.4814) and cooled to 0° 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 hr with vigorous stirring. After 4 hr at 0°, the solution was stirred for 2 hr at 25°. 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) added, followed by 6.4 ml (6.3 g, 103 mmol) of 2-aminoethanol. Immediately the ethanolamine derivative of 9-BBN precipitated. 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 decantates 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° (59 mm), n^{20}D 1.4716 [lit.[10] bp 52° (12 mm), n^{20}D 1.4717], >99% pure by GLC.

In conclusion, it should be pointed out that 9-BBN possesses certain major advantages over other reagents for this transformation. It reduces 2-enones, normally highly susceptible to conjugate reduction, cleanly to the allylic alcohols. Yet it is a very mild reducing agent, similar to sodium borohydride and lithium tri-*tert*-butoxyaluminohydride in its selectivity.

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(2) E. F. Knights and H. C. Brown, *J. Amer. Chem. Soc.*, **90**, 5280, 5281 (1968).
(3) C. G. Scouten and H. C. Brown, *J. Org. Chem.*, **38**, 4092 (1973); H. C. Brown, E. F. Knights, and C. G. Scouten, *J. Amer. Chem. Soc.*, **96**, 7765 (1974).
(4) 9-BBN is now available commercially from the Aldrich Chemical Co., Milwaukee, Wis., both as the solid and the solution in tetrahydrofuran.
(5) An extensive study by Drs. S. Krishnamurthy and N. M. Yoon is underway.
(6) For a recent detailed and critical discussion, see M. R. Johnson and B. Rickborn, *J. Org. Chem.*, **35**, 1041 (1970).
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(8) This convenient precipitation of the 9-BBN–ethanolamine adduct was developed by Gary W. Kramer of our laboratory for a related application.
(9) (a) K. E. Wilson, R. T. Seidner, and S. Masamune, *J. Chem. Soc., Chem. Commun.*, 213 (1970); (b) "The Use of Aluminum Alkyls in Organic Synthesis", Ethyl Corporation, 1970 and 1973; (c) "Specialty Reducing Agents", Texas Alkyls Inc.
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(11) Postdoctoral Research Associate on Grant No. DA-ARO-D-31-124-73G148, supported by the U.S. Army Research Office (Durham).

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Photoannelations with α-Formyl Ketones. Enol Specificity in the Reaction of Acyclic α-Formyl Ketones with Alkenes[1]

Summary: The irradiation of several acyclic α-formyl ketones in the presence of alkenes gives rise to photoproducts derived exclusively from that tautomer enolized toward the aldehyde carbonyl, which can then be cyclized to provide a new cyclohexenone annelation sequence.

Sir: The photochemical cycloaddition of β diketones to alkenes[2a,b] is well documented and has been adequately reviewed.[3a–e] In general this reaction can be viewed as pro-