from the solvent evaporation was purified by silica gel column chromatography (eluant hexane–CH_2Cl_2, 8:1, v/v), affording benzil (385 mg): mp 94–95 °C from benzene–hexane.

3,4-Diphenyl-4-hydroxy-2-isoxazolin-5-one (4b). Methyl 2,3-diphenyl-2-hydroxy-3-(hydroxyimino)propanoate[4] (**3b**; 650 mg) was dissolved in acetone (90 mL), N_2 was bubbled through the solution for 5 min, and irradiation (high-pressure Hg lamp, 125 W, Pyrex filter) was carried out for 5 h. After solvent evaporation, silica gel column chromatography of the residue (eluant hexane–Et_2O, 4:1, v/v) afforded 3,4-diphenyl-4-hydroxy-2-isoxazolin-5-one (215 mg): mp 106–107 °C from Et_2O–pentane, identical with an authentic sample.[2] Unreacted ester **3b** (170 mg) was also recovered.

Registry No. 1, 68708-09-8; **3a**, 89773-82-0; **3b**, 54458-46-7; **4a**, 89773-83-1; **4b**, 80490-41-1.

Communications

A New, Highly Stereoselective Reducing Agent, Potassium 9-(2,3-Dimethyl-2-butoxy)-9-boratabicyclo[3.3.1]nonane

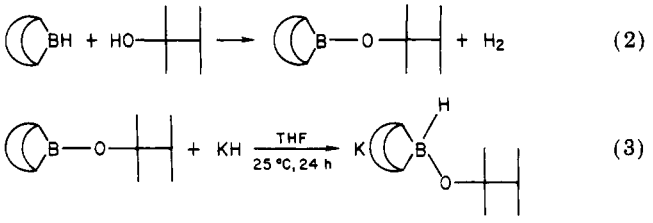
Summary: A new reagent, potassium 9-(2,3-dimethyl-2-butoxy)-9-boratabicyclo[3.3.1]nonane (K9-OThx-9-BBNH), achieves highly stereoselective reductions of cyclic ketones with very simple recovery of the product.

Sir: We have synthesized a new stereoselective reducing agent, potassium 9-(2,3-dimethyl-2-butoxy)-9-boratabicyclo[3.3.1]nonane (K9-OThx-9-BBNH, **1**), and have examined its stereoselectivity toward cyclic ketones. This borohydride reveals an excellent stereoselectivity at 0 °C, comparable to the results previously achieved with lithium tri-*sec*-butylborohydride at that temperature. Moreover, the byproduct 9-BBN derivative is easily removed as an ate complex, greatly simplifying the recovery of the reduction product.

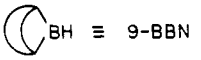
Recently we developed a general method for preparation in high purity of potassium trialkoxyborohydrides containing a wide variety of alkoxy groups from the direct reaction of potassium hydride and the corresponding trialkoxyboranes[1] (eq 1). We were able to extend this

$$KH + (RO)_3B \xrightarrow[\Delta]{THF} K(RO)_3BH \qquad (1)$$

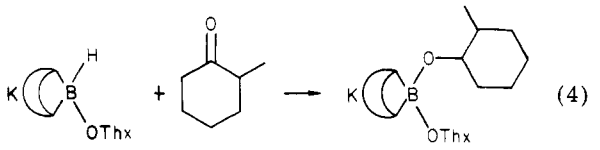
synthesis to the preparation of the borohydrides from B-OR-9-BBN.[2] In the course of this study, we discovered that B-OThx-9-BBN was readily converted into its borohydride, K9-OThx-9-BBNH (eq 2 and 3).[3] The reagent



1



1 is very stable and no disproportionation was observed over more than 1 year when the solution in THF was stored under a positive pressure of nitrogen. This reagent readily reduced ketones at 0 °C and exhibits an excellent stereoselectivity with representative cyclic ketones (eq 4).



98.5% cis

Its stereoselectivity is comparable to the results previously achieved at 0 °C with lithium tri-*sec*-butylborohydride.[4a] However, it still does not approach the exceptionally high stereoselectivity possible with lithium trisiamylborohydride.[4c] The results and comparable data for the other two reagents are summarized in Table I.

Table I. Stereoselective Reduction of Cyclic Ketones with Potassium 9-(2,3-Dimethyl-2-butoxy)-9-boratabicyclo[3.3.1]nonane (K9-OThx-9-BBNH) in Tetrahydrofuran at 0 °C[a,b]

	ratio of less stable isomer, %		
ketone	K9-OThx-9-BBNH	Li-*s*-Bu_3-BH[c]	$LiSia_3$-BH[d]
cyclohexanone			
2-methyl-	98.5	99.3	99.4
3-methyl-	90	85	98
4-methyl-	85.5	80.5	93
4-*tert*-butyl-	87	87.5[d]	96.5
3,3,5-trimethyl-	>99.9	99.8	99
norcamphor	95	99.6	99
camphor	97.5	99.6	>99.9

[a] A 2:1 ratio for reagent:ketone was utilized. [b] The yields of alcohols were quantitative. [c] Data taken from ref 4a. [d] Present study.

In recent years, new developments in the area of stereoselective reduction of cyclic ketones have been exceptionally encouraging.[4] Hindered trialkylborohydrides, such as lithium tri-*sec*-butylborohydride[4a] and lithium trisiamylborohydride,[4c] reduce cyclic ketones containing an α-methyl substitutent to the corresponding alcohols with ≥99% of the less stable isomers. In cases where the alkyl substituent is further removed from the keto group, the stereoselectivity of the reduction is still high, in the 80% to 95% range. Although these trialkylborohydrides are very useful, their byproducts, the trialkylboranes, are often

(1) (a) Brown, H. C.; Nazer, B.; Sikorski, J. A. *Organometallics* **1983**, *2*, 634. (b) Brown, H. C.; Cha, J. S.; Nazer, B. *Inorg. Chem.*, in press.
(2) Research in progress.
(3) Addition of the corresponding potassium alkoxide to 9-BBN did not give these borohydrides in pure form, but the reaction proceeded with disproportionation.

(4) (a) Brown, H. C.; Krishnamurthy, S. *J. Am. Chem. Soc.* **1972**, *94*, 7159. (b) Krishnamurthy, S. *Aldrichimica Acta* **1974**, *7*, 55. (c) Krishnamurthy, S.; Brown, H. C. *J. Am. Chem. Soc.* **1976**, *98*, 3383. (d) Brown, C. A.; Krishnamurthy, S. *J. Organomet. Chem.* **1978**, *156*, 111. (e) Brown, H. C.; Krishnamurthy, S. *Tetrahedron* **1979**, *35*, 567.

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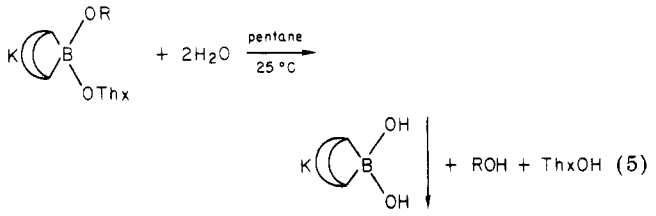
relatively difficult to remove from the reaction mixture. Usually they must be oxidized by alkaline hydrogen peroxide, following reduction, to convert them into the corresponding alcohols and boric acid. This might be an undesirable procedure, particularly in cases where the compound being reduced is itself sensitive to oxidation.

Fortunately, the use of reagent 1 overcomes this problem, while achieving comparable stereoselectivity. The byproduct of the reaction, K9-OThx-9-BBNOR, is readily converted into the hydroxy ate complex by treatment with a slight excess over the theoretical amount of water (eq 5). This simple isolation procedure provides a major



advantage for this reagent in stereoselective reductions where it is desirable to avoid the presence of higher trialkylboranes in the reaction mixture.

The following procedure served to prepare B-OThx-9-BBN. An oven-dried, 250-mL, round-bottomed flask, equipped with a side arm, a condenser, and an adaptor connected to a mercury bubbler, was cooled to room temperature under a stream of nitrogen and maintained under a static pressure of nitrogen. To this flask was added 12.2 g of 9-BBN (100 mmol) and 30 mL of THF; 10.7 g of 2,3-dimethyl-2-butanol (105 mmol) was added to the slurry of 9-BBN and THF dropwise with vigorous stirring at room temperature. After the addition was completed, the reaction mixture was brought to a gentle reflux to ensure completion of hydrogen evolution (1 h). Evaporation of the solvent, followed by distillation from a small piece of potassium metal, yielded 20 g of pure B-OThx-9-BBN (89% yield): bp 95–96 °C (1.3 mm), n^{20}_D 1.4785, ^{11}B NMR δ 55.1 ppm (neat).[5]

The following procedure served for the preparation of the reagent. Into a 100-mL flask was placed 6.4 g of potassium hydride (160 mmol) as an oil suspension by using a double-ended needle. Potassium hydride was washed with THF (3 × 10 mL) to remove the oil medium.[6] To this oil-free potassium hydride was added 50 mL of freshly distilled THF, followed by 18.0 g of B-OThx-9-BBN (80 mmol). The reaction mixture was stirred vigorously at room temperature. The reaction was complete within 24 h, producing the addition compound, K9-OThx-9-BBNH, in pure form: ^{11}B NMR δ −2.8 (d, J_{BH} = 60.3 Hz), IR ν 2000 cm^{-1} (B–H), 1355 cm^{-1} (B–O).

The following procedure was used to explore the stereoselectivity of this reagent. In a 50-mL, round-bottomed flask was placed 2.2 mL of a 0.92 M solution of the reagent in THF (2.0 mmol). The flask was maintained at 0 °C by immersion in an ice–water bath. To the flask was added 1.0 mL of precooled 2-methylcyclohexanone solution in THF (1.0 M in ketone) and the reaction mixture was stirred at 0 °C for 3 h. The reaction was then quenched by addition of 2 mL of 2 N HCl, and the aqueous layer was saturated with anhydrous potassium carbonate. GC analysis of the organic layer showed the presence of a quantitative yield of 2-methylcyclohexanol, containing 98.5% of the cis isomer.

The use of such a large excess of reagent is not necessary, as shown by the following larger scale reaction. In the usual assembly, 5.6 g of 2-methylcyclohexanone (50 mmol) was added dropwise as the neat liquid to 60 mL of the reagent solution in THF (55 mmol) at 0 °C. The reaction was complete in 1 h and the mixture was hydrolyzed with 2.5 mL (140 mmol) of water for 0.5 h at room temperature. All THF was then pumped off by using an aspirator. Then 50 mL of pentane was added to the residue and the mixture was stirred. A white solid precipitated out. The pentane solution was separated and subjected to fractional distillation: 4.8 g of 2-methylcyclohexanol (84%), bp 166–168 °C (753 mm), containing by GC analysis 98.5% of the cis isomer.

Registry No. 1, 89999-86-0; *B*-OThx-9-BBN, 89999-87-1; 9-BBN, 280-64-8; 2-methylcyclohexanone, 583-60-8; 3-methylcyclohexanone, 591-24-2; 4-methylcyclohexanone, 589-92-4; 4-*tert*-butylcyclohexanone, 98-53-3; 3,3,5-trimethylcyclohexanone, 873-94-9; norcamphor, 497-38-1; camphor, 76-22-2; thexyl alcohol, 594-60-5; *cis*-2-methylcyclohexanol, 7443-70-1.

(5) The chemical shifts are reported relative to BF_3·OEt_2 with chemical shifts downfield from BF_3·OEt_2 assigned as positive.
(6) Brown, C. A. *J. Org. Chem.* **1974**, *39*, 3913.

(7) Postdoctoral research associate on Grant ARO DAAG-29-79-C-0027, supported by the U.S. Army Research Office.

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Photoinitiated Additions of Ketones to Bicyclo[1.1.0]butanes. The Existence of Diverse Reaction Pathways

Summary: A radical chain process has been established for the addition of a series of ketones across the C1–C3 bond of bicyclo[1.1.0]butane and its methylated derivatives. For certain ketones, capture of an acyl radical intermediate, generated in a Norrish type I cleavage of the ketone, competes effectively with the radical chain process.

Sir: Recently, we reported the addition of a variety of nucleophiles across the C1–C7 bond of tricyclo[4.1.0.0^{2,7}]heptane in a photoinitiated reaction that involved initial electron transfer to excited state 1-cyanonaphthalene.[1] We have also described the addition of acetone across this same carbon–carbon σ bond.[2] We now report that a variety of different photoinitiated reaction paths can be observed for the addition of ketones across the C1–C3 σ bond of bicyclo[1.1.0]butane and its methylated derivatives.

Table I lists a series of reactions involving the photoinitiated addition of ketones across carbon–carbon single bonds of strained hydrocarbons. Yields appear to depend on the type of methyl substitution on the parent hydrocarbon and on the nature of the ketone. In those cases where methyl substitution was present at the C1(bridgehead) position, only "anti-Markovnikov" addition was observed and the yields were low.[3] Thus, while 1 gave 2

(1) Gassman, P. G.; Olson, K. D.; Walter, L.; Yamaguchi, R. *J. Am. Chem. Soc.* **1981**, *103*, 4977. Gassman, P. G.; Olson, K. D. *Ibid.* **1982**, *104*, 3740.
(2) Gassman, P. G.; Smith, J. L. *J. Org. Chem.* **1983**, *48*, 4438.

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