A NEW CLASS OF STEREOSELECTIVE REDUCING AGENTS, POTASSIUM 9-ALKYL-9-BORATABICYCLO [3,3,1]NONANES

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Summary: A new class of reducing agents, potassium 9-alkyl-9-boratabicyclo[3.3.1]nonanes (K 9-R-9-BENHs) was examined its stereoselectivity toward cyclic ketones. Among these, K 9-TB-9-BENH reveals the most favorable stereoselectivity, comparable to that by lithium trisiamylborohydride at 0° C.

The reaction of potassium hydride with alkyl- or alkoxy-substituted boranes provides a convenicent procedure for preparation of the corresponding potassium tri-substituted borohydrides.¹ These borohydrides possess unique reducing characteristics,^{1-d} especially showing a high degree of stereoselectivity toward cyclic ketones.^{1-e,2}

Recently, we synthesized a new class of reducing agents, potassium 9-alkyl-9-boratabicyclo-[3.3.1] nonanes (K 9-R-9-BBNHs) containing a wide variety of alkyl groups from the reaction of potassium hydride and the corresponding 9-alkyl-9-borabicyclo[3.3.1] nonanes (9-R-9-BBNs).³ In the course of a systematic study of the reducing charcteristics of these reagents, we found that some of these reagents exhibit an excellent stereoselectivity with typical cyclic ketones. The results and comparable data for the other reagents are summarized in Table 1.

All of the reagents examined showed a high stereoselectivity toward the monocyclic and bicyclic ketones. Of these, the selectivity exhibited by potassium 9-<u>t</u>-butyl-9-boratabicyclo-[3.3.1]nonane (K 9-TB-9-BENH) was especially promising, comparable to the results achieved at 0° C with lithium trisianylborohydride^{2,4}. This reagent has \checkmark -methyl substituted tertiary alkyl group on boron, which is more effective than those have β - or γ -methyl substituted bulkier alkyl groups on boron.

It is noteworthy that K 9-R-9-BBNHs are far superior to the reagents, potassium 9-alkoxy-9-boratabicyclo[3.3.1]nonanes (K 9-OR-9-BBNHs). This also strongly indicates an important role of α -substituted alkyl group on boron to exert a high stereoselectivity.

The following procedure was used for preparation of K 9-TB-9-BBNH. Into an oven-dried 100mL flask, equipped with a side arm, a condenser, and an adaptor connected to a mercury bubbler, was placed 3.6 g of potassium hydride (90 mmol) as an oil suspension and the oil medium was removed by washing with THF (3 x 10 mL). To this oil-free potassium hydride were added 25 mL of THF and 10.62 g of 9-TB-9-BBN⁶ (60 mmol). The reaction mixture was stirred vigorously at room temperature for 24 h to give K 9-TB-9-BBNH in a pure form : ¹¹B NMR δ -10.4 (d, J_{B-H} = 75 Hz)⁷; IR \mathcal{V} (B-H) 1980 cm⁻¹.

The reaction of 2-methylcyclohexanone with K 9-TB-9-BBNH is representative explore the stereoselectivity. In a 50-mL flask was placed 1.7 mL of a 1.2 M solution of the reagent in THF (2.0 mmol). The flask was maintained at 0° C and 1.0 mL of a precooled 1.0 M solution of 2-methyl-cyclohexanone solution in THF (1.0 mmol) was added. The reaction mixture was stirred at 0° C for 2 h and then quenched by addition of 0.5 mL of H₂O. The organoborane was oxidized with alkaline hydrogen peroxide. The aqueous layer was satured with anhydrous potassium carbonate, and the

Ketone	R in K 9-R-9-BBNH				K 9-OThx-	Li s-	Li Sia Bh ^d
	<u>n</u> Bu	neohexyl	s-amyl	<u>t</u> -Bu	9-BBNH ^d	Bu ₃ BH ^e	
cyclohexaneone					······································		
2-methyl-	97.5	98	99.5	99.5	98.5	99.3	99.4
3-methyl-	66.5	67	96	98	90	85	98
4-methyl-	61	61.5	90	94	85.5	80,5	93
4-tert-buthy1-	52,5	53	96.5	98.5	87	87.5	96.5
3,3,5-trimethyl-	98	98,5	99	99	99.9	99.8	99
norcamphor	92,5	93,5	95,5	95.5	95	99,6	99
camphor	99.5	99.5	99.9	99.9	97.5	99.6	99.9

Table 1. Stereoselective Reduction of Cyclic Ketones with Potassium 9-Alkyl-9-boratabicyclo-[3.3.1]nonanes (K 9-R-9-BENH) in Tetrahydrofuran at $0^{\circ}C^{a,b,c}$

a) A 2:1 ratio for reagent : ketone was utilized.b) The yields of alcohols were quantitative.c) The figures are percentage of the less stable isomers.d) Data taken from ref 2.e) Data taken from ref 5.

organic layer was separated and dried. GC analysis revealed the presence of 100% 2-methylcyclohexanol containing 99.5% of the <u>cis</u> isomer.

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References and Notes

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