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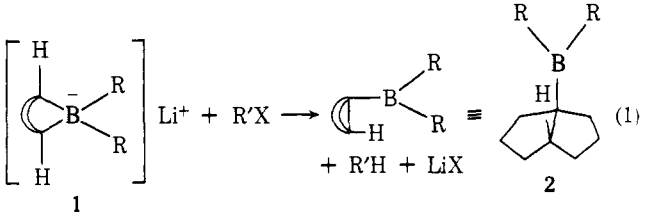
The Facile Rearrangement of Lithium Dialkyl-9-borabicyclo[3.3.1]nonane "Ate" Complexes via Hydride Transfer. A Simple Synthetic Route to *cis*-Bicyclo[3.3.0]oct-1-yldialkylboranes and Derivatives

Sir:

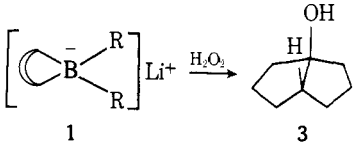
Lithium "ate" complexes (**1**), derived from the addition of alkyllithiums to representative *B*-alkyl-9-borabicyclo-[3.3.1]nonanes (*B*-alkyl-9-BBN), react with a variety of reducible organic substances to form *cis*-bicyclo[3.3.0]oct-1-yldialkylboranes (**2**). This reaction apparently proceeds by the transfer of one of the bridgehead hydrogens on the "ate" complex to the organic substrate followed by subsequent or concurrent migration of the bridge bond from boron to carbon (eq 1). This sequence provides not only a novel means for reducing aldehydes, ketones, alkyl halides, and acid chlorides but also a remarkably simple route to the *cis*-bicyclo[3.3.0]oct-1-yl system.



(1)

1 2

Recently we noted that hydrogen peroxide oxidation of lithium dialkyl-9-BBN "ate" complexes proceeds anomalously, giving rise to a mixture containing variable quantities of *cis*-bicyclo[3.3.0]octan-1-ol (**3**) (eq 2), instead of the expected *cis*-1,5-cyclooctanediol.[1] A rearrangement with formation of a new carbon–carbon bond was evidently



(2)

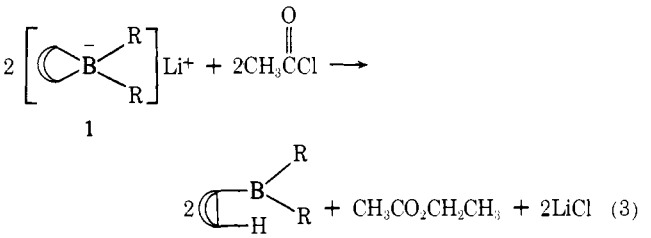
1 3

involved. We undertook to explore the possibility of achieving this rearrangement without the destruction of the postulated organoborane intermediate (**2**). Such organoboranes could provide simple routes to many compounds incorporating the *cis*-bicyclo[3.3.0]oct-1-yl moiety.[2,3]

Almost concurrently with our initial report of the anomalous oxidation of these "ate" complexes, it was reported that the same reagents were capable of reducing certain alkyl halides.[4] Consequently, we examined such halide reductions and established that the rearranged organoborane is indeed produced. Unfortunately, these reductions proceeded well only in hydrocarbon solvent. The presence of even small amounts of ethers inhibited the reaction. This became important in reactions utilizing methyllithium, soluble only in ethers. Removal of the ether to facilitate the desired reaction proved difficult.

Accordingly, another substrate was sought which would react with the "ate" complexes in the presence of ether. Simple aldehydes and ketones were reduced in hydrocarbon solvents, but the reaction was incomplete and sluggish when ether was present. An exception was chloral, which reacted rapidly even in the presence of ether.

The use of acetyl chloride as the reducible substrate offered major advantages. The reaction in hydrocarbon, as well as mixed ether–hydrocarbon solvent, was very vigorous. Analysis of the reaction mixture by GLC showed an essentially quantitative formation of the rearranged organoborane, while analysis by ^{1}H NMR indicated a high yield of ethyl acetate. Apparently 2 equiv of the "ate" complex (**1**) react with 1 equiv of acetyl chloride producing the rearranged organoborane (**2**) and lithium ethoxide. The ethoxide is then scavenged by the remaining equivalent of acetyl chloride to form the ester (eq 3).[5] This result was substantiated by the isolation of *n*-hexyl caproate from a similar reaction with hexanoyl chloride. We used this acid chloride route to examine the generality of this synthesis of *cis*-bicyclo[3.3.0]oct-1-yldialkylboranes. The results are summarized in Table I.[6]



(3)

1

The preparation of *cis*-bicyclo[3.3.0]oct-1-ylethylmethylborane is representative.[7] To an oven-dried, flamed-out, nitrogen-flushed, 50-ml flask fitted with a septum inlet, mag-

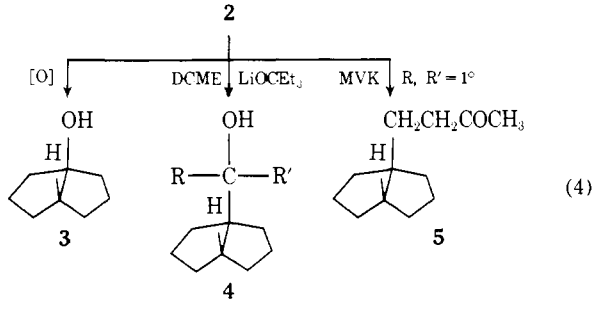
Table I. Preparation and Properties of *cis*-Bicyclo[3.3.0]oct-1-yldialkylboranes (**2**)

Alkyl groups					Physical data			
							^{11}B NMR	
R[a]	R'[b]	% yield[c] (GLC)	% yield[d] (Isolated)	% purity[e] (GLC)	bp, °C	(mmHg)	R_3B,[f] δ	"Ate" complex,[g] δ
Methyl	Methyl	96	94	93[h]	76–78	(20)	−81.9	+20
Ethyl	Methyl	99	97	97	28–32	(0.005)	−82.7	+20.4
Isopropyl	Methyl	92	97	94[h]	39–43	(0.005)	−81.3	+18.2
n-Butyl	Methyl	93	—	—	—		−82.7	+20.8
Methyl	*n*-Butyl	—	95	99	53–56	(0.005)	−82.3	+20.8
tert-Butyl	Methyl	91	97	86[h]	46–49	(0.005)	−80.3	+16.7
n-Butyl	*n*-Butyl	—[i]	94	—[i]	65–68	(0.005)	−81.8	+18.5

[a] *B*-R-9-BBN. [b] R'Li. [c] Reaction scale 4 mmol. [d] Reaction scales of 15–35 mmol. [e] ^{13}C NMR showed only one set of peaks for the bicyclooctyl ring. [f] ^{11}B NMR shift from BF_3:OEt_2 in ppm for **2**. [g] ^{11}B NMR shift from BF_3:OEt_2 for the "ate" complex precursor (**1**). [h] The major impurity appears to be the *B*-R-9-BBN. [i] The organoborane decomposes in the GLC.

netic stirring bar, and a reflux condenser connected to a mercury bubbler maintained under a positive pressure of nitrogen, there was added 5.25 g (35.0 mmol) of *B*-Et-9-BBN and 15 ml of dry, olefin-free pentane. Stirring was begun and the flask was cooled in a dry ice–acetone bath where 19.4 ml of 1.81 M (35.1 mmol) methyllithium (from methyl chloride) in diethyl ether was added slowly via the double-ended needle technique. After stirring about 10 min at −78°, the reaction mixture was allowed to come to room temperature and stir for 1.5 h. The flask was immersed in a cold water bath while 2.75 g (35.0 mmol) of acetyl chloride (freshly distilled from calcium hydride) was added dropwise from a syringe. A vigorous, exothermic reaction occurred, and a white precipitate formed. After stirring about 2 h, the supernatant liquid was decanted via the double-ended needle technique into an evacuated short-path distillation assembly where the volatiles were flash-distilled. The precipitate was washed with dry, olefin-free pentane (3 × 10 ml), and the washings were decanted in like manner into the distillation apparatus. The residual oil was vacuum distilled giving 5.6 g (97%) of a clear, colorless oil, bp 28–32 °C at 0.005 mm. GLC showed the material to be about 97% pure. ^{13}C NMR showed only one set of peaks, indicating that probably only one isomer was present. Alkaline hydrogen peroxide oxidation of a portion of the product in THF solution provided a 95% yield (GLC) of *cis*-bicyclo[3.3.0]octan-1-ol (**3**).

As examples of the synthetic utility of these new organoboranes, we carried out three typical organoborane reactions: alkaline hydrogen peroxide oxidation, the DCME reaction, and 1,4-addition to methyl vinyl ketone. These reactions were carried out under standard conditions[8] and readily provided the products **3, 4,** and **5** (eq 4).



(4)

The unexpected ability of the lithium dialkyl-9-BBN "ate" complexes to reduce a variety of organic substrates not only provides a novel reducing agent,[4,9] but also a new convenient route to the *cis*-bicyclo[3.3.0]oct-1-yldialkylboranes. These bicyclic organoboranes, coupled with the ever expanding battery of organoborane reactions, provide a very simple route to many compounds containing the *cis*-bicyclo[3.3.0]oct-1-yl moiety which have previously been difficult to prepare.

References and Notes

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(2) H. C. Brown, "Boranes in Organic Chemistry", Cornell University Press, Ithaca, N.Y., 1972.
(3) H. C. Brown, G. W. Kramer, A. B. Levy, and M. M. Midland, "Organic Syntheses via Boranes", Wiley-Interscience, New York, N.Y., 1975.
(4) Y. Yamamoto, H. Toi, S.-I. Murahashi, and I. Moritani, *J. Am. Chem. Soc.*, **97**, 2558 (1975).
(5) It has been recently reported that simple lithium tetraalkylboron "ate" complexes smoothly alkylate acid chlorides to give mixed ketones. E. Negishi, K.-W. Chiu, and T. Yoshida, *J. Org. Chem.*, **40**, 1676 (1975). In the present study, no evidence of such a competing alkylation was observed.
(6) Lithium dialkyl-9-BBN "ate" complexes containing secondary or tertiary alkyl groups must be prepared from the *B*-alkyl-9-BBN containing the secondary or tertiary group, since the reaction of secondary or tertiary alkyllithiums with trialkylboranes does not produce the desired "ate" complex in high yield. See ref 5 and E. J. Corey, K. R. Becker, and R. K. Varma, *J. Am. Chem. Soc.*, **94**, 8618 (1972).
(7) For a detailed account of the procedures used in this work, see ref 3, Chapter 9.
(8) Described in ref 3 for similar preparations.
(9) Y. Yamamoto, H. Toi, A. Sonoda, and S.-I. Murahashi, *J. Am. Chem. Soc.*, following paper in this issue.
(10) Graduate Research Assistant on Grant GP 41169X from the National Science Foundation.

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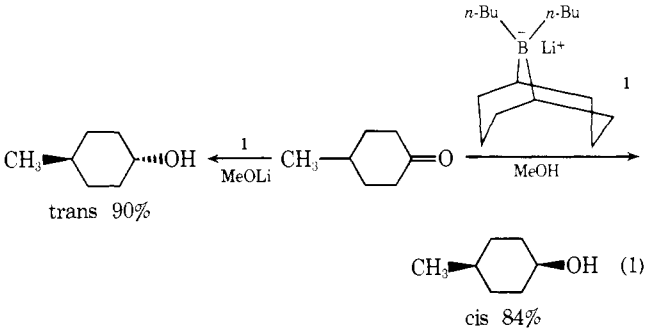
Stereo-, Chemo-, and Regioselective Reductions of Carbonyl Groups via the Lithium Di-*n*-butyl-9-borabicyclo[3.3.1]nonane "Ate" Complex

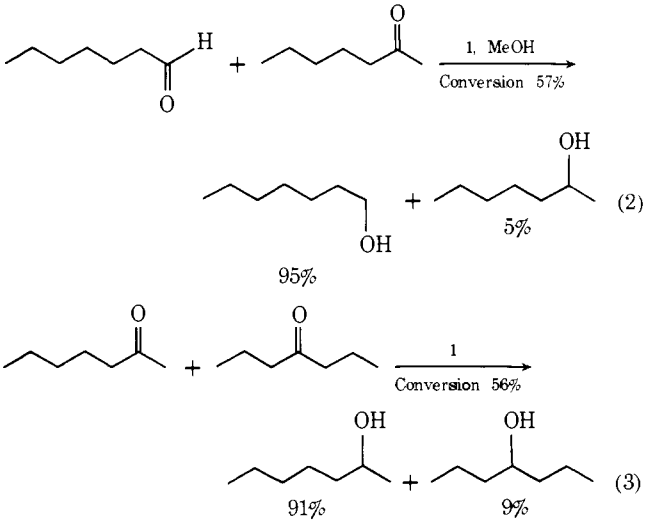
Sir:

The lithium di-*n*-butyl "ate" complex of 9-borabicyclo-[3.3.1]nonane (**1**) (9-BBN "ate" complex), a new type of reducing agent, exhibits high stereo-, chemo-, and regioselectivities[1] in the reduction of carbonyl groups. Thus both *cis*- and *trans*-4-methylcyclohexanols with reasonably high isomeric purity are independently obtainable from 4-methylcyclohexanone with a mere change in additive (eq 1). Such controllable stereoselective reduction via a unitary



(1)

reagent cannot be realized with reagents previously available.[2,5] Furthermore, aldehydes can be chemoselectively reduced in the presence of ketones (eq 2), and the reagent even discriminates between the regioisomers of ketones (eq 3).



(2)

(3)

We recently reported that the bridgehead hydrogen of the 9-BBN ring in **1** acts as a reducing moiety for halides, indicating an obvious difference between **1** and the presently known hydride reagents,[2,5] where the reducing agents contain hydride directly attached to the metal.[6] Therefore,