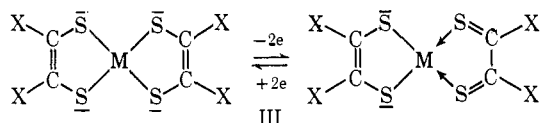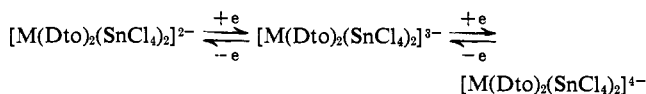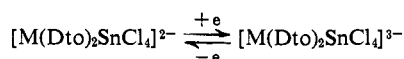$M(Dto)_2{}^{2-}$ complexes could be due to the presence of the carbonyl groups which do not allow a formal thiol-thione interconversion. We have observed that the


III

$SnCl_4$ adducts of the $M(Dto)_2{}^{2-}$ complexes undergo the following *reversible* one-electron reductions.

$$[M(Dto)_2(SnCl_4)_2]^{2-} \underset{-e}{\overset{+e}{\rightleftarrows}} [M(Dto)_2(SnCl_4)_2]^{3-} \underset{-e}{\overset{+e}{\rightleftarrows}}$$

$$[M(Dto)_2(SnCl_4)_2]^{4-}$$

and

$$[M(Dto)_2SnCl_4]^{2-} \underset{-e}{\overset{+e}{\rightleftarrows}} [M(Dto)_2SnCl_4]^{3-}$$

These results can be rationalized, by analogy to the 1,2-dithiolate complexes, if we consider the thioketonic form IV as a formal description for the structure of the adducts. The fact that only one one-electron reduction

IV
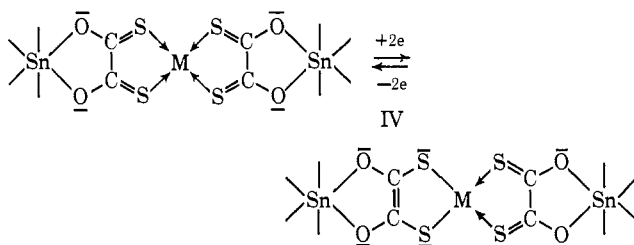
occurs with the 1:1 adducts, while two separate one-electron reductions occur with the 2:1 adducts, suggests that in addition to the ligands, the tin ions are also involved in the observed processes. More definitive information regarding the electronic structures of these complexes must await an epr study of the reduction products. The first set of low energy high intensity absorption bands in the visible spectra of the $M(Dto)_2{}^{2-}$ complexes (Table I) has been assigned by Gray and co-workers[10] to $M \rightarrow L$ charge-transfer processes. This assignment is consistent with the observed bathochromic shifts of these bands in the R_zSnCl_{4-z} adducts, since the introduction of additional metal ions to the $M(Dto)_2{}^{2-}$ complexes is expected primarily to lower the energy of the π and π^* ligand orbitals (Figure 1).[11] The hypsochromic shifts expected for the second set of $L \rightarrow M$ charge-transfer bands was also observed in the spectrum of the $Ni(Dto)_2{}^{2-}(SnCl_4)$ adduct. Electronic effects similar to the above have been reported by Shriver and coworkers[12] in a study of the BX_3 adducts (X = CH_3, Br, Cl, F) of the $Fe(phen)_2(CN)_2$ complex. Similar changes in the spectra of the $M(Dto)_2{}^{2-}$ complexes are also brought about with such Lewis acids as Cl_2SbR_3,

(10) A. R. Latham, V. C. Hascall, and H. B. Gray, *Inorg. Chem.*, 4, 788 (1965).

(11) Shriver and coworkers (ref 12) have calculated the orbital energies of CN^- + H^+ as a function of the N–H distance and found a decrease of the σ, σ^*, π, and π^* orbital energies as the N–H distance decreased. The same workers reported that changes in the d–d transitions in Lewis acid adducts of cyanide complexes are at most about fourfold less than changes in the charge-transfer bands.

(12) (a) D. F. Shriver, S. A. Shriver, and S. E. Anderson, *Inorg. Chem.*, 4, 725 (1965); (b) J. J. Rupp and D. F. Shriver, *ibid.*, 6, 755 (1967), and references therein.

R_3SiCl, $ZrCl_4$, $Ti(C_5H_5)_2Cl_2$, etc.[13] A detailed study of these compounds is currently in progress.
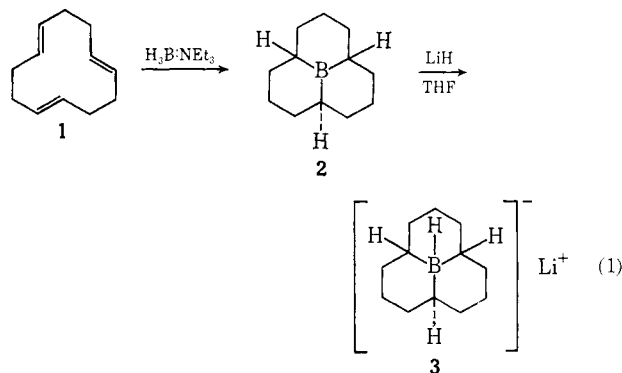
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Lithium Perhydro-9b-boraphenalylhydride. An Active Reducing Agent of Unusually High Stereoselectivity for the Reduction of Cyclic and Bicyclic Ketones

Sir:

Lithium hydride readily reacts with *cis,cis,trans*-perhydro-9b-boraphenalene[1,2] in refluxing tetrahydrofuran (eq 1) to give the corresponding addition compound **3**. This unusual derivative of lithium borohy-

dride, lithium perhydro-9b-boraphenalylhydride, is an active reducing agent which exhibits remarkably high stereoselectivity in the reduction of cyclic and bicyclic ketones, such as 2-methylcyclopentanone, 2-methylcyclohexanone, norcamphor, and camphor.

Since their original discovery[3] relatively little research has been devoted to the trialkylborohydrides. In a brief study of the properties of lithium triethylborohydride[4] it was observed that this material is a stronger reducing agent than the parent compound. The enhanced reducing properties of the derivative presumably arise from the greater ease of transferring hydride ion from the weaker Lewis acid, triethylborane, than from the stronger Lewis acid, borane.[3] It was of interest to explore the hydride transfer ability of a polycyclic boron derivative, such as **3**, with that of a simple trialkylborane derivative, such as lithium triethylborohydride.[5]

In the course of these studies we observed that **3** possessed an unusual ability to introduce steric control into the reduction of ketones. Thus 2-methylcyclopenta-

(1) G. W. Rotermund and R. Köster, *Ann. Chem.*, 686, 153 (1965).

(2) Köster's configuration assignment (*cis,cis,cis*) has been revised: H. C. Brown and W. C. Dickason, *J. Amer. Chem. Soc.*, 91, 1226 (1969).

(3) H. C. Brown, H. I. Schlesinger, I. Sheft, and D. M. Ritter, *ibid.*, 75, 192 (1953).

(4) A. Khuri, Ph.D. Thesis, Purdue University, Lafayette, Ind., 1960.

(5) A detailed study of the reducing characteristics of these derivatives is now underway with S. Krishnamurthy.

Table I. Reduction of Representative Cyclic and Bicyclic Ketones by Lithium Perhydro-9b-borophenalylhydride[a]

Ketone	Alcohol epimer	LiAlH₄[b]	LiAlH-(OMe)₃[b]	IPC₂BH[c]	LiBH-(n-Bu)₃	3
2-Methylcyclopentanone	cis	24	44	94	67	94
2-Methylcyclohexanone	cis	24	69	94	85	97
3-Methylcyclohexanone	trans	16[d]		35		59
3-t-Butylcyclohexanone	trans	15[d]		28		72
4-Methylcyclohexanone	cis	17[d]		33		52
4-t-Butylcyclohexanone	cis	8[e]		37		54
3,3,5-Trimethylcyclohexanone	trans	82[e]				99
Norcamphor	endo	89	98	94	98	99
Camphor	exo	92	99	100	98	99

[a] In THF at 0°. [b] H. C. Brown and H. R. Deck, *J. Amer. Chem. Soc.*, **87**, 5620 (1965). [c] V. K. Varma, Ph.D. Thesis, Purdue University, Lafayette, Ind., 1967. [d] Present work. [e] P. T. Lansbury and R. E. MacLeay, *J. Org. Chem.*, **28**, 1940 (1963).

none gave 94% of *cis*-2-methylcyclopentanol and 2-methylcyclohexanone gave the corresponding *cis* alcohol in 97% epimeric purity. Norcamphor gave 99% pure *endo*-norborneol, whereas camphor gave the *exo* isomer in 99% epimeric purity. 3,5,5-Trimethylcyclohexanone gives the *trans* isomer almost exclusively (99%). Even in the case of simple cyclohexanones containing a single alkyl substituent in the 3 or the 4 position there is observed a significant shift from the usual predominant attack of the reagent from the axial direction toward attack from the equatorial direction. Indeed 3-t-butylcyclohexanone gives 72% of the *trans* isomer as compared to only 15% with lithium aluminum hydride. These results are summarized in Table I.

Previously we had observed that steric control of the reduction of such ketones could be achieved by the use of dialkylboranes, in which the alkyl groups were quite bulky, as in disiamylborane and diisopinocampheyl-borane (IPC₂BH).[6,7] A disadvantage of this approach was the slowness of the reaction using the more hindered dialkylboranes. Thus, the reduction of camphor by diisopinocampheylborane is very slow and requires 24 hr to approach completion.[7] This difficulty is overcome with the present reagent **3**. In all cases, even in the reduction of the highly hindered camphor structure, the reaction is 100% complete within 0.5 hr at 0°.

A further advantage of the reagent is the fact that it contains only one active hydride. This should facilitate kinetic examination of the rates of reaction from the axial and equatorial directions and thereby facilitate resolution of the problem of the factors controlling the formation of epimeric ketones.[8]

Solutions of the trialkylborohydrides were prepared by refluxing for 3 hr in THF 1 equiv of the trialkyl-borane with an excess of finely divided lithium hydride (usually in moderate excess). The resulting solution was cooled and filtered through Celite. (The preparation was carried out under nitrogen and the solutions were stored under that inert gas.) The THF solutions of lithium tri-n-butylborohydride and **3** have a strong, broad absorption in the infrared at 4.95 μ, as has been noted for other alkali metal trialkylborohydrides.[9]

(6) H. C. Brown and D. B. Bigley, *J. Amer. Chem. Soc.*, **83**, 3166 (1961).
(7) H. C. Brown and V. K. Varma, *ibid.*, **88**, 2871 (1966).
(8) J. Klein, E. Dunkelblum, E. L. Eliel, and Y. Senda, *Tetrahedron Lett.*, 6127 (1968).
(9) P. Binger, G. Benedikt, G. W. Rotermund, and R. Köster, *Ann. Chem.*, **717**, 21 (1968), and references therein.

The reductions were carried out by adding 10 mmol of the ketone dissolved in 2.5 ml of THF to 12.5 ml of a 0.8 M solution of the borohydride in THF at 0°. After 30 min at 0°, the reaction mixture was treated with 5 ml of 3 M sodium hydroxide, followed by 5 ml of 30% hydrogen peroxide. The aqueous phase was saturated with potassium carbonate and the THF layer analyzed by glpc for the isomeric alcohols. In all cases the reactions were complete and no evidence for residual ketone was observed.

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Richard B. Wetherill Laboratory
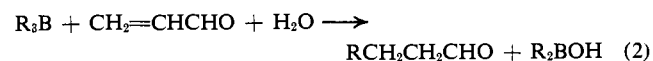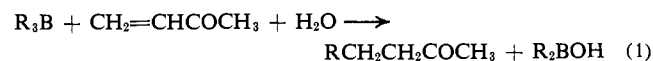*Purdue University, Lafayette, Indiana 47907*
Received October 10, 1969

Inhibition of the Reaction of Organoboranes with α,β-Unsaturated Carbonyl Derivatives by Galvinoxyl. Evidence for a Free-Radical Chain Mechanism

Sir:

We wish to report that the presence of 5 mol % of galvinoxyl completely inhibits the otherwise fast reactions of organoboranes with acrolein, methyl vinyl ketone, and related α,β-unsaturated carbonyl derivatives. Consequently, these facile 1,4-addition reactions must involve a free-radical chain mechanism.

The facile reaction of organoboranes with α,β-unsaturated carbonyl derivatives, such as methyl vinyl ketone[1] (1), acrolein[2] (2), α-methylacrolein[3] (3), α-bromoacrolein[3] (4), and 2-methylenecyclanones[4] (5), offers a convenient synthesis of a wide variety of substituted aldehydes and ketones.

$$R_3B + CH_2{=}CHCOCH_3 + H_2O \longrightarrow$$
$$RCH_2CH_2COCH_3 + R_2BOH \quad (1)$$

$$R_3B + CH_2{=}CHCHO + H_2O \longrightarrow$$
$$RCH_2CH_2CHO + R_2BOH \quad (2)$$

(1) A. Suzuki, A. Arase, H. Matsumoto, M. Itoh, H. C. Brown, M. M. Rogić, and M. W. Rathke, *J. Amer. Chem. Soc.*, **89**, 5708 (1967).
(2) H. C. Brown, M. M. Rogić, M. W. Rathke, and G. W. Kabalka, *ibid.*, **89**, 5709 (1967).
(3) H. C. Brown, M. M. Rogić, M. W. Rathke, and G. W. Kabalka, *ibid.*, **90**, 4165 (1968).
(4) H. C. Brown, M. M. Rogić, M. W. Rathke, and G. W. Kabalka, *ibid.*, **90**, 4165 (1968).