

nally appeared as a doublet (see discussion of compound 3) as an AB pattern with strong coupling from H_1 . By decoupling H_2 and H_6 , $J_{4,5}$ and $J_{4',5'}$ were determined to be equal (3.5 Hz). In addition, the *cis/trans* ratio of the homoallylic coupling constants ($H_1H_{4'}/H_1H_4$) was 1.11 (see ref 12).

Hence, on the basis of (1) small H_4F and $H_4'F$ coupling constants, (2) equality of $J_{4,5}$ and $J_{4',5'}$, and (3) agreement of "predicted" *cis/trans* homoallylic coupling constant ratio with theory, we conclude that 4 is planar¹⁸ with ring inversion not occurring (or involving very shallow boat conformations).

Acknowledgments. We would like to thank the Eli Lilly Co. for a grant-in-aid (to P. W. R.) and for the use of their Varian HA-100 nmr spectrometer.

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Received July 21, 1973

Lithium Dimesitylborohydride Bis(dimethoxyethane). A New Crystalline Reagent for Stereoselective Reduction of Ketones

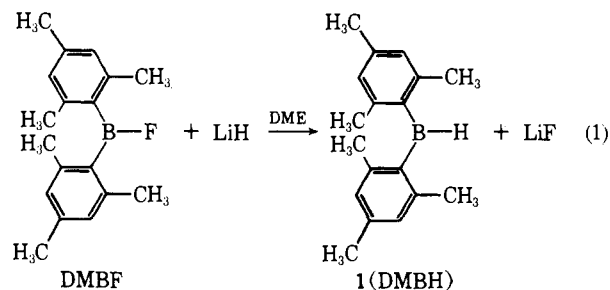
Sir:

The reaction described in detail below between lithium hydride and dimesitylboron fluoride (DMBF) provides the basis for a convenient synthetic route to three easily isolated, new, crystalline diorganoboranes, namely, dimesitylborane (DMBH) (1), lithium dimesitylborohydride (LDMBH₂) (2), and compound 3, lithium dimesitylborohydride bis(dimethoxyethane) (LDMBH₂·2DME).

LDMBH₂·2DME is of special interest since it represents a unique stable diorganoborohydride complex formed between two molecules of dimethoxyethane (DME) and compound 2. The X-ray structure is recorded below. This novel crystalline reagent reduces the carbonyl function of certain cyclic ketones in essentially quantitative yield and with exceptional stereoselectivity, apparently the highest achieved for organoborohydride reducing agents.

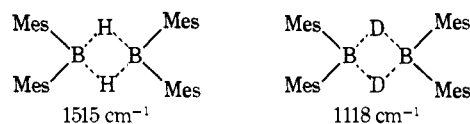
DMBH (mp 164–166° (sealed capillary); mass spectrum, *m/e* 250.1886; Calcd for C₁₈H₂₃B: 250.1892) is isolated in ~80% yield after refluxing (17 hr) a mixture of dimesitylboron fluoride (DMBF)¹ (ca. 0.75 M in DME) with 1.1 equiv of LiH,⁴ adding benzene to precipitate LiF, and crystallizing the evaporated supernatant from DME (eq 1). *Anal.*⁵ Calcd for C₁₈H₂₃B: C, 86.41; H, 9.27; B, 4.32. Found: C, 86.39; H, 9.06; B, 4.16.

The reaction fails in hydrocarbon solvents (benzene or toluene) and other more effective coordinating media such as ether and tetrahydrofuran. The success in DME is doubtless related to the stabilization conferred

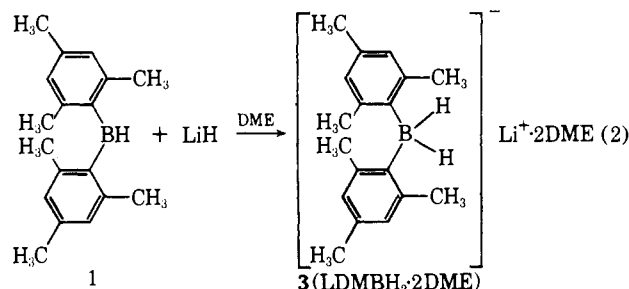


by highly efficient solvent coordination, as clearly evidenced by the X-ray structure (depicted below) for 3.

Despite its bulk, DM BH is a dimer in the crystalline state, as indicated by ir absorption (mineral oil mull) at 1515 cm⁻¹ for 1, 1118 cm⁻¹ for the corresponding deuterio analog (from DMBF and LiD;⁶ mass spectrum *m/e* 251.1951; calcd 251.1956), and no absorption attributable to a B–H stretch in the region (2600–2400 cm⁻¹) for an unassociated monomer⁷ (Mes = mesityl).



Further reduction of 1 (1.1 equiv of LiH in DME, ~30 min reflux) produces complex 3 in 87% yield^{8,9} (mp 129–131° (sealed capillary); ir (mineral oil mull) 2180, 2200, 2280 cm⁻¹. *Anal.*⁵ Calcd for C₂₆H₄₄BLiO₄: C, 71.24; H, 10.11; B, 2.46. Found: C, 71.21; H, 9.88; B, 2.35), eq 2.

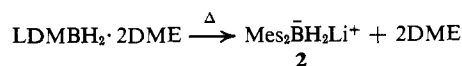


Reduction of several standard cycloalkanones with DM BH at 0° in DME proved slow (incomplete in 8 hr) and, compared to LDMBH₂·2DME, rather nonselective. 2-Methylcyclohexanone, for example, afforded 90% of *cis*-2-methylcyclohexanol. The corresponding *trans* carbinol was formed in 34% yield upon DM BH reduction of 3-methylcyclohexanone (eq 3).^{10–13}

(6) From Fluka Ag, >99 atom % D.

(7) (a) W. J. Lehmann and I. Shapiro, *Spectrochim. Acta*, 17, 396 (1961); (b) E. Negishi, J.-J. Katz, and H. C. Brown, *J. Amer. Chem. Soc.*, 94, 4025 (1972).

(8) By heating and evacuating (130–155° (0.08 mm)) neat samples of 3 for ~4.5 hr (usually on a 5-g scale) "ate" complex 2 is produced in 96% yield (mp 268–270° (sealed capillary); ir (mineral oil mull) 2140 cm⁻¹. *Anal.*⁵ Calcd for C₁₃H₂₄BLi: C, 83.75; H, 9.37; B, 4.19. Found: C, 83.46; H, 9.09; B, 3.90).



(9) Compounds 1 and 2, although more sensitive to air than reagent 3, suffer little deterioration when handled quickly in the atmosphere. Samples of 3 in loosely stoppered vials begin to show ir absorption for >B–OH in ca. 2–3 days. Routinely, we store reagent 3 in sealed vials in a refrigerator (ca. 5°), and such samples have undergone no appreciable loss of hydride activity for 10 months.

(10) Invariably, selectivity of carbonyl reductions induced by bulky R₂BH reagents falls significantly when alkyl substitution in a cyclo-

(1) Prepared by the procedure of Brown and Dodson² from reaction of the Grignard reagent of bromomesitylene³ with boron trifluoride etherate.

(2) H. C. Brown and V. H. Dodson, *J. Amer. Chem. Soc.*, 79, 2302 (1957).

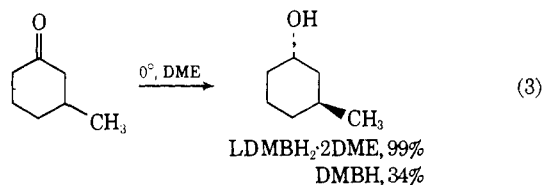
(3) L. I. Smith, "Organic Syntheses," Collect. Vol. II, Wiley, New York, N. Y., 1943, p 95.

(4) Fresh LiH should be employed. In several runs using older exposed samples, either prolonged induction periods were encountered or the reaction was entirely unsuccessful.

(5) Alfred Bernhardt Microanalytisches Laboratorium, 5251 Elbach über Engelskirchen, West Germany.

In contrast, reductions using $\text{LDMBH}_2 \cdot 2\text{DME}$ in DME at 0° of the model series, 2-, 3-, and 4-methylcyclohexanone, proceed in essentially quantitative yield in 3 hr. The reductions may be performed either using the isolated crystalline reagent or by an *in situ* procedure. Results are comparable. In all cases, the corresponding axial OH isomer is produced in at least 94% isomeric purity.

2-Methylcyclohexanone reacted completely with $\text{LDMBH}_2 \cdot 2\text{DME}$ under these conditions to produce the *cis*-carbinol (99%). Similarly, an unhindered ketone such as 3-methylcyclohexanone afforded the corresponding *trans* alcohol (eq 3) in 99% purity.



4-Methylcyclohexanone afforded the product of equatorial attack by the reagent in 94% purity. Selectivities of this magnitude are apparently unprecedented for disubstituted organoborohydride reducing agents.¹⁰⁻¹³

A standard reduction procedure is to add 10 mmol of the ketone dissolved in 10 ml of DME to the reagent formed *in situ* (from reaction of 13 mmol of DMBH and 13 mmol of LiH in 50 ml of DME, 30 min reflux) (eq 2) at 0° under N_2 .¹⁴ After stirring at 0° for 3 hr, the reaction mixture is poured into saturated sodium chloride solution and extracted (two 25-ml portions) with ether. Analysis (glpc) of the dried (Na_2SO_4) organic extracts showed that reductions were complete in all cases and no residual ketone was detected. Distillation of the concentrated extracts affords the pure carbinol in 80-86% yield. The distillation residue (97%) affords dimesitylborinic acid, mp $141-142^\circ$, lit.² mp $140-141^\circ$, after crystallization from Skelly B. Table I summarizes the results.

In addition to the exceptional stereoselectivity observed, a noteworthy feature is the rate response of **3** to ketones of differing structural environments. Although unhindered¹⁵ or moderately hindered¹⁵ ketones are completely reduced in 3 hr at 0° , a highly hindered¹⁵ substrate, such as camphor, is totally inert to the re-

agent after 8 hr at 0° . Approximately 3 days at 25° is required for complete reduction (99.8% *exo*), Table I.

In striking comparison, carbonyl reductions with bulky trisubstituted borohydrides, although highly stereoselective,¹⁶⁻¹⁸ generally proceed at remarkably rapid rates at 0° , even for ketones with widely different steric surroundings.^{19, 20}

As a result of this new development, it may now prove possible to achieve highly stereoselective as well as regiospecific monoreductions of appropriate complex di- or polycarbonyl substrates in unprotected form.

$\text{LDMBH}_2 \cdot 2\text{DME}$ crystallizes in the monoclinic space group *I2/a* with unit cell dimensions $a = 16.157$ (10), $b = 10.059$ (7), $c = 17.020$ (10) Å, $\beta = 95.51$ (6) $^\circ$, and $z = 4$. The 909 significant, independent reflections

(11) H. C. Brown and D. B. Bigley, *J. Amer. Chem. Soc.*, **83**, 3166 (1961).
 (12) H. C. Brown and V. Varma, *J. Amer. Chem. Soc.*, **88**, 2871 (1966).
 (13) An excellent summary account of the numerous developments in borane reagents for selective reductions appears in H. C. Brown, "Boranes in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1972.

(14) Alternatively, the crude mixture formed by treating DMBF with excess LiH (24 hr reflux) may be used directly. The coproduct LiF does not interfere, and results using either method are comparable. However, DMBH is the preferred penultimate intermediate since it is more easily handled.
 (15) The boundaries of this empirical designation, the results of numerous stereochemical studies of nucleophilic attack upon cyclohexanone derivatives, and the various proposals advanced to account for the results, are discussed in J. D. Morrison and H. S. Mosher, "Asymmetric Organic Reactions," Prentice-Hall of Canada, Ltd., Canada, 1971.

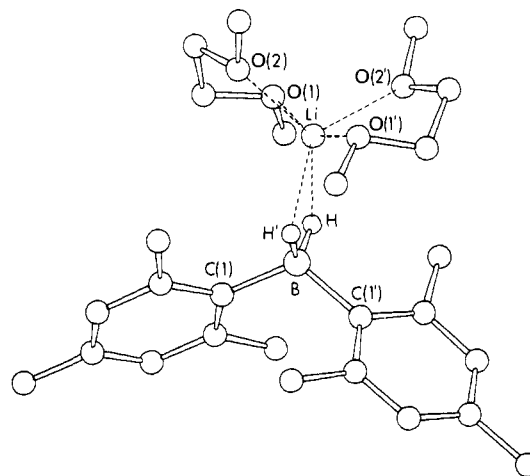


Figure 1. Perspective view of a molecule of $\text{LDMBH}_2 \cdot 2\text{DME}$. Selected distances (Å) and angles (deg) (errors in parentheses): B-H, 1.14 (3); B-C(1), 1.640 (5); B-Li, 2.50 (1); Li-H, 2.06 (4); Li-O(1), 2.353 (4); Li-O(2), 2.000 (7); C(1)-B-C(1'), 116.8 (2) $^\circ$; H-B-H', 110 (3) $^\circ$.

Table I. Reduction of Cycloalkanones with $\text{LDMBH}_2 \cdot 2\text{DME}$ in Dimethoxyethane

Ketone ^a	Temp, $^\circ\text{C}$	Time, hr	Major isomer, ^b %
2-Methylcyclopentanone	0	3	<i>cis</i> , 98
2-Methylcyclohexanone	0	3	<i>cis</i> , 99
3-Methylcyclohexanone	0	3	<i>trans</i> , 99
4-Methylcyclohexanone	0	3	<i>cis</i> , 94 ^c
4- <i>tert</i> -Butylcyclohexanone	0	3	<i>cis</i> , 94
Camphor	25	~72	<i>exo</i> , 99.8

^a The molar ratio of $\text{LDMBH}_2 \cdot 2\text{DME}$ to ketone was 1.3. ^b By glpc analysis. Each result represents the average ($\pm 0.5\%$) of three independent experiments. The absolute yield of alcohol (glpc) in each case was essentially quantitative. ^c At -40° for 3 hr, the *cis* isomer is produced in 96% purity.

(16) H. C. Brown and W. C. Dickason, *J. Amer. Chem. Soc.*, **92**, 709 (1970).

(17) E. J. Corey and R. K. Varma, *J. Amer. Chem. Soc.*, **93**, 7319 (1971).

(18) H. C. Brown and S. Krishnamurthy, *J. Amer. Chem. Soc.*, **94**, 7159 (1972).

(19) For example, 4-methylcyclohexanone and camphor are completely reduced by (*sec*- C_4H_9)₃BH⁻Li⁺ in 1 hr at 0° (80.5% *cis*, and 99.6% *exo*, respectively),¹⁸ and by lithium perhydro-9b-borophenallylhydride in 0.5 hr at 0° .¹⁶

(20) C. A. Brown, *J. Amer. Chem. Soc.*, **95**, 4100 (1973), has observed that the stereoselectivity of carbonyl reductions by bulky borohydrides is also influenced by the cation, and the selectivity achieved using $\text{K}^+\text{HB}^-(\text{sec}-\text{C}_4\text{H}_9)_3$ equals or surpasses that of the lithio derivative.

were collected on a Picker FACS-I automatic diffractometer using Cu K α radiation ($0 < 2\theta \leq 100^\circ$). The structure was solved by direct methods²¹ and has been refined to a conventional *R* factor of 0.058.²² The compound forms as discrete ion pairs in the crystal (Figure 1) with the lithium ion coordinated by two hydridic hydrogens from the [(Mes)₂BH₂]⁻ group and four oxygen atoms from two DME molecules. The molecule possesses twofold symmetry. The structure shows two rather unusual features. One is the markedly asymmetric manner in which the DME molecules bond to the lithium atom, the difference in the two Li-O distances being 0.353 (8) Å. This difference does not find precedent in other complexes, e.g., those alkali metal macrocyclic ethers^{23,24} which do not experience significant intermolecular bonding interactions. A second feature is the opening of the C(1)-B-C(1') angle to 116.8 (2)° from its normal tetrahedral value. It is felt that this is due solely to intramolecular repulsions between the mesityl groups rather than to any partial contribution from boron-lithium direct overlap analogous to that proposed for a Cu-BH₄ complex.²⁵ The structure accounts for the observed increase in $\nu(\text{B-H})$ of LDMBH₂·2DME compared to that for LDMBH₂ since in the former complex the formal positive charge on the lithium ion is partially accommodated by the coordinated DME groups.

Acknowledgment. We thank the National Research Council of Canada for financial support.

Supplementary Material Available. A listing of atomic coordinates will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-274.

- (21) J. Karle and I. L. Karle, *Acta Crystallogr.*, **21**, 849 (1966).
 (22) See paragraph at end of paper regarding supplementary material.
 (23) D. Bright and M. R. Truter, *J. Chem. Soc. B*, 1544 (1970).
 (24) M. A. Bush and M. R. Truter, *Chem. Commun.*, 1439 (1970).
 (25) S. J. Lippard and K. M. Melmed, *Inorg. Chem.*, **6**, 2223 (1967).
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Received August 7, 1973

Hydrogenolysis of Substituted Nortricyclenes over Supported Metal Catalysts. Methyl Migrations and Skeletal Rearrangements

Sir:

Hydrogenolysis of cyclopropyl rings normally occurs with simple ring cleavage.¹ We wish to report that hydrogenolysis of the strained hydrocarbons 3,3-dimethylnorbornene (3,3-dimethyltricyclo[2.2.1.0^{2,6}]heptane (1)) and the related cyclopropyl compound, spiro[tricyclo[2.2.1.0^{2,6}]heptane-3,1'-cyclopropane (5), gives products arising from reactions involving carbon-

carbon bond breaking and re-forming under certain conditions. Hydrogenolysis of either compound over platinum in acetic acid solution gave the products of simple ring cleavage, 2,2-dimethylnorbornane (2) and 7,7-dimethylnorbornane (3), with the latter predominating. These were also the only products from hydrogenolyses of 1 in the temperature range 80–200° over palladium on silica or platinum on either silica or pumice. In contrast, hydrogenolysis of 1 over palladium on pumice in the same temperature range gave di-*exo*-, di-*endo*-, and *trans*-2,3-dimethylnorbornanes (4) in addition to 2 and 3 (see Table I). Samples of 2 and 3 were

Table I. Product Distributions from Hydrogenolyses of 1

Catalyst ^d	H ₂ flow rate, cm ³ min ⁻¹	T, °C	Product composition, % ^a					
			2 + <i>trans</i> - 4	3	<i>cis</i> - <i>exo</i> -4	<i>cis</i> - <i>endo</i> - 4	Recovd 1	
2% Pt/pumice	9	108	20	80				
	9	158	30	70				
	9	200	50	50				
2% Pd/silica	7	100	15 ^b	85				
	7	180	20	80				
2% Pd/pumice	9	108	7.1	5.1	2.0	4.1	81.6	
	9	130	23.2	2.3	8.2	20.2	46.0	
	9	190	44.7 ^c	7.0	14.1	34.1	0.5	
PtO ₂ in acetic acid		30	15	85				

^a A Perkin-Elmer F11 gas chromatograph fitted with a 2-m capillary column packed with Apieson L (10%) on Chromosorb P was used at 16 psi nitrogen pressure and at 110°. Separation of 2 and *trans*-4 could not be achieved. ^b Identified as pure 2,2-dimethylnorbornane after preparative glc using an Autoprep A-700 with a 6-m column of Apiezon L (30%) on Chromosorb P at 110°, with helium pressure 18 psi. ^c Identified by nmr as mainly *trans*-2,3-dimethylnorbornane after preparative glc. ^d Catalysts were prepared by the impregnation of 60–85 mesh (B.S.S.) Whatman S. G. silica gel and of 22–60 mesh pumice stone of Hopkins and Williams Ltd. with aqueous chloroplatinic acid or palladium(II) chloride dissolved in hydrochloric acid. The catalysts were reduced in a stream of hydrogen with the temperature being elevated gradually to 330°.

recovered unchanged after passage over the palladium on pumice catalyst at 140° and the nortricyclene 1 did not react when passed over either silica or pumice in the absence of metal at 120°. The kinetically controlled rearrangement product contains a high proportion of 2,3-*endo*-dimethylnorbornane. The di-*endo* compound was shown to isomerize at higher temperatures over the palladium on pumice catalysts in agreement with previous work,² thus accounting for the increase of di-*exo* and *trans* compounds in the product mixture at these temperatures. Additionally, it was not possible to separate *trans*-2,3-dimethylnorbornane and 2,2-dimethylnorbornane with the glc facilities available, but preparative glc of the product from a reaction at 190° showed that the first eluted peak was pure *trans*-4 and did not contain a detectable amount (by nmr) of 2.

Rearrangement products predominated when the cyclopropylnortricyclene (5) was hydrogenolyzed over palladium or platinum catalysts (see Table II). In addition to the 2,3-dimethylnorbornanes (4), *exo*- and *endo*-2-methylbicyclo[3.2.1]octanes (6) were formed.

- (2) H. A. Quinn, W. R. Jackson, M. A. McKervey, and J. J. Rooney *J. Amer. Chem. Soc.*, **92**, 2911 (1970); H. A. Quinn, J. H. Graham, M. A. McKervey, and J. J. Rooney, *J. Catal.*, **26**, 333 (1972).