

characteristics. It is easy to verify that the resulting $k_{ap}/\{[\pi^{\cdot-}, \text{Na}^+]/[\pi]\}^2 = k_{\text{isom}}K_2'K_5'$ is related to the previously determined $k_{\text{isom}}K_2K_5$ by the relation

$$k_{\text{isom}}K_2'K_5'/k_{\text{isom}}K_2K_5 = (K_{A,\pi})^2$$

where $K_{A,\pi}$ is the equilibrium constant of the reaction



Thus calculated $K_{A,\pi}$ was found to be 140; whereas the direct determination⁷ led to the value of 110.

In conclusion, neither *cis*-stilbene nor its radical anion salt isomerize spontaneously within the time period of our experiments, while its dianion salt does. We derive from Figure 1 $k_{\text{isom}}/k_{-5} = 2 \times 10^{-3} M$ and therefore $k_{\text{isom}} \leq 5 \times 10^6 \text{ sec}^{-1}$ because k_{-5} is probably diffusion controlled, *i.e.*, $k_{-5} \approx 10^{10} M^{-1} \text{ sec}^{-1}$. Hence, the lifetime of the sodium salt is $2 \times 10^{-7} \text{ sec}$ or more. The principle of microscopic reversibility demands therefore the existence of four thermodynamically distinct species: *cis*-stilbene $\cdot^{\cdot-}, \text{Na}^+$, *trans*-stilbene $\cdot^{\cdot-}, \text{Na}^+$, *cis*-stilbene $^{2-}, 2\text{Na}^+$, and *trans*-stilbene $^{2-}, 2\text{Na}^+$. The relative stability of *cis*-stilbene $^{2-}, 2\text{Na}^+$, surprising in view of its endowment with two antibonding electrons, is tentatively attributed to the binding of both phenyl groups by the sodium counterions.

Acknowledgment. The support of this study by the National Science Foundation is gratefully acknowledged.

(7) J. Jagur-Grodzinski, M. Feld, S. L. Yang, and M. Szwarc, *J. Phys. Chem.*, **69**, 628 (1965).

G. Levin, T. A. Ward, M. Szwarc*

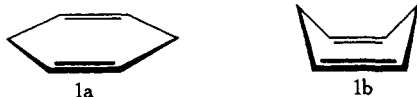
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Stereochemistry of 1,4-Cyclohexadienes. Confirmation via Rare Earth Shift Reagents

Sir:

A considerable amount of controversy exists concerning the conformational preferences of 1,4-cyclohexadiene (**1**) and its derivatives. A planar structure, **1a**, has been proposed by several investigators¹⁻⁷ using various techniques including nmr⁵ and electron diffraction.⁶ However, a subsequent conflicting electron



diffraction study of **1**⁸ and nmr studies of several deriva-

(1) H. Gerding and F. A. Haak, *Recl. Trav. Chim. Pays-Bas*, **68**, 293 (1949).

(2) B. J. Monostori and A. Weber, *J. Mol. Spectrosc.*, **12**, 129 (1964).

(3) H. D. Stidham, *Spectrochim. Acta*, **21**, 23 (1965).

(4) R. C. Lord, Abstracts, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, No. PHYS 74.

(5) G. Dallinga and L. H. Toneman, *J. Mol. Struct.*, **1**, 117 (1967).

(6) E. W. Garbisch, Jr., and M. G. Griffith, *J. Amer. Chem. Soc.*, **90**, 3590 (1958).

(7) Very recently a planar form has been predicted for **1** on the basis of calculations [N. L. Alliner and J. T. Sprague, *J. Amer. Chem. Soc.*, **94**, 5734 (1972)] and for a highly substituted derivative by X-ray analysis [M. J. Bennett, J. T. Purdham, S. Takada, and S. Masamune, *ibid.*, **93**, 4063 (1971)].

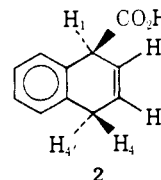
(8) H. Oberhammer and S. H. Bauer, *J. Amer. Chem. Soc.*, **91**, 10 (1969).

tives⁹⁻¹¹ have resulted in the suggestion of a boat conformation, **1b**.

Thus far, the nmr studies on derivatives of **1** have considered only the ratio of the homoallylic *cis* and *trans* (H_1 to H_4) coupling constants. It was on this basis that boat conformations were postulated, and Marshall, *et al.*,¹¹ suggested that 1,4-dihydrobenzoic acid exists in a boat with the substituent pseudoequatorial. Unfortunately, there has been some disagreement^{6,10,11} concerning the "predicted value" of the $J_{\text{cis}}/J_{\text{trans}}$ ratio expected for the planar form.¹²

A major difficulty in the nmr analysis of 1-substituted-1,4-cyclohexadienes is the fact that the several derivatives reported all show a deceptively simple spectrum. Typically, the methine proton appears as a triplet (H_1 , $J \sim 8-9$ Hz) coupled to the methylene protons (H_2, H_4') which appear as a corresponding doublet. Hence, H_4 and H_4' appear to have the same chemical shift and also appear to be equally coupled to H_1 . In addition, the vinyl protons often have approximately the same chemical shift, and neither the vicinal nor allylic coupling constants have been determined. In fact, even the homoallylic coupling constants are difficult to obtain and have only been measured by preparing deuterated compounds.^{12,14,15}

In an attempt to prepare a cyclohexadiene that might be more suitable for nmr analysis, Marshall and Folsom¹⁴ prepared 1,4-dihydro-1-naphthoic acid (**2**) and



concluded, from the vicinal coupling constants ($H_1H_2 = 4.59$ Hz, $H_3H_4 = 4.60$, $H_3H_4' = 2.44$) together with the Karplus equation, that the ring was boat shaped with the CO_2H pseudoaxial. Later, however, the homoallylic coupling constants were accurately determined using deuterium substitution ($J_{1,4} = 3.84$, $J_{1,4'} = 4.36$), and, since the homoallylic *cis/trans* ratio was very close to the predicted value for a flat ring (see ref 12), a "flattened boat" was proposed.¹⁵

We would now like to report the first complete nmr analysis of a 1-substituted-1,4-cyclohexadiene, which we were able to accomplish with the use of the rare earth shift reagent $\text{Eu}(\text{fod})_3$.¹⁶ Birch reduction of benzoic acid followed by LiAlH_4 reduction resulted in 1,4-dihydrobenzyl alcohol (**3**).¹⁷ The complete nmr analysis of **3** was accomplished by adding $\text{Eu}(\text{fod})_3$, and under these conditions the H_4 and H_4' protons appeared as an AB quartet (H_4 assigned to the signal

(9) L. J. Durham, J. Studebaker, and M. J. Perkins, *Chem. Commun.*, 456 (1965).

(10) D. J. Atkinson and M. J. Perkins, *Tetrahedron Lett.*, 2335 (1969).

(11) J. L. Marshall, K. C. Erickson, and T. K. Folsom, *J. Org. Chem.*, **35**, 2038 (1970).

(12) Recently, Sternhell has calculated a value of $J_{\text{cis}}/J_{\text{trans}} = 1.12$ on the basis of an INDO treatment.¹³ See ref 15.

(13) M. Barfield and S. Sternhell, *J. Amer. Chem. Soc.*, **94**, 1905 (1972).

(14) J. L. Marshall and T. K. Folsom, *J. Org. Chem.*, **36**, 2011 (1971).

(15) J. L. Marshall, A. M. Ohrig, and P. N. Jenkins, *J. Org. Chem.*, **37**, 1863 (1972).

(16) For a review, see W. D. Horrocks, Jr., and J. P. Sipe, III, *J. Amer. Chem. Soc.*, **93**, 6800 (1971).

(17) All new compounds gave satisfactory spectral data and elemental analysis.

Table I. 100 MHz Nmr Spectrum of 1,4-Dihydrobenzyl Alcohol (**3**) with Eu(fod)₃

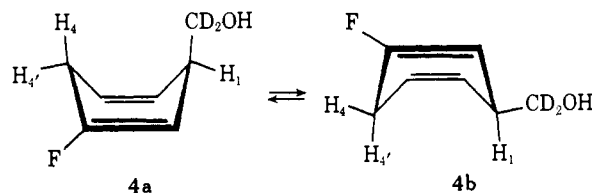
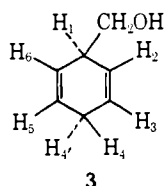
Signal observed	Decoupled protons ^a	Signal pattern	Results
H ₂ ,H ₆ ; H ₃ ,H ₅ ^{b,c}	H ₁ ; H ₄ ,H _{4'}	4 line AB	$J_{2,3} = 10.3$ Hz
H ₂ ,H ₆ ; H ₃ ,H ₅	H ₄ ,H _{4'}	4 lines (AB) each split into a doublet	$J_{1,2} = 3.1$, ^d $J_{1,3} = 1.5$ ^e
H ₂ ,H ₆ ; H ₃ ,H ₅	H ₁	4 lines (AB) each split into a triplet	$J_{3,4} = J_{3,4'} = 3.0$ ^f
			$J_{2,4} = J_{2,4'} = 1.5$ ^g
H ₄ ,H _{4'} ^h	H ₁ ; H ₃ ,H ₅	4 line AB	$J_{4,4'} = 21.7$ ⁱ
H ₄ ,H _{4'}	H ₂ ,H ₆ ; H ₃ ,H ₅	4 lines (AB) ^j each split into a doublet	$J_{1,4} = 7.4$, ^d $J_{1,4'} = 8.6$ ^e

^a Triple irradiation, two external oscillators used. ^b Eu(fod)₃ added until vinyls crossed and become separated. ^c The upfield half of the vinyl AB system moves fastest with Eu(fod)₃ addition, crosses the other half and becomes the downfield portion. Hence, it is assigned to H_{2,6}. ^d From coupling of downfield doublet pairs. ^e From coupling of upfield doublet pairs. ^f Upfield triplet pairs. ^g Downfield triplet pairs not well resolved. ^h More Eu(fod)₃ added until H₄,H_{4'} is observed as an AB system. ⁱ H₂(H₆),H₄(H_{4'}) coupling not observed under these conditions. ^j Appropriately treated as first order, since $\delta_{4,4'} = 35$ Hz at this point (see also footnote c, Table II), confirmed by LAOCN3.

Table II. Nmr Spectrum of 3-Fluoro-1,4-dihydrobenzyl Alcohol-d₂ (**4**) with Eu(fod)₃

Signal Observed	Decoupled nuclei ^a	Signal pattern	Results
H ₄ ,H _{4'}	H ₂ ,H ₆	4 line AB each split into a doublet of doublets ^b	$J_{4,4'} = 22.0$ Hz
			$J_{4,5} = 3.5$
			$J_{4',5} = 3.5$
H ₄ ,H _{4'}	H ₅ ,H ₆	4 line AB each split into doublets ^c	$J_{1,4} = 7.5$
			$J_{1,4'} = 8.3$
H ₅ ,H ₆	H ₁ ,H ₄ ,H _{4'}	4 line AB each split into doublets	$J_{5,6} = 10.5$
			$J_{5,F} = 7.5$
			$J_{6,F} = 4.8$
H ₂	¹⁹ F	Broad singlet	$J_{2,F} = 17.5$
H ₂	H ₁ ,H ₄ ,H _{4'}	Doublet of doublets ^e	$J_{2,6} = 1.4$
			$J_{1,2} = 3.4$

^a Triple irradiation, two external oscillators used. ^b Major secondary coupling from H₁. However, $J_{H_1H_4}$ and $J_{H_1H_4'}$ were more accurately measured by decoupling H₅,H₆. ^c Plus small additional coupling. ^d Appropriately treated at first order, since $\delta_{4,4'} = 42$ Hz at this point and in addition $J_{1,4}$ and $J_{1,4'}$ are unchanged with increased chemical shift (*i.e.*, more shift reagent). ^e In several decoupling attempts, an additional coupling of 1.4 Hz was observed. A similar coupling had also been observed with H₆, and therefore we assigned this to $J_{2,6}$.



moving downfield fastest, *i.e.*, closest proximity to CH₂OH), with further coupling from H₁, H_{2,6}, and H_{3,5}. By performing double and triple irradiation experiments under these conditions, all of the coupling constants were measured and are summarized in Table I. Since the vicinal coupling constants $J_{3,4}$ and $J_{3,4'}$ are equal, H₃ (H₅) must bisect the angle between H₄ and H_{4'}, and, hence, the ring is planar. In addition, the favorable comparison of $J_{2,4}$ and $J_{3,4}$ with $J_{1,2}$ and $J_{1,3}$, respectively, indicates that there is no distortion of the ring at the other end (*i.e.*, around C₁). It should also be noted that the *cis/trans* ratio for the homoallylic coupling constants is 1.16 (*i.e.*, $J_{1,4'}/J_{1,4}$), in good agreement with the value of 1.12 calculated for a planar ring.^{12,18}

In order to investigate the possibility of rapid boat to boat inversion which would lead to equal $J_{3,4}$ and $J_{3,4'}$ values, we prepared 3-fluoro-1,4-dihydrobenzyl alcohol-d₂,^{17,19} (**4**) on the assumption that ring inversion would average in relatively large H₄F and H_{4'}F

(18) The large $J_{4,4'}$ value also supports planarity of the ring. See S. Sternhell, *Quart. Rev., Chem. Soc.*, **23**, 238 (1969), and references therein.

(19) Deuteration was necessary to reduce the peak width of H₁ so that it could be effectively decoupled.

coupling constants (*i.e.*, H₄F and H_{4'}F dihedral angles become small in **4b** and **4a**, respectively).²⁰ Comparison of the ¹H nmr spectrum (60 MHz) with and without ¹⁹F heteronuclear decoupling indicates that there is strong coupling between fluorine and H₂ (17.5 Hz), H₅ (7.5) (note the W relationship), and H₆ (4.8). However, coupling between F and H₄,H_{4'} appears to be quite small, <2 Hz, and could not be measured even though attempts were made under a variety of conditions. Once again, however, using Eu(fod)₃²³ (see Table II) we were able to observe H₄H_{4'} which origi-

(20) The angular dependence of J_{HF} vicinal coupling constants is similar to the Karplus treatment of J_{HH} systems, except the values are much larger in the 0 and 180° range of dihedral angles.²¹ It would be difficult to estimate an "expected" value of J_{HF} for the gauche relationship in a planar **4** because of the double bond, and distortions at C₄ expected for a planar ring. However, we feel that it is reasonable to expect relatively large J_{HF} values from a boat conformation due to the much smaller dihedral angle. In 2-fluoropropene, for example, $J_{F,CH_3} = 16.0$ Hz.²²

(21) K. L. Williamson, Yuan-Fang Li, F. H. Hall, and S. Swager, *J. Amer. Chem. Soc.*, **88**, 5678 (1966).

(22) M. Y. DeWolf and J. D. Baldeschwieler, *J. Mol. Spectrosc.*, **13**, 344 (1964).

(23) In this case, $J_{H_1H_2}$, J_{FH_6} , and J_{FH_4} were measured before and after addition and were found to be unchanged. Hence, the Eu(fod)₃ is not affecting the conformational preferences of **4** or the coupling constants.

nally appeared as a doublet (see discussion of compound **3**) as an AB pattern with strong coupling from H₁. By decoupling H₂ and H₆, 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 (H₁H₄'/H₁H₄) was 1.11 (see ref 12).

Hence, on the basis of (1) small H₄F 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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Lithium Dimesitylborohydride Bis(dimethoxyethane). A New Crystalline Reagent for Stereoselective Reduction of Ketones

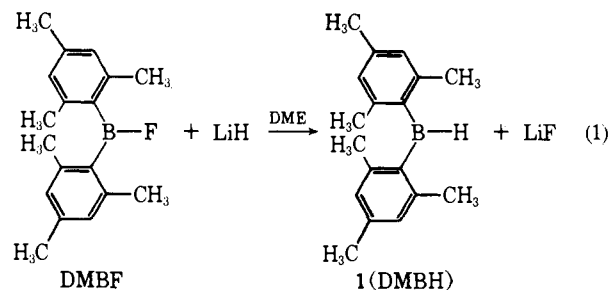
Sir:

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.

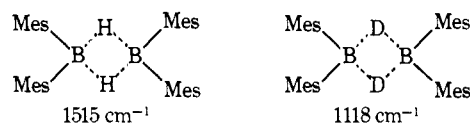
DMBH (mp 164–166° (sealed capillary); mass spectrum, *m/e* 250.1886; Calcd for C₁₈H₂₃B: 250.1892) is isolated in ~80% yield after refluxing (17 hr) a mixture of dimesitylboron fluoride (DMBF)¹ (ca. 0.75 M in DME) with 1.1 equiv of LiH,⁴ adding benzene to precipitate LiF, and crystallizing the evaporated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

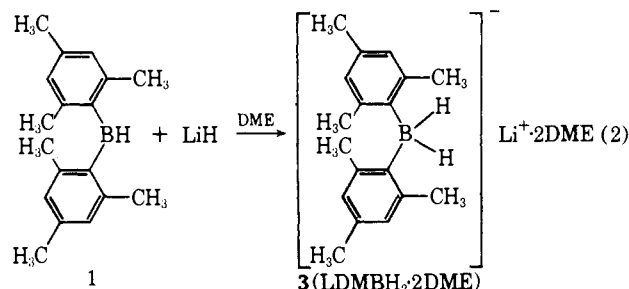


by highly efficient solvent coordination, as clearly evidenced by the X-ray structure (depicted below) for **3**.

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.

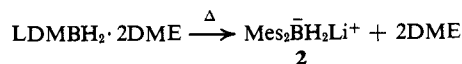


Reduction of several standard cycloalkanones with DM BH at 0° in DME proved slow (incomplete in 8 hr) and, compared to LDMBH₂·2DME, rather nonselective. 2-Methylcyclohexanone, for example, afforded 90% of *cis*-2-methylcyclohexanol. The corresponding *trans* carbinol was formed in 34% yield upon DM BH 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 C₁₈H₂₄BLi: 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.