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

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

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

$$r \cdot \overline{,Na^+ + A} \cong A \cdot \overline{,Na^+ + \pi, K_{A,\pi}}$$

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  $k_{isom}/k_{-5} = 2 \times 10^{-3} M$  and therefore  $k_{isom} \leq 5 \times 10^6 \text{ sec}^{-1}$  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  $2 \times 10^{-7}$  sec<sup>-1</sup> or more. The principle of microscopic reversibility demands therefore the existence of four thermodynamically distinct species: cis-stibene ·-, Na+, trans-stilbene ·-, Na+, cisstilbene<sup>2-</sup>,2Na<sup>+</sup>, and *trans*-stilbene<sup>-2</sup>,2Na<sup>+</sup>. The relative stability of cis-stilbene<sup>2-</sup>,2Na<sup>+</sup>, 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).

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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 investigators<sup>1-7</sup> using various techniques including nmr5 and electron diffraction.<sup>6</sup> However, a subsequent conflicting electron



diffraction study of 18 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).

tives<sup>9-11</sup> 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.,<sup>11</sup> suggested that 1,4-dihydrobenzoic acid exists in a boat with the substituent pseudoequatorial. Unfortunately, there has been some disagreement<sup>6, 10, 11</sup> concerning the "predicted value" of the  $J_{\rm cis}/J_{\rm trans}$  ratio expected for the planar form.<sup>12</sup>

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<sub>1</sub>,  $J \sim 8-9$  Hz) coupled to the methylene protons  $(H_4, H_{4'})$  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 Folsom<sup>14</sup> 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<sub>2</sub>H 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 Eu(fod)3.16 Birch reduction of benzoic acid followed by LiAlH<sub>4</sub> reduction resulted in 1,4-dihydrobenzyl alcohol (3).<sup>17</sup> The complete nmr analysis of 3 was accomplished by adding Eu(fod)<sub>3</sub>, and under these conditions the  $H_4$  and  $H_{4'}$  protons appeared as an AB quartet (H<sub>4</sub> 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  $J_{cis}/J_{trans} = 1.12$ on the basis of an INDO treatment.<sup>13</sup> 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 <sup>a</sup>	Signal pattern	Results
 H2,H6; H3,H5 <sup>b,o</sup>	$H_1; H_4, H_{4'}$	4 line AB	$J_{2,3} = 10.3 \text{ Hz}$
$H_2, H_6; H_3, H_5$	$H_4, H_4$	4 lines (AB) each split into a doublet	$J_{1,2} = 3.1,^d J_{1,3} = 1.5^d$
$H_2, H_6; H_3, H_5$	$\mathbf{H}_{1}$	4 lines (AB) each split into a triplet	$J_{3,4} = J_{3,4'} = 3.0'$
			$J_{2,4} = J_{2,4'} = 1.5^{\circ}$
$H_4, H_4, h$	$H_1; H_3, H_5$	4 line AB	$J_{4,4'} = 21.7^{i}$
$H_{4},H_{4'}$	$H_2, H_6; H_3, H_5$	4 lines (AB) <sup>i</sup> each split into a doublet	$J_{1,4} = 7.4, {}^{d}J_{1,4'} = 8.6^{o}$

<sup>a</sup> Triple irradiation, two external oscillators used. <sup>b</sup> Eu(fod)<sub>3</sub> added until vinyls crossed and become separated. <sup>c</sup> The upfield half of the vinyl AB system moves fastest with Eu(fod)<sub>3</sub> addition, crosses the other half and becomes the downfield portion. Hence, it is assigned to H<sub>2.6</sub>. <sup>d</sup> From coupling of downfield doublet pairs. <sup>e</sup> From coupling of upfield doublet pairs. <sup>f</sup> Upfield triplet pairs. <sup>g</sup> Downfield triplet pairs not well resolved. <sup>h</sup> More Eu(fod)<sub>3</sub> added until H<sub>4</sub>, H<sub>4'</sub> is observed as an AB system. <sup>h</sup> H<sub>2</sub>(H<sub>6</sub>), H<sub>4</sub>(H<sub>4'</sub>) coupling not observed under these conditions. <sup>j</sup> Appropriately treated as first order, since  $\delta_{4,4'} = 35$  Hz at this point (see also footnote c, Table II), confirmed by LAO-CN3.

Table II.	Nmr S	pectrum o	f 3-Fluoro-1.	4-dihvdrobenz	vl Alcohol-d <sub>2</sub>	(4	) with Eu(	fod)
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Signal Observed	Decoupled nuclei <sup>a</sup>	Signal pattern	Results
H4,H4'	$H_2, H_6$	4 line AB each split into a doublet of doublets <sup>b</sup>	$J_{4,4'} = 22.0 \mathrm{Hz}$
			$J_{4,5} = 3.5$
			$J_{4',5} = 3.5$
$\mathbf{H}_{4},\mathbf{H}_{4'}$	$\mathbf{H}_{5},\mathbf{H}_{6}$	4 line AB each split into doublets <sup>e</sup>	$J_{1,4} = 7.5$
			$J_{1,4'} = 8.3$
$H_5, H_6$	$H_1, H_4, H_4'$	4 line AB each split into doublets	$J_{5,6} = 10.5$
		-	$J_{5,\rm F} = 7.5$
			$J_{6,F} = 4.8$
$\mathbf{H}_{2}$	<sup>19</sup> F	Broad singlet	$J_{2,F} = 17.5$
$\mathbf{H}_{2}$	$H_1,H_4,H_{4'}$	Doublet of doublets <sup>e</sup>	$J_{2,6} = 1.4$
2	-, -, -,		$J_{1,2} = 3.4$

<sup>a</sup> Triple irradiation, two external oscillators used. <sup>b</sup> Major secondary coupling from H<sub>1</sub>. However,  $J_{H_1H_4}$  and  $J_{H_1H_4}$ , were more accurately measured by decoupling H<sub>5</sub>, H<sub>6</sub>. <sup>c</sup> Plus small additional coupling. <sup>d</sup> 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). <sup>e</sup> In several decoupling attempts, an additional coupling of 1.4 Hz was observed. A similar coupling had also been observed with H<sub>6</sub>, and therefore we assigned this to  $J_{2,6}$ .



moving downfield fastest, *i.e.*, closest proximity to CH<sub>2</sub>OH), with further coupling from H<sub>1</sub>, H<sub>2,6</sub>, and H<sub>3,5</sub>. 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, H<sub>3</sub> (H<sub>5</sub>) must bisect the angle between H<sub>4</sub> and H<sub>4'</sub>, 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 C<sub>1</sub>). 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.<sup>12, 18</sup>

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- $d_2$ ,<sup>17,19</sup> (4) on the assumption that ring inversion would average in relatively large H<sub>4</sub>F and H<sub>4'</sub>F



coupling constants (*i.e.*, H<sub>4</sub>F and H<sub>4</sub>/F dihedral angles become small in **4b** and **4a**, respectively).<sup>20</sup> Comparison of the <sup>1</sup>H nmr spectrum (60 MHz) with and without <sup>19</sup>F heteronuclear decoupling indicates that there is strong coupling between fluorine and H<sub>2</sub> (17.5 Hz), H<sub>5</sub> (7.5) (note the W relationship), and H<sub>6</sub> (4.8). However, coupling between F and H<sub>4</sub>,H<sub>4</sub>' 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)<sub>3</sub><sup>23</sup> (see Table II) we were able to observe H<sub>4</sub>H<sub>4</sub>' which origi-

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

(23) In this case,  $J_{\rm H_1H_2}$ ,  $J_{\rm FH_5}$ , and  $J_{\rm FH_6}$  were measured before and after addition and were found to be unchanged. Hence, the Eu(fod)<sub>3</sub> is not affecting the conformational preferences of 4 or the coupling constants.

<sup>(18)</sup> 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.

therein. (19) Deuteration was necessary to reduce the peak width of  $H_1$  so that it could be effectively decoupled.

<sup>(20)</sup> The angular dependence of  $J_{\rm HF}$  vicinal coupling constants is similar to the Karplus treatment of  $J_{\rm HH}$  systems, except the values are much larger in the 0 and 180° range of dihedral angles.<sup>21</sup> It would be difficult to estimate an "expected" value of  $J_{\rm HF}$  for the gauche relationship in a planar 4 because of the double bond, and distortions at C<sub>4</sub> expected for a planar ring. However, we feel that it is reasonable to expect relatively large  $J_{\rm HF}$  values from a boat conformation due to the much smaller dihedral angle. In 2-fluoropropene, for example,  $J_{\rm F, CH_4}$ = 16.0 Hz.<sup>22</sup>

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

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 planar<sup>18</sup> with ring inversion not occurring (or involving very shallow boat conformations).

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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 (LDMBH<sub>2</sub>) (2), and compound 3, lithium dimesitylborohydride bis(dimethoxyethane)  $(LDMBH_2 \cdot 2DME).$ 

LDMBH<sub>2</sub>·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 C<sub>18</sub>H<sub>23</sub>B: 250.1892) is isolated in  $\sim 80\%$  yield after refluxing (17 hr) a mixture of dimesitylboron fluoride (DMBF)<sup>1</sup> (ca. 0.75 M in DME) with 1.1 equiv of LiH,<sup>4</sup> adding benzene to precipitate LiF, and crystallizing the evaporated supernatant from DME (eq 1). Anal.<sup>5</sup> Calcd for  $C_{18}H_{23}B$ : 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

(1) Prepared by the procedure of Brown and Dodson<sup>2</sup> from reaction of the Grignard reagent of bromomesitylene<sup>3</sup> 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.



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



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

Despite its bulk, DMBH 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 monomer<sup>7</sup> (Mes = mesityl).



Further reduction of 1 (1.1 equiv of LiH in DME,  $\sim$ 30 min reflux) produces complex 3 in 87% yield<sup>8,9</sup> (mp 129-131° (sealed capillary); ir (mineral oil mull) 2180, 2200, 2280 cm<sup>-1</sup>. Anal.<sup>5</sup> Calcd for C<sub>26</sub>H<sub>44</sub>-BLiO<sub>4</sub>: 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 DMBH at 0° in DME proved slow (incomplete in 8 hr) and, compared to LDMBH<sub>2</sub>·2DME, rather nonselective. 2-Methylcyclohexanone, for example, afforded 90% of cis-2-methylcyclohexanol. The corresponding trans carbinol was formed in 34% yield upon DMBH reduction of 3-methylcyclohexanone (eq 3).<sup>10-13</sup>

(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  $\sim$ 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<sup>-1</sup>. Anal.<sup>6</sup> Calcd for  $C_{18}H_{24}BL_1$ : C, 83.75; H, 9.37; B, 4.19. Found: C, 83.46; H, 9.09; B, 3.90).

$$LDMBH_2 \cdot 2DME \xrightarrow{\Delta} Mes_2\bar{B}H_2Li^+ + 2DME$$

(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.  $5^{\circ}$ ), and such samples have undergone no appreciable loss of hydride activity for 10 months.

(10) Invariably, selectivity of carbonyl reductions induced by bulky  $R_2BH$  reagents falls significantly when alkyl substitution in a cyclo-