

difference in solvation energies is not reflected in the kinetic parameter  $\phi_*$ , which measures the solvation requirements of the transition states, leading to 4 and 5, relative to their respective neutral precursors.<sup>6</sup> However, it appears that the  $\phi_*$  parameter is mostly sensitive to specific solvation interactions such as hydrogen-bonding, and, therefore, it is probably not suited to reveal small differences due to other terms which may contribute to the overall energy of solvation.<sup>19</sup> One could speculate that specific electrostatic interactions with the counterion and/or cavitation energy terms, not influencing  $\phi_*$ , could favor the smaller vinyl cation and contribute to overcome the intrinsic lower basicity of the triple relative to the double bond.

To summarize, the following conclusions can be drawn: (i) arylacetylenes are less basic in the gas phase than the corresponding styrene derivatives by a few kcal mol<sup>-1</sup>; (ii) protonation of the double and triple bonds in these systems under equilibrium conditions in the gas phase is equally sensitive to ring-substitution, and (iii) a reasonably good match is observed between the protonation behavior in the gas phase and in solution so that major differences in the solvation energies of  $\alpha$ -arylvinylium and  $\alpha$ -arylethyl cations are excluded.

### Experimental Section

Compound 1a was a commercial product and was purified by fractional distillation at reduced pressure.

Compounds 1b-h were prepared by literature methods,<sup>20</sup> in some cases with minor modifications, and purified according to standard procedures. Final purification of compound 1b was achieved by preparative GLC.

The purity of all the samples was checked by <sup>1</sup>H NMR and GLC techniques before running the FTICR experiments.

The FTICR experiments were performed on a commercial Nicolet FT-MS 1000 with the magnetic field set at 2 T. The proton affinities were determined by using the bracketing technique and/or, where possible, equilibrium measurements. The compounds were introduced via two different leak valves and their pressures (not corrected) were measured with a Granville-Phylips 280 Bayard Alpert ion gauge. The typical pressure in the experiments was  $3 \times 10^{-6}$  torr with a neutral ratio of about 1.

Reference bases used (and their GB values in kcal mol<sup>-1</sup>) are 4-cyanopyridine (202.4), *sec*-Bu<sub>2</sub>O (200.8), *i*-Pr<sub>2</sub>O (198.0), acetophenone (197.2), NH<sub>3</sub> (196.4), *n*-Bu<sub>2</sub>O (195.5), *t*-BuOMe (194.1), *n*-Pr<sub>2</sub>O (193.7), anisole (192.5), 3-pentanone (192.7), *i*-PrCOMe (192.6), PhCHO (192.2), ethylacetate (192.1), Et<sub>2</sub>O (191.7), 2-butanone (191.2), THF (190.5), methyl acetate (189.5), PhCN (188.2), acetone (188.0), dioxane (185.0), and Me<sub>2</sub>O (183.4).

The protonated reference bases were isolated after a convenient delay by sweeping out all the undesired ions with two consecutive double resonance events.

The reactions between the protonated bases and the samples were followed at different trapping times and, where possible, the equilibrium constants were determined. The estimated average uncertainty in these determinations is  $\pm 0.2$  kcal mol<sup>-1</sup>.

**Acknowledgment.** We acknowledge the collaboration of Dr. Roberto Gabrielli of the Servizio FT-MS of the Area di Ricerca del C.N.R., Roma.

**Registry No.** 1a, 536-74-3; 1b, 768-60-5; 1c, 766-97-2; 1d, 766-98-3; 1e, 873-73-4; 1f, 2561-17-3; 1g, 766-83-6; 1h, 705-28-2.

(19) Taft, R. W.; Wolf, J. F.; Beauchamp, J. L.; Scorrano, G.; Arnett, E. M. *J. Am. Chem. Soc.* 1978, 100, 1240.

(20) (a) Overberger, C. G.; Saunders, J. H. "Organic Syntheses"; Wiley: New York, 1953, Collect. Vol. III, p 204. (b) Mesnard, D.; Bernadou, F.; Miginiac, L. *J. Chem. Res., Synop.* 1981, 270. (c) Dehmow, E. V.; Lissel, M. *Tetrahedron* 1981, 37, 1653. (d) Gorgues, A.; Le Coq, A. *Tetrahedron Lett.* 1976, 4723.

(21) Brown, H. C.; Okamoto, Y. *J. Am. Chem. Soc.* 1958, 80, 4979.

### Application of <sup>13</sup>C NMR Spectroscopy to Acyclic Stereochemical Analysis

James K. Whitesell\*

Department of Chemistry, University of Texas at Austin,  
Austin, Texas 78712

Bernhard Hildebrandt

Department of Chemistry, Philipps University—Marburg,  
D-3550, Marburg, West Germany

Received April 18, 1985

In the past ten years, <sup>13</sup>C NMR spectroscopy has begun to evolve as one of the most powerful tools at the disposal of the synthetic chemist for unraveling stereochemical questions. For example, the difference in congestion experienced by a substituent that is either endo or exo on a bicyclic array is of such a magnitude that it is often possible to decide the stereochemical orientation of a substituent with a high degree of confidence even when only one of the two possible diastereomers is in hand.<sup>1</sup> This situation contrasts very markedly with that in acyclic systems where generally a cyclic derivative is prepared before stereochemical analysis is carried out spectroscopically. This approach is often rationalized on the basis that conformational analysis in complicated, acyclic systems would be so imprecise that reliable predictions could not be made. We suspect that this latter opinion is invoked in the majority of cases without an actual analysis of the situation. As a markedly contrasting example, we would like to provide a relatively simple conformational analysis of the alcohols 1 and then, on the basis of this analysis, to derive predictions for the expected <sup>13</sup>C chemical shifts.<sup>2</sup>

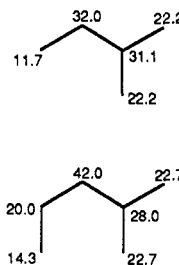
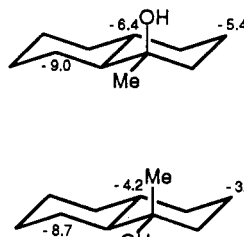
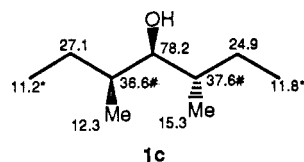
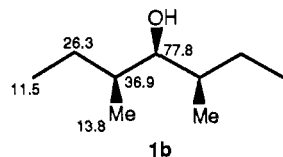
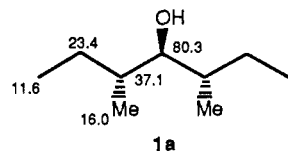
There are two dominant influences on the chemical shift of a carbon: (1) the number and nature of the atoms attached either  $\alpha$  or  $\beta$ ; (2) the steric (and to a lesser extent, electronic) interactions with atoms that are situated  $\gamma$  (as well as those that are more remote). The spacial and bonding relationships between atoms that are either  $\alpha$  or  $\beta$  to one another are invariant with rotation about  $\sigma$  bonds, so long as bond angles are not also changed. Thus, the differences observed between diastereomers result from the interaction of  $\gamma$  as well as more remote substituents. The shift perturbation due to  $\gamma$  substituents has been extensively discussed.<sup>3</sup> The magnitude of these differences is often large as can be seen by comparison of the chemical shifts for the three diastereomeric alcohols 1a-c,<sup>4</sup> where the chemical shift differences between the lowest and highest field C-3, C-5 methyl groups as well as the methylenes (C-2 and C-6) are both  $\delta$  3.7. This is certainly a sufficiently large difference that, with all isomers in hand, a reasonable prediction in a mono- or polycyclic system could be reliably made. It occurred to us that the number of reasonable conformations in such systems might not be as large as would be at first anticipated. If this were indeed the case then the effect of  $\gamma$  substituents observed in rigid bicyclic arrays where spacial relationships are well defined

(1) For example, see: Whitesell, J. K.; Matthews, R. S. *J. Org. Chem.* 1977, 42, 3878.

(2) It is perhaps important to point out that these predictions were arrived at in the absence of the correlation between spectral data and stereochemistry and, therefore, did not evolve intentionally or otherwise along lines so as to arrive at a reasonable fit between prediction and experiment. In addition, the assignment of stereochemistry to 1a-1c is based on the chemistry of their formation and symmetry arguments, not the spectral data.<sup>4</sup>

(3) See: Gorenstein, D. G. *J. Am. Chem. Soc.* 1977, 99, 2254 and references cited therein.

(4) Hoffmann, R. W.; Zeiss, H. J.; Ladner, W.; Tabche, S. *Chem. Ber.* 1982, 115, 2357.



both substituents, resulting in a considerably larger effect,  $-8.7$  and  $-9.0$ , which is quite similar for both diastereomers (avg  $-8.8$ ). In the future, more refined and precise values for these effects may be available, and indeed, the values for the ethyl-substituted decalins lead ultimately to a closer fit between predicted and observed values (the appropriate model with a *sec*-butyl substituent is complicated by the presence of an additional center of chirality). Nonetheless, it must be remembered that the lowest points on conformational energy diagrams do not occur at situations with perfect gauche relationships and that the distortion from  $60^\circ$  will vary from molecule to molecule and thus no empirical model would be anticipated to lead to a perfect fit.

These effects represent the perturbation resulting from the addition of both the methyl and the hydroxyl group onto the decalin framework. For use in predicting the chemical shifts of diastereomers **1a-c** these values were added to the observed shifts for methylbutane, the corresponding hydrocarbon lacking both the R and the hydroxyl groups. The appropriate values were then averaged for the two conformations to obtain the predicted values in Table I. Note that the largest error for **1a** and **1b** is only  $\delta 1.2$ . Considering the derivation of the analysis, we consider this to be an extraordinarily good fit and therefore to lend significant justification to the method. The values predicted for **1c** were based on the assumption that the two conformations are equally populated, a situation which may not necessarily be the case since they differ by whether the methyl or ethyl group is situated gauche to both the hydroxyl and R groups. Nonetheless, the average error is only  $\delta 1.2$ . As would be anticipated, the left-hand side of the molecule is predicted to be the same as **1b** while the right-hand side mimics **1a**.

In arriving at the predictions above, it was assumed that the effect of C-1 and C-7 on the C-3 and C-5 methyl groups ( $\delta$  interaction) would be identical with that found in 2-methylbutane. Clearly, this need not be the case and this effect may account for at least some of the errors. Nonetheless, the qualitative difference between the absorptions for C-4 in the three isomers of **1** can be readily accounted based on interactions with C-1 and C-7. The shielding effect of a  $\delta$  carbon substituent is significant only when there is a hydrogen-hydrogen interaction equivalent to that between the methyl groups in gauche butane. In **1b**, both of the methyls of the ethyl groups can interact with the hydrogen on C-4 in both conformations, while in **1c** only three and in **1a** only two of the four Newman projections have the ethyl groups so oriented. Thus, the upfield shift in the progression from **1a** (80.3) to **1c** (78.2) to **1b** (77.8) for C-4 would be expected.

Application of this approach to the homologous alcohols **2a** and **2c** (Scheme II) leads to chemical shift predictions that have the approximately the same accuracy as those for **1** (Table II). In summary, we feel that the application of  $^{13}\text{C}$  spectroscopy to the direct, stereochemical analysis of acyclic systems is far more promising than would at first appear and encourage others to follow along lines similar to those detailed above.<sup>7</sup>

might be applied to each of the conformations that would be anticipated to be significantly populated.

In the case under consideration, there are for each diastereomer only two reasonable conformations that evolve by rotation about both bonds C-3-C-4 and C-5-C-4. This is due to a "locked step" interaction between substituents on C-3 and C-5, an effect that can be seen in the projection where one of the substituents in both pairs A-A' and B-B' must be hydrogen in order to avoid a serious steric interaction. The magnitude of this interaction would be anticipated to be similar to that experienced when two substituents are 1,3-related and axially substituted on a cyclohexane<sup>5</sup>. Thus, the conformational picture is much simplified for this system, although a similar simplification would be anticipated for other acyclic molecules with three contiguous, tertiary, chiral centers.

In Scheme I we have provided Newman projections along the C-3-C-4 and the C-5-C-4 bonds (each from the perspective looking toward the central carbon, C-4) for each of the diastereomers, **1**. For **1a** the methyl groups are in all cases either anti to the hydroxyl group while gauche to the R group (which represents all of the remaining carbons not specifically illustrated) or vice versa. On the other hand, the methylenes of the ethyl groups are gauche to both the hydroxyl and the R group in one conformation while gauche to the hydroxyl and anti to the R group in the other. Because of the symmetry present in the molecule, these two conformations are enantiomeric and thus identical in energy. The situation in **1b** is precisely reversed, that is it is the methylene group which is either anti to hydroxyl and gauche to R or vice versa, and the methyl group that is gauche to both the hydroxyl and the R group in one conformation while gauche to the hydroxyl and anti to the R group in the other.

The magnitude of the anticipated effects due to the spacial relationship with the carbon substituent (R) and with the hydroxyl group were derived from an analysis of the shift effects on *trans*-fused, bicyclo[4.4.0]decanes.<sup>6</sup> The effect of introducing a carbon anti and an oxygen gauche can be seen to be  $-6.4$  and  $-5.4$  (avg  $-5.9$ ) while the opposite arrangement results in corresponding shifts of  $-4.2$  and  $-3.5$  (avg  $-3.8$ ). In both cases, C-10 is gauche to

(5) It is important that the magnitude of anticipated chemical shift effects as well as the relative energy of any particular conformation be considered hand in hand before the overall effect of that particular conformation on the  $^{13}\text{C}$  spectrum is discarded.

(6) Ayer, W. A.; Brown, L. M.; Fung, S.; Stothers, J. B. *Org. Mag. Reson.* 1978, 11, 73.

Scheme I

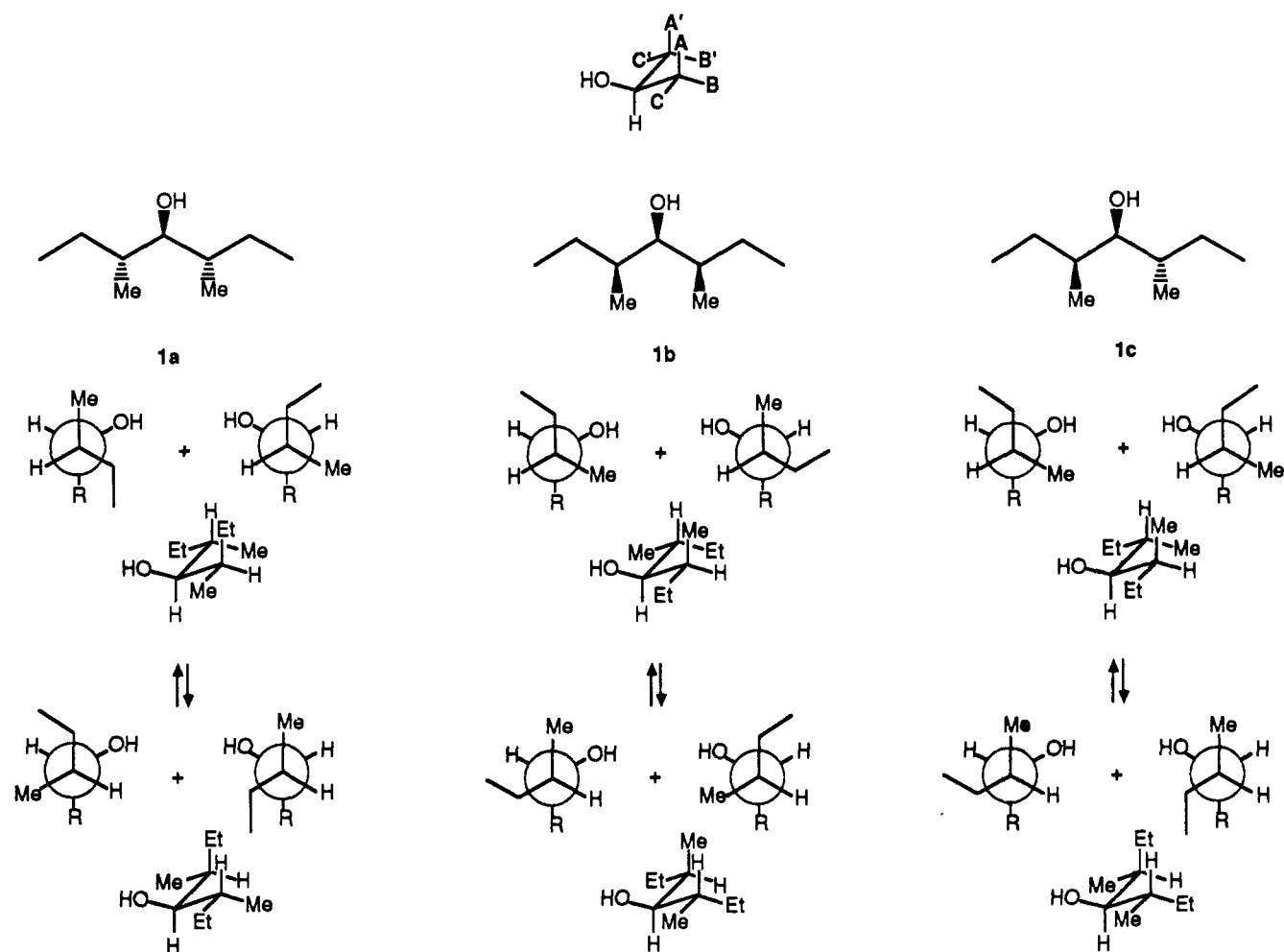


Table I

|    |       | C-2  | C-3 Me | C-5 Me | C-6  |
|----|-------|------|--------|--------|------|
| 1a | obsd  | 23.4 | 16.0   |        |      |
|    | pred  | 24.6 | 17.4   |        |      |
|    | error | 1.2  | 1.4    |        |      |
| 1b | obsd  | 26.3 | 13.8   |        |      |
|    | pred  | 27.2 | 14.8   |        |      |
|    | error | 0.9  | 1.0    |        |      |
| 1c | obsd  | 27.1 | 12.3   | 15.6   | 24.9 |
|    | pred  | 27.2 | 14.8   | 17.4   | 24.6 |
|    | error | 0.1  | 2.5    | 1.8    | -0.3 |

Table II

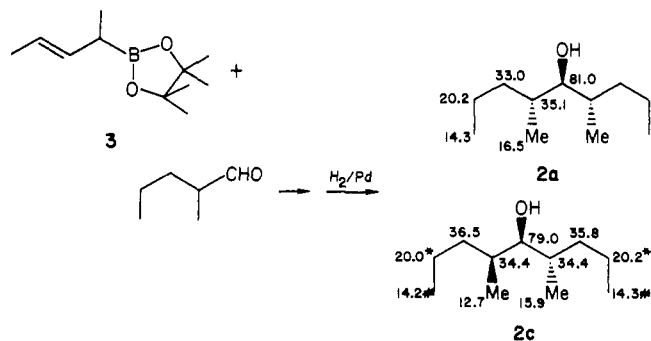
|    |       | C-3  | C-4 Me | C-6 Me | C-7  |
|----|-------|------|--------|--------|------|
| 2a | obsd  | 33.0 | 16.5   |        |      |
|    | pred  | 34.6 | 17.9   |        |      |
|    | error | 1.6  | 1.4    |        |      |
| 2c | obsd  | 36.5 | 12.7   | 15.9   | 35.8 |
|    | pred  | 37.2 | 15.3   | 17.9   | 34.6 |
|    | error | 0.7  | 2.6    | 2.0    | 1.2  |

### Experimental Section

The preparation of the isomeric alcohols 1a-c has been previously described.<sup>4</sup>

2-((*E*)-3-Pentenyl-2)-4,4,5,5-tetramethyl-1,3-dioxaborolane (3). A solution of 38.0 g (0.36 mol) of 2-chloro-3-pentene<sup>9</sup>

Scheme II



in 70 mL of THF was added to a stirred suspension of 46.0 g (1.89 mol) of magnesium in 200 mL of THF at 0 °C. The reaction was warmed to room temperature and after 1 h was filtered, and the filtrate was added with stirring over 1.5 h to a solution of 56.4 g (0.30 mol) of triisopropyl borate in 50 mL of THF at -78 °C. After 2 h the reaction was quenched by the addition of 68 mL (0.30 mol) of a 4.5 M HCl solution in ether followed by 36.0 g (0.30 mol) of pinacol. After 2 h the reaction was added to 150 mL of saturated aqueous NaHCO<sub>3</sub> and stirred for a further 14 h. The organic layer was washed with aqueous NH<sub>4</sub>Cl and brine and then dried over Na<sub>2</sub>SO<sub>4</sub>. Concentration in vacuo at 40 °C afforded 99.0 g of crude product that was purified by chromatography (silica gel, 4:1 petroleum ether (40-60 °C/ether). The resulting colorless oil (39.0 g, 54%) was a 96:4 mixture of *E*:*Z* borolane by GC (30

(7) We have successfully applied these concepts to a limited extent to other, simple acyclic systems where conformational populations were estimated by MM-2 calculations.<sup>8</sup>

(8) Allinger, N. A.; Hirsch, J. A.; Miller, M. A.; Tyminski, I. J.; Van Catledge, F. A. *J. Am. Chem. Soc.* 1968, 90, 1199. Allinger, N. A.; Chung, D. Y. *J. Am. Chem. Soc.* 1976, 98, 6798.

(9) Alexander, E. R.; Kluiber, R. W. *J. Am. Chem. Soc.* 1951, 73, 4304. Coburn, E. R. "Organic Syntheses"; Wiley and Sons: New York, 1955; Collect. Vol. III, p 696.

m × 0.3 mm SE 52 glass capillary column,  $t_R$  19.3 min (*Z*) and 19.7 min (*E*):  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ) 5.49 (dd,  $J_d = 15$  Hz,  $J_a = 7$  Hz,  $J_b = 1$  Hz, 1 H, H-3), 5.36 (dq,  $J_d = 15$  Hz,  $J_a = 7$  Hz,  $J_b = 1$  Hz, 1 H, H-4), 1.63 (d,  $J = 7$  Hz, 3 H,  $\text{CH}_3$ ), 1.22 (s, 12 H,  $\text{CH}_3$ ), 1.04 (d,  $J = 7$  Hz, 3 H,  $\text{CH}_3$ );  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ) 133.2, 122.5, 82.9, 24.6, 18.0, 15.1. Anal. Calcd for  $\text{C}_{11}\text{H}_{21}\text{BO}_2$ : C, 67.36; H, 10.81. Found: C, 67.67; H, 10.92.

**4,6-Dimethylnonan-5-ol (2a and 2c).** To 2.0 g (10 mmol) of **3** in 10 mL of petroleum ether was added at 0 °C 1.0 g (10 mmol) of 2-methylpentanal.<sup>10</sup> The mixture was allowed to warm to room temperature and stirred for 14 h. After addition of 1.5 g (10 mmol) of triethanolamine in 5 mL of  $\text{CH}_2\text{Cl}_2$  the resulting suspension was stirred for 2 h. The mixture was filtered through 45 g of silica gel and the product was eluted with  $\text{CH}_2\text{Cl}_2$ . Concentration afforded 2.1 g of a colorless oil which was taken up in 10 mL of methanol. This solution was stirred with 0.2 g of 5% palladium on charcoal for 1 day at 25 °C under 1 atm of hydrogen. The reaction was filtered, the filtrate concentrated, and the resulting oil distilled to yield 1.3 g (76%, 104–107 °C (14 torr)) of a 25:75 mixture of **2a** and **2b**.

For **2a**:  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ) 81.0, 35.1, 33.0, 20.2, 16.5, 14.3. Anal. Calcd for  $\text{C}_{11}\text{H}_{24}\text{O}$ : C, 76.68; H, 14.04. Found: C, 76.34; H, 14.27.

For **2c**:  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ) 79.0, 36.5, 35.7, 34.4, 34.4, 20.2, 20.0, 15.9, 14.3, 14.2, 12.7.

**Acknowledgment.** Support of this research by the National Institutes of Health (GM-31750) and the Robert A. Welch Foundation (F-626) is gratefully acknowledged.

**Registry No.** **1a**, 98757-88-1; **1b**, 82917-19-9; **1c**, 98757-89-2; **2a**, 98757-90-5; **2c**, 79237-71-1; **3**, 98704-47-3; 2-chloro-3-pentene, 1458-99-7; triisopropyl boronate, 5419-55-6; pinacol, 76-09-5; 2-methylpentanal, 123-15-9.

(10) Skita, A. *Chem. Ber.* 1915, 48, 1491.

## The Conformational Energy of the (Benzene)chromium Tricarbonyl Substituent

Ernest L. Eliel,<sup>\*1a</sup> Muthiah Manoharan,<sup>1a</sup>  
Samuel G. Levine,<sup>1b</sup> and Angelita Ng<sup>1b</sup>

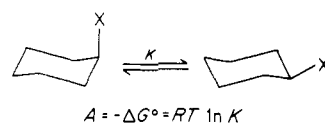
William Rand Kenan, Jr. Laboratories of the University of North Carolina, Chapel Hill, North Carolina 27514, and the Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27607

Received May 15, 1985

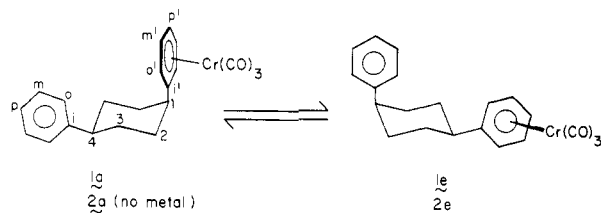
Among the many substituents whose equatorial preference<sup>2</sup> in cyclohexane ( $\Delta G^\circ$ , Scheme I) has been recorded<sup>3-5</sup> there are a few metalloorganic groups such as  $\text{HgBr}$ ,<sup>3</sup>  $\text{SnMe}_3$ ,<sup>6</sup>  $\text{GeMe}_3$ ,<sup>6</sup> and  $\text{PbMe}_3$ <sup>6</sup> but no complexes of transition elements. We report here the equatorial preference of the (benzene)chromium tricarbonyl [ $\text{C}_6\text{H}_5\text{Cr}(\text{CO})_3$ ] substituent, both by itself and when geminal to a methyl group, as determined by low-temperature  $^{13}\text{C NMR}$  spectroscopy.

The equatorial preference of phenyl amounts to 2.87 kcal/mol.<sup>7</sup> Since this value is too large to be measured directly by low-temperature  $^{13}\text{C NMR}$  spectroscopy (the favored methodology) and since we expected the corre-

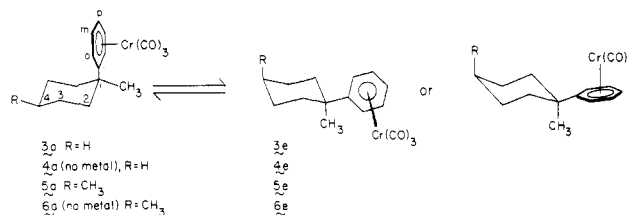
Scheme I



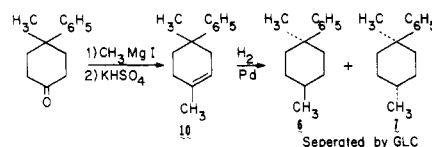
Scheme II



Scheme III



Scheme IV



sponding  $-\Delta G^\circ$  value of the (benzene)chromium tricarbonyl substituent to be of the same order of magnitude, we decided to counterpoise the complexed phenyl group against an uncomplexed one by studying (*cis*-4-phenylcyclohexylbenzene)chromium tricarbonyl (**1**, Scheme II). The parent hydrocarbon **2**<sup>8</sup> was converted to **1** by treatment with chromium hexacarbonyl in refluxing dioxane, the major product (41.5%) being the monocomplex. The  $^{13}\text{C NMR}$  chemical shifts of both the ligand **2** and the complex **1** at room temperature and at  $-100$  °C are given in Table I, and the ratios of corresponding peaks are indicated in Table II. The assignments in the low-temperature spectrum of the ligand are based on known<sup>7</sup> spectra with equatorial and axial phenyl groups; knowledge of the ligand shifts then made possible assignment of most of the signals in the complex. The averaged equilibrium constant of  $1.2 \pm 0.1$  corresponds to  $-\Delta G^\circ = 0.06 \pm 0.03$  kcal/mol at  $-100$  °C; i.e., the equatorial preference of the complexed phenyl group is only marginally larger than that of the uncomplexed one.

This conclusion is reasonable in light of earlier calculations<sup>9</sup> which suggest that the equatorial phenyl ring lies in the symmetry plane of the cyclohexyl ring and the axial one is perpendicular to that plane (cf. Scheme II). In that case, the equatorial phenyl can be complexed sideways (apparently with little steric problem) and the axial one (likewise) from the outside face of the ring. (If there is any steric congestion, it must be about the same for the two different attitudes of the phenyl ring.)

(1) (a) University of North Carolina at Chapel Hill. (b) North Carolina State University.

(2) Alternatively called "conformational energy" or "A-value", cf. ref 3.

(3) Jensen, F. R.; Bushweller, C. H. *Adv. Alicycl. Chem.* 1971, 3, 139.

(4) Schneider, H.-J.; Hoppen, V. *J. Org. Chem.* 1973, 43, 3866.

(5) Corey, E. J.; Feiner, N. F. *J. Org. Chem.* 1980, 45, 765.

(6) Kitching, W.; Doddrell, D.; Grutzner, J. B. *J. Organomet. Chem.* 1976, 107, C5. Kitching, W.; Olszowy, H. A.; Drew, G. M.; Adcock, W. *J. Org. Chem.* 1982, 47, 5153.

(7) Eliel, E. L.; Manoharan, M. *J. Org. Chem.* 1981, 46, 1959.

(8) Levin, S. G.; Ng, A. *J. Org. Chem.* 1985, 50, 390. An alternate synthesis of a mixture of *cis*- and *trans*-1,4-diphenylcyclohexane by hydrogenation of 1,4-dihenyl-1-cyclohexene is described in the Experimental Section and the spectra of both isomers are included in Table I.

(9) Allinger, N. L.; Tribble, M. T. *Tetrahedron Lett.* 1971, 3259.