

Table IV. Ratio of Dimeric to Monomeric Product from *p*-Diisopropylbenzene after *X* h at Room Temperature and *Y* h at Reflux

<i>X</i> , h	<i>Y</i> , h	dimer:monomer
12	3	35:65
24	3	50:50
24	24	80:20

The number of deuterium atoms and positions of substitution were confirmed by mass spectrometry and NMR. Dry nitrogen atmosphere was used for all reactions. The *n*-butyllithium and potassium *tert*-alkoxide solutions were approximately 1.6 M. For the preparation of potassium *tert*-pentoxide solution and 1:1 Bu/LiKO_tPe, see ref 4.

Metalation-Elimination Reactions. The starting material (Table I) was added slowly by syringe to a stirred 4-fold excess of BuLi/KO-*t*-Pe. The mixture was stirred for 24 h at room temperature. During this time the intense color of the metalated olefins and, in the case of radical anions, a metallic mirror developed. The reaction was then slowly heated and refluxed for 24 h. After cooling to room temperature, the reaction mixture was quenched by pouring slowly under nitrogen into a large excess of cooled D₂O. Care was taken not to allow any color to develop. The organic layer was separated, washed twice with water, and dried over calcium chloride. After the hexane was distilled, the products were separated by preparative GLC with a ³/₈ in × 20 ft 30% SE-30 on Chromasorb-W-column or HPLC with Zorbax ODS and light petroleum as solvent.

The ratio of dimeric to monomeric products depends on both the reaction time at room temperature and the time at reflux. Examples are shown in Table IV.

ESR Sample Preparation. The heterogenous reaction mixture (0.1 mL) was transferred by syringe to a nitrogen-flushed ESR-tube. After cooling to -78 °C, 0.1–0.2 mL of THF was added and the whole mixed by a slow current of nitrogen passing through the mixture for a short time. The tube was then sealed.

2,5-Bis(*p*-isopropylphenyl)hexane and 2,5-bis(*m*-isopropylphenyl)hexane were obtained as a mixture of SS, RR, and *meso* enantiomers.

2,5-Bis(*p*-isopropylphenyl)hexane: mp 53–55 °C, ¹H NMR (CCl₄) δ 1.15 (d, ³J = 6 Hz, 6 H, 2CH₃), 1.25 (d, ³J = 6 Hz, 12 H, 4CH₃), 1.35–1.45 (m, ³J = 4 Hz, 4 H, 2CH₂), 2.2–3.1 (2 m overlapping, 4 H,

4CH), 7.0 (s, 8 H, ar); IR (liquid fil) 3050, 3030, 3010, 2985, 2970, 2940 (CH) cm⁻¹; MS (96 eV), *m/e* 322 (100%), 307 (5%), 279 (25%); ¹³C NMR (CDCl₃) δ 22.3, 22.5 (2 q, CH₃), 24.1 (q, CH₃), 33.6 (d, CH), 36.2, 26.6 (2 t, CH₂), 39.6 (d, CH), 126.1, 126.7 (2 d, C-ortho, C-ortho'), 144.8, 144.9 (2 s, C-*ipso*), 145.9 (s, C-*ipso*).

Anal. Calcd for C₂₄H₃₄ (322.5): C, 89.4; H 10.6. Found: C, 89.4; H 10.3.

2,5-Bis(*m*-isopropylphenyl)hexane: Mp 48–50 °C, Bp 0.1 torr 150–160 °C (short path distillation), ¹H NMR (CCl₄) δ 1.15 (d, ³J = 6 Hz, 6H, 2CH₃), 1.25 (d, ³J = 6 Hz, 12H, 4CH₃), 1.35–1.55 (m, ³J = 4 Hz, 4H, 2CH₂), 2.3–3.2 (2 m overlapping, 4H, 4CH), 6.8–7.35 (m, 8H, ar); IR (liquid film) 3010, 2970, 2955, 2930 (CH) cm⁻¹; MS (96 eV) *m/e* = 322 (40%), 320 (15%), 147 (100%).

Anal. Calcd for C₂₄H₃₄ (322.5): C, 89.4; H 10.6. Found: C, 89.0; H, 10.8.

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Registry No. 18, 88158-19-4; 19, 88158-20-7; 20, 88158-21-8; 21, 88158-22-9; 24, 88158-23-0; 25, 88158-24-1; 26, 88158-25-2; 27, 27271-53-0; 28, 52340-00-8; 29, 63949-25-7; 30, 88158-26-3; 31, 88158-27-4; 32, 88158-28-5; (*R**,*R**)-2,5-bis(*p*-isopropylphenyl)hexane, 88158-29-6; *meso*-2,5-bis(*p*-isopropylphenyl)hexane, 88158-30-9; (*R**,*R**)-2,5-bis(*m*-isopropylphenyl)hexane, 88158-31-0; *meso*-2,5-bis(*m*-isopropylphenyl)hexane, 88158-32-1; stilbene radical anion, 34467-73-7; *o*-xylene, 95-47-6; *m*-xylene, 108-38-3; *p*-xylene, 106-42-3; ethylbenzene, 100-41-4; *m*-ethylmethylbenzene, 620-14-4; *p*-ethylmethylbenzene, 622-96-8; *m*-diethylbenzene, 141-93-5; *p*-diethylbenzene, 105-05-5; isopropylbenzene, 98-82-8; *m*-isopropyltoluene, 535-77-3; *p*-isopropyltoluene, 99-87-6; *m*-diisopropylbenzene, 99-62-7; *p*-diisopropylbenzene, 100-18-5; BuLi, 109-72-8; KO_tPe, 53535-81-2.

Supplementary Material Available: Summaries of MNDO calculations (*z*-matrices) for 18–32 (15 pages). Ordering information is given on any current masthead page.

Conformational Analysis. 45.¹ Syn-Axial Methyl/Phenyl and Gauche Methyl/Methyl Interactions[†]

Muthiah Manoharan and Ernest L. Eliel*

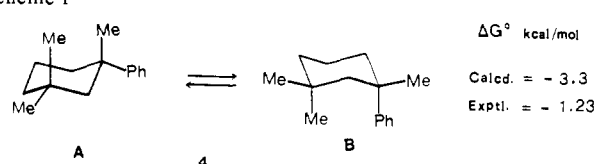
Contribution from the W. R. Kenan, Jr., Laboratories, Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514. Received April 18, 1983.
Revised Manuscript Received September 13, 1983

Abstract: Examination of the conformational equilibria of 1-phenyl-3,3,5-trimethylcyclohexane and 1-phenyl-1,3,3-trimethylcyclohexane by low-temperature ¹³C NMR spectroscopy indicates the 1,3-diaxial interaction of phenyl and methyl to amount to 3.4 ± 0.1 kcal/mol. The *gauche* interaction of the methyl substituents in *trans*-1,2-dimethylcyclohexane is measured as 0.74 kcal/mol through determination, by the same technique, of the conformational equilibrium of *r*-1-phenyl-*t*-3,3,4-dimethylcyclohexane.

The Phenyl/Methyl Syn-Axial Interaction

In the determination of predominant conformations of complex molecules with six-membered rings, 1,3-diaxial (or syn-axial) interactions play an important role. Among 18 such interactions recently tabulated² is the phenyl/methyl interaction, assigned a value of 2.9 kcal/mol. This value is derived from a determination of the excess of a methyl/methyl/H interaction over a phenyl/methyl/H interaction (cf. Scheme I) by NMR spectroscopy of

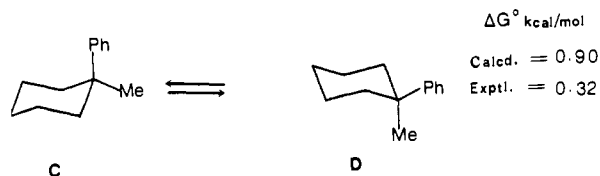
Scheme 1



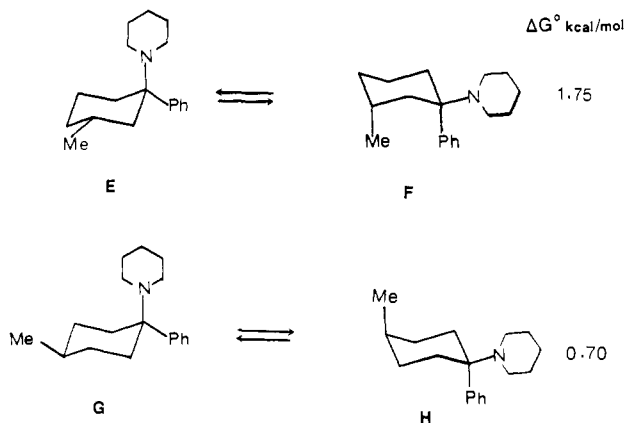
α -fluoro-3-phenyl-3,5,5-trimethylcyclohexanones,³ which yields a difference of 0.9 kcal/mol. Taking the value of the methyl/

[†] Dedicated to Professor Günther O. Schenck in honor of his 70th birthday.

Scheme II



Scheme III

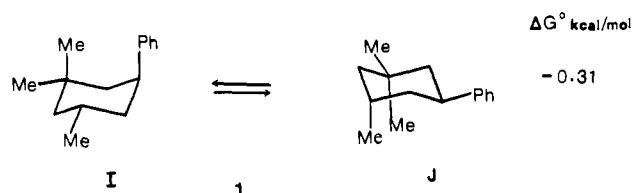


methyl syn-axial interaction as 3.7 kcal/mol as determined experimentally,⁴ the phenyl/methyl interaction is computed to be $3.7 - 0.9 = 2.8$ kcal/mol.⁵ This value must be considered only approximate since the NMR method used was not precise³ and, in any case, refers to a substituted cyclohexane rather than cyclohexane.

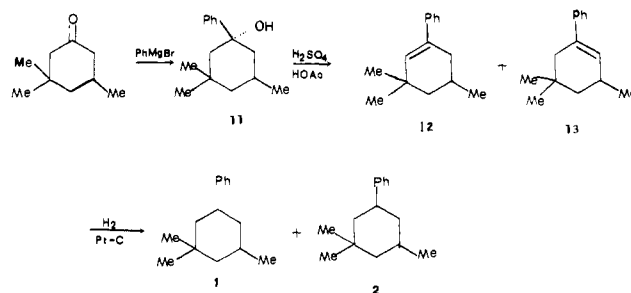
An alternative way of evaluating the Ph/Me interaction is based on a force-field calculation⁶ of the equilibrium depicted in Scheme I; this calculation suggests that $-\Delta G^\circ = 3.2$ – 3.3 kcal/mol. To obtain the Ph/Me interaction (X) from this number, one must also know the Ph/H interaction ($1/2 \times 2.87 = 1.43$ kcal/mol⁷), the Me/H interaction ($1/2 \times 1.74 = 0.87$ kcal/mol⁸), and the differential geminal interaction as between Ph_e/Me_a and Ph_a/Me_e . The latter value (Y) may be derived from the force-field calculation of the equilibrium shown in Scheme II,^{6,9} which suggests $\Delta G^\circ = 0.9$ kcal/mol. Since the interaction in C is 2.87 kcal/mol (two Ph/H) and that in D $1.74 + Y$ kcal/mol (two Me/H plus the differential geminal interaction) the difference is $1.74 + Y - 2.87 = 0.9$ kcal/mol whence $Y = 2.03$ kcal/mol. With this value in hand, one can now evaluate the conformational energy of B and A in Scheme I: That of B is $1.43 + 0.87 + X$ kcal/mol (Ph/H + Me/H + Ph/Me) or $2.3 + X$ and that of A is $1.74 + 3.7 + 2.03$ (2 Me/H + Me/Me + Y) or 7.47 kcal/mol. If the difference is taken as 3.3 kcal/mol, one gets $3.3 = 7.47 - 2.3 - X$ whence $X = 1.87$ kcal/mol. This value is smaller by over 1 kcal/mol than that tabulated by Corey and Feiner.²

A third value for the Ph/Me syn-axial interaction may be calculated from the phenylcyclohexane equilibria shown in Scheme III,

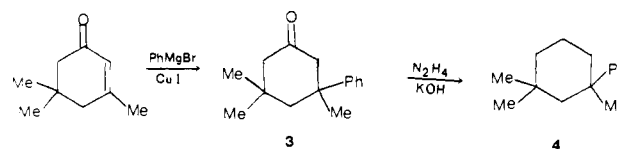
Scheme IV



Scheme V



Scheme VI



determined by Geneste et al.¹⁰ through pK measurements.¹¹ If one assumes that the conformational energy levels of E and G are equal, the conformational energy of F is 1.05 kcal/mol ($1.75 - 0.7$) above that of H. Since geminal interactions in F and H are the same and cancel out, one can compute the conformational energy difference between F and H as follows: $(\text{Ph}/\text{H} + \text{Me}/\text{H} + \text{Ph}/\text{Me}) - (2 \text{ Ph}/\text{H} + 2 \text{ Me}/\text{H}) = 1.05$, or $\text{Ph}/\text{Me} = 1.05 + \text{Ph}/\text{H} + \text{Me}/\text{H} = 1.05 + 1.43 + 0.87 = 3.35$ kcal/mol, a value somewhat larger than that tabulated.² In the light of these discrepancies, we felt that a redetermination of the phenyl/methyl syn-axial interaction was in order.

Results and Discussion

In this work the Ph/Me interaction was determined by measuring the position of the equilibrium shown in Scheme IV by low-temperature ¹³C NMR spectroscopy. A mixture of compound **1** (Scheme IV) and its stereoisomer **2** was easily obtained from dihydroisophorone in three steps as shown in Scheme V: diastereomers **1** and **2** were separated by preparative gas chromatography. The salient NMR data at room temperature and, in the case of **1**, at -100°C (in CD_2Cl_2) are shown in Table I (top). Both conformers of **1** were easily seen and, as shown in Table II, are in a ratio of 2.45 ± 0.22 whence $\Delta G^\circ = -0.31 \pm 0.03$ kcal/mol. If X is the Ph/Me syn-axial interaction, the conformational energy of I (Scheme IV) is $X + 1.43 + 0.87$ or $2.30 + X$ kcal/mol and that of J $3.7 + 1.74$ or 5.44 kcal/mol. Hence $2.30 + X - 5.44 = 0.31$ whence $X = 3.45$ kcal/mol. This value is only slightly higher than that derived from the data of Geneste et al.¹⁰ but appreciably higher than that tabulated^{2,3} and very much higher than that computed by force-field calculation.⁶ It is only slightly smaller than the syn-axial methyl/methyl interaction (3.7 kcal/mol⁴), suggesting that, although the phenyl ring turns its flat face toward the inside of the cyclohexane chair (see below), the interaction between that face and the axial methyl group across the chair is large.

One may now recalculate the equilibrium shown in Scheme I as -1.13 kcal/mol, using experimental instead of calculated values for the Ph/Me 1,3 and geminal interactions.¹² This value differs

(1) Paper 44: Eliel, E. L.; Chandrasekaran, S. *J. Org. Chem.* **1982**, *47*, 4783.

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

(3) (a) Shapiro, B. L.; Chryssam, M. M. *J. Org. Chem.* **1973**, *38*, 880. See also: (b) Shapiro, B. L.; Johnson, M. D., Jr.; Shapiro, M. J. *Ibid.* **1974**, *39*, 796.

(4) Allinger, N. L.; Miller, M. A. *J. Am. Chem. Soc.* **1961**, *83*, 2145.

(5) The source of the (trivial) difference between the original value of 2.8 and the tabulated value of 2.9 kcal/mol is not clear.

(6) Allinger, N. L.; Tribble, M. T. *Tetrahedron Lett.* **1971**, 3259. David Knox in our laboratory has recently recomputed this value using Allinger's MM2 program; the result, 2.32 kcal/mol, is about 1 kcal/mol lower than the earlier one but still about 1 kcal/mol larger than the experimental value. It is clear that the calculation undervalues the Ph/Me syn-axial interaction.

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

(8) Booth, H.; Everett, J. R. *J. Chem. Soc., Chem. Commun.* **1976**, 278.

(9) The calculated⁴ and experimental⁹ values differ by 0.58 kcal/mol. For the sake of consistency, we have used only calculated values in this computation.

(10) Geneste, P.; Kamenka, J. M.; Ung, M. S. N.; Herrmann, P.; Goudal, R.; Trouiller, G. *Eur. J. Med. Chem.-Chim. Ther.* **1979**, *14*, 301.

(11) Cf.: Stolow, R. D. *J. Am. Chem. Soc.* **1959**, *81*, 5806. Tichý, M.; Jonas, J.; Sicher, J. *Collect. Czech. Chem. Commun.* **1959**, *24*, 3434.

(12) See statement regarding supplemental material at end of paper.

Table I. ¹³C NMR Spectra of Tetrasubstituted Cyclohexanes and Derivatives

compd		C-1	C-2	C-3	C-4	C-5	C-6	Me-3e	Me-3a	Me-5	ipso	ortho	meta	para
2 (cis)	RT, ^a CDCl ₃	40.1 ₅	47.2 ₈	30.6 ₈	48.3 ₁	28.7 ₅	43.0 ₆	33.4 ₈	25.4 ₄	22.8 ₃	147.6 ₂	126.9 ₂	128.3 ₂	125.8 ₃
2	calcd ^b	40.2 ₅	47.0 ₆	30.8 ₀	48.5 ₀	28.3 ₅	43.2 ₅	33.7 ₀	24.9 ₀	23.1 ₅	147.9 ₇	126.8 ₃	128.3 ₂	125.8 ₄
1 (trans)	RT, CDCl ₃	35.5 ₄	46.3 ₄	31.4 ₂	45.7 ₀	27.1 ₁	38.8 ₅	32.4 ₉	30.1 ₇	21.9 ₂	147.4 ₂	127.0 ₄	128.2 ₆	125.5 ₆
1	RT, CD ₂ Cl ₂	35.8 ₂	46.6 ₁	31.6 ₆	45.8 ₅	27.5 ₁	39.1 ₅	32.6 ₀	30.2 ₀	21.9 ₉	147.9 ₇	127.3 ₈	128.5 ₂	125.8 ₂
1	calcd ^c	33.9 ₀	45.7 ₅	31.2 ₀	45.4 ₁	26.5 ₉	37.9 ₅	32.5 ₅	31.8 ₅	22.0 ₂	-147.5 ₂	127.5 ₂	128.4 ₂	125.6 ₈
1 1	-100 °C, CD ₂ Cl ₂	31.8 ₈	43.5 ₂	(35.6 ₅) ^d	48.2 ₈	23.9 ₀	(35.5 ₂) ^d	34.1 ₁	26.7 ₄	23.3 ₃	146.2 ₇	127.0 ₅	128.1 ₃	124.9 ₄
1 1	calcd ^b	30.8 ₅	42.5 ₅	31.7 ₀ ^g	49.0 ₀	22.9 ₀	38.6 ₀ ^g	34.5 ^e	27.6 ^e	23.7	<i>f</i>	<i>f</i>	<i>f</i>	<i>f</i>
1 J	-100 °C, CD ₂ Cl ₂	35.0 ₉	47.0 ₆	(28.5 ₈) ^d	43.7 ₂	(28.1 ₇) ^d	39.3 ₉	31.6 ₃	34.8 ₅	21.2 ₆	148.2 ₅	127.3 ₇	128.5 ₉	126.1 ₁
1 J	calcd ^b	34.5 ₀	47.5 ₀	31.7 ₀ ^g	43.9 ₀	28.9	43.0 ^g	33.7 ₀	33.5 ₀	21.5 ₀	148.5 ₄	127.1 ₉	128.6 ₃	126.6 ₀
1	RT, C ₆ D ₅ CD ₃	35.8 ₅	46.4 ₀	31.4 ₈	45.8 ₉	27.3 ₀	38.9 ₂	30.3 ₆	32.3 ₀	22.0 ₆	147.4 ₈	127.3 ₂	128.5 ₂	125.8 ₆
1	+100 °C, C ₆ D ₅ CD ₃	36.2 ₇	46.6 ₇	31.5 ₄	46.2 ₃	27.4 ₈	39.4 ₃	30.4 ₄	32.4 ₈	22.0 ₅	148.0 ₀	127.4 ₁	128.6 ₁	125.9 ₅
1	-50 °C, C ₆ D ₅ CD ₃	35.4 ₉	45.9 ₈	31.5 ₁	45.5 ₉	27.0 ₁	38.1 ₉	30.4 ₅	32.1 ₈	22.1 ₃	147.1 ₂	127.3 ₂	128.5 ₀	125.8 ₃
3	RT, CDCl ₃	210.9 ₃	51.2 ₉	42.5 ₅	51.5 ₆	35.9 ₄	54.4 ₁	32.9 ⁱ	28.4 ⁱ	34.8 ^h	147.8 ₈	125.8 ₆	128.2 ₆	125.9 ₅
3	RT, C ₆ D ₅ CD ₃	208.5 ₆	51.0 ₈	42.3 ₄	51.4 ₂	35.7 ₀	54.1 ₇	32.8 ⁱ	28.3 ⁱ	34.8 ^h	148.2 ₅	126.1 ₂	128.3 ₇	126.0 ₁
3	-80 °C, C ₆ D ₅ CD ₃	210.0 ₁	50.4 ₀	42.2 ₄	50.4 ₀	36.0 ₀	53.7 ₅	33.1 ₅ ⁱ	27.3 ⁱ	35.3 ^h	147.7 ₀	128.0 ₁ ^j	128.8 ₁ ^j	125.1 ₄
3	+100 °C, C ₆ D ₅ CD ₃	208.0 ₂	51.4 ₂	42.3 ₄	51.8 ₆	35.4 ₇	54.3 ₂	32.6 ⁱ	29.26 ⁱ	34.3 ^h	148.8 ₈	126.1 ₁	128.5 ₀	126.1 ₁
4	RT, CDCl ₃	37.8 ₂	51.5 ₀	31.4 ₆	39.9 ₄	19.7 ₈	36.5 ₄	(33.1 ₀) ^d	27.9 ₃	(35.5 ₃) ^{d,k}	149.5 ₀	125.8 ₄	127.9 ₉	125.0 ₇
4	RT, CD ₂ Cl ₂	38.0 ₃	51.6 ₂	31.6 ₃	40.1 ₄	20.0 ₅	36.7 ₃	(33.2 ₇) ^d	27.8 ₉	(35.7 ₉) ^{d,k}	149.7 ₇	126.1 ₃	128.2 ₃	125.2 ₇
4 B	-100 °C, CD ₂ Cl ₂	37.5 ₈	50.7 ₈	31.5 ₈	39.3 ₉	19.5 ₆	35.7 ₆	(34.2 ₉) ^d	25.9 ₇	(35.7 ₆) ^{d,k}	148.3 ₈	127.6 ₁ ^j	128.1 ₉ ^j	124.6 ₆
4 A	-100 °C, CD ₂ Cl ₂	38.8 ₀	49.6 ₀	<i>l</i>	<i>l</i>	<i>l</i>	<i>l</i>	(27.4 ₀) ^d	<i>l</i>	(27.8 ₀) ^{d,k}	<i>l</i>	<i>l</i>	<i>l</i>	<i>l</i>
4	RT, C ₆ D ₅ CD ₃	37.8 ₁	51.5 ₉	31.5 ₄	40.1 ₆	20.1 ₅	36.7 ₀	(33.3 ₆) ^d	27.9 ₀	(35.8 ₂) ^{d,k}	149.2 ₈	125.9 ₂	128.2 ₁	125.3 ₂
4	+100 °C, C ₆ D ₅ CD ₃	38.2 ₄	52.0 ₁	31.6 ₆	40.4 ₉	20.2 ₉	37.1 ₈	(32.9 ₁) ^d	28.7 ₅	(35.1 ₂) ^{d,k}	150.1 ₃	126.0 ₂	128.3 ₃	125.4 ₅

^a RT stands for room temperature. ^b Using appropriate parameters. ^c From low-temperature shift data assuming $\Delta G^\circ = 0.31$ kcal/mol at 25 °C, $n_J = 0.63$, $n_I = 0.37$, and no temperature dependence of the shifts. ^d These assignments may have to be interchanged. ^e Taken from data for 1,1,3,3-tetramethylcyclohexane.²⁹ ^f No basis for calculation. ^g See text. ^h Me-3 in this compound. ⁱ Me-5 (geminal) in this compound. ^j Peaks in 1:1 ratio. ^k Me-1 in this compound. ^l Peak not located.

Table II. Conformer Ratio J/I (Scheme IV)^a

carbon	relative areas		
	J	I	K
C-2	300	110	2.73
C-4	250	100	2.50
C-5	320	135	2.37
Me-3a	260	120	2.17
Me-5	350	150	2.33
C-meta	320	140	2.29
C-para	110	40	2.75
			av 2.45 ± 0.22 ^a

^a $-\Delta G^\circ = 0.31 \pm 0.03$ kcal/mol.

Table III. Conformer Ratio B/A (Scheme I)^a

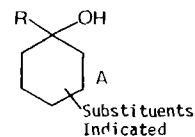
carbon	relative areas		
	B	A	K
Me-1	520	15	34.67
Me-3e	544	15	36.27
			av 35.5 ± 1.1 ^a

^a $-\Delta G^\circ = 1.23 \pm 0.01$ kcal/mol.

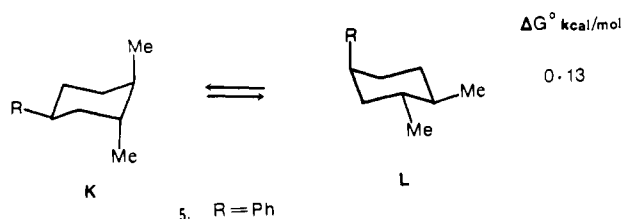
Table IV. ¹³C NMR Shifts of Phenylcyclohexan- τ -1-ols and Related Compounds (A)^a

compd	substituent	R	C-1	C-2	C-3	C-4	C-5	C-6	3-Me	4-Me	5-Me	ipso	ortho	meta	para	other
14	none	Ph	73.2 ₇	39.2 ₃	22.5 ₆	25.8 ₉	22.5 ₆	39.2 ₃				150.1 ₈	124.8 ₆	128.4 ₃	126.8 ₅	
15	<i>c</i> -4- <i>t</i> -Bu ^b	Ph	72.7 ₃	39.3 ₉	22.8 ₉	47.5 ₃	22.8 ₉	39.3 ₉	27.6 ₁ ^c			149.5 ₈	124.4 ₉ ^d	128.1 ₅	126.6 ₀	32.4 ₆ ^e
16	<i>t</i> -4- <i>t</i> -Bu ^b	Ph	73.2 ₂	38.7 ₄	24.9 ₂	47.6 ₈	24.9 ₂	38.7 ₄	27.5 ₄ ^c			144.2 ₀	126.2 ₁ ^d	128.2 ₂	126.6 ₀	32.1 ₅ ^e
11	3,3- <i>t</i> -5-Me ₃	Ph	75.2 ₁	50.4 ₇	31.7 ₂	48.4 ₀	24.4 ₅	47.7 ₄ ^f	27.6 ₀ ^f		22.4 ₄	150.3 ₁	124.5 ₀	128.0 ₂	126.4 ₁	
									34.6 ₁ ^g							
7	<i>t</i> -3, <i>c</i> -4-Me ₂	Ph	73.8 ₂	47.9 ₀	34.2 ₆	38.4 ₈	30.9 ₈	38.7 ₃	19.8 ₅	19.7 ₃		149.5 ₄	124.4 ₈ ^d	128.0 ₅	126.4 ₇	
8	<i>c</i> -3, <i>t</i> -4-Me ₂	Ph	73.8 ₂	47.1 ₅	36.3 ₉	38.7 ₃	32.7 ₅	38.3 ₈	20.1 ₅	19.2 ₈		144.5 ₅	126.3 ₉ ^d	128.3 ₆	127.0 ₆	
17	<i>t</i> -3, <i>c</i> -4-Me ₃	Me	69.9 ₄	48.0 ₁	34.0 ₆	38.6 ₀	30.9 ₃	38.9 ₁	19.7 ₁	19.9 ₀						31.5 ₇ ^h
18	<i>c</i> -3, <i>t</i> -4-Me ₃	Me	71.1 ₅	49.6 ₂	36.7 ₅	38.9 ₁	33.2 ₇	40.5 ₇	20.3 ₂	19.4 ₈						25.9 ₄ ^h

^a Shifts from Me₄Si in CDCl₃. ^b Data taken from ref 28. ^c CH₃ signal of *tert*-butyl group. ^d The large (1.7–1.9 ppm) shift difference in C(ortho) resulting from the conformational interchange of Ph and OH is striking. ^e C(CH₃)₃ signal. ^f CH₃ group cis to OH. ^g CH₃ group trans to OH. ^h 1-CH₃ signal.



Scheme VII

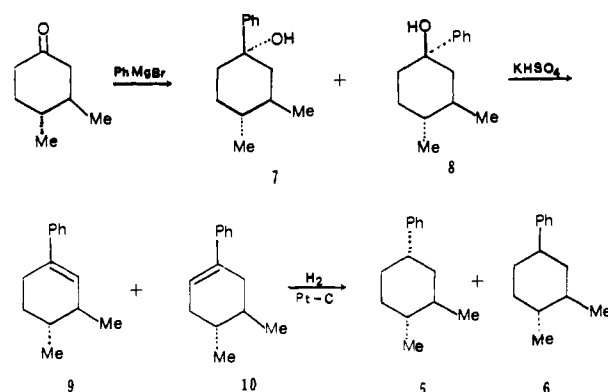


greatly from the calculated one⁶ of 3.3 kcal/mol and suggests that the equilibrium shown in Scheme I should be accessible experimentally by low-temperature ¹³C NMR spectroscopy. We therefore synthesized compound 4 (Scheme I) in two steps from isophorone as shown in Scheme VI and recorded its ¹³C spectrum at room temperature and -100 °C as shown in Table I (bottom). The area ratios in Table III, indicate $K = 35.5 \pm 1.1$ and $\Delta G^\circ = -1.23 \pm 0.01$ kcal/mol, in good agreement with the calculated value. If one now repeats the calculation made at the beginning of this paper but using experimental instead of calculated values for the equilibria shown in Schemes I and II, one obtains $X = 3.36$ kcal/mol for the Ph/Me syn-axial interaction. The three values, 3.36 kcal/mol (from Scheme I), 3.45 kcal/mol (from Scheme IV), and 3.35 kcal/mol (derived from the results of Geneste et al.,¹⁰ Scheme III), are in excellent agreement, despite a number of implicit assumptions, such as additivity of conformational energies, absence of nonchair conformations,¹³ and negligible conformational entropy differences at least in the phenylcyclohexane systems (Scheme III),¹⁴ and despite disregard of complications resulting from differing rotational positions of the phenyl plane. The best recommended value for the Ph/Me syn-axial interaction is thus 3.4 ± 0.1 kcal/mol. It might be noted that the two determinations in the present work are contingent on the Me/Me syn-axial interaction whereas the value derived from Geneste's work is independent of this interaction but rather depends on determination of conformational equilibria in phenylcyclohexanes some of which have been confirmed by ¹³C NMR measurements.¹⁵ Thus the consistency of the data also supports the experimentally determined⁴ value of 3.7 kcal/mol for the Me/Me syn-axial interaction.

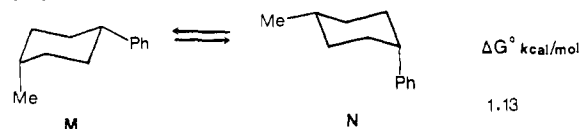
The Methyl/Methyl Gauche Interaction in *trans*-1,2-Dimethylcyclohexane¹⁶

The vicinal Me/Me interaction in *trans*-1,2-dimethylcyclohexane is one of the basic conformational parameters that enters into the equilibrium calculation of the 1,2-dimethylcyclohexanes, a classical conformational problem.¹⁸ Previous approaches,¹⁶ based on the enthalpies of formation of the *trans*-1,2-, *cis*-1,3-, and *trans*-1,4-dimethylcyclohexanes¹⁹ and on conformational equilibria of *t*-2-amino-*c*-4,*t*-5-dimethylcyclohexanols,²⁰ have led

Scheme VIII



Scheme IX



to values of 1.1 kcal/mol¹⁹ in the vapor phase,²¹ 1.0–1.1 kcal/mol¹⁹ in the pure liquid,²¹ and 0.59–0.74 kcal/mol in various solvents.^{20,22} The conformational equilibrium shown in Scheme VII (R = H) should therefore correspond to a ΔG° of 0.59 to 0.74 – (2×1.74) or ca. -2.8 kcal/mol. This is too extreme to be measured directly, and we therefore used a compound (5, Scheme VII, R=Ph) with a phenyl counterpoise (conformational energy⁷ 2.87 kcal/mol) for which the predicted equilibrium corresponds to an equilibrium constant near unity. Compound 5 was synthesized as shown in Scheme VIII. The Grignard addition yielded a 70:30 mixture of epimeric alcohols 7 and 8, which, upon dehydration, gave a mixture of position isomeric olefins 9 and 10. Catalytic hydrogenation gave 5 and its diastereomer 6 in a 55:45 ratio (as judged by ¹³C NMR). Unfortunately the two compounds could not be separated in our hands, and the low-temperature ¹³C NMR analysis of the conformational equilibrium of 5 was carried out with the mixture. Assignment of the signals to 6 and 5 at room temperature and to the two conformations of 5 (K and L) at -100 °C has been described elsewhere;¹⁷ the equilibrium constant, obtained from the areas of the signals at -100 °C, was 0.60 ± 0.07 , corresponding to $\Delta G^\circ = 0.13 \pm 0.03$ kcal/mol. To compute the Me/Me gauche interaction from this value, it is easiest to make comparison with the equilibrium shown in Scheme IX for which $\Delta G^\circ = 1.13 \pm 0.06$ kcal/mol.⁷ K (R = C₆H₅) has one more axial methyl than M; hence, in terms of energy,

$$K = M + 1.74 \text{ kcal/mol}$$

Similarly,

$$L = N + Z$$

where Z is the desired Me/Me gauche interaction. Subtracting:

$$L - K = N - M + Z - 1.74$$

From Schemes VII and IX:

$$0.13 = 1.13 + Z - 1.74$$

whence $Z = 0.74$ kcal/mol, the desired gauche interaction. This value is identical with the highest value determined by Tichý,

(13) Regarding this point, see: St.-Jacques, M.; Bernard, M.; Vaziri, C. *Can. J. Chem.* **1970**, *48*, 2386. Toure, S.; Lapasset, J.; Boyer, B.; Lamaty, G. *Acta Crystallogr., Sect. B* **1979**, *B35*, 2790. Toure, S.; Lapasset, J.; Boyer, B.; Lamaty, G. *Ibid.* **1980**, *B36*, 2168. Anet, F. A. L.; Basus, V. J.; Hewitt, A. P. W.; Saunders, M. J. *J. Am. Chem. Soc.* **1980**, *102*, 3945.

(14) This assumption comes from the comparison of Geneste's values, which were obtained at room temperature, with ours obtained at -100 °C. See also the discussion of the NMR data.¹²

(15) Manoharan, M.; Eliel, E. L.; Carroll, F. I. *Tetrahedron Lett.* **1983**, *24*, 1855.

(16) Since this topic has already been communicated in preliminary form,¹⁷ elaboration of the arguments from the literature is relegated to the supplement material,¹² and the previously reported¹⁷ NMR data are not repeated here.

(17) Manoharan, M.; Eliel, E. L. *Tetrahedron Lett.* **1983**, *24*, 453.

(18) Eliel, E. L.; Allinger, N. L.; Angyal, S. J.; Morrison, G. A. "Conformational Analysis". Reprinted by the American Chemical Society, Washington, DC, 1981, pp 52–56.

(19) (a) Prosen, E. J.; Johnson, W. H.; Rossini, F. D. *J. Res. Natl. Bur. Stand.* **1947**, *39*, 173. (b) Kilpatrick, J. E.; Werner, H. G.; Beckett, C. W.; Pitzer, K. S.; Rossini, F. D. *J. Res. Natl. Bur. Stand.* **1947**, *39*, 523.

(20) Tichý, M.; Vasickova, S.; Arakelian, S. V.; Sicher, J. *Collect. Czech. Chem. Commun.* **1970**, *35*, 1522. Tichý, M. *Collect. Czech. Chem. Commun.* **1973**, *38*, 3631.

(21) These values, being small differences between large numbers, must be considered only approximate.

(22) Note Added in Proof: Since publication of our preliminary communication,¹⁷ Booth and Grindley (Booth, H.; Grindley, T. B. *J. Chem. Soc., Chem. Commun.* **1983**, 1013) have reported a direct determination of the *trans*-1,2-dimethylcyclohexane conformational equilibrium (Scheme VII, R = H) by using both ¹³C enriched substrate and a line-broadening technique. The former approach gave $\Delta G^\circ = 2.75$ kcal/mol, the latter 2.58 ± 0.05 kcal/mol. The corresponding values of the Me/Me gauche interaction Z are 0.73 and 0.90 kcal/mol, the former in excellent agreement with the value determined here, the latter (considered by the authors as more accurate) somewhat less so.

(23) Allinger, N. L.; Hirsch, J. A.; Miller, M. A.; Tyminski, I. J.; Van-Catledge, F. A. *J. Am. Chem. Soc.* **1968**, *90*, 1199.

Table V. ¹³C NMR Shifts of 1-Phenylcyclohexenes and Related Compounds^a

compd	C-1	C-2	C-3	C-4	C-5	C-6	Me-3	Me-4	Me-5	other				
										Me	ipso	ortho	meta	para
19 ^b	136.6 ₇	124.5 ₆	25.9 ₄	22.2 ₇	23.1 ₆	27.4 ₅					142.6 ₇	124.9 ₅	128.1 ₅	126.4 ₉
20	136.2 ₈	124.1 ₇	34.5 ₀	27.4 ₅	31.3 ₆	28.1 ₆		21.6 ₆			142.4 ₆	125.0 ₁	128.1 ₆	127.1 ₅
21 ^c	125.1 ₀	132.1 ₀	32.1 ₀	45.3 ₀	29.6 ₀	39.2 ₀	21.7 ₀		25.4 ₀					
									29.6 ₀					
13	134.8 ₁	129.0 ₇	31.9 ₄	44.4 ₆	29.9 ₅	41.2 ₂	21.6 ₆		25.2 ₅		142.3 ₉	125.0 ₇	127.9 ₂	126.3 ₈
									28.8 ₇					
22 ^c	124.1 ₀	137.5 ₀	33.0 ₀	46.6 ₀	31.3 ₀	34.3 ₀	25.9 ₀		22.4 ₀					
							29.1 ₀							
12	134.0 ₅	134.2 ₉	33.2 ₈	45.7 ₉	31.3 ₄	36.3 ₅	26.1 ₄		22.2 ₇		142.1 ₁	125.0 ₇	127.9 ₂	126.3 ₈
							29.0 ₃							
9	135.6 ₅	130.8 ₇	38.4 ₆	35.6 ₄	31.2 ₇	27.4 ₃	20.0 ₉ ^d	20.2 ₆ ^d			142.4 ₂	125.1 ₃	128.2 ₂	126.6 ₂
10	136.1 ₄	(124.0 ₁)	34.3 ₀	35.0 ₉	34.7 ₇	36.4 ₀		19.6 ₂ ^d	19.3 ₅ ^d		142.3 ₀	126.5 ₂	128.1 ₇	124.9 ₉
23	132.8 ₉	127.7 ₉	37.9 ₀	35.8 ₃	31.2 ₆	30.1 ₇	20.0 ₆ ^d	20.4 ₂ ^d		23.4 ₃				
24	133.4 ₇	120.7 ₂	34.6 ₁	35.0 ₉	34.6 ₁	39.3 ₈		19.6 ₀ ^d	19.4 ₁ ^d	23.5 ₃				

^a Shifts from Me₄Si in CDCl₃. ^b Data from ref 7. ^c Data taken from Bremser catalog.³⁰ ^d These values are interchangeable.

Sicher, et al.²⁰ and close to the value of 0.85, which can be computed from conformational energies calculated by the force-field method.²³ diaxial 1,2-dimethylcyclohexane 3.90 kcal/mol, diequatorial isomer 1.21 kcal/mol, difference 2.69 kcal/mol as against 1.77 kcal/mol (the value calculated for axial methylcyclohexane) × 2 or 3.54 kcal/mol, gauche interaction 3.54 - 2.69 or 0.85 kcal/mol. (It should be taken into account that these particular force-field calculations refer to the gas phase and that the gas-phase energy differences tend to be somewhat greater than the liquid-phase ones because the less stable conformers or isomers generally have the higher heat of vaporization.²⁴) Also, the 0.74 kcal/mol value is lower than the Me/H axial interaction in cyclohexane (0.87 kcal/mol, vide supra) and higher than the liquid-phase gauche interaction in the gauche form of butane, 0.5-0.7 kcal/mol;²⁵ this presumably reflects the ease of energy minimization by torsional deformation; greatest in butane, least in axial methylcyclohexane, intermediate in diequatorial 1,2-dimethylcyclohexane.

Details of NMR spectral assignments are given in the supplemental material.¹²

Experimental Section

Proton NMR spectra were recorded on a Varian XL-100 (100 MHz), Bruker spectrosin WM-250 (250 MHz), or Nicolet NT-360 (360 MHz), located at the NIEHS, Research Triangle Park instrument operated in pulsed Fourier transform mode and locked on solvent deuterium. Carbon-13 NMR spectra were similarly recorded on a Varian XL-100 (25.12 MHz) or Bruker Spectrosin WM-250 (62.89 MHz) instrument. Samples were prepared as 10-25% solutions with the solvents shown in the tables (in the case of carbon spectra) or mentioned below (in the case of proton spectra). All spectra at temperatures other than ambient were recorded in the Bruker instrument; temperature measurements are ± 3 K. For area measurements portions of spectra were expanded and recorded at a sweep width of 200 Hz. The individual peaks were electronically integrated and the ratio of the peaks of the integral tracings taken as peak area ratios.

Boiling points were generally determined either in a short-path column or Kugelrohr apparatus (air-bath temperature) and are uncorrected. Micro analyses were performed by M.H.W. Laboratories. Preparative GLPC was performed in a Varian Aerograph Model 2700 instrument equipped with either a 15 ft x 0.375 in. Apiezon-L (10%) on 30/60 Chromosorb-W or a 12 ft x 0.375 in. 20% DEGS on 80/100 Chromosorb P column. Mass spectra were recorded on a VG-micromass 7070F instrument.

3-Phenyl-3,5,5-trimethylcyclohexanone (3): 3-Phenyl-3,5,5-trimethylcyclohexanone was prepared from isophorone by a modification of a procedure described.^{3,12}

¹³C NMR spectrum, Table I.

1-Phenyl-1,3,3-trimethylcyclohexane (4): 3-Phenyl-3,5,5-trimethylcyclohexanone (3) (4.32 g, 0.02 mol, crude product) and KOH (5 g) were refluxed with 3.5 g of hydrazine hydrate (98%, ca. 0.07 mol) in 50 mL

of triethylene glycol for 2 h. The same amounts again of hydrazine hydrate and KOH were added, and the flask was fitted with a descending condenser and heated in an oil bath at 200 °C for 8 h. After cooling, the reaction mixture was diluted with water (100 mL) and the product extracted with ether (3 × 50 mL). The etheral extracts were combined with the distillate collected during the reaction, washed successively with 2N HCl, saturated aqueous NaHCO₃, and finally with saturated NaCl solution (each about 100 mL), and dried over anhydrous MgSO₄. Distillation of the ether followed by Kugelrohr distillation (160-170 °C (30 mm)) yielded 2.7 g (67%) of **4**, which was purified by GLPC (Apiezon-L column) at 160 °C.

¹H NMR (CDCl₃, 100 MHz) δ 0.39 (s, 3 H, 3-CH₃, cis to Ph), 0.92 (s, 3 H, 3-CH₃, trans to Ph), 1.15 (s, 3 H, 1-CH₃), 2.2-3.4 (m, 8 H), 7.15-7.4 (m, Ph); ¹³C NMR spectrum, Table I; Anal. Calcd for C₁₅H₂₂: C, 89.04; H, 10.96. Found: C, 89.27; H, 10.59.

1-Phenyl-3,3-trans-5-trimethylcyclohexane (1) was prepared according to Scheme V.

1-Phenyl-3,3-*t*,5-trimethylcyclohexan-*r*-1-ol (11). 3,3,5-Trimethylcyclohexanone (Fluka AG, 98%, 14 g, 0.1 mol) in 50 mL of absolute ether was added to 2 equiv of phenylmagnesium bromide prepared from 4.8 g of magnesium turnings and 28.4 g of bromobenzene in 200 mL of absolute ether. The resulting mixture was refluxed for 1 h and stirred overnight. Saturated ammonium chloride (100 mL) was carefully added dropwise, with external cooling. The ether layer was separated and the aqueous layer extracted with ether (3 × 50 mL). The combined etheral solution was washed with saturated sodium chloride solution (100 mL). Drying over anhydrous K₂CO₃, evaporation of ether, and distillation in a short-path column (bp 85-89 °C (0.05 mm)) yielded 17.5 g (81%) of **11**. From ¹³C NMR spectral analysis (Table IV) it was found to be mainly phenyl-3,3-*t*,5-trimethylcyclohexan-*r*-1-ol (>95%) obtained by the favored equatorial approach of the Grignard reagent to 3,3,5-trimethylcyclohexanone.

¹H NMR (CDCl₃, 360 MHz) δ 0.91 (s, 3 H, 3e-CH₃); 0.91-0.93 (d, *J* = 6.5 Hz, 3 H, 5-CH₃), 1.19 (s, 3 H, 3a-CH₃), 0.85-1.05 (m, 1 H), 1.35-1.6 (m, 5 H), 1.7-1.8 (bd, 1 H), 2.0-2.2 (symmetrical, 15 lines, 1 H, H-5), 7.16-7.24 (tt, *J*_{ortho} = 7.2, *J*_{meta} = 1.3 Hz, 1 H, phenylpara), 7.28-7.34 and 7.45-7.49 (m, 4 H, ortho and meta hydrogens); ¹³C NMR spectrum, Table IV; MS, *m/e* 218, 161, 147, 105; elemental composition calcd for C₁₅H₂₂O M⁺ 218.33, found 218.17.

1-Phenyl-3,3,5-trimethylcyclohexene (12) and 1-Phenyl-3,5,5-trimethylcyclohexene (13). To **11** (5.0 g, 0.023 mol) in a round-bottom flask was added 15 mL of 20% (v/v) H₂SO₄ in glacial acetic acid.²⁶ The alcohol dissolved instantly in the acid mixture on stirring and the olefin layer separated; stirring was continued for 10 min. The mixture was poured into 100 mL of ice-cold water and extracted with ether (3 × 25 mL). The combined etheral extract was washed successively with water, saturated aqueous NaHCO₃ solution, and saturated NaCl solution (50 mL each). The ether solution was dried over anhydrous Na₂SO₄, filtered, concentrated, and distilled (Kugelrohr, 175-185 °C (30 mm)) to yield 3.90 g (0.019 mol, 87%) of isomeric olefins **12** and **13** in ca. 2:1 ratio. While the ¹³C NMR shifts of **12** and **13** (Table V) were assigned from the spectrum of the mixture, a small quantity was separated in GLPC using Apiezon-L column at 170 °C for ¹H NMR spectroscopy; **12** emerged first followed by **13**.

12: ¹H NMR (CDCl₃, 250 MHz) δ 1.05-1.07 (d, *J* = 6.5 Hz, 3 H, 5-CH₃), 1.06 (s, 3 H, CH₃), 1.09 (s, 3 H, CH₃), 1.1-1.2 (m, 1 H),

(24) Reference 18, p 54.

(25) (a) Rosenthal, L.; Rabolt, J. F.; Hummel, J. *J. Chem. Phys.* **1982**, *76*, 817 and references therein. (b) Woller, P. B.; Garbisch, E. W., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 5310. See also: Allinger, N. L.; Profeta, S., Jr. *J. Comput. Chem.* **1980**, *1*, 181.

(26) Cf.: Garbisch, E. W., Jr. *J. Org. Chem.* **1961**, *26*, 4165.

(27) Fieser, L. F.; Szmuskovicz, J. *J. Am. Chem. Soc.* **1948**, *70*, 3352.

1.5–1.6 (m, 1 H), 1.8–2.0 (m, 2 H), 2.35–2.5 (doublet or quartet, 1 H, one of the allylic hydrogens), 5.82 (broad singlet, 1 H, olefinic), 7.2–7.4 (m, 5 H, Ph).

13: $^1\text{H NMR}$ (CDCl_3 , 250 MHz) δ 0.96 (s, 3 H, CH_3), 1.08 (s, 3 H, CH_3), 1.08–1.1 (d, $J = 7$ Hz, 3 H, 3- CH_3), 1.45–1.54 (m, 1 H), 1.54 (s, 1 H, probably one of the hydrogens at 4-position having $J_{\text{gem}} = J_{\text{vic}} \approx 0$), 2.03–2.45 (m, 3 H), 5.91 (br s, 1 H, olefinic), 7.2–7.4 (m, 5 H, Ph).

1-Phenyl-3,3,trans-5-trimethylcyclohexane (1) and Its Epimer 2: The olefinic mixture of **12** and **13** (1.0 g, 0.005 mol) was dissolved in 20 mL of 95% ethanol in a hydrogenation bottle, and 100 mg of 10% Pt on carbon was added. The mixture was shaken in a Parr Hydrogenator for 30 min with a starting pressure of 50 psi. It was then filtered through a Celite pad that was washed with 10 mL of ethanol. The solvent was rotoevaporated and the residue distilled in a Kugelrohr (150–160 °C/(30 mm)) to yield 0.82 g (81.8%) of **1** and **2** in a ratio of ca. 3:1 as shown by $^{13}\text{C NMR}$ and GC. This mixture was separated by preparative GLPC using the 20% DEGS column at 160 °C. Compound **2** (25%) emerged first followed by **1** (75%). Anal. Calcd for $\text{C}_{15}\text{H}_{22}$: C, 89.04; H, 10.96. Found: C, 89.18; H, 10.82.

1: $^1\text{H NMR}$ (CD_2Cl_2 , 360 MHz) δ 0.83 (s, 3 H, CH_3), 1.07 (s, 3 H, CH_3), 1.13–1.15 (d, $J = 7.2$ Hz, 3 H, 5- CH_3), 1.22–1.28 (m, 1 H), 1.43–1.48 (q, 1 H), 1.53–1.61 (m, 3 H), 1.81–1.89 (m, 1 H), 2.1–2.13 (m, 1 H), 2.98–3.02 (7 lines, 1 H, benzylic), 7.21–7.42 (m, 5 H, Ph); $^{13}\text{C NMR}$, Table I.

2: $^1\text{H NMR}$ (CDCl_3 , 250 MHz) 0.90–0.93 (d, $J = 6.5$ Hz, 3 H, 5- CH_3), 0.97 (s, 3 H, CH_3), 1.02 (s, 3 H, CH_3), 1.15–1.93 (series of multiplets, 7 H), 2.66–2.82 (tt, A part of AM_2X_2 spectrum, $J_{\text{aa}} = 12$, $J_{\text{ae}} = 4.6$ Hz, 1 H, benzylic), 7.14–7.35 (m, 5 H, Ph); $^{13}\text{C NMR}$, Table I.

1-Phenyl-*t*-3,c-4-dimethylcyclohexan-*r*-1-ol (7) and 1-Phenyl-*c*-3,*t*-4-dimethylcyclohexan-*r*-1-ol (8). A solution of 5 g (0.04 mol) of *trans*-3,4-dimethylcyclohexanone (Wiley Organics, 85% purity, the rest being the *cis* isomer as shown by $^{13}\text{C NMR}$ spectrum) in 20 mL of absolute ether was added to a solution of phenylmagnesium bromide prepared from magnesium turnings (1.92 g, 0.08 mol) and bromobenzene (12.56 g, 0.08 mol) in 100 mL of absolute ether. The resulting mixture was refluxed for 1 h and stirred overnight. Saturated ammonium chloride solution (50 mL) was carefully added dropwise, with external cooling. The ether layer was separated and the aqueous layer extracted with ether (3 \times 20 mL). The combined ethereal solution was washed with saturated sodium chloride solution (50 mL) and dried over anhydrous K_2CO_3 . Evaporation of ether yielded a yellow oil which was shown by $^{13}\text{C NMR}$ to be a mixture of ca. 70% of **7** and ca. 30% of **8**. The epimeric alcohol mixture was directly used in the next step without further purification.

$^1\text{H NMR}$ (CDCl_3 , 250 MHz) δ 0.86–1.00 (overlapping four sets of doublets, 2 \times 2 \times 3 H; CH_3 groups), 1.4–1.82 (m, 2 \times 6 H), 2.1–2.3 (br s, 2 \times 1 H, -OH), 2.3–2.6 (m, 2 \times 2 H), 7.2–7.6 (m, 2 \times 5 H, Ph); $^{13}\text{C NMR}$, Table IV.

1-Phenyl-*trans*-3,4-dimethylcyclohexene (9) and 1-Phenyl-*trans*-4,5-dimethylcyclohexene (10). The epimeric alcohol mixture obtained in the previous step (3 g) was mixed with 3 g of powdered KHSO_4 in a 100-mL round-bottomed flask equipped with a Kugelrohr receiver bulb and placed in the Kugelrohr apparatus. The flask was heated at 150 °C for ca. 1 h, which brings about the dehydration of the alcohol mixture, and the water droplets were collected in the receiver. Then the receiver was changed carefully and aspirator vacuum applied to distill the olefinic mixture (170–180 °C (35 mm)). The mixture thus collected was redistilled to yield 2.4 g (88%) of the desired products. $^{13}\text{C NMR}$ analysis revealed the composition of the mixture to be 45% of **9** and 55% of **10**. For spectral assignment, the mixture was separated by preparative GLPC employing Apiezon-L column at 170 °C. **9** emerged first followed by **10**.

9: $^1\text{H NMR}$ (CDCl_3 , 250 MHz) δ 1.02–1.04 and 1.08–1.1 (two doublets, $J = 6.6$ Hz, 2 \times 3 H, CH_3), 1.23–1.53 (m, 2 H), 1.82–2.00 (m, 2 H), 2.41–2.48 (m, 2 H, two of the allylic hydrogens), 5.90–5.93 (unresolved quartet, 1 H, olefinic), 7.21–7.44 (m, 5 H, Ph); $^{13}\text{C NMR}$, Table V.

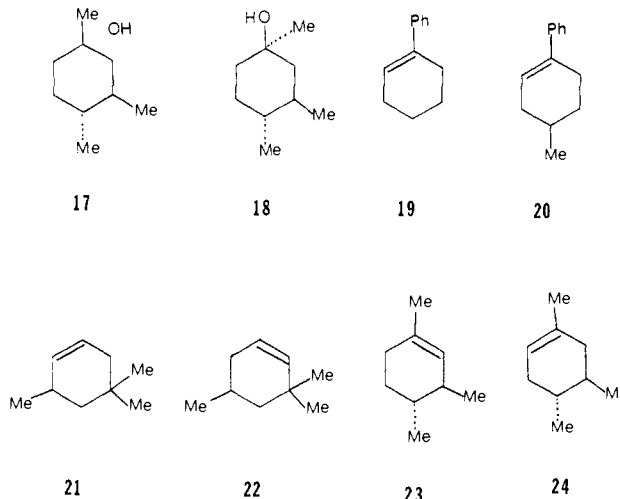
10: $^1\text{H NMR}$ (CDCl_3 , 250 MHz) δ 0.98–1.00 and 1.02–1.04 (two doublets, $J = 6.5$ Hz, 2 \times 3 H, CH_3), 1.36–1.57 (m, 2 H), 1.82–2.54 (four sets of multiplets, 4 H), 6.03–6.09 (m, 1 H, olefinic), 7.2–7.4 (m, 5 H, Ph); $^{13}\text{C NMR}$, Table V.

***r*-1-Phenyl-*t*-3,c-4-dimethylcyclohexane (5) and *r*-1-Phenyl-*c*-3,*t*-4-dimethylcyclohexane (6).** The mixture of olefins from the previous step, **9** and **10** (1.86 g, 0.01 mol), was dissolved in 50 mL of absolute ethanol in a Parr hydrogenation bottle. It was flushed with nitrogen and 200 mg of 10% Pt on carbon catalyst added. The mixture was shaken in a Parr Hydrogenator for ca. 1 h at a starting pressure of 45 psi. It was then carefully filtered through a Celite pad. The solution was rotoevaporated and the residual liquid distilled in a Kugelrohr to yield **5** and **6** as a 55:45 mixture ($^{13}\text{C NMR}$ analysis). The mixture boiled in the range 175–185

°C (50 mm) (Kugelrohr). Attempts to separate the mixture employing a variety of GLPC columns were futile. However, the mixture was purified (from the other diastereomers possible from the *cis*-3,4-dimethylcyclohexanone precursor, which was present to 15%) by preparative GLPC using the Apiezon-L column at 160 °C before the NMR measurements. Anal. Calcd for $\text{C}_{14}\text{H}_{20}$: C, 89.29; H, 10.71. Found: C, 89.49; H, 10.69.

$^1\text{H NMR}$ (CD_2Cl_2 , 360 MHz) (**5** and **6** as a 55:45 mixture) δ 0.92–0.94 (d, $J = 5.9$ Hz, 3 H, CH_3), 0.93–0.95 (d, $J = 6.0$ Hz, 3 H, CH_3), 0.97–0.99 (d, $J = 6.7$ Hz, 3 H, CH_3), 1.01–1.03 (d, $J = 6.7$ Hz, 3 H, CH_3), a series of multiplets in the regions 1.1–1.51 and 1.64–2.01; 2.5–2.6 (tt, A part of AM_2X_2 , $J_{\text{ae}} = 3.3$, $J_{\text{aa}} = 12$ Hz, 1 H, benzylic in **6**), 2.85–2.95 (7 lines, 1 H, benzylic in **5**), 7.12–7.3 (m, 2 \times 5 H, Ph); $^{13}\text{C NMR}$.¹⁷

Compounds Prepared for Comparison of $^{13}\text{C NMR}$ Spectra. In Table IV are recorded the $^{13}\text{C NMR}$ spectra of 1-phenylcyclohexanol (**14**)^{27,28} and its 4-*tert*-butyl homologues, **15** and **16**,²⁸ and the diastereomeric 1,*c*-3,*t*-4- and 1,*c*-3,*t*-4-trimethylcyclohexan-*r*-1-ols (**17** and **18**). The



latter were obtained as a solid mixture (**17**:**18** ratio 2:1) by addition of methylmagnesium iodide to *trans*-3,4-dimethylcyclohexanone, as reported above for the analogous phenyl compounds. In Table V are recorded the $^{13}\text{C NMR}$ spectra of olefins **23** and **24** obtained from the **17**–**18** mixture by KHSO_4 dehydration (bp 145–150 °C (760 mm), Kugelrohr) in the ratio of ca. 45:55. The spectra of **21** and **22** are from the literature.³⁰ Compounds **19**^{28,29} and **20**⁷ have been reported previously but the spectrum of **20** represents a correction in assignment of the olefinic, ipso, and para carbon atoms.

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Registry No. **1**, 87954-30-1; **2**, 87954-31-2; **3**, 25109-54-0; **4**, 33787-24-5; **5**, 86021-34-3; **6**, 86021-33-2; **7**, 87954-32-3; **8**, 87954-33-4; **9**, 87954-34-5; **10**, 87954-35-6; **11**, 60178-86-1; **12**, 87954-36-7; **13**, 87954-37-8; **14**, 1589-60-2; **15**, 17807-26-0; **16**, 21024-55-5; **17**, 52137-11-8; **18**, 52137-15-2; **20**, 16776-31-1; **23**, 87954-38-9; **24**, 87954-39-0; 3,3,5-trimethylcyclohexanone, 873-94-9; phenyl bromide, 108-86-1; *trans*-3,4-dimethylcyclohexanone, 28023-45-2; *trans*-1,2-dimethylcyclohexane, 6876-23-9; isophorone, 78-59-1.

Supplementary Material Available: Recalculation of the equilibrium shown in Scheme I using experimental data, calculation of the methyl/methyl gauche interaction in *trans*-1,2-dimethylcyclohexane from the literature, NMR spectral assignments, modified procedure for preparing 3-phenyl-3,5,5-trimethylcyclohexanone (**3**), and proton NMR data for **3** (11 pages). Ordering information is given on any current masthead page.

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