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

X, h	*Y*, 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*t*Pe, 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 D_2O. 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, ^{1}H NMR(CCl_4) δ 1.15 (d, ^3J = 6 Hz, 6 H, $2CH_3$), 1.25 (d, ^3J = 6 Hz, 12 H, $4CH_3$), 1.35–1.45 (m, ^3J = 4 Hz, 4 H, $2CH_2$), 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%); ^{13}C NMR ($CDCl_3$) δ 22.3, 22.5 (2 q, CH_3), 24.1 (q, CH_3), 33.6 (d, CH), 36.2, 26.6 (2 t, CH_2), 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 $C_{24}H_{34}$ (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), ^{1}H NMR (CCl_4) δ 1.15 (d, ^3J = 6 Hz, 6H, $2CH_3$), 1.25 (d, ^3J = 6 Hz, 12H, $4CH_3$), 1.35–1.55 (m, ^3J = 4 Hz, 4H, $2CH_2$), 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 $C_{24}H_{34}$ (322.5): C, 89.4; H 10.6. Found: C, 89.0; H, 10.8.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft, the SERC, and the Fonds der Chemischen Industrie. ESR experiments were performed during a visit to UCL financed by the British Council. We thank G. W. Spitznagel for computational assistance and the staff of the Regionales Rechenzentrum Erlangen for their cooperation.

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; KOtPe, 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[†]

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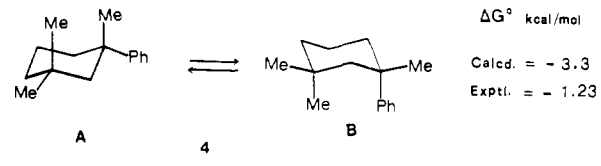
Contribution from the W. R. Kenan, Jr., Laboratories, Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514. *Received April 18, 1983. Revised Manuscript Received September 13, 1983*

Abstract: Examination of the conformational equilibria of 1-phenyl-3,3,*t*-5-trimethylcyclohexane and 1-phenyl-1,3,3-trimethylcyclohexane by low-temperature ^{13}C 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,*c*-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 tabulated[2] 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 I

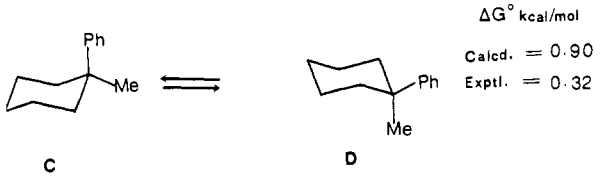


α-fluoro-3-phenyl-3,5,5-trimethylcyclohexanones,[3] which yields a difference of 0.9 kcal/mol. Taking the value of the methyl/

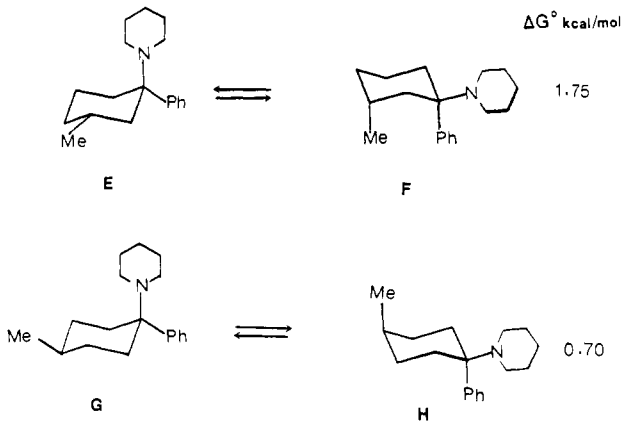
[†] Dedicated to Professor Günther O. Schenck in honor of his 70th birthday.

0002-7863/84/1506-0367$01.50/0

Scheme II



Scheme III

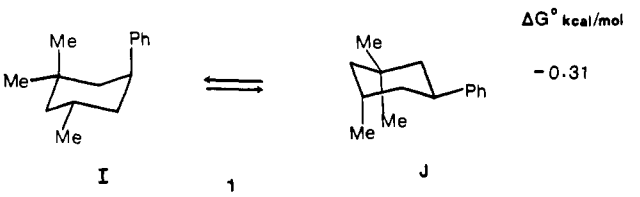


methyl syn-axial interaction as 3.7 kcal/mol as determined experimentally,[4] the phenyl/methyl interaction is computed to be 3.7 − 0.9 = 2.8 kcal/mol.[5] This value must be considered only approximate since the NMR method used was not precise[3] and, in any case, refers to a substituted cyclohexanone rather than cyclohexane.

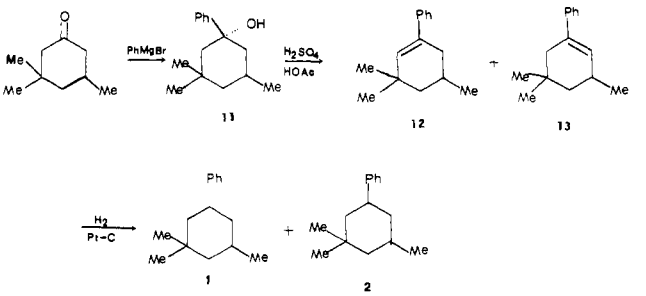
An alternative way of evaluating the Ph/Me interaction is based on a force-field calculation[6] of the equilibrium depicted in Scheme I; this calculation suggests that $-\Delta G^\circ$ = 3.2–3.3 kcal/mol. To obtain the Ph/Me interaction (X) from this number, one must also know the Ph/H interaction ($^1/_2 \times 2.87$ = 1.43 kcal/mol[7]), the Me/H interaction ($^1/_2 \times 1.74$ = 0.87 kcal/mol[8]), 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 ΔG° = 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 phencyclidine equilibria shown in Scheme III, 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: (Ph/H + Me/H + Ph/Me) − (2 Ph/H + 2 Me/H) = 1.05, or Ph/Me = 1.05 + Ph/H + Me/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.

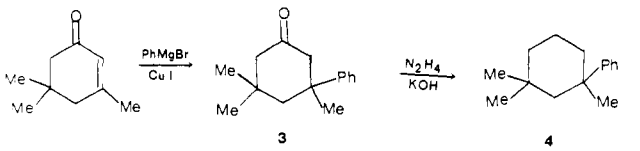
Scheme IV



Scheme V



Scheme VI



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 ^{13}C 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 ΔG° = −0.31 ± 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/mol[4]), 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.; Chrysam, 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 calculated[4] and experimental[7] 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. ^{13}C 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_2Cl_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_6	32.5_5	31.8_5	22.0_2	147.5_2	127.2_5	128.4_2	125.6_8
1 I	−100 °C, CD_2Cl_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 I	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	*f*	*f*	*f*	*f*
1 J	−100 °C, CD_2Cl_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, $C_6D_5CD_3$	35.8_5	46.4_0	31.4_8	45.8_9	27.3_0	38.9_2	30.3_6	32.3_9	22.0_6	147.4_8	127.3_2	128.5_2	125.8_6
1	+100 °C, $C_6D_5CD_3$	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, $C_6D_5CD_3$	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_7^i	28.4_8^i	34.8_8^h	147.8_8	125.8_6	128.2_6	125.9_5
3	RT, $C_6D_5CD_3$	208.5_6	51.0_8	42.3_4	51.4_2	35.7_0	54.1_7	32.8_8^i	28.3_6^i	34.8_2^h	148.2_5	126.1_2	128.3_7	126.0_1
3	−80 °C, $C_6D_5CD_3$	210.0_1	50.4_0	42.2_4	50.4_0	36.0_0	53.7_5	33.1_5^i	27.3_7^i	35.3_9^h	147.7_0	128.0_1^j	128.8_3^j	125.1_4
												126.2_1^j	128.0_1^j	
3	+100 °C, $C_6D_5CD_3$	208.0_2	51.4_2	42.3_4	51.8_6	35.4_7	54.3_2	32.6_9^i	29.26^i	34.3_6^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_2Cl_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_2	125.2_7
4 B	−100 °C, CD_2Cl_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
												125.1_1^g	128.0_7^j	
4 A	−100 °C, CD_2Cl_2	38.8_0	49.6_0	*l*	*l*	*l*	*l*	$(27.4_0)^d$	*l*	$(27.8_0)^{d,k}$	*l*	*l*	*l*	*l*
4	RT, $C_6D_5CD_3$	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, $C_6D_5CD_3$	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]

	relative areas		
carbon	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]

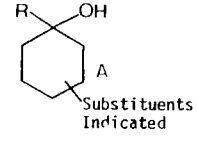
	relative areas		
carbon	B	A	*K*
Me-1	520	15	34.67
Me-3e	544	15	36.27
			av 35.5 ± 1.1[a]

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

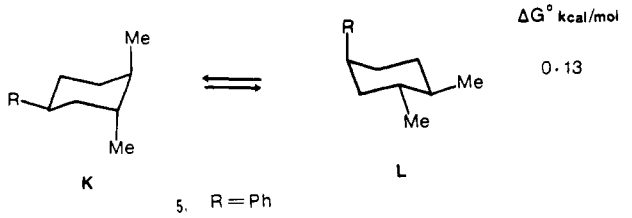
Table IV. ^{13}C NMR Shifts of Phenylcyclohexan-*r*-1-ols and Related Compounds (A)[a]

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	*c*-4-*t*-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	*t*-4-*t*-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-*t*-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	*t*-3,*c*-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	*c*-3,*t*-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	*t*-3,*c*-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	*c*-3,*t*-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 Me_4Si in $CDCl_3$. [b] Data taken from ref 28. [c] CH_3 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] $C(CH_3)_3$ signal. [f] CH_3 group cis to OH. [g] CH_3 group trans to OH. [h] 1-CH_3 signal.



Scheme VII

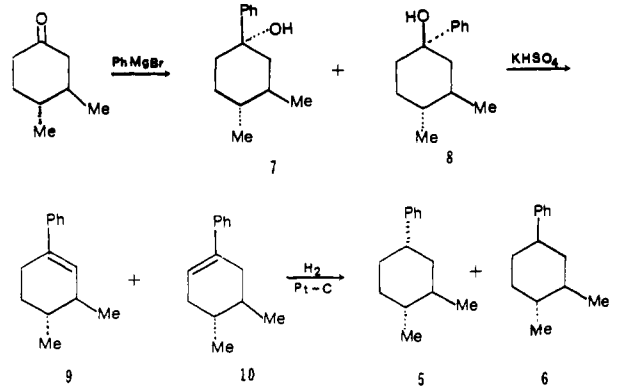


greatly from the calculated one[6] of 3.3 kcal/mol and suggests that the equilibrium shown in Scheme I should be accessible experimentally by low-temperature ^{13}C NMR spectroscopy. We therefore synthesized compound **4** (Scheme I) in two steps from isophorone as shown in Scheme VI and recorded its ^{13}C spectrum at room temperature and −100 °C as shown in Table I (bottom). The area ratios, shown in Table III, indicate $K = 35.5 \pm 1.1$ and $\Delta G° = -1.23 \pm 0.01$ 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), andd 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 phencyclidine 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 phencyclidines some of which have been confirmed by ^{13}C NMR measurements.[15] Thus the consistency of the data also supports the experimentally determined[4] value of 3.7 kcal/mol for the Me/Me syn-axial interaction.

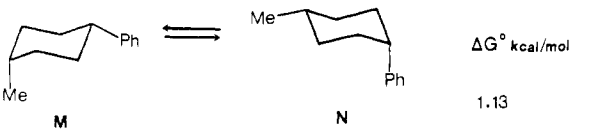
The Methyl/Methyl Gauche Interaction in *trans*-1,2-Dimethylcyclohexane[16]

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-dimethylcyclohexanes[19] 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/mol[19] in the vapor phase,[21] 1.0–1.1 kcal/mol[19] 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 $\Delta G°$ 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 energy[7] 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 ^{13}C NMR). Unfortunately the two compounds could not be separated in our hands, and the low-temperature ^{13}C 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 $\Delta G° = 0.13 \pm 0.03$ 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 $\Delta G° = 1.13 \pm 0.06$ kcal/mol.[7] K (R = C_6H_5) 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.; Hewett, A. P. W.; Saunders, M. *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 reported[17] 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 ^{13}C enriched substrate and a line-broadening technique. The former approach gave $\Delta G° = 2.75$ 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.; VanCatledge, F. A. *J. Am. Chem. Soc.* **1968**, *90*, 1199.

Table V. ^{13}C 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 28.8_7		142.3_9	125.0_7	127.9_2	126.3_8
22[c]	124.1_0	137.5_0	33.0_0	46.6_0	31.3_0	34.3_0	25.9_0 29.1_0		22.4_0					
12	134.0_5	134.2_9	33.2_8	45.7_9	31.3_4	36.3_5	26.1_4 29.0_3		22.2_7		142.1_1	125.0_7	127.9_2	126.3_8
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 Me_4Si in $CDCl_3$. [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 spectrospin 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 Spectrospin 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]

^{13}C 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 $NaHCO_3$, and finally with saturated NaCl solution (each about 100 mL), and dried over anhydrous $MgSO_4$. 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 ($CDCl_3$, 100 MHz) δ 0.39 (s, 3 H, 3-CH_3, cis to Ph), 0.92 (s, 3 H, 3-CH_3, trans to pH), 1.15 (s, 3 H, 1-CH_3), 2.2–3.4 (m, 8 H), 7.15–7.4 (m, Ph); ^{13}C NMR spectrum, Table I; Anal. Calcd for $C_{15}H_{22}$: 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 K_2CO_3, 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 ^{13}C 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 ($CDCl_3$, 360 MHz) δ 0.91 (s, 3 H, 3e-CH_3); 0.91–0.93 (d, J = 6.5 Hz, 3 H, 5-CH_3), 1.19 (s, 3 H, 3a-CH_3), 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); ^{13}C NMR spectrum, Table IV; MS, *m/e* 218, 161, 147, 105; elemental composition calcd for $C_{15}H_{22}O$ 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) H_2SO_4 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 $NaHCO_3$ solution, and saturated NaCl solution (50 mL each). The ether solution was dried over anhydrous Na_2SO_4, 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 ^{13}C 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 ($CDCl_3$, 250 MHz) δ 1.05–1.07 (d, J = 6.5 Hz, 3 H, 5-CH_3), 1.06 (s, 3 H, CH_3), 1.09 (s, 3 H, CH_3), 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.; Szmuszkovicz, 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}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 $J_{gem} = J_{vic} \approx 0$), 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}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 $C_{15}H_{22}$: C, 89.04; H, 10.96. Found: C, 89.18; H, 10.82.

1: ^{1}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}C NMR, Table I.

2: ^{1}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_{aa} = 12, J_{ae} = 4.6 Hz, 1 H, benzylic), 7.14–7.35 (m, 5 H, Ph); ^{13}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}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 × 20 mL). The combined etheral 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}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}H NMR ($CDCl_3$, 250 MHz) δ 0.86–1.00 (overlapping four sets of doublets, 2 × 2 × 3 H; CH_3 groups), 1.4–1.82 (m, 2 × 6 H), 2.1–2.3 (br s, 2 × 1 H, -OH), 2.3–2.6 (m, 2 × 2 H), 7.2–7.6 (m, 2 × 5 H, Ph); ^{13}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 $KHSO_4$[7] 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}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**.

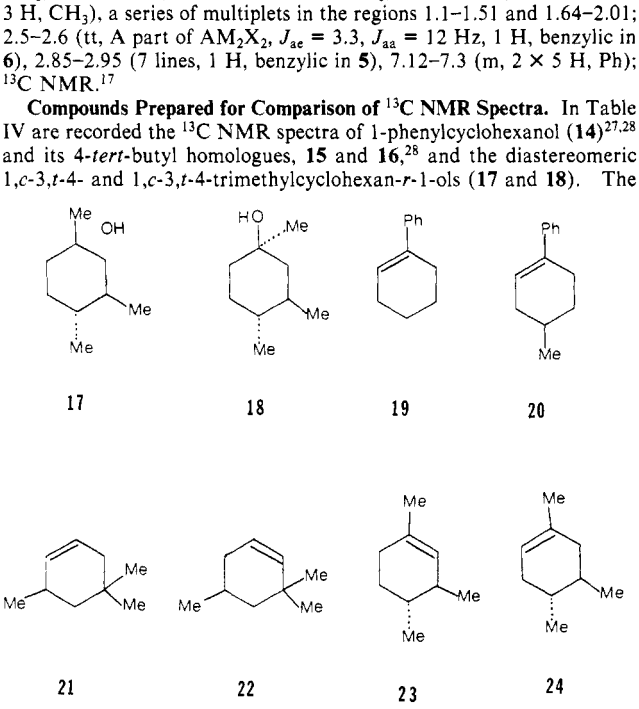
9: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.02–1.04 and 1.08–1.1 (two doublets, J = 6.6 Hz, 2 × 3 H, CH_3), 1.23–1.53 (m, 2 H), 1.82–2.00 (m, 2 H), 2.41–2.48 (m, 2 H, two of the allylic hydrogens), 5.90–5.93 (unresolved quartet, 1 H, olefinic), 7.21–7.44 (m, 5 H, Ph); ^{13}C NMR, Table V.

10: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 0.98–1.00 and 1.02–1.04 (two doublets, J = 6.5 Hz, 2 × 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}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}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 $C_{14}H_{20}$: C, 89.29; H, 10.71. Found: C, 89.49; H, 10.69.

^{1}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_{ae} = 3.3, J_{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 × 5 H, Ph); ^{13}C NMR.[17]

Compounds Prepared for Comparison of ^{13}C NMR Spectra. In Table IV are recorded the ^{13}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}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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