Service (GM 12832), and from National Science Foundation (CHE77-24701A). We also acknowledge the aid of Dr. Joe Murphy in carrying out some early experiments and of Dr. T. C. Hofelich for considerable consultative aid in the later stages of this work.

Registry No. 2,4-Dimethoxybromobenzene, 17715-69-4; 2-methyl-4-methoxybromobenzene, 27060-75-9; tris(2,4-dimethoxyphenyl)methyl alcohol, 76832-37-6; tris(2-methyl-4-methoxyphenyl)methyl alcohol, 76832-38-7; (*o*,*p*-di-MeO)$_3$trityl cation, 14426-26-7; (*o*-Me,*p*-MeO)$_3$trityl cation, 76832-39-8.

Conformational Analysis. 40. Conformation of 1-Methyl-1-phenylcyclohexane and the Conformational Energies of the Phenyl and Vinyl Groups[1]

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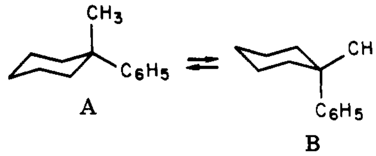
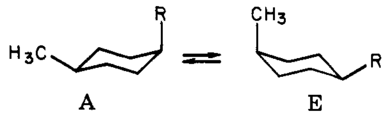
In 1971 Allinger and Tribble[2] calculated, using a force-field approach, that in 1-methyl-1-phenylcyclohexane (1, Scheme I) the conformational energies[3] of methyl (1.7 kcal/mol) and phenyl (3.0 kcal/mol) should not be additive, the conformation with the larger phenyl group in the axial position being preferred at equilibrium by 0.9 kcal/mol. This comes about because the most stable conformation of the axial phenyl group (phenyl perpendicular to the bisector plane of the cyclohexane chair) is not perturbed by introduction of a geminal methyl substituent, whereas considerable perturbation occurs upon introduction of geminal methyl into equatorial phenylcyclohexane whose phenyl substituent is (in the absence of the geminal methyl) most stable in the bisector plane of the cyclohexane chair. The Allinger–Tribble prediction was in qualitative agreement with contemporary NMR data[4] but was not quantitatively borne out by low-temperature proton NMR work subsequently carried out with 1-methyl-1-phenyl-4,4-dimethoxycyclohexane.[5] This work[5] indicated a preference for the axial phenyl group of only 0.34 kcal/mol. However, the experimenters stated:[5] "Whether this discrepancy is due to the presence of the *gem*-dimethoxy group or to some computational insufficiency remains a moot point".

In view of the importance of the prevalence of axial phenyl over geminal methylene in a number of alkaloids of the mesembrine[6] and amarillidacea[7] families, which we are presently investigating, we felt that confirmation of the result of Anteunis' group[5] by low-temperature ^{13}C NMR spectroscopy was desirable. At the same time we decided to reinvestigate the conformational energy of the phenyl group itself, since three discrepant values, 2.0,[8] 2.6,[9] and 3.0 kcal/mol,[10] were in the literature. Although the last $-\Delta G°$ value is the now generally accepted one,[3] it is the composite (at 25 °C) of a rather larger $-\Delta H°$ of 3.61 kcal/mol and an unexpectedly large $-\Delta S°$ of 2.09 gibbs that is not anticipated by the force-field calculations which predict uniquely stable conformations for both equatorial and axial phenylcyclohexane.[2]

Scheme I



Scheme II



2, R = C_6H_5
3, R = $CH{=}CH_2$

Finally we have investigated the conformational energy of the vinyl ($CH_2{=}CH$—) group which could previously be obtained,[5,11] only by assuming the very additivity of $\Delta G°$ values in geminally substituted compounds which is absent in the 1-phenyl-1-methyl case; the two values so computed were 1.5 kcal/mol[5] and 1.4 kcal/mol.[11]

Results

The room-temperature ^{13}C NMR spectral data of 1 is given in Table I (entry 1) as are the low-temperature spectral data of conformers A and B (Scheme I) at −100 °C (entries 2, 3). The two conformational isomers are present in quite unequal amounts and the configurational assignment can be readily made from the upfield shift of the methyl in conformer A and the ipso carbon of the phenyl in B. Measurement of relative areas of various peaks[12] (Table II) gives a K of 2.53 ± 0.33 and $-\Delta G°$ of 0.32 ± 0.04 kcal/mol, favoring conformer B. This result is in excellent quantitative agreement with that of Anteunis' group,[5] whose equilibrium measurement was evidently not perturbed by the presence of the dimethyl ketal function at C(4). The force-field calculations[2] are thus only qualitatively correct in that they overestimate the axial preference of phenyl by nearly 0.6 kcal/mol.

The conformational equilibria in phenyl- and vinylcyclohexanes are too one-sided to be measured directly. We therefore turned to a technique previously used by one of us[13] as well as Booth,[14] involving determination of the conformational equilibrium in a *cis*-4-methylcyclohexyl-R instead of in cyclohexyl-R itself (cf. Scheme II). The technique is particularly attractive since additivity in such 1,4-disubstituted systems does seem to obtain in the cases where it has been tested[13,14] and since a very accurate determination of the conformational energy of the methyl group used as counterpoise—1.74 ± 0.06 kcal/mol—is now available.[15]

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Table I. ^{13}C NMR Signals of Compounds 1-3 and Related Structures[a]

entry	compound	C(1)	C(2,6)	C(3,5)	C(4)[b]	CH_3	C(α)[c]	C(β)[c]	others
1	**1**	38.1_4	38.3_3	23.0_2	26.8_1	31.0_9	149.7_6	126.0_0	128.4_5 meta, 125.4_5 para
2	**1A**[d]	36.7_6	37.3_9	22.3_6	26.1_6	24.0_2	152.7_9	125.3_7	128.1_6 meta, 125.6_5 para
3	**1B**[d]	38.7_0	37.1_9	22.6_5	26.4_3	36.0_2	147.2_1	126.5_2	128.6_5 meta, 125.3_0 para
4	**2**	44.0_2	28.8_9	32.2_4	27.8_7	18.2_3	147.9_9	127.1_4	128.4_5 meta, 125.8_7 para
5	**2E**[d]	45.0_1	28.4_5	31.9_7	26.7_3	17.6_0	148.5_4	127.1_9[e]	128.6_3 meta, 126.2_0 para
6	**2A**[d]	35.4_0	30.0_0	30.5_0	33.6_0	23.4_0	*f*	*f*	*f*
7	**3**	39.3_2	29.1_5	31.2_1	30.6_1	20.5_0	143.8_8	112.7_3	
8	**3**[g]	39.0_6	29.0_2	31.0_5	30.4_7	20.4_9	143.4_1	112.7_4	
9	**3E**[d]	42.6_0	26.3_6	31.2_8	26.8_1	17.3_7	145.2_8	111.6_9	
10	**3A**[d]	36.1_4	(30.3_3)[e]	(30.1_1)[e]	33.2_2	23.2_8	142.3_7	113.8_7	
11	**4**[g]	41.8_0	32.7_8	26.1_9	26.4_0		144.7_7	111.6_4	
12	**5**[g]	44.8_1	34.6_4	27.0_9	26.3_5		147.9_7	126.8_3	128.3_2 meta, 125.8_4 para
13	**6**	44.6_3	34.7_9	36.0_1	32.8_0	22.8_4	148.3_2	127.1_7	128.5_6 meta, 126.0_6 para
14	**7** (trans)[g,h]	48.0_6	27.4_9	36.0_2	32.9_6	22.7_3	32.4_2	27.6_6	
15	**8** (cis)[g,h]	48.8_4	21.4_1	32.6_2	27.5_3	17.5_2	32.6_2	27.5_7	
16	**9** (trans)[g,i]	44.6_1	34.8_2	27.7_4	47.8_1		147.8_0	126.8_1	128.2_6 meta, 125.7_8 para, CMe_3 32.46, CMe_3 27.62
17	**10** (cis)[g,i]	36.4_4	30.7_8	22.8_0	48.2_2		145.2_6	127.7_0	128.0_7 meta, 125.1_4 para, CMe_3 32.60, CMe_3 27.56

[a] Shifts in parts per million from Me_4Si in CD_2Cl_2 unless otherwise indicated. [b] In the 1,4-disubstituted compounds, C(4) is the carbon bearing the methyl substituent except in **9** and **10** where it is the carbon bearing the *tert*-butyl group. [c] In aryl compounds C(α) is C(ipso) and C(β) is C(ortho). [d] At −100 °C. [e] These assignments may have to be interchanged. [f] Not ascertained. [g] In $CDCl_3$. [h] From ref 18. [i] From ref 19.

Table II. Low-Temperature Spectral Data of Compound 1

carbon	rel area B	rel area A	*K*	$-\Delta G°$, cal/mol
C-α (C ipso)	30	10	3.0	378
C-meta	90	39	2.31	288
C-1	33.5	13.5	2.48	313
C-3	67	31	2.16	265
Me	38	14	2.71	343
average			2.53 ± 0.33	317 ± 44

Table III. Low-Temperature Spectral Data of Compound 2

carbon	rel area E	rel area A	*K*	$-\Delta G°$, kcal/mol
CH_3	470	18	26.1	1.12
C(1)	490	24	20.4	1.04
C(2)	990	35	28.3	1.15
C(3)	940	29	32.4	1.20
C(4)	450	17	26.5	1.13
average			26.7 ± 4.3	1.13 ± 0.06

Table IV. Low-Temperature Spectral Data of Compound 3

carbon	rel area[a] E	rel area[a] A	*K*	$\Delta G°$, cal/mol
CH_3	55	69	0.80	78.0
C(1)	52	61	0.85	54.9
C(4)	40	46	0.87	48.1
C(α)	63	75	0.84	60.0
C(β)	73	82	0.89	40.0
C(2) + C(3)[b]	78	95	0.82	67.9
average			0.85 ± 0.04	58 ± 14

[a] Integrations of different peaks were not necessarily carried out with the same expanded spectrum, so areas, say of the E peaks of different carbons, are not comparable. [b] Combined area of C(2) and C(3); the peaks in the A isomer overlapped and were integrated together; corresponding peak areas in the E isomer were added.

The room-temperature ^{13}C shifts of *cis*-4-methyl-1-phenylcyclohexane (**2**, Scheme II) are listed in Table I, entry 4, and the low-temperature shifts of the two conformers **2E** and **2A** in entries 5 and 6. Corresponding shifts are shown for *cis*-4-methyl-1-vinylcyclohexane (**3**, Scheme II) at room temperature (entry 7) and at −100 °C (**3E**, **3A**, entries 9, 10). The spectral data of vinylcyclohexane, **4** (entry 11),[16] phenylcyclohexane, **5** (entry 12),[17] *trans*-4-methyl-1-phenylcyclohexane, **6** (entry 13), *trans*- (**7**) and *cis*- (**8**) 4-*tert*-butylmethylcyclohexane[18] (entries 14, 15), and *trans*- (**9**) and *cis*- (**10**) 4-*tert*-butyl-1-phenylcyclohexane[19] (entries 16, 17) are displayed for comparison. In all cases the signal assignments can be made easily by appropriate correlation and the equilibrium constants are readily obtained by measurement of signal intensities at low temperature. In this way, the equilibrium constant for **2** is found to be 26.7 ± 4.3 (Table III) corresponding to $-\Delta G° = 1.13 \pm 0.06$, favoring equatorial phenyl; with the above-given value for $-\Delta G°_{Me}$ and assuming additivity this implies $-\Delta G°_{Ph} = 2.87 \pm 0.09$ kcal/mol. This value is in between the 2.6[9] and 3.0[10] values given earlier with which it thus appears to be in good agreement. However, if the value in ref 10 is recalculated from 25 to −100 °C, it becomes 3.25 kcal/mol and agreement is less good. This suggests that the large calculated entropy difference in ref 10 (vide supra) is probably in error and that the experimental $-\Delta G°$ value measured at 39 °C of 2.94 kcal/mol[10] is probably close to $-\Delta H°$ with $\Delta S°$ near zero, as expected from first principles.

In the case of **3**, *K* is 0.85 ± 0.04 and $\Delta G°$ is 0.058 ± 0.014 (Table IV) favoring axial vinyl whence, assuming additivity, $-\Delta G°_{vinyl}$ is 1.68 ± 0.06 kcal/mol, only very slightly smaller than the value for methyl. This is in agreement with the observation (Table I, entries 9, 10) that the room-temperature spectrum of **3** (entry 7) corresponds to a nearly 1:1 average of the low-temperature spectra of the two conformers (entries 9, 10). The difference of the conformational energies of geminal methyl and vinyl reported earlier[5] of 0.20 kcal/mol thus suggests slight gem-

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Table V. ^{13}C NMR Spectral Data of Compounds 11–13 and Their Analogues[a]

compd	C(1)	C(2,6)	C(3,5)	C(4)	Me	C(α)[c]	C(β)	NMe$_2$
$C_6H_{11}CH_2COOH$	34.9_4	33.2_7	26.3_0	26.4_2		179.7_3	42.1_8	
11[b]	32.2_8	28.8_0	30.6_9	30.1_1	20.2_8	180.2_3	39.2_2	
trans isomer of **11**[b]	34.5_7	33.0_6	35.0_3	32.5_0	22.6_0	179.7_1	42.0_2	
$C_6H_{11}CH_2CH_2OH$	34.4_4	33.5_1	26.3_8	26.6_9		60.7_6	40.4_3	
12[b]	31.7_7	29.0_0	30.8_9	30.3_7	20.3_8	60.7_5	37.0_6	
trans isomer of **12**[b]	34.1_7	33.4_5	35.3_5	32.8_7	22.7_3	60.3_9	40.2_6	
$C_6H_{11}CH_2CH_2NMe_2$	(35.5_0)[d]	33.6_1	26.4_3	26.7_6		57.6_9	(36.0_3)[d]	45.5_5
13[b]	33.5_1	29.1_3	30.9_4	30.4_2	20.4_0	58.3_2	32.2_1	45.5_9

[a] In parts per million from Me$_4$Si in CDCl$_3$. [b] Peak assignments were made by analogy with *cis*- and *trans*-1,4-dimethylcyclohexane and methylcyclohexane, assignments of monosubstituted compounds and correlation among the series of 1,4-disubstituted species, and, in some instances, from SFORD spectra. [c] Carbon attached to the heteroatom. [d] These assignments may have to be interchanged.

inal nonadditivity with some extra favoring of axial vinyl; an even greater geminal nonadditivity in the case of vinyl and hydroxyl vitiates the previously obtained conformational energy of vinyl reported as 1.39 kcal/mol.[11]

Of spectral interest is the relatively small downfield shift of C(2) of the ring in vinylcyclohexanes, amounting to ca. 3 ppm for axial vinyl and 5 ppm for equatorial (the corresponding values for methyl are[18] 5.5 and 8.9 ppm). Evidently there is an offsetting γ upfield shift due to the terminal methylene of the vinyl. This suggests a substantial population of the conformations of the vinyl group (both equatorial and axial) in which the double bond is eclipsed or nearly eclipsed with the C(1)–C(2) or C(1)–C(6) bond rather than the C(1)–H bond,[20] a finding in accordance with a recent study of proton coupling constants in vinylcyclohexane.[21] It is interesting that the (upfield shifting) γ_a effect of the axial vinyl group is nevertheless in the "normal" ~6-ppm region, based on the observed chemical shift of C(3) in **3A** (Table I, entry 10) and a chemical shift of C(3) of 36.0 ppm in equatorial methylcyclohexanes (cf. entries 13 and 14, Table I). Quite analogous results are seen in the axial phenyl compound **2** where the net β_a effect again is reduced to ca. 3 ppm even though the γ_a effect (ca. 6 ppm) is unexceptional. However, the β_e effect in the equatorial phenyl compounds **5** and **6**—of the order of 7.5 ppm—is more nearly normal, presumably because in the major (bisecting) conformation there is no γ effect of the ortho carbon atoms on C(2,6).

In the proton spectrum of **3**, the upfield position of two ring protons (at 1.21–1.41 ppm) is of note. The absence of a corresponding shift in **4** or any of the other compounds here investigated suggests that the upfield protons are H(3) (axial) and H(5) (axial) in the predominating C/C-eclipsed conformation with an axial vinyl group (**3A**, Scheme II), which evidently shields these protons.

Experimental Section

Proton and ^{13}C spectra were recorded on a Varian XL-100 pulsed Fourier transform NMR spectrometer in the FT mode at 100 and 25.16 MHz, respectively. The proton spectrum of **3** was recorded on a Bruker spectrospin WM-250 FT instrument at 250 MHz. Samples were prepared as 10–15% solutions in CD$_2$Cl$_2$ or CDCl$_3$ (solvent and lock substance) with 2–5% Me$_4$Si as internal reference in 5-mm o.d. tubes. Analytical gas–liquid partition chromatography was carried out with a Hewlett-Packard 5750 instrument equipped with 12 ft × 0.125 in. columns and flame-ionization detector. Preparative GLC was performed in a Varian Aerograph Model 2700 equipped with 12 ft × 0.375 in. columns.

1-Methyl-1-phenylcyclohexane (1). 4-Methyl-4-phenylcyclohexanone was prepared according to the procedure reported by Wellman.[22] ^{1}H NMR (CDCl$_3$) δ 1.16 (s, 3 H, Me), 1.6–2.55 (m, 8 H, ring), 7.1–7.4 (m, 5 H, Ph); ^{13}C NMR (CDCl$_3$) δ 37.76 (C-4) 38.35 (C-2 and C-6), 37.29 (C-3 and C-5), 211.15 (C-1), 31.09 (Me), 146.07 (Ph, ipso), 125.64 (ortho), 128.84 (meta), 126.21 (para).

4-Methyl-4-phenylcyclohexanone (6.3 g, 0.033 mol), 5.0 g of hydrazine hydrate (98%; 0.1 mol), and 7.5 g of KOH were boiled under reflux for 2 h. the same amounts again of hydrazine hydrate and KOH were added, the flask was fitted with a descending condenser, and water was distilled off slowly until the temperature of the reaction mixture reached 195 °C and was maintained until nitrogn evolution ceased (about 6 h). After cooling the reaction mixture was diluted with water and the product extracted with ether. The ethereal extracts were combined with the product that distilled during the reduction, washed successively with dilute HCl, sodium bicarbonate solution, and sodium chloride solution, and dried over anhydrous MgSO$_4$. Evaporation of ether followed by Kugelrohr distillation [65–70 °C (0.5 mm)] gave 4.89 g (86%) of 1-methyl-1-phenylcyclohexane [lit.[23] bp 103 °C (9.5 mm)]: ^{1}H NMR (CDCl$_3$) δ 1.19 (s, 3 H, Me), 1.25–2.2 (m, 10 H, ring), 7.15–7.45 (m, 5 H, Ph).

***cis*- and *trans*-4-Methyl-1-phenylcyclohexanes (2 and 6).** A mixture of *cis*- and *trans*-4-methyl-1-phenylcyclohexanols[10] (5 g) was heated with 5 g of powdered KHSO$_4$ at 120–130 °C.[24] 4-Methyl-1-phenylcyclohexene thus formed was extracted with ether and dried over anhydrous magnesium sulfate. Evaporation of solvent and Kugelrohr distillation [95–100 °C (2 mm)] gave 4.25 g (94%) of the olefin [lit.[23] bp 86–88 °C (0.8 mm)]: ^{1}H NMR (CDCl$_3$) δ 0.98–1.05 (d, 3 H, Me, J = 5.5 Hz), 1.2–2.0 (m, 4 H, ring), 2.05–2.59 (m, 3 H, ring), 6.00–6.15 (m, 1 H, olefinic), 7.1–7.5 (m, 5 H, Ph); ^{13}C NMR (CDCl$_3$) δ 142.46 (C-1), 136.28 (C-2), 127.15 (Ph, ipso), 125.01 (ortho), 128.16 (meta), 124.17 (para), 34.50 (C-3), 27.45 (C-4), 31.36 (C-5), 28.16 (C-6), 21.66 (Me).

Hydrogenation of 3.06 g (0.018 mol) of 4-methyl-1-phenylcyclohexene in 25 mL of absolute ethanol with 200 mg of 5% Pt on carbon catalyst at 40 psi pressure in a Parr hydrogenator was completed in about 10 min. The mixture was filtered through a Celite pad and the solvent evaporated. Kugelrohr distillation of the residue [90–95 °C (2 mm)] gave 2.6 g (84%) of *cis*- and *trans*-1-methyl-4-phenylcyclohexanes. The mixture was separated by preparative GLC on a 20% DEGS on 80/100 Chromosorb P column at 150 °C. The trans isomer (45%) emerged first followed by the cis (55%). The compounds were previously reported[10] to have NMR peaks at δ 1.01 and 2.49 for the cis and at 0.92 and 2.38 ppm for the trans isomer: ^{1}H NMR (CD$_2$Cl$_2$) (cis isomer, **2**) δ 0.96–1.1 (d, J = 7 Hz, 3 H, Me), 1.4–1.98 (m, 9 H, ring), 2.3–2.7 (m, 1 H, benzylic), 7.1–7.4 (m, 5 H, Ph); ^{1}H NMR (CD$_2$Cl$_2$) (trans isomer, **6**) δ 0.9–0.98 (d, J = 4 Hz, 3 H, Me), 1.04–1.98 (m, 9 H,

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[20] This in contrast to the situation in 1-butene where the conformation in which =CH$_2$ eclipses H rather than Me is preferred. However, this difference rests largely on entropy (there are two =CH$_2$/H eclipsed conformations and only one =CH$_2$/CH$_3$ eclipsed one) and the effect of entropy is reversed in vinylcyclohexane where there are two =CH$_2$/CH$_2$ eclipsed but only one =CH$_2$/H eclipsed conformation. Cf.: Bothner-By, A. A.; Naar-Colin, C.; Günther, H. *J. Am. Chem. Soc.* **1962**, *84*, 2748; Karabatsos, G. J.; Taller, R. A. *Tetrahedron* **1968**, *24*, 3923; Kondo, S.; Hirota, E; Morino, Y. *J. Mol. Spectrosc.* **1968**, *28*, 471; Woller, P. B.; Garbisch, E. J., Jr. *J. Org. Chem.* **1972**, *37*, 4281; Durig, J. R.; Compton, D. A. C. *J. Phys. Chem.* **1980**, *84*, 773. See also: Rummens, F. H. A.; Simon, C.; Coupry, C.; Lumbroso-Bader, N. *Org. Magn. Reson.* **1980**, *13*, 33.

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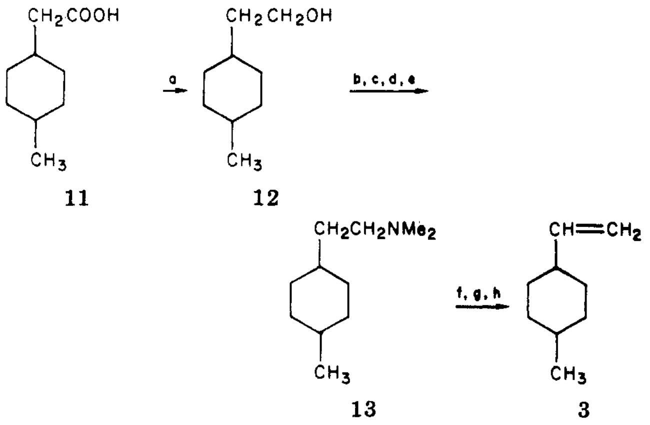
Scheme III[a]



[a] a, $LiAlH_4$/ether; b, TsCl/Py; c, NaN_3/Me_2SO-water; d, $LiAlH_4$-ether; e, HCHO-HCOOH; f, MeI/MeOH; g, Ag_2O; h, pyrolysis.

ring), 2.26–2.60 (m, 1 H, benzylic), 7.1–7.4 (m, 5 H, Ph).

***cis*-4-Methyl-1-vinylcyclohexane (3)** was prepared according to Scheme III. *cis*-4-Methylcyclohexylacetic acid (**11**) was prepared according to the procedure of Stork:[25] ^1H NMR ($CDCl_3$) δ 0.82–0.96 (d, J = 6 Hz, 3 H, Me), 1.04–1.8 (m, 9 H, ring), 1.8–2.2 (m, 1 H, β-CH), 2.2–2.38 (d, J = 5 Hz, 2 H, α-CH_2), 10.85–11.04 (s, 1 H, CO_2H); C-13 spectrum, see Table V.

Reduction of 9.36 g (0.06 mol) of **11** with 1.71 g of $LiAlH_4$ (0.045 mol) in 100 mL of absolute ether gave, after workup and distillation, 7 g (82%) of 2-(*cis*-4-methylcyclohexyl)ethanol, **12**: bp 95–100 °C (15 mm); ^1H NMR ($CDCl_3$) δ 0.82–0.94 (d, J = 6 Hz, 3 H, Me), 1.02–1.8 (m, 12 H, ring and β-CH_2), 3.4–3.66 (m, 2 H, CH_2O), 4.02 (s, 1 H, OH); C-13 spectrum; see Table V.

The alcohol **12** yielded an oily tosylate on treatment with *p*-toluenesulfonyl chloride–pyridine followed by workup.

***N,N*-Dimethyl-2-(*cis*-4-methylcyclohexyl)ethylamine[26–28] (13).** To a solution of 16.25 g of sodium azide (0.25 mol) in 100 mL of Me_2SO and 20 mL of water kept at 70 °C was added 13.3 g (0.045 mol) of the tosylate of **12** in 60 mL of Me_2SO followed by stirring at 70 °C overnight. The mixture was cooled and diluted with water and the product was extracted with ether. The ethereal solution was dried over anhydrous $MgSO_4$ and reduced without further purification by using 19 g (0.5 mol) of $LiAlH_4$ in 200 mL of absolute ether to give 2.75 g (42%) of 2-(*cis*-4-methylcyclohexyl)ethylamine. The amine was dimethylated by using 88% formic acid (10 g) and 37% formaldehyde (10 mL) and heating in an oil bath at 110°C for about 4 h followed by the usual workup to give 2.72 g (84%) of the tertiary amine **13**: bp 115–120 °C (25 mm); ^1H NMR ($CDCl_3$) δ 0.84–0.96 (d, J = 6 Hz, 3 H, Me), 1.2–1.8 (m, 12 H, ring and β-CH_2), 2.24 (s, 6 H, NMe_2); C-13 spectrum, see Table V.

Compound **13** (2.7 g, 0.016 mol) was quaternized[29] by using excess (15 g) methyl iodide in 40 mL of methanol and refluxing the solution for about 3 h. The resulting solution was concentrated and 200 mL of anhydrous ether was added to precipitate the solid methiodide (5 g; quantitative yield), mp 218–220 °C.

A solution of the methiodide (5 g) in 60 mL of distilled water and 10 mL of methanol was stirred with 0.033 mol of freshly prepared silver oxide for 2 h. The resulting quaternary ammonium hydroxide was filtered and concentrated below 40 °C to a yellow oil. This was heated under vacuum (50 mm) at 120 °C in an oil bath. *cis*-4-Methyl-1-vinylcyclohexane was distilled and collected in a dry ice–acetone trap. To the distillate was added 10 mL of 4 N hydrochloric acid and the olefin was extracted with pentane. After the solution was dried over anhydrous K_2CO_3, pentane was evaporated, and Kugelrohr distillation [140–145 °C (760 mm)] gave 1 g (50%) of **3**. Traces of pentane were removed by passing the olefin through a preparative GLC column (12 ft × 0.375 in. 30% SE-30 on 80/100 Chromosorb A) at 140 °C: ^1H NMR (CD_2Cl_2) δ 0.88–0.94 (d, J= 6.3 Hz, 3 H, Me), 1.21–1.41 (m, 2 H, ring), 1.42–1.68 (m, 7 H, ring), 2.13–2.26 (m, 1 H, allylic) (the olefinic region shows a well-resolved ABM part of an ABMX spectrum), 4.91–5.03 (AB part of ABMX system, 10 lines, J_t = 17.36, J_c = 10.5, J_{gem} = 2, $J_{allylic}$ = 1.65 Hz, 2 H, $=CH_2$), 5.81–5.95 (M part of ABMX spectrum, 8 lines, J_t = 17.36, J_c = 10.5, J_{vic} = 6.4 Hz, 1 H, —CH=).

Anal. Calcd for C_9H_{16}: C, 87.01; H, 12.99. Found: C, 87.27; H, 12.82.

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Registry No. 1, 828-45-5; **2**, 76833-24-4; **3**, 34780-47-7; **4**, 695-12-5; **5**, 827-52-1; **6**, 63007-33-0; *cis*-**11**, 7132-95-8; *trans*-**11**, 7132-93-6; *cis*-**12**, 76833-25-5; *cis*-**12** tosylate, 76833-26-6; *trans*-**12**, 76833-27-7; 13, 76833-28-8; **13** methiodide, 76833-29-9; **13** quaternary ammonium hydroxide, 76833-30-2; 4-methyl-4-phenylcyclohexanone, 18932-33-7; *cis*-4-methyl-1-phenylcyclohexanol, 30689-83-9; *trans*-4-methyl-1-phenylcyclohexanol, 30689-84-0; 4-methyl-1-phenylcyclohexene, 16776-31-1; 2-(*cis*-4-methylcyclohexyl)ethylamine, 76833-31-3; $C_6H_{11}CH_2COOH$, 5292-21-7; $C_6H_{11}CH_2CH_2OH$, 4442-79-9; $C_6H_{11}CH_2CH_2NMe_2$, 2358-91-0.

Regioselective Synthesis of α-Alkoxy Ketones from α,α'-Dibromo Ketones

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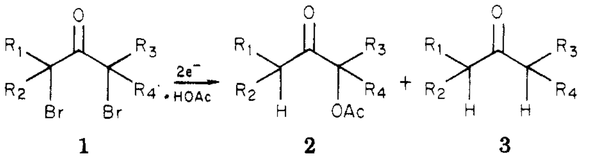
A series of reports from this laboratory has described our studies of the reduction of α,α'-dibromo ketones (**1**), either electrochemically or by ultrasonically dispersed mercury.[1–7] Usually, though not always, these experiments have been carried out in the presence of acetic acid, and in such cases the reaction affords primarily the corresponding α-acetoxy ketones (**2**) and/or the parent ketones (**3**) (eq 1).



(1)

We have adduced considerable evidence[1,3,4,7] that these products are formed via the mechanism shown in Scheme I, in which the key intermediate, enol allylic bromide **4**, is the precursor of both **2** and **3**. For present purposes, we note that in principle any nucleophile might replace acetic acid in this reaction, inasmuch as nucleophilic attack takes place at the end of the mechanistic sequence, resulting in generation of the critical precursor **6**. We have found in a few previous experiments that methanol[2] and some ketones[5] may indeed replace acetic acid in this re-

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