126–127°, $[\alpha]^{22}\mathrm{D}$ −49 ± 2° (*c*, 2.46 in absolute chloroform).

Anal. Calcd. for $C_{22}H_{24}N_2O_5$: C, 66.65; H, 6.10; N, 7.08. Found: C, 66.65; H, 6.29; N, 7.37.

N(Im)-Carbobenzoxy-L-histidyl-L-leucine methyl ester [prepared from 1.39 g. (0.0024 mole) of VII with ammonia] and 0.793 g. (0.002 mole) of carbobenzoxy-L-prolyl-L-phenylalanine were coupled almost as in the case of the compound XVI to carbobenzoxy-L-prolyl-L-phenylalanyl-N(Im)-carbobenzoxy-L-histidyl-L-leucine methyl ester; wt. 1.267 g. (80.0%). Recrystallization from acetone-ether gave a sample for analysis; m.p. 144.5–145° dec., $[\alpha]^{24}\mathrm{D}$ −56.4 ± 1° (*c*, 2.544 in methanol).

Anal. Calcd. for $C_{43}H_{50}N_6O_9$: C, 65.1; H, 6.35; N, 10.6. Found: C, 64.42; H, 6.47; N, 10.71.

Glycyl-N(Im)-carbobenzoxy-L-histidyl-L-phendylalanine Methyl Ester Dihydrobromide (XIX).—A 0.642-g. sample of the compound XII was treated with 3 ml. of 37.5% (w./w. hydrogen bromide in dioxane as in the case of VII to give 0.421 g. of the tripeptide ester dihydrobromide, $\lambda_{\max}^{\mathrm{MeOH}}$ 234 mμ (ε 3640).

Anal. Calcd. for $C_{26}H_{31}N_5O_6Br_2$: C, 46.7; H, 4.68; N, 10.0; Br, 23.9. Found: C, 45.73; H, 4.99; N, 10.40; Br, 22.59.

Carbobenzoxyglycyl-L-histidyl-L-phenylalanine (XX).—To a suspension of 0.642 g. (0.001 mole) of XII in 15 ml. of methanol was added 2.2 ml. of *N* sodium hydroxide and the mixture was shaken at room temperature for 30 min. The resulting clear solution was allowed to stand for additional 30 min., cooled in an ice bath, neutralized with 2.2 ml. of *N* hydrochloric acid, and then concentrated *in vacuo* to dryness. The crystalline residue was washed with ice-cold water and dried; wt. 0.382 g. (77.5%), m.p. 200° dec., $[\alpha]^{30}\mathrm{D}$ +15.4 ± 1.4° (*c*, 1.424 in methanol).

Anal. Calcd. for $C_{25}H_{27}N_5O_6$: C, 60.85; H, 5.52; N, 14.2. Found: C, 60.51; H, 5.65; N, 14.11.

Formyl-γ-methyl-L-glutamyl-L-histidyl-L-phenylalanine (XXI).—A suspension of 0.349 g. (0.5 mmole) of XV in 20 ml. of methanol was submitted to hydrogenation in the presence of palladium black catalyst at room temperature. After the crystal had completely dissolved the hydrogenation was carried on for an additional 8 hr. The catalyst was filtered off and the filtrate was concentrated *in vacuo*. The resulting sirup was dissolved in water and after removal of a slight amount of insoluble precipitate the aqueous solution was concentrated *in vacuo*. Crystallization was effected by repeated concentration with methylene chloride, the product was filtered off, washed with methylene chloride, and dried; wt. 0.212 g. (89.5%), m.p. 185–189° dec., $[\alpha]^{25}\mathrm{D}$ −12.2 ± 2° (*c*, 2.210 in methanol).

Anal. Calcd. for $C_{22}H_{27}N_5O_7 \cdot 2H_2O$: C, 51.9; H, 6.13; N, 13.7. Found: C, 51.28; H, 5.77; N, 13.48.

Carbobenzoxy-γ-*t*-butyl-L-glutamyl-L-histidyl-L-phenylalanine (XXII).—To a suspension of 2.00 g. (0.0026 mole) of XVI in 26 ml. of methanol was added 5.7 ml. of *N* sodium hydroxide at 0°, and the mixture was shaken at room temperature for 15 min. and then cooled in an ice bath. After addition of about 40 ml. of water the solution was neutralized with 5.7 ml. of *N* hydrochloric acid to separate the product as a partially crystallized solid. The precipitate was filtered off, washed with cold water, and dried; wt. 1.41 g. (85.0%). The suspension of this crude product in 20 ml. of acetonitrile was boiled for a few minutes to ensure crystallization. After refrigeration, the crystals were filtered off, washed with acetonitrile and ether, and dried; wt. 1.24 g. (75.0%), m.p. 172–173°, $[\alpha]^{24}\mathrm{D}$ −3.7 ± 1° (*c*, 2.409 in dimethylformamide).

Anal. Calcd. for $C_{32}H_{39}N_5O_8 \cdot H_2O$: C, 60.1; H, 6.46; N, 10.9. Found: C, 59.94; H, 6.44; N, 10.75.

Conformations. I. Synthesis, Proton Magnetic Resonance Spectra, and Ultraviolet Spectra of Substituted 1-Phenylcyclohexenes

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The synthesis of a number of substituted 1-phenylcyclohexenes is described. Proton magnetic resonance and ultraviolet spectra of these compounds are reported.

This is the first of several papers to be published concerning the determination of substituent conformations in cyclohexenes. The synthesis of a number of substituted 1-phenylcyclohexenes will be discussed here. Proton magnetic resonance and ultraviolet spectra of these compounds have been determined and these data are summarized in Table I.

Compounds 1–11 and 13–16 were prepared by dehydration of the corresponding tertiary arylcyclohexanols at room temperature employing usually a sulfuric acid in acetic acid dehydration mixture.[2] In this manner, dehydrations of 2-methyl-1-phenylcyclohexanol,[3] 2-isopropyl-1-phenylcyclohexanol,[3] and 1,2-diphenylcyclohexanol[3] led to mixtures of 6- and 2-substituted—1-phenylcyclohexenes (compounds 6–9 and 13) which were readily separated by conventional methods. Dehydration of 2-*tert*-butyl-1-phenylcyclohexanol[3] afforded only 6-*tert*-butyl-1-phenylcyclohexene (compound 10) as evidenced by a single gas-liquid chromatography band.[4]

The synthetic routes to alkenes 12 and 17–21 are schematically described in Chart I. The preparations of the 6-nitro-1-phenylcyclohexene derivatives (compounds 22–27) have been reported.[5]

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[1] N.S.F. Postdoctoral Fellow, 1961–1962. Present address: Department of Chemistry, University of Chicago, Chicago 37, Ill.

[2] E. W. Garbisch, Jr., *J. Org. Chem.*, **26**, 4165 (1961).

[3] Carbinols are of unknown configurations.

[4] It has not been definitely established whether or not the dehydrations afforded equilibrium mixtures of the possible alkenes.

[5] E. W. Garbisch, Jr., Ph.D. thesis, Northwestern University, 1961. This work will be published shortly. Compound 23 was prepared in the same manner as described for *trans*-4-*tert*-butyl-6-nitro-1-phenylcyclohexene. Compound 26 was furnished by Robert L. Arnold of Northwestern University.

TABLE I^{a}

PROTON MAGNETIC RESONANCE AND ULTRAVIOLET SPECTRA OF SUBSTITUTED 1-PHENYLCYCLOHEXENES

Cpd. no.	1-Phenylcyclohexene substituents (τ)	C-2—H (τ)	C-3—H (τ)	C-4—H (τ)	C-5—H (τ)	C-6—H (τ)	Aryl (τ)	$\lambda_{\max}$(log ϵ)^{t}
1	None	4.00 (W_{H} = 8.5)^{f}	*ca.* 7.75^{b}	8.33	8.33	*ca.* 7.75^{b}	2.83	247 (4.09)
2	4-*t*-Butyl (9.10)	4.00 (W_{H} = 9)^{f}	7.97	7.97^{c}	8.69	7.615 (W_{H} = 15)^{f}	2.81	248 (4.10)
3	4-Methyl (9.01)^{d}	4.01 (W_{H} = 9)^{f}	*ca.* 8.25^{b}	*ca.* 8.25^{b}	*ca.* 8.25^{b}	7.63 (W_{H} = 14.5)^{f}	2.80	247–248 (4.10)
4	4-*t*-Butyl (9.10); *p*-Me (7.70)	4.03 (W_{H} = 9)^{f}	7.97	7.97	8.68	^{i}	2.86; 3.02^{r}	251 (4.18)
5	4,4-Dimethyl (9.04)	4.04 (W_{H} = 8)^{f}	8.04		8.52 (J = 6.5)^{e}	7.63 (W_{H} = 14)^{f}	2.79	247 (4.08)^{v}
6	6-Methyl (9.09; J = 7.0)	4.21 (J = 3.6)^{e}	7.91	8.31	8.31	7.23	2.825	242 (4.05)
7	2-Methyl (8.47)		*ca.* 7.92^{b}	8.31	8.31	*ca.* 7.92^{b}	2.88	237 (3.75)
8	6-Isopropyl (Me; 9.18 and 9.40; J = 6.7)^{y}	4.21 (W_{H} = 9)^{f,s}	7.95	8.355	8.355	7.37	2.86	239.5 (4.02)
9	2-Isopropyl (Me; 9.11; J = 6.9) and (*t*-H; 7.45; J = 6.9)^{z}		7.91	8.33	8.33	7.91	^{aa}	233 (3.68)
10	6-*t*-Butyl (9.24)	4.25 (J = 4.1)^{e}	7.91	8.22	8.22	7.38^{s} (W_{H} = 10.5)^{f}	2.87	239.5 (4.00)
11	6,6-Dimethyl (8.99)	4.62 (J = 3.9)^{e}	7.95	8.39	8.39		2.90	227^{w} (3.65)^{x}
12	6,6-Diethyl (Me; 9.17; J = 6.4)^{e}	4.40 (J = 3.9)^{e}	7.95	^{g}	^{g}		2.89	227^{w} (3.68
13	6-Phenyl (2.92)	3.71 (J = 4.0)^{e}	7.80	8.16^{h}	8.44^{h}	6.08 (W_{H} = 10.5)	2.92	246–247^{l} (4.05)
14	6-Methyl-6-phenyl (Me; 8.64)	3.96 (J = 3.8)^{e}	7.775	8.33	8.33		^{g}	240 (3.99); 270^{w} (3.40)
15	*o*-Methyl (7.77)	4.51 (W_{H} = 8)^{f}	^{i}	8.31	8.31	^{i}	2.99	228^{j,w} (3.75)
16	*o,o*-Dimethyl (7.83)	4.60 (W_{H} = 9)^{f}	^{i}	8.25	8.25	^{i}	3.13	264 (2.38)
17	6-(2-Hydroxy-2-propyl) (Me; 8.98, 9.07) (OH; 8.83)	4.14 (J = 3.8)^{e}	7.915	8.20	8.20	7.18 (W_{H} = 9)	2.82	239–240 (4.02)^{x}
18	4,4-Dimethyl; 6-(2-hydroxy-2-propyl) (Me; 9.05 and 8.99)	4.34 (J = 4.1)^{e}	8.14		^{k}	7.12 (J = 8.6)^{e} (W_{H} = 21)^{f}	2.81	237 (4.01)^{v} 236 (4.01)
19	6-Acetyl (8.195)	3.89 ($J \approx$ 4)^{e}	7.815	^{i}	^{i}	6.405 (W_{H} = 13.5)	2.82	244 (4.05)
20	6-Acetyl (8.31); 4,4-dimethyl (8.97 and 9.03)	3.95 (W_{H} = 9)^{f}	7.95		^{i}	6.37 (W_{H} = 22)^{f}	2.81	244 (4.09)^{x}
21	6-Acetyl (7.89); 6-ethyl (Me; 9.34; J = 7.4)^{e}	3.94 (J = 4.0)^{e}	^{g}	^{g}	^{g}		2.89	242 (3.95)^{x}
22	6-Nitro^{o}	3.66 (J = 3.8)^{e}	^{i}	^{i}	^{i}	4.565 (W_{H} = 9)^{f,s}	2.78	238–239^{o} (4.05)^{u}
23	4-*t*-Butyl (9.10); 6-nitro; *p*-Me (7.70); *trans* stereoisomer	3.64^{n} (J = 2.4 and 4.8)	^{i}	^{i}	8.31	4.57 (W_{H} = 8)^{f}	2.915	246 (4.13)
24	4-Methyl (8.98)^{d}; 6-nitro; *trans* stereoisomer^{o}	3.63^{n} (J = 2.25 and 4.5)	^{g}	^{g}	^{g}	4.57 (W_{H} = 8)^{f}	2.78	239^{o} (4.05)^{u}
25	4-Methyl (8.97)^{p}; 6-nitro *cis* stereoisomer	3.89 (W_{H} = 9)^{f}	^{g}	^{g}	^{g}	4.33 (W_{H} = 19)	2.80	236^{o} (4.05)^{u}
26	4,4-Dimethyl (8.95 and 9.01); 6-nitro	3.88 (J = 3.6)^{e}	^{g}	^{g}	^{g}	4.42 (J = 8.4)^{e} (W_{H} = 21)^{f}	2.79	236.5 (4.05)^{v}
27	6-Bromo; 6-nitro	3.92 (J = 4.0)^{e}	^{g}	^{g}	^{g}		2.74	^{o,q}
28	1-(1-Cyclohexenyl)cyclohexene	4.34	7.89	8.41	8.41	7.89		
29	1-Methylcyclohexene (Me; 8.39)	4.68^{m}	8.11^{m}	^{i,m}	^{i,m}	8.11^{m}		

TABLE I (*Continued*)

[a] Tau values refer to the mid-points of the absorption bands when J-values are not indicated. Coupling constants and widths at half height (W_H) are given in c.p.s. [b] Approximate τ-values are given taking the mid-point of a broad multiplet which includes signals of other protons. [c] The C-4 proton should be deshielded by the C_4—$C_{t\text{-butyl}}$ bond. The band for this proton is thought to be degenerate with that for the allylic protons at 7.97 τ. Relative band areas are consistent with this assignment. [d] Doublet—separation of 4.8 c.p.s. See F. A. L. Anet, *Can. J. Chem.*, **39**, 2262 (1961), for a treatment of the n.m.r. spectra of methyl groups. [e] Triplet (1:2:1). [f] Unresolved band. [g] Complex pattern . [h] Assignments tentatively made after inspection of model. [i] Partially masked. [j] H. P. Landerl, Doctor of Science thesis, September 13, 1948, Carnegie Institute of Technology, reported a shoulder at about 230 mμ log ϵ 3.69. See also ref. 24. [k] The C-5 protons appeared as at least five signals between 94.2 c.p.s. and 60.3 c.p.s. [l] G. P. Mueller, J. G. Fleckenstein, and W. H. Tallent, *J. Am. Chem. Soc.*, **73**, 2651 (1951), and ref. 28 reported λ_{max}^{EtOH} 246 mμ, log ϵ 4.07 and 4.03, respectively. [m] G. V. D. Tiers found 8.40 τ for the methyl and homoallylic protons and 8.14 and 4.70 τ for the allylic and vinyl protons, respectively.[7] [n] Quadruplet (AXY-type with equal intensities and spacings). [o] The ultraviolet spectrum of this compound has been reported.[5] [p] Ill-defined doublet; see reference in footnote *d*. [q] Absorption comes as a broad band: λ^{EtOH} 270–240 mμ, log ϵ 3.23–3.85; $\lambda_{inflection}^{ETOH}$ 230–220 mμ, log ϵ 3.93–3.99. [r] Apparent AB-type quadruplet with apparent *ortho-J* = 8.3 c.p.s. [s] Partially resolved triplet on certain sweeps. [t] The solvent is ethanol unless otherwise indicated. The wave length is given in mμ. [u] Ethanol and cyclohexane. [v] Isoöctane. [w] Inflection. [x] Ethanol and isoöctane. [y] Four signals: 49.6, 42.9, 37.2, and 30.5 c.p.s. [z] A symmetrical five-signal band was seen for this proton; the τ-value refers to the more intense central signal. [aa] Sharp signals at 402 and 399 c.p.s.

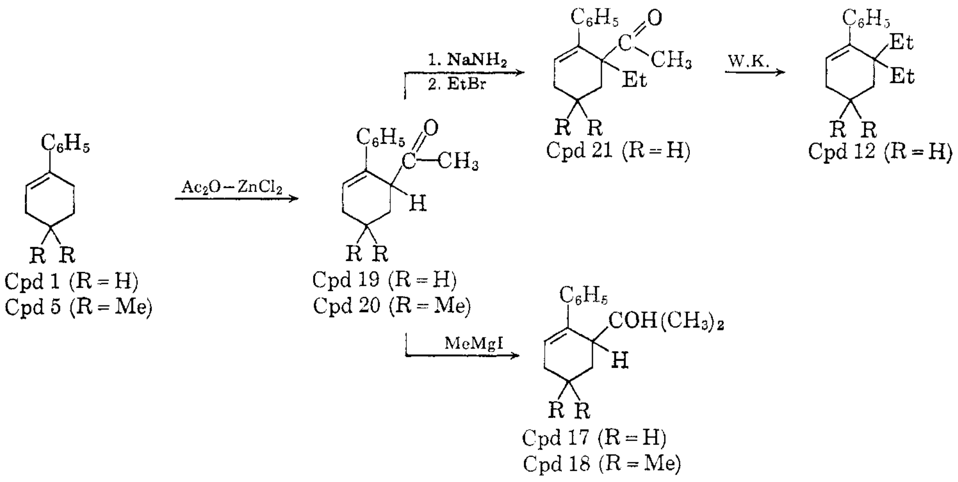

Chart I

The gross structures assigned to prior unknown compounds (compounds 4, 6–12, and 17–22) are in firm accord with their proton magnetic resonance, ultraviolet, and infrared spectra. For example, the sulfuric acid-catalyzed dehydration of 2,2-dimethyl-1-phenylcyclohexanol resulted in one major component together with about 20% of two impurities (by GLC). After adsorption chromatography, the major component was obtained homogeneous to an extent exceeding 95%. The infrared spectrum of this material (compound 11) exhibits no significant absorption for terminal methylene at or about 11 μ.[6] The ultraviolet spectrum exhibits moderate absorption between 225–230 mμ suggesting limited conjugation. The n.m.r. spectrum shows signals for methyl (sharp: 8.99 τ), homoallylic (8.39 τ), allylic (7.95 τ), vinyl (triplet; 4.62 τ), and phenyl (2.90 τ) protons[7] with relative areas of approximately six, four, two, one, and five, respectively. This data is consistent with the assigned structure of 6,6-dimethyl-1-phenylcyclohexene.

Ethylation of 6-acetyl-1-phenylcyclohexene (compound 19) gave, after chromatography, one principal product (compound 21) exhibiting unconjugated carbonyl absorption at 5.86 μ[8] and an ultraviolet spectrum indicative of carbon–carbon double bond conjugation with phenyl. The n.m.r. spectrum shows signals for phenyl (2.89 τ), vinyl (triplet; 3.94 τ), acetyl (sharp; 7.89 τ), homoallylic and ethyl-CH_2 (complex multiplet), and ethyl-CH_3 (triplet; 9.34 τ) protons[7] with intensities (fast sweep) consistent with five, one, five, six, and three protons, respectively (two allylic protons are under the acetyl-CH_3 band). This data complies with requirements for 6-acetyl-6-ethyl-1-phenylcyclohexene.

The proton magnetic resonance assignments made in Table I are consistent with the relative

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(6) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 51.

(7) Representative τ-values for the types of protons encountered in this work may be found in G. V. D. Tiers, "Tables of τ-Values for a Variety of Organic Compounds," Minnesota Mining and Manufacturing Company, Project 737602, 1958. See also: H. Conroy, "Advances in Organic Chemistry," Vol. 2, Interscience Publishers, Inc., New York, N. Y., 1960, p. 287 ff.

(8) R. B. Turner and D. M. Voitle, *J. Am. Chem. Soc.*, **73**, 1403 (1951), report carbonyl absorptions at 5.86 μ for 6-acetyl-1-methylcyclohexene and 5.93 μ for 1-acetyl-2-methylcyclohexene.

signal intensities observed for fast sweeps (and approximate band areas for standard sweeps), and with the tau values assigned to comparable proton absorptions of other compounds.[7] Some comment should be made, however, regarding the characterization of the allylic C-3 and C-6 proton absorptions. The tau value for the allylic protons of 1-methylcyclohexene (compound 28) is 8.11 (8.14[7]) in contrast to the higher value of 8.40[7] for the homoallylic protons. For 1-(1-cyclohexenyl)-cyclohexene, these signals appear at 7.89 and 8.41 τ respectively (compound 28). Because of the anisotropy of the benzene ring,[9] the C-6 protons of 1-phenylcyclohexene would be expected to experience a larger deshielding than would the C-3 protons. Calculation of the shieldings of these protons of 1-phenylcyclohexene (assuming coplanar system) gives[10,11] average values of approximately -0.45 p.p.m. for the C-6 protons and -0.13 p.p.m. for the C-3 protons, with a difference (δ) of 0.32 p.p.m. For 1-phenylcyclohexene the absorptions of these protons were not sufficiently separated to obtain accurate shielding values. For 4,4-dimethyl-1-phenylcyclohexene the C_4-CH_3 bonds were calculated[10,12] to shield the C-6 and C-3 protons by about 0.02 and 0.07 p.p.m., respectively. This serves to separate further the C-6 and C-3 proton bands as compared with 1-phenylcyclohexene (δ now about 0.37 p.p.m.). Tau values to expect taking 1-(1-cyclohexenyl)cyclohexene and 1-methylcyclohexene as references are roughly 7.46 to 7.68 for the C-6 protons and 7.83 to 8.05 for the C-3 protons. The allylic proton bands for 4,4-dimethyl-1-phenylcyclohexene are found at 7.63 and 8.04 τ with δ of 0.41 p.p.m. Assignment of 7.63 τ to the C-6 protons and 8.04 τ to the C-3 protons is made. These assignments are strongly supported as follows. (1) Both 6,6-dimethyl- and 6,6-diethyl-1-phenylcyclohexene have only C-3 allylic protons. The one band readily assigned to allylic protons is found at 7.95 τ for both compounds, and has an area representative of approximately two protons. (2) Substitution of an alkyl, acetyl, or phenyl function for one C-6 proton will lead to a significant deshielding of the remaining C-6 proton and only slightly affect the C-3 protons (relative to 4,4-dimethyl-1-phenylcyclohexene). In addition, the ratios of the C-3 proton and C-6 proton band areas will now be 2 to 1. These effects are observed (see compounds 6, 8, 10, 13, and 17–20 in Table I).

Experimental[13]

N.m.r. Spectra.—A Varian Model 4300 B spectrometer operating at 56.4 Mc. was employed. For calibrations, 564 c.p.s. side bands were imposed on the spectrum with a Hewlett–Packard counter. At least four sweeps were made for each spectrum calibration. Power levels and sweep rates were comparable for all spectra. Samples dissolved in carbon tetrachloride containing 1–2% (by weight) of tetramethylsilane as an internal reference were sealed under vacuum. Sample concentrations (by weight) were: 15% for hydrocarbons and carbonyl derivatives, 10% for alcohols, and 5–10% for nitro derivatives. Spectra run on 5% samples of 1-phenylcyclohexene and 6-(2-hydroxy-2-propyl)-1-phenylcyclohexene (compounds 1 and 17) gave measurements which were not in variance with spectra from samples of higher concentration. Shielding values have a mean deviation of less than ±0.02 p.p.m. Coupling constants and widths at half height (W_{H}) have mean deviations of ±0.3 and ±1.0 c.p.s., respectively.

Ultraviolet absorption spectra were determined in matched 1-cm. quartz cells using a Beckman DK recording spectrophotometer. Molar absorptivity values generally were reproducible to ±2%. The solvents used were spectro grade cyclohexane (Eastman) and isoöctane (Phillips), and U.S.P. grade 95% ethanol.

Cyclohexanones.—The 2-methyl-, 4-methyl-, and 4-*tert*-butylcyclohexanones, and the 2-isopropyl- and 2-*tert*-butylcyclohexanols were obtained from commercial sources. 2-*tert*-Butylcyclohexanone (b.p. 80–82°/13 mm., n^{25}_{D} 1.4561; reported[14] b.p. 75–79°/12 mm., n^{25}_{D} 1.4570), 2-isopropylcyclohexanone (b.p. 139–141°/150 mm., n^{20}_{D} 1.4553, semicarbazone m.p. 193–195°; reported[15] b.p. 72°/15 mm., n^{24}_{D} 1.4526, semicarbazone m.p. 180°), and 2-phenylcyclohexanone (m.p. 58–62°; reported[16] m.p. 60°) were prepared from 2-*tert*-butylcyclohexanol, 2-isopropylcyclohexanol, and 2-phenylcyclohexanol, respectively, by chromic acid oxidation.[17] 2,2-Dimethylcyclohexanone was prepared following the procedure of King, King, and Topliss,[18] and boiled at 168–169°, n^{25}_{D} 1.4460, semicarbazone m.p. 200° (GLC showed *ca.* 8% impurity); reported[18] b.p. 170–171° (765 mm.), $n^{18.5}_{\mathrm{D}}$ 1.4492, semicarbazone, m.p. 199–200°. 2-Methyl-2-phenylcyclohexanone was synthesized according to the method of Newman and Farbman[16] and boiled at 90–91° (1.5 mm.), n^{25}_{D} 1.5342; reported[16] b.p. 95.5–96.5° (1.0 mm.), n^{20}_{D} 1.5357. Hydrogenation of 4,4-dimethyl-2-cyclohexenone[19] (b.p. 55–57°/4.1 mm., n^{28}_{D} 1.4686; reported[20] b.p. 72.5–73.5°/20 mm., n^{14}_{D} 1.4775) in acetic acid using 10% palladium-on-carbon catalyst and 30 p.s.i. of hydrogen, afforded 4,4-dimethylcyclohexanone, m.p. 42–43°; reported[21] m.p. 38°.

The preparation of 1-phenylcyclohexene (compound 1), 4-*tert*-butyl-1-phenylcyclohexene (compound 2), and 4-methyl-1-phenylcyclohexene (compound 3) has been re-

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[9] L. Pauling, *J. Chem. Phys.*, **4**, 673 (1936); J. A. Pople, *ibid.*, **24**, 1111 (1956).

[10] For these calculations the cyclohexene model used was that described by E. J. Corey and R. A. Sneen, *J. Am. Chem. Soc.*, **77**, 2505 (1955). In Fig. 3 of this work, the *y* coordinates for allylic axial and equatorial substituents at both *a* and *d* were taken as -0.175 and 0.109, respectively (a typographical error in signs for these values was confirmed by Professor Corey).

[11] The tables of C. E. Johnson, Jr., and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958), were used to estimate theoretical chemical shifts for a proton at any position (in terms of coördinates ρ and z) in the neighborhood of the phenyl ring.

[12] Shieldings from the carbon–carbon bond were calculated using the appropriate equation by H. M. McConnell, *ibid.*, **27**, 226 (1957), and taking ($\chi_{\mathrm{L}} - \chi_{\mathrm{T}}$) equal to 8.3×10^{-30} cm.^{3}/molecule as given by J. I. Musher, *ibid.*, **35**, 1159 (1961). Distances taken are from the proton to the center of the carbon–carbon bond.

[13] Microanalyses were performed by Mrs. Olga Hamerston and James E. Johnson.

[14] H. L. Goering, R. L. Reeves, and H. H. Espy, *J. Am. Chem. Soc.*, **78**, 4926 (1956).

[15] R. Filler, B. R. Camera, and S. M. Nagvi, *ibid.*, **81**, 658 (1959).

[16] M. S. Newman and M. D. Farbman, *ibid.*, **66**, 1550 (1944).

[17] A. S. Hussey and R. H. Baker, *J. Org. Chem.*, **25**, 1434 (1960).

[18] F. E. King, T. J. King, and J. G. Topliss, *J. Chem. Soc.*, 919 (1957).

[19] The author is indebted to Keith Wellman at Northwestern University for sending improved directions for the synthesis of this material.

[20] E. D. Bergmann and R. Corett, *J. Org. Chem.*, **23**, 1507 (1958).

[21] R. F. Miller and R. Adams, *J. Am. Chem. Soc.*, **58**, 787 (1936).

ported by the author.[2] Samples of these alkenes used for n.m.r. and ultraviolet spectra showed a single gas-liquid chromatography band.

4-*tert*-Butyl-1-*p*-tolylcyclohexene (Compound 4).—This alkene was prepared by sulfuric acid–acetic acid dehydration of the crude tertiary arylcarbinol obtained from the reaction between *p*-tolylmagnesium bromide and 4-*tert*-butylcyclohexanone.[2] The alkene melted at 76.5–77° after three recrystallizations from methanol.

Anal.[22] Calcd. for $C_{17}H_{24}$: C, 89.56; H, 10.44. Found: C, 89.56; H, 10.10.

4,4-Dimethyl-1-phenylcyclohexene (Compound 5).—4,4-Dimethyl-1-phenylcyclohexanol, m.p. 54–56°, was prepared from 4,4-dimethylcyclohexanone by the Grignard reaction. To 5.0 g. of the carbinol in 10 ml. of acetic acid at room temperature was added 5.0 ml. of 30% sulfuric acid–acetic acid (by volume).[2] The alkene separated almost immediately as an oily second phase. The mixture was then stirred for an additional minute and poured into a mixture of pentane (150 ml.) and water (100 ml.). The pentane layer was washed with dilute alkali and water, and then treated with *ca.* 10 g. of activated silica gel. The mixture was filtered and the pentane evaporated under reduced pressure. The entire residue distilled at 79–79.5° (1.2 mm.). A center cut, 2.8 g., n^{25}D 1.5419, was collected for subsequent n.m.r. and ultraviolet measurements and was found to be void of impurities by GLC.[23]

2-Methyl- and 6-Methyl-1-phenylcyclohexene (Compounds 6 and 7).—2-Methyl-1-phenylcyclohexanol, 43 g., b.p. 107° (0.5 mm.),[3,24] was dissolved in 150 ml. of 2.5% sulfuric acid–acetic acid and left for 20 min. at room temperature. By this time the alkene had partially separated as a second oily phase. The mixture was then processed as described above for compound 5. Distillation afforded 30 g. (77%) of a mixture of 2-methyl-1-phenylcyclohexene (20%), 6-methyl-1-phenylcyclohexene (77%), and 3% of higher boiling material (by GLC), b.p. 67–69° (1.2 mm.), n^{25}D 1.5498. This mixture was separated using a Beckman Megachrom gas chromatographic unit[25] or by fractional distillation through a spinning band column.[26]

The 2-methyl-1-phenylcyclohexene boiled at 121° (12 mm.), n^{20}D 1.5472, and was 94% pure by GLC. The n.m.r. spectrum of this material shows no vinyl proton absorption (Table I).

Anal.[22] Calcd. for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.64; H, 9.57.

6-Methyl-1-phenylcyclohexene (99+% pure by GLC) boiled at 121° (12 mm.), n^{20}D 1.5559. The n.m.r. spectrum of this material shows a vinyl proton absorption (Table I).

Anal.[22] Calcd. for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.47; H, 8.90.

2-Isopropyl- and 6-Isopropyl-1-phenylcyclohexene (Compounds 8 and 9).[26]—2-Isopropyl-1-phenylcyclohexanol,[3] m.p. 41–44°, was obtained in 35% (37% recovered ketone) through treatment of an excess of phenylmagnesium bromide in ether with 2-isopropylcyclohexanone. After three recrystallizations from light petroleum (b.p. 30–60°) the carbinol melted at 45–46°.[27]

Anal. Calcd. for $C_{15}H_{22}O$: C, 82.51; H, 10.15. Found: C, 82.09; H, 10.13.

A mixture of 9.0 g. of the carbinol and 75 ml. of 98% formic acid was stirred at room temperature for 0.5 hr. After this time, the mixture was poured into water and the products extracted with pentane. The extract was washed with dilute alkali, dried over sodium sulfate, and the pentane evaporated under reduced pressure. Gas-liquid chromatography showed that the residue consisted of 38% of compound 9 (with about 4% of unidentified material appearing as a shoulder on this band) and 58% of compound 8. One distillation through a spinning band column afforded samples of the alkenes containing less than 1% of impurity (by GLC).

2-Isopropyl-1-phenylcyclohexene boiled at 122° (11.5 mm.), n^{25}D 1.5300. The n.m.r. spectrum of this compound shows no vinyl proton absorption.

Anal.[22] Calcd. for $C_{15}H_{20}$: C, 89.94; H, 10.06. Found: C, 89.80; H, 9.90.

6-Isopropyl-1-phenylcyclohexene boiled at 130° (11.5 mm.), n^{25}D 1.5413. The n.m.r. spectrum of this compound shows a vinyl proton absorption.

Anal.[22] Calcd. for $C_{15}H_{20}$: C, 89.94; H, 10.06. Found: C, 90.50; H, 10.12.

6-*tert*-Butyl-1-phenylcyclohexene (Compound 10).—2-*tert*-Butyl-1-phenylcyclohexanol,[3] b.p. 107–109° (2.5 mm.), was prepared in 50% yield by the reaction between 2-*tert*-butylcyclohexanone and phenyllithium in ether. Without further purification, 5.0 g. (0.022 mole) of this carbinol was treated with 10 ml. of acetic acid which contained 20 drops of sulfuric acid. The resulting solution was left at room temperature for 0.25 hr., during which time the product separated as an oily second phase. The mixture was then processed as described for compound 5. Distillation of the crude product gave 4.3 g. (92%) of 6-*tert*-butyl-1-phenylcyclohexene, b.p. 110–111° (2.2 mm.). The alkene was redistilled and boiled at 110–111° (2.2 mm.), n^{25}D 1.5393. Gas-liquid chromatography showed a single band.

Anal. Calcd. for $C_{16}H_{22}$: C, 89.65; H, 10.35. Found: C, 89.47; H, 10.38.

6,6-Dimethyl-1-phenylcyclohexene (Compound 11).—2,2-Dimethyl-1-phenylcyclohexanol, b.p. 105–106° (0.3 mm.), was prepared in 74% yield by the reaction between 2,2-dimethylcyclohexanone and excess phenyllithium in ether. A solution of 4.0 g. of this carbinol in 15 ml. of acetic acid containing 10 drops of sulfuric acid was warmed at 50° for 10 min. After this time, the reaction mixture was processed as described for compound 5. The crude alkene was found to be about 80% homogeneous by GLC. A portion, 3.10 g., of the product was chromatographed on a 3 × 70 cm. alumina column slurry packed with petroleum ether (b.p. 60–70°). The column was eluted with petroleum ether. The first 700 ml. of eluate contained 2.81 g. of alkene which was found to be 88% pure by GLC. This material was rechromatographed using the same column packed with silica gel in petroleum ether. Elution, as before, afforded in the first 1450 ml., 1.8 g. of 6,6-dimethyl-1-phenylcyclohexene. The alkene was distilled and boiled at 80.5° (0.54 mm.), n^{25}D 1.5324. Gas-liquid chromatography showed this material to be greater than 95% pure.

Anal. Calcd. for $C_{14}H_{18}$: C, 90.26; H, 9.74. Found: C, 90.47; H, 9.74.

1,6-Diphenylcyclohexene (Compound 13).—The alkene was prepared as described for compound 5 using 2.3 g. of 1,2-diphenylcyclohexanol,[3,28] m.p. 56–62°, and 7.0 ml. of 12% sulfuric acid–acetic acid. After two recrystallizations from methanol, pure 1,6-diphenylcyclohexene, m.p. 52.5–53°, was obtained; reported[28] m.p. 51–53°. No attempt was made to isolate the 1,2-diphenylcyclohexene[28] which was formed together with compound 13 in a ratio of about 1:2, respectively (by GLC).

1,6-Diphenyl-6-methylcyclohexene (Compound 14).—Reaction between 2-methyl-2-phenylcyclohexanone (10.0 g.) and excess phenyllithium in ether gave 12.0 g. (78%) of 1,2-diphenyl-2-methylcyclohexanol, b.p. 154–156° (0.35 mm.).

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[22] Microanalysis by Miss Hildegard Beck at Northwestern University.

[23] This alkene, b.p. 77–79° (0.5 mm.), n^{20}D 1.5452, and the carbinol precurser, m.p. 53–55°, were first prepared by Robert Arnold at Northwestern University (forthcoming Ph.D. thesis). The author wishes to thank R. A. for sending his data.

[24] R. B. Carlin and H. P. Landerl, *J. Am. Chem. Soc.*, **75**, 3969 (1953).

[25] The author wishes to thank Dr. W. Penny and J. P. Windey of the Minnesota Mining and Manufacturing Co. for attending to this separation.

[26] Work done at Northwestern University.

[27] It is not certain that this represents a configurationally homogeneous sample.

[28] P. Tomboulian, *J. Org. Chem.*, **26**, 2652 (1961).

This material in 20 ml. of acetic acid was treated with 5.0 ml. of 40% sulfuric acid–acetic acid, and the resulting mixture stirred for 5 min. at room temperature. The product was isolated as described for compound 5. Distillation gave 10.5 g. (94%) of crude 1,6-diphenyl-6-methylcyclohexene, b.p. 131° (0.33 mm.). The alkene slowly crystallized upon standing at room temperature. It melted at 35–37° after one recrystallization from methanol. The melting point was not changed by an additional recrystallization.

Anal. Calcd. for $C_{19}H_{20}$: C, 91.88; H, 8.12. Found: C, 92.00; H, 8.18.

1-*o*-Tolylcyclohexene and 1-(2,6-Dimethylphenyl)-cyclohexene (Compounds 15 and 16).—These alkenes were prepared from the corresponding tertiary arylcarbinols[24] following the procedure described for compound 5. Compound 15 boiled at 69° (1.2 mm.), n^{25}D 1.5406; reported[24] n^{25}D 1.5411, and was found to be homogeneous by GLC. Compound 16 boiled at 87° (1.0 mm.), n^{25}D 1.5342; reported[24] n^{20}D 1.5379, and was found to be homogeneous by GLC.

6-Acetyl-1-phenylcyclohexene (Compound 19).—The procedure used was adapted from that described by Deno and Chafetz[29] for the synthesis of 6-acetyl-1-methylcyclohexene. To a mixture of 20.0 g. (0.15 mole) of zinc chloride in 140 ml. of acetic anhydride at 15° was added 20.0 g. (0.127 mole) of 1-phenylcyclohexene. The mixture was stirred at room temperature for 1.5 hr. and then poured into 800 ml. of water. After the acetic anhydride had hydrolyzed, the products were extracted with ether. The extract was washed with water and dilute sodium bicarbonate, dried over sodium sulfate, and the ether then evaporated under reduced pressure. Distillation of the residue gave 20.5 g. (81%) of 6-acetyl-1-phenylcyclohexene, b.p. 91–93° (0.15 mm.), m.p. 23–27°. After three recrystallizations from petroleum ether (b.p. 30–60°), the alkene melted at 26.5–27°; infrared spectrum (CCl_4), 5.85 μ (s).

Anal. Calcd. for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 84.16; H, 8.32.

6-(2-Hydroxy-2-propyl)-1-phenylcyclohexene (Compound 17).—6-Acetyl-1-phenylcyclohexene, 10.0 g. (0.05 mole), was added to a 20% excess of methylmagnesium iodide in ether. The resulting solution was left for 0.25 hr. and then processed in the usual manner. Distillation of the reaction product gave 9.5 g. of crude carbinol, b.p. 100–105° (0.6 mm.). An infrared spectrum of this material exhibited appreciable carbonyl absorption. A 2.00-g. sample of the crude carbinol was chromatographed on a 2.5 × 14 cm. alumina column packed in 4% ether–petroleum ether (b.p. 60–70°). The first fraction, 500 ml. of 4% ether–petroleum ether, contained 0.581 g. of unchanged 6-acetyl-1-phenylcyclohexene together with approximately 27% of what may be 2-acetyl-1-phenylcyclohexene: infrared spectrum (CCl_4), 5.96 μ (s). The second fraction, 250 ml. of 4% ether–petroleum ether, contained 0.26 g. of carbinol contaminated by a trace of carbonyl material (by infrared). The last fraction, 750 ml. of 30% ether–petroleum ether, contained 1.14 g. of compound 17; infrared spectrum, ($CHCl_3$), 2.83 μ (m), 2.93 μ (w), and no carbonyl absorptions. The last fraction together with a corresponding fraction from a second chromatogram were combined and distilled to give 6-(2-hydroxy-2-propyl)-1-phenylcyclohexene, b.p. 107° (0.25 mm.), n^{25}D 1.5520.

Anal. Calcd. for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 83.12; H, 9.44.

Judging from the ultraviolet spectrum of this material (Table I), there is thought to be little, if any, 2-(2-hydroxy-2-propyl)-1-phenylcyclohexene contaminant.

6-Acetyl-6-ethyl-1-phenylcyclohexene (Compound 21).—A mixture of 8.0 g. (0.04 mole) of 6-acetyl-1-phenylcyclohexene and 1.68 g. (0.043 mole) of sodium amide in 30 ml. of dry benzene was heated at 70–75° for 1 hr. while being stirred. The reaction mixture was then cooled to room temperature and 10.9 g. (0.10 mole) of bromoethane was added. This mixture was stirred at reflux temperature for 20 hr., a second 10.9-g. portion of bromoethane was added after 4 hr. Water (*ca.* 100 ml.) was then added. The benzene layer was washed once with water and the benzene then distilled under reduced pressure. The residue (infrared spectrum showed no detectable absorption for conjugated carbonyl) was chromatographed on a 3 × 70 cm. silica gel column packed in 2% ether–petroleum ether (b.p. 60–70°). The column was eluted with 2% ether–petroleum ether and the following 500-ml. fractions were collected successively and found to contain: (1) void; (2) void; (3) 300 ml. of eluate, void; (4) 0.95 g.; (5) 0.16 g.; (6) 0.45 g.; (7) 1.45 g.; (8) 1.25 g.; (9) 0.77 g.; (10) 0.41 g.; (11) 0.26 g.; (12) 0.14 g.; and (13) 1000 ml. of 20% ether–petroleum ether, 1.64 g. Fraction 13 contained primarily 6-acetyl-1-phenylcyclohexene, m.p. 23–25° after one recrystallization from petroleum ether (b.p. 30–60°). Fractions 6–11 contained compound 21 and were combined and distilled. The 6-acetyl-6-ethyl-1-phenylcyclohexene boiled at 107° (0.15 mm.), n^{25}D 1.5499; infrared spectrum (CCl_4), 5.86 μ (s).

Anal. Calcd. for $C_{16}H_{20}O$: C, 84.16; H, 8.83. Found: C, 84.18; H, 8.88.

6,6-Diethyl-1-phenylcyclohexene (Compound 12).—A mixture of 10.0 g. (0.044 mole) of compound 21, 8.0 g. of sodium hydroxide, 10 ml. of 95% hydrazine, and 60 ml. of diethylene glycol was heated to reflux. Condensate was removed periodically until the temperature of the mixture had risen to 190°. Reflux was continued for 4.5 hr. and then the mixture was cooled and poured into water. The product was extracted with petroleum ether and the extract washed with water and dried over *ca.* 20 g. of silica gel. The solvent was evaporated under reduced pressure and the residue distilled to give 5.5 g. (59%) of 6,6-diethyl-1-phenylcyclohexene, b.p. 95–98° (1.3 mm.). The alkene was redistilled and a center cut boiling at 112.2–112.6° (2.7 mm.) was collected; n^{25}D 1.5358. Gas-liquid chromatography showed this material to be 95–96% pure.

Anal. Calcd. for $C_{16}H_{22}$: C, 89.65; H, 10.35. Found: C, 89.86; H, 10.64.

6-Acetyl-4,4-dimethyl-1-phenylcyclohexene (Compound 20).—The procedure described for the synthesis of compound 22 was followed using 9.0 g. (0.048 mole) of 4,4-dimethyl-1-phenylcyclohexene, 7.0 g. (0.051 mole) of zinc chloride, and 70 ml. of acetic anhydride. The reaction time was 20 min. Distillation of the product gave 8.7 g. (80%) of compound 20, b.p. 113.5–114.5° (0.03 mm.), n^{25}D 1.5411; infrared spectrum ($CHCl_3$), 5.87 μ (s). There was no detectable conjugated carbonyl infrared absorption.

Anal. Calcd. for $C_{16}H_{20}O$: C, 84.16; H, 8.83. Found: C, 84.01; H, 9.04.

4,4-Dimethyl-6-(2-hydroxy-2-propyl)-1-phenylcyclohexene (Compound 18).—6-Acetyl-4,4-dimethyl-1-phenylcyclohexene, 8.7 g. (0.037 mole) was added to 0.042 mole of methylmagnesium iodide in 100 ml. of ether. The solution was stirred for 0.25 hr. and then processed in the usual manner. The crude reaction product was distilled and the material boiling at 108° (0.25 mm.) was collected and weighed 6.0 g. The infrared spectrum of this material exhibited considerable unconjugated carbonyl absorption at 5.86 μ. The distillate was chromatographed on a 2 × 60 cm. alumina column packed in 4% ether–petroleum ether (b.p. 60–70°). Successive elution with 500 ml. of 4%, 2000 ml. of 6%, 500 ml. of 10%, 1500 ml. of 12%, 1000 ml. of 20%, and 500 ml. of 100% ether–petroleum ether solutions gave the following fractions which were found to contain: (1) 500 ml., void; (2) 500 ml., 1.45 g.; (3) 1000 ml., 0.73 g.; (4) 500 ml., 0.45 g.; (5) 1000 ml., 1.79 g., m.p. 52–58°; (6) 1000 ml., 1.01 g., m.p. 65–66°; (7) 1000 ml., 0.43 g., m.p. 65–66°; and (8) 500 ml., 0.06 g., m.p. 65–66°. Fractions 2 and 3 contained unchanged compound 20. From fraction 4 was obtained 0.16 g., m.p. 60–63°, after one recrystallization from petroleum ether

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[29] N. C. Deno and H. Chafetz, *J. Am. Chem. Soc.*, **74**, 3940 (1952).

(b.p. 30–60°). Fractions 5–8 contained essentially pure compound 18 for a total of 3.45 g. (37%). After two recrystallizations from petroleum ether (b.p. 30–60°), the 4,4-dimethyl-6-(2-hydroxy-2-propyl)-1-phenylcyclohexene melted at 66–66.5°; infrared spectrum (CCl_4), 2.82 μ (m) and 2.92 μ (w).

Anal. Calcd. for $C_{17}H_{20}O$: C, 83.55; H, 9.90. Found: C, 83.35; H, 10.00.

***trans*-4-*tert*-Butyl-6-nitro-1-*p*-tolylcyclohexene (Compound 23).**—4-*tert*-Butyl-1-*p*-tolylcyclohexene, 6.84 g. (0.03 mole), was nitrated[5] using 2.6 g. (0.04 mole) of 70% nitric acid, 100 ml. of acetic anhydride, and 5 drops of sulfuric acid. The crude reaction product, after hydrolysis of the acetic anhydride and extraction with ether, was chromatographed on a 3 × 70 cm. silica gel column packed in 1% ether–petroleum ether (b.p. 60–70°). Elution with 4500 ml. of 1% and 2800 ml. of 5% ether–petroleum ether solutions afforded, as the only solid material, 1.83 g. of 1-acetoxy-*cis*-*tert*-butyl-*trans*-2-nitro-1-*p*-tolylcyclohexane, m.p. 124–128.5°. Two recrystallizations from petroleum ether raised the melting point to 131.5–132.5°; infrared spectrum ($CHCl_3$), 8.50 (s), 9.15 (m), 10.32 (m), and 11.02 (w) μ. The infrared spectrum is consistent with the assigned configuration.[5]

Anal. Calcd. for $C_{19}H_{27}NO_4$: C, 68.44; H, 8.16; N, 4.20. Found: C, 68.56; H, 8.13; N, 4.45.

A portion (0.50 g.) of the β-nitroacetate was treated with 15 ml. of acetic anhydride containing 15 drops of sulfuric acid.[5] The resulting solution was left for 10 min. at room temperature and then poured into an excess of water. After hydrolysis of the acetic anhydride was complete, the solid was collected by filtration and weighed 0.41 g., m.p. 67–70°. After one recrystallization from petroleum ether (b.p. 30–60°), the *trans*-4-*tert*-butyl-6-nitro-1-*p*-tolylcyclohexene melted at 73–75°. Two further recrystallizations raised the melting point to 75–76°; infrared spectrum ($CHCl_3$), 6.42 μ (s). Once, a solid form melting at 61–63°, resolidifying at this temperature and then melting again at 75–76° was obtained.

Anal. Calcd. for $C_{17}H_{23}NO_2$: C, 74.69; H, 8.48; N, 5.12. Found: C, 74.13; H, 8.74; N, 5.34.

1-(1-Cyclohexenyl)cyclohexene (Compound 28).—The procedure of Gruber and Adams[30] was followed. The diene obtained boiled at 81.5° (2.0 mm.), $n^{25}\text{D}$ 1.5321; reported[30] $n^{20}\text{D}$ 1.5322. It was 94% pure by GLC.

In Table II are listed the retention volumes (GLC) for a number of 1-arylcyclohexenes relative to 1-phenylcyclohexene. Comparable relationships between V_R and structure have been reported for alkylated biphenyls with regard to noncoplanarity of the conjugated systems.[31]

TABLE II

RETENTION VOLUMES OF 1-ARYLCYCLOHEXENES RELATIVE TO 1-PHENYLCYCLOHEXENE[a]

Compound	V_R/V_R 1-phenylcyclohexene
1-Methyl-2-phenylcyclohexene	0.91
1-*o*-Tolylcyclohexene	1.04
6-Methyl-1-phenylcyclohexene	1.05
4-Methyl-1-phenylcyclohexene	1.24
1-*p*-Tolylcyclohexene	1.49
6,6-Dimethyl-1-phenylcyclohexene	1.08
4,4-Dimethyl-1-phenylcyclohexene	1.34
1-(2,6-Dimethylphenyl)cyclohexene	1.35
1-Isopropyl-2-phenylcyclohexene	1.25
6-Isopropyl-1-phenylcyclohexene	1.67
6-*tert*-Butyl-1-phenylcyclohexene	2.27
6,6-Dimethyl-1-phenylcyclohexene	2.3
4-*tert*-Butyl-1-phenylcyclohexene	3.52

[a] A Perkin–Elmer Vapor Fractometer fitted with a 6-ft. silicone oil DC-200 column was employed. The column temperature was 200° and the helium pressure was 20 p.s.i.

Acknowledgment.—The author is indebted to Dr. W. B. Schwabacher for determining the n.m.r. spectra. The author wishes to thank the National Science Foundation for a postdoctoral fellowship, and Professor M. M. Kreevoy for reading the rough manuscript.

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Conformations. II. Proton Magnetic Resonance Determination of C-6 Substituent Conformations in 6-Substituted 1-Phenylcyclohexenes

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Preferred conformations for C-6 substituents in a number of 6-substituted 1-phenyl(and methyl)cyclohexenes have been determined from the widths at half height of the C-6 proton magnetic resonance bands. Bulky substituents, *e.g.*, 6-*tert*-butyl, were found to be primarily axial. Olefinic proton and C-6 proton coupling constants, extracted from the respective absorptions in a number of instances, were used to approximate dihedral angles between adjacent protons.

Conformations of cyclohexene derivatives have not been widely investigated.[2] Sakashita has concluded recently[3] from infrared and Raman spectra that *axial*-3-halo- and *axial*-4-halocyclohexenes are more stable in the liquid state than their equatorial counterparts. The chair conformation of cyclohexene has been estimated[4] to be favored over the boat form by about 2.7 kcal./mole, and this conformational preference has experimental support for a number of derivatives.[2]

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[1] (a) N.S.F. Postdoctoral Fellow, 1961–1962. (b) Paper I in this series, *J. Org. Chem.*, **27**, 4243 (1962). (c) Present address: Department of Chemistry, University of Chicago, Chicago 37, Illinois.

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[3] K. Sakashita, *Nippon Kagaku Zasshi*, **81**, 49 (1960); *ibid.*, **80**, 972 (1959); *Chem. Abstr.*, **54**, 2008h, 12015b (1960).

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