dihalide was used as the (arbitrary) standard of reference in each case. Fluorine coupling constants (in cycles per second) for the geminal difluorides and proton coupling both geminal and vicinal are listed below. Since $J_{gem} \approx J_{anti} > J_{gauche}$ it follows that axial

F–F (*gem*)	236 ± 3	H–F (*anti*)	44
H–F (*gem*)	46	H–F (*gauche*)	10

fluorine in the monofluorides appears as a quartet (large split) of triplets (small split) whereas the equatorial fluorine in the monofluorides appears as a doublet of two sharp peaks.

The ^{19}F resonance of *cis*-4-*t*-butylcyclohexyl-1-*d* fluoride showed a triplet of triplets, J_{anti} = 40 cps. *trans*-4-Butylcyclohexyl-1-*d* fluoride analogously shows a *single*, somewhat sharp peak. However, it also showed some contamination due to the *cis* isomer and a third component whose signals coincided with that of *cis*-3-*t*-butylcyclohexyl fluoride. Thus a minor amount of rearrangement may have taken place in the displacement of hydroxyl by fluorine.

Conclusion

It is clear from the data here presented that either a 3- or a 4-*t*-butyl group has a strong effect on fluorine resonance at C_1. On the other hand, whereas a 3-*t*-butyl group does somewhat affect proton shift at C_1, a 4-*t*-butyl group in a carbocyclic system apparently does not and it therefore appears that the nmr method as originally proposed[4] is suitable for determining conformational equilibria in cyclohexanes. The reason why a 4-*t*-butyl group has no adverse effect while a 3-*t*-butyl group does has its parallel both in the kinetic[1] and in the equilibrium[41,42] method of conformational analysis and the phenomena may all have a common cause in that the 4-*t*-butyl-substituted compounds (III, IV) and the monosubstituted compound (I $\rightleftharpoons$ II) suffer deformations of a similar kind, whereas the 3-*t*-butyl-substituted compound suffers either no deformation at all or a lesser deformation.[41,43,44] However, these considerations do not seem to apply to a heterocyclic systems such as 1,3-dioxane.[45]

Acknowledgment. This work was supported under National Science Foundation Grant G-20555 and Air Force Office of Scientific Research Grant AF-AFOSR-772-65. We are grateful to Mr. Donald Schifferl for recording the nmr spectra and to the Dow Chemical Co. for supplying us with generous samples of 4-*t*-butylcyclohexanone and 4-*t*-butylcyclohexanoles.

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(42) E. L. Eliel and T. J. Brett, *ibid.*, **87**, 5039 (1965).

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(44) N. L. Allinger, M. A. Miller, F. A. Van Catledge, and J. A. Hirsch, *J. Amer. Chem. Soc.*, **89**, 4345 (1967).

(45) NOTE ADDED IN PROOF. After submission of this paper, a communication appeared elsewhere[46] in which attention is also drawn to the limitations of the nmr method of conformational analysis. However, the authors' argument is incomplete, as they do not consider the possible effect of temperature on chemical shift in comparing low-temperature spectra of dichloro- (and other disubstituted) cyclohexanes with room-temperature spectra of the corresponding *t*-butyl-substituted homologs.

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Conformational Analysis. XIV. Conformational Equilibria of Cyclohexyl Halides[1]

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Abstract: The conformational equilibria of cyclohexyl fluoride, chloride, and bromide have been determined by nuclear magnetic resonance (^1H) as a function of solvent, using the 4-*t*-butylcyclohexyl halides as conformationally rigid models. The $-\Delta G°$ values are: 0.15 kcal/mol for fluorine, 0.43 kcal/mol for chlorine, and 0.37 kcal/mol for bromine, and are remarkably independent of solvent. The value for chlorine was confirmed by an infrared method. 3-*t*-Butylcyclohexyl fluorides and chlorides are not suitable models for conformational equilibrium determinations. ^{19}F nmr spectra can be used for such determination in the 4-*t*-butylcyclohexyl fluoride series only with use of a correction factor computed from the nmr spectra of 1,1-difluorocyclohexanes. A convenient method for the synthesis of *cis*- and *trans*-4-*t*-butylcyclohexyl chlorides and their 3 isomers from the corresponding alcohols *via* the chloroformates is described.

It is well known[2] that conformational equilibrium in a substituted cyclohexane favors the equatorial position of the substituent (Figure 1). Conformational equilibrium in a 1,2-disubstituted ethane (Figure 2) often favors the *anti* conformation over the *gauche*, despite the fact that the latter has a twofold statistical advantage. It would appear that similar steric factors are operative in the two cases and it has often been stated[2c] that the axial interaction in a substituted cyclohexane corresponds to two *gauche* interactions in a 1-substituted propane (Figure 2, X = CH_3). The heavy lines in Figure 1 show these interactions as incorporated in the cyclohexane with axial substituent. In fact, the enthalpy difference[3] between axial and equatorial methylcyclo-

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(2) Reviews on conformational analysis: (a) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Division, John Wiley and Sons, Inc., New York, N. Y., 1965; (b) M. Hanack, "Conformation Theory," Academic Press Inc., New York, N. Y., 1965; (c) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, Chapters 6 and 8; (d) E. L. Eliel, *Angew. Chem.*, **77**, 784 (1965); *Angew. Chem. Intern. Ed. Engl.*, **4**, 761 (1965); (e) E. L. Eliel, *J. Chem. Educ.*, **37**, 126 (1960); (f) J. McKenna "Conformational Analysis of Organic Compounds," Lecture Series No. 1, The Royal Institute of Chemistry, London, 1966.

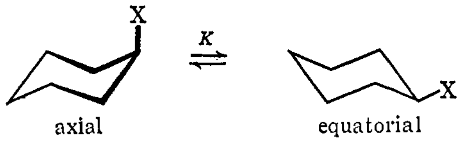

Figure 1.

hexane, 1.7 kcal/mol in the liquid phase or 1.9 kcal/mol in the vapor phase,[2a] is approximately twice the *gauche–anti* difference in butane (0.8–0.9 kcal/mol).

Recently the conformational equilibria in propyl fluoride,[4] propyl chloride,[5] and propyl bromide[5b] (Figure 2, $X = CH_3$, Y = halogen) have been studied by physical methods, such as microwave spectroscopy,[4,5a] infrared spectroscopy,[5b] and electron diffraction (ED),[5c] and it appears in all cases that the *gauche* form is preferred over the *anti* by *more* than a factor of 2; *i.e.*, that it has the lower enthalpy as well as the higher entropy. Calculations[6] also suggest that propyl chloride should have the lower enthalpy in the *gauche* form (as a result of both London forces and dipolar attraction) although they indicate that the bromide should be more stable in the *anti* form. One might think, then, that the halocyclohexanes should be more stable in the axial form, as explained above. (Entropy considerations are unimportant in the halocyclohexanes since there is only *one* axial and *one* equatorial conformation). In fact, however, the literature indicates that cyclohexyl fluoride,[7] cyclohexyl chloride,[7b,8] and cyclohexyl bromide[7b,8a,c,e,f,9] are all more stable in the equatorial conformation. The conformational free energy differences for the above three halocyclohexanes (Figure 1) from the literature are summarized in Table I.

The present work was undertaken to obtain additional data for the conformational equilibria in cyclohexyl halides and, in particular, to determine the conformational equilibrium as a function of solvent, inasmuch as there was a possibility, *a priori*, that solvent effects might have something to do with the breakdown of the relationship between conformational equilibria in propyl halides on one hand and cyclohexyl halides on the other.

Experimental Section

4-*t*-Butylcyclohexyl Chlorides. 4-*t*-Butylcyclohexyl Chloroformates.[10] A three-necked, 500-ml flask containing 100 ml of toluene was equipped with a magnetic stirrer and inlet and outlet tubes, weighed, and placed in an ice–salt bath inside a hood. A rapid stream of phosgene was passed into the toluene; from time to time the flask was disconnected and weighed, and the phosgene flow was stopped when *ca.* 26 g (0.26 mole) had been dissolved in the toluene. A solution of 35 g (0.195 mol) of 4-*t*-butylcyclohexanol (see below for isomeric composition) in 130 ml of dry ether was then added to the cooled solution from a separatory funnel and the mixture allowed to come to room temperature overnight. The ether and part of the toluene were then removed on a rotatory vacuum evaporator at a water bath temperature of 40–60°. The residual chloroformate containing some toluene was used as such.

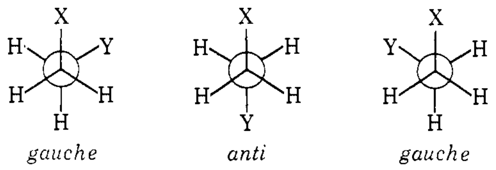

Figure 2.

Table I. Conformational Free Energy Differences for the Cyclohexyl Halides (kcal/mol)

Halogen	$-\Delta G°$	Ref	Method
F	0.15	7c	Nmr
F	0.17	7a	ED
F	0.24	7b	Nmr
F	0.25	7b	Nmr
F	0.24–0.27	7c	Nmr
F	0.40	7d	Microwave
Cl	<0.26	8b	ED
Cl	0.4	8c	Ir
Cl	0.33–0.44	8d	Ir
Cl	0.41	8e	Nmr
Cl	0.42–0.45	8f	Nmr
Cl	0.47	8a	Kerr
Cl	0.48	7b	Nmr
Cl	0.51	7b	Nmr
Cl	0.60	8g	Nmr
Br	0.2	8c	Ir
Br	0.24	9a	Nmr
Br	0.26	8a	Kerr
Br	0.39–0.42	8f	Nmr
Br	0.44	7b	Nmr
Br	0.46	9b	Nmr
Br	0.48	7b	Nmr
Br	0.51	8e	Nmr
Br	0.6 –0.73	9c	Kinetic
Br	0.61–0.63	9b	Ir
Br	0.7	9d	Calcd

***cis*-4-*t*-Butylcyclohexyl Chloride.** The above chloroformate ester prepared from pure *trans*-4-*t*-butylcyclohexanol[11] was cooled in an ice–salt bath and 150 ml of dry pyridine was added rapidly. A reflux condenser was mounted, and the mixture was gently boiled on a heating mantle for 2 hr, carbon dioxide being evolved. The mixture was then cooled, water added, the aqueous layer extracted with ether, and the ether layer separated, washed with water and sodium bicarbonate solution, and dried over calcium chloride. The organic layer, after concentration, was distilled through a spinning-band column to give 9.5 g (31%) of 4-*t*-butylcyclohexene, bp 87° (49 mm) (lit.[12] 55–57° (15 mm)), identified by infrared spectrum,[12] 1.2 g of an intermediate fraction, and 15.1 g (39%) of *cis*-4-*t*-butylcyclohexyl chloride, bp 125.0° (49 mm), $n^{20}\text{D}$ 1.4694 (lit.[13]

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(3) Because of the statistical advantage of the *gauche* form, it is necessary, in the sequel, to compare enthalpies rather than free energies.

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(10) H. E. Carter, R. L. Frank, and H. W. Johnston, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 167.

(11) E. L. Eliel and D. Nasipuri, *J. Org. Chem.*, 30, 3809 (1965); E. L. Eliel, R. J. L. Martin and D. Nasipuri, *Org. Syn.*, in press.

(12) E. L. Eliel and R. S. Ro, *J. Amer. Chem. Soc.*, **79**, 5995 (1957).

(13) F. D. Greene, C. C. Chu, and J. Walia, *J. Org. Chem.*, **29**, 1285 (1964).

bp 80° (0.3 mm)). Gas chromatographic analysis (130°, 10-ft column of 20% QF-1 fluorinated silicone on Chromosorb P) incated this material to be the pure *cis* isomer. Its infrared spectrum was identical with a spectrum of the *cis* chloride[13] kindly provided by Professor Greene. When the starting material was commercial 4-*t*-butylcyclohexanol (70% *trans* isomer), the product contained 92% *cis* and 8% *trans* chloride.

***trans*-4-*t*-Butylcyclohexyl Chloride.** **a.** The crude chloroformate ester (52 g) prepared from *trans*-4-*t*-butylcyclohexanol was heated at 150° for 32 hr. Fractional distillation of the product through a spinning-band column yielded 8.1 g (26%) of forerun (mainly 4-*t*-butylcyclohexene), bp 70–127° (52 mm), 14.2 g (36%) of 4-*t*-butylcyclohexyl chloride, bp 127.0–127.3° (52 mm), and 3.3 g of residue. Gas chromatographic analysis of the chloride (*vide supra*) disclosed it to be 75% *trans* isomer (retention time 49 min) and 25% *cis* isomer (retention time 42 min, at 135°).

b. The chloroformate ester prepared from 76 g of mixed 4-*t*-butylcyclohexanol (70% *trans* isomer) was heated for 19 hr. Toluene was allowed to distil in the early stages and the pot temperature rose from 120 to 200°. Fractional distillation yielded 20.2 g (41%) of 4-*t*-butylcyclohexene, 8.5 g of an olefin–chloride mixture, and 40.7 g (48%) of 4-*t*-butylcyclohexyl chloride, bp 125° (50 mm), containing 68% *trans*, 32% *cis* isomer, and 5.2 g of residue. (The crude material contained the chlorides in a 69:31 ratio.)

c. Attempts to carry out the decomposition at lower temperature were unavailing unless some boron trifluoride was added. Reaction under these conditions afforded no advantage as to chloride yield or isomeric composition.

To purify the *trans* chloride, the crude chloride mixture was passed through a 12 ft × $^3/_8$ in. gas chromatograph column packed with 33% QF-1 on Chromosorb P at a temperature of 130–140°. The chloride so obtained was 97% *trans* isomer; 100% *trans* material ($n^{20}\mathrm{D}$ 1.4656) was obtained by a second passage through the column. The infrared spectrum of the *trans* chloride was identical with one kindly supplied by Professor Greene.[13]

Reaction of 4-*t*-Butylcyclohexyl Chloride with Thiophenol. To a solution of 0.25 g (11 mg-atoms) of sodium in 12 ml of dry methanol was added 1.2 ml (1.3 g, 12 mmol) of thiophenol and 1.75 g (10 mmol) of *cis*-4-*t*-butylcyclohexyl chloride. After boiling at reflux for 3 days, the methanol was removed by flash evaporation, the residue diluted with water, and the product extracted with ether. The ether extract was cleared with aqueous sodium hydroxide, dilute hydrochloride acid, aqueous sodium bicarbonate, and brine and was dried over potassium carbonate. The solution was concentrated and distilled to give *ca.* 0.4 ml of 4-*t*-butylcyclohexane, bp 65° (14 mm), a very small amount of intermediate fraction, and 1.0 g (40%) of *trans*-4-*t*-butylcyclohexyl thiophenyl ether, bp 188–189° (14 mm) (lit.[12] 185–186° (14 mm)), identical in infrared spectrum with an authentic specimen.[12]

trans-4-*t*-Butylcyclohexyl chloride (0.77 g) was similarly treated with sodium thiophenoxide in methanol for 5 days to give *ca.* 0.4 g of *cis*-4-*t*-butylcyclohexyl thiophenyl ether, bp 184° (14.5 mm) (lit.[12] 184–186° (13 mm)), identical in infrared spectrum with an authentic sample.[12] Approximately one-third of the *trans*-chloride was recovered unchanged.

3-*t*-Butylcyclohexyl Chlorides.[14] Pure *cis*-3-*t*-butylcyclohexanol was prepared by equilibration of the epimeric mixture (obtained by catalytic hydrogenation of 3-*t*-butylphenol with 5% rhodium on alumina at 30–60 psi) by lithium aluminum hydride–aluminum chloride.[11,15] The chloroformate ester was prepared from 44.3 g of the alcohol, as described above, and was divided into two approximately equal portions.

***trans* Isomer.** Dry pyridine, 50 ml, was added to approximately half the above chloroformate ester, and the mixture was heated on the steam bath for 15 min and then refluxed (on a heating mantle) for 45 min. Work-up was as described for the 4 isomer. Distillation yielded 5.0 g of crude olefin, bp 70–120° (46 mm), and 8.3 g (*ca.* 33%) of chloride, bp 122° (46 mm), $n^{20}\mathrm{D}$ 1.4692, as well as intermediate and higher boiling fractions (3.3 g). Analysis of the chloride on a 20% QF-1 on Chromosorb P column at 135° indicated its composition to be 96.5% *trans* (retention time 42 min), 3.5% *cis* (retention time 42 min). The material was submitted to ir and nmr spectroscopy as obtained. Its configuration was assigned on the basis of the similarity of its infrared and nmr spectra with those of the conformationally analogous *cis*-4-*t*-butylcyclohexyl chloride (see below). Elemental analysis showed the sample to be somewhat chemically impure.

Anal. Calcd for $C_{10}H_{19}Cl$: C, 68.74; H, 10.96; Cl, 20.30. Found: C, 69.50; H, 11.14; Cl, 19.48.

***cis* Isomer.** The remainder of the chloroformate ester was heated on a mantle under reflux for 5.2 hr during which time the temperature rose to 194°. Decomposition (evidenced by intense frothing) occurred at about 150°. The product which had a slightly acrid odor was washed with water and dried over calcium chloride. Gas chromatographic analysis indicated the following approximate composition: *cis* chloride, 57%; *trans* chloride, 26%; olefin, 17%. Since preparative gas chromatography led to partial decomposition of the chlorides, the *trans* chloride was removed by preferential conversion to thiophenoxide as follows. The above mixture, *ca.* 17 g, was added to 80 ml of methanol containing 1.14 g of dissolved sodium and 5.5 g of thiophenol. The solution was refluxed for 48 hr, cooled, diluted with water, and extracted with petroleum ether (bp 30–60°), and the extract was washed with aqueous potassium hydroxide and water and dried over calcium chloride. Concentration and fractional distillation through a spinning-band column yielded the *cis* chloride, bp 126° (49 mm), with a faint thiophenol odor. The material was percolated through Alcoa F-20 alumina (5 × 0.25 in. column); it had $n^{20}\mathrm{D}$ 1.4696 and, by gas chromatography, was 95% *cis*, 5% *trans* isomer. Its configuration was assigned on the basis of the similarity of its ir and nmr spectra (see below) with the spectra of the configurationally analogous *trans*-4-*t*-butylcyclohexyl chloride.

Anal. Calcd for $C_{10}H_{19}Cl$: C, 68.78; H, 10.96; Cl, 20.30. Found: C, 69.14; H, 11.27; Cl, 20.36.

***cis*-4-*t*-Butylcyclohexyl Bromide.**[16] **a.** ***trans*-4-*t*-Butylcyclohexyl *p*-Nitrobenzenesulfonate.** A solution of 27.1 g (0.12 mol) of *p*-nitrobenzenesulfonyl chloride in 35 ml of dry pyridine was added to 14.3 g (0.09 mol) of *trans*-4-*t*-butylcyclohexanol[11] dissolved in 30 ml of dry pyridine cooled in an ice–water bath. The reaction mixture was kept at 10° for 1 hr and poured into 10% sulfuric acid (35 ml of H_2SO_4, 630 ml of water). The precipitated solid was collected by filtration and dissolved in ether. The ether solution was successively washed with water, aqueous sodium bicarbonate, and water and dried over anhydrous magnesium sulfate. The ether was distilled at room temperature at reduced pressure and the *p*-nitrobenzenesulfonate crystallized from cold benzene to which hexane was added. (The substance readily decomposes when heated.) Reworking of the mother liquors gave a total of 27.1 g (86%), mp 94.5–96° (lit.[16] 92–94° dec).

b. ***cis*-4-*t*-Butylcyclohexyl Bromide.** The above *p*-nitrobenzenesulfonate (27.1 g) was dissolved in 1325 ml of dry acetone contained in a 3-l., three-necked flask equipped with mechanical stirrer and reflux condenser and 8 g of calcium carbonate and 140 g of dry lithium bromide were added. The mixture was refluxed with stirring for 1.25 hr, cooled rapidly in an ice bath, and filtered with the help of a filter aid. Portions of 500 ml of the filtrate were diluted with 1000 ml of ice water each and extracted in series with three 200-ml portions of pentane. The pentane extracts were combined, washed with water and sodium bicarbonate solution, and dried over anhydrous magnesium sulfate. Concentration of the solution followed by fractional distillation yielded 2.5 g (23%) of forerun (*t*-butylcyclohexene) followed by 7.3 g (42%) of *cis*-4-*t*-butylcyclohexyl bromide, bp 99° (8.5 mm.) (lit.[17] 104–110° (14 mm)), identical in infrared spectrum with a sample previously obtained.[17] Gas chromatographic analysis (20% QF-1 at 130°) suggested that the sample contained 90% *cis* bromide, 3% *trans* bromide, and 7% of another impurity of very similar retention time, possibly a rearranged bromide. Since preparative gas chromatography led to hydrogen bromide elimination, the sample was used as such.

***trans*-4-*t*-Butylcyclohexyl Bromide.**[18] A solution of 24.6 g (0.15 mol) of bromine in 50 ml of dimethylformamide (DMF) prepared at the temperature of an ice–salt bath was added to a solution of 39.5 g (0.15 mol) of triphenylphosphine in 200 ml of DMF similarly cooled. The slurry was rapidly added to 23.5 g (0.15 mol) of *trans*-4-*t*-butylcyclohexanol in 50 ml of DMF at room temperature. The reaction mixture was allowed to stand for 2.5 days and then

---

[14] See also J. H. Simons and A. C. Meunier, *J. Amer. Chem. Soc.*, **65**, 1269 (1943), and L. Schmerling, *ibid.*, **69**, 1121 (1957), who identified 3-*t*-butylcyclohexyl chloride of unknown stereochemical identity in mixtures with other isomers.

[15] E. L. Eliel and F. Biros, *ibid.*, **88**, 3334 (1966).

[16] E. J. Corey and L. Haefle, private communication. We thank Professor E. J. Corey for making this method available to us.

[17] E. L. Eliel and R. G. Haber, *J. Org. Chem.* **24**, 143 (1959).

[18] *Cf.* G. A. Wiley, B. M. Rein, and R. L. Hershkowitz, *Tetrahedron Letters*, 2509 (1964); G. A. Wiley, R. L. Hershkowitz, B. M. Rein, and B. C. Chung, *J. Amer. Chem. Soc.*, **86**, 964 (1964); D. Levy and R. Stevenson, *Tetrahedron Letters*, 341 (1965).

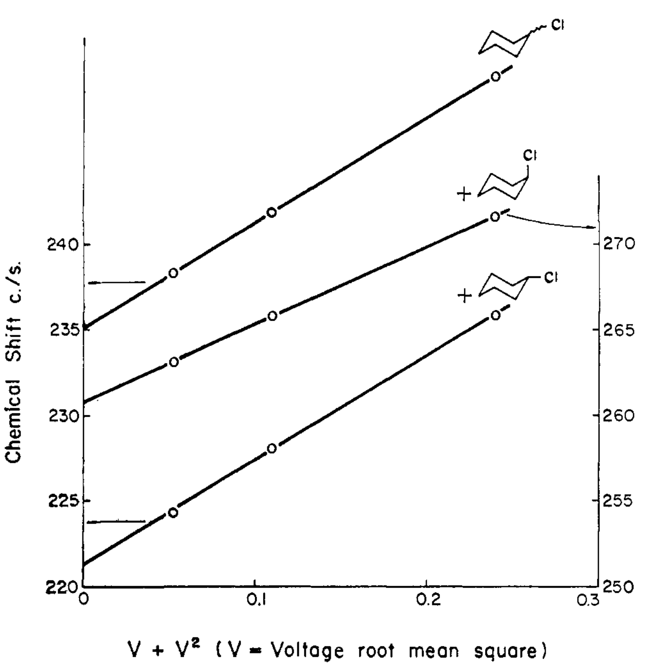

Figure 3.

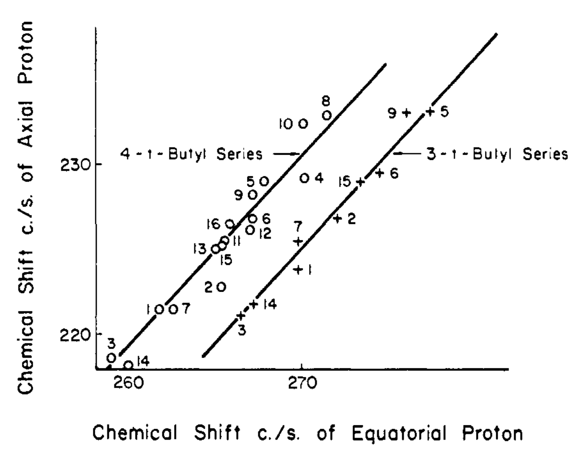

Figure 4. *t*-Butylcyclohexyl chlorides; key to solvents: 1, neat; 2, nitrobenzene; 3, cyclohexane; 4, acetonitrile; 5, trifluoroacetic acid; 6, deuteriochloroform; 7, carbon tetrachloride; 8, N,N-dimethylformamide; 9, N-methylacetamide; 10, 4,4-dimethylamide; 11, methanol; 12, 20% tetra-*n*-butylammonium iodide in methanol; 13, 22% *p*-toluenesulfonic acid in methanol; 14, carbon disulfide; 15, acetic acid; 16, 9% *p*-toluenesulfonic acid in acetic acid; 17, *t*-butyl alcohol.

subjected to distillation at 10 mm. The distillation was completed by lowering the pressure to 1 mm; when a solid began to appear in the condenser, it was stopped. The distillate was diluted with *ca.* 300 ml of water and extracted with petroleum ether (bp 30–60°) and the extract dried over calcium chloride and percolated through a silica gel column (8.5 × 1 in.). The solvent was then distilled and the residue fractionally distilled to give 2.3 g of olefin and 7.1 g (22%) of 4-*t*-butylcyclohexyl bromide, bp 110° (11 mm). Gas chromatography indicated a *trans*:*cis* ratio of 2:1 and there was a small amount of a third impurity.

A bromide mixture containing 67% *trans* isomer, 19% *cis* isomer, and 14% of the third isomer was also obtained from 4-*t*-butylcyclohexanecarboxylic acid by the Hunsdiecker reaction.[19] The *trans* isomer was purified in either case by treatment of the mixture with potassium hydroxide.[17] As finally obtained, the purity of the *trans* isomer (by gas chromatography) was 91% *trans*, 3% *cis*, and 6% other impurity, and its infrared spectrum was identical with one obtained previously.[17]

Other Halides. Cyclohexyl chloride and cyclohexyl bromide were commercial, redistilled materials. Cyclohexyl fluoride and *cis*- and *trans*-3-*t*-butyl and -4-*t*-butylcyclohexyl fluorides were prepared as described in the accompanying paper.[1]

Nmr Spectra. The recording of the nmr spectra is described in the accompanying paper.[1] The signals for the C*H*X protons in the 4-*t*-butylcyclohexyl halides are listed in Tables II, IV, and V, those for the 3-*t*-butyl compounds in Tables III and VI. Shifts are believed to be accurate to ±0.5 cps. The procedure for locating the center of the multiplet has been indicated.[1] As an alternative, the signals were recorded while the cyclohexane protons were saturated at 218 cps and varying radiofrequency. A plot of the apparent shift *vs.* a function of radiofrequency is shown in Figure 3. To obtain the true shift it is necessary to extrapolate to zero radiofrequency. ^{19}F spectra are summarized in Table VII and VIII.

Infrared Spectra. For infrared determination[20–22] of the conformational equilibrium of cyclohexyl chloride, it was assumed[20–22] that *cis*-3- and *trans*-4-*t*-butylcyclohexyl chlorides have the same extinction coefficient for the C–Cl stretching band as the equatorial conformer in cyclohexyl chloride and that the extinction coefficient for the axial conformer in cyclohexyl chloride is the same as for *cis*-4- and *trans*-3-*t*-butylcyclohexyl chlorides. The following bands (e-C–Cl and a-C–Cl, respectively) were measured (in cm^{-1}): cyclohexyl chloride, 737, 689; 4-*t*-butylcyclohexyl chlorides, 728 (*trans* isomer), 693 (*cis* isomer); 3-*t*-butylcyclohexyl chlorides, 723 (*cis* isomer), 670 (*trans* isomer). Optical densities were calculated by the "base-line technique"[23] in which straight lines are drawn tangentially to the peak shoulders and the optical density of the peak is expressed as log [per cent transmittance of base line (center)/per cent transmittance of peak maximum]. Known mixtures of the same total concentration (0.41 *M*) of the chlorides in cyclohexane were prepared, both from *cis*- and *trans*-4-*t*-butylcyclohexyl chlorides and *cis*- and *trans*-3-*t*-butylcyclohexyl chlorides. Transmittance was measured on a Perkin-Elmer Model 421 instrument and a plot was prepared in which the ratio of the base-line optical densities of the *trans* to *cis* isomer (4 series) or *cis* to *trans* isomer (3 series) were plotted against the ratios of concentration of the constituents. The ratio of "base-line optical densities" for the two salient peaks in cyclohexyl chloride were then determined separately in the same fashion at the same molality (0.41) and the conformational equilibrium constant was read directly from the calibration graph.

Discussion

In the present work, conformational equilibria of cyclohexyl fluoride, chloride, and bromide were determined by the nmr method previously described,[2d,24] and the equilibrium of the chloride was also determined by an infrared method based on extinction coefficients.[20–22] The conformational equilibrium value for chlorine derived from the infrared data in the 4-*t*-butyl series (cyclohexane solvent) is

$$K = 1.88\text{–}1.96 \qquad -\Delta G^\circ_{\mathrm{Cl}} = 0.38\text{–}0.40\ \text{kcal/mol}$$

The nmr shifts (C*H*Cl) for cyclohexyl chloride and its 4-*t*-butyl homologs and the derived K and ΔG° values in various solvents are summarized in Table II. These values are remarkably independent of solvent, the average being

$$-\Delta G^\circ_{\mathrm{Cl}} = 0.44\ \text{kcal/mol}$$

A slight but probably significant enhancement of this value is found in the strongly hydrogen-donating solvents trifluoroacetic acid and acetic acid. This en-

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[19] E. L. Eliel and R. V. Acharya, *J. Org. Chem.*, **24**, 151 (1959). The appearance of the third component, not previously found, is puzzling.

[20] R. A. Pickering and C. C. Price, *J. Amer. Chem.*, **80**, 4931 (1958).

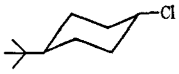
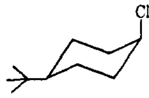
[21] F. R. Jensen and L. H. Gale, *J. Org. Chem.*, **25**, 2075 (1960).

[22] G. Chiurdoglu and W. Masschelein, *Bull. Soc. Chim. Belges*, **69**, 154 (1960).

[23] *Cf.* H. H. Willard, L. L. Merritt, Jr., and J. A. Dean, "Instrumental Methods of Analysis," D. Van Nostrand & Co., Inc. Princeton, N. J., 1965, pp 151–153.

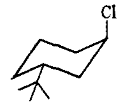
[24] H. Feltkamp and N. C. Franklin, *Angew. Chem.*, **77**, 798 (1965); *Angew. Chem. Intern. Ed. Engl.*, **4**, 774 (1965).

Table II. Chemical Shifts of the Axial and Equatorial Protons of Cyclohexyl and 4-*t*-Butylcyclohexyl Chlorides.[a] Conformational Equilibrium Constant of Cyclohexyl Chloride

Solvent	Cyclohexyl chloride 	*trans*-4-*t*-Butylcyclohexyl chloride 	*cis*-4-*t*-Butylcyclohexyl chloride 	K	$-\Delta G°$, kcal/mol
Neat	235.9	221.5	261.7	1.76	0.34
Nitrobenzene	237.1	222.8	265.3	1.97	0.40
Cyclohexane	231.7	218.6	258.9	2.08	0.43
Acetonitrile	243.0	229.2	270.2	1.97	0.40
Trifluoroacetic acid	240.6	229.0	267.9	2.35	0.51
Deuteriochloroform	239.5	226.8	267.2	2.18	0.46
Carbon tetrachloride	234.4	221.5	262.5	2.18	0.46
N-Methylacetamide	240.8	228.2	267.2	2.10	0.44
N,N-Dimethylacetamide	244.7	232.4	270.1	2.07	0.43
N,N-Dimethylformamide	245.2	232.9	271.5	2.14	0.45
Methanol	238.3	225.5	265.5	2.13	0.45
Methanol-$(n\text{-}C_4H_9)_4N^+I^-$, 20%	240.8	226.1	267.0	1.78	0.34
Methanol-*p*-toluenesulfonic acid 22%	238.2	225.0	265.0	2.03	0.42
Carbon disulfide	231.9	218.2	259.9	2.04	0.42
Acetic acid	237.2	225.2	265.4	2.35	0.51
Acetic acid-*p*-toluenesulfonic acid (9% by wt)	238.3	226.5	265.9	2.28	0.49

[a] In cps downfield from tetramethylsilane at 60 Mcps.

Table III. Chemical Shifts of the Axial and Equatorial Protons of the 3-*t*-Butylcyclohexyl Chlorides.[a] Apparent Conformational Equilibrium Constant of Cyclohexyl Chloride Using 3-*t*-Butyl Compounds as Standards

Solvent	Cyclohexyl chloride 	*cis*-3-*t*-Butylcyclohexyl chloride 	*trans*-3-*t*-Butylcyclohexyl chloride 	K	$-\Delta G°$, kcal/mol
Neat	235.9	223.8	269.8	2.80	0.61
Nitrobenzene	237.1	226.8	272.1	3.40	0.72
Cyclohexane	231.7	221.2	266.5	3.31	0.71
Trifluoroacetic acid	240.6	233.1	277.5	4.92	0.94
Deuteriochloroform	239.5	229.5	274.6	3.51	0.74
Carbon tetrachloride	234.4	225.5	269.8	3.98	0.82
N-Methylacetamide	240.8	233.1	276.1	4.58	0.90
Carbon disulfide	231.9	221.8	267.2	3.50	0.74
Acetic acid	237.2	229.0	273.5	4.43	0.88

[a] In cps downfield from tetramethylsilane at 60 Mcps.

hancement may be caused by a slight entropic advantage of the equatorial halide (which can form hydrogen bonds from three directions) over the axial halide (which might be expected to form hydrogen bonds from two directions only, location of the hydrogen donor over the ring being presumed unfavorable); however, the observed enhancement of about 0.05 kcal/mol is far less than the expected 0.24 kcal/mol at 300°K (corresponding to an entropy difference of $R \ln 3 - R \ln 2$ or 0.81 cal/deg mol). The slightly lower value for $-\Delta G°$ in the neat halide may not be significant, since the measured shifts of the neat halides may be unevenly affected by diamagnetic susceptibility effects in the halide media. A plot of ν_e *vs.* ν_a (in the different solvents) is a straight line (Figure 4).

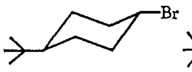
Table III shows corresponding data for 3-*t*-butylcyclohexyl chlorides and cyclohexyl chloride. As explained in the accompanying paper,[1] the $-\Delta G°$ value derived from the 3 series is probably not significant. Surprisingly, the value is also much more solvent dependent than in the 4 series. The infrared value derived from the 3-*t*-butyl standards, $K = 1.57$, $-\Delta G° = 0.27$, also seems out of line, but unlike the nmr value which appears to be too high, the ir value is too low.

The nmr shifts (C*H*Br) for cyclohexyl bromide and its 4-*t*-butyl homologs and the derived K and $\Delta G°$ values are tabulated in Table IV. Again there is little solvent dependence and the average is

$$-\Delta G°_{Br} = 0.37 \text{ kcal/mol}$$

Here again the value for neat bromide is low and the values in acetic acid and trifluoroacetic acid are slightly

Table IV. Chemical Shifts of the Axial and Equatorial Protons of Cyclohexyl and 4-*t*-Butylcyclohexyl Bromides.[a] Conformational Equilibrium Constant of Cyclohexyl Bromide

	Cyclohexyl bromide	*trans*-4-*t*-Butylcyclohexyl bromide	*cis*-4-*t*-Butylcyclohexyl bromide		
Solvent				*K*	$-\Delta G°$, kcal/mol
Neat	249.0	232.9	274.5	1.58	0.27
Nitrobenzene	248.2	231.8	276.7	1.74	0.33
Cyclohexane	243.3	228.3	270.3	1.80	0.35
Acetonitrile	254.2	239.5	282.1	1.90	0.38
Trifluoroacetic acid	252.0	238.1	280.9	2.08	0.43
Deuteriochloroform	251.1	236.4	279.5	1.93	0.39
Carbon tetrachloride	246.9	230.8	274.2	1.70	0.31
N-Methylacetamide	252.9	238.5	280.6	1.92	0.39
N,N-Dimethylacetamide	258.5	244.0	284.4	1.79	0.35
Carbon disulfide	244.4	229.1	272.3	1.82	0.36
Acetic acid	248.7	235.4	277.3	2.15	0.45
Acetic acid–*p*-toluenesulfonic acid (9% by wt)	249.9	236.6	278.1	2.12	0.45

[a] In cps downfield from tetramethylsilane at 60 Mcps.

high, presumably for the same reason as in the chloride series. The $-\Delta G°$ value for bromine is slightly but significantly smaller than that for chlorine. It has been previously explained[2d] why there is not a monotonous relationship between $-\Delta G°$ and group size; in the case of chlorine and bromine, the important factor is probably the greater polarizability of the latter causing a greater attractive London force in the case of bromine which more than compensates for its larger van der Waals radius. However, no categorical statement on this point can be made in the absence of detailed calculations.[25,26] Values for the 3-*t*-butylcyclohexyl bromides were not obtained; infrared values for bromine have been previously recorded[9b] and range from 0.46 to 0.63 kcal/mole. Our earlier value for bromide in the neat liquid obtained by nmr spectroscopy,[9a] −0.24 kcal/mol, is in good agreement with the value recorded in Table I, but the value found in chloroform (−0.94 kcal/mol) was undoubtedly in error, probably due to a reading of a wrongly assigned peak.

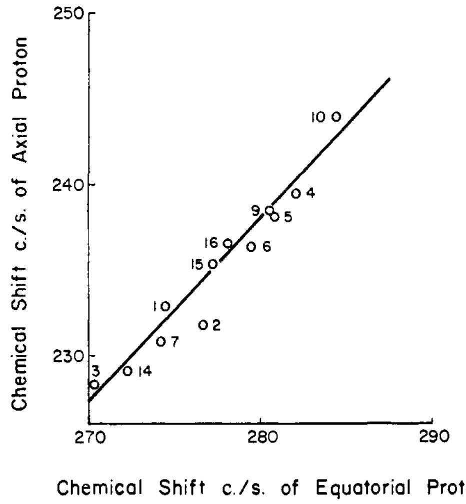


Figure 5. 4-*t*-Butylcyclohexyl bromides; see Figure 4 for key to solvents.

A plot of ν_e *vs.* ν_a in different solvents (Figure 5) is again a straight line.

Proton nmr shifts of cyclohexyl fluoride and its 4-*t*-butyl homologs are shown in Table V, as are the derived *K* and $-\Delta G°$ data. Again the data show little systematic solvent dependence, although there is some scatter. The average value is

$$-\Delta G°_F = 0.15 \text{ kcal/mol}$$

A plot of ν_e *vs.* ν_a displays a straight line (Figure 6). Reasonable $\Delta G°$ data for fluorine are not obtained from the corresponding shifts in the 3 series (Table VI).[1] In Table VII are shown results of fluorine (^{19}F) nmr measurements in mixtures of cyclohexyl fluoride, *cis*-4-*t*-butylcyclohexyl fluoride, and *trans*-4-*t*-butylcyclohexyl fluoride. The calculated *K* and $-\Delta G°$ values are clearly not consonant with the values derived from ^1H spectra. This is not surprising, since it has been previously shown that the 4-*t*-butyl group has a marked effect on the ^{19}F shifts. From the previous work it appears that the apparent *K* derived from ^{19}F shifts should be divided by a correction factor of approximately 1.9 to obtain the true *K*. A more accurate correction factor is obtained by dividing the shift of the equatorial fluorine in 1,1-difluoro-4-*t*-butylcyclohexane (relative to 1,1-difluorocyclohexane) by the shift of the axial fluorine in the same compound (relative to the same standard).[1] The correction factor varies slightly from solvent to solvent. Correction factors calculated from the previous data[1] are included in Table III and the corrected values for *K* and $-\Delta G°$ are also indicated. These corrected values are in fair agreement with ^1H values in Table V and the average conformational free energy of fluorine so calculated is

$$-\Delta G°_F = 0.19 \text{ kcal/mol}$$

Table VIII contains data from ^{19}F nmr spectra in the 3-*t*-butylcyclohexyl fluoride series. Here the correc-

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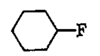
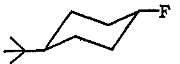
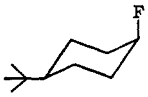
(25) Reference 2a, pp 446–458.

(26) N. L. Allinger, M. A. Miller, F. A. VanCatledge, and J. A. Hirsch, *J. Amer. Chem. Soc.*, **89**, 4345 (1967).

Table V. Chemical Shifts of the Axial and Equatorial Protons of the 4-*t*-Butylcyclohexyl Fluorides.[a] Conformational Equilibrium Constant of Cyclohexyl Fluoride Using 4-*t*-Butyl Compounds as Standards

Solvent	Cyclohexyl fluoride 	*trans*-4-*t*-Butylcyclohexyl fluoride 	*cis*-4-*t*-Butylcyclohexyl fluoride 	K	$-\Delta G°$, kcal/mol
Neat	291.0	281.4	304.1	1.36	0.18
Nitrobenzene	295.8	285.4	308.9	1.17	0.09
Cyclohexane	289.2	279.2	301.9	1.27	0.14
Trifluoroacetic acid	310.8	301.1	322.2	1.18	0.10
Deuteriochloroform	297.1	287.3	310.3	1.35	0.18
Carbon tetrachloride	291.6	281.1	304.6	1.25	0.13
t-Butyl alcohol	293.2	283.4	306.6	1.37	0.19
N-Methylacetamide	294.8	285.6	307.5	1.28	0.19
Carbon disulfide	288.8	278.2	302.0	1.25	0.13
Acetic acid	294.0	284.7	307.0	1.40	0.20

[a] In cps downfield from tetramethylsilane at 60 Mcps.

tion factor to be applied[1] is approximately 0.53. The corrected data in Table VII agree fairly well with the ^1H data for the 3-*t*-butyl series (Table VI) but do not give reasonable values for $\Delta G°_F$.

The data in Tables II–VIII, besides indicating the absence of significant solvent effects on the conformational equilibria of cyclohexyl fluoride, chloride, and bromide, show that the data obtained using 4-*t*-butylcyclohexyl models for the pure axial and equatorial conformers by either nmr or ir spectroscopy are in good agreement with the data recorded in the literature and summarized in Table I. In the case of the ^{19}F spectra it is necessary to apply a correction factor, perhaps to compensate for differential inductive and dipole effects of the 4-*t*-butyl group on equatorial and axial fluorine or for distortion effects of the holding group affecting the ring geometry.[1] The data from the 3-*t*-butyl series are not suitable to compute meaningful conformational equilibria for reasons suggested elsewhere.[1] In any case, the breakdown of the previously suggested relationship $\Delta H°$ (axial → equatorial) = $2\Delta H°$ (*gauche* → *anti*) (*cf.* Figures 1 and 2) is clearly confirmed. The following explanation[2a] is suggested for this breakdown. In the *gauche* form of propyl halides (Figure 2, X = CH_3, Y = halogen) the XY torsional angle τ (Me–C–C–Y) may be *increased* at the energy minimum above the 60° angle which occurs in the staggered form of ethane. While such an increase beyond 60° would increase the torsional potential energy of the molecule, it will decrease the steric repulsion of X and Y. At the energy minimum ($\tau > 60°$), not only will the decrease in steric repulsion have outweighed the increase in torsional potential, but actually, because of the high polarizability of Y (halogen), the net effect may be one of attraction (because of London forces between X and Y) rather than repulsion. Under such circumstances, the *gauche* form (Figure 2) could be more stable than the *anti* in which no such attraction is operative. This picture, in essence, is a qualitative analog of the quantitative considerations presented previously.[6] In the axial conformation of cyclohexyl halide (Figure 1) a corresponding opening up of the torsional angle ($X–C_1–C_2–C_3$) is impossible because the rest of the ring prevents it. There *is* a possibility of a slight flattening of the ring,[7d,27-29] but this, apparently, is nowhere as effective in relieving steric repulsion (or increasing London attraction) at the expense of little angle and torsional strain as is the above-described rotation in propyl halides.

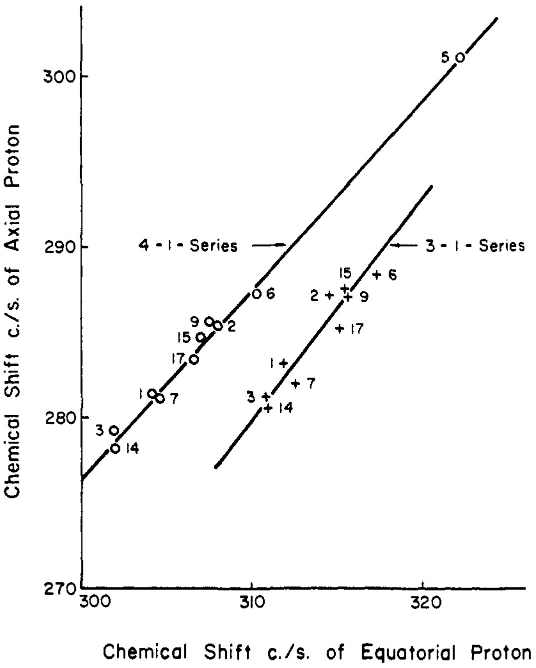


Figure 6. *t*-Butylcyclohexyl fluorides; see Figure 4 for key to solvents.

Preparation of *t*-Butylcyclohexyl Halides. Preparation of stereochemically as well as positionally homogeneous 3- and 4-*t*-butylcyclohexyl halides proved to be a relatively difficult task. *cis*-4-*t*-Butylcyclohexyl bromide had previously been obtained[17] from 4-*t*-butylcyclohexanol (mixed isomers) and phosphorus pentabromide, but the product required tedious repeated low-

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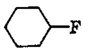
(27) *Cf.* V. A. Atkinson and O. Hassel, *Acta Chem. Scand.*, **13**, 1737 (1959); O. Hassel and E. Wang Lund, *Acta Cryst.*, **2**, 309 (1949).

(28) See also L. Pierce and R. Nelson, *J. Amer. Chem. Soc.*, **88**, 216 (1966).

(29) R. A. Wohl, *Chimia*, **18**, 219 (1964).

Table VI. Chemical Shifts of the Axial and Equatorial Protons of the 3-*t*-Butylcyclohexyl Fluorides.[a] Apparent Conformational Equilibrium Constant of Cyclohexyl Fluoride Using 3-*t*-Butyl Compounds as Standards

Solvent	Cyclohexyl fluoride 	*cis*-3-*t*-Butylcyclohexyl fluoride 	*trans*-3-*t*-Butylcyclohexyl fluoride 	*K*	$-\Delta G^\circ$, kcal/mol
Neat	291.0	283.2	311.8	2.67	0.58
Nitrobenzene	295.8	287.2	314.5	2.17	0.46
Cyclohexane	289.2	281.3	310.8	2.73	0.60
Trifluoroacetic acid	310.8				
Deuteriochloroform	297.1	288.4	317.2	2.31	0.50
Carbon tetrachloride	291.6	282.0	312.5	2.18	0.46
t-Butyl alcohol	293.2	285.2	315.1	2.74	0.60
N-Methylacetamide	294.8	287.1	315.6	2.70	0.59
Carbon disulfide	288.8	280.6	310.9	2.70	0.59
Acetic acid	294.0	287.6	315.4	3.34	0.71

[a] In cps downfield from tetramethylsilane at 60 Mcps.

Table VII. ^{19}F Resonance of Cyclohexyl and 4-*t*-Butylcyclohexyl Fluorides. Derived Conformational Equilibrium Constant

Solvent	K_F	Cor factor	K_F cor	$-\Delta G^\circ_F$ cor, kcal/mol
Neat	2.59	1.90	1.36	0.18
Nitrobenzene	2.90	1.95	1.49	0.24
Cyclohexane	2.40	1.94	1.24	0.13
Deuteriochloroform	3.05	1.96	1.56	0.26
Carbon tetrachloride	2.36	1.96	1.20	0.11
t-Butyl alcohol	2.65	1.97	1.35	0.18
N-Methylacetamide	2.94	1.97	1.49	0.24
Carbon disulfide	2.46	1.94	1.27	0.14
Acetic acid	2.91	1.94	1.50	0.24
Mean				0.19

Table VIII. ^{19}F Resonance of Cyclohexyl and 3-*t*-Butylcyclohexyl Fluorides. Derived Apparent Conformational Equilibrium Constant

Solvent	K_F	$K_F \cdot 1.9$	$-\Delta G^\circ$, kcal/mol
Neat	1.16	2.21	0.47
Nitrobenzene	1.26	2.46	0.53
Cyclohexane	1.11	2.16	0.46
Deuteriochloroform	1.21	2.37	0.51
Carbon tetrachloride	1.13	2.22	0.47
t-Butyl alcohol	1.16	2.28	0.49
N-Methylacetamide	1.24	2.44	0.53
Carbon disulfide	1.14	2.22	0.47
Acetic acid	1.24	2.41	0.52
Mean			0.49

temperature recrystallization. A better method[16] to obtain the *cis* bromide (though only *ca.* 90% pure), kindly communicated to the authors by Professor E. J. Corey, starts with the readily accessible[11] *trans*-4-*t*-butylcyclohexanol which is converted to the *p*-nitrobenzenesulfonate and then treated with lithium bromide. The material could, no doubt, be purified by crystallization if necessary. The *trans* bromide may be obtained in 67% purity from the Hunsdiecker reaction starting with mixed 4-*t*-butylcyclohexanecarboxylic acid. The remaining 33% of the distilled bromide, previously believed to be the *cis* isomer, seems to contain a third, unidentified component as well. The two extraneous components may be preferentially destroyed by treatment with base, leading to a purity of about 91% of the *trans* bromide. Futher purification can be effected[17] by prolonged treatment with base, albeit at the sacrifice of yield. A more convenient method of obtaining *trans* bromide of about 65% purity, also susceptible to purification by base treatment, was by the method recently developed by Wiley[18] using the action of triphenyldibromophosphorane, Ph_3PBr_2 on *trans*-4-*t*-butylcyclohexanol.

4-*t*-Butylcyclohexyl chlorides have previously been obtained[13] by treatment of 4-*t*-butylcyclohexanol with thionyl chloride and by thermal decomposition of 4-*t*-butylcyclohexyldimethylcarbinyl hypochlorites. We have now found that a more convenient method, from the preparative point of view, involves *trans*-4-*t*-butylcyclohexyl chloroformate, readily available from *trans*-4-*t*-butylcyclohexanol and phosgene, as an intermediate. Decomposition of the chloroformate in the presence of pyridine, in conformity with results reported in the literature,[30a] leads to complete inversion of configuration and the formation of pure *cis*-4-*t*-butylcyclohexyl chloride.[27] Starting with a 70:30 *trans–cis* mixture of 4-*t*-butylcyclohexanols interestingly leads to a chloride mixture containing 92% *cis* and only 8% *trans* isomer. Presumably the *cis*-chloride comes from the *trans*-chloroformate whereas the *cis*-chloroformate suffers preferential elimination and yields only little *trans*-chloride. Thermal decomposition of the *trans*-chloroformate proceeds by an SNi pathway[31] and leads largely to *trans*-chloride but not in as high epimeric purity,[30b] the product being contaminated with about 25% of the *cis* isomer. Final purification, in this case, was effected by preparative gas chromatography. In all conversions of chloroformate to chloride, whether pyridine induced or thermal, the chloride is formed along with an approximately

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(30) (a) A. J. H. Houssa and H. Phillips, *J. Chem. Soc.*, 2510 (1929); (b) *ibid.*, 108 (1932) (see also p 1232); K. B. Wiberg and T. M. Shryne, *J. Amer. Chem. Soc.*, 77, 2774 (1955); M. Matzner, R. P. Kurkjy, and R. J. Cotter, *Chem. Rev.*, 64, 645 (1964).

(31) Regarding mechanistic details, *cf.* E. L. Eliel in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p 79.

equimolar quantity of olefin. The 3-*t*-butylcyclohexyl chlorides had previously been obtained[14] only as an epimeric mixture by reaction of *t*-butyl chloride with cyclohexane in the presence of hydrogen fluoride or a Friedel–Crafts catalyst. This reaction involves rearrangement and does not lead to a pure product. In the present work the *trans*- and *cis*-3-*t*-butylcyclohexyl chlorides were prepared through the chloroformates exactly as their conformational analogs (the *cis*- and *trans*-4 isomers); the *trans* isomer was obtained essentially epimerically pure and the *cis* isomer was purified by preferential destruction of the contaminating *trans* (axial) material through reaction with thiophenolate.[32] Gas chromatography in this case led to partial dehydrohalogenation of the chlorides.[33,34]

The preparation of the 4-*t*-butylcyclohexyl fluorides is described in the accompanying paper[1] and the compounds in the 3 series were prepared analogously.

Since rearrangements may occur in the conversion of alcohols to halides, the structures of the 4-*t*-butylcyclohexyl chlorides here prepared were proved by conversion to the known[12] 4-*t*-butylcyclohexyl phenyl thioethers through treatment with thiophenoxide. Since this reaction involves inversion of configuration, it also serves to confirm the configuration of the starting materials, that of the product being known.[12] The structure and configuration of the 4-*t*-butylcyclohexyl bromides had been previously[32] proved in this fashion. The structure, homogeneity, and configuration of the 3-*t*-butylcyclohexyl chlorides was inferred from their gas-chromatographic behavior and the similarity of their infrared and nmr spectra with those of the conformationally analogous 4 isomers. The structure of the 4-*t*-butylcyclohexyl fluorides was established in the accompanying paper[1] and that of the 3 isomers was inferred by analogy.

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(32) *Cf.* E. L. Eliel and R. G. Haber, *J. Amer. Chem. Soc.*, 81, 1249 (1959), regarding the rates of reaction of the corresponding 4-*t*-butylcyclohexyl bromides with thiophenolate.

(33) It is not entirely clear whether the chlorides in the 3 series are more thermally sensitive or whether the column used in their attempted separation for unknown reasons behaved differently from that used for the 4 isomers.

(34) Note Added in Proof. After submission of this paper, an essentially identical synthesis of the 4-*t*-butylcyclohexyl chlorides was published by A. B. Foster, R. Jefferis, and J. M. Webber, *Carbohydrate Res.*, 4, 352 (1967).

Carbon-13 Magnetic Resonance. X.[1a] The Six-Membered Nitrogen Heterocycles and Their Cations[1b]

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Abstract: Carbon-13 chemical shift data on the azines and their protonated cations are presented. Simple additivity parameters were found to account for the effect of nitrogen protonation on the chemical shifts of α-, β-, and γ-carbon atoms. These parameters are highly reproducible with monoprotonation but deviate from additivity quite significantly for diprotonated species. A theoretical analysis of the chemical shift expression indicated that carbon-13 shifts are critically dependent on both charge-transfer features and a variation in the bond-order parameter. The upfield protonation parameter for the α-carbon is explained with a decrease in bonding between $N–C_\alpha$, while the β and γ parameters arise from charge polarization effects. Extended HMO wave functions were used to estimate the carbon-13 shifts. It was found that a protonated nitrogen must be made more electronegative than corresponding basic nitrogens if reasonable agreement between predicted and experimental results are to be obtained in all of the essential features.

Attempts to relate proton and carbon-13 chemical shifts with π-electron densities[2-8] and/or Hammett σ constants[9] in aromatic systems have been reported by several groups of workers. These approaches have been especially successful in accounting for the chemical shifts at the *para* position of monosubstituted benzenes where steric interactions are unimportant and where anisotropic magnetic field effects due to substituent groups are reduced to a negligible value by the remoteness of the substituent group. Reasonable correlations between π-electron densities and the proton chemical shift parameter have also been proposed[2-5] for nitrogen heterocycles where polarization of the π charge is quite

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(1) (a) Previous paper in this series: D. K. Dalling and D. M. Grant, *J. Amer. Chem. Soc.*, **89**, 6612 (1967). (b) Taken in part from the Ph.D. dissertation of R. J. Pugmire, University of Utah, June, 1966.

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