was recrystallized from heptane, (m.p. 45.4–46.0°). Commercial α,3,4-trichlorotoluene was fractionally distilled (b.p. 71° at 1 mm.). The chloromethylation procedure[10] was used in the preparation of α-chloro-4-methoxy-3-nitrotoluene, m.p. 87.0–87.6° (reported,[10] m.p. 85–86°).

α-4-Dichloro-3-nitrotoluene.—Commercial 4-chloro-3-nitrobenzaldehyde was reduced with sodium borohydride in aqueous dioxane to 4-chloro-3-nitrobenzyl alcohol, m.p. 63–64°.

Anal. Calcd. for $C_7H_6ClNO_3$: C, 44.8; H, 3.20. Found: C, 44.8; H, 3.34.

The alcohol was converted with thionyl chloride to the chloride, which was distilled in a Hickman still at 0.05 mm. at a bath temperature of 85° (n^{30}_{D} 1.5805).

Anal. Calcd. for $C_7H_5Cl_2NO_2$: C, 40.8; H, 2.43; Cl, 34.5. Found: C, 40.8; H, 2.38; Cl, 33.7.

α-Chloro-3,4-dinitrotoluene.—Commercial 3,4-dinitrotoluene was oxidized to 3,4-dinitrobenzoic acid,[11] and the latter was converted to the acid chloride using thionyl chloride. Sodium borohydride reduction of the acid chloride in 1,2-dimethoxyethane solution at 10° gave a low yield of impure 3,4-dinitrobenzyl alcohol, m.p. 55.5–57.0°.

Anal. Calcd. for $C_7H_6N_2O_5$: C, 42.5; H, 3.03. Found: C, 40.1; H, 1.95.

Treatment of the alcohol with thionyl chloride, followed by distillation of the product in a Hickman still at 0.05 mm. pressure and a bath temperature of 90° gave α-chloro-3,4-dinitrotoluene, n^{30}_{D} 1.5801.

Anal. Calcd. for $C_7H_5ClN_2O_4$: C, 38.8; H, 2.33; Cl, 16.4. Found: C, 39.4; H, 2.51; Cl, 16.5.

α-Chloro-*m*-nitro-*p*-xylene.—*p*-Tolualdehyde was nitrated[12] to give *m*-nitro-*p*-tolualdehyde, which was reduced with sodium borohydride to 4-methyl-3-nitrobenzyl alcohol, m.p. 42–43°.

Anal. Calcd. for $C_8H_9NO_3$: C, 57.5; H, 5.40. Found: C, 57.8; H, 5.44.

The alcohol and thionyl chloride reacted to produce α-chloro-*m*-nitro-*p*-xylene, which, after recrystallization from hexane melted at 47.0–47.8°; (reported,[13] m.p. 45°).

Kinetic Measurements.—The procedure used in the thiosulfate reactions is that previously described.[2] The solvolysis experiments were carried out in the following manner: in a 250-ml. volumetric flask, 125 ml. of water and approximately 115 ml. of (absolute) ethanol were thermally equilibrated at 60°. An 8-ml. sample of a solution, containing a known weight of the halogen compound (about 0.0013 mole) in ethanol was added, and ethanol was added to bring the total volume to 250 ml. Aliquots of 25 ml. were periodically withdrawn, diluted with cold water, and titrated with 0.02 *N* sodium hydroxide solution using a Sargent-Malmstadt titrator. The reactions were followed to 55–80% completion.

Acknowledgment.—This work was supported by National Science Foundation Grant NSF G-10033.

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[11] H. A. Sirks, *Rec. trav. chim.*, **27**, 221 (1908).

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Conformational Analysis. XXVII. The Conformers of 2-Fluorocyclohexanone[1,2]

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The syntheses and physical properties including dipole moments of *cis*- and *trans*-2-fluoro-4-*t*-butylcyclohexanone are described. From the dipole moment of 2-fluorocyclohexanone it was concluded that the compound is a mixture of equatorial and axial conformers, and that the former predominates in the mixture by an amount which varies with solvent from 52% in heptane to 85% in dioxane.

Previous papers have described the conformations of 2-chlorocyclohexanone,[3] 2-bromocyclohexanone,[4] and related compounds.[5] In each case *cis*-2-halo-4-*t*-butylcyclohexanone was used as a model which was considered to have the halogen exclusively equatorial, while the *trans* isomer had the halogen exclusively axial. Using these models it was possible to measure the equilibrium point in more flexible systems by various methods, most of which had been developed earlier by other workers, including ultraviolet spectra,[6] infrared spectra,[7] polarographic reduction,[8] rotatory dispersion,[9] and especially by dipole moment measurements.[10] The present work describes similar studies with the corresponding fluoroketones.

2-Fluorocyclohexanone (I) itself has been studied by Kende,[11] who has concluded from data of the kind mentioned above that there was no substantial percentage of the axial conformer in benzene solution at 35°. Qualitative support for this sugges-

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[1] Paper XXVI, N. L. Allinger and S. Greenberg, *J. Am. Chem. Soc.*, in press.

[2] This research was supported by the U. S. Army Research Office under Contract No. DA-20-018-ORD 22743.

[3] N. L. Allinger, J. Allinger, L. A. Freiberg, R. Czaja, and N. A. LeBel, *J. Am. Chem. Soc.*, **82**, 5876 (1960).

[4] N. L. Allinger, J. Allinger, and N. A. LeBel, *J. Am. Chem. Soc.*, **82**, 2926 (1960); J. Allinger and N. L. Allinger, *Tetrahedron*, **2**, 64 (1958); *J. Am. Chem. Soc.*, **80**, 5476 (1958).

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[9] C. Djerassi, "Optical Rotary Dispersion," McGraw-Hill Book Co., New York, 1960, p. 115.

[10] W. D. Kumler and A. C. Huitric, *J. Am. Chem. Soc.*, **78**, 3369 (1956).

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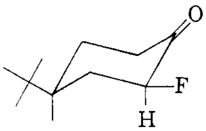
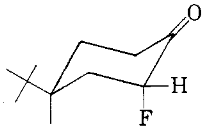
tion was obtained from the fact that equatorial fluoro ketones are generally isolated when prepared in basic solution under what would be expected to be equilibrating conditions.[12]

With suitable models such as the *t*-butyl compounds (II) available, it was known that quantitative measurements of the conformational equilibrium of 2-fluorocyclohexanone (I) could be undertaken. The synthesis of a mixture of the *cis* and *trans* isomers of II was therefore carried out by allowing the sodium salt of 2-hydroxymethylene-4-*t*-butylcyclohexanone to react with perchloryl fluoride in ethanol, according to the method of Kende. The mixture of isomers was separated by fractional distillation to yield a small amount (9%) of the liquid *trans* isomer, b.p. 67° (3.0 mm.), followed by a larger amount (54%) of the *cis* isomer, b.p. 101° (3.2 mm.), which was obtained crystalline, m.p. 41.5°. This order of volatility is as predicted by the dipole rule.[13]



IIe



IIa

The pure *trans* isomer of II was liquid at room temperature. On exposure to air the material was largely converted to a solid. After trituration with pentane the crystals were collected, m.p. 76.5°. This compound was shown to be a hydrate of the ketone by the analysis and the infrared spectrum [which showed a strong O—H stretching band at 2.98 μ (mull) and no C=O stretching absorption]. It slowly dissolved in boiling chloroform, presumably because of the azeotropic removal of water, and gave a solution the infrared spectrum of which was virtually identical with that of IIa in chloroform. The presence of electronegative groups α to a carbonyl is known to stabilize addition compounds such as hydrates.[14]

Calculation of the dipole moments of IIe and IIa proceeded as follows: The dipole moments of cyclohexanone and fluorocyclohexane are 3.06 and 1.94 D, respectively.[15] From the earlier geometrical analysis of the system (in which ideal bond lengths and bond angles were assumed)[16] it was known that the angles between the dipoles are 51° 54′ and 109° 51′, respectively, for IIe and IIa.

Because of the comparatively high polarizability of the carbonyl oxygen (0.84×10^{-24} cm.^{3}),[17] the moment induced in the carbonyl group of IIe by the neighboring C—F dipole must be taken into account. The value of the latter was arrived at by assuming that it would be the same as that induced by the C—Br bond in the analogous bromoketone, since an experimental value is available for that compound (0.17 D along the O—C bond).[10]

Since the polarizability[17] of fluorine (0.38×10^{-24} cm.^{3}) is the same as that of hydrogen (0.42×10^{-24} cm.^{3}), the oxygen would induce the same moment in the C—F and C—H bonds, and therefore the same value for the C—F moment (1.94 D) was used throughout the calculations.

The values calculated for the moments of the two isomers are given in Table I, together with the experimental value. The agreement is good and the assignment of configurations is unambiguous.

TABLE I

DIPOLE MOMENTS OF THE FLUOROCYCLOHEXANONES[a]

	Experimental			
Compound	Heptane	Benzene	Dioxane	Calcd.
IIa	...	2.95	...	3.00
IIe	4.37	4.35	4.39	4.35
I	3.76	4.09	4.20	...

[a] In Debye units at 25°.

The dipole moment of 2-fluorocyclohexanone, which was obtained by the method of Kende, was measured in different solvents. Taking the moments for Ie and Ia as equal to those for IIe and IIa, respectively, the per cent of each conformer in I was calculated for each solvent from the equation:

$$\mu^2_{\text{obs}} = N_a\mu_a^2 + N_e\mu_e^2$$

where N is the mole fraction. It is quite clear that for I the per cent of equatorial conformer increases with the increase in solvent polarity, and the numerical values are heptane 52%, benzene 77%, and dioxane 85%.

The infrared spectra of IIe and IIa were obtained in carbon tetrachloride solution, and they show carbonyl stretching bands which are shifted to higher frequency relative to that of 4-*t*-butylcyclohexanone itself by 27 cm.$^{-1}$ and 18 cm.$^{-1}$, respectively. The shift brought about by the equatorial fluorine is somewhat larger than for bromine (+15 to +22 cm.$^{-1}$) and chlorine (+18 to +25 cm.$^{-1}$), and the shift in the case of the axial epimer is likewise larger than that found for the bromo (−3 to +3 cm.$^{-1}$) and chloro (+2 to +9 cm.$^{-1}$) analogs.[18] The difference between the epimeric fluoro ketones is sufficiently small that conformational assignments by this method may not always be possible.

With 2-fluorocyclohexanone the high resolution infrared spectrum (in carbon tetrachloride) showed a maximum at 1739 cm.$^{-1}$ (+21 cm.$^{-1}$ from parent) with a shoulder at 1730 cm.$^{-1}$ (+12 cm.$^{-1}$). While no extensive studies were carried out regarding this absorption band, the obvious interpretation is that

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[13] N. L. Allinger, *J. Am. Chem. Soc.*, **79**, 3443 (1957).

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[18] E. G. Cummins and J. E. Page, *J. Chem. Soc.*, 3847 (1957).

the 1739-cm.$^{-1}$ maximum indicates the compound is largely in the equatorial conformation, while the shoulder shows a significant amount of the axial conformation is present.

The ultraviolet spectra of I and the epimers of II were examined in various solvents as listed in Table II. The axial compound absorbs at longer wave length than the equatorial, which absorbs at nearly the same place as the parent ketone. It is noteworthy that the extinction coefficients are about the same for both fluoro ketones and the parent compound, contrary to what is found with the chloro and bromo analogs. From the ultraviolet spectrum it appears that fluorocyclohexanone is predominantly in the equatorial form in each solvent, but it is concluded that the ultraviolet spectrum does not appear to be a very sensitive conformational test.

TABLE II

	Ultraviolet Spectra					
	Ethanol		Dioxane		Heptane	
Compound	λ^a	ϵ	λ	ϵ	λ	ϵ
4-*t*-Butylcyclohexanone	283	20	286	17	292	16
IIe	284	16	287	17	291	15
IIa	299	17	299	19	302	19
I	285	21	290	21	295	22

[a] In mμ.

These results, combined with those obtained earlier with other α-halo ketones, show there is an unmistakable trend for the halogen to prefer the axial position to the equatorial which increases as we proceed through the series: fluorine, chlorine, bromine. Attempts to explain this order in terms of classical interactions of dipolar forces have been unsuccessful.[3] Kosower has recently suggested[19] that this order results from the tendency for a nonbonding $2p$ electron on oxygen to be delocalized into the higher empty orbitals of the halogens. In a classical treatment of the problem such a delocalization would be included in the van der Waals interaction, and the only calculations made along these lines predict a stability order for the halogens which is opposite that observed. Since the experimental facts appear quite certain, one is forced to the conclusion that a classical treatment of the system is inadequate. A detailed quantum mechanical treatment is therefore being carried out which is aimed at properly accounting for the interactions of the halogens with the carbonyl system, and will enable quantitative predictions to be made regarding both the ultraviolet spectra and the relative stabilities. The results of this work will be reported later, and a discussion of these properties will be deferred until that time.

TABLE III

DIPOLE MOMENT DATA

N_2	d_{12}	ϵ_{12}
cis-2-Fluoro-4-*t*-butylcyclohexanone (IIe) in *n*-Heptane		
0.00000000	0.678979	1.9126
.00097492	.679349	1.9267
.00185588	...	1.9388
.00334044	.680208	1.9586
.00714494	.681711	2.0111
$\alpha = 13.739$, $\beta = 0.382$, $\epsilon_1 = 1.9130$, $d_1 = 0.67897$, $M_R = 46.06$, $P_{2\infty} = 437.1$, $\mu = 4.37 \pm 0.02$ D.		
cis-2-Fluoro-4-*t*-butylcyclohexanone (IIe) in Benzene		
0.00043369	0.873867	2.2838
.00114441	.874252	2.3033
.00247333	.874491	2.3381
.00301187	.875603	2.3537
$\alpha = 26.941$, $\beta = 0.705$, $\epsilon_1 = 2.2722$, $d_1 = 0.87331$, $M_R = 46.06$, $P_{2\infty} = 433.3$, $\mu = 4.35 \pm 0.04$ D.		
cis-2-Fluoro-4-*t*-butylcyclohexanone (IIe) in Dioxane		
0.00000000	1.028445	2.2122
.00038689	1.027918	...
.00084241	1.028338	2.2338
.00137692	...	2.2489
.00227593	1.028314	2.2729
$\alpha = 26.774$, $\beta = 0.000$, $\epsilon_1 = 2.2119$, $d_1 = 1.0282$, $M_R = 46.06$, $P_{2\infty} = 421.4$, $\mu = 4.39 \pm 0.04$ D.		
trans-2-Fluoro-4-*t*-butylcyclohexanone (IIa) in Benzene		
0.00000000	0.873671	2.2752
.00060493	.873804	2.2822
.00069141	.873876	2.2831
.00164812	.874133	2.2947
$\alpha = 11.866$; $\beta = 0.287$, $\epsilon_1 = 2.2751$, $d_1 = 0.87366$, $M_R = 46.06$, $P_{2\infty} = 224.2$, $\mu = 2.95 \pm 0.03$ D.		
2-Fluorocyclohexanone (I) in *n*-Heptane		
0.00000000	0.678975	1.9129
.90146222	.679328	1.9273
.00284536	.679795	1.9418
.00451486	.680231	1.9581
.00351499	.679894	1.9482
$\alpha = 10.053$, $\beta = 0.280$, $\epsilon_1 = 1.9128$, $d_1 = 0.67895$, $M_R = 27.47$, $P_{2\infty} = 316.4$, $\mu = 3.76 \pm 0.02$ D.		
2-Fluorocyclohexanone (I) in Benzene		
0.00000000	0.873744	2.2721
.00087032	.873986	2.2917
.00169386	.874170	2.3111
.00257231	.874260	2.3309
.00571067	.875412	2.4034
$\alpha = 23.012$, $\beta = 0.297$, $\epsilon_1 = 2.2719$, $d_1 = 0.87367$, $M_R = 27.47$, $P_{2\infty} = 368.7$, $\mu = 4.09 \pm 0.03$ D.		
2-Fluorocyclohexanone (I) in Dioxane		
0.00000000	1.028346	2.2104
.00128716	1.028483	2.2424
.00058443	1.028449	2.2256
.00214510	...	2.2633
.00270849	1.028652	2.2776
$\alpha = 24.653$, $\beta = 0.110$, $\epsilon_1 = 2.2107$, $d_1 = 1.0284$, $M_R = 27.47$, $P_{2\infty} = 387.2$, $\mu = 4.20 \pm 0.03$ D.		

Experimental

2-Fluorocyclohexanone (I).—2-Hydroxymethylenecyclohexanone[20] was converted to the desired product with perchloryl fluoride by the method outlined by Kende. The product was purified by simple distillation, followed by distillation through a 2-ft. Podbielniak type column. The

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[19] E. M. Kosower, G. Wu, and T. S. Sorensen, *J. Am. Chem. Soc.*, **83**, 3147 (1961).

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center fraction was a colorless liquid, b.p. 79° (12 mm.), $n^{25}\mathrm{D}$ 1.4420 (reported b.p. 76–77° (17 mm.)[11]; 83–83.5 (20 mm.)[21]; $n^{25}\mathrm{D}$ 1.4390,[11] $n^{25}\mathrm{D}$ 1.4432[21]). This material was twice redistilled, $n^{25}\mathrm{D}$ 1.4414. The infrared spectrum showed a sharp carbonyl maximum at 1739 cm.$^{-1}$ in carbon tetrachloride, and a shoulder at 1730 cm.$^{-1}$.

Anal. Calcd. for C_6H_9FO: C, 62.05; H, 7.81; F, 16.36. Found: C, 61.78; H, 7.90; F, 16.70.

***cis*- and *trans*-2-Fluoro-4-*t*-butylcyclohexanone (II).**—To an ice bath-cooled solution of 4.6 g. (0.200 g.-atom) of sodium dissolved in 300 ml. of absolute ethanol was added 36.4 g. (0.200 mole) of 2-(hydroxymethylene)-4-*t*-butylcyclohexanone with stirring. After several minutes gaseous perchloryl fluoride was passed through the yellow solution at a moderate rate with stirring and ice bath cooling until the *p*H of the mixture reached 7. During this period of time (*ca.* 0.5 hr.) a white solid precipitated. The mixture was poured into water and was extracted twice with ether. The combined ether extracts were washed twice with water and dried over anhydrous magnesium sulfate. The filtered solution was evaporated to dryness under reduced pressure and the residue was rapidly distilled three times under vacuum to yield 29.4 g. of virtually colorless liquid which was fractionally distilled through a 24-in. Podbielniak-type column with a partial reflux head. The initial fractions yielded 3.0 g. (9%) of *trans*-2-fluoro-4-*t*-butylcyclohexanone (IIa) as a colorless liquid, b.p. 67° (3.0 mm.), $n^{25}\mathrm{D}$ 1.4458. A center fraction of this material was rapidly distilled to yield a sample for analysis and dipole moment studies. It showed an infrared carbonyl maximum at 1734 cm.$^{-1}$ (carbon tetrachloride).

Anal. Calcd. for $C_{10}H_{17}FO$: C, 69.73; H, 9.95; F, 11.03. Found: C, 70.02; H, 10.00; F, 11.48.

After the collection of 2.8 g. of material from the intermediate fractions of the Podbielniak distillation, a total of 16.9 g. (49%) of *cis*-2-fluoro-4-*t*-butylcyclohexanone (IIe) was obtained as a virtually colorless liquid, b.p. 100.5–101° (3.2 mm.), $n^{25}\mathrm{D}$ 1.4558, which solidified on standing in the refrigerator. Several crystallizations from dry *n*-pentane with cooling yielded IIe as small white needles, m.p. 39.5–41.5°. It showed an infrared carbonyl maximum at 1743 cm.$^{-1}$ (carbon tetrachloride). In another run a yield of 54% of IIe was obtained.

Anal. Calcd. for $C_{10}H_{17}FO$: C, 69.73; H, 9.95; F, 11.03. Found: C, 69.92; H, 9.85; F, 11.35.

***trans*-2-Fluoro-4-*t*-butylcyclohexanone Hydrate.**—*trans*-2-Fluoro-4-*t*-butylcyclohexanone, 0.30 g. (0.0017 mole), was partially converted to a solid upon exposure to the air for several hours. A total of 0.22 g. (67%) of hydrate was obtained on filtration with dry *n*-pentane, m.p. 74.5–76.5°. It did not show a carbonyl maximum in the infrared but did show a broad O—H band at 2.98 μ (mull).

Anal. Calcd. for $C_{10}H_{19}FO_2$: C, 63.13; H, 10.07; F, 9.99. Found: C, 63.25; H, 9.95; F, 9.79.

Measurements of Dipole Moments.—The dipole moment apparatus used has been previously described.[22] The dipole moments were measured at 25° and the calculations were carried out by essentially the method of Halverstadt and Kumler[23] utilizing an IBM 650 computer programmed as described earlier.[24] Atomic polarization was neglected. The data are summarized in Table III.

Acknowledgment.—The authors are indebted to Miss M. A. DaRooge for determining the dipole moments reported in this paper, and would also like to thank Dr. A. S. Kende and Dr. E. M. Kosower for helpful discussion.

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Stereospecific Synthesis of *p*-Bornyl- and *p*-Isobornylphenol

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The synthesis of *p*-bornylphenol (I) and *p*-isobornylphenol (II) from camphor is described. Reaction of camphor and *p*-anisylmagnesium bromide afforded *p*-anisylborneol (VI, 26%), which was dehydrated solely to *p*-anisylbornylene (VII, 91%) with 0.3% boron trifluoride etherate in ether. Hydrogenation of VII in the presence of a sponge nickel catalyst afforded isobornylanisole (IX, 72%) exclusively, while chemical reduction with sodium in liquid ammonia gave bornylanisole (VIII, 94%), exclusively. The ethers VIII and IX were converted to the corresponding phenols I and II by fusion with pyridine hydrochloride. The stereochemical configurations of the products were confirmed by an independent unambiguous synthesis of the *endo* isomer I.

The formation in varying proportions of the two epimeric phenols—*p*-bornyl-(I)- or *p*-isobornyl-(II)-phenol from condensation of camphene, pinene, bornene, and related terpenes with phenol has been reported by numerous investigators.[1–9] The *p*-isobornyl- or *p*-bornylphenol structures were

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