Anal. Calcd for $C_{12}H_9Cl_3$: C, 55.53; H, 3.50; Cl, 40.98. Found: C, 55.55; H, 3.52; Cl, 40.87.

Crystal Data. Single crystals of trichloropentacyclododecadiene, $C_{12}H_9Cl_3$, were obtained by slow evaporation of solvent from ethanol solution. The crystals were needles along the *b* axis with prominent forms {010} and {101}. Zero and higher level layer Weissenberg photographs about the *b* axis revealed systematic absences for which the space group was uniquely determined as *Pcab*. Accurate lattice parameters were determined by a least-squares analysis of 20 measurements with a General Electric quarter circle goniostat on an XRD-5 diffractometer. A density measurement of the crystals was made by flotation. There are eight units of $C_{12}H_9Cl_3$ per unit cell. A summary of crystal data is given in Table IV.

Table IV.

$a = 25.56 \pm 0.01$ Å	Habit
$b = 12.148 \pm 0.003$ Å	Needles along *b*
$c = 7.234 \pm 0.002$ Å	Prominent forms {010}, {101}
$\lambda(\text{Cu K}\bar{\alpha}) = 1.5418$ Å	Absences
$V = 2246$ Å^3	$0kl;\ l = 2n + 1$
$\rho_{\text{calcd}} = 1.534$ g cm^{-3}	$h0l;\ h = 2n + 1$
$\rho_{\text{measd}} = 1.539$ g cm^{-3}	$hk0;\ k = 2n + 1$
$Z = 8$	Space group: *Pcab*

Intensity Measurements. Bragg intensities were measured on an XRD-5 G.E. diffractometer with Nb-filtered Mo K$\bar{\alpha}$ radiation. The compound has a substantial vapor pressure; therefore, the crystal was coated with epoxy resin. As a result the background scatter was rather large and contributed strongly to an unfavorable signal to noise ratio for a number of weak reflections. Radiation damage was severe during data collection. Standard intensities changed systematically by as much as 50%. Data were collected for two crystals. A third set was collected with Cu K$\bar{\alpha}$ radiation, but in this case radiation damage was intolerable; the crystal became a powder within 24 hr. The Mo K$\bar{\alpha}$ radiation damage from these measurements dramatically limits the final accuracy of the structure. Diffraction intensity measurements were restricted to the upper octant (the crystal was mounted along b^*). The 2θ scan technique was employed.[25] Data were collected out to $2\theta = 42°$ ($\sin\theta/\lambda = 0.5$ Å^{-1}). Three standard reflections were measured every hour. It was found that the different standards exhibited similar decreases in the net counts.

A quadratic function of time was determined from the distribution of standard reflections. The empirical curve was then used to scale the measured intensities as a function of their sequence. The procedure used here assumes that the standards are representative of the effect of radiation damage to the true structure factors. A preferable treatment has been reported by Ibers[26] where a scale factor for all reflections was given a quadratic time dependence and the corresponding parameters were refined along with the atomic structural parameters. At the time this structure was refined, however, the Ibers' procedure was not known to us. Although the conventional *R* factor would be probably lower by such a treatment, the gross structural results would indeed be the same. The intensity data of the two crystals were put on the same relative scale according to the method of Hamilton, *et al.*[27] Only reflections with net intensities 1.4 times the estimated standard error were used for the crystal structure analysis. Altogether 520 reflections were selected. The weights for each reflection were estimated by the procedure of Stewart and Jensen.[28,29]

Acknowledgments. This work was supported by the National Science Foundation. Spectra were obtained in the Nmr Facility for Biomedical Research (National Institutes of Health Grant No. FR-00292). The technical assistance of Miss Linda Hood and Miss Grazina Maciunas is gratefully acknowledged.

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[24] Spectrum taken on a Varian HA-100 spectrometer operating in the frequency sweep mode.

[25] L. E. Alexander and G. S. Smith, *Acta Crystallogr.*, **17**, 1195 (1964).

[26] J. A. Ibers, *ibid.*, *Sect. B*, **25**, 1667 (1969).

[27] W. C. Hamilton, J. S. Rollett, and R. A. Sparks, *ibid.*, **18**, 129 (1965).

[28] R. F. Stewart and L. H. Jensen, *Z. Kristallogr.*, *Kristallgeometrie, Kristallphys.*, *Kristallchem.*, **128**, 133 (1969).

[29] Listings of structure factors will appear following these pages in the microfilm edition of this volume of the Journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by citing code no. JACS-94-2015. Remit $3.00 for photocopy or $2.00 for microfiche.

Nuclear Magnetic Resonance Spectroscopy. Ring Inversion in 1,1-Difluorocyclodecane[1]

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Abstract: Rates of ring inversion of 1,1-difluorocyclodecane were obtained from line-shape changes in the low-temperature ^{19}F nmr spectra. At −135°, the free energy of activation was 5.7 kcal/mol. The results are interpreted in terms of a boat–chair–boat conformation. Possible pathways for effecting ring inversion are discussed.

Although nmr spectroscopy has been found to be well suited for conformational studies of many cyclic compounds,[3] this method has been used in relatively few cases for the investigation of ten-membered rings. Compounds which have been studied include *trans*-cyclodecene-d_6[4] and several *cis,cis*-1,6-cyclodecadienes.[5] The temperature dependence of the nmr spec-

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[1] Supported by the National Science Foundation.

[2] Summer National Science Foundation Fellow, 1966 and 1968; National Defense Education Act Trainee, 1968–1969.

[3] For recent reviews, see (a) G. Binsch, *Top. Stereochem.*, **3**, 97 (1968); and (b) W. A. Thomas, *Nucl. Magn. Resonance Spectrosc.*, **1**, 43 (1968).

[4] G. Binsch and J. D. Roberts, *J. Amer. Chem. Soc.*, **87**, 5157 (1965).

[5] (a) B. W. Roberts, J. J. Vollmer, and K. L. Servis, *ibid.*, **90**, 5264 (1968); (b) J. J. Vollmer, Ph.D. Thesis, University of Southern California, 1968; (c) J. Dale, T. Ekeland, and J. Schaug, *Chem. Commun.*, 1477 (1968); (d) A. Feigenbaum and J.-M. Lehn, *Bull. Soc. Chim. Fr.*, 3724 (1969).

tra of several ten-membered rings, rather highly substituted with methyl groups, has been discussed briefly.[6] In the work to be described here, we have used the fluorine-labeling technique[7] to obtain information about the conformational properties of cyclodecane in solution.

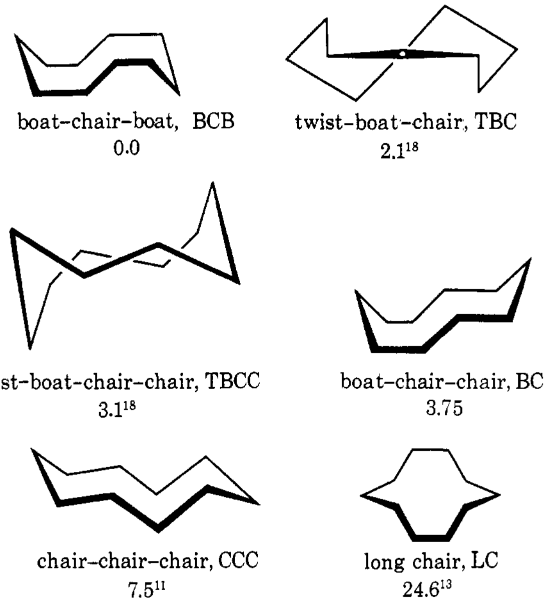
Most of the experimental evidence for the preferred conformation of cyclodecane has come from X-ray diffraction studies of a number of crystalline derivatives.[8] In each case,[9] the ring conformation was the boat–chair–boat (BCB) form. The finding of a single conformation for rings possessing different symmetries and different numbers of substituents implies that this form represents a significant minimum in energy for unsubstituted cyclodecane.


boat–chair–boat
(BCB)

Additional evidence in favor of preference for the boat–chair–boat conformation has come from strain-energy calculations.[10-17] Several conformations for which calculations have been performed are shown in Chart I. Of the conformations for which estimates of the strain energies are available, the TBC and TBCC conformations with energies of 2.1 and 3.1 kcal/mol are closest in energy to the BCB form. Experimental evidence for this order of stability and for the values of the TBC and TBCC strain energies has been obtained.[9,18]

A study of the temperature dependence of the ^{19}F nmr spectrum of 1,1-difluorocyclodecane was undertaken to provide information about the conformations of cyclodecane in solution and the rates of interconversion of substituent positions. *gem*-Fluorides can generally be prepared by treatment of the corresponding ketones with a mixture of sulfur tetrafluoride and hydrogen fluoride,[19,20] but this reaction usually does not work well for the medium-ring ketones. 1,1-Difluorocyclooctane was isolated in only 9% yield from treatment of cyclooctanone with phenylsulfur trifluoride[21] and in 0.5% yield with sulfur tetrafluoride as the fluorinating agent.[22] Attempts to prepare 1,1-difluorocyclodecane by fluorination of cyclodecanone with either sulfur tetrafluoride or phenylsulfur trifluoride were unsuccessful.[23] The lower reactivity of cyclodecanone, relative to cyclooctanone, can be anticipated on the basis of the relative rates and equilibrium constants for other reactions[24,25] of these ketones in which the trigonal carbon is converted into a tetrasubstituted carbon. Electron-withdrawing groups adjacent to a carbonyl group enhance the tendency of carbonyl compounds to undergo addition reactions, and it was anticipated that the presence of an electron-withdrawing substituent adjacent to the carbonyl group in cyclodecanone should facilitate the conversion to the difluoride. A synthesis of 1,1-difluorocyclodecane, based on this idea, is outlined in Scheme I.

Chart I. Conformations of Cyclodecane and Strain Energies[a]


boat–chair–boat, BCB
0.0

twist-boat–chair, TBC
2.1[18]

twist-boat–chair–chair, TBCC
3.1[18]

boat–chair–chair, BCC
3.75

chair–chair–chair, CCC
7.5[11]

long chair, LC
24.6[13]

[a] In kilocalories per mole, relative to the BCB form. The BCC strain energy shown is half that of the CCC form;[11] this relationship was found in Hendrickson's earlier work.[10] The system of nomenclature is that of Hendrickson.[13]

The key step which introduced the *gem*-fluoro group into the ten-membered ring was the fluorination of sebacoin tosylate with a mixture of sulfur tetrafluoride and hydrogen fluoride. The tosylate group in **3** appears to increase the reactivity of the carbonyl group toward the fluorinating agent; the low yield of difluoro tosylate (14%) is nevertheless higher than the yields obtained[21,22] in the fluorination of cyclooctanone.

3,3-Difluoro-*trans*-cyclodecene was prepared in 42% yield by treatment of the tosylate with potassium *tert*-butoxide in *tert*-butyl alcohol. The cycloalkene was

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(6) C. Cordes, V. Prelog, E. Troxler, and H. H. Westen, *Helv. Chim. Acta*, **51**, 1663 (1968).

(7) J. D. Roberts, *Chem. Brit.*, **2**, 529 (1966), and later papers. The application of this technique to the conformational study of cyclooctane has been described: J. E. Anderson, E. S. Glazer, D. L. Griffith, R. Knorr, and J. D. Roberts, *J. Amer. Chem. Soc.*, **91**, 1386 (1969).

(8) (a) For a review, see J. D. Dunitz in "Perspectives in Structural Chemistry," Vol. 2, J. D. Dunitz and J. A. Ibers, Ed., Wiley, New York, N. Y., 1968, p 1; (b) *trans*-1,6-diaminocyclodecane dihydrochloride: E. Huber-Buser and J. D. Dunitz, *Helv. Chim. Acta*, **43**, 760 (1960); **44**, 2027 (1961); **49**, 1821 (1966); (c) *cis*-1,6-diaminocyclodecane dihydrochloride dihydrate: J. D. Dunitz and K. Venkatesan, *ibid.*, **44**, 2033 (1961); (d) cyclodecylamine hydrochloride sesquihydrate: W. Nowacki and M. H. Mladeck, *Chimia*, **15**, 531 (1961); M. H. Mladeck and W. Nowacki, *Helv. Chim. Acta*, **47**, 1280 (1964); (e) *trans*-1,6-dibromocyclodecane: J. D. Dunitz and H. P. Weber, *ibid.*, **47**, 951 (1964); (f) 1-hydroxycyclodecyl dimethyl phosphonate: G. Samuel and R. Weiss, *Tetrahedron*, **26**, 3005 (1970); (g) *trans*-1,6-dihydroxycyclodecane: O. Ermer and J. D. Dunitz, *Chem. Commun.*, **4**, 178 (1971).

(9) 1,1,5,5-Tetramethylcyclodecane-8-carboxylic acid exists in the solid state as a mixture of TBC and TBCC conformations: J. D. Dunitz, H. Eser, M. Bixon, and S. Lifson, *Helv. Chim. Acta*, **50**, 1572 (1967). The failure of this compound to adopt the boat–chair–boat conformation is easily rationalized.

(10) J. B. Hendrickson, *J. Amer. Chem. Soc.*, **86**, 4854 (1964).

(11) J. B. Hendrickson, *ibid.*, **89**, 7036 (1967).

(12) J. B. Hendrickson, *ibid.*, **89**, 7043 (1967).

(13) J. B. Hendrickson, *ibid.*, **89**, 7047 (1967).

(14) K. B. Wiberg, *J. Amer. Chem. Soc.*, **87**, 1070 (1965).

(15) M. Bixon and S. Lifson, *Tetrahedron*, **23**, 769 (1967).

(16) N. L. Allinger, J. A. Hirsch, M. A. Miller, I. J. Tyminski, and F. A. Van-Catledge, *J. Amer. Chem. Soc.*, **90**, 1199 (1968).

(17) N. L. Allinger, M. T. Tribble, M. A. Miller, and D. H. Wertz, *ibid.*, **93**, 1637 (1971).

(18) M. Bixon, H. Dekker, J. D. Dunitz, H. Eser, S. Lifson, C. Mosselman, J. Sicher, and M. Svoboda, *Chem.Commun.*, 360 (1967).

(19) W. R. Hasek, W. C. Smith, and V. A. Englehardt, *J. Amer. Chem. Soc.*, **82**, 543 (1960).

(20) D. G. Martin and F. Kagan, *J. Org. Chem.*, **27**, 3164 (1962).

(21) J. E. Anderson, E. S. Glazer, D. L. Griffith, R. Knorr, and J. D. Roberts, *J. Amer. Chem. Soc.*, **91**, 1386 (1969).

(22) D. R. Strobach and G. A. Boswell, Jr., *J. Org. Chem.*, **36**, 818 (1971).

(23) E. S. Glazer and J. D. Roberts, unpublished work.

(24) V. Prelog and M. Kobelt, *Helv. Chim. Acta*, **32**, 1187 (1949).

(25) H. C. Brown and K. Ichikawa, *Tetrahedron*, **1**, 221 (1957).

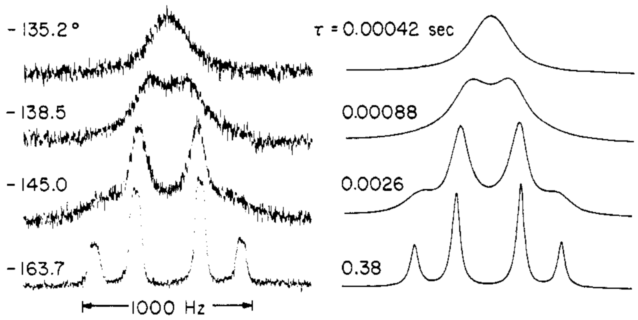


Figure 1. Experimental fluorine nmr spectra (left) of 1,1-difluorocyclodecane in vinyl chloride. On the right are spectra calculated as a function of τ, the mean lifetime before ring inversion.

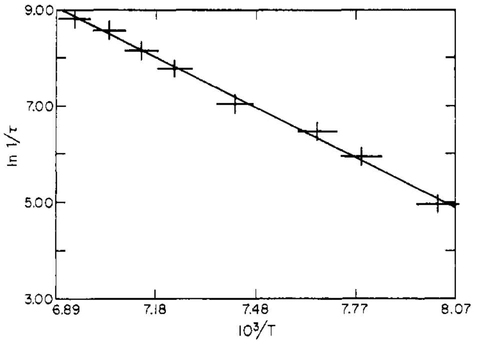
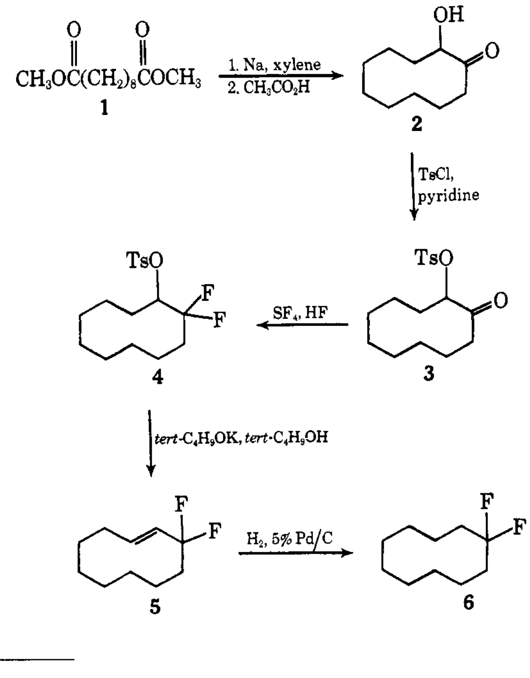


Figure 2. Arrhenius plot for 1,1-difluorocyclodecane.

assigned the trans configuration on the basis of a strong band at 985 cm^{-1} in the infrared spectrum. The trans configuration can also be rationalized as a consequence of the method of synthesis,[26] and the variation with temperature of the ^{19}F nmr spectrum[27] provides further evidence for this configuration.

Scheme I. Synthesis of 3,3-Difluoro-*trans*-cyclodecene and 1,1-Difluorocyclodecane



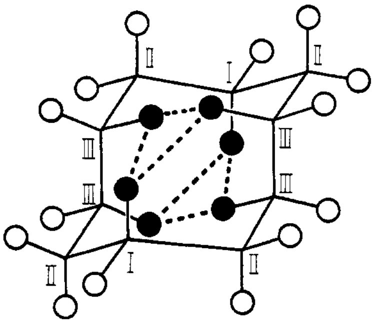


Figure 3. BCB cyclodecane: types of carbons and intraannular (●) and extraannular (○) substituent positions. The mirror plane of symmetry passes through the two carbons of type I. An axis of symmetry bisects the two bonds connecting the type-III carbons.

Experimental Results

The ambient-temperature ^{19}F nmr spectrum of a vinyl chloride solution of 1,1-difluorocyclodecane is a quintet centered 23.24 ppm upfield from internal ethyl chlorodifluoroacetate, with $^3J_{HF}$ = 15.5 Hz. The spectrum broadens below $-129°$ and splits into an AB quartet with a chemical-shift difference of 577 Hz and $^2J_{FF}$ = 243 Hz at $-164°$. Exchange rates between -129 and $-149°$ were determined by comparison of experimental spectra with theoretical spectra calculated as a function of τ, the preexchange lifetime (see Experimental Section). The chemical-shift difference was assumed to decrease by 0.87 Hz per degree rise in temperature.

A proton-decoupled ^{19}F nmr spectrum[28] taken at 94.1 MHz under conditions of slow exchange showed only a simple AB pattern, providing confirmation that only two different fluorine chemical shifts are present.

Representative spectra and an Arrhenius plot of ln $1/\tau$ *vs.* $10^3/T$ are shown in Figures 1 and 2. The activation energy and frequency factor were determined by a least-squares treatment[29] to be $E_a = 7.0 \pm 0.2$ kcal/mol and $\log A = 14.45 \pm 0.35$. At $-135°$, the free energy of activation was 5.74 kcal/mol, and the entropy of activation was 7.1 eu.

Discussion

The three types of carbons in BCB cyclodecane have frequently been labeled I, II, and III, as shown in Figure 3. Six substituent positions are associated with the three kinds of carbons. The positions denoted by an open circle have been referred to as "extraannular"; the others, "intraannular." The six intraannular positions, which form two parallel planes above and below the ring, have severe nonbonded interactions and will be avoided, if possible, by substituents larger than hydrogen.

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[26] E. A. Noe, Ph.D. Thesis, California Institute of Technology, 1971.

[27] E. A. Noe, R. C. Wheland, E. S. Glazer, and J. D. Roberts, *J. Amer. Chem. Soc.*, in press.

[28] We are indebted to Professor Kenneth L. Servis of the University of Southern California for the use of the Varian HA-100 spectrometer and NMR Specialties Model HD-60 decoupler, and for assistance in their operation.

[29] Determinations of the values of E_a and $\Delta S^{\ddagger}$ by nmr spectroscopy are known[30] to be subject to systematic errors, and the uncertainty in E_a is probably not well represented by the root-mean-square error. The potentially most serious source of error in the determination of the activation energy may be the use of the phenomenological T_2 (see Experimental Section). The free energy of activation is estimated to be accurate to ±0.2 kcal/mol.

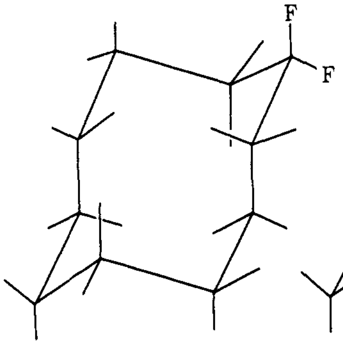
[30] A. Allerhand, H. S. Gutowsky, J. Jonas, and R. A. Meinzer, *J. Amer. Chem. Soc.*, **88**, 3185 (1966).

Table I. ^{19}F Nmr Parameters of Some Difluorocycloalkanes[a]

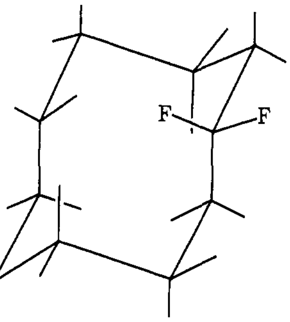
Compound	ν_1	ν_2	$\Delta\nu_{FF}$	J_{FF}	J_{HF}	Ref
1,1-Difluorocyclodecane	808[b]	1385[b]	577	243	15.5	This work
1,1-Difluorocyclooctane[c]			806	240	15.1	*f*
			940	245		
1,1-Difluorocycloheptane					15.5	*g*
1,1-Difluoro-4,4-dimethylcycloheptane			841	237	15.1	*g*
1,1-Difluorocyclohexane	1174[d]	2037[d]	863	231		This work
	638[e]	1522[e]	884	237	12.0	*h*

[a] All values are in hertz, at 56.4 MHz. [b] At −164°, relative to $CF_2ClCO_2C_2H_5$ (internal standard), for a 13% (v/v) solution in vinyl chloride. [c] Two AB's are present for 1,1-difluorocyclooctane at −175°. The smaller values of J_{FF} and $\Delta\nu$ are associated with the major conformation. [d] At −155°, relative to $CF_2ClCO_2C_2H_5$ (internal standard), for a 13% (v/v) solution in vinyl chloride. [e] Relative to CF_3CO_2H (internal standard), for a 1:3 solution in propene. [f] Reference 21. [g] E. S. Glazer, Ph.D. Thesis, California Institute of Technology, 1966. [h] Reference 33.

The observation of a single AB pattern for the ^{19}F nmr spectrum of 1,1-difluorocyclodecane at −164° is consistent with conformation **7** (and its mirror image). Conformations **8** and **9** would place one of the fluorines in an intraannular position, and should not be significantly populated at this temperature. A similar situation was observed[21] for 1,1-difluorocyclooctane, except that here, two of five possible boat–chair conformations, **10** and **11**, were appreciably populated at −175°.



7



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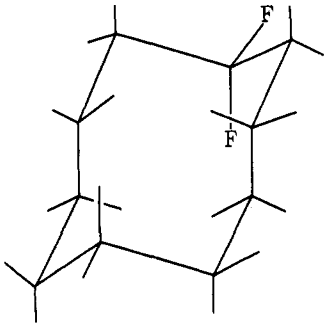

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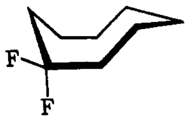

10

11

The two peaks at higher field in the slow-exchange ^{19}F nmr spectra of difluorocycloalkanes generally arise from the axial fluorine.[21,31–33] Only in the case of 1,1,2,2-tetrafluorocyclohexane[33] have the signals at higher field been assigned to the equatorial fluorine. Assignment of the peaks to specific fluorines has been based on the relative line widths, which are usually determined by the extent of coupling to the adjacent protons. The Karplus relationship between dihedral angle and vicinal hydrogen–hydrogen coupling constant appears to be qualitatively applicable to hydrogen–fluorine couplings;[34] as a consequence, in 1,1-difluorocyclohexane and other compounds having similar hydrogen–fluorine dihedral angles, the axial fluorine is more strongly coupled to the adjacent hydrogens and gives rise to considerably broader signals.[21,31–33]

In 1,1-difluorocyclodecane, the two low-field peaks are slightly broader than the high-field peaks. The fact that the peak widths are similar for the axial and equatorial fluorines appears reasonable on examination of a model. Large coupling constants are probably associated with the I-axial hydrogen and the axial fluorine, and with the III-axial hydrogen and the equatorial fluorine. Each of the fluorines will be coupled less strongly to the three remaining hydrogens. Because the line widths for the equatorial and axial fluorines do not differ greatly, there is at present no firm basis for assignment of peaks to specific fluorines.

Spectral parameters for several *gem*-fluorides are compared in Table I. The H–F coupling constants are average values taken from the ambient-temperature ^{19}F nmr spectra. The values of J_{HF} for the seven-, eight-, and ten-membered rings are similar and are larger than for 1,1-difluorocyclohexane. The fluorine–fluorine coupling constants are slightly larger in the medium-ring difluorides. A point of interest in connection with **7** is the more or less "normal" $\Delta\nu_{FF}$ for axial and equatorial *gem*-fluorines, despite the almost identical local environments of the fluorines; *i.e.*, the atoms within three bonds of the fluorines are not only identical, but are also in similar, although not identical, steric relationships. Furthermore, each fluorine has a 1,3-diaxial-type interaction with a hydrogen four bonds away. The nearest major point of difference between the environments of these fluorines is the planar *W* configuration of the axial fluorine with a carbon four bonds away, while the equatorial fluorine lies in a planar *W* configuration with a proton four bonds away. Because of the latter arrangement, there may be a moderate long-range H–F coupling, which could make the equatorial resonance somewhat broader than the axial resonance.

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(31) K. Nagarajan and J. D. Roberts, unpublished; see *Angew. Chem.*, **75**, 20 (1963); *Angew. Chem., Int. Ed. Engl.*, **2**, 53 (1963).

(32) J. T. C. Gerig and J. D. Roberts, *J. Amer. Chem. Soc.*, **88**, 2791 (1966).

(33) A. L. Spassov, D. L. Griffith, E. S. Glazer, K. Nagarajan, and J. D. Roberts, *ibid.*, **89**, 88 (1967).

(34) K. L. Williamson, Y.-F. L. Hsu, F. H. Hall, S. Swager, and M. S. Coulter, *ibid.*, **90**, 6717 (1968), and references therein.

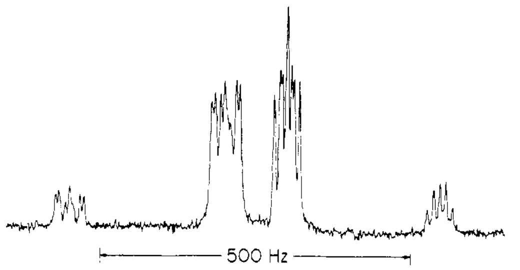
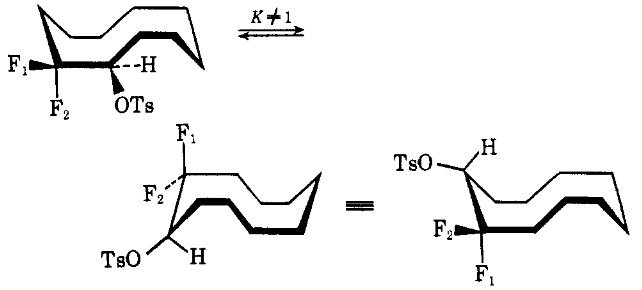


Figure 4. Ambient-temperature ^{19}F nmr spectrum of 1-(*p*-toluenesulfonyloxy)-2,2-difluorocyclodecane. The spectrum was obtained by summing 14 scans on a Varian C-1024 computer.

The ^{19}F nmr spectrum of 1-(*p*-toluenesulfonyloxy)-2,2-difluorocyclodecane (Figure 4) resembles the spectrum of 1,1-difluorocyclodecane with respect to the relative line widths of the signals from axial and equatorial fluorines. The chemical-shift difference was 241 Hz; J_{FF} was 248 Hz. The spectrum can be interpreted in terms of a rapidly equilibrating mixture of the following two conformations, which are the only two structures that do not place a substituent in one of the intraannular positions. The relative line widths for the difluoro tosylate and 1,1-difluorocyclodecane would be expected to be similar because in both conformations the OTs group replaces a hydrogen gauche to each fluorine.

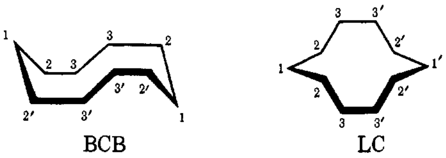


Two AB's in a ratio of about 60:40 were found[35] for the low-temperature ^{19}F nmr spectrum of 1-(*p*-toluenesulfonyloxy)-2,2-difluorocyclohexane. The major AB quartet ($\Delta\nu_{FF}$ = 906 Hz) was tentatively assigned to the conformation with the OTs group equatorial. The minor AB had a chemical-shift difference of 390 Hz. If the assignments are correct, then the conformation with the tosylate group gauche to each fluorine has a larger chemical-shift difference than unsubstituted 1,1-difluorocyclohexane, and a similar situation might be expected for the ten-membered difluoro tosylate. The fact that the chemical-shift difference for the AB pattern in Figure 4 is smaller than for 1,1-difluorocyclodecane can be rationalized in terms of an equilibrium mixture of the two conformations, because a fluorine which is axial in one conformation is equatorial in the other. An energy difference of only 0.4 kcal/mol (0.6 *vs.* 0.2) was calculated[12] for methyl substitution at the I and III equatorial positions of cyclodecane. Even if this difference is low by a factor of two or three (which is possible), there would still be an appreciable amount of the conformation with the tosylate group in the Ie position. Also, the equatorial–axial energy difference for cyclohexyl tosylate (ΔG = 0.515 kcal/mol)[36] is smaller than for methylcyclohexane ($\Delta G \sim 1.7$ kcal/mol).[37]

The activation energy for ring inversion in 1,1-difluorocyclodecane provides an experimental barrier with which the calculated barriers for various ways of accomplishing ring inversion in cyclodecane can be compared.

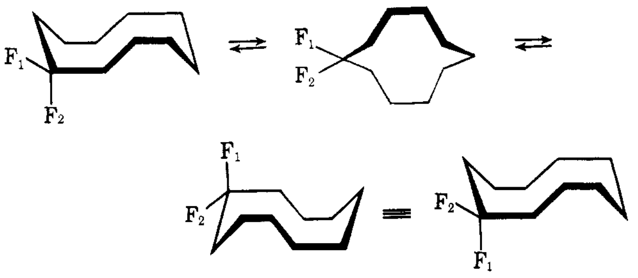
Pseudorotation of the BCB conformation is the simplest way of interconverting substituent positions in cyclodecane. The pseudorotation itinerary of this conformation has been described[13] and is reproduced in Chart II. Interconversion of axial and equatorial fluorine positions in 1,1-difluorocyclodecane by this pathway is shown in Scheme II. An unusual feature of the pseudorotation itinerary is that the BCB form is its own pseudorotation partner. A substituent assumes in sequence the various possible positions on passing through alternate BCB conformations. Although the LC and BCB conformations alternate in the course of pseudorotation, they are not considered pseudorotation partners. As in the case of the BCB form, LC cyclodecane pseudorotates with itself.

Chart II. Numbering System and Pseudorotation Itinerary for BCB and LC Cyclodecane



BCB 1e $\rightleftharpoons$ LC 2′e $\rightleftharpoons$ BCB 3′e $\rightleftharpoons$
LC 3′e $\rightleftharpoons$ BCB 2e $\rightleftharpoons$ LC 1 $\rightleftharpoons$
BCB 2a $\rightleftharpoons$ LC 3′a $\rightleftharpoons$ BCB 3′a $\rightleftharpoons$
LC 2′a $\rightleftharpoons$ BCB 1a $\rightleftharpoons$ LC 2a $\rightleftharpoons$
BCB 3a $\rightleftharpoons$ LC 3a $\rightleftharpoons$ BCB 2′a $\rightleftharpoons$
LC 1′ $\rightleftharpoons$ BCB 2′e $\rightleftharpoons$ LC 3e $\rightleftharpoons$
BCB 3e $\rightleftharpoons$ LC 2e $\rightleftharpoons$ BCB 1e $\rightleftharpoons$ . . .

Scheme II. Interconversion of Equatorial and Axial Fluorine Positions in 1,1-Difluorocyclodecane by Pseudorotation



The calculated strain energy of the LC conformation[13] was 24.6 kcal/mol, relative to BCB cyclodecane. This value is considerably higher than the free energy of activation[38] for ring inversion in 1,1-difluorocyclodecane (5.7 kcal/mol), which suggests that the LC form is not an intermediate in the interconversion of substituent positions in cyclodecane.

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[35] K. Grohmann and J. D. Roberts, unpublished work.

[36] F. R. Jensen, C. H. Bushweller, and B. H. Beck, *J. Amer. Chem. Soc.*, **91**, 344 (1969).

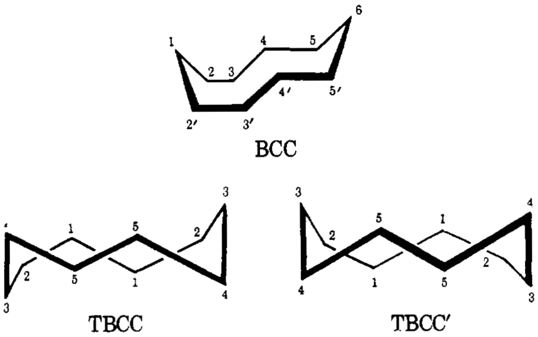
[37] E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience, New York, N. Y., 1965, pp 44, 439–440.

[38] The free energy of activation is used here because of the uncertainty in E_a.

Because the TBC and TBCC conformations of cyclodecane (Chart I) appear to be closest in energy to the BCB form, it is of interest to examine whether these conformations can be used in a low-energy pathway for interconversion of substituent positions in cyclodecane.

Two separate pseudorotation itineraries are required for each of these conformations; the itineraries for BCC–TBCC cyclodecane are given in Chart III. Equilibration of BCB and BCC conformations can be accomplished by flipping one of the methylene groups, maintaining the plane of symmetry which is present in both conformations. The BCB and TBCC conformations are interconverted by rotation of a carbon–carbon bond through the ring. The bonds which can be rotated to equilibrate these conformations are intersected by the symmetry axis, which is maintained during the process.

Chart III. Pseudorotation of BCC Cyclodecane.[a]



I BCC 1a $\rightleftharpoons$ TBCC 1a $\rightleftharpoons$ BCC 2a $\rightleftharpoons$
TBCC′ 2e $\rightleftharpoons$ BCC 3′e $\rightleftharpoons$ TBCC 3e $\rightleftharpoons$
BCC 4e $\rightleftharpoons$ TBCC′ 4e $\rightleftharpoons$ BCC 5′e $\rightleftharpoons$
TBCC 5e $\rightleftharpoons$ BCC 6e $\rightleftharpoons$ TBCC′ 5e $\rightleftharpoons$
BCC 5e $\rightleftharpoons$ TBCC 4e $\rightleftharpoons$ BCC 4′e $\rightleftharpoons$
TBCC′ 3e $\rightleftharpoons$ BCC 3e $\rightleftharpoons$ TBCC 2e $\rightleftharpoons$
BCC 2′a $\rightleftharpoons$ TBCC′ 1a $\rightleftharpoons$ BCC 1a $\rightleftharpoons$ . . .

II BCC 1e $\rightleftharpoons$ TBCC 1e $\rightleftharpoons$ BCC 2e $\rightleftharpoons$
TBCC′ 2a $\rightleftharpoons$ BCC 3′a $\rightleftharpoons$ TBCC 3a $\rightleftharpoons$
BCC 4a $\rightleftharpoons$ TBCC′ 4a $\rightleftharpoons$ BCC 5′a $\rightleftharpoons$
TBCC 5a $\rightleftharpoons$ BCC 6a $\rightleftharpoons$ TBCC′ 5a $\rightleftharpoons$
BCC 5a $\rightleftharpoons$ TBCC 4a $\rightleftharpoons$ BCC 4′a $\rightleftharpoons$
TBCC′ 3a $\rightleftharpoons$ BCC 3a $\rightleftharpoons$ TBCC 2a $\rightleftharpoons$
BCC 2′e $\rightleftharpoons$ TBCC′ 1e $\rightleftharpoons$ BCC 1e $\rightleftharpoons$ . . .

[a] The TBCC and TBCC′ conformations are mirror images of one another.

According to Hendrickson's condensed map of cyclodecane interconversions,[13] a given BCB conformation should be able to enter either of the BCC–TBCC pseudorotation cycles by both the plane-symmetrical and axis-symmetrical processes, but this is not correct. Actually, a given BCB conformation can be directly equilibrated with two TBCC forms in one BCC–TBCC pseudorotation itinerary, or with two BCC conformations in the other BCC–TBCC cycle. These transformations are illustrated below, with the 2e BCB form as an example

TBCC′ 2e $\rightleftarrows$ BCB 2e $\rightleftarrows$ TBCC 4e

BCC 5a $\rightleftarrows$ BCB 2e $\rightleftarrows$ BCC 2e

In this case, the two TBCC forms are in the first pseudorotation cycle of Chart III; the BCC forms are in the second cycle. The TBCC conformations of the first itinerary can equilibrate with BCB conformations as follows

TBCC 1a $\rightleftarrows$ BCB 3′a $\rightleftarrows$ TBCC′ 5e

TBCC′ 2e $\rightleftarrows$ BCB 2e $\rightleftarrows$ TBCC 4e

TBCC 3e $\rightleftarrows$ BCB 1e $\rightleftarrows$ TBCC′ 3e

TBCC′ 4e $\rightleftarrows$ BCB 2′e $\rightleftarrows$ TBCC 2e

TBCC 5e $\rightleftarrows$ BCB 3a $\rightleftarrows$ TBCC′ 1a

Examination of Chart II shows that transformations of types BCB $\rightleftarrows$ TBCC and TBCC $\rightleftarrows$ BCC will not interconvert BCB pseudorotation partners; in particular, ring inversion in 1,1-difluorocyclodecane cannot be accomplished in this way.

As in the case of the axis-symmetrical process, BCB pseudorotation partners cannot be equilibrated by transformations of types BCB $\rightleftarrows$ BCC and BCC $\rightleftarrows$ TBCC. Complete interconversion of cyclodecane positions is possible, however, if the BCB $\rightleftarrows$ TBCC process is included. A pathway which is relevant for 1,1-difluorocyclodecane is: BCB 2e $\rightleftarrows$ BCC 2e $\rightleftarrows$ TBCC′ 2a $\rightleftarrows$ BCB 2a.

A barrier of at least 20 kcal/mol was estimated[13] for conversion of BCB cyclodecane to the BCC form, with the plane of symmetry maintained. Unless a lower energy (unsymmetrical) process exists for the above conversion, or the estimate of the barrier is too high, then interconversions involving only BCB, BCC, and TBCC conformations are not important for complete equilibration of substituent positions in cyclodecane.

The TBC conformation of cyclodecane can be derived from the LC form by moving the two 3 carbons (or the 3′ carbons) of the latter conformation away from the center of the ring, with retention of the symmetry axis. Direct conversion of BCB cyclodecane into the TBC or BC conformations is not possible, and ring inversion cannot be accomplished by equilibria involving only these forms. It is of interest that, according to the calculations, deformation of the LC form to give the TBC conformation results in a decrease in strain energy from 24.6 to 2.1 kcal/mol (for the most stable TBC form). Hendrickson has suggested[13] that asymmetrical modes of conformational transformations may be important for rings larger than cycloheptane. Additional strain-energy calculations will be required for a more complete understanding of the possible routes for interconversion of substituent positions in cyclodecane. It should be noted that, if more than one process is required for complete exchange of substitutent sites in cyclodecane (*e.g.*, as in 1,1-difluorocyclooctane[21]), this would not be revealed in the study of 1,1-difluorocyclodecane. Because only two ring positions are occupied in the difluoride, the effects of only one process can be observed.

Experimental Section

Melting points were taken with a Büchi melting point apparatus and are uncorrected. Preparative vapor-phase chromatographic separations were carried out with a Varian Aerograph Autoprep Model 700 gas chromatograph, using $^3/_8$ in. × 20 ft columns. Analytical vapor-phase chromatograms were obtained with either a Perkin-Elmer Model 154C or a Hewlett-Packard Model 5750 gas chromatograph. Elemental analyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Mich.

Infrared spectra were taken on a Beckman Model IR-7 spectrometer. Proton nmr spectra were obtained with either a Varian A-60A or A-56/60A spectrometer. Chemical shifts are reported in parts per million downfield from internal tetramethylsilane. Fluorine nmr spectra were measured on a Varian A-56/60A spectrometer. The spectra were calibrated by the sideband technique, using a Lenkurt Model 6200 DS audiooscillator and a Hewlett-Packard Model 5216A counter. The signal-to-noise ratio of the low-temperature fluorine spectra was improved with a time-averaging computer, Varian Model C-1024. The Varian Model V-6040 variable-temperature accessory was used to control the temperature. Temperatures were determined by replacement of the sample tube with an open tube containing a suitable solvent and a copper-constantan thermocouple.

Theoretical spectra were generated by an IBM 360/75 computer, using the Gerig program,[32] which is based on the equations of Alexander.[39] The parameters used in calculation of the spectra included the two fluorine chemical shifts, the fluorine-fluorine coupling constant, an "effective" relaxation time, T_2, for each nucleus, and a mean lifetime τ. The value of T_2 was selected to reproduce, as far as possible, the line shape in the slow-exchange spectrum at −163°.

Sebacoin. The acyloin condensation of dimethyl sebacate was carried out on a 1-mol scale according to the procedure of Allinger.[40] The yield of recrystallized product was 102.7 g (60%): mp 39.2–40.8° (lit.[40] mp 38–39°); ir (CCl_4) 1705 (C=O) and 3500 cm^{-1} (O—H).

Sebacoin Tosylate. A solution of 102.3 g (0.601 mol) of sebacoin in 310 ml of pyridine was cooled to 5°, and 154 g (0.807 mol) of *p*-toluenesulfonyl chloride was added with stirring and cooling. After 12 hr at 5° under a nitrogen atmosphere, the mixture was poured into 650 ml of iced 2 *N* hydrochloric acid. The solid product was extracted into methylene chloride. The organic phase was separated and washed five times with 2 *N* hydrochloric acid, twice with saturated sodium bicarbonate solution, and twice with water. The solution was dried over magnesium sulfate, and the solvent was removed with the aid of a rotary evaporator. Recrystallization of the residue from ether gave a first crop of 147.8 g (76%) of white crystals: mp 89–90° (lit.[41] mp 86–87°); ir (CCl_4) 1160, 1182, 1380, and 1599 cm^{-1} (tosylate), 1718 cm^{-1} (C=O). Concentration of the filtrate gave a second crop of 16.9 g, mp 88.8–89.8°.

1-(*p*-Toluenesulfonyloxy)-2,2-difluorocyclodecane. In a 200-ml pressure reaction vessel constructed of Hastelloy C alloy was placed 31 g (95. 7 mmol) of sebacoin tosylate, 69 ml of methylene chloride, and 2.95 g (164 mmol) of water. The bomb was sealed, cooled to Dry Ice-acetone temperature, and evacuated. Sulfur tetrafluoride (113.5 g, 1.05 mol) was condensed into the bomb, and the vessel was rocked for 10.3 hr at ambient temperature (19–23°).[19,20] The reaction mixture was shaken vigorously with a saturated sodium bicarbonate solution and filtered through a pad of Celite. The organic phase was separated and shaken twice more with saturated sodium bicarbonate solution and dried over magnesium sulfate.

Most of the methylene chloride was removed at the rotary evaporator to give a black, viscous residue. The combined residues from 213 g of sebacoin tosylate were chromatographed in two portions over 7.17 kg of neutral alumina. The column was eluted with petroleum ether (30–60°) containing increasingly large amounts of benzene until the product began to elute from the column, and the chromatography was finished with 100% benzene. The brown solid (38.5 g) was dissolved in ether and filtered from a small amount of insoluble material. Three crystallizations (charcoal) from ether gave 28.0 g of white crystals, mp 106.8–108°, and 4.2 g of a second crop of white solid, mp 106.5–107.5°: combined yield, 32.2 g (14.1%); ir (CCl_4), 1177, 1188, 1360, and 1601 cm^{-1} (tosylate). The pmr spectrum of a Silanor C solution showed absorption at δ 1.1–2.5 (19 H), with a sharp peak at 2.43 and a rather sharp peak centered at 1.54, a multiplet at 4.7–5.4 (1 H), and an AA′BB′ pattern at 7.2–8.0 (4 H). The ambient-temperature ^{19}F nmr spectrum was an AB pattern centered 28.0-ppm upfield from internal ethyl trifluoroacetate, with $^2J_{FF}$ = 248 Hz and $\Delta\nu$ = 241 Hz. A thin-layer chromatogram (Eastman silica gel sheet, developed with petroleum ether-ether, 5:2) showed a single spot with an R_f value of 0.6.

Anal. Calcd for $C_{17}H_{24}F_2O_3S$: C, 58.94; H, 6.98; F, 10.97; S, 9.26. Found: C, 59.17; H, 7.13; F, 11.17; S, 9.14.

3,3-Difluoro-*trans*-cyclodecene. A solution of 11.9 g (34.4 mmol) of difluoro tosylate and 7.68 g (68.5 mmol) of potassium *tert*-butoxide in *tert*-butyl alcohol (183 ml) was refluxed for 19 hr. The mixture was cooled to room temperature, poured into 600 ml of ice water, and extracted with ether. The ether solution was washed six times with water and dried over magnesium sulfate. Most of the ether was removed by distillation under reduced pressure, and the residue was diluted to a volume of 35 ml with petroleum ether. A white solid (0.6 g, starting material) separated from solution after storing at −15°, and was collected by filtration. The filtrate was dried (Drierite) and concentrated by distillation under vacuum.

Two-fifths of the product was purified by preparative vpc on a column of 30% FFAP on 45–60 Chromosorb P. The temperatures of the injection port, column, detector, and collector tip were 180, 150, 195, and 152°, respectively. The yield of clear, colorless liquid was 1.01 g (42%): ir (thin film), 985 (trans-disubstituted olefin), 1675 (C=C), and 3050 cm^{-1} (alkenic C–H). The pmr spectrum of a dichlorodifluoromethane solution showed absorption at δ 1.20–2.53 (14 H) with a rather sharp peak at 1.48, and a complex multiplet at 5.30–6.47 (2 H). The ^{19}F nmr spectrum at 14° is a singlet broadened by both H–F couplings and exchange and centered 30.0-ppm upfield from internal ethyl chlorodifluoroacetate. A mass spectrum showed the parent ion at *m/e* 174. An analytical vapor-phase chromatogram[42] indicated a purity of 98% or greater.

Anal. Calcd for $C_{10}H_{16}F_2$: C, 68.93; H, 9.26; F, 21.81. Found: C, 68.89; H, 9.24; F, 21.87.

1,1-Difluorocyclodecane. Most of the petroleum ether was distilled under reduced pressure from half of the crude 3,3-difluoro-*trans*-cyclodecene, and the residue was dissolved in 42 ml of 100% ethanol. Palladium on charcoal (5%, 0.221 g) was added, and the mixture was stirred under hydrogen for 28 hr at room temperature. The hydrogen was supplied by means of a balloon attached to the flask.

The solution was filtered through a Büchner funnel, and most of the solvent was removed by distillation with the aid of the water aspirator. The crude product was purified by preparative vpc using a column of 30% Carbowax on 45–60 Chromosorb P. The temperatures of the injection port, column, detector, and collector were 168, 152, 178, and 143°, respectively. One gram of a clear, colorless liquid was obtained (33% yield from the tosylate). The pmr spectrum of a dichlorodifluoromethane solution showed absorption at δ 1.40–2.50, with a sharp peak centered at 1.60.

Anal. Calcd for $C_{10}H_{18}F_2$: C, 68.15; H, 10.29; F, 21.56. Found: C, 68.22, 68.30; H, 10.21, 10.17; F, 21.52, 21.65.

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(39) S. Alexander, *J. Chem. Phys.*, **37**, 974 (1962).

(40) N. L. Allinger, "Organic Synthesis," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 840.

(41) P. S. Wharton, S. Dunny, and L. S. Krebs, *J. Org. Chem.*, **29**, 958 (1964).

(42) A $^1/_8$ in. × 8 ft column of 20% Carbowax on 45–60 Chromosorb P, and a $^1/_8$ in. × 6 ft column of 20% FFAP on 45–60 Chromosorb P were used.