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The Effect of the Perfluoroalkyl Group on the Nuclear Magnetic Resonance Spectra, Conformational Equilibria, and *cis-trans* Equilibria of 1-Iodo-2-(perfluoroalkyl)-cyclohexanes

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The size and shape of the perfluoroalkyl (R_F) group is an important parameter affecting the stability, preferred conformation, and equilibria of 1-iodo-2-(perfluoroalkyl)-cyclohexanes. *trans* isomers having a linear R_F group of two or more carbons have a diaxial arrangement of R_F and iodine, whereas the isomer with $(CF_3)_2CF-$ has a diequatorial configuration; in both cases, the *trans* groups are somewhat twisted from normal chair positions. *trans* isomer with a CF_3 group exists as an equilibrium mixture of (a,a) and (e,e) conformers, according to n.m.r. spectra studies at 100 to -100° . In all the *cis* isomers the iodo group is axial and the bulkier R_F groups are equatorial. Dipole moments confirm these findings from n.m.r. spectra. Interconversion of *cis* and *trans* isomers occurred at $125-190^\circ$; the rate for those with a $(CF_3)_2CF-$ group was several times as fast as with a $CF_3CF_2CF_2$ group. Reaction: *cis* (a,e) \rightleftharpoons *trans* (e,e); and with a $CF_3CF_2CF_2$ group, *cis* (a,e) \rightleftharpoons *trans* (a,a), gave equilibrium constants from which enthalpy and entropy quantities were calculated. From the magnitude and sign of these energy terms, it is concluded that *trans* isomers are higher energy forms, and that an increase in entropy occurs in going from *cis* to *trans*. Interaction of adjacent bulky and polar R_F and iodo groups with each other and with axial protons can account for these results.

Two kinds of isomer equilibration processes occur with substituted cyclohexanes.¹ During interconversion of stable chair conformations, all substituents exchange axial and equatorial positions without bond breaking and most logically pass through the less stable, flexible boat form.² (Of the many possibilities for the structure of a cyclohexane boat, the so-called "twist-boat" is recognized as the minimum energy form.^{3,4}) *cis-trans* isomerism, of course, involves the breaking and re-forming of shared bonds and is a much higher energy process than mere bending and twisting of ring bonds to accommodate substituents in positions of minimum energy. van der Waals repulsions and electrical effects of the highly polar R_F and iodo substituents in 1-iodo-2-(perfluoroalkyl)-cyclohexanes no doubt also play an important role in these processes, in affecting the position of equilibrium and rate at which they occur. By placing an R_F group of varying size and complexity in proximity to the electronegative, large, and readily deformed iodine atom, unusual and unexpected results were obtained.

In a preliminary communication,⁵ proton n.m.r. spectra of isomers having R_F groups of $CF_3CF_2CF_2-$ and $(CF_3)_2CF-$ were given and some of the behavior of these conformers was very briefly described. Analogs with CF_3- and CF_3CF_2- groups have now been prepared. This paper describes the effect of temperature on n.m.r. spectra of the entire series of compounds, and on *cis-trans* equilibria of the isomeric perfluoropropyl derivatives. Dipole moments of these isomers and of related compounds were determined to provide additional evidence for preferred conformations deduced from n.m.r. spectra.

Results and Discussion

Proton n.m.r. spectra of *trans* isomer Ia (R_F , CF_3CF_2-) are shown in Fig. 1 at various temperatures. Entirely similar spectra were obtained from *trans* isomers with R_F of $CF_3CF_2CF_2-$ (IIa)⁵ or of $CF_3(CF_2)_n-$, $n = 3$ and 6. Neither heating to 100° nor cooling to -100° affected the spectra of Ia and IIa significantly.⁶

(1) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962. This is an excellent treatise of the subject.

(2) (a) P. Hazebroek and L. J. Oosterhoff, *Discussions Faraday Soc.*, **10**, 87 (1951); (b) N. L. Allinger, *J. Am. Chem. Soc.*, **81**, 5727 (1959).

(3) (a) W. S. Johnson, V. J. Bauer, J. L. Margrave, M. A. Frisch, L. H. Dreger, and W. N. Hubbard, *ibid.*, **83**, 606 (1961); (b) J. B. Hendrickson, *ibid.*, **83**, 4537 (1961).

(4) N. L. Allinger and L. A. Freiberg, *ibid.*, **82**, 2393 (1960).

(5) N. O. Brace, *ibid.*, **84**, 3020 (1962).

(6) The values reported are accurate to ± 1 c./sec. Two separate series of measurements gave the same results. The chemical shifts at 26° were identical with the previously reported data⁵ obtained with a Varian Associates A-60 n.m.r. spectrometer.

The small peak in Ia at -277 c./sec. was due to 5% of *cis* isomer known to be present in the sample, and is a measure of the sensitivity of this method. In comparison with iodocyclohexane⁷ and with other cyclohexane derivatives which have been previously reported,^{8,9} the peak at -300 c./sec. is that of an equatorial proton on C-1. *The unusual apparently complete preference of these large substituents for the axial position was without precedent.* Evidence given below shows that the groups are actually twisted from normal chair positions.

There appears to be weak spin-spin coupling between axial and equatorial methylene protons adjacent to C-1 ($J = ca. 3$ c./sec.) in Ia and IIa, consistent with the small coupling constant for protons at a 60 to 130° dihedral angle.^{8,10,11} Line width at half-peak height (H_w) is only 7 c./sec. The triplet centered at -157 c./sec. ($J = 20$ c./sec.) in Ia or IIa is ascribed to the α - CF_2 group coupling with the proton on C-2, since an identical coupling constant appeared in the F^{19} resonance spectrum of Ia.

The spectrum of *trans* isomer IIIa (Fig. 2, CF_3-) was quite different from those of Ia or IIa. Equilibration between (e,e) and (a,a) conformers was clearly evident upon cooling to -90° , where discrete proton resonances of the CHI proton in an equatorial position ((a,a) conformer) at -292 c./sec. and in an axial position ((e,e) conformer) at -236 c./sec. were obtained.¹² The well defined splitting pattern of the C-1 proton centered at -262 c./sec. at 26° may be classified as an AX_2Y type,⁸ with $J_{AX} = 7$ c./sec. and $J_{AY} = ca. 5$ c./sec., where X and Y represent protons on C-6 and C-2 in time-averaged positions. The resonance peak, of course, represents the proton on C-1 in time-averaged equatorial and axial positions.

The splitting pattern, peak separation, and relative areas under the CHI resonance peaks of the "frozen-out" (e,e) and (a,a) conformers at -100° all indicate

(7) (a) A. J. Berlin and F. R. Jensen, *Chem. Ind.* (London), 998 (1960); (b) W. C. Neikam and B. P. Dailey, *J. Chem. Phys.*, **38**, 445 (1963); (c) E. Premuzic and L. W. Reeves, *Can. J. Chem.*, **40**, 1870 (1962).

(8) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959.

(9) (a) A. H. Lewin and S. Winstein, *J. Am. Chem. Soc.*, **84**, 2464 (1962); (b) F. D. Greene, C.-C. Chu, and J. Walla, *ibid.*, **84**, 2463 (1962); (c) E. L. Eliel and M. H. Gianni, *Tetrahedron Letters*, No. 3, 97 (1962); E. L. Eliel, M. H. Gianni, H. Williams, and J. B. Strothers, *ibid.*, No. 17, 741 (1962); (d) L. W. Reeves and K. O. Strömme, *Can. J. Chem.*, **38**, 1241 (1960).

(10) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959.

(11) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

(12) F. R. Jensen, D. S. Noyce, C. H. Sederholm, and A. J. Berlin, *J. Am. Chem. Soc.*, **84**, 386 (1962).

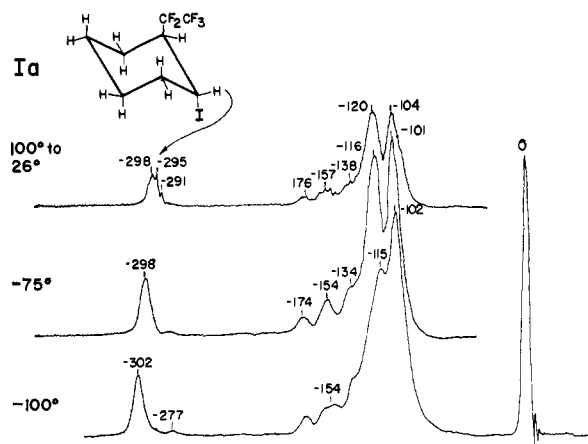


Fig. 1.—Proton n.m.r. spectra of *trans*-1-iodo-2-(perfluoroethyl)-cyclohexane at 60 Mc. in carbon disulfide solution (tetramethylsilane internal reference).

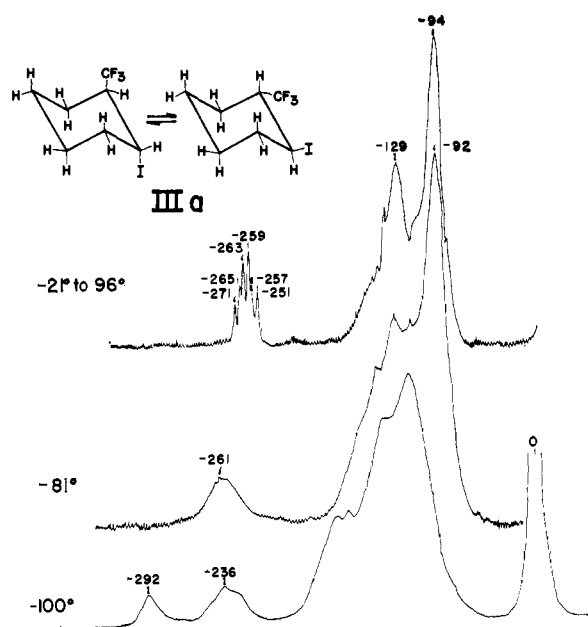


Fig. 2.—Proton n.m.r. spectra of *trans*-1-iodo-2-(trifluoromethyl)-cyclohexane at 60 Mc. in carbon disulfide solution (tetramethylsilane internal reference).

that the (e,e) conformer predominates. Calculations of conformer mixture composition and exchange rates are given in the Experimental.

The previously reported⁵ spectrum of a diequatorial *trans* isomer IVa having a $(CF_3)_2CF-$ group was quite similar to that of IIIa. However, no separation of $-CHI$ resonance peaks of 2 conformers was observed, although the line position shifted from -277 to -258 c./sec. as the temperature was lowered to -95° . This anomalous behavior will require further study.

cis isomers Ib, IIb,⁵ IIIb, and IVb⁵ gave proton n.m.r. spectra (see Fig. 3 for IIIb) which were all similar and remarkably simple. The C-1 proton resonance at -276 ± 1 c./sec. remained unchanged from 100 to -100° which indicated that equilibrium between (a,e) and (e,a) conformers was not occurring, or that the concentration of a second conformer was too small to detect. Preference of the larger and less easily deformed R_F group for the equatorial position was to be expected from thermodynamic considerations (see below). Chemical shift of the equatorial proton on C-1 was to 20 c./sec. higher field than for "pseudo"-diaxial *trans* conformers Ia and IIa, indicating a dif-

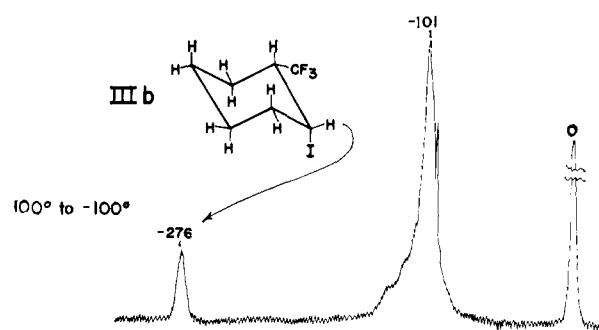
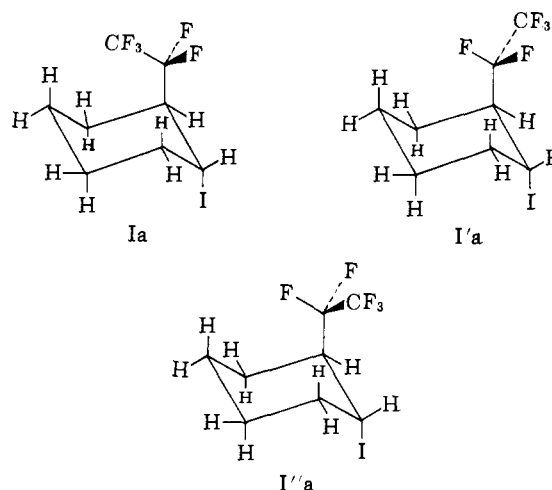


Fig. 3.—Proton n.m.r. spectra of *cis*-1-iodo-2-(trifluoromethyl)-cyclohexane in carbon disulfide solution (tetramethylsilane internal reference).

ference in shielding parameter for an equatorial proton in these *cis* and *trans* conformers.^{9c}

That these are in fact *cis* isomers also is indicated¹³ by the narrow band of methylene proton resonances at -101 or -110 c./sec. in Ib to IVb. The resonance for the proton adjacent to R_F on C-2 was unresolved in Ib, IIb, and IVb. The shoulder just below -120 c./sec. in IIIb, however, was resolved into a 4-line pattern centered at -130 c./sec. ($J_{HF} = 7-8$ c./sec.), corresponding to a similar coupling observed in the F^{19} spectrum (see below). The area under the entire peak was that of 9 protons in each case.

F^{19} Magnetic Resonance Spectra.—The effect of disposition of the R_F group with respect to the ring upon F^{19} n.m.r. spectra was studied. For Ia, three possibilities exist in which eclipsing of the ring to $-CF_2CF_3$ bond is absent.



From well-established conformational rules,¹ conformer Ia, in which trifluoromethyl is over the ring, is of high energy as compared to the forms Ia' and Ia'' in which it is away from the ring; Ia, therefore, contributes little to the over-all structure.¹⁴ An equatorial perfluoroethyl group would not experience a similar restraint, and would be expected to rotate freely. These conclusions, based on results with unfluorinated alkyl groups,^{1,9a,14,15} are nicely confirmed by the present n.m.r. spectra studies.

In F^{19} n.m.r. spectra of Ia and Ib, two sets of lines¹⁶ appear of relative intensities of 3:2. The CF_3 peak in Ia was not coupled to CF_2 , but the CF_2 resonance peak was a complex multiplet of the ABX type.

(13) S. Brownstein and R. Miller, *J. Org. Chem.*, **24**, 1886 (1959).

(14) N. L. Allinger and S.-E. Hu, *ibid.*, **27**, 3417 (1962).

(15) S. Winstein and N. J. Holness, *J. Am. Chem. Soc.*, **77**, 5562 (1955).

(16) All F^{19} n.m.r. spectra were taken at 56.4 Mc. using 1,2-difluoro-1,1,2,2-tetrachloroethane (F-112) as internal reference.

Analysis¹⁷ showed that the F¹⁹ atoms of the CF₂ group were nonequivalent, coupled to each other and to the proton on C-2 of the ring. The chemical shift between geminal F¹⁹ atoms was 200 c./sec. Clearly the two F¹⁹ atoms of CF₂ are shielded to a different degree. The splitting pattern was unaffected by heating to 100° or cooling to -75°.

In Ib the geminal F¹⁹ atoms of CF₂ were nonequivalent, but the narrowness of the line showed that they were very similarly shielded. Varying the temperature from +100 to -75° caused only a 60 c./sec. shift to higher field, without affecting the splitting pattern significantly.

Nonequivalence of identical magnetic nuclei attached to an asymmetric carbon atom has been previously observed.¹⁸ However, in the present case because nearly all the population of *trans* isomer Ia exists in the lower energy conformations Ia' and Ia'', and time-averaging of the environment does not occur, a pronounced chemical shift is obtained. A significant factor which must be considered in comparing rotation of perfluoroalkyl and alkyl groups is the higher barrier to rotation of CF₃-CF₂ as compared with CH₃-CH₂ or CF₃CF₂-CH-. Energy barriers to rotation have been reported. CF₃-CF₃, 3920 cal./mole¹⁹; CF₃-CH₃, 3040 cal./mole²⁰; and CH₃-CH₃, 3.0 kcal./mole.¹

Isomers IIa,b with CF₃CF₂CF₂- groups have, to the first approximation, conformational possibilities¹⁵ similar to those with CF₃CF₂- groups; however, interference of an adjacent iodine with an equatorial CF₃CF₂CF₂- is quite probable. The number of magnetic nuclei in CF₃CF₂CF₂- groups of IIa and IIb made detailed analysis of F¹⁹ spectra difficult. However, the 3 sets of resonances of intensity 3:2:2 observed were clearly those expected. An analysis of the spectra is given in the Experimental.

The isoperfluoropropyl group of IVa and IVb gave three resonance peaks at -80 to 131°. The two nonequivalent CF₃ groups were coupled to each other and to the tertiary fluorine and exhibited chemical shift dependence upon rotation about the CF-ring bond. The shift decreased with an increase in temperature up to the limit of stability of the compounds in carbon disulfide solution. The two CF₃ groups have different chemical shifts and therefore must be shielded to a different extent in IVa and IVb even though they are, approximately, in an equatorial position in both isomers.

It is significant that the same type of F¹⁹ spectrum was observed for the perfluoroisopropyl group in 2-*endo*-iodo-3-*exo*-(perfluoroisopropyl)-norbornane²¹ or in 1-(perfluoroisopropyl)-2-iodo-heptane^{22a} in which (CF₃)₂CF- is also attached to an asymmetric carbon and where some hindrance to free rotation of the (CF₃)₂CF-group also is probable. The iodine-free compound (perfluoroisopropyl)-cyclohexane,^{22b} however, showed an insignificant chemical shift of only 6 c./sec. for (slightly) nonequivalent CF₃ groups. A radical change in their environment was effected by removal of the adjacent iodine. In IVa and IVb, the CF₃ groups are necessarily in an asymmetrical condition with respect to the ring, and also apparently are not freely rotating. For (perfluoroisopropyl)-cyclohexane, *dl*- and *meso*- forms are possible,¹⁴ but averaging of the environment of the CF₃'s

(17) Following ref. 10, p. 89.

(18) J. D. Roberts, "Nuclear Magnetic Resonance, Applications to Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 59. The author is indebted to Prof. Roberts for calling attention to this fact.

(19) (a) D. A. Swick and I. L. Karle, *J. Chem. Phys.*, **23**, 1499 (1955);

(b) J. L. Brandt and R. L. Livingston, *J. Am. Chem. Soc.*, **76**, 2096 (1954).

(20) E. Catalano and K. S. Pitzer, *J. Phys. Chem.*, **62**, 838 (1958).

(21) N. O. Brace, *J. Org. Chem.*, **27**, 3027 (1962).

(22) (a) N. O. Brace, *ibid.*, **28**, 3093 (1963); (b) N. O. Brace, *J. Am. Chem. Soc.*, in press.

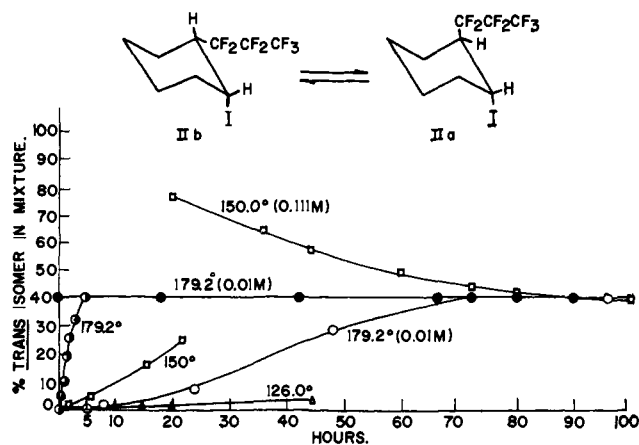
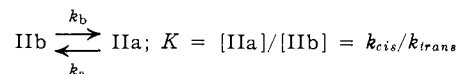


Fig. 4.—Isomerization rate of *cis*- and *trans*-1-iodo-2-(perfluoropropyl)-cyclohexanes: —□—, 150°, 0.111 *M* in benzene; —○— or —●—, 179.2°, 0.01 *M* in cyclohexane; —●—, 179.2°, neat; —▲—, 126°, neat.

through free rotation results in a small chemical shift.

***cis-trans* Isomerization.**—1-Iodo-2-(perfluoroalkyl)-cyclohexanes were considerably less stable to heat or radical attack than acyclic analogs^{22a} such as R_FCH₂CHI-(CH₂)₄CH₃. Equilibration of *cis* and *trans* isomers was observed by heating at 126 to 190°. Since the equilibrium constant for this reaction is a measure of the relative stabilities of the two isomers, the kinetics and energetics of the process were studied.^{1,4,14} For IIb ⇌ IIa the reaction is ostensibly the exchange of an equatorial for an axial position by the R_F group, while for IVb ⇌ IVa the iodine changes positions. As will become evident, more subtle changes are actually involved.



The over-all isomerization rate was dependent on temperature, on the structure of the isomer and the R_F group present, and on the concentration in an "inert" solvent.

Under favorable circumstances the process followed first-order kinetics. Conformers IVa and IVb [R_F = (CF₃)₂CF] isomerized several times faster than IIa and IIb (R_F = CF₃CF₂CF₂-). The ceiling temperature for IVb ⇌ IVa, above which serious decomposition to hydrogen iodide, iodine, and R_FC₆H₁₀ disproportionation products occurred, was near 190°. In preparative work^{22a} IVa and IVb also were much more sensitive to decomposition than were IIa and IIb.

As shown in Fig. 4, the equilibrium composition was approached from the side of pure IIa and pure IIb, and the same holds for IVa and IVb (Fig. 5). More extensive data are given in the Experimental. Because of reaction which occurred with cyclohexane on long heating, benzene solutions were used to determine the equilibrium mixtures. At least four samples each measured twice were used to determine the composition at each temperature. Equilibrium compositions are given in Table I.

Previous workers^{1,14} have demonstrated that the thermodynamic quantities calculated from these equilibrium constants can provide a logical basis for deciding ring structure and conformational changes which occur during the process. *trans*-1,3-Di-*t*-butylcyclohexane, because a very large repulsion energy would be required for a *t*-butyl group to take an axial position in a chair structure, prefers to exist as a boat form.⁴ The entropy associated with the equilibrium *cis* ⇌ *trans*-1,3-di-*t*-butylcyclohexane was found to be +5.0 e.u. Combustion

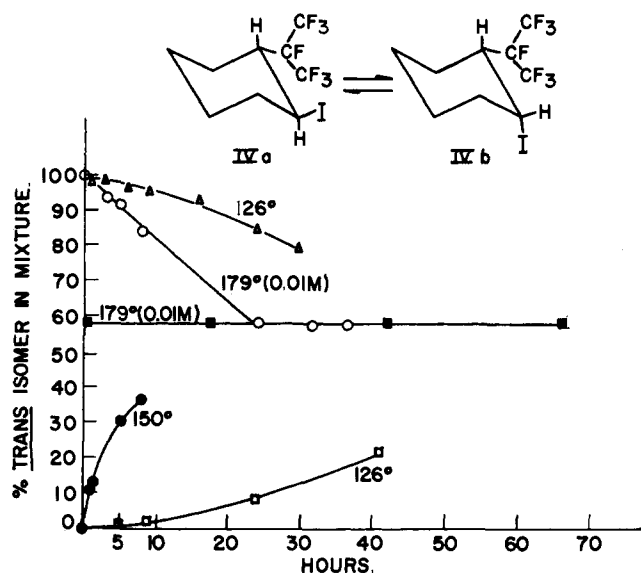


Fig. 5.—Isomerization of *cis*- and *trans*-1-iodo-2-(perfluoroisopropyl)-cyclohexanes; —○— or —■—, 179°, 0.01 *M* in cyclohexane; —●—, 150°, neat; —□— and —▲—, 126°, neat.

tion data^{3a} also support this large positive entropy value. The corresponding value for 1,3-diisopropylcyclohexanes¹⁴ was +3.0 e.u., and for 1,3-dimethylcyclohexanes^{1,14} +1.6 e.u. From these data it has been concluded that a large positive entropy term indicates a nonchair form with a less ordered structure.¹

TABLE I

EQUILIBRIUM COMPOSITION FOR $\text{IIB} \rightleftharpoons \text{IIa}$ AND $\text{IVa} \rightleftharpoons \text{IVb}$ AT 150, 165.8, AND 179.2°			
Isomer pair	150°	165.8°	179.2°
$[\text{IIa}]/[\text{IIB}]^a$	37.8/62.2 ± 0.2	40.5/59.5 ± 0.3	42.65/57.35 ± 0.2
$K = k_{\text{cis}}/k_{\text{trans}}$	0.608	0.681	0.744
$[\text{IVa}]/[\text{IVb}]^b$	53.25/46.75 ± 0.3	54.8/45.2 ± 0.1	56.1/43.9 ± 0.3
$K = k_{\text{cis}}/k_{\text{trans}}$	1.14	1.21	1.28

^a Measured using 0.111 *M* benzene solution. ^b Using 0.057 *M* benzene solution.

By plotting $\ln K$ against $1/T$ and fitting the points by the least squares method to a straight line, the slope = $-\Delta H/R$ and intercept = $\Delta S/R$ were obtained.²³ The straight lines were extrapolated to 25° to obtain ΔF_{298° . Free energy, enthalpy, and entropy quantities for the equilibria $\text{cis-IIb} \rightleftharpoons \text{trans-IIa}$ and $\text{cis-IVb} \rightleftharpoons \text{trans-IVa}$ are listed in Tables II and III, respectively.

TABLE II

THERMODYNAMIC QUANTITIES FOR THE REACTION $\text{cis-IIb} \rightleftharpoons \text{trans-IIa}$

Temp., °K.	ΔF , kcal./mole	ΔH , kcal./mole	ΔS , e.u.
298	+1.02	+2.6 ± 0.3 ^a	+5.08 ^b
423	+0.42 ± 0.015		+5.12 ^c
438.8	+ .34 ± .015		
452.2	+ .27 ± .015		

^a Calcd. from least squares slope of line through 15 points by W. R. Saadeh using machine computation. Error is for 95% confidence limits. ^b Computer calcd. value of intercept at $1/T = 0$; $\Delta S = R$ times (intercept). ^c Calcd. from $\Delta F = \Delta H - T\Delta S$.

Equilibrium constant at 298°K. indicated that 85% of *cis* isomer would be present at room temperature.

It is noteworthy, in the first place, that *IIB* is more stable than *IIa* over the entire temperature range. This is the reverse of the usual situation¹ with 1,2-substituted cyclohexanes for which *trans* (e,e) conformation is

(23) N. L. Allinger and J. L. Coke, *J. Am. Chem. Soc.*, **81**, 4080 (1959); **82**, 2553 (1960).

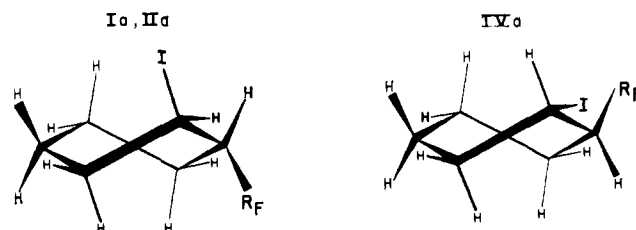


Fig. 6.—*trans*-Twist-boat structures.

generally more stable than *cis* (a,e) conformation, but is quite consistent with the postulated change in position of the R_F group from equatorial (in *IIb*) to higher energy axial position in *IIa*. Secondly, the large positive entropy term (+5.0 e.u.) denotes a significant increase in disorder as *cis-IIb* is converted to *trans-IIa*. This strongly suggests a distortion of the ring has occurred in accordance with the thermodynamic behavior already established for such a transformation. The enthalpy change (2.6 kcal./mole) which accompanies $\text{IIb} \rightleftharpoons \text{IIa}$, however, is only half that found^{1,3,4} (5.0 kcal./mole) for conversion of chair to "twist-boat" forms. It appears, therefore, that ground-state energy level of *IIb* is higher than for a normal chair structure due to iodine- R_F interactions, or that *IIa* does not attain a true "twist-boat" structure.

Similar conclusions are drawn from the thermodynamic relationships of *IVa* and *IVb* (Table III).

TABLE III

THERMODYNAMIC QUANTITIES FOR THE REACTION $\text{cis-IVb} \rightleftharpoons \text{trans-IVa}$

Temp., °K.	ΔF , kcal./mole	ΔH , kcal./mole	ΔS , e.u.
298	+0.37	+1.48 ± 0.2 ^a	+3.77 ^b
395	.00		
423	-.11 ± 0.02	+1.48 ± 0.2 ^a	+4.04 ^c
438.8	-.17 ± .02		
452.2	-.21 ± .02		

^a Calcd. from least squares slope of line through 18 points by W. R. Saadeh. ^b Calcd. from intercept of computed line. ^c Calcd. from $\Delta F = \Delta H - T\Delta S$.

Extrapolation gave an equilibrium constant of zero at 395°K., and presumably below this temperature the *cis* isomer becomes more stable than the *trans*. The entropy term at 423°K. (+4.04 e.u.) is again a fairly large positive value. The small positive enthalpy term at 423° results from the fact that the positive entropy change is greater than the quite small favorable negative free energy change. Disorder is increased as *cis* is transformed into *trans* isomer.

Since these equilibrations apparently do not actually involve moving an R_F group (or iodine) from "true" equatorial to axial positions of an undistorted chair, free energy and enthalpy quantities do not carry the significance at first contemplated.²⁴ However, the free energy change in $\text{IVb} \rightarrow \text{IVa}$ of +0.37 kcal./mole is quite close to the reported^{1,7a} value (0.4 kcal.) for moving iodine from axial to an equatorial position.

Since in both cases there is an increase in entropy and enthalpy for *trans* isomers over that of *cis* conformers, it appears that *cis* isomers *Ib* or *IVb* are normal chair structures, but that *trans* isomers *Ia* and *IIa* have twisted rings with pseudo-axial substituents, whereas *IVa* has the groups in pseudo-equatorial positions. One possible representation of these structures as "twist-boat" forms is shown in Fig. 6. A "half-chair" structure^{3b} may afford an equally valid

(24) It will be necessary to study the isomerization of *cis*- and *trans*-1-*t*-butyl-3-(or 4)-(perfluoroalkyl)-cyclohexanes to ascertain these quantities for the R_F group.

representation.²⁵ The angles calculated from dipole moment data (see below) accord reasonably well with estimated angles in a "twist-boat" structure of 87° for vicinal pseudo-diequatorial and 147° for pseudo-diaxial substituents (Dreiding stereomodels).²⁶

Dipole Moments of Conformers.—Additional evidence for the preferred conformations of Ia,b to IVa,b was sought by means of dipole moment measurements. This method has been much used to study structure problems²⁷ and in appropriate cases can give a definitive answer. Dipole moments of Ia,b, IIa,b, and IVa,b, the necessary reference compounds, and data available from the literature are listed in Table IV. Dielectric constants were measured in dilute benzene solution²⁸ and as neat liquids²⁹ when possible. By checking one method against the other, as recommended by Smyth,³⁰ values closer to the dipole moment of the isolated molecules in the gaseous state may be obtained, and the reliability of the data increased.

TABLE IV
DIPOLE MOMENTS OF 1-IODO-2-(PERFLUOROALKYL)-
CYCLOHEXANES AND ALLIED COMPOUNDS AT 25°

Compound	Dipole moment, Debyes
Iodocyclohexane	1.93, ^a 2.0, ^b 2.2 ^c
Trifluoromethylcyclohexane	2.50 ^d
Trifluoromethylbenzene	2.60 ^d
Pentafluoroethylbenzene	2.65 ^e
Heptafluoropropylcyclohexane (V)	2.7 ^f
Heptafluoroisopropylcyclohexane	2.8 ^f
1-Heptafluoropropyl- and 3-heptafluoropropyl- cyclohexane (VI and VII)	2.75, ^a 2.9 ^f
Ia (R _F = CF ₃ CF ₂ -; <i>trans</i> -a,a)	2.00 ^a
Ib (R _F = CF ₃ CF ₂ -; <i>cis</i> -a,e)	3.71, ^a 3.5 ^f
IIa [R _F = CF ₃ (CF ₂) ₂ -; <i>trans</i> -a,a]	1.91, ^a 2.1 ^f
IIb [R _F = CF ₃ (CF ₂) ₂ -; <i>cis</i> -a,e]	3.54, ^a 3.4 ^f
IVa [R _F = (CF ₃) ₂ CF-; <i>trans</i> -e,e]	3.00, ^a 3.3 ^f
IVb [R _F = (CF ₃) ₂ CF-; <i>cis</i> -a,e]	3.4 ^f

^a Calcd. from dielectric constant (ϵ') of neat liquid. ^b Ref. 31, 32. ^c Ref. 33. ^d Ref. 31. ^e Ref. 34. ^f Calcd. from dielectric constant of dilute benzene solution measured at two concentrations and extrapolated to zero concentration.

The dielectric constant of the pure polar liquids at 10 and 100 Kc. was measured by Kegelman and the moments calculated from the relation³⁰

$$\text{dipole moment} = 0.01281 \times$$

$$10^{-18} \left[\frac{TM(2\epsilon' + nD^2)(\epsilon' + 2)}{d} \frac{(\epsilon' - 1 - \frac{nD^2 - 1}{nD^2 + 2})}{3\epsilon'(nD^2 + 2)} \right]^{1/2}$$

where d = density, T = temperature, nD = refractive index for the D sodium line, M = molecular weight, and ϵ' = the measured dielectric constant. As Smyth has shown by appropriate examples,³⁰ values obtained by this method are frequently more reliable

(25) M. Tichy, J. Sipos, and J. Sicher, *Collection Czech. Chem. Commun.*, **27**, 2907 (1962). The dihedral angle between *trans* substituents in a "twist-boat" form is not 49.3 or 86.9° as given, but closer to 147° and 86.9°. This is an excellent article.

(26) W. Büchi, Glasapparate-Fabrik Flawil; available from Swissco Instruments, Greenville, Ill.

(27) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1955.

(28) The author is indebted to C. G. Wortz and Naomi Schlichter for making these measurements.

(29) The author is indebted to Dr. M. R. Kegelman for determining dielectric constants of pure polar liquids and for several helpful discussions of dipole moment data.

(30) Reference 27, pp. 226 and 227.

(31) J. D. Roberts, R. L. Webb, and E. A. McElhill, *J. Am. Chem. Soc.*, **72**, 408 (1950).

(32) Reference 27, p. 274.

(33) J. M. Eckart and R. J. W. Le Fèvre, *J. Chem. Soc.*, 1081 (1962).

(34) A. E. Pavlath and A. J. Leffler, "Aromatic Fluorine Compounds," Reinhold Publ. Corp., New York, N. Y., 1962, p. 25.

and closer to the gas values. In our case they also corresponded more closely to theoretical values calculated from the group moments for *cis* isomers in which conformational equilibria should not affect the result.

Calculation from the polarization of dilute solution was made using the expression²⁷

$$\text{dipole moment} = 0.01281 \times 10^{-18} [(P_{\infty} - R_D)298]^{1/2} \text{ e.s.u.}$$

where P_{∞} , the polarization at infinite dilution, was obtained by extrapolation and R_D , the molar refraction, was calculated from atomic refractions.

The theoretical relationship between dipole moment of a molecule and group moments is²⁷

$$\mu \text{ (dipole moment)} = (m_1^2 + m_2^2 + 2m_1m_2 \cos \theta)^{1/2}$$

where θ is the angle between vectors of group moments m_1 and m_2 . However, calculation of the moment of a molecule containing two or more dipoles which may change their directions relative to one another by rotation around bonds requires special consideration.²⁷

Dipole moments for the conformers Ia and IVb listed in Table VI were estimated from group moments, assuming theoretical tetrahedral carbon bond angles, undistorted cyclohexane rings, and no interaction of adjacent polarizable substituents.

The calculated dipole moment of Ia using an angle of 180° for anticoplanar substituents is 0.7 D., and for IIa, 0.8 D., while the observed moments were 2.0 and 1.9 D., respectively. This large difference may be attributed to: (1) the "time-averaged" position of the R_F group is not anticoplanar with iodine because (a,a) conformer is in equilibrium with (e,e) conformer; or (2) the ring is twisted into a configuration in which *trans*-R_F and iodo substituents are at some angle less than 180°. However, results of n.m.r. temperature studies definitely exclude (1), and thermodynamic energy relationships support (2) as a principal cause. It is possible to calculate from the observed moment what the "effective" dihedral angle is in Ia or IIa. This turns out to be 133° for Ia (from $\cos \theta = -0.675$) and 137° for IIa (from $\cos \theta = -0.735$).

From an examination of Dreiding stereomodels²⁶ of cyclohexane chair structures, it is readily seen that bending of R_F and iodine in *trans*-(a,a) conformers away from axial hydrogens can be accomplished at the expense of some bond angle strain and torsional energy³⁵ (perhaps 2 to 4 kcal./mole). As shown above, equilibrium entropy and enthalpy terms for IIa do indicate a strained configuration.

The *cis*-(a,e) conformer Ib has a dipole moment of 3.7 D. as pure polar liquid, and for IIb the moment is 3.5 D. The calculated value for Ib and IIb (a,e) chair structure is 3.9 ± 0.1 D. using the theoretical angle of 70° 32' (the *projected* angle of 60° is commonly used), and making the assumptions of no distortion of the ring or interaction of the substituents as above.

Calculation of the dihedral angle from the observed moments gave 77° for Ib and 86° for IIb. Because of proximity of substituents in this (a,e) conformation and the likelihood of mutual polarization, these estimated angles are probably several degrees too high.³⁶

The moment for the *trans*-(e,e) isomer IVa (3.00 or 3.3 D.) is consistent with a diequatorial disposition of

(35) Reference 1, p. 252. Torsional energy for a bond deformation of 10° is 1.8 kcal./mole (calculated); see also ref. 3b.

(36) There are three *gauche* positions over a rotation of 360° for CF₂ fluorines of CF₃CF₂ of Ib with respect to the ring bond, but in one of these the CF₃ is close to iodine with the CF₃-CF₂ bond parallel to the ring-iodine bond. In the other two positions the CF₃-CF₂ bond makes an angle of 108° with iodine. Though it is impossible to say what the time-averaged position of an equatorial CF₃CF₂ is, if CF₃ spends more time away from iodine than near it, as seems most likely, the resultant vector will make an angle greater than 70° with iodine. It should be noted that in a true diaxial chair form (*i.e.*, Ia, I'a, and I''a), since iodine and CF₃CF₂ are coplanar, rotation of CF₃ should be without effect on the dipole moment.

substituents in a "twist-boat" form. From F^{19} spectra and evident interaction of these two groups as shown by isomerization rates and thermodynamic values, both hindered rotation of $(CF_3)_2CF$ and some bending away of iodine and R_F groups from each other in IVa appear probable. From the dipole moments an angle between groups in IVa of 95 – 104° may be calculated.

It is interesting to observe that the relative stabilities of IIa,b and IVa,b are not correctly predicted by the "conformational rule"³⁷ or the "isomer sequence rule."³⁸ Since these isomers differ in dipole moment, a necessary condition is missing. The "dipole rule,"³⁹ however, does apply, according to which the isomer of higher dipole moment has the higher physical constants,^{22a} regardless of heat content. For IVa and IVb the differences in stability and physical properties^{22a} are smaller, but the "dipole rule," nevertheless, holds.

Experimental

Source of Materials.—The preparation and gas chromatographic analysis of Ia,b to IVa,b has been reported^{5,22}; the samples used for n.m.r. and *cis-trans* equilibration were of 99% purity except for Ia which contained 5% of Ib. Iodocyclohexane was redistilled, 99% pure. The 1- and 3-heptafluoropropylcyclohexane mixture (VI and VII) was obtained from IIa,b by alkaline hydrolysis,^{22b} and (heptafluoroisopropyl)-cyclohexane (V) from IVa,b by zinc reduction.^{22b}

N.m.r. Spectra.—Compound IVa (0.45 g., 0.00119 mole), carbon disulfide (0.78 g., 1.00 ml.), and *ca.* 0.1 g. of a mixture of equal parts of tetraethylsilane (TMS), difluorotetrachloroethane (F-112), and chloroform (ν_{HCCl_3} , -440 c./sec. from TMS) was cooled to -80° in a glass n.m.r. tube, evacuated and filled with nitrogen twice, and sealed *in vacuo*. The concentration was 0.83 *M*. Samples of IVb and IIIa,b for n.m.r. spectrum analysis were similarly prepared. The concentration of IIa, IIb was 1.7 *M*; for iodocyclohexane and for IIIa, IIIb it was 2.9 *M*.

Proton spectra of IVa, IVb previously reported⁵ were obtained with a Varian Associates A-60 spectrometer at 25° , and spectra at other temperatures were taken by C. B. Matthews using an HR-60 Varian Associates high-resolution n.m.r. spectrometer fitted with a thermostated insert as previously used by others.^{7b} The more concentrated solutions (*ca.* 2 *M*, 75% by wt. of IVa, IVb) used in the prior work⁵ gave at a temperature below -50° only a broad resonance of the C-1 proton in IVa for which accurate chemical shift measurement was not obtained. The spectra of IVa (0.83 *M* in carbon disulfide) recorded down to -95° were well defined and the shift measurement interpolated between TMS and chloroform. However, at -95° a solid phase was present in IVa. There may have been some separation of a

phase rich in IVa above -95° which may have caused some shift in the proton resonance. Table V records chemical shift data.

In Table VI are listed the chemical shifts for the axial proton and the equatorial proton on C-1 of the two conformation isomers of IIIa. The coalescence temperature was $-80 \pm 1^\circ$ (see Fig. 2).

TABLE VI
CHEMICAL SHIFTS OF *trans*-1-IODO-2-TRIFLUOROMETHYLCYCLOHEXANE CONFORMATION ISOMERS (IIIa)

Temp., °C.	δ_e , c./sec.	δ_a , c./sec.	$(\nu_a - \nu_e)$, c./sec.
-80 to -82	Could not detect 2 peaks		
-85	-278	-242	36
-87	-279	-238	40
-89	-280	-238	42
-90.5	-283	-237	46
-91.5	-285	-236	49
-93	-293	-236	57
-93	-291	-234	57
-97	-293	-236	57
-100	-292	-236	56

The area under the two proton resonances of spectra obtained at -93 , -97 , and -100° was measured by the triangle approximation. The -293 c./sec. peak area to -236 c./sec. peak area ratio was 30 to 70 in each case; therefore $(a,a)/(e,e) = 30/70$. The expression⁴⁰

$$\delta_M = X_e \delta_e + X_a \delta_a$$

(where δ_M is the measured chemical shift at 26° and the X_e and X_a are mole fractions of the conformers having an equatorial CHI proton, respectively) was also used to calculate the ratio of equatorial to axial protons; $X_e = 0.33$ and $X_a = 0.67$, or $(a,a)/(e,e) = 0.33/0.67$.

A plot of the change in chemical shift difference with temperature was made. The curve is somewhat S-shaped as obtained for cyclohexane.¹² From an examination of the shapes of the curves given in ref. 8, the value of $2\pi\tau(\nu_a - \nu_e) = ca. 3$ corresponds most closely to the peak separation achieved with IIIa (Fig. 2); $\tau = 0.0084$.

The $\tau = \sqrt{2}/2\pi(\nu_a - \nu_e) = 1/k$ relation⁴¹ gave $\tau = 0.00394$ and $k = 253.8$ sec.⁻¹ at coalescence temperature of -80° for both forward and reverse steps. For one step,¹² $k = \pi(\nu_a - \nu_e)/\sqrt{2} = 124$ sec.⁻¹. At -90° (approximately half the peak separation occurred at this temperature) we have⁴¹

$$\frac{\text{separation of peaks}}{\text{sepn. of peaks for large } \tau} = \left[1 - \frac{1}{2\pi^2\tau^2(\nu_a - \nu_e)^2} \right]^{1/2}$$

$\tau = 0.0486$; $k = 20.6$ sec.⁻¹ at -90° . Limits of error of this method and other considerations related to this interconversion have been discussed in detail.^{12,41}

F^{19} N.m.r. Spectra.— F^{19} magnetic resonance spectra of Ia to IVb were recorded by C. B. Matthews at 56.4 Mc. using FCCl₂-CFCl₂ (F-112) as internal reference over a temperature range.

(a) **F^{19} Spectra of Ia,b.**—In Ia spectrum the CF_3 peak was at 846 c./sec. and CF_2 resonances were centered at 2580 c./sec. Analysis showed that the nonequivalent F^{19} atoms of CF_2 had $J_{FF'} = 275$ c./sec. and were coupled to the ring proton ($J_{HF} 20 =$ c./sec.). The chemical shift was 200 c./sec. The ratio of intensity of outer to inner lines was 1 to 9.3 (calcd. 9.5). In Ib the CF_3 peak was at 913 c./sec. and the *single* CF_2 peak was at 3088 c./sec. At high resolution a splitting of *ca.* 5 c./sec. was seen in the CF_2 peak of Ib.

(b) **F^{19} Spectra of IIa,b.**—In IIa [$CF_3(a)$ - $CF_2(b)$ - $CF_2(c)$] the CF_3 peak (a) was split into a triplet by CF_2 (J 10 c./sec.)⁴² while the CF_2 peak (b) at 2460 c./sec. had 8 lines of 10 c./sec. spacing, indicating coupling⁴³ with both the CF_3 and the adjacent CF_2 (c). The $-CF_2$ peak (c) had a more complex splitting pattern of the ABX_n type resulting from nonequivalent geminal F^{19} atoms coupling to each other and to other F^{19} atoms. Since there was a triplet having $J = 20$ c./sec. in the proton n.m.r. spectrum of IIa, this splitting also would be expected to appear in the F^{19} resonance spectrum of peak (c) of IIa. The satellite peaks or "wings" (the outer pair of the AB pattern at 2995 and 3580 c./sec.) were very weak (1:26 intensity) but were observed at high resolution. Calculation⁴⁷ of the parameters for CF_2 peak (c)

(40) L. W. Reeves and K. O. Strømme, *Trans. Faraday Soc.*, **57**, 390 (1961).

(41) Reference 8, p. 224.

(42) L. Petrakis and C. H. Sederholm, *J. Chem. Phys.*, **35**, 1243 (1961). Coupling constants, $J_{FF} = 7$ to 10 c./sec. for 1,3- F^{19} atoms in a chain are given; $J_{FF} \sim 0$ for 1,2- F^{19} atoms.

(43) S. L. Manatt and D. D. Ellemen, *J. Am. Chem. Soc.*, **84**, 1305 (1962).

TABLE V

PROTON N.M.R. DATA AT 100 TO -100°

<i>trans</i> Isomer	R_F	Peak position (c./sec.) below TMS at 60 Mc.			
		100°	-100°	100°	-100°
Ia	CF_3CF_2-	-297	-302	-120 -104	-115 -102
IIa	$CF_3(CF_2)_2-$	-300	-303	-116 -101	-116 -102
IIIa	CF_3-	-265	-293	<i>a</i>	<i>a</i>
IVa	$(CF_2)_2CF-$	-277	-258 ^b	-131 -95	-148 -95
<i>cis</i> Isomer	R_F				
Ib	CF_3CF_2-	-278	-278	-105	-105
IIb	$CF_3(CF_2)_2-$	-284	-278	-112 -107	-105 -109
IIIb	CF_3-	-276	-276	-101	-101
IVb	$(CF_3)_2CF-$	-284	-278	-119 -116 -112 -110	-109 -109 -109 -109

^a See Fig. 2 and Table VI. ^b At -95° , one broad peak only.

(37) N. L. Allinger, *J. Am. Chem. Soc.*, **79**, 3443 (1957).

(38) H. van Bekkum, A. van Veen, P. E. Verkade, and B. M. Wepster, *Rec. trav. chim.*, **80**, 1310 (1961).

(39) A. E. van Arkel, *ibid.*, **51**, 1081 (1932); **53**, 246 (1934).

TABLE VII
APPROXIMATE FIRST-ORDER RATE CONSTANTS FOR THERMAL
ISOMERIZATION OF *cis*- AND *trans*-1-IODO-2-(PERFLUOROPROPYL)-
CYCLOHEXANES

Isomer pair	Concn., <i>M</i>	Solvent	Temp., °C.	k_{cis} (sec. ⁻¹ × 10 ⁷)	k_{trans}
IIa, IIb	...	None	126	2.1	...
IIa, IIb	...	None	150	39.0	62.8 ^a
IIa, IIb	...	None	179.2	416	583 ^a
IIa, IIb	0.111	Benzene	150	14.7 ^b	23.9
IIa, IIb	.111	Benzene	150	15.6 ^b	25.2
IIa, IIb	.111	Benzene	185	269	386
IIa, IIb	.010	c-C ₆ H ₁₂	179.2	10.0 ^c	14.4 ^a
IVa, IVb	...	None	126.0	11.4	...
IVa, IVb	...	None	150.0	269	194
IVa, IVb	0.010	c-C ₆ H ₁₂	179.2	83 ^b	63.9

^a k_{trans} was calculated from K and k_{cis} . ^b k_{cis} was calculated from K and k_{trans} . ^c Calculated from rate curve extrapolated to zero time.

other magnetic nuclei. The ratio of intensity of the outer to inner lines of the AB pattern was 1:30. F¹⁹ spectra of IIa and IIb were insensitive to temperature over the range of 100 to -70°.

It seems probable that nonequivalence of F¹⁹ atoms of CF₂ (c) peaks in IIa and IIb derives from attachment to an asymmetric carbon atom. However, the chemical shift of (c) peaks are greater in IIa,b than for CF₂ peaks in Ia,b. Hindrance to free rotation, by analogy to Ia, is very likely to be present in IIa as well, since conformations in which an *axial* perfluoropropyl is kept away from axial protons would be of lower energy than those in which axial repulsions can occur.

(c) F¹⁹ Spectra of IIIa,b.—Equivalent F¹⁹ of the CF₃ group in IIIa gave a doublet at zero and 13 c./sec. from F-112 (or -630 and -617 c./sec. from trifluoroacetic acid), resulting from coupling with the C-2 proton ($J_{HF} = 13$ c./sec.). In IIb the doublet was at 202 and 210 c./sec. from F-112; $J_{HF} = 8$ c./sec.

(d) F¹⁹ Spectra of IVa,b.—The CF₃(a)CF(c)CF₃(b) group of IVa and IVb gave 3 resonances at -80 to 131°; the chemical shift between nonequivalent CF₃ groups was smaller for IVa than for IVb and decreased with an increase in temperature. Free rotation of the group was not attained, however, as in the iodine free compound (isoperfluoropropyl)-cyclohexane.^{22b} The 5-line

TABLE VIII
ISOMERIZATION RATE IIa ⇌ IIb
At 150 ± 0.1° (0.111 *M* in benzene)

Time, min.	% IIa	Time, min.	% IIa	Time, min.	% IIa	Time, min.	% IIa
0	84.86	0	50.37	0	34.5 ± 0.1 ^a	0	42.9 ± 0.5 ^a
1200	76.0	390	48.98	1020	35.6 ± .1 ^a	6900	40.5 ± .4 ^b
2160	63.8	1455	43.74	1380	36.2 ± .1 ^a	7560	39.8 ± .4 ^c
2640	55.4	2825	41.6	1800	36.4 ± .1 ^a	8640	37.8 ± .5 ^c
3600	49.8	3240	41.3	2160	36.5 ± .1 ^a	Final	37.8 ± .4
4320	44.0	4320	40.2	2520	37.7 ± .1 ^a		
4800	42.4	6000	38.8	Final	37.7 ± .1		

At 165.8 ± 0.2° (0.111 *M* in benzene)

0	34.5 ± 0.1 ^a
1275	36.4 ± .5 ^a
1500	40.2 ± .3 ^a
2460	40.7 ± .1 ^a
2760	40.2 ± .5 ^a
Final	40.5 ± .3

At 179.0 ± 0.2° (0.111 *M* in benzene)

0	32.46 ± 0.1 ^a
540	42.56 ± .2 ^a
540	42.60 ± .2 ^a
540	42.80 ± .3 ^a
Mean	42.65 ± .2

At 179.2 ± 0.2° (0.0100 *M* in cyclohexane)

Time, min.	% IIa	% C ₆ H ₁₁ I	Time, min.	% IIa	% C ₆ H ₁₁ I	Time, min.	% IIa	% C ₆ H ₁₁ I
0	0.00	...	0	100.0	...	0	41.7	0.0
360	0.89	...	435	94.8	2.3	1080	39.5	3.6
480	2.15	...	1440	90.5	2.0	2520	37.8	4.8
1440	7.10	1.9	4320	53.0	1.8	3960	38.0	6.5
2880	29.0	...	5760	48.7	2.0	5400	38.8	5.2
4320	39.2	4.0	7200	45.6	5.6	Final	42 ^d	
4770	42.0	1.3						
5760	39.5	0.7						
7200	40.7	3.0						

At 182 ± 2° (0.111 *M* in benzene)

0	0.00		0	100.0
60	3.22		60	99.2
120	15.76		120	88.76
180	16.6		180	84.96
390	36.64		300	64.05
450	38.47		390	57.73
510	37.48		480	46.4
1320	40.22		900	42.42

^a Average of 2 or 3 analyses. ^b Average of 8 analyses of 4 tubes. ^c Average of 6 analyses of 3 tubes. ^d Corrected for C₆H₁₁I.

gave the constants: $J_{FF'} = 285$ c./sec.; $\delta_F - \delta_{F'} = 76.3$ c./sec.; $\delta_F = 3250$ c./sec.; $\delta_{F'} = 3327$ c./sec. An F-F spin interaction of $J \sim 190$ c./sec. was found for different geminal F¹⁹ atoms in certain fluorinated cyclohexanes⁴⁴; a value of 158 c./sec. also has been given.¹⁰

The CF₃CF₂CF₂ group in IIb showed similar resonance patterns. CF₃ peak (a) was at 793, CF₂ peak (b) at 2910, and CF₂ peak (c) at 3314 c./sec. Nonequivalent F¹⁹ atoms of CF₂ peak (c) were coupled to each other ($J_{FF'} = 285$ c./sec.; $\delta_F - \delta_{F'} = 116$ c./sec.; $\delta_F = 3252$ c./sec.; $\delta_{F'} = 3386$ c./sec.) and to

splitting pattern of CF₃(a) at 250 c./sec. in IVa gave F¹⁹ coupling constants⁴⁵ $J_{ab} = 9$ c./sec. for coupling to CF₃(b) and $J_{ac} = 9$ c./sec. for coupling to CF(c). The CF₃(b) in IVa at 405 c./sec. gave $J_{ba} = 9$ c./sec. and $J_{bc} = 4.5$ c./sec. (8 lines of equal spacing). The 10-line pattern found for the CF peak (c) at 6115 c./sec. has the predicted⁴⁵ complexity. The F¹⁹ spectrum of IVb had 8-line multiplets for both CF₃ peaks (a) at 220 c./sec. and (b) at 450 c./sec., but the spectrum of the CF peak (c) at 6695 c./sec. had 7 lines of 8 c./sec. spacing; J_{ac} and J_{bc} both appear to be 8 c./sec. and J_{ab} was about 4 c./sec.

(44) J. Feeney and L. H. Sutcliffe, *Trans. Faraday Soc.*, **56**, 1559 (1960).

(45) The author is indebted to Prof. J. D. Roberts for this analysis.

TABLE IX

THERMAL ISOMERIZATION OF IIA,b; ACCELERATION OF RATE BY AIR AT $179.2 \pm 0.1^\circ$ (SEALED IN GLASS TUBES OPEN TO AIR AT -70°)

Time, min.	% olefin	% IIA	$k/2.303 \times 10^7$ sec. ⁻¹		Time, min.	% olefin	% IIA	$k/2.303 \times 10^7$ sec. ⁻¹		
0	1.01	98.9			31	1.07	92.1			
10	1.04	97.2	101		60	1.27	83.5	214		
	0.96	97.5							1.07	81.6
	.94	97.5							1.25	83.3
	.87	97.5					126		2.16	64.8
20	.82	96.0	111		182	4.4	47.4	278		
	.51	96.0								
	1.05	95.6								

TABLE X

IIa \rightleftharpoons IIb at $150.0 \pm 0.1^\circ$ in *vacuo*;^a RADICAL DISPROPORTIONATION PRODUCTS BY G.L.C. ANALYSIS^b

Time, min.	% V ^b	% VI ^b	% VII ^b	% IIA ^b
0.00	0.20	0.30	0.49	46.01
240	0.15	.31	.46	45.9
420	Trace	.57	.62	45.2
600	Trace	.76	1.08	43.4
720	0.3	.93	1.40	42.4
1380	Trace	2.68	2.87	39.98

^a Starting mixture was IIA,b distilled after lithium aluminum hydride treatment.^{22b} ^b G.l.c. analysis done using a 2-m. "R" column at 150° , 15 p.s.i. helium applied pressure; V, retention time (r.t.), 3.55 min.; VI, 4.40 min.; VII, 4.85 min.; IIA, 23.0 min.

TABLE XI

ISOMERIZATION OF IVA \rightleftharpoons IVb

Neat			Neat		
At $126.0 \pm 0.1^\circ$			At $150.0 \pm 0.1^\circ$		
Time, min.	% olefin	% IVA	Time, min.	% olefin	% IVA
0	1.67	97.1	0	...	0.74
60	1.87	96.1	60	...	11.33
180	1.61	97.0	120	...	13.24
360	1.54	94.9	300	...	27.8
540	1.53	93.7	420	0.94	28.4
960	1.75	92.2	480	1.4	35.5
1440	2.20	83.4	1380	41.8 ^a	0 ^a
1800	2.92	76.4			

At $150.0 \pm 0.2^\circ$			(0.057 M in benzene)			At $179.1 \pm 0.1^\circ$		
Time, min.	% IVA		Time, min.	% IVA		Time, min.	% IVA	
0	53.9 \pm 0.3 ^b		0	53.9 \pm 0.3 ^b		0	53.9 \pm 0.3 ^b	
240	54.2 \pm .5 ^b		960	53.9 \pm .5 ^c		462	56.1 \pm .7 ^b	
960	53.1 \pm .3 ^b		1440	53.9 \pm .6 ^c		462	56.1 \pm .2 ^b	
1200	52.8 \pm .1 ^b		2400	54.0 \pm .6 ^c		462	56.3 \pm .1 ^b	
7500	53.1 \pm .1 ^b		3610	54.8 \pm .1 ^c		462	56.1 \pm .5 ^b	
7500	53.5 \pm .2 ^b		Final	54.8 \pm .1		Mean	56.1 \pm .3	
7500	53.4 \pm .5 ^b							
8700	53.6 \pm .3 ^b							
Final	53.3 \pm .3							

At $179.2 \pm 0.2^\circ$ (0.0100 M in cyclohexane)

Time, min.	% IVA	% C ₆ H ₅ I	Time, min.	% IVA	% C ₆ H ₅ I
0	0.00	...	0	99.9	Absent
180	3.60	Absent	180	93.6	Absent
480	6.95	Absent	300	92.1	Absent
1440	49.3	3.4	480	84.3	Absent
1890	54.2	4.7	1440	57.2	Absent
2190	56.0	3.5	1890	56.7	Absent
			2190	56.9	Absent

^a The olefin mixture, 32% of IVb, and higher retention time products, 17.1 and 19.8%, obtained; free iodine (41%), hydrogen iodide (28%), and organic iodine (30%) present in a sample. ^b Average of 2 analyses. ^c Average of 4 analyses of 2 separate tubes.

Thermal Isomerization of *cis* and *trans* Isomers.—Samples of IIA, IIb and IVA, IVb, as neat liquids or dissolved in benzene or cyclohexane, were sealed *in vacuo* at -70° in glass capillary tubes which had been evacuated and filled with nitrogen three times. Known mixtures of the isomers were also weighed and the com-

TABLE XII

ISOMERIZATION OF *cis*- AND *trans*-1-iodo-2-(PERFLUOROBUTYL)-CYCLOHEXANE AT $180 \pm 0.1^\circ$ (NEAT)

Time, min.	% olefin	% <i>trans</i>	Time, min.	% olefin	% <i>trans</i>	Time, min.	% olefin	% <i>trans</i>
0	3.4	92.5	0	0.6	18.8	0	...	43.9
30	3.4	82.1	30	0.7	19.9	30	0.38	43.0
60	1.6	77.6	60	0.6	23.3	60	.50	43.2
225	3.58	43.6	195	4.2	35.3	300	.74	42.2
340	3.80	43.1	315	29.3	17.0 ^a	330	.76	43.9
			420	46.3	6.7 ^b			

^a Products included 39.6% of *cis* isomer, 11.9% and 1.7% of two higher retention time compounds. ^b Also 22% of *cis* isomer, 19.0% and 5.65% of the higher retention time compounds.

TABLE XIII

BENZENE SOLUTION DIPOLE MOMENT DATA

Mole fract. solute	d^{25}_4	Diell. const. at 25°	P_2
Ib (μ 3.5 D., R_D 50.36, P_∞ 303.50; N. Schlichter)			
0.01116	0.88350	2.3674	291.50
0.00541	0.89401	2.4620	297.68
IIa (μ 2.2 D., R_D 55.2, P_∞ 162.3; C. G. Wortz)			
0.0102772	0.8969	2.3495	162.25
0.0054900	0.8870	2.3166	159.95
IIb (μ 3.4 D., R_D 55.2, P_∞ 297.7; C. G. W.)			
0.010445	0.8973	2.4475	292.28
0.006463	0.8889	2.3836	294.34
IVa (μ 3.3 D., R_D 55.2, P_∞ 283.7; C. G. W.)			
0.0051787	0.8837	2.3534	283.7
IVb (μ 3.4 D., R_D 55.2, P_∞ 293.8; C. G. W.)			
0.0052190	0.8850	2.3603	293.8
V (μ 2.7 D., R_D 42.42, P_∞ 191.32; N. S.)			
0.01084	0.88222	0.38188	202.18
0.00545	0.87862	2.32860	196.74
Iso-(heptafluoropropyl)-cyclohexane (μ 2.8 D., R_D 42.42, P_∞ 208.68; N. S.)			
0.01034	0.88258	2.38144	205.90
0.00430	0.87697	2.31968	207.52
VI (60%) and VII (40%) (μ 2.9 D., R_D 41.958, P_∞ 224.78; N. S.)			
0.01087	0.88263	2.40526	230.16
0.00528	0.87928	2.34095	227.42

position of all samples determined by gas chromatography before and after heating for the time specified in the tables. The conditions and chromatographic columns used were those given previously.^{5,22a} The *cis* and *trans* isomers showed identical weight/areas ratios and the peaks were separated completely; the ratio of areas was therefore used to calculate composition. Replicate analyses were run in those cases where an equilibrium composition was determined. Precision of analysis was in most cases greater than $\pm 0.2\%$. Side reactions occurred after long heating time at 126 or 150° or in a few minutes at 180° . The color of iodine appeared and varying amounts of V, VI, and VII were formed. The total relative areas of these side products are listed under "olefin" in Table IX; in Table X the individual amounts of these side products are listed. Analogous side products from IVA,b are listed in Table XI and from 1-iodo-2-(perfluorobutyl)-cyclohexane in Table XII. There were also higher-boiling side products obtained in experiments where gross decomposition occurred. These products were not further investigated. Side reactions were noticeably suppressed in benzene solution.

The isomerization rate was strongly affected by traces of foreign substances and appeared to be accelerated by the decomposition products. Samples which were sealed in the presence of air isomerized at an increasing rate as the reaction proceeded (Table IX), and developed a dark iodine color in a few minutes at 179° . It was not possible to reach the equilibrium mixture from both sides starting with pure isomers because of decomposition of the samples. However, mixtures near the equilibrium value on both sides were prepared and constant composition attained in this way. In cyclohexane a minor side reaction which gave iodo-

cyclohexane occurred after several hours at 179°. However, an equilibrium mixture was unaffected by this reaction.

A Dow-Corning silicone oil (No. 550) was used in the heating bath which was stirred rapidly. The temperature was controlled by a Magnaset relay-activating mercury thermometer. A high-low heating cycle gave temperature control of $\pm 0.2^\circ$ or better. Samples taken from the bath were quenched at -70° , opened, and liquid removed by hypodermic syringe for gas chromatographic analysis.

Rate constants were calculated from the kinetic data using a procedure employed previously.^{46,47} $[I\text{Ib}]_0/[I\text{Ib}]_t$ and $\log [I\text{Ib}]_0/[I\text{Ib}]_t/t = k/2.303$, for example, were calculated from the amount of IIb present in the mixture at zero time and after intervals of time (t). A plot of $k/2.303$ against time was made. The intercept at zero time when only IIb was present represents the initial rate constant free from back reaction of IIa. The results of similar calculations are recorded in Table VII.

(46) H. L. Goering, J. P. Blanchard, and E. F. Silversmith, *J. Am. Chem. Soc.*, **76**, 5409 (1954).

(47) The author is indebted to Dr. E. F. Silversmith for pointing out this method of making these rate computations.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY, ITHACA, N. Y.]

Lewis Acid Induced Rapid Allylic Rearrangements of 2-Halo-3-hydroxy-2,4-dimethylcyclobutenones. An Unusually Reactive α -Haloketone¹

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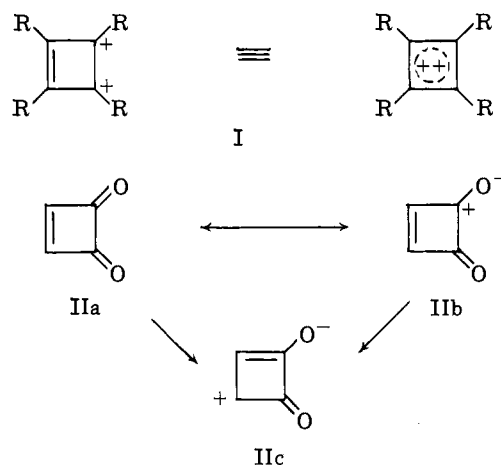
The n.m.r. spectrum of 3-hydroxy-2,4-dimethylcyclobutenone (X) demonstrates a long-range coupling constant of 2.5 c.p.s. through one double and four single bonds. The spectroscopic properties of X are discussed with reference to its essentially complete enolization. The sharp singlet observed for the methyl resonance in the n.m.r. spectra of 2-bromo-3-hydroxy-2,4-dimethylcyclobutenone (IX) and related compounds in the presence of Lewis acids is interpreted in terms of an allylic rearrangement taking place with a frequency of 100–200 sec.⁻¹. These observations are discussed with reference to the carbonium ion XVIII, a relative of the cyclobutadiene dication I.

Polyhalogenated cyclobutenes and cyclobutenones have enjoyed the attention of several groups of researchers for some years.^{3–8} This attention may be ascribed, in part, to an interest in the compound types as relatives or precursors of derivatives of the potentially stable cyclobutadiene dication I⁷ (R = H). Thus the Blomquist group³ and the Roberts group⁴ have prepared several derivatives of cyclobutene-3,4-dione (II) and have investigated their reactions in some detail. The relationship of the π -electron system of these substances to the 2π -electron cyclobutadiene dication system has been discussed by Roberts⁹ with reference to the several resonance contributors of type IIa–IIc, and has been popularized in the name "cyclobutadienoquinone."¹³ Further, the preparation of stable salts of substituted cyclobutadiene dications has been attempted both by Katz⁷ for I (R = CH₃) and by Freedman⁸ for I (R = C₆H₅).

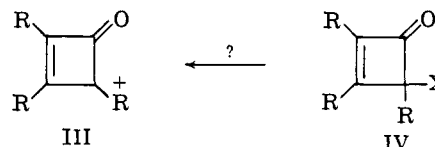
The possibility that there might be unusual stability associated with α -ketocarbenium ions of type III and, therefore, unusual reactivity associated with α -haloketones of type IV seemed a natural extrapolation from the above considerations. Further encouragement was afforded by the observations by Roberts that, although enol ether V, for which hydrolysis must proceed through the α -ketocarbenium ion VII,¹⁰ is stable to prolonged

Dipole Moment Measurements.—The dielectric constants of the neat liquids were measured by M. R. Kegelmann²⁹ using a General Radio Co. Type 716-C capacitance bridge and a Balsbaugh electrical measuring cell of 10-ml. capacity (Type 2TN-20LV) with nickel electrodes. Dissipation factors at 10 and 100 kc. were less than 0.5%. The measured ϵ' values were employed in the calculation of dipole moments listed in Table VI.

The dielectric constants for benzene solutions of the compounds at two concentrations were determined²⁸ by C. G. Wortz and by Naomi Schlichter using Dipolemeter Type DM 01 manufactured by the Wissenschaftlich-Technische Werkstätten, Weilheim, Oberbayern, Germany. Densities of the benzene solutions were measured by weighing 50 ml. in a volumetric flask. Molar refractions were calculated from the atomic refractions, and the polarization P_∞ extrapolated from the measured polarizations. Because the amount of the pure compounds was limited, measurements were made at only two concentrations. However, these values were checked by comparison with the moments calculated from the dielectric constants of the pure polar liquids.



heating with aqueous alcoholic acid,¹¹ enol ether VI, for which hydrolysis probably proceeds through the related carbonium ion VIII, is readily hydrolyzed on brief heating with this reagent. The present article is concerned with some reactions of derivatives of the haloketone IV which could lead through or to carbonium ions of type III.



The starting point for our investigation was the known bromoketone, 2-bromo-3-hydroxy-2,4-dimethylcyclobutenone (IX).¹² This substance was chosen

(11) E. I. Silversmith and J. D. Roberts, *J. Am. Chem. Soc.*, **80**, 4083 (1958).

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(3) J. D. Roberts, *Record Chem. Progr.*, **17**, 95 (1956).

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(10) J. Hine, "Physical Organic Chemistry," 2nd Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 169.