#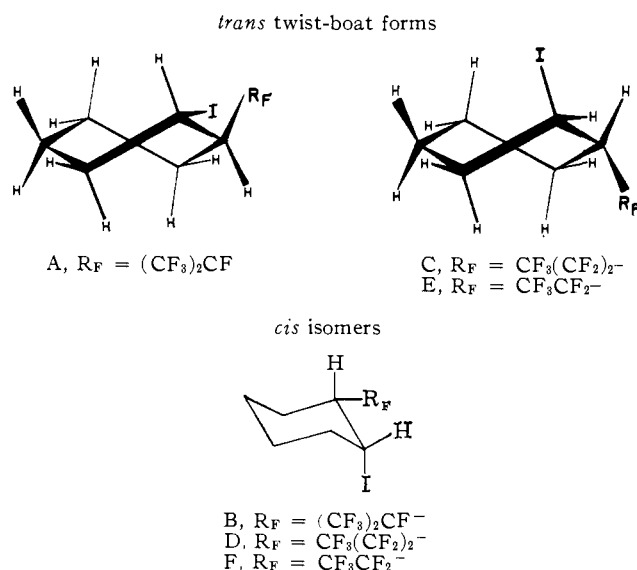 Reactions of 1-Iodo-2-(perfluoroalkyl)cyclohexane Conformers. Products of Elimination and Reduction. Rates and Mechanisms

BY NEAL O. BRACE

Base-induced elimination of cis- and trans-1-iodo-2-(perfluoroalkyl)cyclohexanes gave Δ^1- and Δ^2-olefins in high yield by a clean second-order reaction. cis Isomers, with axial iodine in a chair conformation, gave almost exclusively Δ^1-olefin at a rate accelerated tremendously by the favorable anti-coplanar geometry and by the perfluoroalkyl (R_F) group. trans Isomers, which exist as twist-boat forms, gave a mixture rich in Δ^2-olefin at a rate comparable to the very slow cis elimination from "β-benzene hexachloride" which cannot have anti-coplanar proton and halogen. This indicates that the proton being attacked by base in the twist-boat form is not anti-coplanar with the R_F group or iodine. The rate of the predominantly cis elimination to Δ^1-olefin from trans-1-iodo-2-(perfluorobutyl)cyclopentane was very nearly the same as for iodocyclohexane or for 1-iodopentane; a very much faster rate was anticipated for a concerted bimolecular syn-coplanar elimination mechanism. Zinc reduction of 1-iodo-2-(perfluoroalkyl)cyclohexanes gave (perfluoroalkyl)cyclohexanes of normal chair structures.

Reactions of 1-iodo-2-(perfluoroalkyl)cyclohexanes reveal consequences of steric and polar interactions of iodine and the large electronegative perfluoroalkyl (R_F) group in these unusual compounds.[1] As an example, thermal equilibration of cis and trans isomers having an isoperfluoropropyl group occurred at a rate several times that of isomers with an n-perfluoropropyl group. The preferred conformation of isomers having R_F groups of varying size and shape was deduced from n.m.r. spectra and dipole moments.[1] Isomers with bulky R_F groups appear to rest almost exclusively in only one of the two possible conformations over a wide temperature range. trans Conformers having isomeric perfluoropropyl groups differ in the positions occupied by R_F and iodine. Dipole moments, n.m.r. spectra, and equilibrium heat content data[1] indicate a "psuedo"-diequatorial arrangement for the isomer with a $(CF_3)_2$-CF— and a "pseudo"-diaxial configuration for the isomer with a $CF_3CF_2CF_2$— group, with the cyclohexane ring in both isomers being twisted into a shape having a higher energy and entropy than for a normal chair.

trans twist-boat forms

A, R_F = $(CF_3)_2CF$

C, R_F = $CF_3(CF_2)_2$—
E, R_F = CF_3CF_2—

cis isomers

B, R_F = $(CF_3)_2CF^-$
D, R_F = $CF_3(CF_2)_2^-$
F, R_F = $CF_3CF_2^-$

Only in an untwisted chair can concerted *trans* elimination of a proton and iodine at the preferred dihedral angle of 180° occur.[2-6] In accordance with the Curtin–Hammett principle,[7,8] however, it is generally assumed that reaction will take place in this conformation no matter how small the concentration may be, if the transition state free energy level for reaction is favorable. It was of interest, therefore, to determine the rates and products of elimination of the novel cis and trans isomers in order to assess the importance of the various possible factors.

In order to provide a solid basis for the interpretation of kinetic data, the rate of elimination from iodocyclohexane was determined under conditions identical with those used by Cristol[4] in his classic study of elimination rates of hexachlorocyclohexanes. The isomeric 1-iodo-2-(perfluoroalkyl)cyclohexanes and an acyclic analog ($CF_3CF_2CF_2CH_2CH_2I$) were hydrolyzed in the same system, as was also the corresponding trans-1-iodo-2-(perfluorobutyl)cyclopentane. These data afford an unusual opportunity to observe the effects of stereochemistry and the proximity of perfluoroalkyl groups on the course of a well-established chemical reaction.

Reduction of the isomeric 1-iodo-2-(perfluoroalkyl)-cyclohexanes to iodine-free (perfluoroalkyl)cyclohexanes was carried out in order to answer the question: "What effect will removal of the adjacent iodine have on rotation of the perfluoroalkyl group and on the conformational equilibrium of the cyclohexane ring"?

Results

Olefin Product Ratios.—The relative amount of Δ^1- and Δ^2-olefin obtained from isomeric 1-iodo-2-(perfluoroalkyl)cyclohexanes by dehydrohalogenation with sodium methoxide in methanol at 70° is listed in Table I. Hydrolysis in 92.6% ethanol at 30° gave identical results in the instance tested.

Alkaline hydrolysis of cis conformers B and D might be expected[6] to give a mixture of 1- and 3-heptafluoropropylcyclohexenes H to L, since the β-protons on C-2 and C-6 are both anti-coplanar with the iodine on

(2) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, p. 472.

(3) J. F. Bunnett, Angew. Chem. Intern. Ed. Engl., **1**, 225 (1962).

(4) (a) S. J. Cristol, J. Am. Chem. Soc., **69**, 338 (1947); (b) S. J. Cristol, N. L. Hause, and J. S. Meek, ibid., **73**, 674 (1951).

(5) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp. 140, 232.

(6) Cf. the menthyl chloride and neomenthyl chloride case (ref. 2 and 5).

(7) D. Y. Curtin, Record Chem. Progr., **15**, 111 (1954).

(8) See ref. 5, p. 151.

(1) N. O. Brace, J. Am. Chem. Soc., **84**, 3020 (1962); (b) ibid., **86**, 665 (1964); (c) J. Org. Chem., **28**, 3093 (1963).

Table I

Relative Amount of Δ^1- and Δ^2-Olefin from Dehydrohalogenation of *cis*- and *trans*-1-Iodo-2-(perluoroalkyl)cyclohexanes by Sodium Methoxide in Methanol at 70°

| | ─────Substituted cyclohexane───── | | Subst. cyclohexene, % | |
Isomer	Conform.	R_F	Δ^1	Δ^2
A	*trans* twist (e,e)	$(CF_3)_2CF-$	23	77
B	*cis* chair (a,e)	$(CF_3)_2CF-$	96	4
C	*trans* twist (a,a)	$CF_3(CF_2)_2-$	15	85
D	*cis* chair (a,e)	$CF_3(CF_2)_2-$	100	0
E	*trans* twist (a,a)	CF_3CF_2-	15[a]	85
F	*cis* chair (a,e)	CF_3CF_2-	100[a]	0

[a] In 92.6% ethanol at 30.0° also.

C-1. The stereoelectronic preference for base-induced *trans* elimination of a proton and halogen in halogen-substituted cyclohexanes is well known.[3-5] A transition state having axial iodine and β-proton in an *anti*-coplanar relationship, and therefore in which synchronized, concerted attack and elimination steps can occur, is recognized as a favorable configuration.[3,4]
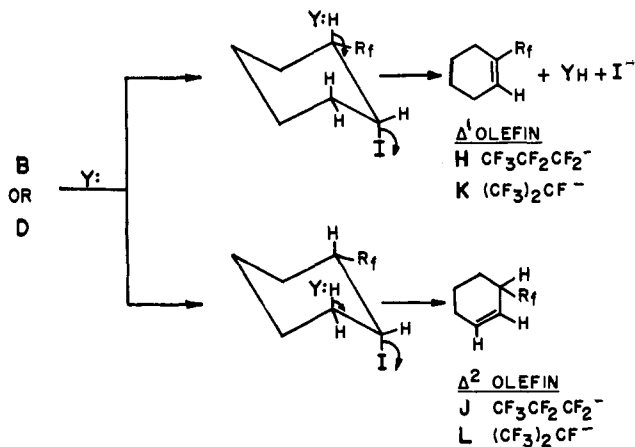
The olefinic product actually obtained from D, however, was at least 99% Δ^1-olefin (H) according to gas–liquid phase chromatography (g.l.c.). About 4% of Δ^2-olefin L was present in the mixture of K and L obtained from B.

There was no detectable isomerization of Δ^1- or Δ^2-olefin under the reaction conditions, and no higher boiling products of solvolysis were isolated by distillation or indicated by g.l.c. analysis (B and D were 99% pure).

Stereospecificity of hydrolysis was also observed with F. In this instance incomplete reaction only was permitted in order to determine if any isomerization to the *trans* isomer occurred. The *cis* isomer F recovered (40%) contained no increase in concentration of E. It is apparent that the attack of base on the proton at C-2 was greatly favored over C-6.

Hydrolysis of *trans* twist-boat isomers A, C, and E gave in high yield a mixture of Δ^1- and Δ^2-olefins in each case. A gave more Δ^1-olefin (23%) than did C or E (15%). Data are given in Table I. The relative amount of the two olefins was determined by g.l.c. and n.m.r. spectra analysis, and the results were consistent with infrared spectra, which showed a strong band at 6.00 μ in the Δ^1-isomers only. The same Δ^1- and Δ^2-olefins were obtained from A and B and the Δ^1-olefin from C had an infrared spectrum and g.l.c. retention time identical with olefin from D. This
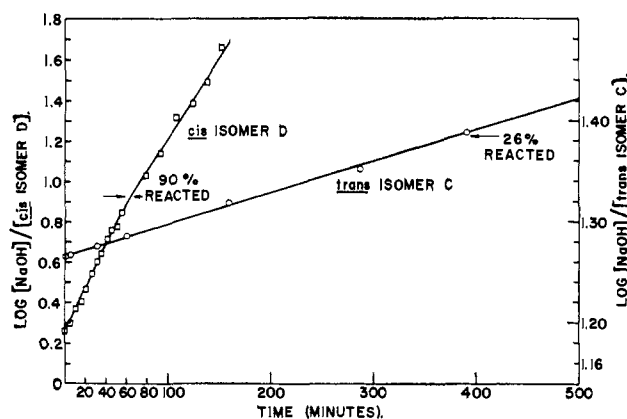

Fig. 1.—Hydrolysis rates for *cis*-1-iodo-2-(perfluoropropyl)-cyclohexane (D) and *trans*-1-iodo-2-(perfluoropropyl)cyclohexane (C) at 30.00° in 92.6% ethanol.

constitutes at once a proof of the *cis–trans* relationship of A and B, and of C and D, and renders unlikely the possibility that these could have been position isomers. An analogous conclusion applies to E and F and to *cis*- and *trans*-1-iodo-2-(perfluoroheptyl)cyclohexane which also gave only Δ^1- and Δ^2-olefins. The proton n.m.r. spectra of H and K were quite similar, as were the proton n.m.r. spectra of J and L. Chemical shifts for proton and F^{19} n.m.r. spectra are recorded in the Experimental. The surprising lack of stereoelectronic control of elimination from the *trans* isomers is discussed in detail below.

Rate Studies.—In order to assess properly the significance of the olefin product ratios, rate studies at 30.00° were done in 76.1 and 92.6% ethanol. It was determined that: (1), the elimination reactions were all second order, since good straight line plots of log [NaOH]/[isomer] against time passing through the original concentration ratio were obtained up to 90% reaction (see Fig. 1); (2), the rate of reaction of *cis* conformers was about 10,000 times greater than that of *trans* isomers which varied among themselves by a factor of only about three; (3), *cis* conformers hydrolyzed at a slightly slower rate beyond 90% reaction; and (4), model compounds: iodocyclohexane, 1-iodopentane, $CF_3CF_2CF_2CH_2CH_2I$ (G), and from the literature, "β- and γ-benzene hexachloride"[4] and *t*-amyl iodide[9] $[CH_3CH_2C(CH_3)_2I]$, gave hydrolysis rates quite consistent with these results. Rate of hydrolysis in 76.1% ethanol was about half that in 92.6% ethanol. The data are recorded in Table II. Relative rates calculated using iodocyclohexane rate = 1.00 and partial rate factors for Δ^1- and Δ^2-olefin formation are given in Table III.

Measurement of reaction rates by the procedure used previously[4] which employed the well-known Volhard titration[10] for determination of iodide concentration was satisfactory for isomers A to F. With iodocyclohexane and 1-iodopentane, however, rapid solvolysis occurred after the addition of silver nitrate and entirely erroneous results were obtained. Extraction into cyclohexane gave troublesome emulsions, but was otherwise satisfactory.[11]

(9) H. C. Brown and I. Moritani, *J. Am. Chem. Soc.*, **76**, 455 (1954).

(10) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1948, p. 475.
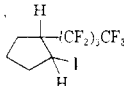
(11) T. D. Nevitt and G. S. Hammond, *J. Am. Chem. Soc.*, **76**, 4124 (1954).

TABLE II

DATA AND REACTION RATE CONSTANTS FOR DEHYDROHALOGENATION OF ALKYL AND CYCLOALKYL HALIDES BY SODIUM HYDROXIDE IN 76.1 AND 92.6% ETHANOL AT 30.00°

Compound, R_F	[Halide], M	[NaOH], M	$k_{30.00}°$, l./sec. mole, 92.6%	$k_{30.00}°$, l./sec. mole, 76.1%
"β-Benzene hexachloride"	0.001046	0.05621	2.11×10^{-5a}	
	.000838	.03782		3×10^{-6b}
"γ-Benzene hexachloride"	.001	.005609	0.151^a	
	.000939	.00471		0.0435^b
Iodocyclohexane^c	.0286	.2497	7.9×10^{-5}	
	.02176	.2299		7.75×10^{-5}
1-Iodopentane^c	.01576	.2790	5.0×10^{-5}	
	.0206	.2423		3.5×10^{-5}
$CF_3CF_2CF_2CH_2CH_2I$ (G)	.00489	.005016	0.155	
A, trans twist e,e (CF_3)$_2CF-$	.006956	.9603		7.55×10^{-6}
	.00598	.908	1.5×10^{-5}	
B, cis a,e (CF_3)$_2CF-$	.004038	.01253		0.055
	.00394	.01254	0.14^d	
	.003925	.005016	0.11^d	
C, trans twist a,a $CF_3(CF_2)_2-$	.05430	.998	1.30×10^{-5}	
D, cis a,e $CF_3(CF_2)_2-$	.00532	.00538	0.11^d	
	.00529	.00974	0.092^e	
E, trans twist, a,a CF_3CF_2-	.01313	.991	1.05×10^{-5}	
F, cis a,e CF_3CF_2-	.002228	.009557	$(0.21)^{d\,f}$	
M (a cyclopentane), $CF_3(CF_2)_3-$	.00971	.999	5.60×10^{-5}	

^{a} See ref. 4a. ^{b} See ref. 4b. ^{c} t-Amyl iodide [$CH_3CH_2C(CH_3)_2I$] is estimated from the data given in ref. 9 for hydrolysis in t-butyl alcohol solution to have $k_2 = 10.4 \times 10^{-5}$ l. mole^{-1} sec.$^{-1}$ at 25° in ethanol solution. ^{d} Data obtained by Volhard titration; error in measuring the slope was about $\pm 10\%$. ^{e} Data obtained by potentiometer method of analysis; the rate constant is for 90% hydrolyses of D; error in measuring slope was about $\pm 3\%$. ^{f} The limits of error for this value are greater than the precision of the other data.

TABLE III

RELATIVE RATES AND PARTIAL RATE FACTORS FOR HYDROLYSES OF cis- AND trans-1-IODO-2-(PERFLUOROALKYL)CYCLOHEXANES TO Δ^1- AND Δ^2-OLEFIN (IODOCYCLOHEXANE RATE = 1.00)

| Cyclohexane isomer Conformation	R_F	Rel. rate	Partial rate factor Δ^1-Olefin	Partial rate factor Δ^2-Olefin
A, trans twist e,e	(CF_3)$_2CF-$	0.19	0.044	0.15
C, trans twist a,a	$CF_3(CF_2)_2-$	.16	.024	.136
E, trans twist a,a	CF_3CF_2-	.133	.020	.113
B, cis chair a,e	(CF_3)$_2CF-$	1770	1700	70
D, cis chair a,e	$CF_3(CF_2)_2-$	1170	1170	...
G, $CF_3CF_2CF_2CH_2CH_2I$		1960	1960	...
M, (cyclopentane structure with $(CF_2)_3CF_3$, H, I, H)		0.71	0.475	0.234
Iodocyclohexane		1.00	0.5	0.5
$CH_3CH_2CH_2CH_2CH_2I$		0.63	...	...
"β-Benzene hexachloride"		0.27	...	...
"γ-Benzene hexachloride"		1901	...	...

An elegantly suitable procedure was devised employing a potentiometric method of analysis[12]; it also gave more precise data for isomers A to F. A silver electrode and a mercury–mercurous sulfate couple as reference electrode were used, with sodium sulfate as supporting electrolyte. The change in potential of the cell upon the addition of silver nitrate solution was measured with a pH meter, which gave a sharp break at the equivalence point. The midpoint of the curve occurred at about 300 mvolts.

Discussion

The product and rate studies demonstrate that the electrophilic R_F group activates the proton of C-2,

promoting attack by base. There is of course a strong preference for concerted trans-elimination of anti-coplanar groups, as shown by the great acceleration in rate of elimination from the favorably constituted cis isomers. The rates for iodocyclohexane or 1-iodopentane,[13,14] which have no activating R_F group, were comparable and much less than that of $CF_3CF_2CF_2$-CH_2CH_2I (G). Like the cis conformers, G may readily assume a conformation of the favorable type in which one β-proton is anti-coplanar to iodine and attack by base is promoted by the R_F group. As cited above,
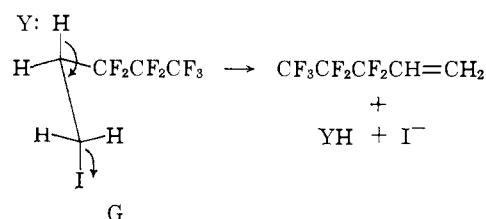
the cis isomers appear from n.m.r. studies to prefer the conformation having the trans arrangement of axial iodine and a proton on C-2. It is necessary for trans isomers to shift from the more stable e,e-chair conformation or a twist form into an a,a-chair conformation in order to place a proton and adjacent iodine in anti-coplanar position.[2,5]

When the rate data for trans twist-boat isomers A, C, and E are considered, one is immediately confronted with the fact that dehydrohalogenation occurs one-fifth to one-sixth of that for iodocyclohexane. One might assume that for concerted attack and elimination from A, C, or E with twisted rings, additional energy over that required for iodocyclohexane must be supplied to bring the substituents on C-1 and C-6 into anti-coplanar position.[5] But then one is puzzled by the fact that the twist-boat isomer A with the groups in "pseudo" e,e-positions actually reacts slightly faster than the twist-boat isomers C or E in which the groups are "pseudo"-diaxial. The partial rate factors for Δ^2-olefin formation (which may involve the assumed anti-coplanar transition state) are almost identical, however, and the chief difference is in the Δ^1-olefin rate factors (0.044 for A vs. 0.02 for C or E) for which trans elimination is not possible. This confused picture is clarified considerably by reference to the relative rate of hydrolysis of "β-benzene hexachloride," which has no anti-coplanar proton and halogen in either conformation.[4] The relative value is 0.27, about twice that of the trans twist-boat isomers.

"β-Benzene hexachloride" must undergo cis elimination, which involves a carbanion intermediate as an extreme transition state structure made more probable by the stabilizing influence of the electrophilic halogen.[4] The two steps in cis elimination may be concerted, but removal of the proton precedes in time sequence removal of halogen.[5] These data clearly imply that the anti-coplanar transition state is not involved in any of the trans isomer hydrolyses. If it were, the rate should have been greater, and not less, than that of "β-benzene hexachloride." It should be understood, of course, that if Δ^1- and Δ^2- olefin are formed by two different mechanisms as predicted from previous

(12) The author is indebted to L. A. Williams, who first demonstrated the suitability of this method of analysis.

(13) These data are more in line with the rate for t-pentyl iodide (ref. 9) than the old values for iodocyclohexane (see ref. 14).

(14) B. W. Tronow and L. W. Ladigina, Chem. Ber., 63B, 3060 (1930).

concepts, it is also to be expected that the rate for A would be smaller than for C and E.

The reluctance for the twist-boat isomers to assume a conformation in which the R_F and iodine groups are truly diaxial and maximally crowded by axial hydrogens, therefore, appears to direct the reaction to the *cis* elimination mechanism. The energy barrier to rotation for A, C, and E evidently has a magnitude comparable to the activation energy for *cis* elimination. From the higher partial rate factor for Δ^1-olefin from A over C or E, one may conclude that approach of base to the proton adjacent to the *branched* R_F is less hindered than in the case of *straight-chain* perfluoroalkyl groups. It is interesting to note that one interpretation of the F^{19} n.m.r. spectral data of these isomers is that straight chain R_F groups are rotating more freely with respect to the ring than is the isoperfluoropropyl group.[2]

While carbanion mechanism for Δ^1-olefin has in its favor the activating influence of the α-R_F group, one must also consider the possibility that prior isomerization of *trans* to *cis* structure may occur, induced by iodide ion. It was not possible to find evidence for isomerization of *trans* to *cis* during hydrolysis, but also it is unlikely that the *cis* isomer would be recovered from partially reacted mixtures in view of its 10,000 times faster rate of hydrolysis. No hydrolysis of *trans* conformers occurred under conditions that gave complete reaction of the *cis* conformers. The rate of exchange[15] of radioactive sodium iodide with iodocyclohexane in absolute ethanol at 25° was 0.84×10^{-7} l. mole^{-1}. This is about 1/900 as fast as the rate of hydrolysis of iodocyclohexane and 1/180 that of A or C in 92.6% ethanol. Hence, it is not likely that iodide exchange and concomitant isomerization could account for Δ^1-olefin.

Carbanion mechanism for Δ^1-olefin formation has been postulated for elimination from other cyclohexanes with α-electrophilic groups. According to Bunnett,[3] an aryl substituent on C-2 should cause a shift toward carbanion character in the transition state. Elimination of a tosylate group from *trans* isomers with β-phenyl[16] or β-p-toluenesulfonyl substituent[17] gave Δ^1-olefin in both cases.

We would like to enquire further what implications the carbanion mechanism may have for the rate and products of elimination from the analogous *trans*-substituted cyclopentane M. The second-order rate constant (Table III) for M was four times[18] that of twist-boat isomers A and C, but only 1/3000 that of *cis* chair compounds B or D, and a little less that the rate for iodocyclohexane. The ratio of Δ^1- to Δ^2-olefin was 3/1 using sodium hydroxide in 92.6% ethanol, or 2/1 with sodium methoxide in anhydrous methanol.

The proton on C-2 of M can be readily made to eclipse iodine with only slight twisting,[19,20] but only a proton

(15) S. F. Van Straten, R. V. V. Nichols, and C. A. Winkler, *Can. J. Chem.*, **29**, 372 (1951).

(16) S. J. Cristol and F. R. Stermitz, *J. Am. Chem. Soc.*, **82**, 4692 (1960); (b) S. J. Cristol and D. I. Davies, *J. Org. Chem.*, **27**, 293 (1962).
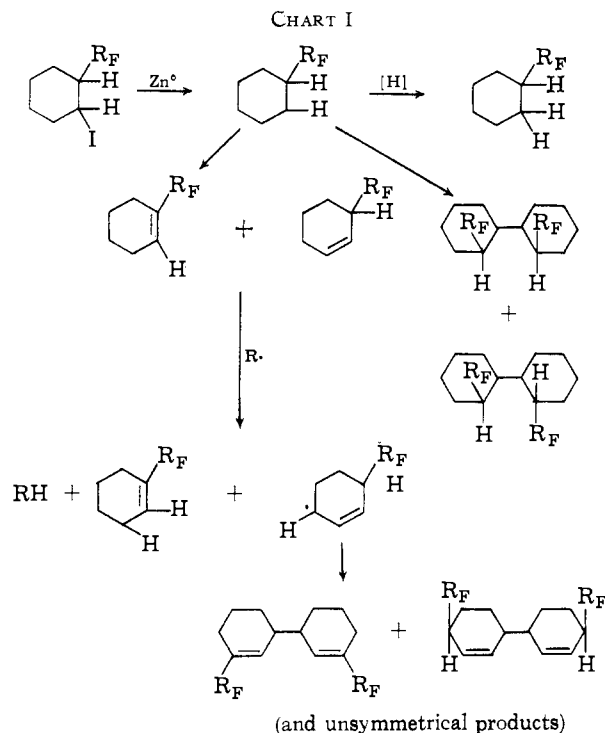
(17) J. Weinstock, R. G. Pearson, and F. G. Bordwell, *J. Am. Chem. Soc.*, **76**, 4748 (1954).

(18) J. D. Roberts and V. C. Chambers, *ibid.*, **73**, 5034 (1951). Bimolecular rate constants for cyclopentyl bromide reactions were greater than for cyclohexyl bromide reactions by a factor of six.

(19) F. V. Brutcher and W. Bauer, Jr., *J. Am. Chem. Soc.*, **84**, 2233 (1962).

(20) C. H. DePuy, R. D. Thurn, and G. F. Morris, *ibid.*, **84**, 1314 (1962).

on C-5 can be twisted into a *trans*-like position. *cis* Elimination of the proton adjacent to the R_F group is evidently favored over *trans* elimination of the unactivated proton on C-5.
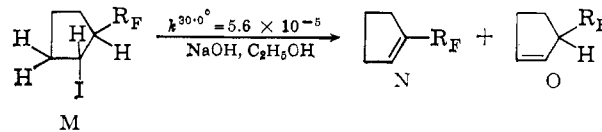
According to a theory recently put forward,[20] concerted bimolecular elimination with the leaving group at a 0° dihedral angle to the proton in a cyclopentane should occur at a rate comparable to that of the well-recognized *anti*-coplanar transition state with the groups at a 180° dihedral angle in a cyclohexane. However, the over-all rate observed for M is more like that of *cis* elimination in the cyclohexane system involving a noncoplanar transition state. *Therefore, a carbanion mechanism for cis elimination from M appears to be operating.* In this connection the previously determined[1] olefin product ratio for tri-*n*-butylamine elimination (16% of N and 83% of O) from M clearly shows the effect of a bulky attacking base, which is directed away from the sterically shielded proton of C-2 in spite of stabilization of the carbanion by the R_F group.

Reduction of Isomers A to D.—Lithium aluminum hydride in refluxing ether solution failed to react with C and D to any appreciable extent,[21] but zinc and hydriodic acid in ethanol gave rapid reduction. Unfortunately, replacement with hydrogen was accompanied by disproportionation of the (heptafluoropropyl)cyclohexyl radical to Δ^1- and Δ^2-olefins and a mixture of bi[2-(heptafluoropropyl)cyclohex-1-yl] and bi[3- or 4-(heptafluoropropyl)cyclohexen-2-yl] isomers. Reduction of A and B gave quite similar results. Identity of the primary products was established by elementary and g.l.c. analysis and by n.m.r. spectra. It is significant that the two CF_3 groups of (heptafluoroisopropyl)cyclohexane in F^{19} n.m.r. spectrum were chemically shifted only 0.07 p.p.m., indicating very similar shielding for the now rapidly rotating $(CF_3)_2CF$ group. In A or B the two CF_3 groups were nonequivalent and showed separate peaks 2.75 to 4.1 p.p.m. apart.[1] Hindrance to free rotation and probably to inversion of the ring were drastically reduced by the removal of iodine.

The higher boiling coupled products consisted of five compounds (g.l.c.), some of which were unsaturated (decolorized dilute potassium permanganate solution in acetone in 1 min.). The infrared spectrum indicated a small amount of unsaturation of the type with an R_F group attached to the double bond. A scheme by which these results may be rationalized is shown in Chart I.

Abstraction of allylic hydrogen from Δ^1- and Δ^2-olefins by, for example, the (heptafluoropropyl)cyclohexyl radical, would give isomeric (heptafluoropropyl)cyclohexenyl radicals which could couple in several ways. In view of the possible complexities and the viscous nature of the coupled products, further investigation was not considered appropriate.

(21) N. G. Gaylord, "Reduction with Complex Metal Hydrides," Interscience Publishers, Inc., New York, N. Y., 1956, p. 890.

CHART I

(and unsymmetrical products)

Experimental

Starting Materials.—*cis*- and *trans*-1-iodo-2-(perfluoroalkyl)-cyclohexane pure isomers were obtained from preparative gas chromatography,[1] followed by treatment with activated alumina and a short path distillation to free the compounds from polar impurities and any of the liquid phase material eluted from the g.l.c. column. 1-Iodopentane and iodocyclohexane were obtained from Distillation Products, Ind., and redistilled; analysis by g.l.c., >99% pure. 1-Iodo-3,3,4,4,5,5,5-heptafluoropentane, b.p. 62° (100 mm.), n^{25}D 1.377, was obtained from the addition of 1-iodoperfluoropropane to ethylene.[22] Anhydrous ethanol was diluted to the desired concentration. Sodium hydroxide was dissolved in the aqueous ethanol and the normality of the solution determined by titration prior to use. All g.l.c. analyses were performed using a Perkin–Elmer vapor fractometer Model 154-C, with helium carrier gas.

Rate Measurements.—A procedure similar to that used by Cristol[4] was employed. The bath temperature was controlled to ±0.01°. Titration of iodide ion in most cases was by the normal Volhard procedure.[10] There was no detectable solvolysis to cyclohexanols; titration with silver nitrate by a conductometric method gave precise and compatible results. Ethanol (96.2% by weight) was used in most experiments in order to give a reasonable rate for the *trans* isomers; the rate of hydrolysis in 76.1% (by wt.) ethanol was measured for one *cis* and one *trans* isomer.

A typical experiment was conducted as follows: *cis*-1-iodo-2-(perfluoropropyl)cyclohexane (D, 0.20861 g., 0.0005518 mole) was dissolved in 92.6% (by wt.) ethanol at 30.00° in a 100-ml. volumetric flask. 5.00 ml. of 0.2545 N sodium hydroxide solution (0.00125 mole) at 30.00° was added, and brought to volume at 30.00°. After 3- and 5-min. intervals thereafter a 10-ml. aliquot was added to 5 ml. of 1.5 N nitric acid; 5 ml. of 0.0301 N silver nitrate solution and a drop of ferrous ammonium sulfate solution were added and the excess of silver nitrate titrated with 0.0201 N potassium thiocyanate solution. The concentrations of the alkali, iodide ion, and unreacted D were calculated for each sample, and the extent of reaction also calculated. Hydrolysis attained 98% in 140 min. in this case.

With the *trans* isomers it was necessary to increase the concentration of the reactants by 10³ in order to have measurable rates at 30°. Thus, *trans*-1-iodo-2-(perfluoropropyl)cyclohexane (C, 0.2053 g., 0.000543 mole) was weighed in a 10-ml. volumetric flask which was then filled with 0.998 N sodium hydroxide (0.00998 mole) in 92.6% (by wt.) ethanol at 30.00°. One-ml.

aliquots were removed and titrated as above using 0.01 N silver nitrate and potassium thiocyanate solutions. The results are given in Table IV.

TABLE IV
RATE OF HYDROLYSIS OF C AT 30.00°

Time, min.	Titer 0.01004 N KCNS, ml.	I, mequiv./ml.	% C reacted	[C]	[NaOH]/[C]
0.0				0.05430	18.4
5.0	9.95	0.00052	0.95	.0538	18.5
30.0	9.85	.00156	2.87	.0527	18.9
60.0	9.75	.00260	4.78	.0514	19.3
160.0	9.36	.00671	12.3	.0476	20.8
287.0	9.00	.0104	19.2	.0439	22.5
392.0	8.65	.0140	28.8	.0403	24.4
649.0	8.00	.02080	38.3	.0335	29.2
948.0	7.40	.02704	49.8	.02735	35.6
1463	6.50	.0364	67.0	.0179	53.7

A plot of log $[NaOH]_t/[C]_t$ *vs.* time (t) (see Fig. 1) gave a straight line of slope 3.194×10^{-5}/min.; k was calculated from the expression[23]

$$k = \frac{2.303 \text{ slope}}{60([NaOH]_0 - [C]_0)} = 1.30 \times 10^{-5} \text{ l. mole}^{-1} \text{ sec.}^{-1}$$

An estimate of the error in measuring the slope was determined using the least squares method by W. R. Saadeh. For Volhard titrations it ranged ±3 to 10% and for potentiometric titrations it was ±3.0% (95% confidence limits).

Potentiometric Titration of Iodide.[12]—A 5.00-ml. aliquot of sodium iodide, sodium hydroxide, and iodocyclohexane (or 1-iodopentane, or isomer A to F) in 96.2% ethanol containing about 0.006 mequiv. of sodium iodide/ml. was added to 5.0 ml. of 1.5 N nitric acid in a 250-ml. beaker (if the solution was yellow, a crystal of sodium bisulfite was added); 50 ml. of 2 N sodium sulfate solution was added, and the contents diluted to about 100 ml. The pH was adjusted to 2.0 ± 0.2 by the addition of 1.5 N nitric acid if necessary. A silver electrode and a mercury–mercurous sulfate[24] reference electrode covered with sodium sulfate solution were inserted in the solution and electrical connections attached to the pH meter (Beckman Model G). Silver nitrate solution (0.1 N) was added from a microburet dipping into the solution, following the drop of potential across the electrodes, while stirring with a Teflon-covered magnet bar. At the near equivalence point the microburet was removed from the solution, and the potential drop *vs.* titrant curve was used to calculate ΔV/ml. of silver nitrate solution and to determine the difference in the amount of titrant added and the amount required for exact equivalence (*e.g.* at 300 mvolts). This amount was then added to or subtracted from the actual titer as indicated by the mvolt difference between the reference and the observed potential. The results agreed well with the Volhard method. Titration of iodocyclohexane or 1-iodopentane solution, however, gave meaningful results only by the potentiometric method.

1-Perfluoropropylcyclohexene (H) and 3-Perfluoropropyl-cyclohexene J.—*cis*-1-Iodo-2-(perfluoropropyl)cyclohexane (99% pure isomer D by g.l.c. analysis, 7.0 g., 0.0185 mole) was added to a stirred mixture of sodium methoxide (analytical reagent, 2.2 g., 0.04 mole) and anhydrous methanol (25 ml.). The mixture was heated at 70° under a reflux condenser connected to a trap kept at −70° for 4 hr., cooled to 25°, and poured into 50 ml. of water. The aqueous layer was extracted three times with dichloromethane, and the organic extract dried over magnesium sulfate. Distillation in a 16-in. platinum spinning band column (column A) gave 3.60 g. (77% of theory) of H, b.p. 83° (127 mm.), n^{25}D 1.3598; g.l.c. analysis (see below) showed that 99.8% of the total area was under 1 peak and none of J was indicated. There was no residue. Physical constants previously reported[25] for H are; b.p. 134–135°, n^{25}D 1.3629.

(22) J. D. Park, E. R. Larsen, H. V. Holler, and J. R. Lacher, *J. Org. Chem.*, **23**, 1166 (1958).

(23) S. Glasstone, "Text Book of Physical Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1940, p. 1036.

(24) J. J. Lingane, "Electroanalytical Chemistry," Interscience Publishers, Inc., New York, N. Y., 1953, p. 262.

(25) E. T. McBee, C. W. Roberts, and A. F. Meiners, *J. Am. Chem. Soc.*, **79**, 335 (1957).

The refractive index of a mixture of H and J was slightly higher, and they did not differ sufficiently in boiling point to be separated (see below).

An infrared spectrum of H had a weak band absorbing at 3.20 μ, a strong band at 6.00 μ, and a band at 10.38 μ but not at 10.10 μ. The n.m.r. spectrum obtained at 60 Mc. with an A-60 Varian Associates instrument showed only one vinyl proton resonance at -6.30 p.p.m. (all proton n.m.r. peaks were measured relative to tetramethylsilane), and two proton resonance peaks (area, 4 protons each) at -2.18 and -1.75 p.p.m. (30 c./slc. separation). These peaks represent the time-averaged *axial* and *equatorial* methylene proton resonances. The F[19] n.m.r. spectrum[26] of H at 56.4 Mc. (trifluoroacetic acid was used as external reference in all cases) gave three resonances: CF$_3$ at $+3.74$ p.p.m. (a triplet, $J_{FF} = 10$ c./sec.); a CF$_2$ peak at $+37.07$ (a 4-line multiplet of the AB type, $J_{FF} = 10$ c./sec., with an additional splitting of 1 c./sec. of each peak); and a CF$_2$ peak at $+49.13$ p.p.m. with no evident splitting.

Anal. Calcd. for C$_9$H$_9$F$_7$: C, 43.21; H, 3.63. Found: C, 43.3; H, 3.9.

trans-1-Iodo-2-(perfluoropropyl)cyclohexane (99.8% pure isomer C by g.l.c. analysis, 7.0 g., 0.0185 mole) by a procedure identical with the above gave 3.57 g. (77.3% of theory) of H and J, b.p. 78–82° (132 mm.), n^{25}D 1.3604. The composition of the mixture was determined by g.l.c. analysis using a 2-m. bis-β-methoxyethyl phthalate column (20%) on Chromosorb packing operated at 65° with 7 p.s.i. of applied helium pressure at 45.8 ml./min. flow. The identity, retention times, and areas were: H at 12.0 min., 16.5%; J at 14.65 min., 83.0%. This column gave better separation of H and J than other columns used.[1b]

An infrared spectrum showed a band at 6.00 μ (from H) and bands at 10.10 and 10.4 μ. An n.m.r. spectrum showed 2 resonances for vinyl protons; the —HC=CR$_F$ proton at -6.30 p.p.m. (area of 0.17 proton) from H and the —HC=CH—CHR$_F$ protons at -6.10 to -5.55 p.p.m. (area of 1.4 protons) from J. The complex splitting pattern of the latter protons was not resolved, inasmuch as the ratio of chemical shift to coupling constant was too small. Nevertheless, the relative areas agreed with the composition of the mixture as determined by g.l.c. analysis. The –CHR$_F$ proton resonance of J was at -2.99 p.p.m. (area 0.85 proton). The F[19] n.m.r. spectrum[26] of J taken at 56.4 Mc. as for H also gave three resonance peaks: CF$_3$ (a triplet) at $+4.24$ p.p.m., an exceedingly complex CF$_2$ multiplet at $+40.23$ p.p.m., and an AB type 4-line pattern at $+47.85$ p.p.m.

When H was heated with sodium methoxide under the conditions used above, the recovered olefin was unchanged in composition; a mixture of 16.5% of H and 83% of J was likewise unaffected by this treatment. Equilibration therefore did not occur during synthesis.

The dipole moment of a mixture of 59% H and 40.2% J measured in dilute benzene solution at 25° was 2.9 debye units.[1] The pure liquid (d^{25}_4 1.327; n^{25}D 1.3504) at 25° gave 2.75 D.[1]

1-Perfluoroisopropylcyclohexene (K) and 3-Perfluoroisopropyl-cyclohexene (L).—This procedure illustrates the small-scale technique empoyed in cases where insufficient pure isomer was available for fractionation of products. *cis*-1-Iodo-2-(perfluoro-isopropyl)cyclohexane (98% pure B by g.l.c. analysis, 0.35 g., 0.00092 mole) was added to a slurry of sodium methoxide (0.30 g., 0.0056 mole) in anhydrous methanol (3.0 ml.) and heated at 70° while stirring as in previous experiments. Water (10 ml.) was added the the organic layer extracted into cyclohexane (4 ml.) in four portions. The total organic extract (2.61 g.) was dried over magnesium sulfate (0.2 g.) and g.l.c. analysis performed (2-m. Perkin-Elmer "R," "Ucon" polypropylene glycol oil LB-550-X column at 150°; 15 p.s.i. helium pressure at 45 ml./min. flow rate). Replicate analyses gave (area %) cyclohexane (95.2), K (4.59) at 3.1 min. retention time, and L (0.19) at 3.5 min. A weighed mixture of the olefins in cyclohexane was also analyzed by g.l.c. The weight–area factors showed that the recovery was 91% of theory and the relative amount of K was 96% and L was 4%. The water solution was found to contain the theoretical amount of sodium iodide (Volhard analysis).

trans-1-Iodo-2-(perfluoroisopropyl)cyclohexane (A) under identical conditions gave K (22.2%) and L (77.8%). A twofold increase in amount of reactants gave 21.6/78.4. A tenfold

increase in amount of reactants and isolation by distillation gave an olefin mixture (1.76 g., 58% recovery, and no residu e or higher boiling products) which had b.p. 66–72° (140 mm.), n^{25}D 1.3667, and contained 22% of K and 78% of L by g.l.c. analysis.[27]

When the K/L mixture (0.68 g.) was heated for 4 hr. at 70° with alkali as above and recovered, the ratio of isomers was unchanged according to g.l.c. analysis.

A mixture of B (20%) and A (80%) (15.1 g., 0.04 mole) and sodium methoxide (5.4 g., 0.1 mole) in methanol (50 ml.) in analogous manner gave a mixture (8.9 g., 90% yield) of K (41.1%) and L (58%), b.p. 128–134° (1 atm. pressure) of b.p. 84–87° (170 mm.), n^{25}D 1.3645 to 1.3658 (4 different fractions, column A).

An infrared spectrum of this mixture showed a weak (vinyl) carbon–hydrogen stretching band at 3.20, a weak vinyl double bond band at 6.00, and bands at 10.20 to 10.40 μ (not resolved). The n.m.r. spectrum (at 60 Mc.) was analogous to that of the H/J mixture, but notable differences appeared also. The proton resonance of —HC=CR$_F$ was at -6.37 p.p.m. (0.42 proton area) and the resonance pattern of —HC=CHR$_F$ protons (0.84 proton area) appeared at -5.86 p.p.m. with "wings" at -5.65 and -6.10 p.p.m. (The vinyl proton resonance of cyclohexene is at -5.57 p.p.m.) A broad resonance peak of the -CHR$_F$ proton was at -2.90 to -3.4 p.p.m. (0.70 proton area). Methylene protons gave a complex pattern from -1.6 to -2.35 p.p.m. (9 protons area). These areas correspond to the composition of the olefin mixture.

Anal. Calcd. for C$_9$H$_9$F$_7$: C, 43.21; H, 3.62. Found: C, 43.6; H, 3.8.

(Heptafluoropropyl)cyclohexane.—A slurry of zinc (30 mesh, 5.0 g., 0.077 g.-atom), anhydrous ethanol (25 ml.), and C and D mixture (17/82, 10.0 g., 0.0264 mole) was heated to 80° while 55% aqueous hydriodic acid (3.0 ml.) was added in 1-ml. portions to moderate the evolution of hydrogen. After 1 hr. the addition of acid was repeated. The liquid was decanted into 100 ml. of water, unreacted zinc was rinsed with ethanol, and the aqueous solution was extracted three times with 10 ml. of dichloromethane. The organic extract was shaken with saturated sodium bicarbonate solution, dried over magnesium sulfate, and distilled in column A. (Perfluoropropyl)cyclohexane, b.p. 90° (169 mm.), n^{25}D 1.3525, retention time 19.5 min., 4.1 g. (62% of theory), was obtained. The product also contained H (1.2%), retention time 20.7 min., and J (5.0%), retention time 21.85 min., and less than 1% of several other impurities (g.l.c. analysis using a 2-m. R column at 80°, 15 p.s.i. helium pressure, 5.0 flow). Peak enhancement with H and J was used for positive identification. A mixture of coupled products, 1,1'-bis[2-(perfluoropropyl)cyclohexanyl] and -cyclohexenyl] isomers, was also distilled; b.p. 50° (3.0 mm.), n^{25}D 1.4182, 0.47 g. The column hold-up was 0.32 g. (total 13% of theory). The coupled products decolorized 1% potassium permanganate in acetone solution and showed a weak vinyl absorption band near 6.00 μ in the infrared.

A proton n.m.r. spectrum of (heptafluoropropyl)cyclohexane at 60 Mc. had a 6-proton peak at -1.90 p.p.m. and a 5-proton group of three peaks centered at -1.30 p.p.m. The F[19] n.m.r. spectrum[26] at 56.4 Mc. with trifluoroacetic acid external reference showed a CF$_3$ triplet peak at $+4.08$ p.p.m. ($J = 10$ c./sec.), a highly complex CF$_2$ multiplet at $+27.84$ p.p.m. (>16 lines) composed of six peaks separated by 11 to 12 c./sec., each split into three with 3 to 4 c./sec. splittings, and a CF$_2$ peak at $+33.69$ p.p.m. containing an inner set of three lines and an outer pair at 17 c./sec. spacing from the center.

Anal. Calcd. for C$_9$F$_7$H$_{11}$: C, 42.9; H, 4.40. Found: C, 43.1; H, 4.3. Calcd. for C$_{18}$H$_{20}$F$_{14}$: C, 43.0; H, 4.0. Found (coupled product): C, 42.9; H, 4.3.

(Heptafluoroisopropyl)cyclohexane.—By an identical procedure a mixture of A and B (16/84, respectively, 10.0 g., 0.0264 mole) gave (heptafluoroisopropyl)cyclohexane, b.p. 88° (166 mm.), n^{25}D 1.3602, retention time 15.45 min. at 80°, 4.53 g. (68% of theory), which was mixed with 17.8% of L (retention time 17.6 min. at 80°). A "coupled" product, b.p. 86–90° (1.2 mm.), n^{25}D 1.3979, 0.68 g., and hold-up, 0.36 g., was also obtained (total 16% of theory). This was a complex mixture as shown by g.l.c. analysis. There were obtained five peaks having relative areas and retention times of 34.3% at 56.7 min., 27.7% at 59.3 min., 18.7% at 65.0 min., 14.4% at 67.9 min., and 4.78% at

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(26) F[19] n.m.r. were taken at 25° by T. E. Beukelman using a Varian Associates high resolution spectrometer.

(27) The ratio K/L from A was erroneously reported as 60/40 (ref. 1a).

73.3 min. (2-m. R column at 150° with 54 ml./min. of helium). The coupled products decolorized 1% potassium permanganate in acetone solution.

A proton n.m.r. spectrum of (heptafluoroisopropyl)cyclohexane was essentially the same as for the n-propyl analog. An F^{19} n.m.r. spectrum[28] at 56.4 Mc. had a $(CF_3)_2$ peak at -3.87 p.p.m. relative to trifluoroacetic acid and a CF peak at $+100.04$ p.p.m. The latter was very complex (>18 lines) showing 2 c./sec. splittings; the nearly identical CF_3 groups gave on close examination separation into two peaks 4 c./sec. apart and three small satellites spaced 7 c./sec. apart, above and below the CF_3 peaks. A very small difference in shielding of the rotating CF_3 groups appears to be responsible for the fine structure in the spectrum.

Anal. Calcd. for $C_9F_7H_{11}$: C, 42.9; H, 4.4. Found: C, 43.4; H, 4.3. Calcd. for $C_{18}H_{20}F_{14}$: C, 43.0; H, 4.01. Found: C, 43.7; H, 3.9.

1-Perfluoroethylcyclohexene and 3-Perfluoroethylcyclohexene.—1-Iodo-2-(perfluoroethyl)cyclohexane (91% E and 7.0% F, g.l.c. analysis, 7.2 g., 0.022 mole) was added to a mixture of sodium methoxide (2.5 g., 0.046 mole) and methanol (20 ml.). After 6 hr. at 70°, water (50 ml.) was added, the olefin mixture was extracted into 1,2-dichlorotetrafluoroethane (F-113), and the ratio determined by g.l.c. analysis (2-m. bismethoxyethyl phthalate column at 60°, 5 p.s.i. helium pressure, 4.0 flow). Recovery was 4.4 g. (100%) and the ratio of Δ^1-olefin (retention time 18.4 min.) to Δ^2-olefin (retention time 21.3 min.) was 22/78. Correcting for *cis* isomer F giving all Δ^1-olefin (see below), the Δ^1/Δ^2 ratio from *trans* isomer E was 15/85. The olefin mixture distilled at b.p. 72° (170 mm.), $n^{25}D$ 1.3702, 3.94 g. (90% of theory). An infrared spectrum had CH bands at 3.21, 3.45, and 3.52 μ, vinyl CH bands (moderate) at 5.88, 5.98, and 6.02 μ, and associated band at 10.1 to 10.2 μ, consistent with the Δ^1/Δ^2 ratio above. The bands at 3.21 and 10.10 μ are from Δ^2-olefin. An F^{19} n.m.r. spectrum at 56.4 Mc. gave a CF_3 peak at $+5.05$ p.p.m. (Δ^2-olefin) and a CF_3 peak at $+7.27$ p.p.m. (Δ^1-olefin) of relative areas 4 to 1, corresponding to g.l.c. analysis of Δ^2- and Δ^1-olefins, respectively. The CF_2 peak of Δ^2-olefin was a 4-line (w-s-s-w) AB pattern centered at $+41.68$ p.p.m. with a 16 c./sec. splitting of each peak due to $J_{HF} = 16$ c./sec. The "wings" were at $+36.52$ and $+46.82$ p.p.m. Hence, $J_{FF'} = 290$ c./sec.; and $\delta_F - \delta_{F'} = 1.95$ p.p.m. A proton n.m.r. spectrum at 60 Mc. gave a peak at -6.40 p.p.m. (0.24 proton area of $R_FC=CH-$), an AB pattern at -6.14 to -5.61 p.p.m. (1.46 proton of $R_FCH-CH=CH-$), a broad resonance at -3.3 to -2.5 p.p.m. (0.8 proton of R_FCH-), and a complex set at -2.3 to 1.5 p.p.m. (6.6 protons of $(CH_2)-$).

Anal. Calcd. for $C_8H_9F_5$: C, 48.0; H, 4.5; F, 47.4; Found: C, 47.6; H, 4.5; F, 47.5.

Partial Hydrolysis of *trans* Isomer E.—1-Iodo-2-(perfluoroethyl)cyclohexane (95% E and 5% F by g.l.c. analysis, 0.3146 g., 0.00083 mole) in 50 ml. of 0.991 N sodium hydroxide solution was kept at 30.0° for 3.5 hr. and 5.0 ml. of 1.5 N nitric acid and 100 ml. of water were added. The layers were extracted with cyclohexane (3×2.5 ml.) with salt added to aid in separation. The liquid (5.93 g.) was distilled in column A. Cyclohexane (5.1 g.) containing 0.015 g. of Δ^1- and Δ^2-olefin (12% of theory) and an oil residue (0.8521 g.) were obtained. Analysis by g.l.c. showed the latter to contain 0.62 g. of cyclohexane, 0.016 g. of 3-perfluoroethylcyclohexene (12% of theory), and 0.23 g. of E (75% recovery). No higher boiling compound was found.

There was no F present, which is reasonable, since its rate of hydrolysis is 10^4 that of E.

Partial Hydrolysis of *cis* Isomer F.—1-Iodo-2-(perfluoroethyl)cyclohexane (98.3% F and 1.7% E, g.l.c. analysis, 2.0293 g., 0.00618 mole) in 10 ml. of 0.3231 N sodium hydroxide solution (0.00323 mole) was kept at 30.0° for 180 min. The clear solution was diluted with 100 ml. of water, the oil layer removed, and the aqueous layer extracted with cyclohexane (3×3.0 ml.). The organic liquid (8.2833 g.) contained 6.50 g. of cyclohexane, 0.788 g. (51% conversion) of 1- perfluoroethylcyclohexene, 0.03 g. of E, and 0.814 g. (41% recovery) of F. There was a slight decrease in the *cis–trans* ratio. This was confirmed by removing the cyclohexane and olefin by distillation, leaving 0.6 g. of oil which by g.l.c. analysis contained 2.5% of E and 97.5% of F. There was no other higher boiling compound present.

Hydrolysis of *trans*-1-Iodo-2-(perfluorobutyl)cyclopentane (M).—In quite similar fashion a solution of M^1 (1.00 g., 0.00241 mole) in 50 ml. of 92.6% ethanol with 2.0 g. (0.05 mole) of sodium hydroxide at 65° for 7.5 hr. gave, upon work-up, a cyclohexane solution (4.15 g.) of 1-perfluorobutylcyclopentene (N) and 3-perfluorobutylcyclopentene (O). Three separate determinations of the relative areas of the two olefins gave $74 \pm 1\%$ of N and $26 \pm 1\%$ of O using the g.l.c. column and conditions reported.[1] The retention times were unchanged by admixture with the same olefins obtained previously.[1] The recovery of N and O was 60%. Compound M (1.00 g., 0.0024 mole), sodium methoxide (0.30 g., 0.005 mole), and anhydrous methanol (3.0 ml.) at 70° for 7 hr. extracted into F-113 gave a mixture of $67 \pm 0.5\%$ of N and $33 \pm 0.5\%$ of O (g.l.c. analysis of three samples). Distillation in column A gave N and O (0.54 g., 80% yield).

1-Perfluoroheptylcyclohexene and 3-Perfluoroheptylcyclohexene.—1-Iodo-2-(perfluoroheptyl)cyclohexane (a 1:1 mixture of *cis* and *trans* isomers, 23.0 g., 0.03 mole) and potassium hydroxide (5.0 g., 0.089 mole) dissolved in 50 ml. of 90% alcohol was heated under reflux for 5 hr. at 80°. Water and hydrochloric acid were added; the oil was extracted into chloroform, washed with sodium sulfite solution, dried, and fractionated in column A. A foreshot, b.p. 76–96° (20 mm.), $n^{25}D$ 1.3621, 2.5 g., was collected and 1-perfluoroheptyl- and 3-perfluoroheptylcyclohexene distilled at b.p. 98° (20.0 mm.), $n^{25}D$ 1.3461, 12.7 g. (89%). A residue of 1.8 g. remained; g.l.c. analysis (150°, helium at 20 ml./min. using a 10-ft. Apiezon M column[1]) showed a mixture of two olefins. By analogy to the perfluoropropylcyclohexenes, the Δ^1-isomer at 9.2 min. (60% of the total area) and Δ^2-olefin at 10.0 min. (40%) were obtained.

A proton n.m.r. spectrum at 60 Mc. gave an $R_F-C=CH$ vinyl proton resonance peak at -6.30 p.p.m. (0.6 proton) and a complex vinyl proton resonance pattern of $R_F-CH-CH=CH-$ centered at -5.75 p.p.m. (0.4 proton), a broad resonance of R_FCH- at -3.93 p.p.m., and (CH_2) peaks at -2.18 and -1.71 p.p.m. (3.5 protons each).

Infrared spectra of the olefins showed CH stretching bands at 3.25 and 3.45 μ, an olefinic $R_FC=C$ stretching band at 6.02 μ, CH deformation bands at 7.35 and 7.45 μ, and associated bands at 10.08 and 10.80 μ.

The mixture of *cis*- and *trans*-1-iodo-2-(perfluoroheptyl)cyclohexane was heated with 10% aqueous sodium hydroxide solution at 104–131° for 0.5 hr. without appreciable hydrolysis.

Anal. Calcd. for $C_{13}F_{15}H_9$: C, 34.7; H, 2.0; F, 63.3. Found: C, 34.9; H, 2.0; F, 63.2.