Relative Reactivities and Stereochemistry of Addition of Iodoperfluoroalkanes to Cyclic Olefins

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The relative reactivity of cyclic olefins toward the free-radical addition of 1-iodoperfluoropropane at 70° using azonitrile initiator was *cis*-cyclooctene (2.70) > cyclopentene (2.22) > cycloheptene (1.40) > cyclohexene (1.00). Under these conditions 1-heptene (a typical acyclic olefin) reacted 14 times faster than cyclohexene. *cis*-Cyclooctene gave four adducts: *cis*- and *trans*-1-iodo-2-perfluoropropylcyclooctane and, by 1,5 shift of the intermediate radical, *cis*- and *trans*-1-iodo-4-perfluoropropylcyclooctane. Zinc reduction of this mixture gave only perfluoropropylcyclooctane, and dehydrohalogenation formed two olefins in nearly equal amounts. By contrast, cyclopentene gave only a trans adduct, while cyclohexene and cycloheptene formed both cis and trans 1,2 adducts, probably as a result of ring flipping. These results are interpreted as the consequence, first, of preferred trans addition (with the bulky and electronegative R_F and iodine groups as far as possible from each other) and, secondly, a combination of steric strain and pseudorotation of the rings.

In a previous study[1] perfluoroalkyl iodides (R_FI) and cyclopentene or cyclohexene gave 1-iodo-2-perfluoroalkylcycloalkanes having marked differences in properties, depending on the size and shape of the perfluoroalkyl group. The nmr spectra,[2,3] rate of hydrogen iodide elimination, partial rate factors for Δ^1 and Δ^2 olefin formation, and equilibration between cis and trans isomers of 1-iodo-2-perfluoroalkylcyclohexanes[4] varied with the conformation of the ring. It was concluded that trans adducts having bulky R_F groups assume twist-boat conformations which are surprisingly stable at room temperature, while cis adducts appear to be locked into a stable chair form. The twist-boat conformation was subsequently observed by other workers in the analogous case of *trans*-1-bromo-2-trichloromethylcyclohexane.[5]

While reactions of cycloheptene and *cis*-cyclooctene with carbon tetrachloride or bromotrichloromethane have been reported,[5-7] addition of R_FI to these cyclic olefins has not been investigated. We were particularly interested in the influence that the greater mobility of these medium-size rings would have on the relative ease of addition, since cyclopentene and cyclohexene were unusually sluggish in their reactions with R_FI. Addition of R_FI to norbornene or norbornadiene occurred very readily,[8] probably as a result of relief of ring strain, and side reactions which were noted[1] in the case of cyclohexene were not important. It has been shown that bromotrichloromethane gave only 1,2 addition to *cis*-cyclooctene, while carbon tetrachloride gave 1,4 adduct by transannular rearrangement of the intermediate radical, and trichloromethanesulfonyl chloride gave both 1,2 and 1,4 adducts.[5,6] Study of the behavior of these cyclic olefins toward R_FI addition should contribute to our understanding of free radical reactions.

Results and Discussion

Synthesis of Adducts.—Azonitrile-initiated [2,2'-azobis(2-methylpropionitrile), ABN] reaction of 1-iodo-

perfluoropropane with the individual cyclic olefins at 70° gave adducts as shown in Chart I. (Charts II and

CHART I

$$R_F = CF_3CF_2CF_2$$

1, n = 3
2b, n = 4
3b, n = 5

n = 4, 5

2a, n = 4
3a, n = 5
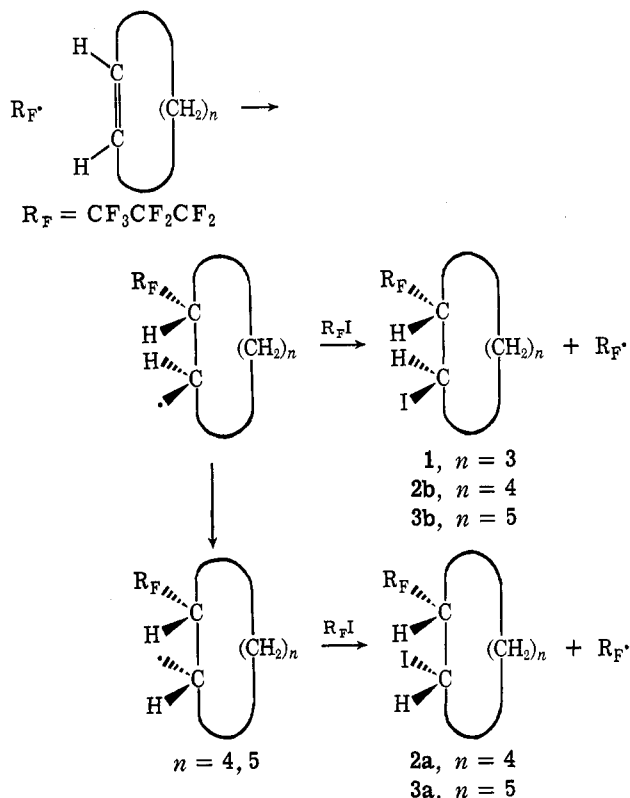
III give more detailed structural data.) It was necessary to isolate and characterize the new compounds from cyclopentene, cycloheptene, and *cis*-cyclooctene. One reason was to quantify the gas–liquid phase chromatographic (glpc) analysis used to determine the amounts formed in competitive reactions. Cyclohexene adducts had been previously prepared; their unusual structures and properties provided further incentive to extend the synthesis to higher homologs.

Cyclopentene gave a trans adduct (1) in 19% conversion (4 mol/mol of ABN). Its ir and nmr spectra resembled closely those of the *n*-perfluorobutyl analog which was characterized previously.[1]

Cycloheptene adducts (3a,b) were formed in a 27:72 ratio (cis–trans), at 29% conversion (7.1 mol/mol of

(1) N. O. Brace, *J. Org. Chem.*, **28**, 3093 (1963).

(2) N. O. Brace, *J. Amer. Chem. Soc.*, **84**, 3020 (1962).

(3) N. O. Brace, *ibid.*, **86**, 665 (1964).

(4) N. O. Brace, *ibid.*, **86**, 2428 (1964).

(5) J. G. Traynham, A. G. Lane, and N S. Bhacca, *J. Org. Chem.*, **34**, 1302 (1969).

(6) J. G. Traynham and T. M. Couvillon, *J. Amer. Chem. Soc.*, **87**, 5806 (1965); **89**, 3205 (1967).

(7) L. H. Gale, *J. Org. Chem.*, **34**, 81 (1969).

(8) N. O. Brace, *ibid.*, **27**, 3077 (1962).

ABN). These isomers were separated by glpc and were thermally unstable. In the nmr spectrum of **3a,b** the resonance for CHI protons was at δ 4.95, comparable in chemical shift to trans-"twist" isomer 1-iodo-2-perfluoropropylcyclohexane (**2b**).[1] In glpc analyses this trans isomer **2b** always eluted from the column first, as did the principal isomer, **3b**. From these data it is concluded that **3b** has the trans configuration.

cis-Cyclooctene adducts proved to be particularly troublesome to isolate in pure condition, as they were very sensitive to heat, light, and air. By exercising necessary precautions, however, a 70–80% conversion (70–80 mol/mol of ABN) was obtained of the pure adducts **4a,b** and **5a,b** (glpc). Choice of conditions for reaction and for glpc analysis was critical. Samples of the isomer pairs were trapped by glpc for analysis and for study of their ir spectra. The entire mixture was converted to stable derivatives (Chart II).

CHART II

$$4a,b + 5a,b \xrightarrow{Zn/H^+} $$

$$(R_F = CF_3CF_2CF_2)$$
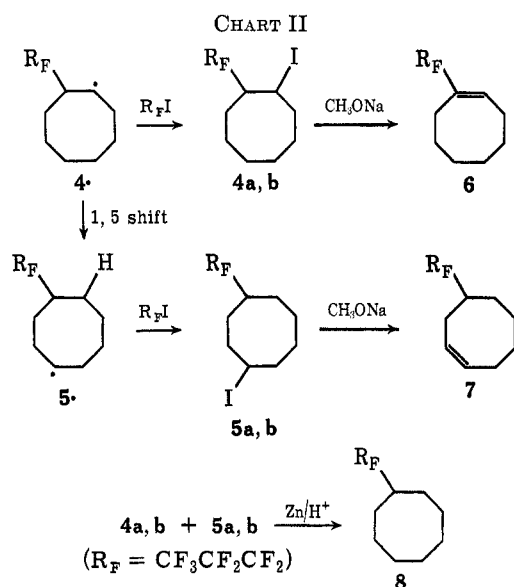
A mixture of isomers **4a,b** and **5a,b**, when treated with zinc and acid, gave a single substance, perfluoropropylcyclooctane (**8**). Hence, the differentiating features in **4a,b** and **5a,b** were the position of the iodine atom and the cis–trans arrangement of the two groups. By reaction with base, the isomer mixture **4a,b** and **5a,b** (41:57) gave a pair of olefins, 1-perfluoropropylcyclooctene (**6**) and 4- (or 5-) perfluoropropylcyclooctene (**7**), in about equal amount. The position of the double bond in **7** is not known, but only one of the two possible isomers (Δ³ or Δ⁴) was formed. A sample of **7** was trapped by glpc. The ir spectrum showed $\nu_{CH=CH}$ 3025, δ_{CH} 1460, 1440, 1340, and $\gamma_{CH=CH}$ 995, 920, 892, and 710 cm^{-1}. Bands at 3025, 895, and 710 cm^{-1} are also present in *cis*-cyclooctene, and bands at 990 and 920 cm^{-1} appear in 3-perfluoropropylcyclohexene.[4] The mixture of **6** and **7** showed (in addition to those in **7**) absorptions of $\nu_{CH=}$ 3035 and $\nu_{R_FC=C}$ 1660 and bands at 755, 722, and 690 cm^{-1}. Bands at 1667, 755, 717, and 683 cm^{-1} are also present in 1-perfluoropropylcyclohexene.[4] The bands at 3035 and 1667 cm^{-1} are in accord with a Δ¹ double bond position for **6**. The nmr spectrum of **6** and **7** (equal amounts) showed olefinic protons at δ 5.5–6.3 (1.5 protons) in a complex splitting pattern. These

data conform to the anticipated behavior of **4a,b** and **5a,b** and for structures **6** and **7**.

Relative Rates of Reaction.—Mixtures of cyclopentene with each of the other cyclic olefins, competing for 1 mol of 1-iodoperfluoropropane and catalyzed by ABN at 70°, were run under standard conditions. Cyclopentene was chosen as reference olefin because it formed only one adduct, which facilitated comparison. A summary of results is given in Table I.

TABLE I
RELATIVE RATES OF REACTION OF CYCLIC OLEFINS

Olefin pair	Ret time^a		Adducts, mmol^b		Ratio of C₅/Cₓ
	C₅	Cₓ	C₅	Cₓ	
C₅/C₆	4.3	7.0, 10.4	7.99	3.57	1.00/0.450
C₅/C₇	4.3	12.5, 13.9	1.67	1.04	1.00/0.622
C₅/C₈	4.3	14.1, 15.6	1.52	1.87	1.00/1.23

^{a} Retention time in minutes; the trans isomer eluted first in each case, except for cyclooctene adducts which were not resolved into four peaks on these conditions. ^{b} Average of three replicate determinations, ±0.02 mmol in most cases.

From these data the order of reactivity was found to be cyclo-C₈ > C₅ > C₇ > C₆, with proportions 2.70: 2.22:1.40:1.00. Under identical reaction conditions 1-heptene reacted with 1-iodoperfluoropropane 14 times as fast as cyclohexene.[1] As shown by Gale,[7] this order corresponds to the irreversible addition of radicals and is comparable to the results obtained with acetaldehyde or BrCCl₃ with these cyclic olefins.

Significance of Results.—Free radical addition of R$_F$I in a trans mode to cyclopentene conforms to the pattern observed in reactions of this type.[8] Since the bulky and electronegative groups cannot bend away from each other in the cis arrangement, transfer occurs only in the trans manner (Chart I). Norbornene (a rigid cyclopentene model) reacted similarly, and the dipole moments of several related compounds support this conclusion (Table II).

For the norbornane derivatives **9** and **10**, using the proper dihedral angle and the correction for geometry
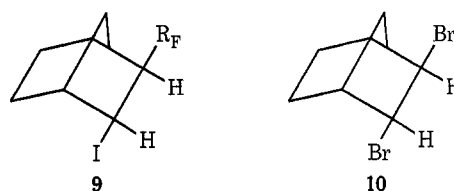
of the ring as applied by Krieger,[9] calculated dipole moments were obtained in excellent agreement with experimental values. These results clarify the confused picture obtained for bromotrichloromethane adducts of cyclopentene and norbornene.[5]

Group moment of D(C–I) = 2.06 D from iodocyclopentane[10] and group moment of D(ring–R$_F$) = 2.8 D were used.[4] Calculation was done using the equation

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

When applied to **1**, agreement between calculated and observed dipole moments again was satisfactory. Reported data[9] for *exo*-2-*endo*-3-dibromonorbornane (**10**), and two sets of isomers of **2a,b** are listed for comparison.

(9) H. Kreiger, *Suom. Kemistilehti B*, **31**, 348 (1958); *Chem. Abstr.*, **53**, 13195 (1959)
(10) M. T. Rogers and J. D. Roberts, *J. Amer. Chem. Soc.*, **68**, 843 (1946).

TABLE II

DIPOLE MOMENTS OF CYCLIC ADDUCTS

		Dipole moment, D			
		Found[a]			θ,
Compd	R_F	Benzene solution	Neat	Calcd[b]	Dihedral angle
9	$CF_3(CF_2)_2$	3.09	2.86	2.85	123°21'
9	$(CF_3)_2CF$	3.21	2.99	2.85	123°21'
1	$CF_3(CF_2)_3$	2.99[c]	2.58[c]	2.55	123°21'
2a	$CF_3(CF_2)_2$	3.45[b]	3.54[b]	4.00	70°32'
(cis, e, a)					
2b	$CF_3(CF_2)_2$	2.28[b]	1.91[b]	1.55	147°
(trans twist a, a)					
2a	$(CF_3)_2CF$	3.42[b]		4.00	70°32'
(cis, e, a)					
2b	$(CF_3)_2CF$	3.35[b]	3.00[b]	3.59	86°54'
(trans twist e, e)					
10		2.30[d]		2.33[d]	
Iodocyclopentane		2.06[e]			

[a] Unpublished work with M. R. Kegelmann. [b] See ref 4 for the method used. [c] Reference 1. [d] H. Kreiger, *Suom. Kemistilehti B*, **31**, 348 (1958); *Chem. Abstr.*, **53**, 13195 (1959). [e] M. T. Rogers and J. D. Roberts, *J. Amer. Chem. Soc.*, **68**, 843 (1946).

Correlation of dipole moments with structures of isomers **2a,b** and sources of error have been discussed previously.[4]

For cyclohexene, both cis and trans addition occurred, as previously shown.[1] Since flipping of the ring (**2·** → **2·′**) may occur before transfer of the intermediate radical with R_FI, a mixture of isomers somewhat dependent on the size and shape of the R_F group was obtained (Chart III). Twisting of the ring into twist-boat forms was observed, consistent with dipole moments and other data.[3,4] Again, the addition of $BrCCl_3$ conforms to this behavior.[5,11]

Cycloheptane has twist-chair and twist-boat conformations as its lowest energy forms.[12] The barrier to flipping from chair to boat family is 8.50 kcal/mol and the twist-boat is 2.49 kcal/mol less stable than the twist-chair. Due to pseudorotation, a substituent in one position may pass to every other, as detailed by Hendrickson.[12] In 1,2-disubstituted cycloheptanes it is possible to distinguish between two cis and two trans forms, but by pseudorotation these reduce to only one of each, separated by a high energy barrier. It thus becomes reasonable that cycloheptene adds R_FI more rapidly than does cyclohexene. The barrier to flipping is lower for cycloheptane than for cyclohexane (calcd, 12.7 kcal/mol),[12] and the trans-diequatorial arrangement of ordinary 1,2 substituents is preferred.[13] The intermediate radical may readily pseudorotate to relieve crowding and repulsion by R_F and I groups in the transfer step. Adducts **3a,b** having these bulky electro-
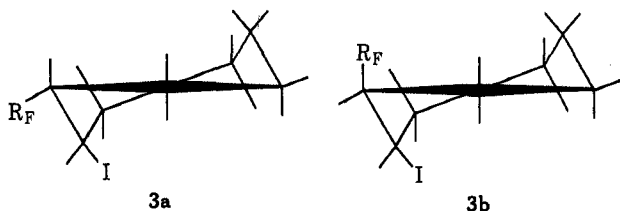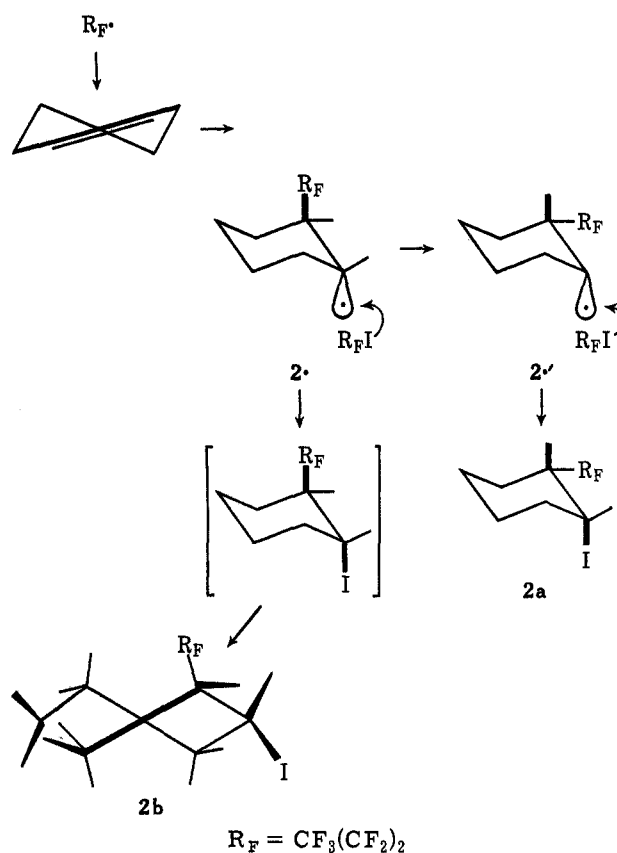
CHART III

$R_F = CF_3(CF_2)_2$

negative substituents may be tentatively represented in preferred conformations as shown.

It is odd that $BrCCl_3$ has been reported[5] to give cis addition (only) to cycloheptene; orientation was based on coupling constants for vicinal protons in comparison to predicted values. Gale, however, gave nmr data which could be interpreted to mean that a trans adduct was obtained.[7] The chemical shifts for protons adjacent to Br and to CCl_3 in the cycloheptene adduct were closer to values found for the *trans*-1-bromo-2-trichloromethylcyclohexane than for the cis isomer.[5,7] In view of the discrepancy in these two sets of data, and the predicted lower energy for trans forms, it seems probable that trans addition had occurred.

cis-Cyclooctene was the most reactive of the four cyclic olefins studied toward R_FI addition. The same order of reactivity was found for CH_3CHO or $BrCCl_3$ addition. Gale[7] attributed this to the "medium-ring effect," in which two sp² carbons are converted to sp³ carbons, and stated that the principal result is a great decrease in the rate of abstraction of the substituted cyclooctyl radical without affecting the rate constant for addition of the $CCl_3·$ radical to *cis*-cyclooctene. It was suggested that the presence of one sp² carbon center imparts sufficient flexibility to minimize hydrogen-hydrogen nonbonded interactions. In radical addition of carbon tetrachloride to *cis*-cyclooctene, transannular rearrangement of the intermediate radical (analogous to **4·** → **5·**) was attributed by Traynham and Couvillon[6] to destabilization of the radical center by neighboring trichloromethyl substituent. This destabilization energy was estimated to be more than 3.5–4.0 kcal/mol. With a more active transfer agent ($BrCCl_3$) very little transannular addition occurred. In this re-

3a　　　　**3b**

(11) The BrCCl₃–norbornene adduct is *endo*-2-bromo-*exo*-3-trichloromethylnorbornane, and its dipole moment is 2.60 D, in line with that of **9** and **10**.

(12) J. B. Hendrickson, *J. Amer. Chem. Soc.*, **83**, 4537 (1961).

(13) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience, New York, N. Y., 1965, p 208.

spect R_FI addition more closely resembled that of Cl_3CSO_2Cl, which also gave a mixture of both 1,2- and 1,4-addition products.[5,6] It is then somewhat surprising that relative rates of reaction of R_FI with *cis*-cyclooctene *vs.* the other cyclic olefins parallels so closely that found for CH_3CHO or $BrCCl_3$, which occurred without transannular rearrangement.

Rationalization of the order of reactivity found with R_FI may be summarized as follows. Because the cyclooctyl radical is flexible, having several conformations only about 2.0 kcal/mol higher in energy than the most stable boat–chair form,[14] trans addition to vicinal carbons can occur with only little energy expenditure. More important, however, is the fact that transannular reaction places the bulky and electronegative addends far apart. This minimizes the repulsions which tend to reduce rate of transfer with R_FI. Since torsional and nonbonded strain in cyclopentane is less than for cyclooctane or cycloheptane,[13] addition of R_F radicals to cyclopentene does not require as much energy. The transfer step with R_FI, however, is restricted to non-eclipsing of these groups and therefore must go in a trans manner. Hence, cyclopentene is less reactive than cyclooctene. Cycloheptene is next most reactive because total strain energy in the adduct radical is higher than in cyclopentane, and transannular rearrangement cannot take place as with the cyclooctyl radical. Pseudorotation, while present, may be somewhat restricted by the bulky vicinal substituents; the preferred trans orientation of the cycloheptyl radical and R_FI may be more difficult to achieve as well. Cyclohexene is the least reactive for the following reasons: (1) trans addition requires both the R_F group and the approaching R_FI molecule to occupy crowded axial positions (Chart III); (2) formation of cis isomer **2a** necessitates ring flipping of **2·** to **2·'** to place the bulky R_F group in an equatorial position before axial approach of R_FI occurs; (3) instead of obtaining a trans-diequatorial cyclohexane chair conformer, one actually obtains a twist-boat compound (**2b**) which must pass through a higher energy barrier before it can be formed.

A tentative conclusion from these results is that addition of the R_F radical and transfer with R_FI are coupled processes, which must both be considered in determining overall reaction rates of olefins with perfluoroalkyl iodides.

Experimental Section

Analyses, Sources, and Purification of Materials.—All experiments were carried out in an atmosphere of nitrogen. Cyclopentene was obtained from Columbia Organic Chemicals and redistilled in a 2-ft platinum spinning band column (column A), bp 44°, $n^{25}D$ 1.4198; cyclohexene (99%) was from Phillips Petroleum Co., $n^{25}D$ 1.4439; cycloheptene (99%) was from Chemical Samples Co., $n^{25}D$ 1.4562; *cis*-cyclooctene was from Cities Service Development Co. and redistilled in column A, bp 145°, $n^{25}D$ 1.4683, ir bands at 893 and 885 cm⁻¹;[15] 1-iodoperfluoropropane (11) was from Pierce Chemical Co., redistilled, bp 41°; 2,2'-azobis(2-methylpropionitrile) (12) was from Eastman Kodak Co. Infrared spectra were recorded on a Perkin-Elmer Model 337 grating spectrophotometer using KBr cells. Nmr spectra were obtained using a Varian A-60 spectrometer at ambient temperature.

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

(15) A. C. Cope, R. A. Pike, and C. F. Spencer, *ibid.*, **75**, 3212 (1953).

trans-1-Iodo-2-(perfluoropropyl)cyclopentane (1).[16]—Cyclopentene (13.41 g, 17.5 ml, 0.200 mol), 11 (22.23 g, 11.84 ml, 0.0800 mol), and 12 (0.6568 g, 4.00 mmol) were charged to a Fischer-Porter aerosol tube, cooled to −78°, evacuated, filled with nitrogen three times, and sealed. The tube was heated at 70° for 24 hr in a stirred oil bath. The cloudy mixture was filtered through a sintered glass funnel and distilled in a variable take-off distilling head without a column. Cyclopentene and 11, bp 35–40°, 24.1 g; adduct 1, bp 58° (8 mm), $n^{25}D$ 1.4180, 5.4 g, bp 34° (2 mm), 0.3 g (19% conversion), 4 mol/mol of 12; residue (0.9 g); and trap liquid (2.26 g, also cyclopentene and 11) were recovered. The product 1 was 96% trans isomer (retention time 4.3 min) by glpc analysis; three other substances of about 2% each were also present, at 8.0, 9.6, and 10.2 min. Pure 1 was trapped from repetitive injections on a 6 ft × 0.25 in. column packed with 10% silicone oil (QF-1), operated at 120°. An ir spectrum showed ν_{CH} 2980, 2890, δ_{CH} 1450, 1350, ν_{CF} 1240, 1200, 1180, and bands at 1120, 1070, 790–760, and 730 cm⁻¹. An nmr spectrum showed δ 1.7–2.3 [6 protons, m, $(CH_2)_3$], 2.7–3.8 (1 proton, m, CHR_F), 4.58 (1 proton, q, $J = 5$ Hz, $CH_2CHICHR_F$).

Anal. Calcd for $C_8H_8F_7I$: C, 26.39; H, 2.21. Found: C, 26.53; H, 2.36.

cis- and *trans*-1-Iodo-2-(perfluoropropyl)cycloheptane (3a,b).[16]—Cycloheptene (48.0 g, 58.4 ml, 0.500 mol), 11 (29.6 g, 14.8 ml, 0.100 mol), and 12 (0.6568 g, 4.00 mmol) were processed as above and heated in the bath at 48–50° for 24.5 hr. The clear liquid product (75.8 g) was decanted from some solid precipitate and distilled in column A. Starting materials, bp 41–72°, 20 g, were removed; and, under reduced pressure, cycloheptene, bp 54–56° (100 mm), $n^{25}D$ 1.4561, 35.7 g; 3a,b, bp 72–78° (3.5–4.2 mm), $n^{25}D$ 1.4405, 7.58 g, and bp 64–66° (2.0 mm), $n^{25}D$ 1.4421, 3.94 g (29% conversion). Reaction at 70° gave a 25% conversion to 3a,b. A residue (0.70 g) and trap liquid (5.71 g of additional starting materials) were also obtained. 3a,b was passed down alumina to remove color, rinsed with ligroin (bp 30–60°), and redistilled, bp 52–53° (0.55 mm), $n^{25}D$ 1.4394, 9.57 g. An ir spectrum gave ν_{CH} 2950, 2980, δ_{CH} 1460, 1450, 1350, ν_{CF} 1220, 1180, and bands at 1115, 1090, 980, 960, 950, 930, and 730 cm⁻¹. Glpc analysis gave at 12.5 min, 72.0%; 13.8 min, 27.3%; 15.2 min, 0.21%; and 18.8 min, 0.28% relative areas. An nmr spectrum of 3a,b showed δ 1.4–2.4 [10 protons, m, $(CH_2)_5$], 2.5–3.7 (1.0 proton, m, $CHCF_2CF_2CF_3$), 4.95 [1.0 proton, partly resolved five-line pattern, $J = 5$ Hz, $(CH_2)_2CHI$].

Anal. Calcd for $C_{10}H_{12}F_7I$: C, 30.63; H, 3.09; F, 33.91; I, 32.36. Found: C, 30.70; H, 3.10; F, 33.72; I, 32.48.

cis- and *trans*-1-Iodo-2-(perfluoropropyl)cyclooctane (4a,b) and *cis*- and *trans*-1-Iodo-4-(perfluoropropyl)cyclooctane (5a,b).—*cis*-Cyclooctene (20.0 g, 23.6 ml, 0.180 mol), 11 (30.0 g, 15.0 ml, 0.100 mol), and 12 (0.164 g, 1.00 mmol) were processed as above. The tube was heated for 7 hr at 70.0° in the oil bath. The colorless product mixture (49.5 g) was distilled in column A, under reduced pressure; *cis*-cyclooctene, $n^{25}D$ 1.4679, 1.16 g; 4a,b and 5a,b, bp 56–66° (0.30 mm), $n^{25}D$ 1.4495, 28.5 g (70% conversion); and a solid residue (0.30 g) were obtained. Volatile compounds (21.75 g) collected in the −78° trap. The entire adduct mixture was analyzed by glpc using a 6 ft × ³/₁₆ in. stainless steel column, filled with Carbowax 400 on Porosil (100–200 mesh) at 105°. Peaks of 7.1, 34.1, 27.8, and 29.4% relative areas were obtained at 8.6, 9.4, 15.0, and 16.7 min, respectively: ir (entire mixture, KBr, liquid film) ν_{CH} 2920, 2850, δ_{CH} 1460, 1430, 1340, ν_{CF} 1230, 1195, 1180, 1150, 1110, bands at 1110, 990, 965, 950, 935, 908, 860, 845, 810, 750, 740, 710, 670, 650, 595, 565, and 535 cm⁻¹.

Reaction of 0.500 mol of *cis*-cyclooctene and 0.10 mol of 11 (3.00 mmol of 12) at 76° for 22 hr gave an 84% conversion to 4a,b and 5a,b. Fractionation in column A gave four cuts, b p 67–72° (0.50 mm), containing three or four substances according to glpc analysis (6 ft × 0.25 in. column, Carbowax 20 M, 20% on Chromosorb W, 160° and 25-psi helium pressure). The adducts were sensitive to heat and light and tended to decompose. Individual peaks were trapped and infrared spectra were recorded: peak 1, 7, retention time 1.3 min, 5.0%, ir $\nu_{CH=C-}$ 3025, ν_{CH_2} 2960, 2940, 2860 (overtone 1750), δ_{CH} 1460, 1440, 1340, ν_{CF} 1230 (vs), 1196, 1175, 1118, and bands at 1015, 995, 980, 962, 950, 920, 905, 892, 710, 668, and 642 cm⁻¹; peak 2, 4a,b, 8.4 min, 40%, ir (KBr, CCl₄ solution), ν_{CH} of CH_2 2940, 2860; δ_{CH} 1460, 1440, 1340; ν_{CF} 1230, 1220 (vs), 1196, 1175, 1165, 1122, 1110, and

bands at 1010, 1000, 970, 945 (w), 925, 890 (w), 865, 745, 710, 670, and 665 cm^{-1}; peak 3, **5a,b**, 17 min, 55%, ir (KBr, CCl$_4$ solution) same as 2 from 4000 to 1000 cm^{-1}, bands at 990, 950, 940, 910, 860, 845, 750, 710, 670, 650, 595, 570, and 540 cm^{-1}. Nmr spectra of mixtures of **4a,b** and **5a,b** of varying isomer composition were recorded. All were similar: nmr (neat, A-60) δ 1.00–1.36 (13.0 protons, unresolved), 4.58 (1.0 proton, partially resolved multiplet of CHI).

Anal. Calcd for C$_{11}$H$_{14}$F$_7$I: C, 32.53; H, 3.47; F 32.75; I, 31.25. Found (mixture): C, 32.60; H, 3.37; F, 32.17; I, 30.98. Found (peak no. 2): C, 32.53; H, 3.47. Found (peak no. 3): C, 32.71; H, 3.60.

Dehydrohalogenation of Adduct Mixture 4a,b and 5a,b to 1-Perfluoropropylcyclooctene (6 and 7).[17]—**4a,b** and **5a,b** (7.00 g, 0.0172 mol), 25 ml of methanol, and 2.0 g (0.037 mol) of sodium methoxide were refluxed for 4 hr at 68°, and poured into 50 ml of water. The product was extracted with 10 ml of dichloromethane three times, dried over magnesium sulfate, and distilled to give **6** and **7**, bp 73° (18 mm), n^{25}D 1.3856, 2.6 g (55% of theory). Glpc analysis (5 ft XE-60 silicone oil column, 15% on Chromosorb W, 115°, 25-psi helium) gave peaks at 5.8 (53.5%) and 6.2 min (46.5%). Similar results were obtained with a 10-ft SE-30 silicone oil column or a 4 ft "UCON Polar" LB550-X column, which gave peaks at 12.4 (2.15%), 14.0 (54.1%), and 15.3 min (43.8%); ir (KBr, liquid film) $\nu_{CH=C}$ 3040, ν_{CH} 2960, 2940, 2880, $\nu_{C=C}$ 1660 (w), δ_{CH} 1480, 1455, 1350, ν_{CF} 1220, 1180, 1120, bands at 1015, 982, 955, 940, 920, 908, 895, 845, 825, 775, 755, 745, 738, 722, and 710 cm^{-1}, weak bands appeared at 690, 670, 655, and 535 cm^{-1}. Comparison showed that **6** and **7** were present in small amount in the original adduct mixtures. Nmr (neat) showed proton resonances at δ 1.2–1.9 and 1.9–2.85 [11.4 protons, m, (CH$_2$)$_5$ or (CH$_2$)$_6$] and 5.3–6.4 (1.5 protons, -CH=CH- and R$_F$C=CH).

Anal. Calcd for C$_{11}$H$_{13}$F$_7$: C, 47.48; H, 4.71; F, 47.81. Found (isomer mixture): C, 47.52; H, 4.78; F, 47.60.

Zinc Reduction of 4a,b and 5a,b Adduct Mixture to Perfluoropropylcyclooctane (8).—**4a,b** and **5a,b** (10.8 g, 0.0266 mol), ethanol (25 ml), and zinc (30 mesh, 5.0 g, 0.077 g-atom) were heated to reflux with stirring, and 3 ml of 55% hydriodic acid was added; after 1.5 hr another 1 ml of acid was added. Later (0.5 hr) the mixture was poured into 100 ml of water, made acidic with hydrochloric acid, and extracted three times with 10 ml of dichloromethane. The organic layer was rinsed with dilute aqueous sodium bicarbonate, dried over magnesium sulfate, and distilled to give **8**, bp 93–94° (39 mm), n^{25}D 1.3802, 3.4 g (45%).

Adduct mixture **4a,b** and **5a,b** (8.3 g, 0.020 mol), zinc dust (5.0 g, 0.076 mol), diethylene glycol (25 ml), and 36% aqueous HCl (5 ml) at 70–80° for 3 hr, followed by azeotropic distillation, gave **8** (4.0 g, 71%). Glpc analysis showed a single peak using a variety of columns and conditions; ir (liquid film on KBr plates) ν_{CH} 2960, 2940, 2880, δ_{CH} 1470, 1450, 1350, ν_{CF} 1220, 1180, 1120, 1110, and bands at 1020, 1010, 1000, 970, 950, 940, 915, 860, 845, 820, 808, 745, 738, and 705 cm^{-1}; nmr (neat) δ 1.6 [14 protons, s, (CH$_2$)$_7$] and 2.0–2.8 [1 proton, m, CH(CF$_2$)$_2$CF$_3$].

Anal. Calcd for C$_{11}$H$_{15}$F$_7$: C, 47.14; H, 5.40. Found: C, 47.14; H, 5.29.

Competition Reactions,[16] **1 and 2a,b.**—Cyclopentene (0.8364 g, 0.01228 mol), cyclohexene (1.0357 g, 0.0126 mol), **11** (3.0843

g, 0.0104 mol), and **12** (0.0823 g, 0.5 mmol) were placed in a heavy-walled glass ampoule, chilled to −78°, filled with nitrogen and evacuated three times, and sealed with a hand torch at 0.5 mm. The reaction tube was placed in an oil bath heated at 70° for 20 hr, and the liquid (4.45 g) was decanted from some flocculent precipitate and distilled in a small stillhead connected to a −78° trap. All the volatile material (3.37 g, n^{25}D 1.4111) was pumped to the trap and the adduct mixture (**1** and **2a,b**) was distilled, bp 28–39° (1.5 mm), 0.51 g (9.7% conversion). The residue was 0.06 g. Reaction occurred with an efficiency of 2.76 mol of adducts/mol of **12**. Glpc analysis, using 0.1088 g (0.2933 mmol) of adduct mixture and 0.0186 g of chlorobenzene (internal reference), showed that there were 7.99 mmol of **1** and 3.57 mmol of **2a** and **2b**, in a ratio of 1.00:1.27, respectively. The ratio of **1** to **2a,b** was 1.000:0.4497. Glpc analyses were performed using a Perkin-Elmer Model 881 gas chromatograph with hydrogen flame detector, fitted with a 6-ft × 0.125 in. column packed with "UCON Polar" LB 550 (20%) on Chromosorb W (60–80 mesh), and temperature-programmed (4°/min to 150°) after 5 min at 105°. Nitrogen carrier gas at 28 ml/min and 0.2-μl samples were employed. These conditions were established after an extensive survey of columns and operating parameters to enable separation of all the components of mixtures.

1 and 3a,b.—Cyclopentene (1.7028 g, 0.0246 mol), cycloheptene (2.4043 g, 0.0247 mol), **11** (6.0036 g, 0.02028 mol), and **12** (0.1640 g, 0.100 mmol) gave adducts **1** and **3a,b**, bp 35–49° (1.15–0.60 mm), 1.06 g (13.8% conversion); the −78° trap contained 5.47 g of recovered starting materials, and the residue was 0.24 g. The efficiency of reaction was 2.8 mol/mol of **12**. Glpc analysis using 0.0946 g (2.50 mmol) of adduct mixture and 0.0293 g of chlorobenzene showed that there were 1.68 mmol of **1** and 1.04 mmol of **3a** and **3b** in a ratio of 1.00:3.62, respectively. The ratio of **1** to **3a,b** was 1.000:0.6223.

1 and 4a,b, 5a,b.—Cyclopentene (0.8427 g, 0.01237 mol), cyclooctene (1.3854 g, 0.01257 mol), **11** (3.0527 g, 0.01035 mol), and **12** (0.0823 g, 0.500 mmol) gave adducts, bp 36–65° (0.95–0.075 mm) (bath 72–86°), 1.18 g (29.6% conversion). The −78° trap contained 1.90 g and the residue was 0.21 g. Glpc analysis, using 0.1040 g of adduct mixture and 0.0115 g of benzene, showed that there were 1.519 mmol of **1** and 1.805 mmol of **4a,b** and **5a,b** (1.00:1.10). The ratio of **1** to **4a,b** and **5a,b** was 1.000:1.227. Benzene was used as internal standard in this analysis.

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