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(35) For example, with an increase in population of A, our analysis would predict a relative shift of C_4 to higher field at lower temperature. If B were favored, a low-field shift of C_4 would result.

(36) C_4 appears to have undergone no shift change, while C_8 and C_α have suffered −0.02 and +0.9 ppm shifts, respectively.

(37) The proton spectrum of 1-naphthylmethyl bromide has been examined at lower temperatures [M. D. Bentley and M. J. S. Dewar, *J. Org. Chem.*, **35**, 2707 (1970)] and over the range 40 to −100 °C, the $-CH_2Br$ resonance suffered a 0.4 ppm low-field shift. This was interpreted in terms of a steric effect displacing the Br group out of the plane of the ring, apparently implying B to be favored at lower temperatures. However, the possibility of significant molecular layering at lower temperatures and the effects of specific molecular organization would need careful evaluation. The effects of lower temperatures on the ring-proton shifts were not discussed, but may have indicated aggregation, or specific collision complexes.[38]

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(41) (a) For a discussion and examples of the effect of this structural manipulation on mesomerism in other naphthyl systems see W. Adcock and M. J. S. Dewar, *J. Am. Chem. Soc.*, **89**, 379 (1967). (b) The ^1H NMR spectra of arylmethyl anions have been investigated in some detail [F. J. Kronzer and V. R. Sandel, *Chem. Ind.* (*London*), 210 (1972); F. J. Kronzer and V. R. Sandel, *J. Am. Chem. Soc.*, **94**, 5750 (1972); V. R. Sandel and H. H. Freedman, *ibid.*, **85**, 2328 (1963)], and in the case of 1-naphthylmethyllithium (THF) (compared with 1-methylnaphthalene[21] in $CDCl_3$) H_4 and H_5 suffer high-field shifts of 1.90 and 0.74 ppm, respectively. These relative shifts are in somewhat poor agreement with HMO parameters (0.200 and 0.05, respectively) but more agreeably with SCF-π parameters (0.263 and 0.092, respectively) (Table II). Ion pairing and specific molecular aggregation could be troublesome, as could the known sensitivity of ^1H shifts to long-range magnetic perturbations of various kinds. In addition, substantial field effects may also operate in addition to any conjugation. Careful studies of the ^{13}C spectra of 1- and 2-naphthylmethyllithium would be most informative.

(42) There is evidence (ref 40) that in the case of ^{19}F shielding in the 5α-naphthyl system, field effects and steric crowding may contribute to the overall ^{19}F SCS. These would be less important for ^{13}C SCS.

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(44) T. E. Peacock and P. T. Wilkinson, *Proc. Phys. Soc., London*, **83**, 525 (1964).

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(49) We at first suspected that the assumptions regarding bond lengths in the naphthyl framework may have been partly to blame for the overestimation of mesomerism to the second ring. A calculation with self-consistency in bond lengths was not enlightening, and if anything, aggravated the situation. More thorough (and expensive) calculations are required.

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(51) For a related situation, see K. Takahashi, Y. Kondo, and R. Asami, *Org. Magn. Reson.*, **6**, 580 (1974).

Evidence for Free-Radical Reductive Dehalogenation in Reaction of Zinc and Acid with 1-Perfluoroalkyl-2-iodoalkanes and with 1-Perfluoroalkyl-2-iodoalkenes[1]

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Reductive dehalogenation of 7-perfluorobutyl-6-iodo-1-heptene by either tri-*n*-butyltin hydride or zinc and acid gave partial cyclization to *cis*- and *trans*-1-methyl-2-(perfluorobutyl)methylcyclopentane, and at a rate consistent with previously studied free-radical cyclizations. Cyclization was slower for 8-perfluorobutyl-7-iodo-1-octene, while 6-perfluorobutyl-5-iodo-1-hexene gave only unrearranged product. Reductive dehalogenation of 1-perfluoropropyl-2-iodo-1-hexene was not stereospecific but inversion of the intermediate vinyl radicals occurred. Free-radical addition of perfluoropropyl iodide to 1-heptyne did not give internal hydrogen transfer and cyclization as had been observed for analogous reaction of CCl_4 or of $HCCl_3$.

The purpose of this research was (1) to synthesize iodine-free perfluoroalkyl-substituted alkanes and alkenes of various types; (2) to compare the behavior of a homologous series of 1-perfluoroalkyl-2-iodo terminal alkenes and of 1-perfluoroalkyl-2-iodo-1-alkenes during dissolving metal reduction, in which free radicals might be involved; and (3) to compare reductive dehalogenation of tri-*n*-butyltin hydride with that given by zinc and acid in this series of compounds.[2]

It is important to recognize that in most chemical reactions the perfluoroalkyl group retains its integrity, as a result of the high C–F bond strength. Rearrangement, loss of fluorine, or C–C bond cleavage are seldom observed. Hence, reductive defluorination is not anticipated in these reactions, in which C–I bonds are broken.

By way of background it would be helpful to review the state of the art as summarized in a recent text. "The mechanism of carbon–halogen cleavage has been studied extensively for reductions effected with solutions of alkali metals, with chromium(II) salts, zinc, magnesium and iron, and by electrolysis. Dissolving metal reductions are considered to involve transfer of an electron from the metal surface (or from metal in solution), or from a lower valence state of certain metal ions, e.g. Cr(II). Such reactions are probably related to the formation of organometallic derivatives (or dimeric products) when alkyl halides are allowed to react with metals. The possibility that free radicals or organometallic derivatives may be short-lived intermediates in these reductive cleavage reactions is suggested, since elimination rather than cleavage is usually observed if a substituent (halogen, -OH, -OR, -OCOR) that can be lost as a stable anion is present at an adjacent carbon atom."[3] The reaction paths have been diagrammed as follows.[3]

$$\begin{tikzcd} \mathrm{RBr} \arrow[r, "\mathrm{M}\cdot"] & \mathrm{R{-}Br\cdot^{-}M^{+}} \arrow[d, "-\mathrm{M}^{+}\,\mathrm{Br}^{-}"] & \\ \mathrm{R^{-}\,M^{+}} \arrow[d, "\mathrm{H}^{+}"] & \mathrm{R}\cdot \arrow[l, "\mathrm{M}\cdot"'] \arrow[r] & \mathrm{R{-}R} \\ \mathrm{R{-}H} & & \end{tikzcd}$$

Results

Free-radical addition of iodoperfluoroalkanes (R_FI) to terminal alkenes provided novel 1-perfluoroalkyl-2-iodoalkanes in excellent yield.[4] Similar reaction with 1-alkynes gave (*Z*)- and (*E*)-1-perfluoroalkyl-2-iodo-1-alkenes (**1a,b** and **2a,b**). Addition was stereoselective but not stereospecific as it was formerly believed to be.[4] In the case of terminal alkadienes, structure of the reaction product depended on the distance between the end groups. With 1,6-heptadiene cyclization of the intermediate radical occurred in part and a mixture of open-chain (**3**) and cyclic products (**4**) was isolated[5] (Chart I). While reductive dehalogenation of certain 1-perfluoroalkyl-2-iodoalkanes by zinc and acid has already been described,[4–7] evidence has now been obtained which tends to confirm the suspected free-radical nature of the process.

In orientation experiments 2-iodooctane and 5-iodo-1-hexene were dehalogenated using the well-known free-radical reducing agent, tri-*n*-butyltin hydride (TBTH).[8] Reduction in both cases gave the normal products (*n*-octane and 1-hexene). With 7-perfluorobutyl-6-iodohept-1-ene (**3**), however, a substantial amount of cyclization occurred (Chart II). Gas–liquid phase chromatography showed that 32.5% of open-chain product **5** was formed and 67.5% of cyclic product **6a,b**; the ratio of **5**/**6** was 0.480. This is consistent with abundant evidence from previous studies[9–12] showing the intermediacy of radicals in this reaction. The next higher homologue, 8-perfluorobutyl-7-iodooct-1-ene (**7**), with TBTH gave 98% of linear product **8** and not more than 2% of cyclic product **9a,b**.

These same reductions were then performed using zinc and acetic acid in ether as the reducing system;[13] see Chart III. 6-Perfluorobutyl-5-iodohex-1-ene (**10**) gave only open-chain product **11**. There were no extraneous peaks in GLC analysis and the NMR spectra showed no methyl group resonance. However, **3** again cyclized during reduction and the ratio of **5**/**6** formed was 0.297. Area measurements in GLC analysis and NMR spectra were in good agreement.

Chart I. Preparation of 1-Perfluoroalkyl-2-iodo-1-alkenes and of 7-Perfluoroalkyl-6-iodohept-1-ene and 1-Iodomethyl-2-(perfluoroalkyl)methylcyclopentanes

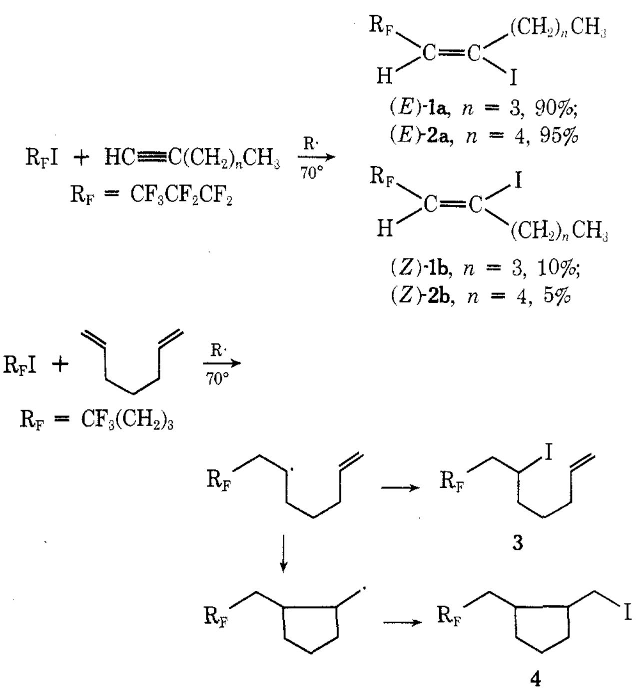
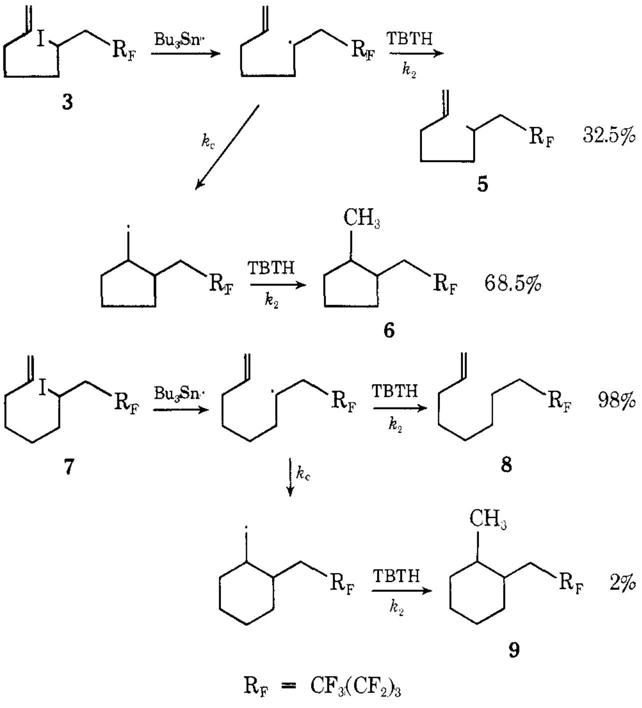


Chart II. Tri-*n*-Butyltin Hydride Reduction of Iodoalkenes



Proton resonances for the CH_3CH coupling (doublet, $J = 7$ Hz) in the cis and trans isomers of **6** were clearly defined; cis/trans = 1:2. Zinc reduction of **7** gave a significant amount of cis and trans isomers of 1-methyl-2-(perfluorobutyl)methylcyclohexane (**9a,b**). Proper choice of GLC column and operating conditions permitted separation of two peaks of identical area (8.0%). NMR spectra also showed the expected resonances for two methyl groups, and ir spectra gave CH_3 group absorption bands.

Clearly, reductive dehalogenation of iodoalkenes by zinc and acid has characteristics of a free-radical process.

Reduction of 1-Perfluoroalkyl-2-iodo-1-alkenes. De-

Chart III. Zinc and Acid Dehalogenation of Iodoalkenes

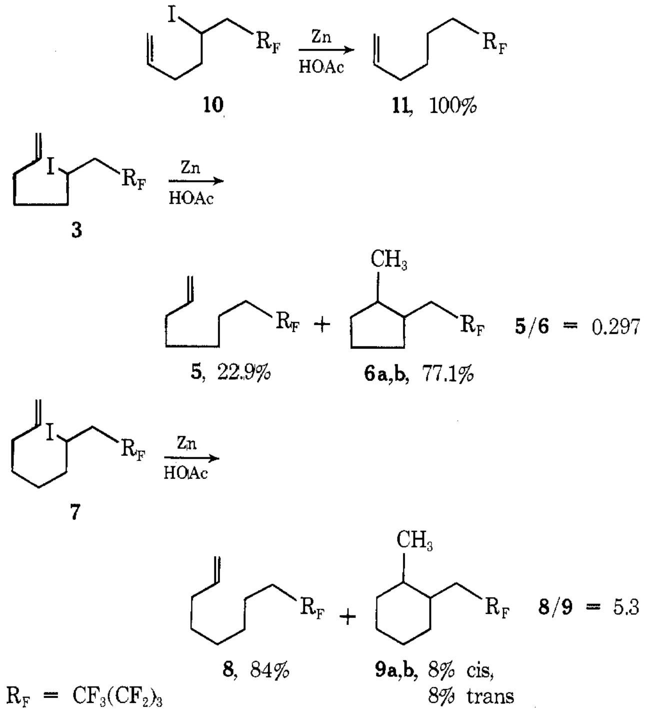
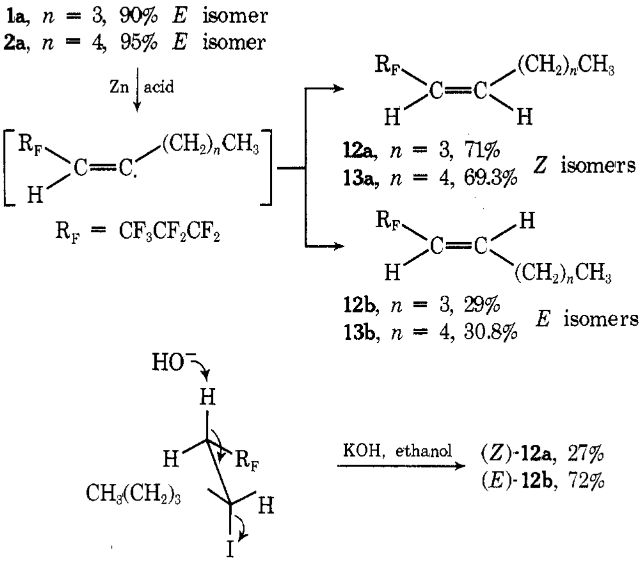


Chart IV. Nonstereospecific Reduction of 1-Perfluoroalkyl-2-iodo-1-alkenes. Exclusive α-Dehydrohalogenation of 1-Perfluoroalkyl-2-iodoalkanes



14 (preferred conformation)

halogenation of 1-perfluoroalkyl-2-iodo-1-alkenes afforded additional evidence for the intermediacy of free radicals. 1-Perfluoropropyl-2-iodo-1-hexene (90% *E* isomer, **1a**) gave $CF_3CF_2CF_2CH{=}CH(CH_2)_3CH_3$, 71% *Z* isomer **12a**, and 29% *E* isomer **12b**, by reaction with zinc and hydrogen chloride in alcohol solution at 78° (Chart IV). A similar reaction of 1-perfluoropropyl-2-iodo-1-heptene (95% *E* isomer **2a**) gave reduction to 1-perfluoropropyl-1-heptene, 69.3% *Z* isomer **13a** and 30.7% *E* isomer **13b**. These reactions show that a substantial loss of configuration occurs during reduction. Evidence for structures was obtained by synthesis of **12a,b** from 1-perfluoropropyl-2-iodohexane (**14**) by dehydrohalogenation. Isomers of **12a,b** obtained by GLC trapping were distinguished by their ir spectra; *Z* isomer **12a** had double bond stretching frequency at 1660 cm^{-1} and *E* isomer **12b** had this band at 1680 cm^{-1}. Two additional points of interest should be noted. Exclusive α-dehydrohalogenation was observed, as shown by the identity of **12a,b** obtained from **1a,b** and from **14**, and the absence of significant side products (GLC analysis). There was a preference for *E* isomer **12b**, from anti elimination of **14** in the conformation having the R_F and alkyl groups also anti to each other, to minimize crowding. The ratio of **12a**/**12b** was 1:2.67.

In most of these experiments using zinc and acid small amounts of higher boiling products were formed. They are believed to be the result of radical coupling, as indicated previously. Such products have been frequently obtained and appear to be favored by slow reaction and minimal contact of the iodoalkane at the reacting metal surface. These are conditions which would obtain in a two-phase liquid system. A further example is the reduction of 1-perfluoroheptyl-2-iodohexadecane (**15**) in benzene and aqueous hydrochloric acid by zinc and magnesium powder to 1-perfluoroheptylhexadecane (**16**) in 62% yield and to 15,16-[bis(perfluoroheptyl)methyl]triacontane in 28% yield.

The homogeneous organic phase which is formed using an anhydrous alcohol and hydrogen chloride (gas) has given less coupling, rapid reaction, and high yields of reduced, uncoupled product (85–92%).[14,15] In several of the experiments reported herein the solvent system acetic acid–diethyl ether, recommended by Hassner,[13] was used with good success. However, removal of the acetic acid was somewhat troublesome. It may be of interest to note that in one attempted Grignard reaction using *endo*-2-iodo-*exo*-3-perfluoropropylnorbornane, where crowding may have been a problem, a good yield of coupling product, 2,2′-bis(3-perfluoropropylnorbornyl), was obtained.[6] Here, too, loss of configuration occurred, as two forms having syn and anti fusion of the two rings were isolated.

Discussion

These experiments closely link the solid evidence[9–12] for free-radical mechanism of dehalogenation by TBTH with the zinc and acid heterogeneous systems we have frequently used. Since the rate constant for transfer of hydrogen from TBTH to an alkyl radical was determined[10] to be $k_2 = 1.1 \times 10^6\ M^{-1}\ \mathrm{sec}^{-1}$ at 25°, it is possible to estimate the rate constant for cyclization at 50° of **3**:

$$\mathbf{5}/\mathbf{6} = k_2/k_c[\mathrm{TBTH}];\ k_c = 4 \times 10^6\ \mathrm{M}^{-1}\ \mathrm{sec}^{-1}$$

For the 5-hexenyl radical $k_c = 1 \times 10^{-1}\ \mathrm{sec}^{-1}$ and for the 4-(cyclohexenyl)butyl radical $k_c \simeq 4 \times 10^4\ \mathrm{sec}^{-1}$.[10] The rate constant for cyclization of **7** at 50° is similarly

$$\mathbf{8}/\mathbf{9} = k_2/k_c[\mathrm{TBTH}];\ k_c = 4 \times 10^4\ \mathrm{sec}^{-1}$$

These values are indeed close to the previously determined constants for related reactions.

By comparing the **5**/**6** ratio in zinc reduction of **3** with that obtained in TBTH reduction we may estimate the "effective concentration" of active reducing agent. Using the calculated value for k_c we have

$$\mathbf{5}/\mathbf{6} = 0.297 = \frac{1.0 \times 10^6}{4 \times 10^6}\ [\text{reducing agent}]$$

From this the [reducing agent] is found to be about 1.2 *M*. The iodooctene **7** yields an estimate for [reducing agent] of about 0.21 *M*. Of course, one would expect that the "effective concentration" would vary widely according to the experimental conditions employed.

It had previously been reported[16] that zinc and acid gave stereospecific reduction of 1-perfluoroalkyl-2-iodo-1-alkenes such as **1a,b** and **2a,b**. The present results show that such is not the case. It was necessary to be able to separate

Table I
Sources and Physical Constants of Starting Materials

Compd	Code	Bp, °C (mm)	$n^{25}D$	Source
Tri-*n*-butyltin hydride		80 (0.50)		ref 20
5-Iodo-1-hexene		38–40 (15)	1.5100	ref 22
$CF_3CF_2CF_2CH{=}CI(CH_2)_3CH_3$	**1a,b**	94 (50)	1.4095	ref 4
$CF_3CF_2CF_2CH{=}CI(CH_2)_4CH_3$	**2a,b**	95 (25)	1.4135	This paper
$CF_3(CF_2)_3CH_2\underset{I}{C}H(CH_2)_3CH{=}CH_2$	**3**	90 (8)	1.4065	ref 6
$CF_3(CF_2)_3CH_2CHI(CH_2)_4CH{=}CH_2$	**7**	56 (0.25)	1.4080	ref 21
$CF_3(CF_2)_2CH_2CHI(CH_2)_3CH_3$	**14**	85 (23)	1.4029	ref 23

the two isomers by GLC, since the ir spectra could not be used to distinguish them in a mixture. Both *Z* and *E* isomers of **1** or **2** had the double bond stretching frequency at 1640 cm^{-1}. Once the two isomers were separated the fingerprint region did show significant differences. The reduced product **12a,b** from **1a** was more readily identified by ir, but there was considerable merit in using the more accurate and sensitive GLC method to determine product composition.

Isomerization of the vinyl radical from **1a** or **2a** is not expected to be a high-energy process. Similar radicals also equilibrate. Hay summarizes some recent work involving isomerization and cyclization of substituted vinyl radicals.[17] In this connection it was surprising to find that radical addition of R_FI to 1-heptyne did not give any cyclization product analogous to that obtained by Heiba and Dessau in the reaction of CCl_4 or $HCCl_3$ with 1-heptyne.[18] It appears that the rate of transfer from R_FI to the intermediate vinyl radical is considerably faster than hydrogen abstraction. This finding may in fact make it possible to determine rate constants for transfer from these small molecules to carbon radicals.

Experimental Section[19]

Source of Materials and Physical Measurements. Table I lists the sources and physical constants of starting materials. TBTH was prepared from tri-*n*-butyltin chloride (Aldrich) and lithium aluminum hydride (Ventron) in 52% yield,[20] and redistilled in a 3-ft spinning band column. Less pure material did not react properly. Infrared spectra were recorded on a Perkin-Elmer Model 337 spectrophotometer. NMR spectra were done using a Varian A-60 spectrophotometer. Gas chromatographic analyses were performed using a Sargent-Welch thermal conductivity or a Perkin-Elmer Model 881 unit fitted with a hydrogen flame detector, and under conditions which are listed as appropriate.

Reduction of 5-Iodo-1-hexene with Tri-*n*-butyltin Hydride. A 50-ml flask was fitted with a variable takeoff, total reflux distilling head, thermometer, magnetic stirrer, Claisen adapter, dropping funnel, and a dry ice cooled trap. 2,2′-Azobis-2-(methylpropionitrile) (ABN, 0.25 g, 1.5 mmol) and 5-iodo-1-hexene[22] (10.01 g, 47.20 mmol) were added and while cooling to 0–10° with an ice bath, TBTH (14.8 g, 51.1 mmol) was added cautiously over a period of 5 min. The mixture was stirred for 4 hr while heating to 50° with an oil bath. 1-Hexene (2.75 g, 69.3%, $n^{25}D$ 1.3850) was collected in the dry ice trap at 20 mm of mercury pressure, using a water aspirator. Characteristic infrared absorption of 1-hexene at 3075, 1645, 998, and 914 cm^{-1} was observed.

Reduction of 7-Perfluorobutyl-6-iodohept-1-ene (3) with TBTH. In similar fashion **3** (6-iodo-8,8,9,9,10,10,11,11,11-nonafluoro-1-undecene, 2.43 g, 5.50 mmol) containing **4** [1-iodomethyl-2-(perfluorobutyl)methylcyclopentane, 1.99 g, 4.50 mmol], ABN (0.0328 g, 0.200 mmol), and TBTH (3.77 g, 13.0 mmol, a 1.93 *M* solution) gave 8,8,9,9,10,10,11,11,11-nonafluoro-1-undecene (**5**) and *cis*- and *trans*-1-methyl-2-(perfluorobutyl)methylcyclopentane (**6a,b**), bp 62–66° (15 mm), 2.63 g, $n^{25}D$ 1.3504 (83%). Ir showed ν_{CH} (olefinic) at 3100, $\nu_{C=C}$ at 1640 (weak), and out-of-plane bending at 992 and 910 cm^{-1}. GLC analysis (using a 6 ft × 0.125 in. column packed with 20% "Ucon Polar" LB 550-X on 60–80 mesh Gas Pack WA at 60°) showed **5**, retention time 11.2 min, 17.8% relative area, and **6** at 15.7 min, 81.5% relative area (replicate analyses). The conversion of **3** to **6** was 67.5% and of **3** to **5** was 32.5%; **5/6** then was 0.480.

Anal. Calcd for $C_{11}H_{13}F_9$: C, 41.78; H, 4.14. Found (**5/6** mixture): C, 41.77; H, 4.00.

Zinc Reduction of 7-Perfluorobutyl-6-iodohept-1-ene (3). Using a similar apparatus but with a 100-ml flask, **3** (4.86 g, 11.0 mmol) and **4** (3.98 g, 9.00 mmol), and, while stirring, powdered zinc (100 mesh, 5.0 g, 80 mmol) and glacial acetic acid (25 ml, dropwise) were added and the mixture heated to reflux temperature (62°) using an oil bath, for 4 hr. The slurry was cooled and decanted, the zinc washed with 10 ml of ether, and the layers separated with the aid of 25 ml of saturated salt solution. Saturated sodium bicarbonate solution (25 ml) was added to the organic layer, 5 ml at a time, shaken carefully. The water layer was washed with 10 ml of ether, and the combined ether extracts dried over magnesium sulfate. Distillation gave **5** and **6a,b**, bp 66° (14 mm), 4.33 g, $n^{25}D$ 1.3517 (68.5%). A residue of 1.31 g of oil remained. GLC analysis showed **5**, 12.6% relative area, and **6a,b**, 87.5%. Ir spectra were identical for both reduction product mixtures. An NMR spectrum of the **5/6a,b** mixture gave resonances at δ 0.85, d, J = 7 Hz, 1.81 proton, CH_3CH of **6a**; 1.10, d, J = 7 Hz, 0.57 proton, CH_3CH of **6b**; 1.2–2.6, m, 10 protons, $(CH_2)_n$ and CH; 4.8–6.2, m, 0.5 proton, $CH_2{=}CH$ of **5**. Correcting for the amount of **4** originally present, the conversion of **3** to **5** was 22.9% and of **3** to **6** was 77.1%; hence, the ratio of **5/6** was 0.297.

Reduction of 8-Perfluorobutyl-7-iodooct-1-ene (7) with TBTH. **7** (7-iodo-9,9,10,10,11,11,12,12,12-nonafluoro-1-dodecene, 11.0 g, 24.1 mmol), ABN (0.0203 g, 1.25 mmol), and TBTH (9.00 g, 31.0 mmol, 1.90 *M* in the resulting solution) gave exothermic reaction at 31–43° under a nitrogen atmosphere. Distillation in a 16-in. spinning band column afforded 9,9,10,10,11,11,12,12,12-nonafluoro-1-dodecene (**8**) and *cis*- and *trans*-1-methyl-2-(perfluorobutyl)methylcyclohexane (**9**), bp 83° (13 mm), 6.41 g (81%). Tri-*n*-butyltin iodide (13.92 g) remained in the pot flask. GLC analysis (10 ft, 10% QF-1 fluorosilicone oil on Chromosorb W, at 90°) showed **8**, 98%, and **9**, 2% relative areas.

Anal. Calcd for $C_{12}H_{15}F_9$: C, 43.64; H, 4.58. Found: C, 43.81; H, 4.76.

Zinc Reduction of 8-Perfluorobutyl-7-iodooct-1-ene (7) to 8 and 9a,b. **7** (7.66 g, 16.8 mmol), zinc dust (1.57 g, 26.0 mmol), acetic acid (15 ml), and ether (15 ml) were heated to reflux for 5 hr. Distillation gave **8** and **9a,b**, bp 79–83° (14 mm), $n^{25}D$ 1.3551, 3.57 g (64%), and a liquid residue of 2.44 g. Ir showed ν_{CH}(olefinic) 3070, $\nu_{C=C}$ 1640, δ_{CH_3} 1460 and 1380 cm^{-1}, and bands at 1440, 1415, 1350, 1300, 1250–1200, 1140, 1040, 1020, 996, 918, 880, 850, and 720 cm^{-1}. An NMR spectrum showed proton resonances at δ 0.90, d, 0.28 proton, CH_3CH of **9a**; 1.2–2.6, m, 11.9 proton, (CH_2), CH (and CH_3CH of **9b**); 4.9, m, 1.75, $CH_2{=}CH$ of **8**; 5.2–6.2, m, 1.0 proton, CH= of **8**. GLC analysis (10-ft QF-1 column, 90°) gave peaks for **9a**, 14.6 min, 8.41%; **9b**, 15.8 min, 8.04%; and **9**, 18.8 min, 83.26% relative area. GLC analysis using the "Ucon Polar" column and several others failed to resolve the mixture.

Preparation of 6-Perfluorobutyl-5-iodohex-1-ene (10). 1,5-Hexadiene (16.4 g, 200 mmol), 1-iodoperfluorobutane (17.8 g, 50.0 mmol), and ABN (0.300 g, 1.82 mmol) were charged to a Fischer-Porter aerosol tube, cooled to −78°, evacuated and filled with nitrogen three times, and heated in an oil bath for 21 hr at 70.0°. Distillation in a 2-ft platinum spinning band column gave 1,5-hexadiene (11.6 g, 70.6% of the amount charged) and 5-iodo-7,7,8,8,9,9,10,10,10-nonafluoro-1-decene (**10**), bp 85° (12.0 mm), $n^{25}D$ 1.4010, 13.88 g (64.8%) in three fractions: the bis adduct,[6,21] bp 54° (0.10 mm), $n^{25}D$ 1.4350, 2.17 g, and residual oil, mostly bis adduct, 2.3 g. GLC analysis (6-ft "Ucon Polar" column, 128°) showed **10**, 98.7%, ir $\nu_{CH=CH}$ 1640 cm^{-1} and bands at 990, 920, 880, 850, 740, 730, 690, and 515 cm^{-1}.

Anal. Calcd for $C_{10}H_{10}F_9I$: C, 28.05; H, 39.94. Found: C, 28.23; H, 2.48.

Zinc Reduction of 10. **10** (6.60 g, 15.4 mmol), acetic acid (15 ml), and diethyl ether (15 ml) were stirred while zinc dust (100 mesh, 1.57 g, 24.0 mmol) was added. Work-up and distillation gave 7,7,8,8,9,9,10,10,10-nonafluoro-1-decene (**11**), bp 39–44° (18 mm), n^{25}D 1.3374, 2.02 g (44%). Part of the volatile product was lost. A residue of 0.56 g remained. Ir showed bands similar to **8**. An NMR spectrum gave proton resonances at δ 1.3–3.2, m, 8 protons, and at 4.8–6.1, m, 3 protons, in agreement with structure **11**. The R_FCH_2 group was indicated by a triplet at δ 2.75, the last of a triplet of triplets at δ 2.4; J_{HF} = 22 and J_{HH} = 7 Hz. No methyl group resonance appeared at δ 0.8–1.2. GLC analysis (6-ft "Ucon Polar" column, 62°) gave a single peak at 6.4 min.

Anal. Calcd for $C_{10}H_{11}F_9$: C, 39.75; H, 3.67. Found: C, 39.85; H, 3.80.

Zinc Reduction of 1-Perfluoropropyl-2-iodohex-1-ene (1a,b). **1a,b** (1,1,1,2,2,3,3-heptafluoro-5-iodonon-4-ene, 89.8% *E* isomer **1a** and 10.9% *Z* isomer **1b**, 10.9 g, 39.2 mmol), zinc (30 mesh, 10.0 g, 154 mmol), and ethanol (75 ml) were stirred in a flask fitted with a gas inlet tube, reflux condenser, and a paddle stirrer. Hydrogen chloride was introduced above the slurry occasionally, until gas evolution began, and the zinc began to react. The mixture was kept at 76–78° by heating as necessary. Samples taken after 1 and 2 hr both showed that very little of **1a,b** remained. The cooled liquid was decanted into 100 ml of water and extracted three times with dichloromethane (25 ml) and dried ($MgSO_4$). Distillation (16-in. spinning band column) gave (*Z*)- and (*E*)-1,1,1,2,2,3,3-heptafluoro-4-nonene (**12a,b**), bp 77° (138 mm), n^{25}D 1.3400, 5.35 g (63.2%). There was no residue. GLC analysis (10-ft QF-1 column, 85°) showed **12a** at 6.4 min, 70.6%, and **12b** at 7.2 min, 29.4%. **1a,b** was at 23.5 min retention time. Varying ratios of **12a,b** appeared in the distilled fractions. NMR gave proton resonances at δ 0.94, m, 3 protons, CH_3; 1.4, 4 protons, m, $(CH_2)_2$; 2.3, 2 protons, m, $CH_2CH{=}$; 5.0–7.0, m, 2 protons, $CH{=}CH$.

Anal. Calcd for $C_9H_{11}F_7$: C, 42.86; H, 4.40. Found: C, 42.98; H, 4.35.

Preparation of 1-Perfluoropropyl-2-iodo-1-heptene (2a,b) by Addition of 1-Iodoperfluoropropane to 1-Heptyne. 1-Iodoperfluoropropane (12.0 g, 40.0 mmol), 1-heptyne (4.80 g, 50.0 mmol), and ABN (0.0820 g, 0.500 mmol) were charged to a pressure tube and processed as for **10**. Fractionation gave **2a,b**, bp 95° (26 mm), n^{25}D 1.4135, 14.3 g (91%), in four fractions; the first three fractions contained 90.3% of **2a** and 9.67% of **2b**. The last fraction (1.9 g) contained 60.0% of **2a** and 40.0% of **2b** and was used for trapping these isomers on a GLC column (6-ft QF-1, 125°, 4-μl injections). A drop of **2a** (3.8-min retention time) on KBr plates showed ir bands: ν_{CH} 3080, 2980, 2950, 2880; $\nu_{CH=CI}$ 1640; δ_{CH} 1480, 1380, 1350; ν_{CF} 1270, 1230, 1180, 1140, 1120; bands at 1080, 975, 950, 940, 915, 820, 740, 725, 680, and 640 cm^{-1}. **2b** (5.6-min retention time) gave ir bands at $\nu_{CH=CI}$ 1640; δ_{CH} 1470, 1380, 1350; ν_{CF} same; bands at 1050, 1020, 970, 948, 915, 850, 820, 790, 740, 675, and 655 cm^{-1}. An NMR spectrum of **2a** (96%) showed proton resonances at δ 0.9, t, *J* = 5 Hz, 3 protons, CH_3; 1.4, m, 6 protons, $(CH_2)_3$; 2.68, m, 2 protons, $CH_2CI{=}C$; 6.40, t, *J* = 15 Hz, 1 proton, $CF_2CH{=}CI$.

Zinc Reduction of 1-Perfluoropropyl-2-iodo-1-heptene (2a,b). **2a,b** (1,1,1,2,2,3,3-heptafluoro-5-iodo-4-decene, 6.50 g, 16.6 mmol, 95.5% of *E* and 4.5% of *Z* isomers), zinc (30 mesh, 15.0 g in three portions, 230 mmol), ethanol (75 ml), and hydrogen chloride were employed as in the experiment with **1a,b**. Distillation afforded (*Z*)- and (*E*)-1,1,1,2,2,3,3-heptafluoro-4-decene (**13a,b**), bp 141–143° (1 atm), n^{25}D 1.3535, and bp 81° (95 mm), n^{25}D 1.3501, 3.40 g (77%). A residue of 1.2 g remained. GLC analysis (10-ft QF-1 column, 85°) gave (*Z*)-**13a** at 10.8 min, 69.3%, and (*E*)-**13b** at 12.5 min, 30.7%; **2a,b** was at 16.1-min retention time. For NMR and ir spectra see below.

Anal. Calcd for $C_{10}H_{13}F_7$: C, 45.11; H, 4.92. Found: 44.91; H, 5.09.

Preparation of 1,1,1,2,2,3,3-Heptafluoro-5-iodononane (14).[23] 1-Hexene (16.82 g, 200 mmol), 1-iodoperfluoropropane (29.6 g, 100 mmol), and ABN (0.164 g, 1.00 mmol) were charged to a pressure tube, processed as for the preparation of **10**. Distillation (2-ft platinum spinning band column) gave 1-hexene (7.55 g, 90.0 mmol), 1,1,1,2,2,3,3-heptafluoro-5-iodononane (**14**), bp 85° (23 mm), n^{25}D 1.4029, 36.1 g; and bp 73° (12 mm), n^{25}D 1.4036, 1.2 g (98%); and an oil residue (1.3 g). GLC analysis (6-ft Carbowax 1500, 20% on Chromosorb WA, 150°) gave **14** at 6.0 min, 98.14%; and an unknown at 7.6 min, 1.86%. NMR δ 0.92, m, 3 protons, CH_3; 1.12–2.2, m, 6 protons, $(CH_2)_3$; 2.82, 6 lines, 2 protons, J_{HF} = 20, J_{HH} = 7 Hz, CF_2CH_2; 4.33, 5 lines, 1 proton, *J* = 7 Hz, CH_2CHICH_2.

Preparation of (*Z*)- and (*E*)-1,1,1,2,2,3,3-Heptafluoro-4-nonene (12,a,b) by Dehydrohalogenation of 14. A solution of KOH (3.00 g, 53.5 mmol) in 60% aqueous ethanol (75 ml) was stirred by magnet bar while **14** (10.0 g, 26.4 mmol) was added and kept at 70° for 22 hr. Two layers formed which were poured into water (50 ml) and 6 *N* HCl (10 ml). The mixture was extracted into CCl_4 (three times, 10 ml) and dried ($MgSO_4$). Distillation (16-in. spinning band column) gave (*Z*)- and (*E*)-**12a,b**, bp 129°, n^{25}D 1.3392, 4.48 g, in three fractions (68%); and a residual oil (1.5 g). GLC analysis and trapping of peaks was done using a 10-ft QF-1 fluorosilicone column at 85°. (*Z*)-**12a** at 9.2 min, 27%, (*E*)-**12b** at 10.9 min, 72%, and two peaks in small amount were obtained. (*Z*)-**12a** gave ir bands at 2970, 2940, 2890, 2870; $\nu_{CH=CH}$ 1660; δ_{CH} 1470, 1350; ν_{CF} 1230, 1180, 1120; bands at 960, 670, 650, and 535 cm^{-1}. (*E*)-**12b** gave $\nu_{CH=CH}$ 1680; δ_{CH} 1465, 1350; ν_{CF} 1230, 1180, 1115; and bands at 970, 925, 735, 710, and 540 cm^{-1}.

Addition of 1-Iodoperfluoroheptane to 1-Hexadecene. Zinc Reduction of 1-Perfluoroheptyl-2-iodohexadecane (15) to 1-Perfluoroheptylhexadecane (16) and to 15,16-Bis[(perfluoroheptyl)methyl]triacontane (17). 1-Iodoperfluoroheptane (24.8 g, 50.0 mmol), 1-hexadecene (Humphrey Chemical Co, 22.4 g, 100 mmol, n^{20}D 1.4388), and ABN (0.200 g, 1.20 mmol) were heated at 80° under nitrogen for 7 hr. GLC showed only a trace of unreacted R_FI. The product (**15**) was a white solid; it was converted directly to **16** and **17**. A slurry of **15**, hexadecene (47.0 g, combined), zinc dust (65 g, 1.0 mol), magnesium powder (4.0 g, 120 mmol), and benzene (25 ml) was heated to 70° and stirred rapidly while 16% hydrochloric acid (42 ml) was added dropwise during 0.75 hr. Exothermic reaction occurred. Zinc dust (10 g), magnesium powder (1.0 g), and hydrochloric acid (43 ml) were added after 1 hr at 75°. After 3 hr, benzene (100 ml) was added, the slurry decanted and the organic layer rinsed with water twice, dried ($MgSO_4$), and distilled in a 3-ft spinning band column. 1-Hexadecene (10.6 g, 100%) was recovered, bp 87.5–90° (0.45 mm), n^{25}D 1.4390; an intermediate fraction, bp 108–127.5° (0.6 mm), n^{25}D 1.3959, 1.4 g; and 1-perfluoroheptylhexadecane (**16**), bp 122–124° (0.3 mm), 18.3 g (61.6%), a white solid. The high-boiling residue was distilled without a column, giving 15,16-bis[(perfluoroheptyl)methyl]triacontane (**17**), bp 240° (0.1 mm), 6.1 g, and bp 260° (0.1 mm), 2.2 g (total 28% of theory). The structures of **16** and of **17** were assumed to be consistent with their properties and molecular weight determination.

Anal. Calcd for $C_{23}H_{33}F_{15}$: C, 46.47; H, 5.6; F, 47.94. Found: C, 46.5; H, 5.4; F, 44.3.

Anal. Calcd for $C_{46}H_{64}F_{30}$: C, 46.5; H, 5.4; F, 47.9; mol wt, 1187. Found: C, 48.7; H, 6.0; F, 45.8; mol wt (bp in acetone) 1088, 1062.

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Hydride Transfer Reduction–Rearrangements of Tricyclodecylcarbinols and Tricycloundecanols. Formation of Tricyclo[6.2.1.0^{2,6}]undec-2(6)-ene under Phosphoric Acid Catalysis

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Hydride transfer reduction–rearrangements of 5,6-*exo*-trimethylene-2-norbornylcarbinol (**1**), 2- and 3-hydroxy-6,7-*exo*-trimethylenebicyclo[3.2.1]octane (**2** and **3**), and 2-hydroxy-5,6-*endo*-trimethylenebicyclo[2.2.2]octane (**4x** and **4n**) in 95% sulfuric acid and excess *n*-pentane at room temperature gave 4-homoisotwistane (tricyclo[5.3.1.0^{3,8}]undecane, **5**) with high selectivity (92–97%). In contrast to this, treatment of **1**, **2**, **3**, and **4** with refluxing 85% phosphoric acid–*n*-heptane resulted in the predominant formation of a novel olefin, tricyclo[6.2.1.0^{2,6}]undec-2(6)-ene (**6**). The structure of **6** was established by an independent synthesis of the hydrogenation product (**6h**) of **6**. The olefin **6** selectively (94%) isomerized to **5** in sulfuric acid–*n*-pentane. The result suggests that tricyclo[6.2.1.0^{2,6}]undec-2-yl cation (**6c**) would be a key intermediate in the rearrangement sequence leading to **5**.

In the course of the identification of intermediates in adamantane rearrangement of 2,3-*exo*-tetramethylenenorbornane and 2,3-trimethylenebicyclo[2.2.2]octane, it was necessary for us to prepare an authentic specimen of 6,7-*exo*-trimethylenebicyclo[3.2.1]octane.[1] A synthesis was planned involving hydride transfer reduction–rearrangement[2–4] of 5,6-*exo*-trimethylene-2-norbornylcarbinol (**1**). This route seemed quite promising, since the isomerization of the cation (**1a**) from the carbinol **1** could give rise to the hoped-for 6,7-*exo*-trimethylenebicyclo[3.2.1]octane system, in view of the well-documented ring expansion of 2-norbornylcarbinyl to bicyclo[3.2.1]octyl cation.[5]

Sulfuric Acid Catalyzed Rearrangements of Carbinols. 5,6-*exo*-Trimethylene-2-norbornylcarbinol (**1**) was prepared from 2-*exo*-chloro-5,6-*exo*-trimethylenenorbornane[6] via Grignard reaction followed by addition to formaldehyde.[7] The carbinol thus obtained consisted of two epimers in 53:47 ratio, as shown on conventional VPC. The mixture **1** was then stirred with 95% sulfuric acid and *n*-pentane at room temperature. Samples were withdrawn at intervals from the pentane layer of the reaction mixture and examined on Golay column GC–MS, which determined the composition and established the identities of the products. Results are shown in Table I. Contrary to our expectation, no 6,7-*exo*-trimethylenebicyclo[3.2.1]octane was obtained, but 4-homoisotwistane (tricyclo[5.3.1.0^{3,8}]undecane, **5**)[1,3,4] was found to be the main product (95%) (Scheme I).

Since the first step in the rearrangement of **1** should be ring expansion to a bicyclo[3.2.1]octyl cation (**2a**),[4,5,8] reaction of 2-hydroxy-6,7-*exo*-trimethylenebicyclo[3.2.1]octane (**2**) was also examined. The alcohol **2** was prepared from 5,6-*exo*-trimethylene-2-norbornene (**7**)[6] by the application of the method of Bergman[9] (dichlorocarbene ring expansion,[1] hydrolysis of allylic chlorine atom, and dechlorination–hydrogenation). The alcohol **2** thus synthesized was a mixture (89:11) of two epimers separable on conventional VPC. Reaction of **2** with sulfuric acid and *n*-pentane also gave **5** predominantly (90%) (Table I).

Table I. Sulfuric Acid Catalyzed Hydride Transfer Reduction–Rearrangement[a]

Run	Reactant	Reaction time, min	Product,[b] %[c] 15	Unknown D[d]	5	Others[e]
1	1	1	2.1	3.1	93.7	1.1
		10	2.0	2.9	94.9	0.2
		30	1.7	2.4	95.0	0.9[f]
2	2	1	1.8	2.8	89.7	5.7
		10	2.2	2.8	89.2	5.8
		30	1.8	2.7	89.0	6.5[g]
3	3	1	1.1	2.9	94.0	2.0
		15	0.8	1.3	96.8	1.1
4	4x	1	1.9	2.7	89.7	5.7[h]
		10	2.1	2.6	89.8	5.5[i]
		30	1.9	2.7	89.8	5.6[j]
5	4n	1	0.8	2.5	94.4	2.3
		10	2.0	2.4	92.1	3.5[k]
11	2Δ	30	1.1	2.2	85.0	11.7[l]
12	6	1	1.6	2.3	92.3	3.8
		5	1.4	2.1	91.7	4.5
		10	1.1	2.2	91.8	5.8[m]

[a] 100 mg of reactant, 1 g of 95% sulfuric acid, and 5 ml of *n*-pentane stirred vigorously at room temperature (~25 °C). Combined yields of pentane-soluble products were 25–35%, the balance being tarry materials. [b] Identified on Golay GC–MS by comparison with authentic specimens.[13] [c] Calculated from Golay VPC peak areas. [d] A tricycloundecane (M$^+$ *m/e* 150) of unknown structure detected in adamantane rearrangement of various precursors.[1,12,13] [e] Consisting of several, unidentified compounds with M$^+$ *m/e* 146, 148, or 150. [f] Including 0.8% 2-methyladamantane (2-Me-Ad). [g] 0.4% 2-Me-Ad. [h] 0.3% 1,2-*exo*-tetramethylenenorbornane (B_2)[13] and 1.0% 1,2-*endo*-tetramethylenenorbornane (B_3).[13] [i] 0.6% B_2, 0.4% B_3, 0.5% 2-Me-Ad, and 0.3% 6,7-*exo*-trimethylenebicyclo[3.2.1]octane (**2h**).[1] [j] 0.5% B_2, 0.5% B_3, 0.2% 2-Me-Ad, and 0.1% **2h**. [k] 1.0% 1,2-*exo*-trimethylene-*cis*-bicyclo[3.3.0]octane (B_1).[13] [l] 0.7% 2-Me-Ad and two tricycloundecadienes (M$^+$ *m/e* 146) in 6.2 and 1.4%, respectively. [m] 0.4% 2-Me-Ad.