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Effect of a Perfluoroalkyl Group on the Elimination and Substitution Reactions of Two Homologous Series of Perfluoroalkyl-Substituted Iodoalkanes[1]

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Substitution and elimination reactions of two homologous series of compounds, induced by strong bases, were studied in aqueous alcohol and anhydrous methanol solution. Series I compounds, $R_F(CH_2)_nI$ having $n = 2$ (R_F = a perfluoroalkyl group, also named an *F*-alkyl group), gave only $R_FCH{=}CH_2$ under all conditions. By contrast, $R_F(CH_2)_3I$ gave 4–10 times as much substitution as elimination products. Isomerization of $R_FCH_2CH{=}CH_2$ (**6**) to $R_FCH{=}CHCH_3$ (**7**) occurred; this result may account, in part, for the extremely high **7**/**6** alkene ratios (37–81/1) obtained from elimination reactions of $R_FCH_2CHICH_3$. All series II compounds, $R_FCH_2CHI(CH_2)_nCH_3$ (n = 0–5), gave entirely elimination, and principally toward the R_F group. *E*/*Z* isomer ratios varied from 2.65 to 5. These results were compared to those obtained from 1- and 2-iodooctane under the same conditions. A practical synthesis of $CF_3(CF_2)_5CH_2CH_2CH_2I$ is described; the isomeric (*F*-alkyl)propenes **6** and **7** were also separately prepared. Rates of reactions under standard conditions for both series I and II compounds were measured. Kinetically, only second-order processes were observed, but a sharp break occurred in rate as the R_F group was separated more than two carbons from the departing iodine atom, in series I compounds. Series II compounds reacted about one-tenth as fast as series I compounds. These results are discussed in the context of previous work with *F*-alkyl-substituted compounds.

A study of *F*-alkyl-substituted iodoalkanes was begun several years ago, using two homologous series of compounds. Several members of the first series (i.e., $CF_3(CF_2)_m(CH_2)_nI$, n = 2, 4, 6) had been prepared by free radical telomerization of iodo-*F*-alkanes (R_FI) with ethene.[2] Rates of dehydrohalogenation and substitution of these compounds were then measured, but unfortunately a key member of the series having $n = 3$ ($R_FCH_2CH_2CH_2I$) was not known. Subsequently, the compound $CF_3(CF_2)_5(CH_2)_3I$ was synthesized and we can now report some of its chemistry. (The first member of the series, R_FCH_2I is well-known but, of course, does not undergo dehydrohalogenation under ordinary circumstances.)[3] Similarly, compounds of the series II were obtained from the free radical addition of iodo-*F*-alkanes to various terminal alkenes.[2,4] These series afforded a unique opportunity to observe the effect of proximity of the strong electron-withdrawing *F*-alkyl group on the course and rate of some simple substitution and elimination reactions. Furthermore, a quantitative product and rate study was needed to facilitate further work. An investigation of two related series of compounds will be reported separately.[5]

series I $CF_3(CF_2)_m(CH_2)_nI$				series II $CF_3(CF_2)_m$- $CH_2CHI(CH_2)_nCH_3$	
m	n	m	n	m	n
2	2	5	3	2	3
3	2	6	4	3	3
5	2	6	8	3	4
6	2			6	0
				6	5

Results

Reactions of series I and II compounds were carried out under standard conditions to set the new results in the frame of previous quantitative studies. (*F*-Alkyl)alkanoic acids and 1-iodo-2-(*F*-alkyl)cycloalkanes[6,7] of known configurations had been examined under conditions that were originally chosen to conform to classical studies in the field.[8] In the present work, products were isolated and characterized, and as required, synthesized independently. Quantitative measurement of all significant volatile products was accomplished by GC analysis using known mixtures and an internal reference with appropriate response factors.

Series I homologous having $n = 2$ (i.e., $R_FCH_2CH_2I$) with various *F*-alkyl (R_F) groups gave only the elimination product, $R_FCH{=}CH_2$ (99% yield), by reaction with strong base, confirming our earlier results.[6] Reactions of 1-iodo-2-(*F*-hexyl)ethane (**1**) were done by using NaOH (an excess) in 92.6% ethanol, in 76.1% aqueous ethanol at 50 °C, or with sodium methoxide in anhydrous methanol at 30 °C. Table I lists conditions and results of several experiments. In one experiment the reaction mixture was "spiked" with 2-(*F*-hexyl)-1-ethanol to see whether it would be recovered by the method of extraction used. Satisfactory recovery was found. Thus, no more than traces of this product could have been formed. GC gave (*F*-hexyl)ethene (**2**) as the only product and **2** was recovered in 91.5% of theory. None of the methyl ether was found from reaction of **1** with sodium methoxide.

In rate studies done in 92.6% ethanol, reaction with NaOH was followed out to 80–95% conversion of $R_FCH_2CH_2I$. Rate constants are listed in Table II, and it was found that the size of the *F*-alkyl group had only a small effect on rate. All substances gave clean second-order kinetics (first order in $R_FCH_2CH_2I$ and first order in base)

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(1) Presented in part at the 6th International Symposium on Fluorine Chemistry (ISFC), Durham, England, July 18, 1971 and at the 8th International Symposium on Fluorine Chemistry, Kyoto, Japan, August 22, 1976.

(2) (a) Brace, N. O. U.S. Patent 3016406, Jan. 9, 1962 (to E.I. du Pont de Nemours and Co. (b) Brace, N. O. U.S. Patent 3145222, August 8, 1964.

(3) Nakai, T.; Tanaka, K.; Ishikawa, N. *J. Fluorine Chem.* **1977**, *9*, 89–93.

(4) Brace, N. O.; Van Elswyk, J. E. *J. Org. Chem.* **1976**, *41*, 766–771.

(5) Brace, N. O. *J. Org. Chem.* **1973**, *38*, 3167–3172.

(6) Brace, N. O. *J. Am. Chem. Soc.* **1964**, *86*, 2428–2434.

(7) Brace, N. O. *J. Org. Chem.* **1971**, *36*, 1904–1909.

(8) Streitwieser, Jr., A. "Solvolytic Displacement Reactions"; McGraw-Hill Book Co.: New York, 1962; p 10 and p 30.

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Table I. Dehydrohalogenation of 1 in Alcohol Solution

1, M	base	M	solvent	time, h	temp, °C	2, %[a]
0.16	NaOH	0.64	92.6% EtOH	6.5	30.0	99
0.16	NaOH	0.32	92.6% EtOH	1.0	30.0	99[b]
0.21	NaOH	1.0	76.1% EtOH	4.0	50	98.7
0.77	NaOMe	1.6	100% MeOH	1.0	50	98.9

[a] By titration of I^-. [b] Product recovered by extraction, weight, and GC analysis.

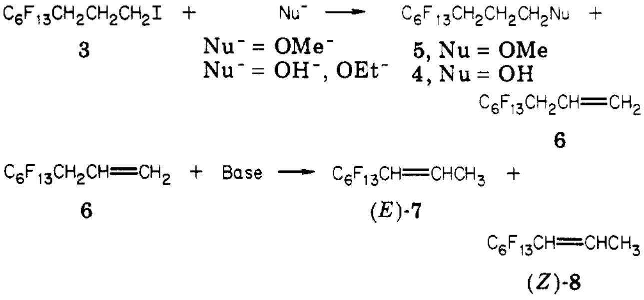
Table II. Rate of Dehydrohalogenation of $R_FCH_2CH_2I$ by NaOH in 92.6% Ethanol at 30.0 °C

$R_FCH_2CH_2I$					
R_F	10^3 M	NaOH, 10^3 M	time, min	rxn,[a] %	k[b], L/mol s
C_3F_7	4.89	5.016			0.155[c]
C_4F_9	2.829	12.97	16	89	0.107
C_4F_9	2.946	12.97	65	95	0.111
C_6F_{13}	3.095	5.186	83	80	0.136
C_7F_{15}	3.095	5.186	70	81	0.116

[a] Extent of reaction as determined by I^- titration. [b] Rate constants obtained from least-squares analysis of data (see Figure 1). [c] Reference 6.

under the conditions used. An example of the type of data obtained is shown in Figure 1 for compound **1**. For comparison, the rate of reaction of 1-iodopentane was reported as $k = 5.0 \times 10^{-5}$ L/mol s.[6]

Substitution and Elimination Reactions of 3-(*F*-Hexyl)-1-iodopropane (3) with Nucleophiles. Rearrangement of 3-(*F*-Hexyl)-1-propene (6) to (*E*)-1-(*F*-Hexyl)-1-propene (7). A synthesis of **3** (n = 3 homologue) is given below. Reactions of **3** with the nucleophiles present in anhydrous methanol and in aqueous ethanol were examined under several conditions to determine some of the variables of the system. It was found that at lower temperature and concentrations substitution predominated over elimination by methoxide or hydroxide ion. Extent of primary reactions and of secondary reaction [isomerization by methoxide ion or hydroxide ion of 3-(*F*-hexyl)-1-propene (**6**)] also was affected. Table III summarizes some of these results.



$$\underset{\mathbf{3}}{C_6F_{13}CH_2CH_2CH_2I} + Nu^- \longrightarrow C_6F_{13}CH_2CH_2CH_2Nu + C_6F_{13}CH_2CH{=}CH_2\ (\mathbf{6})$$

$Nu^- = OMe^-$ — **5**, Nu = OMe

$Nu^- = OH^-, OEt^-$ — **4**, Nu = OH

$$\underset{\mathbf{6}}{C_6F_{13}CH_2CH{=}CH_2} + \text{Base} \longrightarrow \underset{(E)\text{-}\mathbf{7}}{C_6F_{13}CH{=}CHCH_3} + \underset{(Z)\text{-}\mathbf{8}}{C_6F_{13}CH{=}CHCH_3}$$

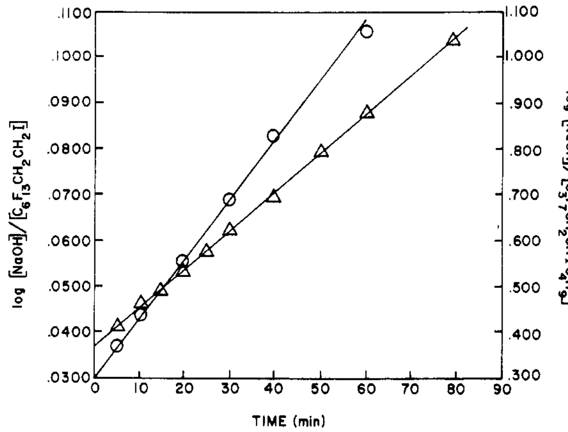


Figure 1. Reaction of $C_3F_7CH_2CHIC_4H_9$ with NaOH in 92.6% ethanol at 30.0 °C. See Tables II and V (△, $C_3F_7CH_2CHIC_4H_9$; ○, $C_6F_{13}CH_2CH_2I$).

In methanol complete conversion of **3** occurred at 50 °C in 16.7 h, giving chiefly substitution (85.8%) to **5**; about half of **6** isomerized to the more stable trans isomer, (*E*)-1-(*F*-hexyl)-1-propene (**7**). It is probable that some of (*Z*)-1-(*F*-hexyl)-1-propene (**8**) was also formed, but the small amount was not detected in the GC. At 30 °C, and lower concentrations of substrate and nucleophile, partial reaction of **3** occurred and isomerization was not observed.

In alcohol solutions of NaOH, complete reaction of **3** was achieved in 92.6% ethanol at 30 °C, with small variations in the amounts of substitution and elimination products. It was also noted that more isomerization of **6** occurred by KOH in 70% ethanol at 50 °C, but less reaction of **3** was found than for reactions done in 92.6% ethanol at 30 °C. Of possible significance was the cloudiness and a white precipitate that formed in those reactions in aqueous alcohol that gave the most isomerization. Ionic association is known to have an effect on orientation in anti eliminations from 2-haloalkanes.[9]

Table III. Substitution and Elimination Reactions of 3

Methoxide Ion in Methanol

				conversion, %			
NaOMe	3, M	time, h	temp, °C	5	6[a]	7	3[b]
1.3	0.75	16.7	50	85.8	8.6	4.5	0[c]
0.71	0.36	24	30	62.0	12.0		21.0[c]

Hydroxide Ion in Aqueous Ethanol

				conversion, %			
base, M	3, M	time, h	temp, °C	4	6[a]	7	3[b]
0.82[d]	0.16	30	30	78.0[c]	17.7	4.3	0
0.63[e]	0.26	24	50	50.2	29.1	26.7	19.2
0.76[f]	0.15	23	30	84.0	15.7	10.4	0.3

[a] Original amount of **6** before isomerization to **7**. [b] Per cent of **3** recovered. [c] 4.3% of **4** was present in the original sample of **3**. [d] NaOH in 92.6% ethanol gave a clear, colorless solution throughout the reaction. [e] KOH in 70% ethanol gave a cloudy, white precipitate throughout the reaction. [f] NaOH in 92.6% ethanol gave a cloudy, white precipitate throughout the reaction.

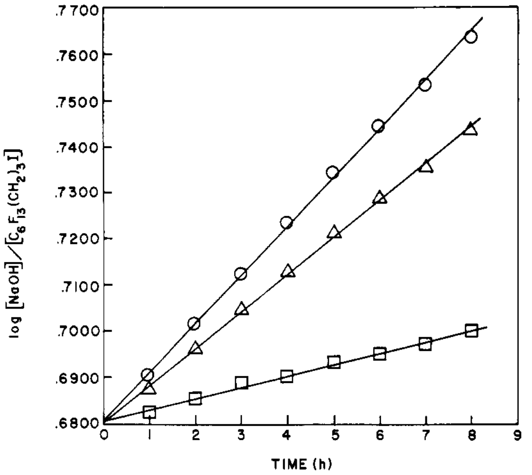


Figure 2. Reaction of $C_6F_{13}(CH_2)_3I$ with NaOH in 92.6% ethanol at 30.0 °C. See Table III (○, overall rate; △, rate of S_N2 reaction; □, rate of E-2 reaction).

Table IV. Reaction Rates of $CF_3(CF_2)_m(CH_2)_nI$ (n = 3-8) with NaOH in 92.6% Ethanol at 30.0 °C

m	n	concn, 10^3 M	NaOH, 10^2 M	rxn,[a] %	10^4 k,[b] L/mol s
5	3	5.526	2.461	21	3.47[c]
6	4	5.227	2.461	85	2.73
6	4	6.094	2.461	80	2.96
6	8	2.516	2.461	85	1.29

[a] Extent of reaction by titration of I^-. [b] k obtained from least-squares analysis of data. [c] From product analysis, $k(S_N2)$ = 2.69×10^{-4} and k(E-2) = 0.78×10^{-4}.

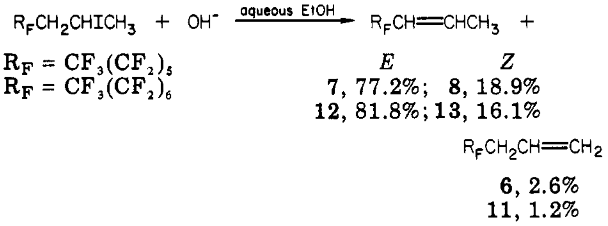
The base-induced isomerization of **6** to **7** has important consequences for elimination reactions of an isomer of **3**, $R_FCH_2CHICH_3$, as seen below.

Rate of Reaction of 3 in 92.6% Ethanol. Second-order kinetics were again observed for reaction of NaOH with **3** in 92.6% ethanol at 30.0 °C, as for its lower homologue **1**. A linear plot (Figure 2) of the appropriate quantities was obtained out to 21% reaction. Accordingly, both displacement and elimination appear to be normal bimolecular processes. Total rate of reaction, $k = 3.47 \times 10^{-4}$ L/mol s (Table IV), was substantially less than that of **1** under these conditions.

Series I Higher Homologues. Three additional members of the series $R_F(CH_2)_nI$ (n = 4, 6, 8) were obtained by telomerization of R_FI with ethene.[2b] Rates of reaction of the n = 4 and 8 homologues with NaOH in 92.6% ethanol were measured at 30.0 °C (Table IV). Products of reaction were not isolated but would be expected to conform to the pattern set by previous studies of these substances.[10,11] Rates decreased from the n = 3 to the n = 8 homologue, as expected, but even the slowest rate ($k = 1.29 \times 10^{-4}$ L/mol s) was greater than that of 1-iodopentane ($k = 5.0 \times 10^{-5}$ L/mol s) previously found under these conditions.[6]

Reaction of 1-Iodooctane. The model compound, 1-iodooctane, with NaOH in 92.6% ethanol gave 1-octene (7.3%), 1-octanol (56.4%), and unreacted 1-iodooctane (27.8%, mol amounts). With NaOMe in anhydrous methanol at 30 °C for 24 h, the reaction products were 1-octene (6.1%) and 1-methoxyoctane (69.7%). The identity of 1-octene (and the absence of octane or (E)-2-octene) was demonstrated by time coincidence in GC. 1-Methoxyoctane was identified by NMR and IR.

Series II (F-Alkyl)iodoalkanes. Base-induced elimination of series II homologues occurred by preferential attack at the more acidic proton of R_FCH_2CHIR. For reaction of $CF_3(CF_2)_5CH_2CHICH_3$ (**9**) with NaOH in



9, R_F = $CF_3(CF_2)_5$
10, R_F = $CF_3(CF_2)_6$

E Z
7, 77.2%; 8, 18.9%
12, 81.8%; 13, 16.1%

6, 2.6%
11, 1.2%

92.6% ethanol at 50 °C for 24 h, the E and Z products **7** and **8**, respectively, and the terminal alkene **6** were obtained in a ratio of **7**,**8**/**6** = 37. An even higher selectivity was found for reaction of $CF_3(CF_2)_6CH_2CHICH_3$ (**10**) with KOH in 76.1% ethanol at 50 °C; the E,Z isomer mixture, **12**, **13**, predominated over the terminal alkene **11** by 81/1.

However, it must be remembered that the conditions of reaction were the same as those that were found to give substantial isomerization of the first formed terminal alkene to the mixture of *cis*- and *trans*-1-(F-alkyl)-1-propenes from **3**. Thus, to obtain initial values, the observed E/Z ratios have to be corrected for an unknown amount of isomerization. As seen by results listed in Table III, the rate of isomerization was very sensitive to reaction conditions. Accordingly, more precise information will require a considerable number of experiments.

Dehydrohalogenation of the higher homologue $CF_3(CF_2)_2CH_2CHICH_2(CH_2)_2CH_3$ (**16**) at 50 °C in 92.6% ethanol gave the E isomer **17** and Z isomer **18** of structure $CF_3(CF_2)_2CH{=}CHCH_2(CH_2)_2CH_3$[4] in a ratio of **17**/**18** = 2.65. This is the same ratio as was previously found for reaction of **16** in 75% ethanol at 50 °C.[4] A third isomer (presumably $CF_3(CF_2)_2CH_2CH{=}CH(CH_2)_2CH_3$) (**19**) was now obtained in a 2% yield as well.

The E/Z ratios for reaction of **9** as given above were **7**/**8** = 4.1 in 92.6% ethanol and **12**/**13** = 5.1 in 76.1% ethanol. These E/Z ratios were both somewhat higher than those for **17**/**18** and are also greater than those reported for reaction of 2-iodohexane at 100 °C with methoxide in methanol (3.6)[12] or for reaction of 2-bromobutane and ethoxide ion in ethanol at 50 °C (3.21).[9] Probably more **7** than **8** was formed by isomerization of **6**.

The IR spectrum of the E isomer **7** showed CH= at ν 3050 cm^{-1} and CH=CH at 1680 cm^{-1} with a band at 965 cm^{-1} and many additional significant bands in the skeletal vibration region. These data confirm the previously observed[4] absorptions for the E isomer **17**. Z isomer **18** had CH=CH at ν 1660 cm^{-1}.[4] In the NMR of **7** the coupling constant for vinyl protons was found to be 16 Hz by means of decoupling and expansion of the spectrum. This value of J is consistent with an anti orientation of the two protons attached to the double bond.[13]

Rate Constants for Series II Compounds. Reaction rates for $CF_3(CF_2)_mCH_2CHI(CH_2)_nCH_3$ (n = 0–5) with NaOH in 92.6% ethanol at 30.0 °C are listed in Table V. Rate constants were calculated by the usual least-squares treatment of the data, obtained by titration of the iodide

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(9) Bartsch, R. A. *Acc. Chem. Res.* **1975**, *8*, 239–245.

(10) Brace, N. O. U.S. Patent 3 257 407, June 21, 1966 (to E.I. du Pont de Nemours and Co.). Reaction of $R_F(CH_2)_4I$ with pyridine gave $[R_F(CH_2)_4Pyr]^+I^-$ in quantitative yield.

(11) Brace, N. O. *J. Org. Chem.* **1962**, *27*, 4491–4498. Reaction of $R_F(CH_2)_6I$ with NaCN in alcohol solution gave $R_F(CH_2)_6CN$ in better than 90% yield.

(12) Bartsch, R. A.; Bunnett, J. F. *J. Am. Chem. Soc.* **1968**, *68*, 408–417.

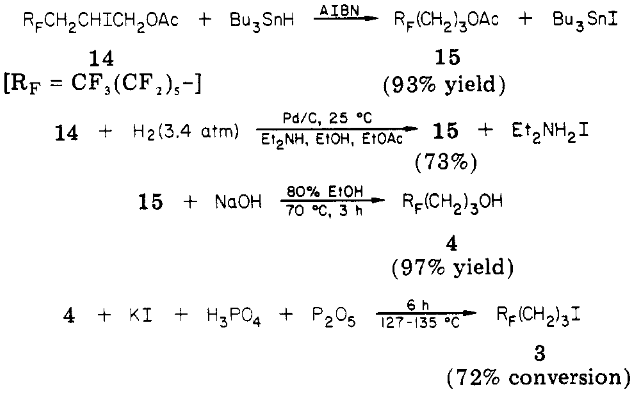
(13) Von Werner, K.; Wrackmeyer, B. *J. Fluorine Chem.* **1981**, *19*, 163–180.

Table V. Reaction Rates of Series II Homologues with NaOH in 92.6% Ethanol at 30.0 °C

$CF_3(CF_2)_mCH_2CHI-(CH_2)_nCH_3$					
m	n	concn, 10^3 M	NaOH, 10^2 M	rxn,[a] %	10^2 k,[b] L/mol s
6	0	3.691	2.385	95	5.84
2	3	6.017	1.296	82	3.81
2	3	5.317	1.296	90	4.10
3	3	5.501	2.480	76	3.38
3	3	4.952	2.480	77	3.54
3	3	6.247	2.476	74	3.54
3	3	4.636	1.189	65	3.70
3	4	4.523	2.476	70	3.10
3	4	6.024	2.519	72	3.40
3	4	4.681	2.480	74	3.31
3	4	5.705	2.490	72	2.92
6	5	1.409	0.2593	76	3.41

[a] Extent of reaction by I^- titration. [b] Least-squares analysis of data.

Scheme I. Synthesis of 3-(*F*-Hexyl)-1-iodopropane (3)



$$\underset{\mathbf{14}}{R_FCH_2CHICH_2OAc} + Bu_3SnH \xrightarrow{AIBN} \underset{\substack{\mathbf{15}\\(93\%\ \text{yield})}}{R_F(CH_2)_3OAc} + Bu_3SnI$$

$[R_F = CF_3(CF_2)_5-]$

$$\mathbf{14} + H_2(3.4\ \text{atm}) \xrightarrow[Et_2NH,\ EtOH,\ EtOAc]{Pd/C,\ 25\ °C} \underset{(73\%)}{\mathbf{15}} + Et_2NH_2I$$

$$\mathbf{15} + NaOH \xrightarrow[70\ °C,\ 3\ h]{80\%\ EtOH} \underset{\substack{\mathbf{4}\\(97\%\ \text{yield})}}{R_F(CH_2)_3OH}$$

$$\mathbf{4} + KI + H_3PO_4 + P_2O_5 \xrightarrow[127\text{-}135\ °C]{6\ h} \underset{\substack{\mathbf{3}\\(72\%\ \text{conversion})}}{R_F(CH_2)_3I}$$

ion. Rates of several of the homologues were determined by three different persons at different times. For $CF_3(CF_2)_3CH_2CHI(CH_2)_3CH_3$ (prepared by the free radical addition of $CF_3(CF_2)_3I$ to 1-hexene)[5] four values of the rate constant averaged $3.5 \pm 0.2 \times 10^{-2}$ L/mol s, which is a measure of the reproducibility of the method used. Straight line plots were obtained for all compounds out to 65–90% bimolecular reaction. The plot for $CF_3(CF_2)_2CH_2CHI(CH_2)_3CH_3$ is shown in Figure 1. The values of k ($3–4 \times 10^{-2}$ L/mol s) were about one-tenth of that for series I compounds (as indicated by the ordinates of Figure 1). $CF_3(CF_2)_6CH_2CHICH_3$ (**10**) reacted with NaOH a little faster than its higher homologues ($k = 5.84 \times 10^{-2}$ L/mol s), perhaps because of decreased steric hindrance in the preferred anti conformation.

Reaction of 2-Iodooctane with Sodium Hydroxide in 92.6% Ethanol. Hydrolysis of the model compound, 2-iodooctane, under standard conditions gave 2-octanol (3.9%), (*E*)-2-octene (61%), 1-octene (9.1%), and a 25.9% recovery of 2-iodooctane. (*Z*)-2-Octene and 2-ethoxyoctane were not detected in the GC. The identity of the octenes was shown by addition of known compounds to the GC. The rate constant for reaction of 2-iodooctane under these conditions was previously reported as 7.88×10^{-5} L/mol s.[7] This value is considerably smaller than any of the series II homologues listed in Table V.

Synthesis of $R_FCH_2CH_2CH_2I$. A practical method for preparation of the 3-(*F*-alkyl)-1-iodopropane family was found, as given in Scheme I. The alcohol $CF_3(CF_2)_5(CH_2)_3OH$ (**4**)[14] was converted to $CF_3(CF_2)_5(CH_2)_3I$ (**3**) by reaction with KI in anhydrous phosphoric acid.[15] The terminally fluorinated alcohol **4**, under the best conditions found, gave a 72% conversion to **3** along with unreacted **4**. Separation of the two substances was difficult and the best sample was 93.5% pure. Reaction conditions were first established using 1-heptanol or 1-octanol as starting compounds, and a 92% conversion was achieved.

Synthesis of 1-(*F*-Hexyl)-2-iodopropane (9), (*E*)-1-(*F*-Hexyl)-1-propene (7), and 3-(*F*-Hexyl)-1-propene (6). The same compound ($CF_3(CF_2)_5CH_2CHICH_2OAc$, **14**) used for the synthesis of **3** also gave **6** in 88% yield by reaction with zinc in oxydiethanol.[16] Dehydrohalogenation of **9** to (*E*)- and (*Z*)-1-(*F*-hexyl)-1-propenes was described above. Free-radical addition of 1-iodo-*F*-hexane to propene was conveniently done in the laboratory at atmospheric pressure by using a process discovered by Knell.[17] Benzoyl peroxide (BPO) rather than an azonitrile initiator[2] is required, however. Reaction at 100 °C gave 96% conversion to **9**. 4-(*F*-Hexyl)benzoic acid (mp 191 °C, 0.25% yield) and iodobenzene, about 90% yield on BPO, were also isolated.

Table VI. Kinetic Data of the Reaction between Fluoroalkyl Bromides and KI[a]

substance	relative k at 35 °C
$CH_3CH_2CH_2Br$	4.95
$CF_3CH_2CH_2Br$	1.00
$C_3F_7CH_2CH_2Br$	0.81
CF_3CH_2Br	0.00078
$C_3F_7CH_2Br$	0.000064

[a] Data were reported for reaction at 20, 35, 115, and 160 °C; E_a and ΔS^* (eu) were calculated as well. See ref 18.

Discussion

In compounds of series I, the inductive effect of the R_F group seems to express itself in two ways: (1) by loosening the C–H bonds of the CH_2 group adjacent to R_F; (2) by strengthening the C–I bond of the terminal CH_2I group. Evidence for these two behaviors is seen in the acceleration in rate of elimination of $R_FCH_2CH_2I$ over that of $R_F(CH_2)_3I$ ($k(R_FCH_2CH_2I)/(R_F(CH_2)_3I = 9.9 \times 10^3$) and the increase in rate of substitution along the series $R_FCH_2I < R_FCH_2CH_2I < R_F(CH_2)_3I < R_F(CH_2)_4I < R_F(CH_2)_8I$.

There was a striking contrast between elimination of 1-iodooctane and a series I homologue having a β-*F*-alkyl group. The rate of reaction was about 10^4 faster and the elimination/substitution ratio was greater than 4×10^3 for $R_FCH_2CH_2I$ over 1-iodooctane. This contrast diminished greatly when $R_FCH_2CH_2CH_2I$ (**3**) and 1-iodooctane were compared. Reaction rate was only about 10 times greater and the elimination/substitution product ratio just 1.4 times greater for the *F*-alkyl compound than for 1-iodooctane.

This great diminution of the inductive effect could not have been correctly or exactly predicted from previous studies. Rates of nucleophilic substitution by iodide ion in the fluoroalkyl bromide series R_FCH_2Br and $R_FCH_2CH_2Br$ are given in Table VI. Thus, the rate decreased by a factor of 1280 with $R_F = CF_3$ or by 12630 with $R_F = C_3F_7$, when the R_F group was placed one CH_2 group nearer the reaction center.[18] CF_3CH_2I reacted 1.7×10^4 times more slowly than CH_3CH_2I with sodium benzene-

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[14] Brace, N. O. *J. Fluorine Chem.* **1982**, *20*, 313–327.

[15] Stone, H.; Schechter, H. *J. Org. Chem.* **1950**, *15*, 491–494.

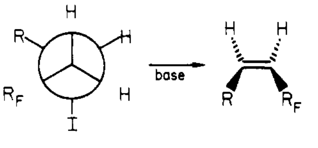
[16] Knell, M.; Brace, N. O. U.S. Patent 3843735, October 22, 1974 (to Ciba-Geigy Corp.).

[17] Knell, M. U.S. Patent 4058573, November 15, 1977 (to Ciba-Geigy Corp.). Dr. Knell kindly provided $C_7F_{15}CH_2CHICH_3$.

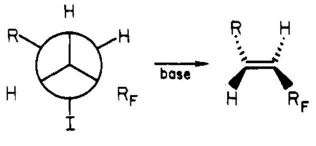
[18] McBee, E. T.; Battershell, R. D.; Braendlin, H. P. *J. Am. Chem. Soc.* **1962**, *84*, 3157–3160.

thiolate in methanol solution.[19] Reaction of CF_3CH_2I with $C_6H_5O^-$, in contrast to $C_6H_5S^-$, did not occur in DMF at room temperature. At 80 °C in 20 h, HF elimination and substitution both occurred.[3] In these reports the R_F group was only one or two carbon atoms removed from the reaction center, and extrapolation to a homologue having a three carbon or greater segment would have given an inaccurate result.

In dehydrohalogenation of series II compounds [R_FCH_2CHIR], the bulk of the R group had a small effect on the rate of reaction. The homologue with R = Me reacted about twice as fast as the homologues with larger R groups. All homologues reacted about one-tenth as fast as series I compounds that lack a branching group. No substitution products were observed from series II compounds. The decrease in rate of dehydrohalogenation, going from $R_FCH_2CH_2I$ to R_FCH_2CHIR would be consistent with the strong preference for anti elimination of series II compounds. The energy needed to bring the attacking base to within bonding distance in the intermediate complex would be greater with a gauche R group than with a hydrogen atom on the α carbon atom.



series I, R = H



series II, R = Me to heptyl

The preference for *E* over *Z* isomer in the products, $R_FCH{=}CHR$, is similarly explained; in the transition state leading to the *Z* isomer, the alkyl and *F*-alkyl groups are gauche or nearly eclipsed, depending on how complete product development has become. This would not be true for the intermediate leading to the *E* isomer. However, this restriction is not present in series I compounds, and a faster rate of reaction obtains in spite of the stronger C–I bond in the primary iodoalkane.

Mechanism of Elimination. Concerted E-2 mechanism for anti elimination of I^- from 1-iodo-2-(*F*-alkyl)cyclohexane conformers was strongly suggested by reaction rate order and the stereochemical results of previous studies.[6,20] By contrast, isomers in which the preferred geometry was not readily achieved (twist boat conformers or *trans*-1-iodo-2-(*F*-alkyl)cyclopentanes) gave syn elimination by a carbanion mechanism.[6] Reactions were first order each in base and in substrate. In a thorough study of strong base induced olefin formation from 2-hexyl halides, Bartsch and Bunnett concluded that the middle E2 transition-state mechanism adequately accounted for all the results.[12] This conclusion has been generally accepted for such simple substances up to now.[21,22] More recently, Keefe and Jencks have concluded, on the basis of extensive studies ranging over a large number of different structures, that a concerted E2 mechanism is followed even in the 2-(*p*-nitrophenyl)ethyl halide series, except possibly for the fluoride derivative.[23] It might have been expected that an E1cB mechanism would be found here. Elimination in the phenylethyl series has some analogy to dehydrohalogenation in series I compounds, in which stabilization of the carbanion at the β carbon atom could occur.[21] In the absence of further evidence (e.g., isotope effects), it is tentatively assumed that the mechanism of elimination of series I and II homologues is similar to that of the previously studied compounds.[6,7]

Conclusions

The inductive effect of an R_F group was manifest in the $R_F(CH_2)_nI$ series by an increase in rate of substitution by hydroxide ion with an increase in *n* from one to three and by a change in products of reaction from elimination when *n* was two to predominant substitution when *n* was three or higher. Rates and products of reaction were independent of the R_F group. Substantial isomerization of $R_FCH_2CH{=}CH_2$ to (*E*)-$R_FCH{=}CHCH_3$ occurred during reaction. Series II homologues, $R_FCH_2CHI(CH_2)_nCH_3$, gave mostly (*E*)-$R_FCH{=}CH(CH_2)_nCH_3$ at a rate decreasing from $n = 0$ to $n = 5$; $R_FCH_2CHICH_3$ gave both $R_FCH_2CH{=}CH_2$ and (*E*)- and (*Z*)-$R_FCH{=}CHCH_3$. These results were contrasted with those obtained from 1-iodooctane and 2-iodooctane: the former gave chiefly substitution products and the latter almost entirely elimination product by reaction with NaOH in 92.6% ethanol. Both unfluorinated compounds reacted at a rate substantially slower than their fluorinated analogues.

Experimental Section

Source of Materials and Methods. Substances of the type $CF_3(CF_2)_m(CH_2)_nI$ were obtained by free-radical addition of $CF_3(CF_2)_mI$ to ethene.[2] It should be noted that a convenient laboratory procedure has now been disclosed for the preparation of $CF_3(CF_2)_mCH_2CH_2I$ and of $CF_3(CF_2)_mCH_2CHICH_3$ (m = 5, 6, and 7) using ethene or propene, respectively, at atmospheric pressure.[17] Compounds of series II were similarly prepared by the addition of $CF_3(CF_2)_mI$ to the appropriate alkene.[2,4,5,24] Physical constants for substances of interest with literature references are listed in Table VII to facilitate their further study. Infrared spectra were obtained using a Perkin-Elmer grating spectrometer, IR-337; NMR spectra were taken using Varian T-60 or HA-100 spectrometers. Gas chromatography (GC) was done using either a Sargent-Welch thermal conductivity instrument, temperature-programmed as described below, or a similar Gow-Mac instrument, operated at different temperatures as required. Potentiometric titration of iodide ion in aqueous solution was done by using the method described previously that employed a bright silver electrode (Beckman 39261), 3 N KNO_3 salt bridge, and a calomel reference electrode.[6,7] Least-squares analysis of the data by machine program gave the slope of the plot of $\log_{10}$ [NaOH]/[compd] vs. time and an estimate of error. For example, for $CF_3(CF_2)_5CH_2CH_2I$ (Figure 1) the slope was 1.27×10^{-3}/min with $\sigma = 0.02 \times 10^{-3}$, $k = 1.36 \times 10^{-1} \pm 0.02 \times 10^{-1}$. An estimate of *total* error in weighing and other measurements was less than 1–2%.

Standard Mixtures for GC Analysis. Samples were run on three columns as required for separation of compounds: Silicone oil (SE 30), a 6-ft by $^1/_4$-in. column packed with 10% of SE 30 silicone oil on 60–80 mesh Chromosorb WA, treated with "DMAC", at 70–150 °C (after 5 min), and 24 mL/min helium flow; Silicone oil (QF-1), an 8-ft by $^1/_4$-in. column, otherwise the same as above; Silicone oil (W-98), a 5-ft by $^1/_4$-in. column, 10% on Chromosorb WA, 100–150 °C (after 5 min), and 30 mL/min helium flow. **Mixture 1** (QF-1): **2**, retention time 4.1 min, response factor 0.4305; toluene, retention time 6.4 min, 1.000; $CF_3(CF_2)_5CH_2CH_2OH$, retention time 10.3 min, 0.4794; **1**, retention time 11.2,

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(19) Hine, J.; Ghirardelli, R. G. *J. Org. Chem.* **1958**, *23*, 1550–1552.

(20) Brace, N. O. *J. Org. Chem.* **1962**, *27*, 4491–4498.

(21) Saunders, Jr., W. H. *Acc. Chem. Res.* **1976**, *9*, 19–25.

(22) Lowry, T. H.; Richardson, K. S. "Mechanism and Theory in Organic Chemistry", 2nd ed.; Harper and Row: New York, 1981; p 530 et seq.

(23) (a) Keefe, J. R.; Jencks, W. P. *J. Am. Chem. Soc.* **1983**, *105*, 265–279. (b) **Note added in proof**: Gandler and Yokoyama [Gandler, J. R.; Yokoyama, T. *J. Am. Chem. Soc.* **1984**, *106*, 130–135] found that *all* the 2-(2,4-dinitrophenyl)ethyl halides (F, Cl, Br, I) gave E-2 elimination in water, in CF_3CH_2OH, in $(CF_3)_2CHOH$ or in ethanol. Kinetics, lack of deuterium exchange, and product analysis were used to support this conclusion.

(24) Brace, N. O. *J. Org. Chem.* **1963**, *28*, 3093–3102.

(25) Day, R. I. U.S. Patent 3 283 012, November 1, 1966 (to E.I. du Pont de Nemours and Co.).

(26) Foulletier, L.; Lalu, J.-P. Fr. Patent 1 532 284, July 4, 1968 (to Ugine Kuhlmann Co.); *Chem. Abstr.* **1969**, *71*, 101289.

Table VII. Sources and Properties of Starting Materials and Other Compounds

substance	bp, °C (mmHg)	n^{25}_D (mp, °C)	source	ref
$CF_3(CF_2)_3I$	67	1.3252	*a*	20
$CF_3(CF_2)_5I$	66 (300)	1.3268	*a*	20
$CF_3(CF_2)_6I$	70 (70)	1.3270	*b*	20
$CF_3(CF_2)_5CH_2CHICH_3$ (**9**)	69 (11)	1.3705	*c*	17
$CF_3(CF_2)_6CH_2CHICH_3$ (**10**)	120 (13)	1.3630	*a*	17
$CF_3(CF_2)_5CH_2CHICH_2OAc$ (**14**)	62 (0.05)	1.3822	*c*	14
$CF_3(CF_2)_5CH_2CH_2CH_2OAc$ (**15**)	93 (11)	1.3320	*c*	14
$CF_3(CF_2)_3CH_2CH_2I$	140		*a*	2, 25
$CF_3(CF_2)_5CH_2CH_2I$ (**1**)	180 107–110 (100)	1.3590	*a*	2, 25
$CF_3(CF_2)_6CH_2CH_2I$	89 (23)	(40–45)	*c*	2, 25
$CF_3(CF_2)_6(CH_2)_4I$	108 (8)	(35–45)	*d*	2
$CF_3(CF_2)_6(CH_2)_6I$	136 (8)	(36–39)	*d*	2
$CF_3(CF_2)_6(CH_2)_8I$	104 (0.45)		*d*	2
$CF_3(CF_2)_2CH_2CHI(CH_2)_3CH_3$ (**16**)	82 (20)	1.4029	*c*	2, 4
$CF_3(CF_2)_3CH_2CHI(CH_2)_3CH_3$	81 (10)	1.3942	*c*	2, 5
$CF_3(CF_2)_3CH_2CHI(CH_2)_4CH_3$	95 (10)	1.3982	*c*	2
$CF_3(CF_2)_6CH_2CHI(CH_2)_5CH_3$	85 (0.02)		*e*	2
$CF_3(CF_2)_5CH_2CH{=}CH_2$ (**6**)	60 (70)	1.3051	*c*	16
$CF_3(CF_2)_6CH_2CH{=}CH_2$ (**11**)	142	1.3090	*c*	16, 28
$CF_3(CF_2)_5CH{=}CH_2$	56 (160)	*f*	*c*	26
$CF_3(CF_2)_5CH_2CH_2OH$	93 (35)	1.3161	*c*	25

[a] Ciba-Geigy Corp., Ardsley, NY, courtesy of Dr. E. K. Kleiner. [b] Columbia Organic Chemicals Co. [c] This work. [d] E.I. du Pont de Nemours and Co., Wilmington, DE. [e] Sample from Dr. M. Knell, Ciba-Geigy Corp. [f] n^{25}_D below 1.300.

0.3832. **Mixture 2** (SE 30): **6**, retention time 4.5 min, 0.4160: *n*-octane, retention time 8.3 min, 1.000; **4**, retention time 10.5 min, 0.4023; **3**, retention time 14.0 min, 0.3401. **Mixture 3** (QF-1): **6** (2.7%), retention time 3.6 min, and **7** (96.6%), retention time 4.3 min, 0.4778; toluene, retention time 7.6 min, 1.000; **4**, retention time 10.4 min, 0.4676; **9**, retention time 10.8 min, 0.4126. **Mixture 4** (QF-1): toluene, retention time 3.1 min, 1.000; **1**, retention time 7.5 min, 0.3472; 1-octanol, retention time 9.6 min, 0.9552; 1-iodooctane, retention time 12.0 min, 0.6246. **Mixture 5** (W-98): 1-octene, retention time 3.5 min, 1.167; cyclooctane, retention time 6.7 min, 1.000; 2-octanol, retention time 8.1 min, 1.055; 2-iodooctane, retention time 12.5 min, 0.7480. **Mixture 6** (SE 30): 1-octene, retention time 10.5 min, 0.7587; (*E*)-2-octene, retention time 11.6 min, 0.8103; cyclooctane, retention time 17.0 min, 1.000.

Reaction of 1 with Sodium Hydroxide in Aqueous Alcohol. **1** (1.896 g, 4.00 mmol) was added to NaOH (0.64g, 16.0 mmol) dissolved in 25 mL of 92.6% ethanol (a 0.16 M solution) and stirred in a sealed tube at 30.0 °C for 2.5 h. GC analysis of a sample gave **2** as the only detectable substance. After 6.5 h at 30.0 °C the remaining solution was added to 100 mL of 0.03 M HCl; the product layer (0.6163 g) was 99% of **2**. The aqueous layer was extracted with CCl_4 (1.00 mL, twice); GC showed a total of 78% of **2** and 0.18% of 2-(*F*-hexyl)-1-ethanol. This substance was added to the aqueous layer and extracted with CCl_4 (1 mL). GC showed that 82.4% and 86% of the alcohol was recovered (toluene, internal reference).

1 (1.9118 g, 4.033 mmol) and NaOH (0.32 g, 8.0 mmol) in 12.5 mL of 92.6% ethanol (a 0.36 M solution) was stirred at 30 °C for 1 h. The product mixture was added to dilute HCl (27 mL, 0.4 M) and chilled to 10 °C for 1 h; the **2** layer weighed 1.2007 g, 86.0% of theory; GC, 100% purity. Extraction with CCl_4 (1.00 mL, 3 times) gave a total of 95.1% of theory of **2** (GC analysis, toluene reference).

Reaction of **1** with NaOH at 50 °C for 4 h in 76.1% ethanol (0.21 M in iodoalkane and 1.0 M in NaOH) gave 99.9% conversion to **2**.

Reaction of 1 with Sodium Methoxide in Methanol. **1** (20.33 g, 42.2 mmol) was added to a solution of sodium methoxide (4.76 g, 88.0 mmol) in anhydrous methanol (55 mL) at 50 °C, under nitrogen, while stirring. After 110 min a sample was added to dilute acid and the oil layer was dried. GC indicated 98.9% of **2** and unknown substances of 0.81% and 0.23%. These substances were probably derived from impurities known to be present in the starting material.

3-(*F*-Hexyl)-1-methoxypropane (5). **3** (2.1720 g, 4.166 mmol, containing 0.3066 mmol of **4**) and sodium methoxide (0.5400 g, 10.00 mmol) in anhydrous methanol (12.50 mL) were stirred by a magnet bar in a sealed tube at 30.0 °C for 24 h, poured into 0.4 M HCl (27 mL), and chilled for 1 h at 10 °C. A layer weighing 1.638 g separated; the aqueous layer was extracted with dichloromethane (2.0 mL, twice). GC (toluene reference, QF-1) indicated **6**, retention time 4.9 min, 11.7% of theory, **5**, 9.5 min, 59.4%, **4**, 10.8 min, 59.6% recovery, and **3**, 14.0 min, 23.0% recovery. No **7** was found.

3 (2.00 g, 3.835 mmol, as above) was added to sodium methoxide (0.4 g, 8.8 mmol) in 5.5 mL of methanol at 30 °C and stirred at 50 °C for 16.7 h. The solution, added to 0.46 M HCl (13 mL), gave a product mixture (1.2428 g). GC (QF-1): **5**, 87.3%; **6**, 4.0%; **7** (and **8**), 4.5%; **4**, 4.3%. Distillation in a microstill at 10 mm gave I, (bath temp, 65–72 °C), 0.65 g, and II, (bath temp 75 °C), 0.54 g. I contained **6**, 3.9%, **5**, 95.1%, and unreacted **3**, 0.85%. II contained **6**, 1.15%, **5**, 93.9%, **3**, 1.1%, and **4**, 3.65%. Extraction of the aqueous layer (diethyl ether 3 mL, 3 times) gave residual oil, 0.40 g, containing 63.4% of **5**. The total recovery was thus 93% of theory for **5**, and that of **6** and **7** (and **8**) was 7% of theory.

NMR (100 MHz, $CDCl_3$) (fraction I): δ 1.51–2.71 (4 H, broad complex multiplet of $R_F\mathit{CH_2CH_2}OMe$), 3.42 (3 H, s, OCH_3), 3.52 (2 H, t (partially obscured), $R_FCH_2CH_2\mathit{CH_2}OMe$). Vinyl proton resonances were below the detectable limit of the instrument. Anal. Calcd for $C_{10}H_9F_{13}O$: C, 30.6; H, 2.3; F, 63.0. Found: C, 30.4; H, 2.3; F, 62.8.

Reaction of 3 with Sodium Hydroxide in Ethanol at 30 °C. **3** (2.0120 g, 3.859 mmol, containing 0.283 mmol of **4**) and 1.1% of **15** were added to NaOH (0.82g, 20.5 mmol) in ethanol (25 mL, 92.6%) while stirring at 30.0 °C. The mixture was sealed in a glass tube, stirred for 30 h at 30 °C, poured into 0.23 M HCl (52 mL), and gave **4** (1.1629 g, 77% yield). The aqueous layer was extracted with dichloromethane (2.5 mL, twice). Toluene (internal reference) was added. GC (combined amounts): **6**, 4.3 min, 19.2% of theory; **7** (and **8**), 4.6 min, 3.25%; **4**, 10.4 min, 81.6% (not including the original amount). No **3** remained.

Reaction of 3 at 50 °C in Aqueous Ethanol with Potassium Hydroxide. **3** (2.00 g, 3.85 mmol, as above) in ethanol (7.89 g, 10 mL) was added to KOH (6.4 g, 10 mmol) dissolved in water (6 mL, the solution was thus 57% by weight of ethanol), stirred at 50 °C for 24 h, and worked up as above. The product weighed 1.18 g. GC (SE30, combined amounts): **6** (with a shoulder of **7**) 26.0%; **4**, 50.2%; unreacted **3**, 15.1%; unknown, 1.1%.

(*F*-Heptyl)propene Isomers from Reaction of 1-(*F*-Heptyl)-2-iodopropane (10) with Base. **10** (10.76 g, 20.00 mmol) was added to KOH (2.24 g, 40.0 mmol) in ethanol (50 mL, 76.1%), stirred at 50 °C for 24 h, poured into 1 M HCl (60 mL), and gave **11** and (*E*)- and (*Z*)-1-(*F*-heptyl)-1-propene (**12** and **13**), 7.04 g (85.8% of theory). GC, QF-1, 50 °C, 5 min, to 120 °C, 22 mL/min helium flow: **11**, retention time 6.3 min, 1.21%; **13**, 8.0 min, 16.1%; **12**, 8.8 min, 81.8%; **10**, 11.5 min, 0.87%. **11** increased the area of the 6.3 min peak only. The aqueous layer was extracted with CCl_4, (5 mL, twice) and was distilled in a 16-in. spinning band column to yield **12** and **13** (a small amount **11**), bp 61–64 °C (30 mm), $n^{25}{}_D$ 1.3110, 6.57 g (GC, 98.6% purity), and a residue, 0.19 g. IR (cm^{-1}) CH= 3050, CH 2990, 2970, 2930, 2870, C=C 1680, CH 1450, 1380, 1360, 1350, CF 1300–1120. Bands at 984 and 964 are not present in **11**; bands at 1030, 1018, 890, 840, 750–700, 665, 645, 570, and 530 cm^{-1} were also obtained. NMR (100 MHz, $CDCl_3$) δ 1.90 (complex multiplet, 3 H, CH_3), 5.62 and 6.42 (complex multiplet, 2 H, CH=CH, $J_{H1,H2}$ = 16 Hz). Decoupling and expansion of the spectrum showed a signal at δ 6.42 was due to the proton adjacent to the *F*-heptyl group, and that H_1 and H_2 were chiefly trans.[27]

(*E*)- and (*Z*)-1-(*F*-Hexyl)-1-propene (7 and 8). **9** (2.57 g, 5.18 mmol, containing impurities of 0.67 and 1.04%) and NaOH (0.42 g, 10 mmol), dissolved in ethanol (12.5 mL, 92.6%) were stirred (sealed tube) at 50 °C for 24 h, poured into 0.8 M HCl (14.5 mL), and yielded product, 1.5854 g (83.6% of theory). GC, QF-1, 70 °C, 8 min to 180 °C, at 10 °C/min, 25 mL/min helium flow rate (no other conditions or columns would separate this mixture): **6**, 5.2 min, 2.6%; *Z* isomer of **8**, 6.2 min, 18.9%; *E* isomer of **7**, 7.0 min, 77.2%; **9**, 11.0 min, 0.71%. **6** added to the sample increased the area of the peak at 5.2 min only. The aqueous layer extracted with dichloromethane (1.0 mL, twice) and chilled to 10 °C gave a product (1.373 g). GC: dichloromethane, 94.0%; **6**, **7**, and **8**, 6.0%; **9**, 0.3%. Anal. Calcd for $C_9H_5F_{13}$: C, 30.0; H, 1.4; F, 68.6. Found: C, 2.96; H, 1.3; F, 68.1.

3-(*F*-Hexyl)-1-propene (6). Zinc dust (Baker's, 60–80 mesh, 10.47 g, 150 mmol) and 2,2′-oxydiethanol (20 mL) were stirred by a magnet bar in a 100-mL flask, fitted with a dropping funnel having a needle valve and a total reflux, partial take-off head, and heated in an oil bath kept at a constant temperature. At a pressure of 113 mmHg, **14** (44.0 g, 80.0 mmol, 24 mL) was added during 0.5 h at 126 °C, and **6** distilled, bp 80–85 °C (113 mm). Additional product distilled during 1 h at 35 mm (136 °C bath temp): total 25.35 g, 88.0% yield. GC (8-ft QF-1): impurities at 2.2 min (0.96%) and 5.3 min (0.21%). IR CH= 3100 and 3040 cm^{-1}, C=C 1650, deformation bands at 992, 935, and 890, impurities gave C=O at 1730 and 1750 cm^{-1}. Redistillation (16-in. spinning band column): I, bp 45–54 °C (70 mm), 0.88 g; II, bp 54–59 °C (70 mm), 0.32 g; III, bp 59 °C (70 mm), $n^{25}{}_D$ 1.3051, 11.38 g; IV, bp 60 °C (70 mm), $n^{25}{}_D$ 1.3051, 9.58 g; holdup in column, 0.63 g. GC: III, impurity at 1.8 min, 2.12%; **6**, 97.9%; **IV**, **6**, 100%. Total yield was 72.7% of **6**. NMR (100 MHz, $CDCl_3$) δ 2.85, doublet of triplet, 2 H, CF_2CH_2CH=), 5.1 and 6.3 (2 multiplets, 3 H, CH=CH_2). Anal. Calcd for $C_9H_5F_{13}$: C, 30.0; H, 1.4; F, 68.6. Found: C, 30.3; H, 1.3; F, 68.0.

Reaction of 1-Iodooctane with NaOH in 92.6% Ethanol at 30.0 °C. 1-Iodooctane (2.4073 g, 10.02 mmol, 99% pure) was added while stirring to a solution of NaOH (0.8205 g, 20.92 mmol) in 92.6% ethanol (25 mL) that had been made up as follows: water (0.75 mL, 41.6 mmol) was added to NaOH and then diluted by gradual addition of ethanol (95%). The cloudy reaction mixture was stirred in a sealed glass tube at 30.0 °C for 24 h, poured into water (50 mL) and 6 M HCl (2 mL), chilled to 10 °C, and extracted with dichloromethane (2.5 mL, twice). The solvent was evaporated at 25 °C in part. An aliquot (0.3464 g from 2.8785 g) and cyclooctane (reference liquid, 0.1540 g) gave molar amounts by GC as follows (SE 30): unknown (an artifact not from reaction), 9.3 min, 8.4%; 1-octene, 11.0 min, 7.3%; cyclooctane, 17.2 min; unknown, 22.2 min, 1.5%; 1-octanol, 23.3 min, 56.4%; 1-iodooctane, 27.2 min, 27.8%. 1-Octene added to the sample increased the 11.0 min peak, but (*E*)-2-octene gave a peak at 13.0 *min not in* the sample. *n*-Octane was not present in the original 1-iodooctane nor did it coincide with the unknown substance at 9.3 min.

Reaction of 2-Iodooctane with NaOH in 92.6% Ethanol at 30.0 °C. 2-Iodooctane (2.3989 g, 9.991 mmol) and NaOH (0.8369 g, 20.92 mmol) as for 1-iodooctane above gave molar amounts (% of theory) by GC (cyclooctane reference, SE 30): 1-octene, 11.8 min, 9.1%; (*E*)-2-octene, 13.0 min, 61%; unknown, 19.1 min, 0.25%; 2-octanol, 20.2 min, 3.9%; 2-iodooctane, 22.8 min, 25.9%. Again, addition of 1-octene and (separately) (*E*)-2-octene to the sample increased their respective peaks. Similar results were obtained on the "W-98" and "QF-1" silicone oil columns.

1-(*F*-Propyl)-2-iodohexane (16). **16** (1.00 g, 2.63 mmol) and NaOH (0.32 g, 8.0 mmol) in ethanol (92.6%, 10 mL) were stirred by a magnet bar at 50.0 °C in a tightly capped tube for 18 h. Workup as above gave (GC, QF-1, relative areas) the following: a new isomer, **19**, retention time 10.5 min, 1.95%; (*Z*)-1-(*F*-propyl)-1-hexene (**18**, 27.0%, avg of 2), 11.5 min; (*E*)-1-(*F*-propyl)-1-hexene (**17**, 72.0%) 12.3 min; unreacted **16**, 0.17%, 21.5 min. Samples of the previously prepared **17** and **18** product mixture[4] were injected under the same conditions and gave the same retention times; the relative areas also were unchanged.

1-Iodooctane and Sodium Methoxide. 1-Iodooctane (2.3935 g, 9.968 mmol) and NaOMe (1.0132 g, 18.76 mmol), a slurry in anhydrous methanol (12.5 mL, 1.50 M in NaOMe), were stirred by a magnet bar in a sealed tube for 24 h at 30.0 °C. The white slurry was worked up as above and gave (GC, W-98, cyclooctane reference) the following: 1-octene, 10.3 min, 6.1%; 1-methoxyoctane, 15.9 min, 69.7%; unreacted 1-iodooctane, 19.6 min, 24.2%. Analysis on a 4-ft × $^{1}/_{8}$-in. OV-101 Silicone oil column gave 1-octene, 6.2%, two unknowns, ca. 0.2%, 1-methoxyoctane, 69.1%, and 1-iodooctane, 24.0%. Heating of half of the mixture with NaOMe (0.50 g, 9.2 mmol) and 5.0 mL of MeOH for 21 h at 60 °C gave complete reaction of the remaining 1-iodooctane. GC: 1-octene, 4.9%; 1-methoxyoctane, 94.8%; spiking with 1-iodooctane gave a new peak. IR 1115 and 950 cm^{-1} CH_3O (ν_{as} and ν_s), bands not in 1-iodooctane. NMR (60 MHz, CCl_4) 0.98 (3 H, m, CH_3), 1.15 (12 H, m, $(CH_2)_6$), 3.21 (5 H, distorted s, CH_3OCH_2). Anal. Calcd for $C_9H_{20}O$: C, 75.0; H, 13.9. Found: C, 75.0; H, 13.3.

3-(*F*-Hexyl)-1-propanol (4). **14** (undistilled, 25.31 g, 46.3 mmol, 92.1% pure by GC) was converted to **15** by catalytic dehalogenation using a diethylamine acid acceptor as described previously.[14] GC showed only one peak for **15**. A solution of KOH (7.84 g, 139 mmol) dissolved in 20 mL of water and 80 mL of ethanol was added to the oil residue that remained after the solvent had been stripped off. The mixture was stirred for 3 h at 69–70 °C, the solvent was stripped off, water (50 mL) was added, and the oil was extracted into diethyl ether (3 times, 25 mL). Distillation gave **4**: bp 86–88 °C (12 mm); $n^{25}{}_D$ 1.3250; 11.76 g (GC, one peak); 67.1% overall yield. When distilled **15** was used, the yield of product was 92.6% of theory.

3-(*F*-Hexyl)-1-iodopropane (3). **4** (28.70 g, 75.9 mmol) and KI (26.25 g, 158 mmol) were added while stirring to a solution of phosphoric acid (23.09 g, 200 mmol, 85%) and phosphoric anhydride (4.58 g, 32.3 mmol) that had been cooled in an ice bath. The mixture became dark in color as it was heated to 127–135 °C during 6 h. Material sublimed to the upper sides of the flask and was occasionally scraped down. After cooling in an ice bath, diethyl ether (10 mL) and water (15 mL) were added, and the aqueous layer was shaken with ether (15 mL) and benzene (50 mL). The organic layer was washed with sodium bisulfite and saturated NaCl solutions to remove iodine. Distillation (16-in. spinning band column operated at a high reflux ratio) gave the following: fractions I–III, bp 80–82 °C (12 mm), $n^{25}{}_D$ 1.3510–1.3540, 0.91 g, 4.97 g, and 8.89 g, contained **4** (about 30%) and **3** (about 60%); fraction IV, bp 82–84°/12 mm, $n^{25}{}_D$ 1.3639, 17.80 g, contained 93.5% of **3**, 5.34% of **4**, and 1.1% of **15** (GC, SE 30). This was a 71.9% conversion to **3** and a yield of 88.2% based on recovered material. NMR (100 MHz, $CDCl_3$) δ 2.20 (complex multiplet, 4 H, $R_FCH_2CH_2$), 3.25 (t, 2 H, CH_2I). Anal. Calcd for $C_9H_6F_{13}I$: C, 22.1; H, 1.24; F, 50.6; I, 26.0. Found: C, 19.8; H, 1.15; F, 52.1; I, 23.8.

A subsequent experiment gave material, bp 76 °C (9.0 mm), that contained 95.9% of **3** and 4.05% of **4**. Prior to these experiments the method was used to prepare 1-iodoheptane or 1-iodooctane as follows. 1-Octanol (22.41 g, 172 mmol) and KI (57.16 g, 344 mmol) were added to phosphoric acid (50.24 g, 436 mmol) and P_2O_5 (9.90 g, 70 mmol) and heated at 135–145 °C for 5.5 h. Workup and distillation gave 1-iodooctane, bp 119/12 mm, 34.15 g, containing by GC 8.0% of 1-octanol and 92% of 1-iodooctane.

1-(*F*-Hexyl)-2-iodopropane (9). 1-Iodo-*F*-hexane (93.58 g, 209.8 mmol) [containing 4.04 g (11.7 mmol) of 1-iodo-*F*-butane,

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[27] We thank Dr. Ronald Rodebaugh for ^{13}C NMR spectra and Dr. Robert Grulich for ^{19}F NMR spectra.

(28) Anello, L. G.; Sweeney, R. F. U.S. Patent 3 576 885, April 27, 1971 (to Allied Chemical Corp.).

ca. 2.5% of 1-iodo-*F*-octane, and 1-iodo-*F*-decane] and benzoyl peroxide (1.0155 g, 4.198 mmol) were charged in a reactor tube[29] with a sintered disk gas inlet at the bottom and a sampling port on the side, attached to a dry ice cooled trap, and immersed in an oil bath at 100 °C. Propene (Matheson, C. P., from a cylinder) was bubbled through the oil at a rate of 10–20 bubbles/s; the rate of addition was adjusted to maintain a small excess of propene. After 40 and 86 min, respectively, GC (SE 30) showed that 50.3% and 73.7% conversion to **9** had occurred. After 2 h, 1-iodo-*F*-hexane (2.12%, retention time 3.5 min) and **9** (89.4%, 10.5 min) were present. After 1.5 h of additional time, the trap contained about 5 mL of propene; the reaction mixture was cooled and filtered from white, solid 4-(*F*-hexyl)benzoic acid, 0.23 g, mp 191°, and recrystallized from benzene, 0.25% conversion. NMR (acetone-d_6, 60 MHz) δ 7.87 and 8.30 (AA′BB′ pattern of p-substituted benzene), 5.10 (1 H, broad, exchangeable COOH). Anal. Calcd for $C_{13}H_5F_{13}O_2$: C, 35.5; H, 1.15; F, 56.1. Found: C, 35.0; H, 1.1; F, 57.6. The liquid filtrate (107.0 g) (GC indicated 2.63% of $C_6F_{13}H$, 0.78% of 1-iodo-*F*-hexane, 1.75% of 1-(*F*-butyl)-2-iodopropane, 91.8% of **9**, and 2.38% of iodobenzene; retention time 12.5 min) was fractionated using a 16-in. spinning band column operated at high reflux ratio. Fractions I and II, bp 70–74 °C (19 mm), 14.0 g, contained 75% and 89% of **9** and several side products listed above; fractions III–VI, bp 74–76 °C (19.5 mm), n^{25}_{D} 1.3670, 83.5%, contained 99.4% **9** and 0.6% iodobenzene. ^{13}C NMR (200 MHz) 94.277 ppm (the same spectrum as iodobenzene). A residue of soft, gummy solid (3.25 g) and trap liquid (5.34 g) were also recovered. The total conversion to **9** (GC) was 98.2 g or 96.3% of theory; 92.1% of **9** was recovered by distillation. NMR (100 MHz and 200 MHz, $CDCl_3$)[27] δ 2.04 (3 H, d, J = 7 and 1.25 Hz, long range coupling, CH_3), 2.47–3.21 (2 H, broad coupling, multiplet, CH_2), 4.45 (complex multiplet, 1 H, CHI). ^{13}C NMR (200 MHz) CH_3, 10.705 (q), CH, 29.269 and 29.218 (d, long range coupling to F), CH_2, 43.316 (t, splitting by CF_2). Anal. Calcd for $C_9H_6F_{13}I$: C, 22.1; H, 1.24; F, 50.6; I, 26.0. Found: C, 21.8; H, 1.3; F, 50.4; I, 25.8.

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[29] Kharasch, M. S.; Friedlander, H. N. *J. Org. Chem.* **1969**, *14*, 239–247.

Photochemical Transformations. 37. Electron-Transfer Requirements for Photosolvolysis and Photo-Wagner–Meerwein Reactions of Some Dichlorodibenzobicyclo[2.2.2]octadienes in Singlet and Triplet Excited States[1]

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Substituted *trans*-7,8-dichloro-10-X-2,3:5,6-dibenzobicyclo[2.2.2]octa-2,5-dienes (X = $COCH_3$, CN, and NO_2) and corresponding dinitro-substituted compounds (10,15-dinitro and 10,14-dinitro) were solvolyzed with silver acetate in acetic acid and were irradiated in glacial acetic acid or acetonitrile with 254- and 300-nm light. The structures of the monoring-substituted diastereoisomeric dichlorides were demonstrated by proof of structures of the daughter solvolysis products. Unlike compounds previously studied, these compounds were either photochemically inert or photoinactive with respect to Wagner–Meerwein rearrangement or to solvolysis. These results have been rationalized in terms of the inability of the excited states of the light-absorbing chromophores in these compounds to transfer electrons to the carbon–chlorine bonds remote from these chromophores. While triplet states of a variety of *cis*- and *trans*-7,8-dichloro-2,3:5,6-dibenzobicyclo[2.2.2]octa-2,5-dienes are reported to be similarly inert, the 10,11-dimethoxy derivatives all were photoactive with acetone sensitization. The migration stereochemistries of the sensitized reactions were quite different from those of direct irradiations or of ground-state reactions. Estimations of the free energies of electron transfer were consistent with these and previously reported results.

Reports concerning the photosolvolyses of organic compounds have been numerous.[2] With only a few exceptions, these reports deal with compounds possessing at least two chromophores, one being the carbon–nucleofuge bond and the other often an aromatic ring or a carbonyl group. In general, the second chromophore absorbs the light, which is usually in a region of the spectrum where the carbon–nucleofuge bond does not absorb or has a relatively low extinction coefficient. After the initial excitation process, some or all of the excitation is transferred to the carbon–nucleofuge bond, which ultimately cleaves to form a carbocation and an anion (when the substrate is an uncharged species). The mechanism of this excitation transfer from

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[1] Paper 36. Cristol, S. J.; Ali, M. Z. *Tetrahedron Lett.*, in press.

[2] For a review, see: Cristol, S. J.; Bindel, T. H. In "Organic Photochemistry"; Padwa, A., Ed.; Marcel Dekker: New York, 1983; Vol. 6, pp 327–415.