sulfonate, the glass tube was tightly stoppered with a glass stopper and the lower portion of the reaction tube was immersed in a temperature bath. After the desired time period, the reaction mixture was poured into water. A weighed amount of cyclohexene (internal standard) was added and the mixture was extracted with pentane. As before, the pentane solution was kept in a freezer until analysis.

Gas Chromatographic Analysis of Hydrocarbon Products. The pentane solutions were analyzed on a $^1/_8$ in. × 10 ft column of 20% SE-30 on Chromosorb P operated at 70–80 °C, which gave satisfactory separation of cyclohexene (internal standard), bicyclo[2.2.1]hept-2-ene (**6**), and nortricyclene (**7**). Relative peak areas were determined by integration and were corrected for molar response, if necessary. The molar responses of cyclohexene to **6** and **7** were both 0.973. Relative peak areas from 2–5 chromatograms were averaged.

Deuterium Analysis. The pentane solutions of hydrocarbon products were injected onto a $^1/_8$ in. × 10 ft column of 20% SE-30 on Chromosorb P operated at an appropriate temperature and the bicyclo[2.2.1]hept-2-ene peak was introduced into the mass spectrometer to determine the deuterium content of the bicyclo[2.2.1]hept-2-ene obtained in elimination from the deuterated bromide **10** and arenesulfonate **11**. Relative intensities of the M^+ and $(M + 1)^+$ peaks from 10–40 mass spectra were averaged as a data set. Several (2–5) data sets were averaged in the determination of deuterium content for which it was assumed that relative intensities of M^+ and $(M + 1)^+$ peaks are the same for bicyclo[2.2.1]hept-2-ene and 2-deuterobicyclo[2.2.1]hept-2-ene.

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The Effect of Conjugation on Hydrogen Iodide and Hydrogen Fluoride Elimination from 1-(*F*-Alkyl)-2-iodoalkenes: From 5-(*F*-Butyl)-4-iodo-1-pentene to 5-(*F*-Butyl)pentadienes and Further to 1-Fluoro-1-(*F*-propyl)-1,3,5-hexatrienes[1]

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Dehydrohalogenation of homologous 1-(*F*-butyl)-2-iodoalkenes, $[R_FCH_2CHI(CH_2)_nCH{=}CH_2$ (n = 2–4)] under defined conditions gave (*F*-butyl)-substituted alkadienes $[R_FCH{=}CH(CH_2)_nCH{=}CH_2]$ in high yield. By contrast, $R_FCH_2CHICH_2CH{=}CH_2$ (**1**) gave *E,Z* isomers of 1-fluoro-1-(*F*-propyl)-1,3,5-hexatriene (**3**) in 95% yield by way of isomeric 5-(*F*-butyl)pentadienes (**2** and **4**). Trapping and identification of organic products by GC/MS and FT/IR gave rate of conversion of **1** to intermediate dienes **2** and **4** and of dienes to triene isomers **3**. Samples were separately titrated for HI and HF. Kinetic order of reactions and rates by these independent methods were concordant. IR, UV, and mass spectra were useful in identifying separated GC peaks, and NMR spectra of isolated triene **3** confirmed its structure. Conjugated diene 3*E*-**2** was the major intermediate on the path from **1** to **3**; rate of disappearance of **2** and formation of **3** were almost identical. Surprisingly, elimination of HF from **2**, and its unconjugated isomer 4*E*-**4**, occurred at similar rates. Elimination from 4*E*-**4** may have involved a *concerted* loss of proton and fluoride ion, with a shift of the double bond to give the all-conjugated triene **3**. Novel stereochemistry in these elimination reactions, mass spectrum fragmentation patterns, and other spectroscopic results are reported.

Introduction

Chemistry of perfluoroalkyl-substituted compounds is not well-known and frequently cannot be predicted from analogous hydrocarbon compounds. The integrity of the perfluoroalkyl (*F*-alkyl or R_F) group is usually assumed, since an R_F group remains unaffected by common chemical reactions such as reduction,[2,3] elimination,[4] substitution,[4,5] and other modifications of functional derivatives. In two homologous series of R_F-substituted alkanes $[R_F(CH_2CH_2)_nI$ and $R_FCH_2CHI(CH_2)_nCH_3$, n = 0–5], elimination and substitution reaction rates and products differed greatly depending on proximity of the iodine and R_F substituents,[4] but in no case was HF lost. Conditions of reaction were used that had given reproducible, clean hydrogen iodide elimination from several classes of R_F-substituted iodoalkanes[4,6] and had been originally chosen to conform to classical studies. Previously, in one specific instance, facile elimination of HF occurred during reaction of excess base with 4-(*F*-alkyl)-3-iodobutanoic acids.[6] Initial attack of base to eliminate HI occurred at the C-2 proton, and not α to the R_F group as in previous cases, and the intermediate reacted further with base to eliminate HF. Though apparently the rate of HF elimination was

$$R_FCF_2CH_2CHICH_2COOH \xrightarrow[-HI]{} R_FCF_2CH_2CH{=}CHCOO^- \xrightarrow[-HF]{} R_FCF{=}CHCH{=}CHCOO^-$$

slower than HI, what factors were responsible for the differing behaviors of these compounds? The answers are important to an understanding of fluorinated compounds.

Free-radical addition of iodo-*F*-alkanes (R_FI) to terminal alkadienes gave good yields of mono- and bis-adducts in two homologous series.[7] Dehydrohalogenation of the

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[1] Presented in part at the 8th International Symposium on Fluorine Chemistry, Kyoto, Japan, 1976, and at the 10th Winter Fluorine Conference ACS, St. Petersburg, FL, 1987.

[2] Brace, N. O.; van Elswyk, J. E. *J. Org. Chem.* **1976**, *41*, 766.

[3] Brace, N. O. *J. Fluorine Chem.* **1982**, *20*, 313.

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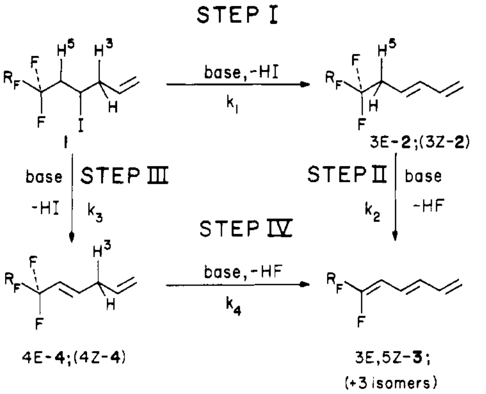
Table I. Product Separation and Identification by GC/MS and Tandem FTIR, from Experiment 1[a,b]

peak no.	substance	t_R, min	rel area, %
1	3*Z*-**2**	11.06	1.273
2	3*E*-**2**	12.84	2.296
3	3*E*,5*E*-**3**	14.00	4.733
4	3*Z*,5*Z*-**3**	15.33	26.350
5	3*E*,5*Z*-**3**	15.92	59.650
6	4*E*-**4**	18.817	–[c]
7	4*Z*-**4**	18.817	–[c]

[a] Reaction of **1** (0.2219 M) and NaOH (0.7144 M) in 92.6% ethanol (25 mL) at 29.1 °C for 208 min. [b] Organic products (94.8% of theory) were separated by capillary GC on the "DB-5" column (see Experimental Section). [c] 4*Z*-**4** and 4*E*-**4** gave combined area of 3.144%; these isomers were separated on the "DB-1" column. See Table II.

Scheme I. Four-Step Reaction for Dehydrohalogenation of 5-(*F*-butyl)-4-iodo-1-pentene



homologous mono-adduct series of 1-(*F*-alkyl)-2-iodoalkenes [$R_FCH_2CHI(CH_2)_nCH{=}CH_2$, $n = 1$–4] has now revealed some interesting effects not seen with (*F*-alkyl)-iodoalkanes.[4] In preliminary work, homologues of the series (n = 2 and 4) gave the expected products, $R_FCH{=}CH(CH_2)_nCH{=}CH_2$, under "standard"[4] conditions. However, the first homologue, 5-(*F*-butyl)-4-iodo-1-pentene (**1**), was anomalous. Elimination of both HI and HF occurred and were quantified, but organic products were more difficult to quantify. Finally, high-resolution GC/MS and tandem GC/FTIR,[8] gave a nearly complete analysis of the complex product mixture from **1**. Three key experiments are the primary focus of this work, and the results are discussed in the broader context of higher homologues and related substances.

Results

Reaction of 5-(*F*-butyl)-4-iodo-1-pentene (**1**) with NaOH in 92.6% ethanol gave (3*E*,5*Z*)-1-fluoro-1-(*F*-propyl)-1,3,5-hexatriene (3*E*,5*Z*-**3**) as major product. All identified products from experiment 1 are listed in Table I. Scheme I outlines two competitive routes for dehydrohalogenation of **1** to the isomeric trienes **3**. Likely intermediates were (3*E*)- and (3*Z*)-5-(*F*-butyl)-1,3-pentadiene (3*E*-**2** and 3*Z*-**2**) and the nonconjugated dienes, (4*E*)- and (4*Z*)-5-(*F*-butyl)-1,4-pentadiene (4*E*-**4** and 4*Z*-**4**).

In experiment 2, samples taken at intervals of time gave rates for reaction steps of Scheme I. Mole amounts of volatile products are given in Table II. Figure 1 displays the rapid disappearance of **1** and the simultaneous, rapid build up and slow decay of conjugated *trans*-diene, 3*E*-**2**. Both *cis*-diene 3*Z*-**2** and nonconjugated dienes 4*Z*-**4** and 4*E*-**4** were minor products and are not plotted. However, Table II lists all volatile products and their concentrations. By interpolation, diene isomer 3*E*-**2** reached a maximum of about 70 mol % in 3.5 min; 3*E*-**2** and 3*Z*-**2** disappeared at a rate that was reciprocal to formation of triene isomers **3**. Since *trans*-diene 3*E*-**2** predominated in step I, triene isomers derived from 3*E*-**2** also predominated. Trienes **3** reached 96.4 mol % in 61 min. **1** decreased to 0.44 mol % after 14.6 min.

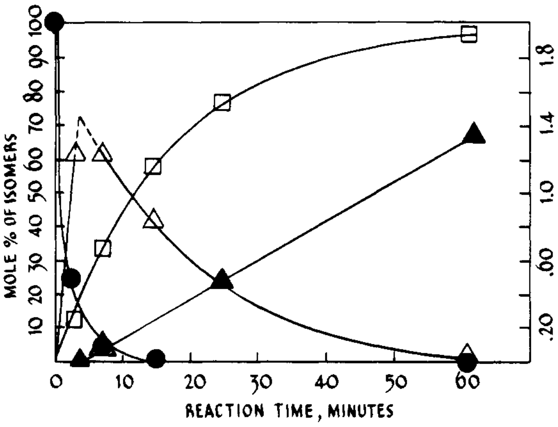


Figure 1. Dehydrohalogenation reaction of **1**. Disappearance of 3*E*,3*Z*-**2** and formation of 3*E*,3*Z*-**3**; 5*E*,5*Z*-**3** isomers. Closed circles, mol % of **1** remaining; open triangles, total conj dienes, 3*E*-**2** and 3*Z*-**2**; open squares, total trienes **3**, formed; closed triangles, log $[2]_o/[2]_t$, data from experiment 2 and Table II.

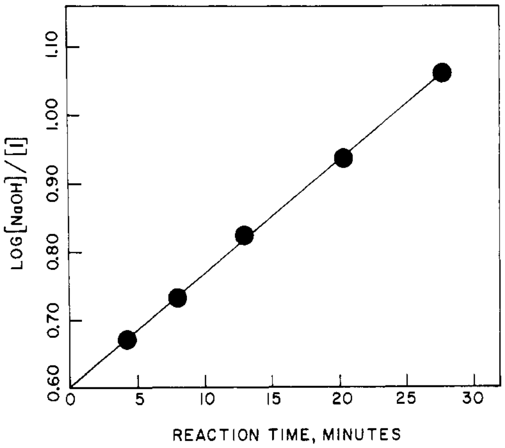


Figure 2. Dehydrohalogenation reaction of **1**. Rate of HI formation by titration, corrected for reaction of base with diene.

Rate constants for each step of Scheme I are listed in Table III; see also Table IV for mole amounts and quantities used for calculations. For step I of Scheme I, titration of iodide ion, making use of dilute reaction mixture and the sensitive potentiometric method previously employed,[4] gave greater accuracy in measurement of rate. A calibration experiment gave a linear correction plot for HF formed and base used up in reaction with dienes, as a function of time (Table V). Corrected quantities for reaction of **1** gave a linear plot presented as Figure 2. The rate constant, k_1, was 4.44×10^{-2} L mol^{-1} s^{-1} at 30 °C.

Because of rapid reaction rate and few available data points, similar analysis of titration and GC data of experiment 2 gave an approximate rate constant for k_1 (see Table IV, k_1 = ca. 3×10^{-2} L mol^{-1} s^{-1} at 30 °C). However, Figure 3 illustrates the coincidence of HI formation and disappearance of **1** in this reaction.

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[7] Brace, N. O. *J. Org. Chem.* **1973**, *38*, 3167.

[8] Access to instruments was provided by Argonne National Laboratory, through the Regional Instrumentation Sharing Program in the Division of Educational Programs, 1985. We are indebted to Dr. J. Demergian for valuable assistance in obtaining GC, FT-IR, and MS results.

Table II. Capillary GC Analysis of Experiment 2[a,b]

		reaction time: mol % of substances in each sample				
substance	GC ret time, min	3.10	7.13	14.6	25.0[c]	61.0
3*Z*-**2**	10.9	1.50	0.42	0.23	–	0.13
3*E*-**2**	12.81	59.8	60.5	41.3	22.5	3.21
3*E*,5*E*-**3**	14.12	7.73	17.6	28.0	32.2	37.3
3*Z*,5*Z*-**3**	15.07	1.24	4.66	9.38	11.5	24.1
3*E*,5*Z*-**3**	15.60	3.48	10.9	19.6	29.1	34.9
1	24.59	24.0	4.56	0.44	–	0.010
4*E*-**4**	25.74	1.91	1.07	0.50	–	–
4*Z*-**4**	28.64	0.29	0.27	0.26	–	0.25

	summation for kinetic analysis				
	3.10	7.13	14.6	25.0[c]	61.0
dienes					
log [**2**,**4**]$_i$/[**2**,**4**]$_t$	0.00[d]	0.0692	0.240	0.501[c]	1.32
trienes[e]					
(100 − [**3**]$_t$)	87.55	66.81	42.97	25.1	3.58
log (100/(100 − [**3**]$_t$))	0.0577	0.176	0.367	0.600	1.46

[a] Reaction of **1** (0.09704 M) and NaOH (0.2926M) in 92.6% ethanol at 29.5 °C; see Experimental Section. [b] Retention times from the "DB-1" column. [c] GC on "Ucon Polar" packed column. [d] At time = 3.5 min, when [**2**] + [**4**] reached a maximum. [e] Total trienes, **3**, at time = *t* were subtracted from **3** at end of reaction (**3** = 100%). This gave the amount of unformed **3** at time = *t*.

Table III. Rate Constants for Reactions of Scheme I and Related Rate Constants[a]

			least-squares[a]	
step	*k*	rate constant: 30 °C, L/mol^{-1} s^{-1}	sd slope	correlation
I	k_1	4.44×10^{-2} [b,c]	0.0002	0.9997
II	k_2	6.9×10^{-3} [d]	0.0016	0.9988
		(6.1×10^{-3} [e])	0.0003	0.9998[e]
III	k_3	(1.4×10^{-3})[f]	–	–[f]
IV	k_4	6.6×10^{-3} [g]	0.0034	0.9992
$R_FCH_2CHI(CH_2)_2CH{=}CH_2$[h]		4.23×10^{-2}	0.0001	1.000[h]
$R_FCH_2CHICH_2COOH$[i]		1.1×10^{-2}		–[i]
$R_FCH_2CHI(CH_2)_3CH_3$[j]		3.54×10^{-2}		–[j]
$CH_3CHI(CH_2)_5CH_3$[k]		7.88×10^{-5}	0.0000	0.9994

[a] See Tables II, IV, and VI. [b] By titration; see Table V and Experimental Section. Another expt gave $k_1 = 4.6 \times 10^{-2}$ L mol^{-1} s^{-1}. [c] From GC analysis, k_1 = ca. 3×10^{-2} L mol^{-1} s^{-1}; see Table IV. [d] See Table IV; calcd from ln [NaOH]/[**2**] against time (min); 4 points. [e] Plot of log (100/100 − [**3**]) against time (min); $k = 9.7 \times 10^{-4}$/s; $Y = 0.0240X + 0.0005$; sd residuals = 0.0141. k_2 from $k = 9.7 \times 10^{-4}$ s^{-1}/[NaOH]$_{av}$; [NaOH]$_{av}$ = 0.157. See Tables II and IV. [f] Extrapolation of [**2**]/[**4**] to time = 0; k_1/k_3 = 31 and k_3 = 0.0444/31. [g] From ln [NaOH]/[4*E*-**4**] against time; see Table IV. [h] Compound **5**. $R_F = C_4F_9$. Rate constant from titration; two experiments (see Experimental Section). [i] $R_F = C_3F_7$ or C_4F_9; *k* values of 1.02, 1.13, and 1.15×10^{-2} L mol^{-1} s^{-1} from three titration experiments; see ref 6. Error limits are given. [j] $R_F = C_4F_9$; *k* values from four titration experiments were 3.38, 3.54, 3.54, and 3.70×10^{-2} L mol^{-1} s^{-1} (mean value 3.54), from ref 4; see error estimate. [k] See refs 4 and 6; error estimate from original data.

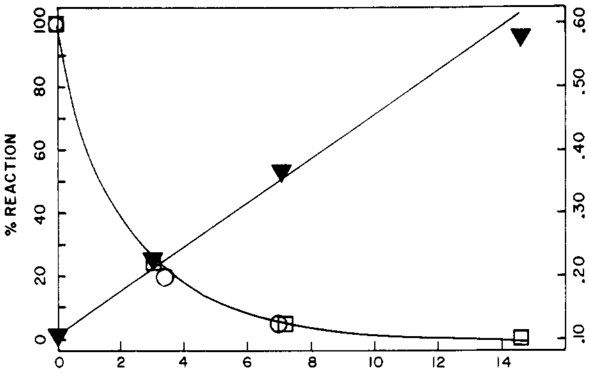

Figure 3. Dehydrohalogenation reaction of **1**. Disappearance of **1** (from Tables II and IV) and hydrogen iodide formation (from Table V). Open squares, mol % of **1** remaining; open circles, iodide ion by titration, % of total remaining; closed triangles, ln [NaOH]/[**1**].

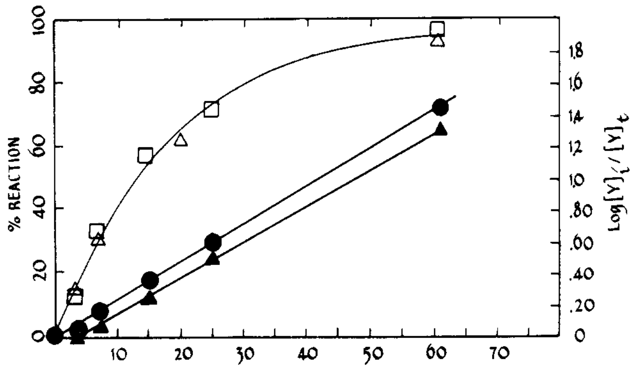

Figure 4. Dehydrohalogenation reaction of **1**. Formation of HF and *total* triene isomers, **3**. Open triangles, mol % HF by titration (from Table V); open squares, mol % of **3** (from Table II). log functions were calcd on Table II: closed circles, log $[Y]_i/[Y]_t$ = log (100/(100 − [**3**]$_t$)); closed triangles, log [**2**,**4**]$_i$/[**2**,**4**]$_t$.

Rate constant for step II of Scheme I was found in several ways. Figure 1 shows the linear plot of log $[\mathbf{2}]_0/[\mathbf{2}]_t$ against time, from which an approximate rate constant may be estimated (see Table III). However, a least-squares plot of ln [NaOH]/[**2**] or of ln [NaOH/[**2** + **4**] against time gave $k_2 = 6.9 \times 10^{-3}$ L mol^{-1} s^{-1} at 30 °C. This was confirmed by an identical rate constant for the formation of triene isomers **3**. Concentrations of each substance, calculated from the GC data of experiment 2, are listed in Tables II and IV, together with quantities used for rate plots of Figure 1 and Figure 4.

Experiment 3 was interesting, in that change in hydrogen fluoride concentration was coincident with formation of **3** (Figure 4). This demonstrates the relationship between formation of HF and trienes **3** in step II (Scheme

Table IV. Dehydrohalogenation Reactions of **1**: Kinetic Results from GC Analysis[a-c]

time, min	[**1**]	$[I^-]$[d]	total [**2**]	total [**3**][e]	[NaOH][f]	ln [NaOH]/[**1**][g]	ln [NaOH]/[**2**][h]	ln [NaOH]/[4*E*-**4**][i]
0.00	0.09704	0.000	0.000	0.000	0.296	1.12	0.00	0.000
3.10	0.0233	0.0738	0.0595	0.0121	0.210	2.20	1.26	4.73
7.13	0.00443	0.0926	0.0591	0.0322	0.171	3.65	1.06	5.10
14.6	0.00043	0.0966	0.0403	0.0553	0.144	5.82	1.28	5.69
25.0[j]	–	–	0.0223	0.0706	0.129	–	1.75	–
61.0	0.97E-4	0.0970	0.00323	0.0936	0.106	9.29	3.49	–

[a] See Table II for GC results. [b] The second-order rate expression, $\ln([\mathrm{NaOH}]_i - x)/[\mathrm{compd}]_i - x) = kt([\mathrm{NaOH}]_i - [\mathrm{compd}]_i)$ was solved for k: k ($\mathrm{L\ mol^{-1}\ s^{-1}}$) = (slope)/(60 s/min)($[\mathrm{NaOH})_i - [\mathrm{compd}]_i$). Least-squares analysis of the data is given for each set of data. [c] Rate constants are given in Table III. [d] $[I^-]_t$ was calcd from GC analysis of $[\mathbf{1}]_t$. [e] From Scheme I, $[\mathbf{3}]_t = [F^-]_t$; $[F^-]$ and ($[\mathbf{2}]_t + [\mathbf{4}]_t$) are reciprocal. [f] $[\mathrm{NaOH}]_t$ was calcd from $[\mathrm{NaOH}]_i - ([I^-]_t + [F^-]_t)$. [g] ln [NaOH]/[**1**] against time; least-squares, $Y = 0.3216X + 1.2007$; correlation, 0.9984; sd slope = 0.0129; sd residuals = 0.1407 (only first four points used); k_1 = ca. $3 \times 10^{-2}\ \mathrm{L\ mol^{-1}\ s^{-1}}$. [h] ln [NaOH/[**2**] from 7.13 min against time: $Y = 0.0466X + 0.6583$; correlation 0.9982; sd slope = 0.0019; sd residuals, 0.0791. [i] ln [NaOH]/[4*E*-**4**] from 3.1 min against time: $Y = 0.0831X + 4.4882$; sd slope = 0.0034; sd residuals = 0.0281; correlation 0.9992 (only three points). [j] GC on "Ucon Polar" column; see Experimental Section.

Table V. Dehydrohalogenation Rate of **1** by HI and HF Titration[a]

	reaction time, min				
	3.38	6.96	19.71	60.59	120.68
% $[F^-]$[b]	14.59	30.42	62.22	93.95	100.0
$(100 - F^-)$	85.41	69.583	37.78	6.05	–
$\log(100/(100 - F^-))$[c]	0.0685	0.158	0.423	1.22	–
% $[I^-]$[b]	80.7	95.5	99.9	100	100

	dehydrofluorination of **1**: calibration expt, rate in dilute soln[d]						
	8.20	15.72	23.78	31.75	39.75	47.77	55.90
$[F^-]$[e]	0.182	0.270	0.364	0.499	0.625	0.750	0.885
% $[F^-]$[f]	4.77	7.08	9.55	13.1	16.4	19.7	23.2

	HI elimination rate of **1** in dilute soln[g]								
	4.25	8.08	13.00	20.33	27.75	33.25	40.25	50.00	61.0
$[I^-]$[e]	1.027	1.674	2.415	3.088	3.592	3.848	4.096	4.303	4.526
[NaOH][e]	18.32	17.69	16.95	16.27	15.77	15.52	15.27	15.06	14.83
[**1**][e]	3.885	3.238	2.497	1.824	1.320	1.064	0.8194	0.6094	0.3862
$[F^-]$[e,h]	0.13	0.18	0.29	0.43	0.56	0.65			
[NaOH]/[**1**][i]	4.682	5.408	6.672	8.684	11.52	13.96			
log [NaOH]/[**1**][j]	0.6704	0.7330	0.8242	0.9387	1.061	1.145			

[a] Experiment 3; **1**, 0.1035 M, NaOH, 0.3646 M in 92.6% ethanol at 30 °C. [b] % of total, titrated. [c] See Figure 1 and footnote *e* of Table II. [d] **1**, 3.811×10^{-3} M; NaOH, 14.02×10^{-3} M in 92.6% ethanol at 30.0 °C. See Experimental Section. [e] Concentration, M × 10^{-3}. [f] Theory, % of fluoride ion. [g] **1**, 4.912×10^{-3} M; NaOH, 19.36×10^{-3} M; 92.6% ethanol at 30.0 °C. [h] 4.912×10^{-3} M times % fluoride from previous experiment. [i] Used [NaOH] corrected for HF formation. [j] See Figure 2 and Experimental Section, for details, error analysis.

Table VI. Configuration of Products of Experiment 2 as a Function of Reaction Time

	isomer ratio at reaction time, min				
	3.10	7.13	14.58	61.05	208[a]
dienes **2**: 3*E*/3*Z*	39.9	145.8	178.9	24.7	1.80
Trienes **3**					
3*E*/3*Z* at 3-position	10.3	6.21	5.08	2.99	2.44
5*Z*/5*E* at 5-position	0.61	0.88	1.02	1.58	18.2
combined isomers **2** and **3**					
3*E* config, mol %	71.0	89.0	89.1	76.1	66.7
3*Z* config, mol %	2.74	5.09	9.61	25.6	27.6
3*E*/3*Z* (all isomers)	25.9	17.6	9.27	2.97	2.41

[a] Data are from Experiment 1 of Table I.

I). The two parallel log $[Y]_i/[Y]_t$ plots of Figure 4 (see also Figure 1 for **2**) have the same slope and represent the combined disappearance of **2** and **4** and the formation of **3**.

Because of insufficient data, rate constant for step III could not be calculated directly. An estimate, based on extrapolation of [**2**] and [**4**] to time = zero, gave an approximate value for $k_3 = 1.4 \times 10^{-3}\ \mathrm{L\ mol^{-1}\ s^{-1}}$ at 30 °C ($k_3 = k_1/31$; see Table III). This assumes that [**2**] and [**4**] formed from **1** represents the only source of these substances. See below for a discussion of this point.

Constant k_4 of step IV was evaluated from rate of disappearance of 4*E*-**4**. A second-order plot of ln [NaOH]/[4*E*-**4**] against time gave: $k_4 = 6.6 \times 10^{-3}\ \mathrm{L\ mol^{-1}\ s^{-1}}$ at 30 °C (Table III). The least-squares equation and correlation are given in Table IV. The similarity of k_2, obtained from triene formation *and* diene disappearance, and of k_4 for step IV is a result of considerable surprise.

Stereochemistry. Stereochemical factors and reaction rates are much used in the study of elimination reactions and their mechanisms.[9-11] The rate preference for *trans*-diene 3*E*-**2** over *cis*-diene 3*Z*-**2** reached a ratio as high as 178:1 in 14.6 min (Table VI; see also Figure 5). However, as 3*E*-**2** increased in concentration, its utilization rate

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(10) (a) Saunders, W. H.; Cockrell, A. F. *Mechanism of Elimination Reactions*; John Wiley and Sons: New York, 1973. (b) Saunders, W. H. *Acc. Chem. Res.* **1976**, *9*, 19.

(11) Bunnett, J. F. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 225–280.

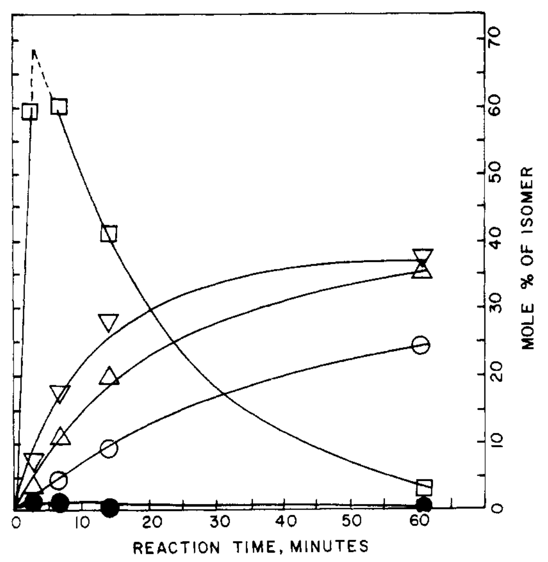


Figure 5. Dehydrohalogenation reaction of 1. Formation and disappearance rates for 3*E*-**2**, 3*Z*-**2** and formation rates for triene isomers **3**, from capillary GC. Open squares, 3*E*-**2**; closed circles, 3*Z*-**2**; open triangles, down, 3*E*,5*E*-**3**; open triangles, up, 3*E*,5*Z*-**3**; open circles, 3*Z*,5*Z*-**3**. From experiment 2.

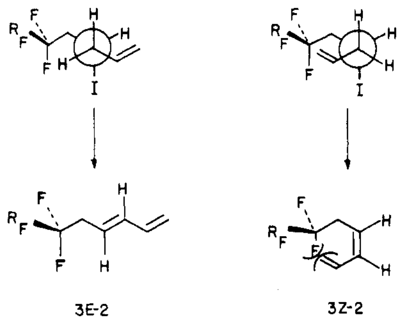
also increased. The 3*E* configuration of *combined* isomers of **2** and **3** remained relatively constant at 70–89 mol % over a 1-h period; it fell to 67% after 208 min. As pointed out above, the sum of triene isomers formed equalled that of diene originally present. Accordingly, the final 3*E*/3*Z* ratio for *all* **2** and **3** isomers represents more accurately the overall relative rates of formation of trans and cis isomers. The combined 3*E*/3*Z* ratio fell from 26, initially, to 3 after 1 h. After 208 min it was 2.41. Figure 5 shows vividly the changes in amounts of the various **2** and **3** isomers as a function of time.

With regard to stereochemistry of step II (Scheme I), *isolated* trienes with trans configuration (5*Z*) predominated. However, the 5*Z*/5*E* ratio was 0.60 after 3.10 min, reached 1.02 after 14.6 min, and was 1.58 in 1 h of reaction time. The isomer ratio for long reaction times was much higher; after 208 min the 5*Z*/5*E*-**3** ratio was 18.2. This change in configuration with long reaction time was observed in previous dehydrohalogenation reactions and was apparently caused by base-induced isomerization.[4]

Identification of Dienes and Trienes by Spectroscopic Methods. Mass Spectrum Analysis.[12] These new reaction products were at first exceedingly difficult to identify. The mixture was not separated cleanly by GC on packed columns, the trienes polymerized in a short time when purified, and elemental analysis gave obviously erroneous results, because of incomplete combustion. The first breakthrough occurred when tandem GC/MS analysis gave the mol ions (*m*/*e*) of individual isomers as listed in the supplementary material (Table VII).[12,13-15]

A more detailed analysis of the mass spectra of products **2**, **3**, and **4** was made possible by fragmentation at higher field conditions.[8] The substances were separated by capillary GC (baseline separations), and a partial listing of ion fragments and their relative abundances is given in Table VIII of the supplementary material.[12] Fragmentation patterns that show the relationship between starting compound and pathways to ion fragments are given in Schemes II, III, and IV (supplementary material), for one each of the corresponding isomers of **2**, **3**, and **4**.[12]

Scheme V. 3*Z*-2 and 3*E*-2 Configuration Controlled by Steric Congestion in the Transition State



Dehydrohalogenation of Higher Homologues of the Series $R_FCH_2CHI(CH_2)_nCH{=}CH_2$. In previous work with 1-(perfluoroalkyl)-2-iodoalkanes, there was a strong preference for attack of base at the proton adjacent to the R_F group.[4] All members of the 1-(perfluoroalkyl)-2-iodoalkane series gave only elimination of HI, even though they could theoretically have given both HI and HF.[4] The homologue, 6-(*F*-butyl)-5-iodo-1-hexene (**5**, *n* = 2) and NaOH in 92.6% ethanol at 30 °C gave 97.7% reaction (I^-), and a 90.6% distilled yield of (5*E*)- and (5*Z*)-6-(*F*-butyl)-1,5-hexadiene (5*E*-**6** and 5*Z*-**6**; 7.2 *E*/*Z*). **5** and sodium methoxide in methanol at 70 °C gave 5*E*-**6** and 5*Z*-**6** and no HF or methyl ether from solvolysis (NMR and IR analysis). A second-order rate constant for **5** and NaOH in 92.6% ethanol at 30 °C was $k = 4.23 \times 10^{-2}$ L mol^{-1} s^{-1} (Table III), in the range previously found for (saturated) 1-(perfluoroalkyl)-2-iodoalkanes.[4] It is a matter of some interest that HI elimination from 2- iodooctane is 10^3 times slower than **5** ($k = 7.88 \times 10^{-5}$ L mol^{-1} s^{-1}) in 92.6% ethanol at 30 °C.[4,6] The enhancing effect of an R_F group on rate of attack by base, and elimination of HI, is clearly evident.

The next homologue, 8-(*F*-butyl)-7-iodo-1-octene (**7**) gave (7*E*)- and (7*Z*)-8-(*F*-butyl)-1,7-octadienes (**8**; 3.3 *E*/*Z*, by GC). With both **6** and **8**, IR stretching frequency of the *E* isomer was at 1675 cm^{-1} and for the *Z* isomer at 1640 cm^{-1}; NMR spectra were in accord with the expected structures. These results once again point up the unusual behavior of **1** in dehydrohalogenation reactions.

Discussion

Relationship to Previous Dehydrohalogenation Studies. Homologue **1** in the (*F*-alkyl)-2-iodoalkene series most closely resembles the 4-(*F*-alkyl)-3-iodobutanoic acids in structural character and behavior in reaction with base.[6] HI comes off first to form a conjugated diene (or carbonyl) in either case, and only a minor amount of nonconjugated product could be isolated. Elimination of HI from **1** or from the iodobutanoic acid was clearly a bimolecular process and followed second-order kinetics in both cases. The corresponding rates at 30 °C (see Table III) were of the same order of magnitude, and the slightly slower rate of the iodobutanoic acid may be attributed to repulsion of base by the negatively charged substrate, $R_FCH_2CHICH_2COO^-$.

Stereochemical preference for anti-elimination of HI from **1** (Table VI; 3*E*-**2**/3*Z*-**2**) was as high as 178, or from the iodobutanoic acid was very large; only a trace of the *cis*-4-(*F*-alkyl)-2-butenoic acid (as ethyl ester) was trapped by GC. In a slow, dilute dehydrohalogenation reaction, none of the cis isomer was found, nor was the nonconju-

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(12) See paragraph at end of paper for suppmementary material.

(13) We are indebted to Mr. Paul Campbell and to the Du Page County Crime Laboratory for assistance.

(14) Spangler, C. W.; Woods, G. F. *J. Org. Chem.* **1963**, *28*, 2245; **1965**, *30*, 2218. Spangler, C. W.; Jondahl, T. P.; Spangler, B. *Ibid.* **1973**, *38*, 2478.

(15) Bellamy, L. J. *The Infrared Spectra of Complex Molecules*, 3rd ed.; Chapman and Hall: London, 1975; Vol. I, p 41ff.

gated compound seen in isolated samples.[6]

In reaction of **1** with base, preference for 3*E*-**2** configuration probably has a stereochemical basis.[9-11] As the Newman projections of Scheme V show, steric congestion in the syn rotamer leading to 3*Z*-**2** would tend to raise the energy of the corresponding transition state; the anti rotamer has less crowding and would thus react faster with base. This effect was observed in a study of the related 1-(*F*-alkyl)-2-iodoalkanes.[4]

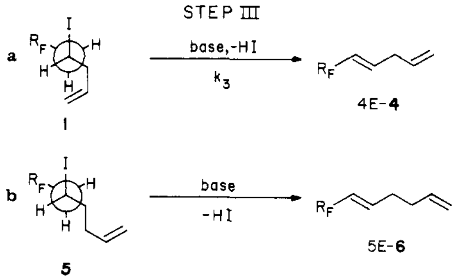
Referring now to Scheme I, HI elimination from **1** by competitive attack of base in step I and step III would account for the products formed. Increased stability of the conjugated dienes, 3*E*-**2** and 3*Z*-**2** from **1** over the nonconjugated dienes, 4*E*-**4** and 4*Z*-**4**, is the most obvious reason for the 30-fold difference in rate. To a first approximation, a 1,3-pentadiene such as 3*E*-**2** has about 6.7 kcal/mol lower energy than a 1,4-pentadiene such as 4*E*-**4**, based on the parent hydrocarbons. In terms of transition-state theory, activation energy for elimination of HI from **1** is lowered by formation of a 1,3-pentadiene, as compared with a 1,4-pentadiene. The assumption that a concerted, base-promoted 1,2-elimination has a faster rate than a stepwise reaction has been questioned.[16] To test this hypothesis, it is proposed to measure the Arrhenius activation energy for dehydrohalogenation of **1**, the 4-(*F*-alkyl)-3-iodobutanenitriles,[6] and possibly the 4-(*F*-alkyl)-3-iodo-2-butanones. Making use of short reaction times and capillary GC techniques, a more accurate picture may be developed of intermediates and their rates of formation and disappearance under different reaction conditions.

Steps I and III Rate Constants. Elimination rates of HI from **1** in step I and step III of Scheme I seemed difficult to reconcile with those of 1-(*F*-alkyl)-2-iodoalkanes or of **5** (see Table III). Rates for the *saturated* analogue, $C_4F_9CH_2CHI(CH_2)_3CH_3$, and for **5** were about 25 times faster than that of **1** in step III. In all cases the proton attacked is adjacent to the R_F group.[4] This being the case, it is puzzling why HI elimination of **1** is not equally as fast in step III. By contrast, results from $R_FCH_2CHICH_2COOH$ when compared to those of **1** are clear and consistent: HI elimination to *conjugated* products have comparable rates, but the nonconjugated products are formed at slower rate.[6]

A reviewer has suggested that 4*Z*-**4** and 4*E*-**4** may *actually* be formed at a comparable or faster rate than 3*Z*-**2** and 3*E*-**2**, but then the nonconjugated isomer rearranges rapidly to the conjugated isomer. This could account for the low amounts of **4**. The answer to this question may emerge from the detailed product studies proposed above. It is difficult to see how the decay of 3*E*-**2** (Figure 1) would so closely relate to the build up of triene **3**, if there were the additional step in going from **1** to **4** to **2** to **3**.

Another plausible explanation is based on stereoelectronic effects. The "apparent" slower rate of step III could result from proximity of the 2-propenyl group in **1** to the proton at C-5 in the transition state. A rotamer with the C-5 proton and the 4-iodo groups *anti* to each other (Scheme VI), would have the π-electron cloud of the 2-propenyl group proximate to the C-5 proton. For the analogous rotamer (Scheme V) leading to 3*E*-**2** in step I, a proton *at C-3* is being attacked, and the *vinyl* group does not interfere. In fact, the very presence of the vinyl group may be responsible for accelerated reaction with base, through resonance with the forming double bond. For 3*E*-**2** there is an additional CH_2 separating R_F and iodine.

Scheme VI[a]



[a] (a) HI elimination from **1**: attack of base at C-5 proton slowed by repulsion from π-electrons of the 2-propenyl group. (b) HI elimination from homologue **5**: repulsion of base absent in rotamer having a 3-butenyl group.

This same reasoning would apply to the iodobutanoic acids, but in greater force, since the negatively charged COO^- group would be proximate to the similarly charged attacking base as in **1** of Scheme VI. It should also be pointed out that the bulk of the alkyl group in the R_FCH_2CHIR series[4] had only a small effect on rate of HI elimination. The rate decreases from 5.84 to 4.10×10^{-2} L mol^{-1} s^{-1} at 30 °C in going from R = Me to *n*-Bu; and further to 3.41×10^{-2} L mol^{-1} s^{-1} with R = *n*-hexyl. In the case of *unsaturated* homologue **5**, its elimination rate (Table III) is not appreciably changed with respect to its *saturated* analogue, 1-(*F*-butyl)-2-iodohexane ($C_4F_9CH_2CHI(CH_2)_3CH_3$, Table III). This result may have its basis in the nonproximate position of the double bond π-electrons of **5**, as indicated in the drawing of Scheme VI.

Step II of Scheme I. Elimination of HF from the diene intermediates formed in either step I or step III follows second-order kinetics. In extensive work on dehydrofluorination reactions, Koch, Tumas, and Knoll[17] obtained rate constants at 50 °C, and activation parameters for sodium ethoxide promoted reaction in ethanol, of $PhCH_2CF_3$ and of $PhCH_2CF_2CF_3$.[18] These substances have a close similarity to conjugated dienes 3*E*-**2** and 3*Z*-**2** in that the phenyl ring becomes conjugated with the double bond formed during reaction to give an extended conjugated system very much like the reaction of 3*E*-**2** to give **3**. The rate constant, 5.41×10^{-5} L mol^{-1} s^{-1}, for

$$PhCH_2CF_2CF_3 \rightarrow PhCH{=}CFCF_3$$

2,2,3,3,3-pentafluoropropylbenzene is about 100 times smaller at 50 °C than that of 3*E*-**2** at 30 °C; the rate for $PhCH_2CF_3$, $k_{-HF} = 3.45 \times 10^{-7}$ L mol^{-1} s^{-1} at 50 °C, is about 10^4 times slower. It is instructive to observe that Koch, Tumas, and Knoll found the same dehydrofluorination reactions run in ethanol or in *tert*-butyl alcohol gave different activation enthalpy and entropy parameters. A two-step proton-transfer reaction, in which internal return plays an important part in determining rates and kinetics of the dehydrofluorination reaction, was proposed, based on evidence from isotope effects and thermodynamic measurements. The authors state, "since internal return is a competition between a reprotonation step, k_{-1}, and the ejection of halide, k_2, the use of fluoride ion as a leaving group from different environments could give large differences in observed experimental results".[17]

With these cautions in mind, we do not offer a mechanism for step II of Scheme I, based on present results. In future studies, attention should be given to isotope effects

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(16) Bordwell, F. G. *Acc. Chem. Res.* **1972**, *5*, 374.

(17) Koch, H. F.; Tumas, W.; Knoll, R. *J. Am. Chem. Soc.* **1981**, *103*, 5423–5429.

(18) We are grateful to a reviewer for pointing out ref 17 to us.

and activation parameters of the reaction along with product studies.

Step IV of Scheme I. A 1,4-elimination of HF and simultaneous shift of the double bond was considered for the analogous step in dehydrofluorination of 4-(*F*-alkyl)-3-iodobutanoic acids.[6] This reaction mode was thought *not* to pertain, since the intermediate, $R_FCH=CHCH_2COOH$, could not be found among the products. However, 4*E*-4 and 4*Z*-4 were definitely present though in small amount, in product mixtures from 1. 4*E*-4, but not 4*Z*-4, reacted with base and disappeared at a rate nearly identical with that of 3*E*-2 (Table III; $k_2 = 6.9 \times 10^{-3}$ and $k_4 = 6.6 \times 10^{-3}$ L mol^{-1} s^{-1} at 30 °C). Thus, both for 1 and in the iodobutanoic case,[6] 1,4-elimination of HF remains a distinct possibility for step IV. Rates and products of reaction are consistent. To look further into this subject, it is proposed to synthesize 4*E*-4, or the analogous $R_FCH=CHCH_2COOH$, probably by a more suitable method, and directly observe dehydrofluorination rates and products.

Summary. A high-yield synthesis of novel fluorine-substituted dienes and hexatrienes by a simple dehydrohalogenation reaction was discovered. Factors that affect the facile elimination of fluoride ion from perfluoroalkyl-substituted molecules have been further identified and illustrated. Quantitative measurement of formation and reaction rates of intermediates and products, and of GC trapping and spectroscopic (UV, IR, NMR, and MS) properties of these substances, have revealed new results in the chemistry of fluorine-substituted hydrocarbons. Reaction behavior of iodoalkene 1 was contrasted with 1-(*F*-alkyl)-2-iodoalkanes, 4-(*F*-alkyl)-3-iodobutanoic acids, and higher members of the homologous series, $R_FCH_2CHI(CH_2)_nCH=CH_2$, where $n = 1$–4. Those members with $n = 2$–4 did not eliminate hydrogen fluoride in reaction with base but gave dienes of the type $R_FCH=CH(CH_2)_nCH=CH_2$.

Experimental Section

Sources of Materials and Physical Methods. Mono-adduct homologues 5 and 7 were prepared as described.[7] An improved procedure for the preparation of homologue 1 is given below. IR spectra were obtained by means of Perkin-Elmer spectrometer No. 1430 or by FT-IR, making use of a Nicolet 60 SX Fourier transform infrared spectrometer, interfaced with a Hewlett-Packard 5840 capillary column gas chromatograph, and with a Nicolet 1280 computer data system.[8] NMR spectra were taken on a Varian HA-100 spectrometer with the assistance of Dr. Ronald Rodebaugh of CIBA-GEIGY Corp., Ardsley, NY. GC analyses (*n*-hexane as internal reference) utilized a Gow-Mac thermal conductivity instrument, fitted with a 6 ft × $^1/_4$ in. column packed with UCON POLAR LB-550X oil, 20% on Chromosorb P. A Perkin-Elmer Sigma 3 gas chromatograph (3-ft glass column, fluorosilicone "OV-210" polymer) was temperature programmed from 160 to 350 °C and attached to a Hewlett-Packard mass spectrometer Model No. 5992.[13] Quantitative capillary GC and mass spectra were obtained by a Hewlett-Packard Model No. 5984, used in tandem with a Hewlett-Packard Model No. 5840 gas chromatograph; the data system was an HP 5934A Model 21 MX computer, 5948B data subsystem (A/D and D/A converters). Capillary columns, 30 m × 0.322 mm i.d., "DB-1" and "DB-5", from the J and W Scientific Co. were employed. Distillation on a Nester-Faust 16-in. stainless steel spinning band column, operated at high reflux ratio, provided pure materials. Rate determinations by titration of iodide ion and fluoride ion were done as described.[4,6] UV spectra were obtained by the use of Beckman DK-2 or Cary 219 spectrometers.

Preparation of 6,6,7,7,8,8,9,9,9-Nonafluoro-4-iodo-1-nonene (1). A heavy-wall glass pressure tube, cooled to −78 °C, was charged with 1,4-pentadiene (13.7 g, 0.197 mol), 1-iodo-1,1,2,2,3,3,4,4,4-nonafluorobutane (1-iodoperfluorobutane, 34.5 g, 0.0997 mol), and azobis-2-methylpropionitrile (1.3145 g, 8.005 mmol). The pressure tube was evacuated and filled with nitrogen three times, evacuated, and sealed. The reaction mixture was heated at 70 °C for 16 h. It was distilled in a total reflux, variable take-off column, heated with an oil bath. Materials recovered were 1,4-pentadiene (5.18 g); crude 1, bp 77–85 °C (14 mm), 24.4 g, and bp 75–68 °C (6–4.5 mm), 4.84 g; a residue, 7.62 g of mostly bis-adduct; and trap liquid (19.1 g), a mixture of 1-iodoperfluorobutane, 1.4-pentadiene, and some solid tetramethylsuccinonitrile. The crude yield of 1 was 70.8%. 1 was redistilled in a 16-in. spinning band column, operated at a reflux ratio of 15/1 and a bath temperature of 102 °C. A fraction, bp 87 °C (15 mm), $n^{25}{}_D$ 1.3970, was 99.4% pure by GC analysis.

Dehydrohalogenation of 5-(*F*-butyl)-4-iodo-1-pentene (1). Product Separation and Identification by GC/MS and Tandem FT-IR. Experiment 1. 1 (2.2973 g, 5.548 mmol, 0.2219 M) was added to a solution of sodium hydroxide (0.7147 g, 17.86 mmol, 0.7144 M) in 92.6% ethanol in a 25-mL volumetric flask at 29.1 °C. The mixture was stirred by magnet bar for 208 min; water (22 mL) and hydrochloric acid (6 mL, 3 N) were added, and the mixture was chilled. A lower layer (1.3992 g, 94.8% of theory for 6,7,7,8,8,9,9,9-octafluoronona-1,3,5-trienes, 3) was drawn off. Additional product (3.0%) was extracted by dichloromethane (1 mL). GC analyses were performed by means of capillary columns, "DB-1" and "DB-5". GC peaks identified by GC/MS and FT-IR are given in Table I. Mass spectra (*m*/*e* and intensities) for each identified substance are listed in Table VIII.[12] FT-IR results are listed in Table IX.[12] Individual peaks and mixtures from distillation fractions are described below.

Aliquot Samples for GC Trapping, Iodide, and Fluoride Analyses. Experiment 2. Sodium hydroxide (0.2962 g, 7.405 mmol, 0.2926 M) in 92.6% ethanol (25 mL) was equilibrated at 29.5 °C, and at a time $t = 0$, added to 1 (1.0045 g, 2.426 mmol, 0.097 04 M) in a 50-mL, round-bottom flask, stirred by magnet bar at 29.5 °C. Aliquots (5 mL) were removed and immediately diluted with cold water (5 mL); then, seven drops of 1.5 M hydrochloric acid and about 0.015 g of sodium bisulfite (to prevent oxidation of iodide ion) were added. The samples were chilled to 0 °C; the oil droplets drawn up by capillary pipet and placed in preweighed vials (92.23% recovery). Quantitative GC analysis, with *n*-hexane internal reference, gave mole amounts of identified compounds given in Table II and IV, as a function of reaction time. The aqueous solution of each aliquot sample was washed into a 500-mL volumetric flask to give a suitable dilution. Aliquots of 25 mL were titrated for iodide ion, as previously described.[4] The aliquot sample taken at 61.05 min was analyzed by FT–IR.

Experiment 3. Sodium hydroxide (2.6 mL of a 49.08 M solution in water) was diluted with 32.6 mL of ethanol to give 35.0-mL total volume. The clear solution (12.76 mmol, 0.3640 M) was added to 1 (1.5004 g, 3.624 mmol, 0.1035 M) while stirring and kept at 30.0 °C. Aliquots were taken for fluoride ion titration, and separately, for iodide ion titration. Sodium fluoride standard solutions of concentrations from 0.1 to 0.0001 M were used for reference. Acetic acid/sodium acetate (5 M), buffered to a pH of 5 (15 mL), was added to standard solutions (10 mL). Titration of the sample aliquots (1 mL), added to 25 mL of "TSIAB" buffer, gave the results listed in Table V. Results agreed well with GC analysis and iodide ion titration of experiment 2.

Spinning Band Column Distillation of 6,7,7,8,8,9,9,9-Octafluoro-1,3,5-nonatriene (3 Isomer) Mixture. 1 (7.2305 g, 17.46 mmol) in 43.0 g of ethanol was diluted to 90 mL with 92.6% ethanol at 30 °C. Sodium hydroxide (3.50 g, 87.5 mmol) in water (3.50 g) was added, while the mixture was stirred and diluted to 100 mL by 92.6% ethanol. The mixture was kept at 30 °C for 7 h, diluted with water (100 mL), and extracted with carbon tetrachloride (3 times, 15 mL). Titration gave 93.9% of theory of iodide ion. Distillation (3-ft, stainless steel spinning band column) gave fractions as follows: I, bp 64–65 °C (15 mm), 0.28 g; II, bp 66–67 °C (15 mm), $n^{25}{}_D$ 1.3835, 1.75 g; III, bp 67 °C (15 mm), $n^{25}{}_D$ 1.3854, 1.07 g; IV, bp 42–67 °C (0.75–0.16 mm), 0.69 g. Final bath temperature, 175 °C; residue, 0.80 g of a dark, thick gum. Recovery of trienes 3 was 81.7%. GC: II comprised 94.4% of two isomers of 3. Combustion analysis (two different samples by two different Analyatical Laboratories) gave inaccurate results, owing to incomplete combustion. Anal. Calcd for $C_9H_6F_8$: C, 40.6; H, 6.0; F, 57.1. Found: C, 32.7; H, 1.6; F, 56.5 (total 90.8%). See experiment 1 for GC/MS and FT-IR identification of 3 isomers. Fractions II and III, kept cold and dark, gradually thickened to an insoluble white solid. IR (freshly distilled II and III, CCl_4 solution or liquid film): CH, CH_2, 3080, 3060, 3035, 3010, 2960, 2940, 2910, 1835 (overtone); CF=CH, CH=CH, conj. 1730, 1675, 1625, 1590; CH, 1440, 1415, 1380, 1355, 1330, 1300; CF, 1220, 1180, 1150, 1110; deformation bands, 995, 950, 935, 910, 870; and bands at 1050, 1030, 1020, 850, 800, 790, 780, 740, 730, 650, 515, and 500 cm^{-1}. ^1H NMR (60 MHz, CCl_4): II and III δ 5.3 (2 H, CH_2=), 5.9 (m, 0.5 H, (*E*)-R_FCF=CH), 6.5 (m, 3.5 H, (*Z*)-R_FCF=CH).

GC Trapping, UV, and IR Analyses of 6,6,7,7,8,8,9,9,9-Nonafluoro-1,3-nonadienes (3*Z*-2 and 3*E*-2), 6,6,7,7,8,8,9,9,9-Nonafluoro-1,4-nonadienes (4*Z*-2 and 4*E*-4), and 6,7,7,8,8,9,9,9-Octafluoro-1,3,5-nonatriene Isomers 3. 1 (1.7771 g, 4.292 mmol) was added while stirring to a solution of NaOH (0.8264 g, 20.66 mmol) in ethanol (92.6%, 25 mL) at 30 °C, and stirring was continued at 30 °C for 4 h. The cloudy suspension was made acidic with HCl (3 mL, 6 M) and chilled to 10 °C, and the yellow layer was removed (0.9230 g, 80.8% of theory). GC analysis (6 ft by $^1/_4$ in. "UCON POLAR" column, 100 °C (5 min), 5 °C/min to 125 °C) gave peaks as follows (retention times, area %). Dienes 2 and 4, 5.9, 2.8%; 6.8, 5.5%; 9.7, 1.3%; and 11.7, 1.8%; triene 3 isomers, 3*E*,5*E*-3, 14.3, 23.0%; 3*E*,5*Z*-3, 18.0, 65.5%. Levy-Lang pipets (200 μL) were cooled in dry ice and attached to the exit port. Three repetitive injections of 3 μL (0.0144 g) of the mixture gave combined dienes 2 and 4 (first four peaks), 0.0030 g; 3*E*,3*E*-3, 0.0028 g; and 3*E*,5*Z*-3, 0.0086 g (quantitative recovery). Data from UV spectra in cyclohexane solution are given in Table IX.[12] IR spectra were recorded on a grating instrument, and that of 3*E*,5*Z*-3 appears in the supplementary material.[12]

Dehydrohalogenation of 6,6,7,7,8,8,9,9,9-Nonafluoro-4-iodo-1-nonene (1): Rate Determinations and Error Analysis of Titration. A 100-mL volumetric flask was charged with 1 (0.2304 g, 0.4912 mmol), and 92.6% ethanol was added to within 10 mL of the mark and equilibrated to 30.0 °C. At time = zero, 5.00 mL of 0.3871 N sodium hydroxide solution in 92.6% ethanol was added, the flask was quickly filled to the mark, and the solution was shaken. At 5–6-min intervals, a 5.00-mL aliquot was pipetted into 5 mL of 1.5 M nitric acid, and about 0.01 g of sodium bisulfite was added (to prevent air oxidation; if omitted, a yellow color appeared, and inaccurate results were obtained). The capped vials were kept at −78 °C and titrated as done previously,[4,6] making use of a bright silver electrode and 0.03000 N silver nitrate solution as titrant. Reaction times in minutes and seconds were converted to decimal minutes; the quantities found and calculated are listed in Table V.

Least-squares analysis of the data (10 points) gave a calcd slope of 0.0160 min^{-1}, correlation of 0.9990, standard deviation of slope of 0.0003, and calcd $k_1 = 4.27 \times 10^{-2}$ L mol^{-1} s^{-1}. A calibration experiment (see Table V) gave values for HF elimination by titration as described above; these results were used to set up a straight-line calibration plot that related the amount of base used up in reaction with diene, with the extent of reaction. Thus, corrected [NaOH]/[1] quantities listed in Table V and presented as Figure 2 gave a straight line, slope = 0.0167, correlation, 0.9997; $Y = 0.0167X + 0.5994$; sd slope, 0.0002; sd residuals, 0.0049. The k_1 was calcd = 4.436 × 10-2 L mol^{-1} s^{-1}. Subsequently, using freshly distilled 1, but otherwise identical means, five reaction samples to 85% reaction of 1 gave (corrected) least-squares slope of 0.0238/min; correlation, 0.9958; sd slope, 0.0011; sd residuals, 0.0299. The k_1 was 4.6×10^{-2} L mol^{-1} s^{-1}.

Precision and Accuracy of Potentiometric Titration. Potassium iodide (primary standard) was titrated in the same manner with 0.03000 M silver nitrate. Three samples, over the range of 0.7965–2.240 E-5 mol/L of KI gave an average accuracy of −1.72%; variance was from −1.85 to −1.65%. The average error in precision was ±0.877%. This would cause an absolute error in the quantity log [NaOH]/[compound] from ±0.008 in the region near 0.850×10^{-5} M to ±0.004 in the region of values near 1.41 $\times 10^{-5}$ M. Accordingly, rate constants obtained in those experiments in which these techiniques and reagents of this purity were used should have comparable accuracy and precision.

Dehydrohalogenation of 1: Reaction with Sodium Methoxide in Methanol. 1 (0.4576 g, 1.105 mmol) was added to sodium methoxide in methanol (3.0 mL, 1.0 M) in an ampoule, flushed with nitrogen while cold, and sealed in vacuo. The tube was heated at constant temperature of 70 °C for 4 h, poured into water (10 mL), and extracted with carbon tetrachloride (1 mL, three times). The extract was dried by passing over alumina and magnesium sulfate. The products were examined by NMR and IR spectroscopy and found to be identical with those obtained from reaction in ethanol. Specifically, all proton resonances appeared between δ 5.2 and 6.8; IR absorption bands were those listed for 3, including vinyl CH bands at 990, 950, 935, 910, 870, and 850 cm^{-1}. Only traces of solvolysis products (methyl ethers) could have been present. Titration of the aqueous layer gave 92.44% of theory for iodide ion.

Dehydrohalogenation of 7,7,8,8,9,9,10,10,10-Nonafluoro-5-iodo-1-decene (5). 5 (7.4325 g, 17.36 mmol) and sodium hydroxide (3.00 g, 74.8 mmol) in 92.6% ethanol (100 mL) at 30 °C (as for 1 above), gave 97.7% reaction in 4.5 h (iodide titration). Fluoride ion, none; no difference from blank. Workup and distillation gave (5*Z*)- and (5*E*)-7,7,8,8,9,9,10,10,10-nonafluoro-1,5-decadiene (5*Z*-6 and 5*E*-6), bp 69 °C (48 mm), n^{25}_D 1.3426, 4.72 g, 90.6% of theory. GC (Gow-Mac, 6-ft fluorosilicone column, QF-1): 5*Z*-6, 5.6 min, 12.0% area, and 5*E*-6, 5.6 min, 86.6%. IR: CH, 3080, 2980, 2920, and 2850; CH=CH, 1675; CH=CH_2, 1640; and bands at 990, 920, and 880 cm^{-1}. ^1H NMR (100 MHz, $CDCl_3$): δ 2.25 (m, 4 H, $(CH_2)_2$), 5.0 (m, 2 H, =CH_2), and 5.2–6.5 (m, 3 H, R_FCH=CH and CH=). Anal. Calcd for $C_{10}H_9F_9$: C, 40.0; H, 3.0; F, 57.0. Found: C, 39.9; H, 3.06; F, 56.1.

Rate Determinations. 5 (0.2307 g, 0.5389 mmol) and NaOH (0.07744 g, 1.396 mmol) in 100 mL of 92.6% ethanol at 30 °C gave 85.2% reaction in 56.9 min, a calcd slope of 0.0154/min for reaction to 20.42 min; and a least-squares calcd correlation of 1.0000. See section above for error analysis. Rate constant, $k = 4.23 \times 10^{-2}$ L mol^{-1} s^{-1}. A second determination, making use of new materials, gave a calcd slope of 0.0223/min, a least-squares correlation of 0.9987, and $k = 3.96 \times 10^{-2}$ L mol^{-1} s^{-1} (see Table III).

Dehydrohalogenation of 9,9,10,10,11,11,12,12,12-Nonafluoro-7-iodo-1-dodecene (7). 7 (7.51587 g, 16.477 mmol, 1.648 M in 92.6% ethanol) and NaOH (1.98 g, 49.4 mmol) gave 93.9% reaction in two hours at 30.0° (iodide titration). Workup and distillation gave 9,9,10,10,11,11,12,12,12-nonafluoro-1,7-dodecadiene (7*Z*-8 and 7*E*-8), bp 57–60 °C (15 mm), 3.46 g (after two distillations), 62% of theory. IR: very similar to 5*Z*-6 and 5*E*-6. GC (same as for 6): 7*Z*-8, 6.6 min, 23.45% area; 7*E*-8, 7.4 min, 76.6% and two impurities of 0.76% each. ^1H NMR (CCl_4, 100 MHz): δ 1.5 (m, 4 H, $(CH_2)_2$, 2.15 (m, 4 H, (CH=$CHCH_2$ and CH_2CH=CH_2), 4.98, (d, 2 H, CH=CH_2, and 5.2–6.7 (m, 3 H, R_FCH=CH and CH=CH_2). Anal. Calcd for $C_{12}H_{13}F_9$: C, 43.9; H, 4.0; F, 52.1. Found: C, 46.5; H, 4.47; F, 48.0.

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Supplementary Material Available: Details of the identification of dienes and trienes by spectroscopic methods, Schemes II–IV, Tables VII–X, and the printed IR spectrum of triene isomer 3*E*,5*Z*-3 (13 pages). Ordering information is given on any current masthead page.