Facile Elimination of Fluoride Ion in the Dehydrohalogenation of 3-Iodo-4-(perfluoroalkyl)butanoic Acids. Preparation of Fluorinated Sorbic Acid Analogs

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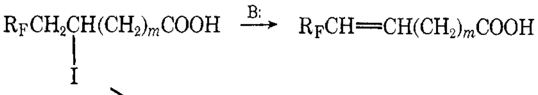
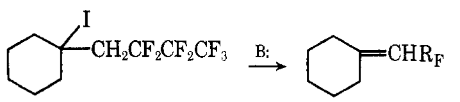
Free-radical addition of perfluoroalkyl iodides (R_FI) to 3-butenoic acid gave $R_FCH_2CHICH_2COOH$ in quantitative yield. Dehydrohalogenation of the adduct by base removed both HI and HF, forming $R_FCH_2CH{=}CHCOOH$ and $R_F'CF{=}CHCH{=}COOH$; the dienoic acid was the sole product from reaction with an excess of base. Kinetic studies showed that loss of HI preceded HF. Formation of a 1,4-dienoic acid appears to be the driving force for this reaction, since $R_FCH_2CHICH_2CH_2COOH$ with an excess of base gave only $R_FCH{=}CHCH_2CH_2COOH$.

Reactions of β-iodoperfluoroalkyl-substituted alkanes have received very little attention even though such compounds are readily obtained by the free-radical addition of perfluoroalkyl iodides to alkenes. Base-induced dehydrohalogenation of β-iodo(perfluoroalkyl)alkanoic acids[1] (**1**) and of 1-iodo-1-heptafluorobutylcyclohexane[2] (**2**) gave exclusively the α,β olefin by



$$R_FCH_2\underset{\displaystyle I}{C}H(CH_2)_mCOOH \xrightarrow{B:} R_FCH{=}CH(CH_2)_mCOOH$$

1, $m \geqq 2$



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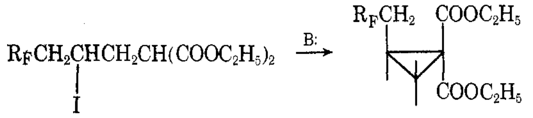
B is a strong base, $R_F = CF_3(CF_2)_n-$, $n = 2$ and higher

attack of the proton adjacent to the strong electron-withdrawing perfluoroalkyl (R_F) group. One exception is the malonic ester **3**, where the more highly activated



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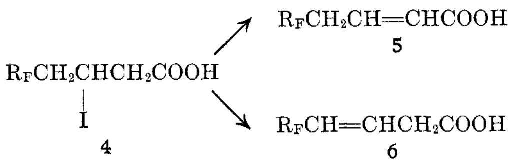
proton α to the ester function is attacked, giving a cyclopropane.[3] Steric hindrance or conformational effects also gave anomalous results with 1-iodo-2-(perfluoroalkyl)cycloalkanes,[4] which led to both Δ^1 and Δ^2 olefins. *In no instance has elimination of fluoride from a perfluoroalkyl group been observed.*

Reactions of $R_FCH_2CHICH_2COOH$ (**4**) presented a special problem. One might assume that dehydrohalogenation would occur *via* attack at the proton adjacent to the carboxyl group, but the evidence cited above demonstrates that the proton α to R_F is also quite acidic.



Both from the synthetic point of view and mechanistically the behavior of **4** under hydrolysis conditions appeared interesting. For reasons which will become apparent this study was extended to the nitrile, $R_FCH_2CHICH_2CN$ (**7**).

Results and Discussion

Our previously reported method[1,5] was utilized for the preparation of **4**. Azobisisobutyronitrile initiator

$$R_FI + CH_2{=}CHCH_2COOH \longrightarrow \underset{\textbf{4}}{R_FCH_2CHICH_2COOH}$$

(2 mol %) at 70–80° gave quantitative yields of 3-iodo-5,5,6,6,7,7,7-heptafluoroheptanoic acid (**4**, $R_F = CF_3CF_2CF_2$) and of 3-iodo-5,5,6,6,7,7,8,8,8-nonafluorooctanoic acid [**4**, $R_F = CF_3(CF_2)_3-$] as crystalline solids. Analogous reaction of 3-butenenitrile and 1-iodoperfluoropropane gave 50% conversion (98% yield) of $R_FCH_2CHICH_2CN$ (**7**).

The proton nmr spectra of **4** and **7** (Chart I) were

CHART I

	δ, ppm	Lines	J, Hz
$R_FCH_2CHICH_2COOH$ (**4**) 4 3 2 1	H_4, 3.00	(6)	$J_{HF} = 20, J_{HH} = 7$
	H_3, 4.52	5	$J_{H_3H_4} = 7, J_{H_2H_3} = 7$
	H_2, 3.30	2	$J_{H_2H_3} = 7$
	H_1, 11.9	1	
$R_FCH_2CHICH_2CN$ (**7**) 4 3 2	H_4, 3.00	6	$J_{HF} = 20, J_{HH} = 7$
	H_3, 4.50	5	$J_{H_3H_4} = 7, J_{H_2H_3} = 7$
	H_2, 3.30	2	$J_{H_2H_3} = 7$

very similar. The six-line pattern at about δ 3.0 was partially obscured by the strong, sharp doublet of H_2 at δ 3.3. In **4** the acid proton resonance appeared at δ 11.9.

Reaction of **4** with bases was attempted under various conditions.[6] With *1 equiv* of KOH in aqueous ethanol, the solution became strongly acidic from release of HI and HF and a mixture of 5,5,6,6,7,7,7-heptafluoro-2-heptenoic acid (**5**) and 5,6,6,7,7,7-hexafluoro-*trans*,-*trans*-2,4-heptadienoic acid (**8**) (and unreacted **4**) was obtained (Scheme I).

It is postulated that the strong base (OH^-) first converted **4** to its conjugate base (**4'**) and then loss of HI by attack of another base on **4'** occurred. Similar steps resulted in elimination of HF from **5** or **6**. The stronger acids then reequilibrated with the conjugate

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[1] N. O. Brace, *J. Org. Chem.*, **27**, 4491 (1962).

[2] N. O. Brace, *ibid.*, **31**, 2879 (1966).

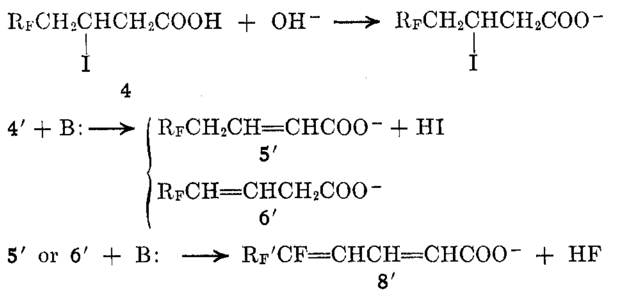
[3] N. O. Brace, *Tetrahedron Lett.*, **20**, 1697 (1970).

[4] N. O. Brace, *J. Amer. Chem. Soc.*, **86**, 2428 (1964).

[5] N. O. Brace, to E. I. du Pont de Nemours and Co., U. S. Patent 3,145,222 (Aug 18, 1964).

[6] N. O. Brace, Abstracts of Papers, 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969, FLUO 42.

SCHEME I



$$\underset{4}{R_FCH_2\underset{I}{C}HCH_2COOH} + OH^- \longrightarrow R_FCH_2\underset{I}{C}HCH_2COO^-$$

$$4' + B\colon \longrightarrow \begin{cases} \underset{5'}{R_FCH_2CH{=}CHCOO^-} + HI \\ \underset{6'}{R_FCH{=}CHCH_2COO^-} \end{cases}$$

$$5' \text{ or } 6' + B\colon \longrightarrow \underset{8'}{R_F'CF{=}CHCH{=}CHCOO^-} + HF$$

bases present in the system to liberate the weaker carboxylic acids. Kinetics of halide elimination and product rate studies given below showed that **8** followed the formation of **5**.

When two or more equivalents of strong base were used, the conjugated dienoic acid $R_F'CF{=}CHCH{=}CHCOOH$ (**8**) was obtained in better than 95% yield; **8** was also obtained in 98% yield by the addition of 3 mol of sodium methoxide to a solution of **4** in methanol at reflux temperature. We were unable to isolate **6** from any of these reaction mixtures.

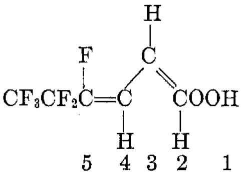
Separation of **5** and **8** proved troublesome. A mixture of **5** (40%) and **8** (60%), mp 52–53°, crystallized from the crude product mixture in ligroin. Repeated recrystallization did not change the melting point and it was unchanged by changing the solvent to CCl_4. This mixture was converted in high yield to ethyl esters **9** and **10**; nmr and ir spectra of the mixture agreed with analysis by gas–liquid phase chromatography (glpc) from which pure samples of **9** and **10** were trapped for ir spectra and analysis. $CF_3CF_2CF_2CH_2CH{=}CHCOOC_2H_5$ (**9**) thus obtained showed ν C=O 1730, ν trans C=C 1660, and characteristic bands at 982, 932, 918, and 882 cm^{-1}. A C=C stretching vibration of 1659 cm^{-1} in methyl *trans*-2-butenoate[7,8] confirms the structural assignment of **9**. The cis isomer of **9**, present in very small amount, was also trapped by glpc: ir ν C=O 1720, ν cis C=C 1650, out-of-plane CH olefinic bending at 812 cm^{-1}. Methyl *cis*-2-butenoate has reported[7] bands at ν C=O 1721, ν cis C=C 1644, and γ CH=CH 812 cm^{-1}.

Nmr spectra of **5** (or **9**) showed the anticipated six-line pattern for H_4 of **5** at δ 3.1, showing coupling with both CF_2 and adjacent vinyl proton.

	δ, ppm	Lines	J, Hz
$CF_3CF_2CF_2CH_2CH{=}CHCOOH$ 4 3 2 1	H_4, 3.1	6	$J_{HF} = 18$, $J_{HH} = 8$
5	$H_{2,3}$, 6.8–7.4	5	m
	H_1, 2.4	1	

Identification of **8** ($R_F' = CF_3CF_2$) as 5,6,6,7,7,7-hexafluoro-*trans,trans*-2,4-heptadienoic acid was based on its infrared spectrum which showed ν C=O 1710, ν C=C 1675 and 1630, and characteristic bands at 990, 962, and 895 cm^{-1}. The band at 988 cm^{-1} has been assigned to the *trans,trans*-diene CH rocking frequency[9] and is present in *trans,trans*-2,4-hexadienoic acid.[7] A band at 960 cm^{-1} is associated with CH out-of-plane vibrations in *trans*-$R_FCH{=}CHCF_3$ and $R_FCH{=}CHCH_3$.[10,11] The C=C stretching frequencies in **8** are higher than those observed for the unfluorinated acid (1642 and 1614 cm^{-1}), but this is consistent with the known effect of fluorine substitution.[8,10]

An nmr spectrum of **8** showed proton resonances of the expected complexity and shifts. The quartet at δ 7.75 could be interpreted as arising from a 16-Hz coupling of H_4 with F_5 and 11-Hz coupling of H_4 with the trans proton H_3. An 11-Hz coupling also appeared to be present in the six-line multiplet of H_2, H_3. More detailed analysis would require isolating the resonances of H_2 and H_3.



δ, ppm	Lines	J, Hz
H_2H_3, 6.5	6	*m*
H_4, 7.75	4	$J_{HF} = 16$, $J_{H_3H_4} = 11$
H_1, 12.58	1	

Identification of **8** was facilitated by conversion to its ethyl ester **10**, a single substance (by glpc) obtained in 92% yield, having an ir and an nmr spectrum consistent with the postulated structure. From crude product mixtures containing **5** and **8**, ethyl esters having retention times differing from **9** and **10** were also obtained in very small amount. One such substance was an isomer of **10**, probably ethyl 5,6,6,7,7,8,8,8-octafluoro-*cis*-2-*trans*-4-octadienoate ($CF_3CF_2CF_2CF{=}CHCH{=}CHCOOC_2H_5$), having infrared bands at ν C=O 1720, ν C=C 1670 and 1605, and bands at 965 and 935 cm^{-1}. The band at 1605 cm^{-1} is at the frequency anticipated for a cis α,β double bond in this conjugated structure.[8,10]

Kinetic Studies.—In order to place these synthetic results in perspective, elimination rates of **4** under standard conditions were determined.[6] The method used previously[4] for comparison of alkyl and cycloalkyl iodides having β-perfluoroalkyl groups was employed. Two types of kinetic experiments were performed. To determine the rate of organic product formation, samples were taken at intervals, and the organic acids were extracted into CCl_4 and identified by ir spectra. In the second type of experiment, run on a micro scale, the rate of iodide elimination was followed accurately by a sensitive potentiometric titration method.[12]

The first type of experiment was limited by the fact that, at sufficiently high concentrations of **4** to permit isolation of products, reaction was too rapid to follow at the high, required base concentration. Thus, when **4** (0.2008 *M*) and NaOH (0.3984 *M*) in 92.6% ethanol at 30° were mixed, reaction occurred to the extent of 48.3% in 5 min; a mixture of **4**, **5**, and a little **8** was obtained. Further reaction occurred much more slowly as the excess alkali had been used up; in 1200 min **5** and **8** were the chief constituents (70% utilization of base). After 4010 min 88% reaction had occurred and **8** was the principal product. Second-order kinetics

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[7] J. L. H. Allan, G. D. Meakins, and M. C. Whiting, *J. Chem. Soc.*, 1874 (1955).

[8] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Wiley, New York, N. Y., 1958, p 35.

[9] R. T. Conley, "Infrared Spectroscopy," Allyn and Bacon, Boston, Mass, 1966, p 104.

[10] J. K. Brown and K. J. Morgan in "Advances in Fluorine Chemistry," Butterworths, London, 1965, p 253.

[11] R. N. Haszeldine, *J. Chem. Soc.*, 2504 (1952).

[12] Assistance by Miss Gail Van Wingerden in obtaining these data is gratefully acknowledged.

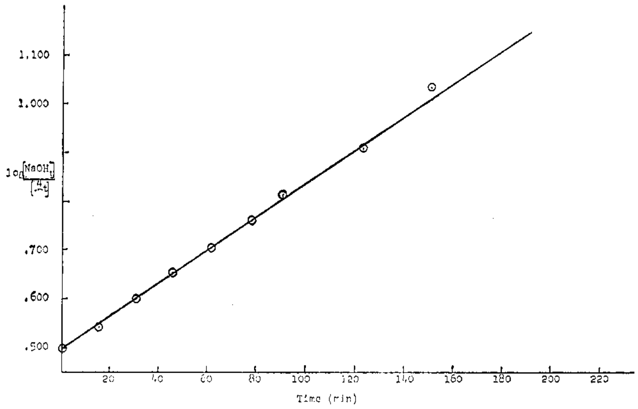


Figure 1.—Rate of iodide elimination of **4** in 92.6% ethanol at 30.0°.

were followed. The rate constant was calculated as 1.91 × 10^{-5} l. mol^{-1} sec^{-1} for reaction beyond 200 min, under conditions where H_2O and **4′** (or other conjugate bases) would be the expected attacking species.

In the kinetic runs on a small scale, reaction of **4** with 2 equiv of NaOH in dilute 92.6% ethanol solution at 30° was followed out to 90% iodide elimination (hydroxide ion, attacking species). Clean second-order kinetics were observed, giving good reproducibility of rate in three separate experiments. A typical plot is shown in Figure 1. Data for **4** and some related compounds are listed in Table I. The rate constant for **4**, k_{I^-} = 1.10 ± 0.05 × 10^{-2}, showed that under these conditions approximately 1 hr was required for half of the iodide to be eliminated. It was somewhat surprising to find that the rate for iodide elimination from iodoalkanoic acid **4** did not differ much from that from compounds such as $R_FCH_2I(CH_2)_3CH_3$ which could not form an α,β unsaturated acid. These data also showed that such β-(perfluoroalkyl)iodoalkanes reacted very much faster than unfluorinated iodoalkanes such as 1-iodopentane or 2-iodooctane. Unfortunately, comparable rate data for elimination of HI from 2-iodoalkanoic acids, RCH_2CHICH_2COOH, are not available.

TABLE I

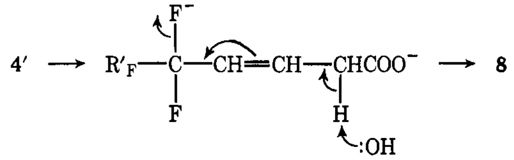
ELIMINATION RATES FOR $R_FCH_2CHICH_2COOH$ (4) AND OTHER IODO COMPOUNDS[a]

Compd	$M \times 10^3$	NaOH, $M \times 10^3$	k, l. sec^{-1} mol^{-1}
4 (run 1)	6.11	12.97	1.02 × 10^{-2}
4 (run 2)	5.45	12.97	1.13 × 10^{-2}
4 (run 3)	6.24	12.97	1.15 × 10^{-2}
$CF_3(CF_2)_2CH_2CHI(CH_2)_3CH_3$	5.317	12.97	4.1 × 10^{-2}
$CF_3(CF_2)_2CH_2CH_2I$[b]	4.89	5.016	1.55 × 10^{-1}
$CH_3(CH_2)_4I$[b]	157.6	279.0	5.0 × 10^{-5}
$CH_3CHI(CH_2)_5CH_3$	6.892	49.22	7.9 × 10^{-5}

[a] At 30° in 92.6% ethanol. [b] See ref 4.

In an attempt to follow the rate of fluoride ion elimination an experiment was done under identical conditions, determining the fluoride ion directly with a specific ion electrode. In 1 hr at 30°, about 20% of the expected fluoride was obtained (50% iodide elimination) confirming that the reaction proceeds, at least in part, stepwise from **5** to **8**. The order of the fluoride ion elimination reaction appeared to be complex, however.

These data cannot exclude the possibility that the sequence **4** → **6** → **8** was also being followed to a small extent. However, this is not consistent with the isolation of **5** and not **6** from a series of samples of incomplete reaction. If the rate for this process were much greater than for **5** → **8**, it would help to explain why none of **6** was found in reaction products. The postulated 1,4 elimination of HF and simultaneous shift of the double bond has not been previously observed and does not seem too likely to occur.



$$4' \longrightarrow R'_F-\overset{F^-}{\underset{F}{C}}-CH{=}CH-\underset{\underset{:OH}{H}}{CHCOO^-} \longrightarrow 8$$

6′

These results should be contrasted with those obtained by base-induced elimination of $CF_3CF_2CF_2CH_2CHI(CH_2)_2COOH$ (**1**, m = 2), the next higher homolog of **4**. With 2.6 mol of sodium hydroxide (1.6 M in 90% aqueous ethanol) $CF_3CF_2CF_2CH{=}CH(CH_2)_2COOH$ was the only product. There was no evidence for fluoride ion elimination, in contrast to **4**, but in agreement with previous experience.[1] The *trans*-olefinic $R_FCH{=}CH$ group was clearly evident from the ir spectrum, ν C=C 1675 and γ CH=CH 965 cm^{-1}, as discussed above. The nmr spectrum was consistent with the assigned structure, giving the anticipated lines and chemical shifts.

	Proton	δ, ppm
$CF_3(CF_2)_2CH{=}CHCH_2CH_2COOH$	H_3, H_3	2.52
5 4 3 2 1	H_4, H_5	5.0–6.6
	H_1	11.8

Here, of course, the acidic proton α to the carboxyl group cannot enter into the 1,2-elimination reaction, and a 1,3-conjugated diene structure would not also be conjugated with the carbonyl group. These appear to be the significant differences between **4** and $CF_3CF_2CF_2CH_2CHI(CH_2)_2COOH$.

Dehydrohalogenation of $R_FCH_2CHICH_2CN$.—In order to overcome the difficulties inherent in studying the behavior of a mixture of bases and conjugate bases of carboxylic acids, analogous reactions were carried out with 3-iodo-4-(perfluoropropyl)butanenitrile. A complex product mixture resulted which was analyzed by ir spectroscopy and separated by glpc; trapping of peaks gave 5,6,6,7,7,7-hexafluoro-*trans,trans*-2,4-heptadienitrile ($CF_3CF_2CF{=}CHCH{=}CHCN$) and 5,5,6,6,-7,7,7-heptafluoro-*trans*-2-heptenenitrile ($CF_3CF_2CF_2CH_2CH{=}CHCN$). Several other products were also present. An attempt to follow the kinetics of iodide elimination failed because of interference with the silver ion electrode, possibly by the nitrile group.

Experimental Section[13]

Source of Materials.—1-Iodoperfluoropropane (**11**), Pierce Chemical Co., was redistilled, bp 41°, and kept cold and dark before use. 1-Iodoperfluorobutane (**12**), bp 67°, $n^{25}D$ 1.3248, was a gift from the E. I. du Pont de Nemours and Co. 3-Butenoic acid (**13**) and 4-pentenoic acid (**14**) from Peninsular Chem-Research Co. were fractionated in a 16-in. stainless steel spinning-

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[13] Infrared spectra were recorded on a Perkin-Elmer Model 337 grating spectrometer. Nmr spectra were taken using a Varian 60 MHz A-60 spectrometer and are recorded in the format: δ in ppm (multiplet, number of protons, J = Hz, group, with protons being observed boldfaced).

band column (column A). **13**, bp 86–87° (34 mm), n^{25}_{D} 1.4201, and **14**, bp 111–112° (50 mm), n^{25}_{D} 1.4265, were used. Azobisisobutyronitrile (**15**), Eastman Organic Chemicals, was used as received; 3-butenenitrile (**16**) (same source) was redistilled, bp 117°, n^{25}_{D} 1.4036.

3-Iodo-5,5,6,6,7,7,7-heptafluoroheptanoic Acid (4).—11 (29.6 g, 0.10 mol), **13** (4.61 g, 0.050 mol), and **15** (0.164 g, 0.0010 mol) were charged into a cold Fischer-Porter Aerosol tube, cooled to −78°, evacuated, and filled with nitrogen twice. The evacuated tube was heated in an oil bath at 78 ± 1° for 21 hr and the cold liquid transferred to a flask (34.9 g, 100% recovery). Excess **11** (11.4 g) was removed *in vacuo* up to a pot temperature of 70° leaving **4** ($R_F = CF_3CF_2CF_2$) (19.8 g, 100%): mp 30–33°; ir (CCl_4) bonded OH of COOH 3500–2500, ν C=O 1710, δ CH 1425, 1400, and 1350, and bands at 1310, 1280, 1202, 1180, 1120, 965, 950, 930, and 905 cm^{-1}. A 5.0-g aliquot was distilled in two parts [no. 1, bp 78–82° (0.25 mm), n^{25}_{D} 1.4156, 1.45 g; and no. 2, bp 82° (0.25 mm), n^{25}_{D} 1.4173, 2.6 g] leaving undistilled product, 1.0 g. The ir spectra of the original sample and the two cuts were identical. Cut no. 2 solidified, mp 31–33°.

Anal. Calcd for $C_7F_7H_6O_2I$: C, 22.01; H, 1.58. Found: C, 22.15; H, 1.70.

3-Iodo-5,5,6,6,7,7,8,8,8-nonafluorooctanoic Acid.—12 (35.0 g, 0.10 mol), **13** (4.61 g, 0.0535 mol), and **15** (0.164 g, 0.0010 mol) in like manner gave **4** [$R_F = CF_3(CF_2)_3$–] (24.0 g, 100%) which solidified when cooled. A 1.5-g portion of the solid was recrystallized from ligroin (bp 60–90°): mp 40°; ir (KBr plates) bonded OH of COOH, ν C=O 1710, δ CH, 1440, and 1350, ν CF 1230 and 1135, and bands at 1025, 1010, 930, 880, 840, 780, 740, 730, 690, and 685 cm^{-1}; nmr (50% CCl_4, 60 MHz) δ 3.00 (6-line multiplet, 2, partly obscured by resonance at δ 3.3, $J_{HF} = 19$, $J_{HH} = 7$ Hz, CF_2CH_2), 3.3 (d, 2, $J = 7$ Hz, CH_2-COOH), 4.52 (5-line multiplet, 1, $J_{HH} = 7$ and 7 Hz, CH_2-$CHICH_2$), and 11.9 (s, 1, COOH). Titration of 0.2104 g in 25 ml of 50% aqueous ethanol against 0.02810 *N* NaOH gave a sharp break at pH 8.3, 17.90 ml (neut equiv 418, calcd 432).

Anal. Calcd for $C_8H_6F_9O_2I$: C, 22.24; H, 1.40. Found: C, 22.49; H, 1.52.

4-Iodo-6,6,7,7,8,8,8-heptafluorooctanoic Acid (1, *m* = 2).—11 (29.6 g, 0.10 mol), **14** (8.00 g, 0.080 mol), and **15** (0.246 g, 0.00150 mol) similarly gave **1** [$R_F = CF_3(CF_2)_2$, $m = 2$] (27.1 g, 100%), mp 42–4° before and mp 43–44.5° after carbon treatment in *n*-pentane solution, which was evaporated off and cooled: ir (KBr plates) ν C=O 1710, δ CH 1430 and 1350, ν CF 1230, 1180, and 1120, and bands at 950, 920, and 732 cm^{-1}.

Anal. Calcd for $C_8H_8F_7O_2I$: C, 24.26; H, 2.03. Found: C, 24.64; H, 2.31.

Base-Induced Elimination of 1 (*m* = 2).—$CF_3(CF_2)_2CH_2CHI$-$(CH_2)_2COOH$ (10.6 g, 0.030 mol) was added to a solution of NaOH (3.2 g, 0.080 mol) in 50 ml of 80% ethanol and kept at 73° for 6 hr while stirring. The product was worked up and distilled to give *cis*- and *trans*-$CF_3(CF_2)_2CH{=}CH(CH_2)_2COOH$: bp 68–69° (0.30 mm); n^{25}_{D} 1.3620; 5.8 g (72% yield); ir (KBr) ν COOH 3300–2700, ν C=O 1715, ν C=C 1675, δ CH 1430, 1410, and 1350, and bands at 1225, 1180, 1120, 970 (s), 945 (s), 740, and 720 cm^{-1}; nmr (50%, CCl_4) δ 2.52 [s, broadened, 4, $(CH_2)_2$], 5.0–6.6 (m, 2, CH=CH), 11.8 (s, 1, COOH).

Anal. Calcd for $C_8H_7F_7O_2$: C, 35.83; H, 2.63. Found: C, 35.72; H, 2.75.

5,6,6,7,7,7-Hexafluoro-*trans,trans*-2,4-heptadienoic Acid (8, $R_F' = CF_3CF_2$–).—4 ($R_F = CF_3CF_2CF_2$–) (13.3 g, 0.034 mol) in methanol (60 ml) was heated on a steam bath, and portions of sodium methoxide (5.3 g, 0.095 mol) were added during a 5-min period and then kept at 67° for 5 hr. The mixture foamed and a white precipitate formed. Water (100 ml) was added to the cooled mixture which was acidified with 10 ml of concentrated hydrochloric acid and extracted three times (25 ml v/v of ether and benzene). The organic extract was washed with water (10 ml) and dried over $MgSO_4$. Solvent was removed down to 70° (12 mm) giving $CF_3CF_2CF{=}CHCH{=}CHCOOH$ (**8**) (7.8 g, 98%), mp 58–63°. The reaction was repeated with identical results. Under modified conditions (see below), however, a mixture of products was obtained: ir (CCl_4) ν OH (bonded) of COOH 3100–2550, ν C=O 1702, ν CH=C 3090, ν C=C 1675 and 1625, δ CH 1420 and 1350, and bands at 1315, 1270, 1265, 1210, 1180, 1150, 1095, 990, 960, 940, 895, 732, 690, 560, and 525 cm^{-1}; nmr (20% in CCl_4) δ 5.9–6.6 (6-line unsym, 2, **CH**=CHCOOH), 7.65 (q, 1, $J_{HH} = 11$, $J_{HF} = 16$ Hz, CF_2**CH**=CH), 12.23 (s, 1, COO**H**). **8** sublimed at 90° (9 mm). Recrystallization from benzene and from cyclohexane containing a little benzene raised the melting point to 64–65°. No change in melting point occurred after successive recrystallizations but the mother liquors gave lower mixture melting points. Titration in 50% aqueous ethanol solution gave an equivalence point at pH 6.4.

Anal. Calcd for $C_7H_4F_6O_2$: C, 35.81; H, 1.77; neut equiv, 234.1. Found: C, 35.81; H, 1.77; neut equiv, 232 ± 1.

Alternate Methods of Dehydrohalogenation.—4 [$R_F = CF_3$-$(CF_2)_2$–] (9.3 g, 0.024 mol) was added to a solution of sodium methoxide (4.5 g, 0.079 mol) in 55 ml of methanol at 45°. The temperature rose to 50° and a white solid precipitated. The mixture was heated on a steam bath at 67° for 6 hr. A yellow solution and precipitate were obtained in contrast to the colorless solution and white precipitate obtained by portionwise addition of $NaOCH_3$ (see above). The reaction mixture was worked up as above, and the solid acid was obtained as a low melting point mixture: wt 5.7 g (100%); ir ν CH=C 3090, COOH 3000–2800 (also 2720, 2680, 2620, and 2550), ν C=O 1700 (somewhat broadened), ν C=C 1625, and bands at 1410, 1350, 1320, 1275, 1250, 1220, 1180, 1150, 1095, 1035, 985, 960, 940, 890, 730, and 685 cm^{-1}. Fractional crystallization in ligroine gave a series of fractions of increasing melting point, from 45–50° to 127–135°, without achieving clean separation of products.

5,6,6,7,7,8,8,8-Octafluoro-*trans,trans*-2,4-octadienoic Acid (8, $R_F' = CF_3CF_2CF_2$).—4 [$R_F = CF_3(CF_2)_3$–] (19.3 g, 0.045 mol) was added to a solution of 8.4 g (0.15 mol) of KOH in 100 ml of 90% aqueous ethanol and heated at 70° for 20 hr. The mixture was acidified at 10° with 15 ml of concentrated hydrochloric acid, extracted into chloroform, and dried over $MgSO_4$. A dark red mixture distilled, bp 87–120° (13 mm), 12.2 g (95%). A portion of the solid (3.6 g) in 25 ml of CCl_4 was decolorized with carbon, cooled to 10°, and gave 1.1 g, mp 69–70°; recrystallization twice gave mp 73–74°. A reaction mixture of **4** (13.0 g, 0.030 mol) and KOH (3.34 g, 0.0595 mol) in 90% ethanol (50 ml) kept at 70° for 24 hr was acidified and extracted into ether and benzene (30 ml each time) and then rinsed with aqueous sodium sulfite solution (10 ml). Evaporation of solvent gave colorless **8**, 9.1 g (100%), mp 68–70°; recrystallization from ligroine (bp 60–90°) raised the melting point to 72–73°. Titration in 50% aqueous ethanol gave an equivalence point at pH 6.4: ir (10% in CCl_4) bonded COOH 3300–2800, ν CH 3100, 3050, 3000, and 2940, (also weak bands at 2680, 2630, and 2560), ν C=O 1705, ν CH=CH 1675 and 1630, δ CH 1420, 1360, and 1330, and bands at 1280, 1260, 1240, 1220, 1190, 1130, 1065, 1040 (d), 990, 945, 915, 895, and 735 cm^{-1}; nmr (20% CCl_4) δ 6.0–6.8 (6-line multiplet, 2, unresolved, **CH**=CHCOOH), 7.7 (q, 1, $J_{HH} = 11$, $J_{HF} = 16$ Hz, CF=**CH**), 12.35 (s, 1, COO**H**).

Anal. Calcd for $C_8F_8H_4O_2$: C, 33.82; H, 1.42; neut equiv, 284.1. Found: C, 33.39; H, 1.46; neut equiv, 286.5.

Mixture of 5 and 8 from 4 [$R_F = CF_3(CF_2)_3$–].—4 [$R_F = CF_3$-$(CF_2)_3$–] (8.65 g, 0.0200 mol), KOH (1.121 g, 0.0200 mol), and 90% ethanol (16.7 ml) kept at 70° for 24 hr became progressively darker red in color and acidic. The mixture was worked up as above and became colorless when the benzene–ether solution was rinsed with dilute sulfite solution. Evaporation of the solvent gave **4**, **5**, and **8**, 5.7 g (94%, crude). Recrystallization three times from ligroin (bp 60–90°) gave **5** and **8**, mp 52–53°, 2.6 g, and the melting point did not change when subsequently recrystallized twice from CCl_4. The ligroin filtrates were used below for esterification, and in a separate experiment the recrystallized acid mixture was also converted to ethyl esters. An infrared spectrum of the mixture clearly indicated **5** and **8** (ν C=C 1675, 1660, and 1625 cm^{-1}); nmr δ 3.1 (6-line multiplet, 1.33, $J_{HF} = 18$, $J_{HH} = 8$ Hz, CF_2**CH_2** of **5**), 6.0–6.6 (6-line multiplet, 1.33, **CH**=CHCOOH of **8**), 6.8–7.4 (5-line multiplet, 0.66, **CH**=CHCOOH of **5**), 7.7 (q, 0.43, $J_{HF} = 28$, $J_{HH} = 11$ Hz, CF=**CH** of **8**), 12.4 (s, 1, COOH of **5** and **8**).

The mixture of **5** and **8**, mp 52–53° (0.80 g, 0.0027 mol), ethanol (5.0 ml), benzene (2.0 ml), and 1 drop of sulfuric acid was refluxed, the azeotrope removed during 8 hr, and the product worked up. The ethyl ester mixture (0.55 g) was analyzed by glpc on 10 ft × 0.25 in. Carbowax 20M (10% on Chromosorb W) and on Apiezon M (20% on Chromosorb W) columns at 130°, with 15-psi helium carrier gas. **9** [$R_F = CF_3(CF_2)_3$–] eluted at 23.8 min, 57.3% (ir matched, see below), and **10** [$R_F' = CF_3(CF_2)_2$–] eluted at 26.2 min, 37.5% (ir matched, see below).

Ethyl 5,5,6,6,7,7,7-Nonafluoro-*cis*- and -*trans*-2-octenoates.—Similarly, the ligroin filtrate (above) was converted to ethyl esters and distilled, 3.0 g. Analysis by glpc on a 10 ft × 0.25 in. silicone oil (SE-30, 10% on Chromosorb W) column as above showed four substances: peak no. 1 at 16.5 min, 12.8%; peak no. 2 at 18.9 min, 14.4%; peak no. 3 at 23.0 min, 34.0%; peak no. 4 at 26.0 min, 39.3%. Infrared spectra confirmed that no. 3 was **9** and no. 4 was **10**. Compound of peak no. 1 showed ir (CCl_4) ν CH 3050, ν C=O 1720, ν C=C 1650, δ CH 1410, 1330, and 1300, and bands at 1240, 1220, 1190, 1170, 1140, 1115, 1065, 1035, 1015 (w), 895, 855 (w), 812, and 735 cm^{-1}. From the ν C=O and ν C=C and out-of-plane CH olefinic bending frequency at 812 cm^{-1}, this substance appeared to be the cis isomer of **9**, $CF_3(CF_2)_3CH_2CH{=}CHCOOC_2H_5$, by comparison with methyl *cis*-2-butenoate[7] (ν C=O 1721, ν C=C 1644, and γ CH=CH 812 cm^{-1}). Peak no. 2 was shown to be actually two substances by analysis on 10-ft Apiezon M and silicone oil (SF-96) columns, but insufficient material was obtained for identification.

A small quantity of ethyl 5,5,6,6,7,7,8,8,8-nonafluoro-*trans*-2-octenoate (**9**) (peak no. 3) was trapped for elemental analysis and the ir spectrum showed ν CH=C 3050, ν CH 2990, 2950, 2910, 2880, ν C=O 1730, ν C=C 1660, δ CH 1475, 1465, 1448, 1425, 1380, 1370, 1350, and 1320, ν CF 1270, 1240, and 1220, and bands at 1200, 1190, 1170, 1140, 1100, 1045, 1020, 982, 945, 932, 918, 882, 860, 835, and 690 cm^{-1}.

Anal. Calcd for $C_{10}H_9F_9O_2$: C, 35.10; H, 2.65; F, 49.98. Found: C, 35.30; H, 2.44; F, 50.30.

Ethyl 5,6,6,7,7,7-Hexafluoro-*trans,trans*-2,4-heptadienoate (10).—**8** ($R_F{}' = CF_3CF_2$–) (2.58 g, 0.011 mol), ethanol (2.3 g, 0.050 mol), benzene (30 ml), and 2 small drops of sulfuric acid were heated under reflux 5 hr, while azeotrope was removed slowly. After the usual work-up procedure **10** distilled in column A: bp 80° (20 mm); $n^{25}D$ 1.3980; 2.05 g (78%); ir (CCl_4 solution or film on KBr) ν CH=C, 3095 and 3050, ν CH 3000, 2950, 2925, and 2880, ν C=O 1725, ν C=C 1675 and 1620, δ CH_3 1475 and 1360, δ CH_2 1450, 1440, and 1320, ν CF 1290, 1265, 1240, and 1215, and bands at 1170, 1140, 1095, 1045, 995, 985, 890, 865, 812, 790, 770, and 740 cm^{-1}; nmr (neat) δ 1.24 (t, 3, J = 7 Hz, CH_3), 4.21 (q, 2, J = 7 Hz, CH_2CH_3), 6.0–6.8 (6-line multiplet, 2, unresolved CH=CH), 7.5 (q, 1, J_{HH} = 11, J_{HF} = 16 Hz, CF=CH). Glpc analysis using a 6 ft × 0.25 in. Carbowax 20M (20% on Chromosorb W) column, 135°, with 12-psi helium carrier gas gave 99% area under one peak at 8.0 min.

Anal. Calcd for $C_9F_6H_8O_2$: C, 41.23; F, 43.48; H, 3.07. Found: C, 41.17; F, 43.16; H, 3.12.

Ethyl 5,6,6,7,7,8,8,8-Octafluoro-*trans,trans*-2,4-octadienoate (10) and Its Isomer.—**8** [$R_F = CF_3(CF_2)_3$–] (6.50 g, 0.023 mol of crude sample, mp 68–70°) esterified as above gave **10**, bp 98° (33 mm), $n^{25}D$ 1.3855, 6.6 g (92%). Glpc analysis as above gave 95.3% under one peak at 7.4 min and three other substances, 0.75%, 3.2% at 4.0 min, and 0.86%: ir (CCl_4) was the same as **10** ($R_F{}' = CF_3CF_2$) to 1300 cm^{-1}, ν CF 1290, 1270, and 1240, and bands at 1190, 1160, 1140, 1120, 1100, 1060, 1040, 985, 945, 920, 890, and 732 cm^{-1}; nmr δ 1.40 (t, 3 protons, J = 7 Hz, CH_3), 4.38 (q, 2 protons, J = 7 Hz, OCH_2), 6.2–7.0 (6-line multiplet, 2 protons unresolved, CH=CHCO), 7.7 (q, 1 proton, $J_{HF} = J_{HH}$ = 11 Hz, CF=CH).

The peak at 4.0-min retention time also was trapped. An ir spectrum gave ν C=O 1720, ν C=C 1670 and 1605, δ CH 1460, 1440, and 1350, and bands at 1220, 1190, 1125, 1045, 1030, 965, and 935 cm^{-1}. Bands at 1060, 1040, 985, 945, and 890 cm^{-1} in **10** were absent. These data indicate that the second substance was an isomer of **10**, possibly ethyl 5,6,6,7,7,8,8,8-octafluoro-*cis*-2-*trans*-4-octadienoate, since the 1605-cm^{-1} band is lower in the 4.0-min peak than in the 7.4-min peak.[8] Reported values are 1642 and 1614 cm^{-1} for the trans,trans isomer and 1623 and 1587 cm^{-1} for the cis,cis isomer of hexadienoic acids.[8]

Anal. Calcd for $C_{10}H_8F_8O_2$: C, 38.47; H, 2.58. Found (**10**): C, 38.25; H, 2.51.

Table II

Rate of Iodide Elimination of 4

Time, min	$AgNO_3$, ml	% reaction	Equiv of $AgNO_3$ × 10^{-6}	$NaOH_t$ × 10^{-4}	C_t × 10^{-4} [a]
0				18.499	6.1108
15.0	0.184	18	5.5715	17.3847	4.9965
30.0	0.323	32	9.7804	16.5429	4.1547
45.0	0.423	42	12.8084	15.9373	3.5491
61.0	0.503	50	15.2308	15.4528	3.0646
77.0	0.582	58	17.6230	14.9744	2.5862
90.0	0.637	64	19.2884	14.6413	2.2531
122.5	0.723	72	21.8924	14.1205	1.7323
150.5	0.773	77	23.4064	13.8177	1.4295
255.0	0.862	86	26.1014	13.2787	0.8905

[a] C = moles of **4**.

Base-Induced Elimination of 4. Product-Rate Studies.—**4** (8.6734 g, 20.08 mmol) was added to 10 ml of 92.6% ethanol at 30.00° in a 100-ml volumetric flask, and 80.00 ml of 0.4980 N sodium hydroxide solution (39.84 mmol) was added and brought to volume at 30.00° (mole ratio 1.00:2.00). After 5 min, 200 min, 1080 min, and suitable intervals thereafter, a 5-ml aliquot was added to 25.00 ml of 0.1007 N hydrochloric acid, the separated oil extracted with three 3-ml portions of CCl_4, and the water layer titrated with 0.02810 N sodium hydroxide solution, using phenolphthalein indicator. Assuming that the amount of base used was equal to the amount of organic acid hydrolyzed, concentrations of alkali and acid remaining were calculated. A plot of log $[cpd]_t/[NaOH]_t$ *vs.* time after 200 min gave a straight line of slope 9.85 × 10^{-5}/min; k was calculated from the expression[4]

$$k = \frac{2.303}{60[\mathrm{cpd}]_0 - [\mathrm{NaOH}]_0}\left(\log\frac{[\mathrm{NaOH}]}{[\mathrm{cpd}]} + \log(\mathrm{slope})\right) = 1.91 \times 10^{-5}\ \mathrm{l.\ mol^{-1}\ sec^{-1}}$$

Titration showed that 48.3% of NaOH had been used in 5 min, 54.5% in 200 min, 67.8% in 1080 min, and 88% in 4010 min. Ir showed **4**, **5**, and a little **8** in the 5- and 200-min samples, very little **4** in subsequent samples, and a decreasing amount of **5** after 75.9% of the base had been used. **8** was the principal product after 81% reaction. The identification of **5** was based on bands at 1040, 880, and 690 cm^{-1}; **8** gave a shoulder at 1675, sharp band at 1625, and bands at 1065, 915, and 895 cm^{-1}. The ir spectra compared closely with an analogous mixture obtained in the preparative reaction above, shown to contain only **5** and **8**.

Iodide Elimination of 4. Kinetic Studies.[4,12]—**4** (0.2640 g, 0.6111 mmol) was placed in a 100-ml volumetric flask, diluted with 50 ml of 92.6% ethanol, and equilibrated at 29.90° (mole ratio 0.248:1.00). At t = 0, 5.00 ml of 0.4922 N NaOH (2.46 mmol) in 92.6% ethanol was added and diluted to 100 ml with more 92.6% ethanol. At timed intervals thereafter a 5.00-ml aliquot was placed in a 250-ml beaker containing 5 ml of 1.5 N nitric acid, 50 ml of 2 N sodium sulfate solution, and about 0.1 g of sodium bisulfite. The iodide ion was titrated with 0.03028 N silver nitrate, using a Beckman 39261 bright silver electrode *vs.* a saturated calomel. Typical data are recorded in Table II. It was found necessary to correct the initial concentration of NaOH for the amount reacted with **4** to give the carboxylate salt of **4**. The slope and intercept obtained from least-squares treatment of the data were used to calculate k as above.[4] Three separate runs were made using different standard solutions of $AgNO_3$ and NaOH. The values of k were determined as k_{I^-} = 1.146 × 10^{-2}, 1.128 × 10^{-2}, and 1.023 × 10^{-2} l. mol^{-1} sec^{-1}, indicating the degree of accuracy achieved. A typical plot of the data is given in Figure 1. It will be noted that with the large excess of base used hydrolysis of **4** occurred at a much faster rate than when only an equivalent or less of base was present.

Iodide Elimination Rates of 2-Iodooctane, 1-Iodopentane, and 1,1,1,2,2,3,3-Heptafluoro-5-iodononane.[12]—In similar fashion as with **4** the rates of hydrolysis of the title compounds were measured in 92.6% ethanol. Each gave good straight line plots for second-order rates. The data are summarized in Table I.

Elimination of 4. Fluoride Determination.—**4** (0.2306 g, 5.34 × 10^{-4} mol) was dissolved in 70 ml of 92.6% ethanol in a 100-ml volumetric flask equilibrated to 30.00°, and 5.00 ml of 0.4922 N NaOH solution was added and made up to volume. At timed intervals 5.00-ml aliquots were added to 4.00 ml of 1.5 N nitric acid and a few drops of sodium bisulfite solution in a separatory funnel and extracted twice with 5 ml of CCl_4, and the aqueous layer was rinsed out with water (total volume 10.00 ml). The samples were adjusted to pH 5.0, sodium acetate–acetic acid buffer was added, and the solutions were diluted to known volume. Fluoride concentration was measured directly by use of an Orion fluoride electrode. A calibration curve was prepared using solutions containing the same concentrations of ethanol and nitrate. Results are given in Table III. After analysis known amounts of fluoride were added to samples 2 and 5 and recovery was quantitative. However, samples taken after 75.0 min gave erratic results and the fluoride added after titration was not recovered quantitatively. This indicates that interference may have been present in these samples.

TABLE III

FLUORIDE DETERMINATION

Sample	Reaction time, min	Total fluoride, 10^{-6} mol	% reaction
1	16.0	3.42	(12.8)
2	30.0	3.53	13.2
3	45.0	4.21	15.8
4	60.2	5.47	20.5
5	75.0	10.8	40.5

3-Iodo-5,5,6,6,7,7,7-heptafluoroheptanenitrile (7).—**11** (30.0 g, 0.10 mol), **16** (3.35 g, 0.05 mol), and **15** (0.25 g, 0.0015 mol) were charged to a Fischer-Porter Aerosol tube, filled with nitrogen, evacuated three times at −78°, and sealed. The tube was heated for 15 hr at 72°. The product was fractionated in a 2-ft platinum spinning-band column. **11** (19.7 g, 0.066 mol) and **16** (1.67 g, 0.025 mol) were recovered, and **7**, bp 60° (0.60 mm), $n^{25}\mathrm{D}$ 1.4148, 8.55 g (48% conversion, 98% yield), solidified on cooling to 10°: ir (10% CCl_4) ν CH 2980 and 2950, ν C≡N 2260, δ CH 1450, 1435, 1400, 1380, 1355, and 1340, ν CF 1280–1180, and bands at 1125, 1070, 1010, 990, 965, 950, 900, 845, and 830 cm^{-1}; nmr δ 3.00 (6-line multiplet, 2, J_{HF} = 20, J_{HH} = 7 Hz, CF_2CH_2CH), 3.30 (d, 2, J = 7 Hz, $CHCH_2CN$), 4.50 (5-line multiplet, 1, J = 7 Hz, CH_2CHICH_2).

Anal. Calcd for $C_7F_7H_5NI$: C, 23.15; H, 1.39; I, 34.95. Found: C, 23.34; H, 1.47; I, 35.21.

Hydrolysis of 3-Iodo-5,5,6,6,7,7,7-heptafluoroheptanenitrile (7).—**7** (4.20 g, 0.012 mol) was added to a solution of KOH (0.822 g, 0.0146 mol) in 10.0 ml of 90% aqueous ethanol and kept at 65–70° for 7 hr. Solid separated from the orange, acidic solution in the stoppered flask. Water (10 ml) was added and benzene (three 10-ml portions) and ether (10 ml) was used to extract the organic products. The red color was removed by shaking with a dilute aqueous sodium sulfite solution. Distillation in column A gave product fractions: no. 1, bp 77° (32 mm), $n^{25}\mathrm{D}$ 1.3577, 0.80 g; no. 2, bp 82–87° (32 mm), $n^{25}\mathrm{D}$ 1.3684, 0.60 g; no. 3, hold-up pumped over, $n^{25}\mathrm{D}$ 1.4160, 0.95 g (total 95% recovery). Infrared spectra (KBr plates) showed that no. 1 contained principally 5,6,6,7,7,7-hexafluoro-*trans,trans*-2,4-heptadienenitrile (**17**): ν CH 3090, ν C≡N 2230 (conj), ν C=C 1680 and 1630, δ CH 1455, 1428, 1355, and 1340, and bands at 990, 980, 960, 950, 920, 880, 828, 810, 770, 750, 735, and 725 cm^{-1}. No. 2 contained both **17** and 5,5,6,6,7,7,8,8,8-heptafluoro-*trans*-2-heptenenitrile (**18**): ν CH 3080, 3010, and 2960, ν C≡N 2245 (m, unconj) and 2230 (w), ν C=C 1680 (w) and 1648 (ms), and bands at 982, 970, 960 (s), 920, 890 (w), 810, 800, 765, 760, 755, 730, 655, 635, 545, and 530 cm^{-1}. No. 3 showed only conjugated C=CCN, ν C≡N 2230 (m), ν C=C 1648 (m), and bands at 965 (m), 760 (w), 740 (m), and 730 cm^{-1}. Glpc analysis was done using a 10 ft × 0.25 in. Apiezon M column (20% on Chromosorb W), operated at 160° with 15-psi helium carrier gas. Cut no. 1 eluted 70.3% of **17** at 4.2 min, 6.1% at 5.0 min, and 22.0% of **18** at 5.5 min. Cut no. 2 eluted 28.0% of **17** at 4.2 min, 50.4% of **18** at 5.5 min, and 16.2% of **7** at 17.0 min. Cut no. 3 eluted 2.68% of **17** at 4.2 min, 19.1% of **18** at 5.5 min, and 5 peaks from 17 to 46.8 min. Taken together these results indicate that cut no. 1 was mostly **17** and **18**; cut no. 2 contained some **17**, mostly **18**, and some **7**; and cut no. 3 was a mixture of a little **17**, some **18**, **7**, and several unidentified higher boiling substances.

Registry No.—**1** (m = 2; R_F = $CF_3(CF_2)_2$), 29370-66-9; **4** (R_F = $CF_3(CF_2)_2$), 2093-44-9; **4** (R_F = $CF_3(CF_2)_3$), 29260-81-9; **5** (R_F = $CF_3(CF_2)_2$), 29260-82-0; **7** (R_F = $CF_3(CF_2)_2$), 2357-48-4; **8** (R_F' = CF_3CF_2), 29260-84-2; **8** (R_F' = $CF_3(CF_2)_2$), 29260-85-3; **8** (R_F = CF_3CF_2) ethyl ester, 29260-86-4; **9**, 29260-87-5; *cis*-**9**, 29260-88-6; **10**, 29260-89-7; *cis,trans*-**10**, 29370-67-0; **17** (R_F = CF_3CF_2), 29370-68-1; **18** (R_F = $CF_3(CF_2)_2$), 29260-90-0; *cis*-6,6,7,7,8,8,8-heptafluorooct-4-enoic acid, 29260-91-1; *trans*-6,6,7,7,8,8,8-heptafluorooct-4-enoic acid, 29260-92-2.

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Sulfoxide–Carbodiimide Reactions. X.[1] Further Studies on the Mechanism of the Oxidation Reaction

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Several new pieces of evidence concerning the course of the DMSO–DCC oxidation reaction have been considered and have led to some modification of the previously proposed mechanism. By nmr studies it has been shown that, in the absence of an alcohol, the initial DMSO–DCC adduct **1** is formed in very low equilibrium concentrations. During oxidation of an alcohol using DMSO-d_6 the resulting dicyclohexylurea is found to contain one atom of deuterium. This had led to the conclusion that the abstraction of the $-SCH_3$ proton leading to the oxysulfonium ylide **3** occurs *via* an intramolecular mechanism involving either an ionic or a tetracovalent sulfur intermediate.

Previous work from this laboratory has demonstrated that efficient oxidation of primary and secondary alcohols to the corresponding aldehydes and ketones can be achieved under mild conditions through reaction with dimethyl sulfoxide (DMSO) and dicyclohexylcarbodiimide (DCC) in the presence of an appropriate proton source.[2,3] These same reagents also effect interesting, mechanistically related reactions with phenols,[4] enols,[5] oximes,[6] and a variety of other nucleophilic nitrogenous functional groups.[7]

The mechanism originally proposed[2a] for the oxidation of alcohols is outlined in Scheme I below and both the initial formation of the DMSO–DCC adduct **1** and the intramolecular nature of the proton abstraction step *via* the oxysulfonium ylide **3** have been confirmed by isotope experiments.[8]

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[1] For part IX, see U. Brodbeck and J. G. Moffatt, *J. Org. Chem.*, **35**, 3552 (1970).

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