Reactions of Fluoroalkyl Radicals Generated Electrochemically. Part 1. Additions of Trifluoromethyl Radicals to Olefinic and Acetylenic Bonds

By **Christopher J. Brookes, Paul L. Coe, Alan E. Pedler,** * and **John Colin Tatlow,** Chemistry Department, University of Birmingham, P.O. Box 363, Birmingham B15 2TT

Trifluoromethyl radicals, generated by the electrolysis of trifluoroacetic acid in acetonitrile–water–sodium hydroxide reacted with olefins $CH_2=CHX$ ($X = C_3H_7$. C_4H_9. C_5H_{11}. CO_2CH_3. CN. and $CH_2CO_2CH_3$) to give a mixture of products of the type $CF_3CH_2CH_2X$. $CF_3CH=CHX$. $CF_3CH_2CH(CF_3)X$. and $(CF_3CH_2CHX)_2$. Where $X = CO_2CH_3$ trimeric products were also isolated. With hex-1-yne. electrolysis of trifluoroacetic acid gave a mixture of Z- and E-$CF_3CH=CHC_4H_9$ and E-$CF_3CH=C(CF_3)C_4H_9$. In contrast cyclopentene produced only cyclopentyl trifluoro-acetates.

IN a preliminary note [1] we summarised our studies of the reactions with alkenes of trifluoromethyl radicals generated electrochemically. There are many reports [2] of the additions to a wide variety of alkenes of fluoroalkyl radicals generated thermally or photochemically. However, prior to our earlier note there had been no recorded examples of the use in addition reactions of such radicals electrolytically generated. Subsequently, a report [3] has appeared of some electrochemical reactions involving alkenes and fluoro-acids, which complements those we now describe.

There have been many examples of the formation of fluoroalkyl radicals by electrochemical methods,[4] usually involving the production of dimeric products in the classical Kolbe manner. The reactions of hydrocarbon radicals generated electrochemically with alkenes and dienes,[5] and more recently, electro-deficient alkenes [6] (*e.g.* methyl acrylate) have also been described, leading to the formation of various addition products as well as more complex oligomeric compounds. The present work describes the products arising from the addition of trifluoromethyl radicals to a range of alkenes, resulting in the formation of some novel trifluoromethyl-substituted compounds.

The addition of trifluoromethyl radicals followed essentially the same course with all the linear terminal alkenes and we shall discuss in detail only the reaction with pent-1-ene. Trifluoroacetic acid was electrolysed, using approximately constant current conditions and platinum electrodes in acetonitrile–water containing a little sodium hydroxide in the presence of pent-1-ene (200 mmol). A complex mixture of products was obtained which contained four major components (separated by preparative scale g.l.c.), and a large number of minor products. The most volatile of the major products was the known [7] 1,1,1-trifluorohexane,

[1] C. J. Brookes, P. L. Coe, D. M. Owen, A. E. Pedler, and J. C. Tatlow, *J.C.S. Chem. Comm.*, 1974, 322.

[2] R. N. Haszeldine, *J. Chem. Soc.*, 1949, 2856; R. N. Haszeldine and B. R. Steele, *ibid.*, 1953, 1199: C. Walling, ' Free Radicals in Solution ', J. Wiley and Sons, New York, 1957, p. 251; N. O. Brace, *J. Org. Chem.* 1962, **27**, 4491; K. Leedham and R. N. Haszeldine, *J. Chem. Soc.*, 1954, 1634; D. S. Ashton, J. M. Tedder, and J. C. Walton, *ibid.*, 1974, 299 and references therein.

[3] R. N. Renaud and P. J. Champagne, *Canad. J. Chem.*, 1975, **53**, 529.

[4] F. Swarts, *Bull. Sci. Acad. Roy. Belg.*, 1931, **17**, 27; 1933, **42**, 102; A. I. Levin, O. N. Chechina, and S. V. Sokalov, *Zhur. obshchei Khim.*, 1965, **35**, 1776: A. I. Levin, S. V. Sokalov, O. N. Chechina, and K. I. Bil'dinov, *ibid.*, 1969. **39**, 413; V. V. Berenblit, V. I. Grachev, D. S. Rondarev, R. M. Ryazanova, and and S. V. Sokalov, *Zhur. Vseroyuz. Khim. obshch. im D. T. Mendeleeva*, 1970, **15**, 575: M. S. Toy, *J. Electrochem. Soc.*, 1967, **114**, 1042; D. E. Sullivan and R. N. Renaud, *Canad. J. Chem.*, 1973, **51**, 772.

[5] H. Schafer and R. Pistorius, *Angew. Chem. Internat. Edn.*, 1972, **11**, 841.

[6] M. Chkir and D. Lelandais, *Chem. Comm.*, 1971, 1369.

[7] J. H. Atherton and R. Fields, *J. Chem. Soc. (C).* 1967, 1450.

characterized by elemental analysis, mass spectrometry, and ^{19}F and [1]H n.m.r. spectroscopy, all of which were consistent with the proposed structure and in agreement with literature values. The second two products could not be separated by preparative scale g.l.c. Elemental analysis of the mixture was consistent with the empirical formula $C_6H_9F_3$, confirmed by mass spectrometry (which showed a peak at 138). There was an absorption at 1 679 cm^{-1} in the i.r. spectrum ($\rangle$C=C$\langle$). The [19]F n.m.r. spectrum showed four signals, two with triplet splitting (J 10.4 Hz) and two more complex signals; these we ascribe to the presence of two pairs of E- and Z-isomers. The ^{1}H spectrum contained a band at δ 2.7 which was a doublet of quartets (J 7 and 10.5 Hz); a similar signal was found [8] in compounds obtained from the decomposition of perfluoroalkylcopper compounds in the presence of terminal alkenes, and was shown to be due to the grouping CF_3CH_2–CH=CH–. The remaining n.m.r. data were consistent with the mixture consisting of two pairs of trifluoromethyl substituted alkenes differing in the position of the double bond (this was confirmed for the products from hex-1-ene by hydrogenation studies, which gave only a single product, $viz.$ 1,1,1-trifluoroheptane). Thus the mixture consisted of E/Z-1,1,1-trifluorohex-2-ene (A) and E/Z-1,1,1-trifluorohex-3-ene (B). Integration of the n.m.r. signals in either the ^{19}F or ^{1}H spectrum suggested the ratio A : B = 2 : 1 (closer to 1 : 1 in the products from hex- and hept-1-ene). The assignment of signals to the individual E- and Z-isomers was tentatively made on the basis of the chemical shifts for the trifluoromethyl signals. From the reaction of CF$_3$ radicals with methyl vinylacetate (see below) we isolated a compound identified as E-methyl 5,5,5-trifluoropent-3-enoate, with the $trans$-configuration, since the olefinic protons formed an AB system in the [1]H n.m.r. spectrum, J 16 Hz typical for a $trans$-system (cis J_{HH} 4—9 Hz). The chemical shift for the fluorine signal in this compound was ϕ 65.2 p.p.m. (ddt, J 6.4, 2.1, 2.1 Hz). From the splitting of two of the fluorine signals at ϕ 64.8 and 58.9 p.p.m. in the mixture of alkenes obtained for pent-1-ene we could assign both these to the 2-ene. Provided that the shielding of the trifluoromethyl group is generally greater in $trans$ than in cis-alkenes we can then assign the former signal to the $trans$ and the latter to the cis-compound. This argument may be extended to the 3-alkenes and the remaining 1,1,1-trifluoromethyl-2-alkenes derived from the other substrates, $i.e.$ the compound containing the trifluoromethyl group with the larger chemical shift is the $trans$-form.

The fourth and principal component isolated was shown by elemental analysis and mass spectrometry to have the empirical formula $C_{12}H_{20}F_6$ with no unsaturation (i.r. spectroscopy). N.m.r. spectroscopy was consistent with the structure 4,5-bis-(2,2,2-trifluoroethyl)octane, a dimeric product.

Structurally analogous products were obtained from

hex-1-ene and hept-1-ene, although with both these an additional compound was also isolated, which was shown by analytical and spectrometric methods to contain two trifluoromethyl groups. [19]F N.m.r. spectroscopy gave peaks for two trifluoromethyl groups in the intensity ratio 1 : 1, one with a triplet of doublets coupling pattern (J_t 10.7, J_d 2.3 Hz), the other a simple doublet (J_d 8.4 Hz). Together with the [1]H n.m.r. spectrum this indicated that the products were 1,1,1-trifluoro-3-(trifluoromethyl)heptane and 1,1,1-trifluoro-3-(trifluoromethyl)octane respectively.

We next investigated the reaction of cyclopentene under the same conditions. A mixture was obtained containing two major components in the ratio 3 : 2. The first was identified as the known [9] cyclopentyl trifluoroacetate. The second, which analysed correctly for a cyclopentenyl trifluoroacetate, showed a C=C stretching band in the i.r. spectrum and a [1]H n.m.r. spectrum containing a signal due to two identical vinylic protons, and a set of signals due to an AA'BB'X system (analysed as an ABX spectrum). This is consistent only with cyclopent-3-enyl trifluoroacetate.

From the electrolysis of trifluoroacetic acid in the presence of an excess of methyl acrylate, three major components were obtained together with much polymeric material. The most volatile compound isolated was shown to have the empirical formula $C_5H_7F_3O_2$ with a strong carbonyl absorption in the i.r. spectrum but no other unsaturation indicated. [19]F N.m.r. spectroscopy showed an absorption due to a CF$_3$ group at ϕ 66.0 J 10 Hz) with a [1]H n.m.r. spectrum consistent with the presence of an ester group (CO$_2$CH$_3$) and two contiguous CH$_2$ groups, one of which was adjacent to the trifluoromethyl group. These data indicated that the product is methyl 4,4,4-trifluorobutyrate. The second compound obtained crystallized with time and after recrystallization was shown to have the empirical formula $C_{10}H_{12}F_6O_4$ (chemical analysis). The i.r. spectrum showed a carbonyl absorption at 1 740 cm^{-1} with no other unsaturation. The [19]F n.m.r. spectrum of the crystallized material showed two triplet signals in the ratio 7 : 3 at ϕ 66.32 and 66.37 (both J 9.9 Hz): the uncrystallized material showed the same signals but in the ratio 1 : 1. The proton spectrum showed a signal typical of a methoxy-group, and a series of signals ascribed to CH$_2$–CH. These results are consistent with the product being a mixture of ($\pm$)- and $meso$-dimethyl 2,3-bis-(2,2,2-trifluoroethyl)succinate. The 1 : 1 ratio of isomers in the unrecrystallized mixture was subsequently confirmed by g.l.c.[10] The structure of the ester was confirmed by hydrolysis to the corresponding acid. The third component was also a solid, the analysis and spectra of which suggested it was a mixture of the isomers of dimethyl 3-carboxymethyl-2,5-bis-(2,2,2-trifluoroethyl)adipate. This product incorporates three methyl acrylate residues representing the commencement of a polymerization sequence.

[8] P. L. Coe and N. E. Milner, $J.$ $Organometallic$ $Chem.$, 1972, **39**, 395.

[9] U.S.P. 2,858,331 and B.P. 776,073.
[10] G. M. Bruce and A. E. Pedler, unpublished observations.

In an attempt to reduce the proportion of high polymer, the electrolysis was repeated using an excess of trifluoroacetic acid: the amount of polymer was, in fact, considerably reduced by this, although the yield of the other products was not significantly changed. However an additional product was isolated in low yield. Elemental analysis and mass spectrometry gave an empirical formula $C_6H_6F_6O_2$ with a carbonyl absorption at 1 760 cm^{-1} (i.r. spectroscopy), typical of an ester. The ^{19}F n.m.r. spectrum showed the presence of two CF_3 groups in the ratio 1 : 1, one with triplet, the other with doublet, splitting suggesting the presence of CF_3CH_2 and CF_3CH. The ^{1}H spectrum showed a signal at δ 3.86 (MeO) and a series of signals δ 3.65—2.24 (CH_2–CH) in the ratio 1 : 1. These data suggest the compound to be methyl 4,4,4-trifluoro-2-trifluoromethyl-butyrate. A sample of the mixture of ($\pm$)- and meso-dimethyl 2,3-bis-(2,2,2-trifluoroethyl)succinate isomers obtained from this reaction was recrystallized from petroleum to afford a pure sample of one of the isomers (n.m.r. spectroscopy), which on hydrolysis with aqueous KOH gave one of the isomers of 2,3-bis-(2,2,2-trifluoro-ethyl)succinic acid.

Electrolysis of trifluoroacetic acid in the presence of acrylonitrile gave a mixture containing two principal constituents. The most volatile of these was shown to be 4,4,4-trifluoro-2-trifluoromethylbutyronitrile by the usual techniques and the second, a crystalline solid, was 2,3-bis-(2,2,2-trifluoroethyl)succinonitrile. The ^{19}F n.m.r. spectrum of the recrystallized succinonitrile contained two signals, both triplets (J ca. 10 Hz) at ϕ 64.85 and 64.97 due to the presence of ($\pm$)- and meso-isomers. From the intensity ratios of the signals in the re-crystallized mixture and the residue recovered from the mother liquors, the isomer ratio in the succinonitrile as formed was 1.6 : 1. The structure of the nitrile was confirmed by hydrolysis to 2,3-bis-(2,2,2-trifluoroethyl)-succinic acid (with a correct analysis and i.r. and ^{19}F and ^{1}H n.m.r. spectra). The ^{19}F n.m.r. spectrum contained two triplet (J ca. 11 Hz) signals at ϕ 65.00 and 65.08, in the ratio 1.2 : 1, ascribed to the presence of ($\pm$)- and meso-isomers. The spectral data for the single isomer of the succinic acid obtained earlier by hydrolysis of dimethyl 2,3-bis-(2,2,2-trifluoroethyl)succinate were consistent with those of the isomer mixture.

The electrolysis was carried out also in the presence of methyl vinylacetate. Even using a large excess of trifluoroacetic acid there was a high yield of polymer (and consequently a lower yield of volatile products). Four principal products were isolated: the first of these was shown by elemental analysis to have the empirical formula $C_6H_9F_3O_2$, and ^{19}F and ^{1}H n.m.r. spectroscopy confirmed the structure as methyl 5,5,5-trifluoro-pentanoate. The empirical formula of the second compound isolated was $C_6H_7F_3O_2$ and the i.r. spectrum showed a carbonyl absorption at 1 740 cm^{-1} and C=C absorption at 1 685 cm^{-1}. The ^{19}F n.m.r. spectrum showed the presence of a CF_3 group at ϕ 65.2, with con-siderable spin–spin coupling. The ^{1}H spectrum showed
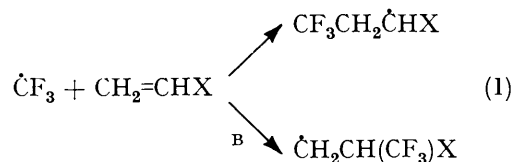
bands at δ 3.19, 3.75, and an AB system at δ 5.84 and 6.55 (J_{AB} 15.2 Hz) attributable to =CH–CH_2CO$_2$CH$_3$, OCH$_3$ and trans CH=CH, respectively from a consider-ation of coupling patterns and coupling constants (J_{cis} 4—9, J_{trans} 13—16 Hz [11]). Thus the compound was identified as E-methyl 5,5,5-trifluoropent-3-enoate.

The third component was shown to be an isomer of this by chemical analysis. The ^{19}F n.m.r. spectrum indicated a CF_3 group adjacent to a CH_2 group, since it showed the expected triplet splitting with a coupling constant of 10.5 Hz, similar to that found in 1,1,1-tri-fluorohex-2-ene. The ^{1}H spectrum was consistent with this and indicated that the compound contained an E-CH=CH arrangement (J_{AB} 16 Hz in an AB system), as well as a signal due to CH_2 and OCH$_3$, so identifying the compound as E-methyl 5,5,5-trifluoropent-2-enoate.

The less volatile fractions of the reaction mixture afforded a crystalline solid, identified by the usual methods as a dimeric product with the structure di-methyl 3,4-bis-(2,2,2-trifluoroethyl)adipate.

It was demonstrated finally that the scope of these reactions could be extended to include alkynes as sub-strates. Using hex-1-yne, however, a large number of products were formed, only two being present in sig-nificant amounts. The first was shown by elemental analysis, and i.r. and n.m.r. spectroscopy to be a mixture of E- and Z-1,1,1-trifluorohept-2-ene in the ratio 1 : 4, with a ^{19}F n.m.r. spectrum identical with that of a similar mixture obtained from the products of hex-1-ene and trifluoroacetic acid. The structure was confirmed by hydrogenation to the known 1,1,1-trifluoroheptane, identified by i.r. spectroscopy. The second product isolated from reaction with hex-1-yne was shown to be 1,1,1-trifluoro-3-(trifluoromethyl)hept-2-ene with a correct elemental analysis and consistent i.r. spectrum. The ^{19}F n.m.r. spectrum showed two fluorine signals, ratio 1 : 1 at ϕ 58.8 and 63.8 with a splitting pattern consistent with the proposed structure, and a correct ^{1}H n.m.r. spectrum.

The formation of the products of reactions of trifluoro-methyl radicals with alkenes and hex-1-yne may be readily understood in terms of radical addition, dimeriz-ation, hydrogen atom abstraction, and anodic oxidation reactions. Trifluoromethyl radicals, generated by anodic oxidation of trifluoroacetate ions may, in addition to dimerizing in the normal Kolbe manner, react with the double bond of the alkene in two ways [(1) A and B]

$$\dot{C}F_3 + CH_2{=}CHX \begin{array}{c} \nearrow \quad CF_3CH_2\dot{C}HX \\ \\ {}_B\searrow \quad \dot{C}H_2CH(CF_3)X \end{array} \quad (1)$$

In the gas phase (A) is preferred [2] since the more stable secondary radical results, and it seems that similar considerations apply here. Thus we isolated no branched-chain monosubstituted products consistent

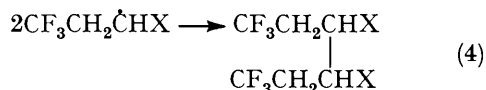[11] T. Schaefer, Canad. J. Chem., 1962, **40**, 1.

with route (1B) (*e.g.* 2-trifluoromethylheptane) from any reaction. Though not all our products were identified it seems clear that compounds arising from route (1B) can be present in small proportions only, if at all. The radical formed in (A) may now undergo one of several reactions: (i) abstraction of hydrogen atom either from solvent or monomer, reaction (2), leading to the
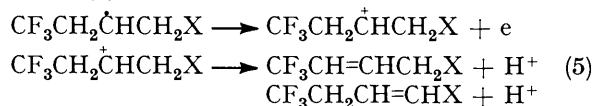
$$CF_3CH_2CHX + RH \longrightarrow CF_2CH_2CH_2X + \dot{R} \quad (2)$$

$$RH = \text{monomer or solvent}$$
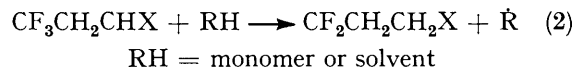
formation of saturated products; (ii) further reaction with a second trifluoromethyl radical as in reaction (3);

$$CF_3CH_2\dot{C}HX + \dot{C}F_3 \longrightarrow CF_3CH_2CH(CF_3)X \quad (3)$$

or (iii) dimerization according to reaction (4).

$$2CF_3CH_2\dot{C}HX \longrightarrow \begin{array}{c} CF_3CH_2CHX \\ | \\ CF_3CH_2CHX \end{array} \quad (4)$$

Additional products from the reaction are 2- and (where possible) 3-enes. These may arise by transfer of a hydrogen atom to a suitable receptor or by radical disproportionation, although we regard the latter as unlikely to be a significant contributor to alkene formation in view of the failure to identify the presence of alkenes in the products from acrylonitrile and methyl acrylate. We believe a more probable reaction to be further electrochemical oxidation of the radical formed in (1) to a carbonium ion followed by loss of a hydrogen ion as in (5):

$$CF_3CH_2\dot{C}HCH_2X \longrightarrow CF_3CH_2\overset{+}{C}HCH_2X + e$$
$$CF_3CH_2\overset{+}{C}HCH_2X \longrightarrow CF_3CH=CHCH_2X + H^+ \quad (5)$$
$$CF_3CH_2CH=CHX + H^+$$

Further oxidation of radical intermediates formed in Kolbe-type reactions has been suggested previously, provided that the ionization potential of the radical is below *ca.* 8 eV.[12] This process is in competition with the normal dimerization of the radicals. Thus the products obtained from the reaction of acetic acid with 3,3-dimethylbut-1-ene under electrolytic conditions are best explained in terms of a carbonium-ion intermediate.[13] Although we isolate alkenes from the reaction with straight-chain alk-1-enes and methyl vinylacetate, albeit in only low yield, we have been unable to isolate any unsaturated compounds when using acrylonitrile and methyl acrylate. Presumably the presence of an electron-withdrawing group (CN or CO$_2$Me) attached directly to the free-radical centre of the intermediate from process (1A) renders further oxidation to a carbonium ion unlikely. Alternatively greater radical stability in the intermediates from acrylonitrile and methyl acrylate (leading to an increased probability of dimerization) may be ascribed to resonance stabilization of the unpaired electron with the unsaturated polar systems.

Finally, the reaction in the presence of cyclopentene affords no products arising from addition of trifluoro-

methyl radicals, but two products, both trifluoroacetate esters which we suggest are formed as a result of oxidation of cyclopentene itself. The first, cyclopentyl trifluoroacetate could then be formed according to reactions
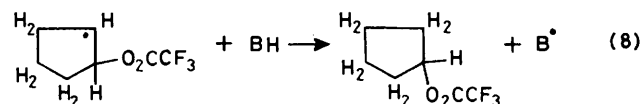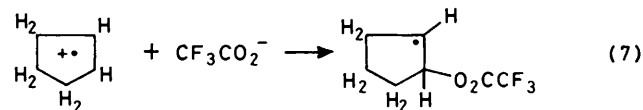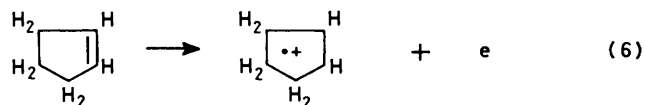
(6)—(8). The second compound was identified as cyclopent-3-enyl trifluoroacetate, but it is difficult to suggest a mechanism to account for the formation of this.

EXPERIMENTAL

Electrolyses were carried out under constant current conditions at 0 °C in a four-necked flask (140 cm³) fitted with a magnetic stirrer, two platinum electrodes (2.5 × 2.5 cm), and a reflux condenser, the outlet of which was connected to a trap cooled in liquid air. The cathode was enclosed in dialysis tubing (Visking 32/32; The Scientific Instrument Centre Ltd.) so that the apparatus functioned as a divided cell.

N.m.r. spectra were measured on Varian HA 100, Perkin-Elmer R10, and R12 n.m.r. spectrometers, with the samples in CCl$_4$ (unless otherwise stated). ^{1}H Chemical shifts are reported in δ values (p.p.m. from tetramethylsilane internal standard) and ^{19}F chemical shifts in ϕ values (p.p.m. from chlorotrifluoromethane internal standard). I.r. spectra were recorded on a Perkin-Elmer 257 i.r. spectrophotometer.

G.l.c. was carried out using a Pye 104 gas chromatograph with nitrogen as carrier gas and a flame-ionization detector using the following columns and stationary phrases: column A, 9.1 m × 7 mm i.d., Carbowax 6000 : Chromosorb P = 1 : 5; column B, 9.1 m × 7 mm i.d., polyethyleneglycol adipate : Chromosorb P = 1 : 6; column C, 9.1 m × 7 mm i.d., Ucon LB550X : Chromosorb P = 1 : 4; column D, 9.1 m × 7 mm i.d., silicone gum SE 30 : Universal B = 1 : 40.

General Procedure.—To a mixture of acetonitrile (40 cm³) and water (5.6 cm³) was added the substrate, trifluoroacetic acid, and sodium hydroxide; the mixture was electrolysed at 0 °C. After electrolysis the mixture was poured into water (100 cm³) and the aqueous solution extracted with ether (4 × 70 cm³). The ethereal extracts were washed

[12] L. Eberson, *Acta. Chem. Scand.*, 1963, **17**, 2004; H. R. Weinberg and N. L. Weinberg, *Chem. Rev.*, 1968, **449**.
[13] W. B. Smith and Y. Hyon Yuh, *Tetrahedron*, 1968, **24**, 463.

with sodium hydrogen carbonate solution (7% w/v; 3 × 50 cm³) and water (4 × 50 cm³), and then dried (MgSO₄) and the ether distilled off. The residue was then separated by distillation and preparative scale g.l.c. into components.

Pent-1-ene.—Trifluoroacetic acid (22.8 g), sodium hydroxide (0.4 g), and pent-1-ene (14.0 g) were electrolysed at 0.7—1.0 A for 9 h to afford a residue (19.2 g) which was fractionally distilled to give six fractions.

Fraction (I) (2.3 g), b.p. 34—72 °C, was shown by g.l.c. to be principally ether. A portion (1.13 g) of fraction (II) (2.7 g), b.p. 72—78 °C, was separated (g.l.c., column A; 65 °C; N₂ 6.5 l/h) into (*a*) ether (trace), (*b*) 1,1,1-trifluoro-hexane (0.26 g), b.p. 69—70 °C (lit.,⁷ b.p. 70—71 °C) (Found: C, 51.4; H, 7.9; F, 40.5. Calc. for C₆H₁₁F₃: C, 51.4; H, 7.9; F, 40.7%) with a consistent ¹⁹F n.m.r. spectrum: (*c*) a mixture (0.11 g) of 1,1,1-trifluorohex-2-ene (A) and 1,1,1-trifluorohex-3-ene (B) (Found: C, 52.2; H, 6.7; F, 41.1. C₆H₉F₃ requires C, 52.2; H, 6.6; F, 41.3%); *M*⁺ 138 (required); ν_max. 2 960, 2 930, 2 875 (aliphatic CH), 1 679 (C=C), and 1 350—1 050 cm⁻¹ (CF); φ 58.9 [m, CF₃, *cis*-(A)], 64.8 [dq, *J*₁,₄ 6.5, *J*₁,₃ 2 Hz, CF₃, *trans*-(A)], 67.1 [t, *J*_HF 10.4 Hz, CF₃, *cis*-(B)], and 67.5 [t, *J*_HF 10.4 Hz, CF₃, *trans*-(B)]; integration of the fluorine signals was in the ratio 1 : 34; 3.5 : 14.5; δ 0.95 (m, CH₃), 1.50 (m, CH₃–*CH*₂–CH₂), 2.1 (m, CH=CH–*CH*₂), 2.7 (dq, *J* 7 and 10.5 Hz, CF₃–*CH*₂), and 5.6—6.3 (m, *CH=CH*); integration of the proton signals was consistent with a ratio A : B = 2 : 1.

Fraction (III) (0.4 g), b.p. 78—94 °C, and fraction (IV) (0.4 g), b.p. 30—40 °C/12 mmHg were both complex mixtures inseparable by g.l.c. A portion (0.61 g) of fraction (V) (2.9 g), b.p. 40—72 °C/12 mmHg was separated (column B; 120 °C; N₂ 6.9 l/h) to afford (*a*) a mixture (0.12 g), and (*b*) 4,5-*bis*-(2,2,2-*trifluoroethyl*)*octane* (0.25 g), b.p. 190—191 °C (Found: C, 52.1; H, 7.0; F, 41.1. C₁₂H₂₀F₆ requires C, 51.8; H, 7.2; F, 41.0%); *M*⁺, 139 (C₁₂H₂₀F₆⁺ requires 278); ν_max. 2 960, 2 875 (aliphatic CH), and 1 450—1 000 cm⁻¹ (aliphatic CF); φ 64.8 (tr, *J*_HF 10.5 Hz); δ 0.95 (3 H, complex, *CH*₃), 1.35 (4 H, broad, CH₃–*CH*₂CH₂), and 1.95 (3 H, complex m, CF₃–*CH*₂–*CH*–); and (*c*) a mixture (0.03 g) of four components. Fraction (VI) (5.2 g), b.p. 72—140 °C/12 mmHg was shown to be essentially (80%) 4,5-bis-(2,2,2-trifluoroethyl)octane by g.l.c. analysis and i.r. spectroscopy.

Hex-1-ene.—Trifluoroacetic acid (22.8 g), sodium hydroxide (0.4 g), and hex-1-ene (8.4 g) were electrolysed for 8 h, 1.0 A initially being passed, this falling steadily to 0.65 A. The residue (13.7 g) after work-up was distilled to afford six fractions. Fraction (I) (1.4 g), b.p. 34—65 °C, was shown by g.l.c. to consist of ether, acetonitrile, hex-1-ene, and traces of products present in later fractions. Of fraction (II) (3.5 g), b.p. 65—85 °C, a portion (0.46 g) was separated (g.l.c. column A; 120 °C; N₂, 6.4 l/h) to give (*a*) a mixture (0.02 g) of ether and hex-1-ene (g.l.c. retention times), (*b*) 1,1,1-*trifluoro-3-trifluoromethylheptane* (0.03 g), b.p. 126—127 °C (Found: C, 43.4; H, 5.1; F, 51.3. C₈H₁₂F₆ requires C, 43.2; H, 5.4; F, 51.3%); *M*⁺ 203 (*M* − F); ν_max. 2 960 and 2 870 (aliphatic CH) and 1 450—1 150 cm⁻¹ (CF); φ 65.7 (3 F, tr of d, *J*_HF 10.7, *J*₁,₃ 2.3 Hz, CF₃–CH₂), and 72.7 (3 F, d, *J* 8.4 Hz, CF₃–CH); δ 0.95 (3 H, CH₃), 1.45 [6 H, CH–(*CH*₂)₃–CH₃], and 2.36 [3 H, CF₃–*CH*₂–*CH*(CF₃)] all m; (*c*) 1,1,1-trifluoroheptane (0.12 g),

¹⁴ W. R. Hasek, W. S. Smith, and V. A. Engelhardt, *J. Amer. Chem. Soc.*, 1960, **82**, 543.

b.p. 100—101 °C (lit.,¹⁴ b.p. 101 °C) (Found: C, 54.8; H, 8.0; F, 37.2. Calc. for C₇H₁₃F₃: C, 54.5; H, 8.5; F, 37.0%); φ 67.9 (tr, *J* 10.6 Hz); δ 0.91 (3 H, CH₃), 1.35 [8 H, CH₃–(CH₂)₄], and 2.05 (2 H, CF₃–CH₂), all complex signals; (*d*) a mixture of 1,1,1-trifluorohept-2-ene (A) and 1,1,1-trifluorohept-3-ene (B) (0.04 g); *M*⁺ 152 (required); ν_max. 2 960, 2 930, 2 865 (aliphatic CH), 1 678 (C=C), and 1 450—1 050 cm⁻¹ (C–F); φ 59.6 [d, *J ca.* 8 Hz, *cis*-(A)], 65.3 [ddt, *J* 5.9, 2.0, and 2.0 Hz, *trans*-(A)], 67.5 [t, *J* 10.7 Hz, *cis*-(B)], and 68.0 [t, *J* 10.8 Hz, *trans*-(B)] in the ratio 1 : 29 : 10 : 35; δ 0.94 (m, CH₃), 1.43 [m, CH₃–(CH₂)ₙ–CH₂–CH=], 2.10 (m, CH=CH–CH₂–), 2.75 (ddq, *J* 6.6, 0.7, 10.6 Hz, CF₃–CH₂–CH=CH), and 5.6—6.4 (m, *CH=CH*); integration of these signals was consistent with the ratio A : B = 1 : 1.1.

Fraction (III) (1.05 g) had b.p. 30—40 °C/13 mmHg; a portion (0.41 g) was separated by g.l.c. (column A; 120 °C; N₂ 6.4 l/h) to give (*a*) 1,1,1-trifluoro-3-(trifluoromethyl)-heptane (0.11 g), (*b*) 1,1,1-trifluoroheptane (0.10 g) both identified by i.r. spectroscopy, and (*c*) a mixture (0.07 g) of 1,1,1-trifluorohept-2- and -3-ene, identified by n.m.r. spectroscopy. Fraction (IV) (1.05 g), b.p. 40—92 °C/13 mmHg was separated by g.l.c. (column B; 180 °C; N₂, 6 l/h) to afford (*a*) a mixture of components (0.24 g) and (*b*) 5,6-*bis*-(2,2,2-*trifluoroethyl*)*decane* (0.51 g), b.p. 218—219 °C (Found: C, 54.6; H, 7.6; F, 37.3. C₁₄H₂₄F₆ requires C, 54.9; H, 7.9; F, 37.2%); *M*⁺ 153 (C₁₄H₂₄F₆⁺ requires 306); ν_max. 2 960, 2 930, 2 870 (aliphatic CH), and 1 400—1 100 (CF); φ 65.5 (tr, *J*_HF 11.7 Hz); δ 0.93 (3 H, c, CH₃), 1.30 [6 H, broad, (CH₂)₃], and 1.95 (3 H, cm, CF₃–*CH*₂–*CH*). Fraction (V) (2.3 g), b.p. 94—96/13 mmHg was shown by g.l.c. and i.r. spectroscopy to be 90% 5,6-bis-(2,2,2-trifluoro-ethyl)decane and fraction (VI) (2.0 g), b.p. 96—100 °C/13 mmHg, was a mixture (g.l.c.) of this decane and other compounds, not separable by g.l.c.

Hept-1-ene.—Trifluoroacetic acid (22.8 g), sodium hydroxide (0.4 g), and hept-1-ene (19.6 g) were electrolysed for 8 h at 0.9 A. The residue (34.0 g) obtained after work-up was fractionally distilled to give two fractions and a residue. Fraction (I) was a mixture (13.7 g), b.p. 34—120 °C, of ether, acetonitrile, and hept-1-ene, together with traces of other components (analytical g.l.c.). Fraction (II) (2.05 g) had b.p. 120—124 °C; a portion (1.8 g) was separated by g.l.c. (column A; 100 °C; N₂ 5.8 l/h) to give (*a*) a mixture (0.15 g), (*b*) 1,1,1-*trifluoro-octane* (0.63 g), b.p 129—130 °C (Found: C, 57.2; H, 9.0; F, 33.8. C₈H₁₅F₃ requires C, 57.1; H, 9.0; F, 33.9%); *M*⁺ 168 (required); ν_max. 2 960, 2 920, 2 865 (aliphatic CH), and 1 450—1 000 cm⁻¹ (aliphatic CF); φ 67.2 (tr, *J*_HF 10.4 Hz); δ 0.90 (3 H, c, CH₃), 1.31 (10 H, br, CH₂), and 2.05 (2 H, cm, CF₃–CH₂), and (*c*) a mixture (0.44 g) of 1,1,1-trifluoro-oct-2-ene (A) and 1,1,1-trifluoro-oct-3-ene (B) (Found: C, 57.7; H, 8.0; F, 34.2. C₈H₁₃F₃ requires C, 57.8; H, 7.9; F, 34.3%); *M*⁺ 166 (required); ν_max. 2 960, 2 930, 2 870 (aliphatic CH), 1 675 (C=C), 1 450—1 150 cm⁻¹ (CF); φ 60.6 [d, *J ca.* 6 Hz, *cis*-(A)], 64.7 [cm, *trans*-(A)], 66.9 [tr, *J*_HF 10.7 Hz, *cis*-(B)], and 67.3 [tr, *J*_HF 10.7 Hz, *trans*-(B)] in the ratio 1 : 57 : 17 : 43; δ 0.93 (cm, CH₃), 1.39 [cm, CH₃–(CH₂)ₙ–CH₂–CH=], 2.13 [cm, (CH₂)ₙ*CH*₂–CH=], 2.78 (ddq, *J* 6.9, 0.8, 11.0 Hz, CF₃–CH₂–CH=CH), 5.6—6.5 (cm, *CH=CH*); integration of these signals was consistent with the ratio A : B = 1.2 : 1. Sub-fraction (IIa) was subsequently separated by g.l.c. (column A; 80 °C; N₂ 5.8 l/h) to afford 1,1,1-trifluoro-3-(trifluoromethyl)octane (0.07 g); ν_max. 2 960, 2 930, 2 870 (aliphatic CH), and 1 460—1 120 cm⁻¹ (CF);

ϕ 65.3 (3 F, t, J_{HF} 9.6 Hz, CF_3–CH_2) and 72.2 (3 F, distorted d, CF_3–CH); δ 0.96 (3 H, c, CH_3), 1.39 [8 H, broad, $(CH_2)_4$], and 2.34 (3 H, m, CF_3–CH_2–CH).

Further fractionation of the residue of the original product under reduced pressure (12 mmHg) gave fraction (III), a mixture (0.6 g), b.p. 30—45 °C/12 mmHg shown to contain compounds already identified and fraction (IV) (1.25 g), b.p. 50—112 °C/12 mmHg, consisting principally of 6,7-bis-(2,2,2-trifluoroethyl)dodecane (50% by g.l.c. analysis, see below). A fraction (V) (6.15 g), had b.p. 114—128 °C/12 mmHg: a portion (1.02 g) was separated by g.l.c. (column B; 180 °C; N_2 4.75 l/h) to afford (a) 6,7-bis-(2,2,2-trifluoroethyl)dodecane (0.66 g), b.p. 248—249 °C (Found: C, 57.5; H, 8.7; F, 33.8. $C_{16}H_{28}F_6$ requires C, 57.5; H, 8.4; F, 34.1%), $\nu_{max.}$ 2 960, 2 930, 2 860 (aliphatic CH), and 1 470—1 100 cm^{-1} (CF); M^+ 167 ($C_{16}H_{28}F_6^+$ requires 334); ϕ 64.8 (tr, J_{HF} 10.8 Hz); δ 0.95 (3 H, c, CH_3), 1.30 [8 H, broad, $(CH_2)_4$], and 1.95 (3 H, cm, CF_3–CH_2–CH); and (b) a mixture of compounds (0.09 g), not identified. The remainder of the original product was involatile and not further investigated.

Hydrogenation of the Mixture of E- *and* Z-1,1,1-*Trifluoro-hept*-2- *and* -3-*ene.*—A portion (0.4 g) of the title compounds (obtained from the electrolysis involving hex-1-ene) in ethanol (30 cm³) was hydrogenated (10% Pd/C, 0.1 g) at room temperature. Ether (80 cm³) was then added and the mixture washed with water (3 × 50 cm³), dried ($MgSO_4$), and the ether evaporated to leave a residue (0.65 g). A portion (0.59 g) of this was separated by g.l.c. (column A; 70 °C; N_2 6.4 l/h) to afford (i) ether (0.15 g) and (ii) 1,1,1-trifluoroheptane (0.26 g), both identified by i.r. spectroscopy.

Hex-1-*yne.*—Trifluoroacetic acid (34.2 g), hex-1-yne (8.2 g), and sodium hydroxide (0.6 g) were electrolysed for 9 h at 1.0 A. The liquid residue (18.0 g) was distilled to give two fractions. Fraction (I) (3.35 g), b.p. 34—96 °C, was a mixture of principally ether and acetonitrile. Fraction (II) (3.30 g) had b.p. 96—104 °C; a portion (1.9 g) was separated by g.l.c. (column A; 70 °C; N_2 5.6 l/h) into (a) a mixture (0.32 g) of three inseparable saturated tri-fluoromethyl-substituted compounds (n.m.r.), (b) a mixture of E- and Z-1,1,1-*trifluorohept*-2-*ene* (0.65 g), b.p. 96—97 °C (Found: C, 55.2; H, 7.1; F, 37.6. $C_7H_{11}F_3$ requires C, 55.3; H, 7.3; F, 37.5%); M^+ 152 (required); $\nu_{max.}$ 2 960, 2 930, 2 860 (aliphatic CH), 1 680 (C=C), and 1 350—1 100 cm^{-1} (CF); ϕ 59.0 (dt, J 8.2 and 2.5 Hz, cis-CF_3), 64.8 (ddt, J 6.1, 2.1, 2.0 Hz, trans-CF_3) these signals being in the ratio 1 : 4; δ 0.95 (3 H, c, CH_3), 1.40 [4 H, c, $(CH_2)_2$], 2.15 (2 H, c, =C–CH_2), and 5.6—6.3 (2 H, c, CH=CH); and (c) Z-1,1,1-*trifluoro*-3-*trifluoromethylhept*-2-*ene* (0.40 g), b.p. 122—123 °C (Found: C, 43.8; H, 4.7; F, 51.7. $C_8H_{10}F_6$ requires C, 43.6; H, 4.6; F, 51.8%); $\nu_{max.}$ 2 960, 2 940, 2 870 (aliphatic CH), 1 685 (C=C), and 1 400—1 100 cm^{-1} (CF); ϕ 58.8 (3 F, p, $J_{1,2}$ 9, $J_{1,4}$ 11 Hz, CF_3), 63.8 (3 F, q, $J_{1,4}$ 11 Hz, CF_3); δ 0.98 (3 H, m, CH_3), 1.47 [4 H, m, $(CH_2)_2$], 2.3

$$\left(2\ H,\ m,\ \begin{array}{c} F_3C \\ \diagdown \\ H \end{array} C{=}C \begin{array}{c} CF_3 \\ \diagup \\ \diagdown CH_2{-} \end{array} \right)$$ and 5.88 (1 H, trq, $J_{1,4}$ 2, $J_{1,2}$ 9 Hz).

The remainder of the volatile product (2.55 g), b.p. 40—130 °C (13 mmHg), was an inseparable mixture of components.

Hydrogenation of a Mixture of E- *and* Z-1,1,1-*Trifluoro-hept*-2-*ene.*—A sample (0.30 g) of the mixture of alkenes

obtained from the electrolysis using hex-1-yne was hydrogenated as above to leave a residue (0.45 g) which was separated by g.l.c. to give (i) ether (0.12 g) and (ii) 1,1,1-trifluoroheptane (0.19 g), both identified by i.r. spectroscopy.

Cyclopentene.—Trifluoroacetic acid (22.8 g), cyclopentene (13.6 g), and sodium hydroxide (0.4 g) were electrolysed for 9 h at a current of 1.0—0.20 A to give, after work-up, a residue (13.9 g). Distillation (in the presence of B.D.H. silicone Antifoaming A) gave two fractions. Fraction (I) (1.6 g), b.p. 34—90 °C, was a mixture of ether, cyclopentene, and acetonitrile (g.l.c.). Fraction (II) (3.2 g) had b.p. 110—140 °C; a portion (1.92 g) was separated by g.l.c. (column A; 120 °C; N_2 3.75 l/h) into (a) a mixture (0.45 g) of ether and cyclopentene (g.l.c.), (b) an unidentified mixture (0.03 g), (c) cyclopentyl trifluoroacetate (0.30 g), b.p. 127—128 °C (lit.,[9] 125—127 °C) (Found: C, 45.4; H, 4.9; F, 31.5. Calc. for $C_7H_9F_3O_2$: C, 46.2; H, 5.0; F, 31.1%); ϕ 76.12 (s, O·CO·CF_3); δ 5.36 (1 H, m, CHO·CO·CF_3) and 1.7—2.1 [8 H, m, $(CH_2)_4$]; (d) a mixture (0.30 g), and (e) an inseparable mixture of six components (0.27 g). Mixture II (d) was separated (g.l.c., column C; 130 °C; N_2 2.5 l/h) to give (i) acetonitrile (0.06 g) (i.r. spectroscopy), and (ii) *cyclopent*-3-*enyltrifluoroacetate* (0.19 g), b.p. 126—127 °C (Found: C, 46.9; H, 3.9; F, 31.5. $C_7H_7F_3O_2$ requires C, 46.7; H, 3.9; F, 31.7%); $\nu_{max.}$ 3 070 (=CH), 2 920, 2 860 (aliphatic CH), 1 775 (C=O), 1 400—1 100 cm^{-1} (CF); ϕ 76.0 (s, CF_3); δ 5.74 (2 H, br,s, olefinic H), and signals analysed as an approximate ABX system at δ_x 5.54 (1 H, tr of tr, J_{AX} 6.5, J_{BX} 3.0 Hz, tertiary H), δ_A 2.25 (2 H, J_{AB} 17.0, J_{AX} 6.5 Hz, CH_2), and δ_B 2.54 (2 H, J_{AB} 17.0, J_{BX} 3.0 Hz, CH_2). The remainder of the volatile product (5.25 g), b.p. 30—110 °C (12 mmHg), from the original residue was an inseparable complex mixture of saturated and unsaturated trifluoroacetoxy-substituted compounds.

Methyl Acrylate.—(a) *Excess of methyl acrylate.* Tri-fluoroacetic acid (11.4 g), methyl acrylate (25.8 g), and sodium hydroxide (0.2 g) were electrolysed at 1.0 A for 6.5 h. Work-up afforded a residue (34.5 g) which was distilled to give five fractions. Fraction (I) (14.3 g), b.p. 34—85 °C, was identified (g.l.c.) as a mixture of ether, acetonitrile, and methyl acrylate: fraction (II) (0.7 g), b.p. 30—40 °C (13 mmHg), was separated by g.l.c. (column C; 130 °C; N_2 3.5 l/h) into (a) an unidentified mixture (0.03 g), (b) methyl acrylate (0.10 g), (c) acetonitrile (0.17 g) (both by i.r. spectroscopy), and (d) *methyl* 4,4,4-*trifluoro-butyrate* (0.25 g), b.p. 114—115 °C (Found: C, 38.8; H, 4.2; F, 36.5. $C_5H_7F_3O_2$ requires C, 38.5; H, 4.5; F, 36.5%); $\nu_{max.}$ 3 000, 2 950, 2 850 (aliphatic CH), 1 740 (C=O), and 1 400—1 100 cm^{-1} (CF); ϕ 68.0 (tr, J_{HF} 10 Hz); δ 2.5 [4 H, c, $(CH_2)_2$], and 3.67 (3 H, s, CH_3O).

Fraction (III) (6.9 g), b.p. 110—140 °C/13 mmHg, was a solid. Recrystallization of a portion (1.0 g) from light petroleum (b.p. 60—80 °C) afforded a mixture of (±)- and meso-*dimethyl* 2,3-*bis*-(2,2,2-*trifluoroethyl*)*succinate* (0.77 g), m.p. 83—85 °C (Found: C, 38.8; H, 3.6; F, 36.9. $C_{10}H_{12}F_6O_4$ requires C, 38.7; H, 3.9; F, 36.8%); $\nu_{max.}$ 2 910, 2 840 (aliphatic CH), 1 740 (C=O), and 1 400—1 100 cm^{-1} (CF); the ^{19}F n.m.r. spectrum showed two triplet signals (J_{HF} 9.9 Hz) in the ratio 3 : 3 at ϕ 66.32 (isomer A) and 66.37 (isomer B), with proton signals at δ 3.71 (3 H, s, OMe) and 3.29—1.69 (3 H, c, CH_2–CH). The ^{19}F n.m.r. spectrum of the uncrystallized reaction product showed the two triplet fluorine signals corresponding to isomers A and B in the ratio 1 : 1.

Fraction (IV) (0.7 g), b.p. 120—130 °C/0.4 mmHg, was

shown by g.l.c. to be a mixture of dimethyl 2,3-bis-(2,2,2-trifluoroethyl)succinate, dimethyl 3-carboxymethyl-2,5-bis-(2,2,2-trifluoroethyl)adipate (see below) and two other unknown components in trace amounts. Fraction (V) (1.3 g), b.p. 130—143 °C/0.4 mmHg, contained principally (90%) one component (g.l.c.): a portion (1.0 g) was separated by g.l.c. (column D; 195 °C; N_2 2.6 l/h) to afford *dimethyl 3-carboxymethyl-2,5-bis-(2,2,2-trifluoroethyl)adipate* (0.69 g) (Found: C, 42.5; H, 4.7; F, 28.6. $C_{14}H_{18}F_6O_6$ requires C, 42.4; H, 4.6; F, 28.8%); $\nu_{max.}$ 3 000, 2 960, 2 850 (aliphatic CH), 1 735 (C=O), and 1 450—1 050 cm^{-1} (CF). The ^{19}F n.m.r. spectrum was complex, consisting of lines comprising eight overlapping triplet signals; ϕ 65.71—66.41; δ 3.72 (6 H, s, OMe), 3.70 (3 H, s, OMe), and 1.5—3.1 (9 H, c, CH$_2$–CH).

The residue from the distillation (8.5 g) was polymeric.

(b) *Excess of trifluoroacetic acid.* Trifluoroacetic acid (34.2 g), methyl acrylate (8.6 g), and sodium hydroxide (0.6 g) were electrolysed at 1.0 A for 8 h, the residue (17.9 g) after work-up being distilled. Fraction (I) (1.7 g), b.p. 34—60 °C, was ether and acetonitrile; fraction (II) (1.95 g), b.p. 60—85 °C, contained ether, acetonitrile, methyl acrylate, and two other components in trace amounts. Fraction (III) (0.43 g), b.p. 85—112 °C, was separated (1.12 g) by g.l.c. (column A; 90—150 °C; N_2 6 l/h) to afford (a) ether (trace), (b) a mixture (0.46 g), (c) two unidentified components (0.05 g), (d) methyl 4,4,4-trifluoro-butyrate (0.10 g), and (e) acetonitrile (0.12 g), the last two being identified by i.r. spectroscopy. The mixture III (b) was re-separated by g.l.c. (column C; 100 °C; N_2 3.6 l/h) to give (i) *methyl 4,4,4-trifluoro-2-trifluoromethylbutyrate* (0.31 g), b.p. 107—108 °C (Found: C, 32.2; H, 2.4; F, 51.2. $C_6H_6F_6O_2$ requires C, 32.2; H, 2.7; F, 50.9%); $\nu_{max.}$ 3 010, 2 960, 2 870 (aliphatic CH), 1 760 (C=O), and 1 440—1 070 cm^{-1} (CF); ϕ 66.9 (3 F, t, J_{HF} 10.4 Hz, CF$_3$–CH$_2$) and 69.7 (3 F, d, J_{HF} 8.5 Hz, CF$_3$–CH); δ 3.86 (3 H, s, OMe) and 3.65—2.24 (3 H, complex, CH$_2$–CH).

Fraction (IV) (0.55 g) from the distillation had b.p. 40—100 °C/12 mmHg; by g.l.c. and i.r. spectroscopy it was principally dimethyl 2,3-bis-(2,2,2-trifluoroethyl)succinate. Fraction (V) (7.2 g), b.p. 110—158 °C/12 mmHg, was recrystallized from petroleum (b.p. 60—80 °C) to give dimethyl 2,3-bis-(2,2,2-trifluoroethyl)succinate (3.1 g), m.p. 83—85 °C; ^{19}F n.m.r. spectroscopy showed this to be isomer A. The mother liquor was evaporated to give a mixture (3.8 g) which was recrystallized from methanol to afford a mixture of isomers A and B (2.2 g) in the ratio 1 : 6 (^{19}F n.m.r. spectroscopy). The methanol was evaporated to leave a residue (1.5 g), shown by g.l.c. to be a mixture of dimethyl 2,3-bis-(2,2,2-trifluoroethyl)succinate and dimethyl 3-carboxymethyl-2,5-bis-(2,2,2-trifluoroethyl)adipate. The residue (1.0 g) from the distillation was a brown tar, not investigated further.

Saponification of Dimethyl 2,3-Bis-(2,2,2-trifluoroethyl)-succinate.—The title compound (isomer A; 1.0 g) and KOH (0.9 g) in aqueous ethanol (8.0 cm³, 25% v/v) was refluxed for 6 h. The solution was acidified (30 cm³; 50% HCl), extracted with ether (3 × 50 cm³), and the combined extracts dried (MgSO$_4$) and evaporated to give a solid (1.05 g). This was sublimed (115—125 °C/12 mmHg) and recrystallized from water to give *2,3-bis-(2,2,2-trifluoro-ethyl)succinic acid* (0.65 g), m.p. 202—209 °C (Found: C, 34.0; H, 2.9; F, 40.1. $C_8H_8F_6O_4$ requires C, 34.1; H, 2.8; F, 40.4%); $\nu_{max.}$ 3 400—2 600 (broad, OH), 2 910, 2 850 (aliphatic CH), 1 725 (C=O), 1 450—1 050 cm^{-1} (CF);

ϕ([^{2}H$_6$]acetone) 65.0 (tr, J_{HF} 10.7 Hz); δ 7.58 (1 H, br,s, OH), and 3.15—2.20 (3 H, complex, CH$_2$–CH).

Acrylonitrile.—Trifluoroacetic acid (34.2 g), acrylonitrile (freshly distilled from CaH$_2$, 5.3 g), and sodium hydroxide (0.6 g) were electrolysed for 8 h at 1 A. The liquid residue after work-up (16.6 g) was distilled to remove ether and acetonitrile (1.2 g). Fractionation gave (I) (1.85 g), b.p. 70—86 °C, consisting principally of ether and acetonitrile with a trace of the major component of the next fraction. Fraction (II) (2.9 g) had b.p. 86—90 °C; a portion (0.38 g) was separated by g.l.c. (column A; 100 °C; N_2 6.0 l/h) to afford (a) acetonitrile (0.10 g), identified by i.r. spectroscopy and (b) *2-trifluoromethyl-4,4,4-trifluorobutyronitrile* (0.18 g), b.p. 107—108 °C (Found: C, 31.1; H, 1.6; F, 59.9; N, 7.3. $C_5H_3F_6N$ requires C, 31.4; H, 1.6; F, 59.7; N, 7.3%); $\nu_{max.}$ 3 002, 2 970, 2 940 (aliphatic CH), and 1 450—1 060 (CF); ϕ 66.2 (3 F, q of tr, J_{FF} 1.3, J_{HF} 9.8 Hz, CF$_3$–CH$_2$), and 70.7 (3 F, q of d, J_{FF} 1.3, J_{HF} 7.5 Hz, CF$_3$CH); δ 3.61 (1 H, sex, J 7 Hz, CH), and 2.97—2.41 (2 H, m, CH$_2$).

Fraction (III) (0.8 g), b.p. 92—110 °C, was a mixture, shown by g.l.c. to consist of ca. 50% of 2,3-bis-(2,2,2-tri-fluoroethyl)succinonitrile (see below) and other components: this was not separated. Fraction (IV) (3.1 g), b.p. 110—135 °C/12 mmHg, was a solid, a portion (0.50 g) of which was recrystallized from ethanol to afford *2,3-bis-(2,2,2-tri-fluoroethyl)succinonitrile* (0.38 g) (Found: C, 39.0; H, 2.3; F, 46.4; N, 11.2. $C_8H_6F_6N_2$ requires C, 39.4; H, 2.5; F, 46.7; N, 11.5%); M^+ 244 (required); $\nu_{max.}$ 2 920, 2 850 (aliphatic CH), 2 260 (C≡N), 1 450—1 100 cm^{-1} (CF); ϕ([^{2}H$_6$]acetone) 64.85 (tr, J_{HF} 9.9 Hz, CF$_3$, isomer A) and 64.97 (tr, J_{HF} 9.8 Hz, CF$_3$, isomer B), the signals in the ratio 3 : 1; δ 3.86 (1 H, m, CH–CH$_2$), and 3.25—2.82 (2 H, c, CH–CH$_2$).

The mother liquors were evaporated: ^{19}F n.m.r. spectroscopy showed the ratio of isomers to be A : B = 1 : 4.

The reaction product (13.3 g) from a repeat electrolysis was distilled in vacuum (0.2 mmHg) to give a liquid distillate (3.6 g), shown by g.l.c. to be a mixture of ether, acetonitrile, and 4,4,4-trifluoro-2-trifluoromethylbutyro-nitrile and a residue (9.5 g) shown by g.l.c. to consist of 2,3-bis-(2,2,2-trifluoroethyl)succinonitrile (70%). The residue was heated at 120 °C with aqueous H$_2$SO$_4$ (60 cm³; 60% v/v) for 15 h, when the solution was diluted with water (100 cm³) and extracted with ether (4 × 100 cm³). The extracts were washed with water (100 cm³), dried (MgSO$_4$), and evaporated to leave a solid (5.1 g) which was recrystallized from water to afford a mixture of the isomers of 2,3-bis-(2,2,2-trifluoroethyl)succinic acid (4.2 g) (Found: C, 34.0; H, 2.7; F, 40.2. Calc. for $C_8H_8F_6O_4$: C, 34.1; H, 2.8; F, 40.4%); ϕ([^{2}H$_6$]acetone) 65.00 (tr, J 10.7 Hz) and 65.08 (tr, J 11.0 Hz), the signals in the ratio approximately 1.2 : 1; δ 8.16 (1 H, broad s, OH) and 3.16—2.28 (3 H, complex m, CH$_2$–CH).

Methyl Vinylacetate.—Trifluoroacetic acid (34.2 g), methyl vinylacetate (10.0 g), and sodium hydroxide (0.6 g) were electrolysed for 8 h at initially 1.0 A, this falling to 0.2 A. The standard work-up gave a residue (21.05 g), which was distilled *in vacuo* (0.05 mmHg) to afford a distillate (7.65 g) and a residue (13.35 g).

The distillate was shown to be principally ether, acetonitrile, and methyl vinylacetate. The residue was separated by vacuum distillation (0.35 mmHg) into fractions (I) (5.2 g), b.p. 30—40 °C; (II) (1.45 g), b.p. 70—87 °C; (III) (1.7 g), b.p. 87—110 °C; (IV) (3.2 g), b.p. 118—132 °C, and a residue (0.9 g), not investigated further.

A portion (3.13 g) of fraction (I) was separated by g.l.c. (column C; 130 °C; N_2 2.5 l/h) to afford (*a*) a mixture (0.49 g), containing principally acetonitrile (g.l.c.), (*b*) methyl vinylacetate (0.75 g) (i.r. spectroscopy), (*c*) *methyl 5,5,5-trifluoropentanoate* (0.51 g), b.p. 142 °C (Found: C, 42.7; H, 5.6; F, 33.3. $C_6H_9F_3O_2$ requires C, 42.4; H, 5.3; F, 33.5%); $\nu_{max.}$ 2 960 (aliphatic CH), 1 740 (C=O), and 1 450—1 100 cm^{-1} (CF); ϕ 67.04 (tr, J 10.2 Hz); δ 3.69 (3 H, s, OCH$_3$), and 2.49—1.70 [6 H, complex m, $-(CH_2)_3^-$]; (*d*) E-*methyl 5,5,5-trifluoropent-3-enoate* (0.23 g), b.p. 147 °C (Found: C, 43.0; H, 4.3; F, 33.8. $C_6H_7F_3O_2$ requires C, 42.9; H, 4.2; F, 33.9%); $\nu_{max.}$ 3 000, 2 960, 2 900, 2 850 (aliphatic CH), 1 740 (C=O), 1 685 (C=C), 1 350—1 050 (CF); ϕ 65.2 (ddtr, J 6.4, 2.1, 2.1 Hz); δ 3.75 (3 H, s, OCH$_3$), 3.19 (2 H, ddq, J 1.6, 6.6, and 2.1 Hz, CH_2CO$_2$CH$_3$) and an AB system δ_A 6.55, δ_B 5.84, J_{AB} = 15.2 Hz, signal A further split into tr of q J 6.6 and 2.1 Hz, signal B into q of tr J 6.4 and 1.6 Hz, total intensity 2 H (CH=CH), and (*e*) E-*methyl 5,5,5-trifluoropent-2-enoate* (0.19 g), b.p. 148.5 °C (Found: C, 42.8; H, 4.3; F, 33.8. $C_6H_7F_3O_2$ requires C, 42.9; H, 4.2; F, 33.9%); $\nu_{max.}$ 3 000, 2 960, 2 850 (aliphatic CH), 1 730 (C=O), 1 665 (C=C), and 1 440—1 050 cm^{-1}

(CF); ϕ 66.22 (tr, J 10.5 Hz); δ 3.76 (3 H, s, OCH$_3$), 3.04 (2 H, ddq, J 1.5, 7.4, 10.5 Hz, CH$_2$), and an AB system δ_A 6.86, δ_B 6.09, J_{AB} = 16 Hz, signal A further split into a triplet, J 7.4 Hz, total intensity 2 H (CH=CH).

Fraction (II) (1.45 g), b.p. 70—87 °C, and fraction (III) (1.7 g), b.p. 87—110 °C, were multicomponent inseparable (g.l.c.) mixtures, although fraction (III) was shown (g.l.c.) to be *ca.* 50% of the adipate from fraction (IV). The final fraction (IV) (3.2 g), b.p. 118—132 °C, solidified and was recrystallized from light petroleum (b.p. 60—80 °C) to afford a mixture of the stereoisomers of dimethyl 3,4-*bis*-(2,2,2-*trifluoroethyl*)*adipate* (0.63 g), m.p. 66—67 °C (Found: C, 42.9; H, 4.5; F, 34.0. $C_{12}H_{16}F_6O_4$ requires C, 42.6; H, 4.8; F, 33.7%); M^+ 338 (required); $\nu_{max.}$ 2 950, 2 930, 2 860 (aliphatic CH), 1 725 (C=O), and 1 450—1 130 (CF); ϕ 64.6 (tr, J 10.4 Hz); δ 3.70 (3 H, s, OCH$_3$), and 2.53—2.0 (5 H, cm, CH$_2$–CH$_2$–CH$_2$).