

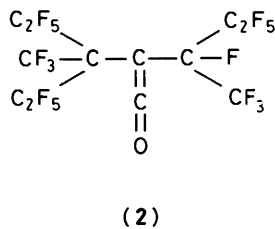
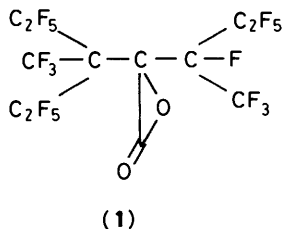
Reactions of Tetrafluoroethene Oligomers. Part 9.¹ Some Reactions of Perfluoro-(1-ethyl-1-methylpropyl)(s-butyl)ethanolide (an α -Lactone)

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The ethanolide (1), prepared by hypochlorite-mediated epoxidation of the ketene $\text{CF}_3(\text{C}_2\text{F}_5)_2\text{C}[\text{C}_2\text{F}_5(\text{CF}_3)\text{CF}]\text{C}=\text{C}=\text{O}$ (2), decomposed when warmed at 90 °C for 30 min to give the ketone $\text{CF}_3(\text{C}_2\text{F}_5)_2\text{CCOCF}(\text{CF}_3)\text{C}_2\text{F}_5$ (3). Reaction of compound (1) with either triethylamine or trimethylamine afforded the olefin (*E/Z*)- $\text{CF}_3(\text{C}_2\text{F}_5)_2\text{CCH}=\text{C}(\text{CF}_3)\text{C}_2\text{F}_5$ (4). Treatment of compound (1) with secondary amines R_2NH ($\text{R} = \text{Et}, \text{R}_2[\text{CH}_2]_5$) or primary amines RNH_2 ($\text{R} = \text{c-C}_6\text{H}_{11}$ or Bu^t) afforded oxo amides of the type $\text{CF}_3(\text{C}_2\text{F}_5)\text{CFCOCONR}_2$ (5) and (6) and $\text{CF}_3(\text{C}_2\text{F}_5)\text{CFCOCONHR}$ (7) and (8). With ethylamine and isopropylamine the isolated products were the corresponding oxamides and the olefin (4). With sodium methoxide three products were formed, a trace of olefin (4), 2,4-dimethoxyperfluoro-3-methylpent-2-ene (10), and the oxo ester $\text{CF}_3(\text{C}_2\text{F}_5)\text{CFCOCO}_2\text{Me}$ (11). Sodium ethoxide yielded the olefin (4), the oxo ester $\text{CF}_3(\text{C}_2\text{F}_5)\text{CFCOCO}_2\text{Et}$ (12), and the olefin $\text{CF}_3\text{CF}=\text{C}(\text{CF}_3)\text{CF}(\text{CF}_3)\text{OEt}$ (13). Reaction of compound (1) with methylmagnesium iodide and ethylmagnesium iodide afforded the esters $\text{C}_2\text{F}_5(\text{CF}_3)\text{C}=\text{C}(\text{CO}_2\text{Me})\text{C}(\text{Me})(\text{CF}_3)\text{C}_2\text{F}_5$ (14) and $\text{C}_2\text{F}_5(\text{CF}_3)\text{C}=\text{C}(\text{CO}_2\text{Et})\text{C}(\text{Et})(\text{CF}_3)\text{C}_2\text{F}_5$ (15) respectively. Treatment of compound (1) with methyl-lithium gave a mixture of two products, the esters (14) and $\text{C}_2\text{F}_5(\text{CF}_3)(\text{Me})\text{CC}(\text{CO}_2\text{Me})=\text{C}(\text{Me})\text{CF}_3$ (16), by what appears to be an unusual attack on the ring oxygen. Reaction of compound (1) with ethanethiol gave the ester $\text{C}_2\text{F}_5(\text{CF}_3)\text{CFCOCOSet}$ (17) and the olefin $\text{C}_2\text{F}_5(\text{CF}_3)\text{C}=\text{C}(\text{CF}_3)\text{SEt}$ (18). Compound (1) on reaction with ammonia gave oxamide and the unusual cyanodi-imine $\text{CF}_3\text{C}(\text{=NH})\text{CH}(\text{CN})\text{C}(\text{=NH})\text{CF}_3$ (9). Reaction of compound (1) with tributyl- or triphenyl-phosphine gave olefin (4) again by reaction on the ring oxygen.

In a preliminary communication² we described the preparation of the first isolable α -ethanolide (α -lactone), perfluoro-(1-ethyl-1-methylpropyl)(s-butyl)ethanolide (1) by the epoxidation, using sodium hypochlorite, of perfluoro (1-ethyl-1-methylpropyl)(s-butyl)ketene (2). We now describe some reactions of this novel species.



Ethanolides have been postulated as intermediates in a number of reactions, the ozonolysis of ketenes,³ the photodecomposition of β -peroxy lactones,⁴ and the hydrolysis of α -bromopropionic acid derivatives.⁵ Only recently however, with the work of Adam,⁶ has an α -lactone with some degree of

stability been obtained, when a solution of $(\text{CF}_3)_2\text{C}=\text{C}=\text{O}$ was prepared. A theoretical study by Liebman and Greenberg⁷ indicated that bulky electron-attracting groups were important in stabilising the ring form rather than the open chain $\text{R}_2\text{C}^+-\text{CO}_2^-$ structure, and our synthesis supported this view.

Thus, we report an investigation of the reactions of compound (1) with a range of nucleophiles of differing steric requirements.

Results and Discussion

In some earlier work,⁸ we had shown that addition of triethylamine enhances the solubility and increases the

reactivity of tetrafluoroethene oligomers towards nucleophiles. Since the α -lactone (1) was not very soluble in many solvents we tested this effect with compound (1). A vigorous reaction ensued even at -10 °C, and on work-up a product was obtained which had lost all the characteristic i.r. bands for the α -lactone, but was identical with a product previously obtained in some earlier work with the tetrafluoroethene hexamer,⁸ namely 4*H*-heneicosafuoro-5-ethyl-3,5-dimethylhept-3-ene (4).

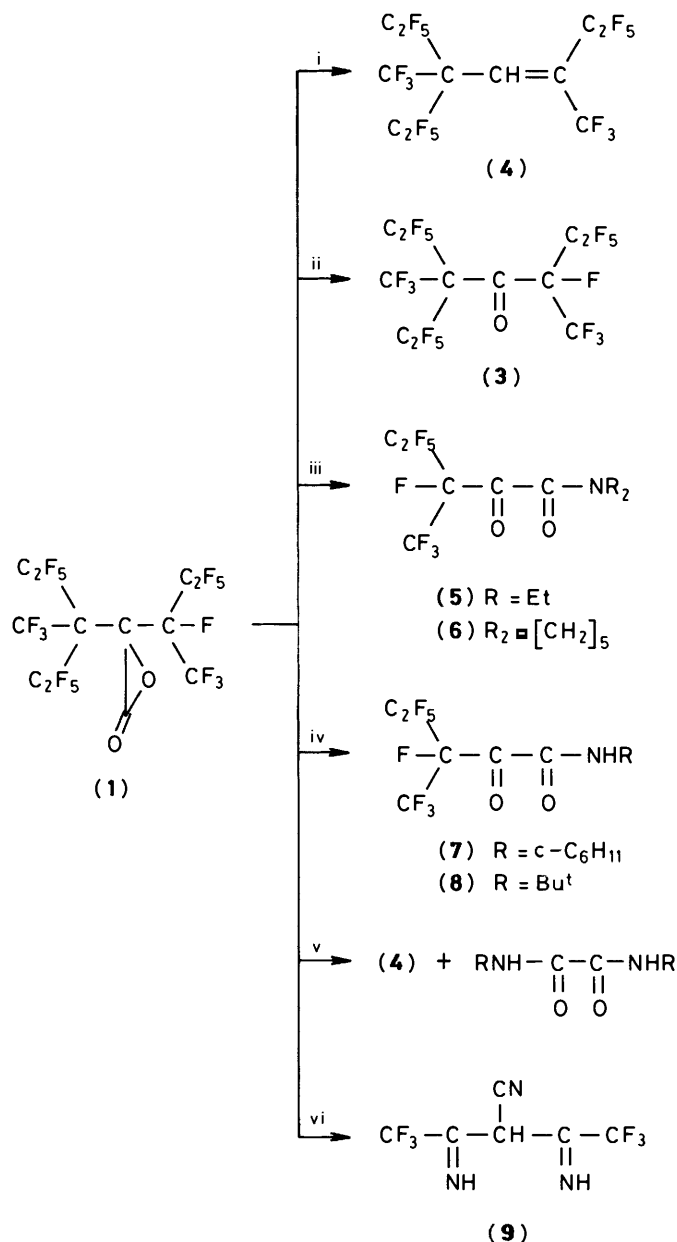
We next checked the thermal stability of the α -lactone and found that it was stable (up to 1 year) at -10 °C, but that (i) at room temperature and above it decomposed with loss of carbon monoxide and (ii) at 90 °C for 30 min decomposition was complete to yield perfluoro-3-ethyl-3,5-dimethylheptan-4-one (3). Thus, it was clear that substitutions must be studied at low temperatures.

We first studied the reactions of compound (1) with a series of primary and secondary amines (Scheme 1). With diethylamine at -10 °C, a smooth reaction occurred and g.l.c. indicated two products were formed, the minor component readily being shown to be the olefin (4). The major component was shown by ¹⁹F n.m.r. spectroscopy to have lost the $\text{CF}_3(\text{C}_2\text{F}_5)_2\text{C}$ group and to contain C_2F_5 and CF_3 groups and a tertiary fluorine atom. The ¹H n.m.r. spectrum showed the presence of an ethyl group. The i.r. spectrum indicated the presence of two strong carbonyl bands. Mass spectral and elemental analysis confirmed the product as *N,N*-diethylperfluoro-3-methyl-2-oxopentanamide (5).

Reaction of compound (1) with piperidine followed a similar pattern to yield *N,N*-pentamethyleneperfluoro-3-methyl-2-oxopentanamide (6).

Treatment of compound (1) with cyclohexylamine and *t*-butylamine gave essentially the same pattern as the secondary amines, yielding the corresponding *N*-cyclohexyl and *N-t*-butyl-2-oxo amides (7) and (8) respectively.

Reaction of compound (1) with ethylamine and isopropylamine showed considerable superficial differences; in each case



Scheme 1. Reagents and conditions: i, Et_3N , Me_3N , Ph_3P , or Bu_3P ; ii, 80°C ; iii, Et_2NH or $\text{HN}[\text{CH}_2]_5$; iv, $c\text{-C}_6\text{H}_{11}\text{NH}_2$ or Bu^tNH_2 ; v, EtNH_2 or Pr^tNH_2 ; vi, NH_3

the only fluorocarbon product isolated was the olefin (4); the main product was the oxamide derivative.

In none of these reactions was any product associated with the $\text{CF}_3(\text{C}_2\text{F}_5)_2\text{C}$ group isolated. In this respect, the reaction of compound (1) with ammonia proved to be very interesting. A solid was precipitated and was shown to be oxamide. Evaporation of the solvent gave a volatile solid, which on ^{19}F n.m.r. spectroscopy showed a single uncoupled CF_3 resonance. The proton n.m.r. spectrum showed a sharp singlet at δ 3.4 and complex signal at δ 5.45 in the ratio 1:2. The peak at δ 5.45 disappeared when the sample was shaken with D_2O . The i.r. spectrum showed a broad peak at 3250 cm^{-1} , a sharp signal at 2200 cm^{-1} , and a broad band at 1610 cm^{-1} attributable to NH , $\text{C}\equiv\text{N}$, and $\text{C}=\text{N}$ absorptions respectively. Mass spectrometry and elemental analysis confirmed $\text{C}_6\text{H}_3\text{F}_6\text{N}_3$ as the empirical formula. These data suggested the product to be 4,4,4-trifluoro-

3-imino-2-(2,2,2-trifluoro-1-iminoethyl)butanenitrile (9). It is possible (see below) to rationalise the formation of this product by reaction of $\text{CF}_3(\text{C}_2\text{F}_5)_2\text{C}=\text{C}(\text{CF}_3)\text{F}$, derived from $\text{CF}_3(\text{C}_2\text{F}_5)_2\text{C}^-$ (lost from the original reaction) by loss of fluoride ion, with ammonia.

The reaction of compound (1) with sodium methoxide gave two major products; the first again showed loss of the $\text{CF}_3(\text{C}_2\text{F}_5)_2\text{C}$ group and retention of the $\text{C}_2\text{F}_5\text{CF}_3\text{CF}$ function in its ^{19}F n.m.r. spectrum. The i.r. spectrum with strong bands at 1780 and 1795 cm^{-1} indicated an oxo ester, and the product was confirmed as methyl perfluoro-3-methyl-2-oxopentanoate (11). The second product showed three signals for CF_3 groups and the signal for a single fluorine atom; those of the CF_3 groups were in positions we would anticipate for CF_3 groups on a double bond. The tertiary fluorine was to low field and previously we have seen such signals on a carbon atom bearing alkoxy groups. The ^1H spectrum showed the presence of two methoxy groups one of which was coupled to fluorine (J 4 Hz) as a doublet. Mass spectrometry and elemental analysis confirmed the structure as 2,4-dimethoxyperfluoro-3-methylpent-2-ene (10). In a similar reaction with sodium ethoxide the corresponding oxo ester (12) was obtained, together with an olefin. The ^{19}F n.m.r. spectrum of this olefin showed the presence of three CF_3 groups, and one olefinic and one tertiary fluorine atom. We thus assign the product to be 4-ethoxyperfluoro-3-methylpent-2-ene (13), *i.e.* the mono-substituted product of the trimer of tetrafluoroethene (TFE). We could not in this case or indeed in any of the other olefins determine the stereochemistry of the olefins from n.m.r. spectroscopy since the signals were too complex for analysis.

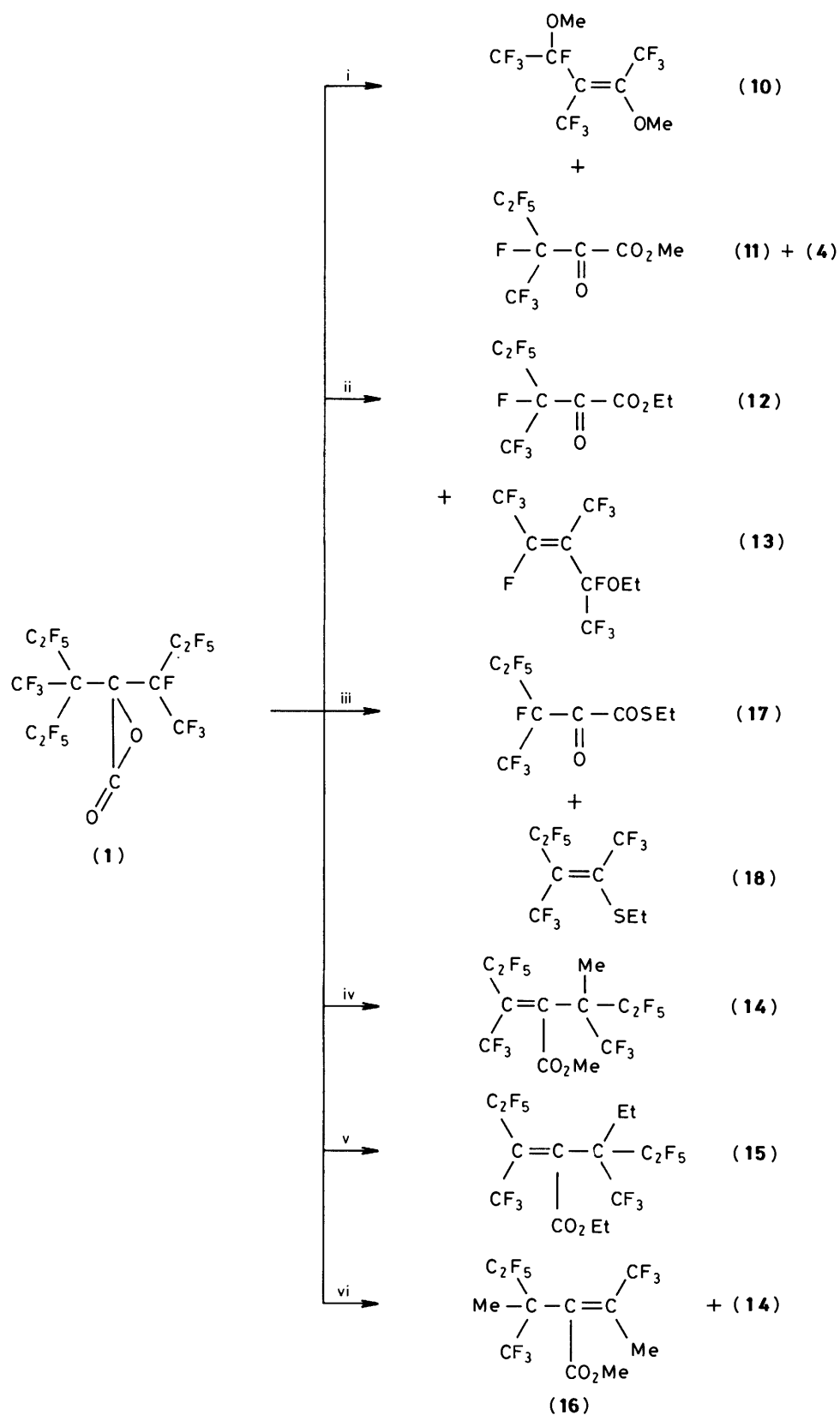
Reaction of compound (1) with ethanethiol gave the expected oxo thioester (17) and an olefin, the ^{19}F n.m.r. spectrum of which showed three signals for CF_3 groups and a CF_2 group, no olefinic fluorine signals, and no signals for tertiary fluorine. This suggests the product to be 2-ethylthioperfluoro-3-methylpent-2-ene (18).

When the ethanolate (1) was treated with methylmagnesium iodide in ether a single product was obtained. Its i.r. spectrum showed a strong band for an ester function, and mass spectrometry and elemental analysis gave an empirical formula $\text{C}_{12}\text{H}_6\text{F}_{16}\text{O}_2$. The ^1H n.m.r. spectrum showed two signals, one complex and one a sharp singlet in the ratio 1:1, the latter signal being at the region expected for an ester. The ^{19}F spectrum showed signals for four CF_3 groups and two CF_2 groups. One CF_3 group and one C_2F_5 group were in the region of the spectrum we expect for fluoroalkyl groups on double bonds. We thus conclude that the product is methyl 2-(2,2,3,3,3-pentafluoro-1-methyl-1-trifluoromethylpropyl)perfluoro-3-methylpent-2-enoate (14). It was at first difficult to envisage how this product formed, but as a result of further studies (see below) a rationale can be advanced as is indicated later.

In a similar experiment, but using the ethyl Grignard reagent, a similar product (15) to (14) but with ethyl rather than methyl groups was obtained. The structure was confirmed by spectroscopic methods as above.

Reaction of compound (1) with methyl-lithium gave two products, the minor component being readily identified as (14). The major component was shown by elemental analysis and mass spectrometry to have the formula $\text{C}_{11}\text{H}_9\text{F}_{11}\text{O}_2$ and to contain an ester carbonyl function. The ^1H n.m.r. spectrum in this case showed signals for three methyl groups, one of which was an ester methyl. The ^{19}F spectrum showed bands for two CF_3 groups and only one C_2F_5 group. We conclude that the product is methyl 4,4,4-trifluoro-3-methyl-2-(2,2,3,3,3-pentafluoro-1-methyl-1-trifluoromethylpropyl)but-2-enoate (16) (Scheme 2).

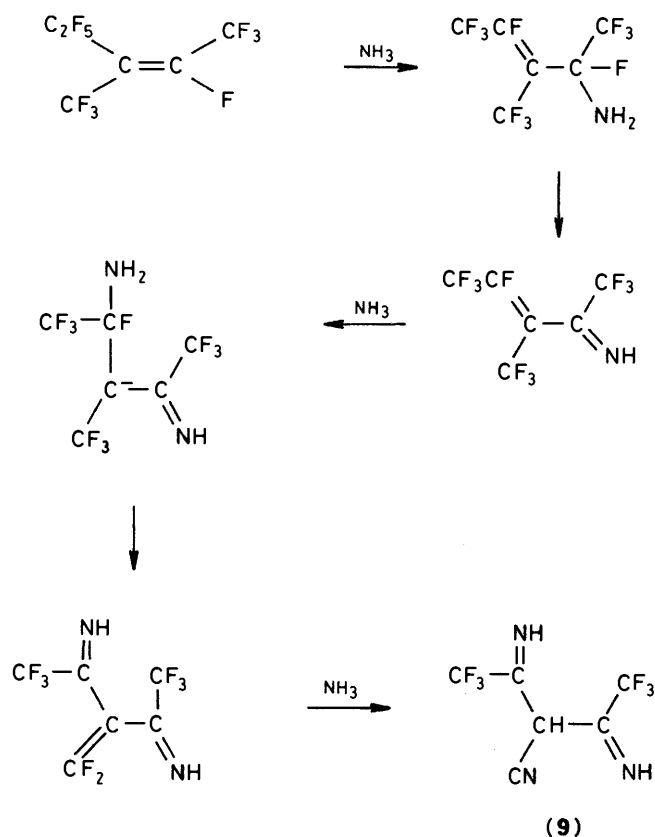
When compound (1) in dry ether was treated with triphenylphosphine or tributylphosphine a precipitate was formed immediately, but disappeared after a time; attempts to



Scheme 2. Reagents: i, MeO^- ; ii, EtO^- ; iii, EtS^- ; iv, MeMgI ; v, EtMgI ; vi, MeLi

isolate the solid have so far failed. When a ^{31}P n.m.r. spectrum was run on the solution immediately after mixing, a resonance was observed which indicated the presence of a phosphonium

salt being formed, but we have so far been unable fully to confirm this observation. Work-up of these solutions gave the olefin (4) as the only isolable product.



Scheme 4.

apparent ready loss of C_2F_5 , either as $C_2F_5^-$ or as $C_2F_4 + F^-$ when the nucleophile is $MeMgBr$, $MeLi$, or $EtMgBr$ [compounds (14), (15), (16)] (Scheme 1) rather than protonation. Such eliminations are rare in fluorocarbon chemistry, but this is the second time we have encountered this ready loss, the first being the decomposition of $CF_3-(C_2F_5)_2CCHN_2$ in ethanol.⁹ It is possible this could be due to the relief of steric strain in the bulky $CF_3(C_2F_5)_2C$ group.

Thus, we conclude that the reactivity of the ethanolid is to some extent governed by the ready loss of $CF_3(C_2F_5)_2C^-$, but shows the unusual effect of the alternative ring opening. We are currently studying routes to other α -lactones in order to discover the minimum size and electronegativity of the groups necessary to obtain a stable structure and to follow further their reactivity.

Experimental

Preparation of Perfluoro-(1-ethyl-1-methylpropyl)(s-butyl)ethanolid.—Perfluoro-(1-ethyl-1-methylpropyl)(s-butyl)ketene (2) (100 g, 0.17 mol), acetonitrile (200 cm³), and sodium hypochlorite solution (450 cm³) were vigorously stirred at 0 °C for 3 h. The lower fluorocarbon layer was washed with water (50 cm³) to yield perfluoro-(1-ethyl-1-methylpropyl)(s-butyl)ethanolid (α -lactone) (1) (94.4 g, 92%). This product was stable at -20 °C indefinitely. ¹⁹F N.m.r. spectroscopy showed the typical patterns for $CF_3(C_2F_5)_2C$ and $CF_3C_2F_5CF$ groups we have described previously.¹ I.r. spectroscopy showed strong bands in the region 1900—2060 cm⁻¹.

Thermolysis of the Ethanolid (1).—The ethanolid (1) (10 g, 0.018 mol) was heated at 90 °C for 30 min; a gas (carbon monoxide) was rapidly evolved. The mixture was cooled to give

a liquid (9.1 g, 95%), which on distillation afforded perfluoro-3-ethyl-3,5-dimethylheptanone (3), b.p. 155 °C, identical with an authentic sample.¹

Reaction of the Ethanolid (1) with Amines.—(a) *Triethylamine.* To a solution of the ethanolid (1) (5 g, 0.009 mol) in dry ether (25 cm³) at -10 °C was added a solution of triethylamine (1 g, 0.01 mol) in dry ether (25 cm³) during 15 min. The mixture was stirred at -10 °C for 1 h and then allowed to warm to 18 °C during 12 h. The mixture was washed with 4M-hydrochloric acid (20 cm³), dried ($MgSO_4$), and the ether distilled off to yield 4H-heneicosafuoro-5-ethyl-3,5-dimethylhept-3-ene (4) (3.1 g, 69%), identical with an authentic sample.²

(b) *Trimethylamine.* In a similar experiment but at -30 °C trimethylamine and (1) afforded the olefin (4) in 88% yield.

(c) *Diethylamine.* A solution of diethylamine (1 g, 0.013 mol) in dry ether (25 cm³) was added during 30 min to a stirred solution of the α -ethanolid (5 g, 0.009 mol) in dry ether (25 cm³) at -10 °C. The mixture was stirred at -10 °C for 1 h and then allowed to warm to 18 °C during 20 h. The solution was filtered, dried ($MgSO_4$), and the ether evaporated off to give an oil (2.82 g). A portion (2.5 g) was separated by preparative g.l.c. (p.l.c.) to give (i) olefin (4) (0.22 g) and (ii) N,N-diethylperfluoro-3-methyl-2-oxopentanamide (5) (1.7 g), b.p. 86—88 °C/20 mmHg (Found: C, 34.6; H, 2.9; N, 3.9; F, 49.8. $C_{10}H_{10}F_9NO_2$ requires C, 34.6; H, 2.9; N, 4.0; F, 49.3%). ¹⁹F and ¹H n.m.r. spectra were both consistent with the structure.

(d) *Piperidine.* In a similar experiment to (c) the ethanolid (1) (5 g) and piperidine afforded a mixture of (i) olefin (4) (0.3 g) and (ii) N,N-pentamethylenepfluoro-3-methyl-2-oxopentanamide (6) (1.6 g), b.p. 47—49 °C/0.2 mmHg (Found: C, 36.9; H, 2.9; N, 3.9; F, 48.0. $C_{11}H_{10}F_9NO_2$ requires C, 36.7; H, 2.8; N, 3.9; F, 47.6%). ¹⁹F and ¹H n.m.r. spectra were consistent with the proposed structure. Mass spectrometry gave peaks at m/z 359 (M^+), and 69 (CF_3) as the base peak.

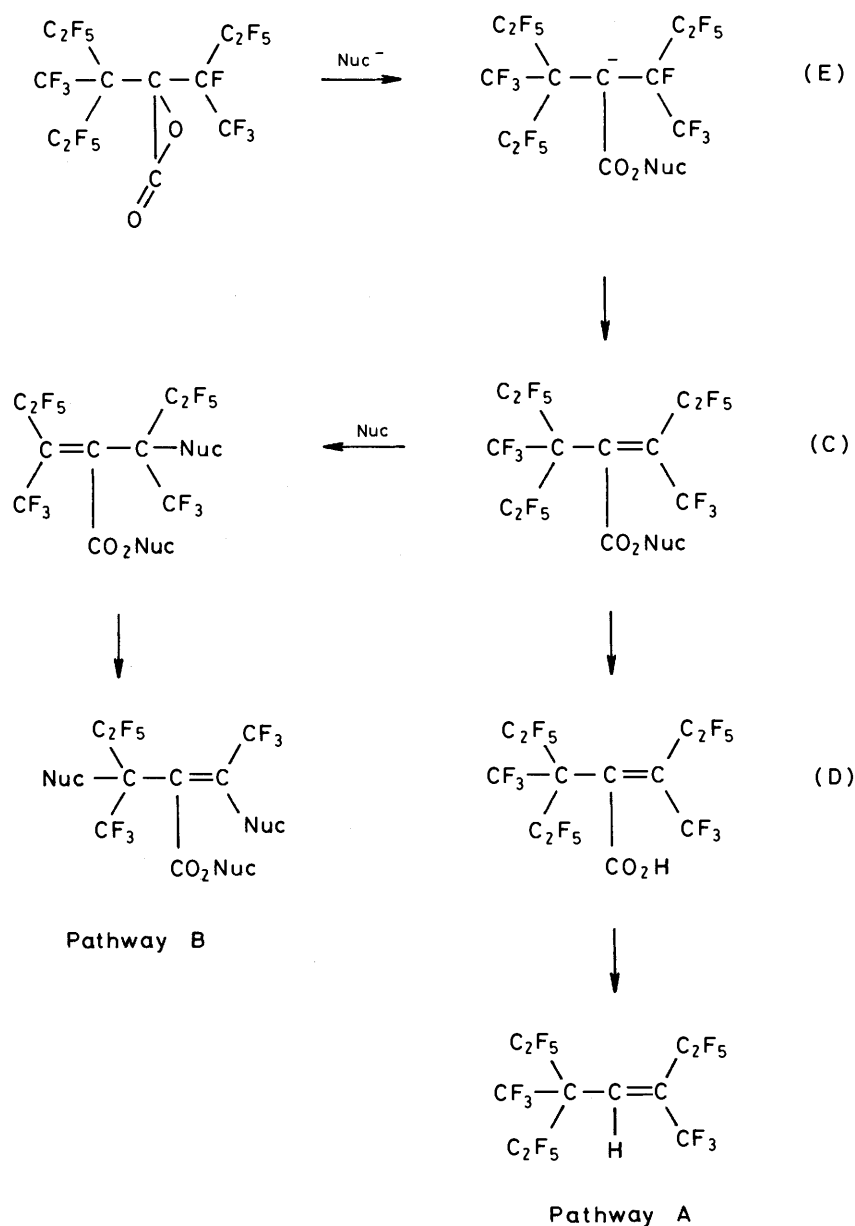
(e) *Cyclohexylamine.* In a similar experiment cyclohexylamine (0.34 g, 0.003 mol) and the ethanolid (1) (2 g, 0.0036 mol) but in Freon 113 ($CCl_2F-CClF_2$) as solvent at -40 °C afforded N-cyclohexylperfluoro-3-methyl-2-oxopentanamide (7) (1.1 g, 85%), m.p. 124—125 °C (Found: C, 38.3; H, 3.4; N, 3.7. $C_{12}H_{14}F_9NO_2$ requires C, 38.5; H, 3.2; N, 3.8%). ¹⁹F and ¹H n.m.r. spectra were in accord with the structure.

(f) *t-Butylamine.* In a similar experiment to (e) the ethanolid (1) (10 g, 0.018 mol) and t-butylamine (1.3 g, 0.018 mol) gave N-t-butylperfluoro-3-methyl-2-oxopentanamide (8) (5.8 g, 99%), b.p. 91—92 °C/20 mmHg (Found: C, 34.7; H, 3.0; N, 4.0. $C_{10}H_{10}F_9NO_2$ requires C, 34.6; H, 2.9; N, 4.0%).

(g) *Ethylamine.* Reaction of the ethanolid (1) (5 g, 0.009 mol) with ethylamine (1 g, 0.02 mol) at -10 °C afforded two products: (i) a solid identified as N,N'-diethyloxamide (1 g), m.p. 175 °C and (ii) olefin (4) (0.2 g).

(h) *With isopropylamine.* In a similar experiment but using isopropylamine (1.2 g, 0.02 mol) two products were again formed: (i) N,N'-di-isopropyloxamide (0.9 g), m.p. 212 °C and (ii) olefin (4) (0.23 g).

Reaction of the α -Lactone (2) with Sodium Methoxide.—A solution of the ethanolid (6 g, 0.11 mol) in Freon 113 (30 cm³) was added to a vigorously stirred solution of sodium methoxide (2 g, 0.04 mol) in dry methanol (30 cm³). The mixture was stirred for 12 h, water (100 cm³) was added, the fluorocarbon layer was separated, and the Freon was evaporated off to yield a pale green oil (4.2 g). Separation by p.l.c. afforded (i) olefin (4) (0.3 g), (ii) 2,4-dimethoxyperfluoro-3-methylpent-2-ene (10) (1.6 g) identical with an authentic sample,¹ and (iii) methyl perfluoro-3-methyl-2-oxopentanoate (11) (1.6 g), b.p. 101—103 °C/10 mmHg (Found: 26.9; H, 1.2. $C_7H_3F_9O_3$ requires C, 27.4; H, 1.0%).



Scheme 5. Pathway A: Nuc = Ph₃P, Bu₃P, Me₃N, Et₃N. Pathway B: Nuc = MeMgI, EtMgI, MeLi

Reaction of Ethanolide (1) with Sodium Ethoxide.—In a similar experiment to the above the α -lactone (1) (10 g, 0.018 mol) afforded an oil (6.2 g), which on separation gave (i) olefin (4) (0.4 g), (ii) ethylperfluoro-3-methyl-2-oxopentanoate (12) (1.7 g), b.p. 116–117 °C/20 mmHg (Found: C, 30.4; H, 1.3. C₈H₅F₉O₃ requires C, 30.4; H, 1.6%), and (iii) 4-ethoxyperfluoro-3-methylpent-2-ene (13) (1.2 g), identical with an authentic sample.

Reaction of the Ethanolide (1) with Methylmagnesium Iodide.—Methylmagnesium iodide [from methyl iodide (1.2 g)] in ether was added to a solution of the α -lactone (1) (5 g, 0.009 mol) in ether (30 cm³) at –10 °C. The mixture was stirred at –10 °C for 1 h, and poured into a mixture of 2M-sulphuric acid (50 cm³) and ice (50 g). The ether layer was separated and the aqueous layer was extracted with ether (2 × 50 cm³). The combined extracts and mother liquor were dried (MgSO₄) and evaporated to leave an oil (2.1 g), distillation of which afforded methyl-

2-(2,2,3,3,3-pentafluoro-1-methyl-1-trifluoromethylpropyl)perfluoro-3-methylpent-2-enoate (14) (1.6 g, 39%), b.p. 101–102 °C/20 mmHg (Found: C, 31.7; H, 1.9. C₁₂H₆F₁₆O₂ requires C, 31.4; H, 1.5%). ¹⁹F N.m.r. spectroscopy showed bands (rel. CCl₃F) at ϕ_F 65.2 (3 F, c, CF₃C=), 66.3 (3 F, c, CF₃), 78.1 (3 F, c, CF₃CF₂), 78.8 (3 F, CF₃CF₂), 107.3 (2 F, c, CF₃CF₂), and 110.8 p.p.m. (2 F, c, CF₃CF₂). The ¹H n.m.r. spectrum showed signals at δ 1.75 (3 H, c, Me) and 3.68 (3 H, s, MeO). Mass spectrometry showed peaks at m/z 486 (M^+) and 471 ($M - CH_3$)⁺.

Reaction of the Ethanolide (1) with Ethylmagnesium Bromide.—In a similar experiment but using ethylmagnesium bromide (3 mol equiv.) with the α -lactone (10 g, 0.018 mol), there was obtained ethyl-2-(1-ethyl-2,2,3,3,3-pentafluoro-1-trifluoromethylpropyl)perfluoro-3-methylpent-2-enoate (15) (7.61 g, 88%), b.p. 121–123 °C/20 mmHg (Found: C, 31.6; H, 1.8. C₁₄H₁₀F₁₆O₂ requires C, 32.6; H, 1.9%); δ_H 1.12 (3 H, t, J_{HH} 6 Hz, CCH₂Me), 1.35 (3 H, t, J_{HH} 7 Hz, OCH₂Me), 3.7 (2 H, q, J_{HH}

6 Hz, CCH_2Me), and 4.26 (2 H, q, J_{HH} 7 Hz, OCH_2Me). The ^{19}F n.m.r. spectrum showed a similar pattern of peaks for that found in ester (14).

Reaction of the Ethanolide (1) with Methyl-lithium.—Methyl-lithium (3 mol equiv.) was added during 15 min to a solution of the α -lactone (1) (5 g, 0.009 mol) in dry ether (100 cm³) at $-10^\circ C$ in dry nitrogen. The mixture was stirred at $18^\circ C$ for 10 h, when 4M-hydrochloric acid (50 cm³) was added, and the ether layer and the combined ether extracts (2×25 cm³) of the aqueous layer were dried and distilled to give an oil (4.1 g). Separation by p.l.c. afforded two products: (i) methyl 4,4,4-trifluoro-3-methyl-2-(2,2,3,3,3-pentafluoro-1-methyl-1-trifluoro-methylpropyl)but-2-enoate (16) (2.31 g), b.p. $86-87^\circ C/20$ mmHg (Found: C, 34.4; H, 2.3. $C_{11}H_9F_{11}O_2$ requires C, 34.6; H, 2.4%; m/z 382 (M^+) and 363 ($M - F$)⁺; δ_H 1.62 (3 H, CMe), 2.1 (3 H, =CMe), and 3.73 (3 H, MeO); ϕ_F 65.8 (3 F, s, CF_3), 66.2 (3 F, c, CF_3), 79.6 (3 F, c, CF_2CF_3), and 109.8 (2 F, c, CF_2CF_3); and (ii) compound (14) (0.9 g).

Reaction of the Ethanolide (1) with Ethanethiol.—A solution of the ethanolide (1) (10 g, 0.018 mol) in dry ether (50 cm³) and sodium ethanethiolate [from ethanethiol (3.2 g) and sodium] in dry ether (50 cm³) were stirred together at $-10^\circ C$ for 15 h. The solution was washed with water (2×25 cm³) and dried ($MgSO_4$), and the ether was distilled off to leave a yellow oil. Distillation under reduced pressure afforded (i) 4H-perfluoro-5-ethyl-3,5-dimethylhept-3-ene (4) (1.4 g), identical with an authentic sample; (ii) s-ethylperfluoro-3-methyl-2-oxopentanthioate (17) (1.6 g), b.p. $64-66^\circ C/9$ mmHg (Found: C, 28.9; H, 1.15. $C_8H_5F_9SO_2$ requires C, 28.6; H, 1.5%; ^{19}F and 1H n.m.r. spectra were consistent with the structure; and (iii) 2-ethylthioperfluoro-3-methylpent-2-ene (18) (2.1 g), b.p. $77^\circ C/9$ mmHg (Found: C, 28.1; H, 1.2; F, 61.1. $C_8H_5F_{11}S$ requires C, 28.1; H, 1.5; F, 61.1%; m/z 342 (M^+), 314 ($M - C_2H_4$)⁺, and 223 ($M - C_2F_5$); δ_H 1.08 (3 H, t, Me), and 2.75 (2 H, q, J 7 Hz, CH_2); ϕ_F 59.1 (3 F, CF_3), 59.2 (3 F, CF_3), 81.2 (3 CF, CF_3CF_2), and 103.7 (2 F, CF_3CF_2).

Reaction of the Ethanolide (1) with Ammonia.—Dry ammonia was bubbled through a solution of the ethanolide (10 g, 0.018 mol) in dry ether (100 cm³) at $-10^\circ C$ for 1 h, and then the mixture was stirred at $20^\circ C$ for 20 h. The solid (1.01 g) which precipitated was filtered off and shown to be oxamide. The ether was evaporated to yield a slurry (1 g). Vacuum transfer afforded a liquid, shown to be the olefin (4) (0.26 g). The residual solid was sublimed to give 4,4,4-trifluoro-3-imino-2-(2,2,2-trifluoro-1-iminoethyl)butanenitrile (9) (0.31 g), m.p. $65^\circ C$ (Found: C, 31.8; H, 1.7; N, 18.9. $C_6H_3F_6N_3$ requires C, 31.1; H, 1.3; N, 18.2%).

Reaction of the Ethanolide (1) with Triphenylphosphine.—A solution of the ethanolide (1) (5 g, 0.009 mol) in dry ether (25 cm³) was treated at $-10^\circ C$ with solution of triphenylphosphine (2.2 g) in dry ether (25 cm³). The white precipitate which formed was filtered off in a dry bag; however, it liquified rapidly and all attempts to remove and characterise it have so far failed. The combined liquid and ether layers were evaporated to yield the olefin (4) (2.9 g, 65%), identical with an authentic sample.

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