

FLUOROKETENES

VII.* SYNTHESIS AND REACTIVITY OF TRIFLUOROMETHYLFLUOROKETENE, PERFLUOROACRYLOYL FLUORIDE, PERFLUOROMETHACRYLOYL FLUORIDE, METHYL PERFLUOROACRYLATE AND METHYL PERFLUOROMETHACRYLATE

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SUMMARY

Trifluoromethylketene has been detected by trapping reactions, but has not been isolated. In the absence of a trapping agent, reactions designed to give the ketene gave its isomer, perfluoroacryloyl fluoride. Convenient syntheses are described for saturated precursors to perfluoroacryloyl fluoride, methyl perfluoroacrylate and methyl perfluoromethacrylate, and conditions are given for the dehydrofluorination of these precursors to the acrylates. Some chemistry of perfluoromethacryloyl fluoride [available from bis(trifluoromethyl)ketene through equilibration], perfluoroacryloyl fluoride and the related methyl esters are reported, particularly Michael additions, 1,2 cyclo-additions and free-radical reactions.

INTRODUCTION

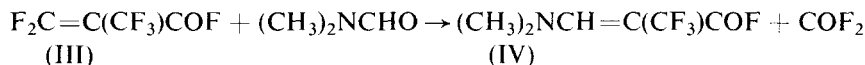
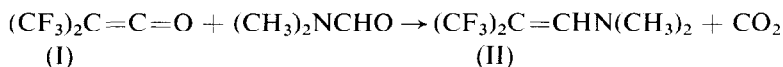
The simplest perfluoroketene, difluoroketene, decomposes readily (carbon monoxide and tetrafluoroethylene being found²) and has been detected only through its derivatives. Bis(trifluoromethyl)ketene, (I), is a stable compound which equilibrates in the vapor phase over sodium fluoride with its isomer, perfluoromethacryloyl fluoride, (III), which is also a stable compound^{3,4}. Dehydrochlorination of $\text{CF}_3\text{CFHCOCl}$ with triethylamine in cyclopentadiene was earlier reported to trap trifluoromethylfluoroketene, (IX), as 7-fluoro-7-trifluoromethylbicyclo-[3,2,0]hept-2-en-6-one⁵. Although we have not been able to isolate (IX), we have similarly detected it through trapping reactions as described below. In addition,

* For Part VI, see ref. 1.

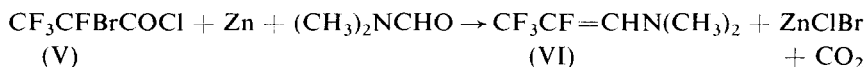
we have found evidence for the isomerization of (IX) to its stable isomer, perfluoroacryloyl fluoride, (VII). Other syntheses of perfluoroacryloyl fluoride have been described^{6,7}, but none is as amenable to straightforward synthesis of large amounts as the catalytic dehydrofluorination of $\text{CF}_3\text{CHF}\text{COF}$, also described below.

ADDITION OF FLUORINATED KETENES AND ACRYLOYL FLUORIDES TO CARBONYL COMPOUNDS

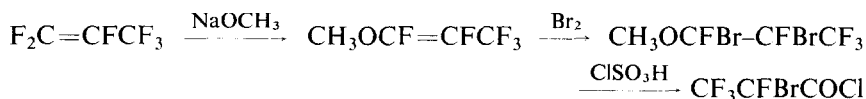
Bis(trifluoromethyl)ketene, (I), is reported to give the unsaturated amine (II) and carbon dioxide with dimethylformamide⁸. In our hands, this reaction gave not only (II) but also some unsaturated acid fluoride (IV). The latter is obtained in high yield from the reaction of (III) with dimethylformamide.



Similarly, we find that dehalogenation of α -bromotetrafluoropropionyl chloride, (V), with zinc in dimethylformamide gives the trifluoromethylfluoroketene derivative (VI) and carbon dioxide.

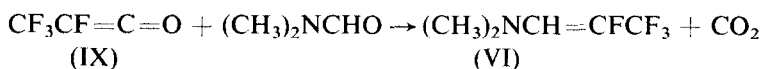
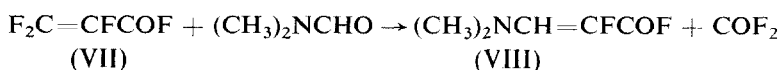


The bromoacid chloride (V) was prepared previously in several steps starting with α -hydrotetrafluoropropionitrile⁹. We used a convenient three-step route from hexafluoropropene,

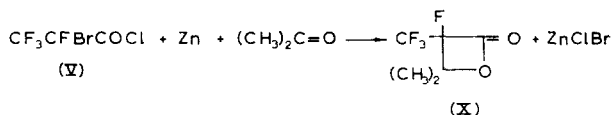


as described in the experimental section.

Reaction of perfluoroacryloyl fluoride, (VII), with dimethylformamide gave the acryloyl fluoride derivative (VIII) and, in one experiment, some of the ketene derivative (VI) also. Formation of (VI) may have resulted from partial isomerization of perfluoroacryloyl fluoride to trifluoromethyl fluoroketene, (IX), prior to reaction with dimethylformamide, or possibly from direct attack of dimethylformamide on the carbonyl carbon of (VII).



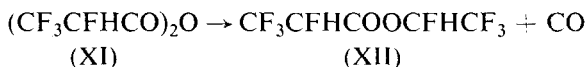
Additional evidence for the transitory existence of (IX) was provided by the dehalogenation of (V) with zinc in the presence of acetone. A 6% yield of α -fluoro- α -(trifluoromethyl)- β,β -dimethylpropiolactone, (X), was obtained in a cyclo-addition similar to that observed with difluoroketene².



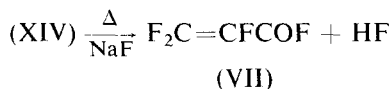
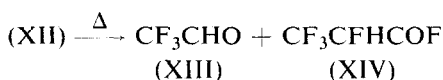
Dehalogenation of (V) by iron in the vapor phase led not to the ketene (IX) but to its isomer, perfluoroacryloyl fluoride, (VII), indicating a rearrangement.

SYNTHESIS OF FLUORINATED ACRYLATE ESTERS AND ACID FLUORIDES

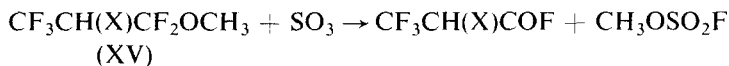
Bis(trifluoromethyl)ketene, (I), is best prepared by heating hexafluoroisobutyric acid with phosphorus pentoxide³. The anhydride of the acid formed as an intermediate is easily pyrolyzed to 1 mol of acid and 1 mol of ketene. Analogously, ketene (IX) might be formed by pyrolysis of α -hydrotetrafluoropropionic anhydride, (XI). However, this pyrolysis gave carbon monoxide and tetrafluoroethyl tetrafluoropropionate, (XII).



Further pyrolysis of (XII) gives fluoral, (XIII), and tetrafluoropropionyl fluoride, (XIV). If this pyrolysis is carried out over sodium fluoride, the acid fluoride (XIV) is converted to perfluoroacryloyl fluoride, (VII), by dehydrofluorination.

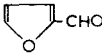
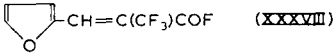
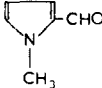
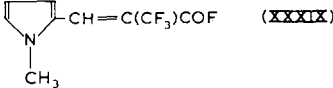
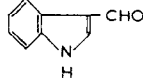
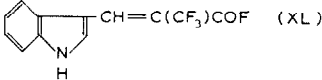
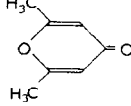
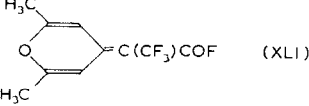
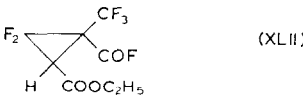


This high-temperature dehydrofluorination provides the most convenient synthesis of perfluoroacryloyl fluoride, (VII). The precursor (XIV) is best prepared by reaction of sulfur trioxide with methyl tetrafluoropropyl ether, (XV) (X = F). Although the preparation of (XV) (X = F) in sealed autoclaves has been reported¹⁰, it is easily made by base-catalyzed addition of methanol to hexafluoropropene under atmospheric pressure conditions as described in the experimental section. Some interesting by-products are also characterized. Sulfur trioxide reacts similarly with methyl hexafluoroisobutyl ether, (XV), (X = CF₃); the latter is available from the reaction of perfluoroisobutylene with methanol^{11,12}.

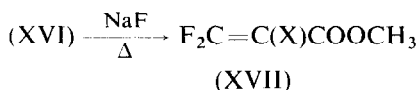
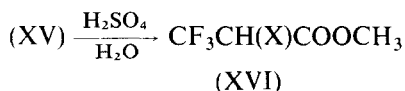


Preparation of perfluoroacrylic acids or esters from the corresponding acryloyl fluorides (III) and (VII) is not practical because nucleophilic attack on these compounds proceeds on the terminal CF_2 groups in preference to the acid fluoride groups. For example, reaction of (III) with excess methanol gives the expected methyl ester, $\text{CH}_3\text{OCF}_2\text{CH}(\text{CF}_3)\text{COOCH}_3$ ¹³, whereas methanol in equimolar amounts leads to a good yield of $\text{CH}_3\text{OCF}_2\text{CH}(\text{CF}_3)\text{COF}$, (XXIX). Such reactions of (III) with alcohols and thiols are given in Table 1. Reaction of

TABLE I
REACTIONS OF PERFLUOROMETHACRYLOYL FLUORIDE

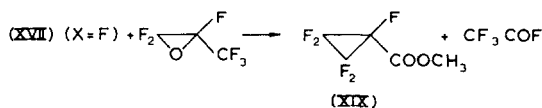
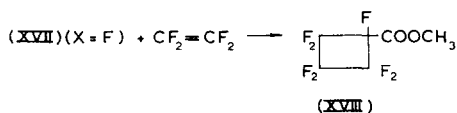
Reactants	Products
CH_3OH	$\text{CH}_3\text{OCF}_2\text{CH}(\text{CF}_3)\text{COF}$ (XXIX)
$\text{C}_6\text{H}_5\text{OH}$	$\text{C}_6\text{H}_5\text{OCF}_2\text{CH}(\text{CF}_3)\text{COF}$ (XXX)
$\text{H}_2\text{C}=\text{CHCH}_2\text{OH}$	$\text{H}_2\text{C}=\text{CHCH}_2\text{OCF}_2\text{CH}(\text{CF}_3)\text{COF}$ (XXXI)
$\text{CH}_3\text{OCOCH}_2\text{OH}$	$\text{CH}_3\text{OCOCH}_2\text{OCF}_2\text{CH}(\text{CF}_3)\text{COF}$ (XXXII)
$\text{HSCH}_2\text{COOCH}_3$	$\text{CH}_3\text{O}_2\text{CCH}_2\text{SCF}_2\text{CH}(\text{CF}_3)\text{COF}$ (XXXIII)
$\text{C}_6\text{H}_5\text{SH}$	$\text{C}_6\text{H}_5\text{SCF}_2\text{CH}(\text{CF}_3)\text{COF}$ (XXXIV)
$\text{HSCH}_2\text{CH}_2\text{OH}$	$\text{HSCH}_2\text{CH}_2\text{OCF}_2\text{CH}(\text{CF}_3)\text{COF}$ (XXXV)
$p\text{-(CH}_3)_2\text{NC}_6\text{H}_4\text{CH}=\text{CHCHO}$	$\text{FOCCH}(\text{CF}_3)\text{CF}_2\text{SCH}_2\text{CH}_2\text{OCF}_2\text{CH}(\text{CF}_3)\text{COF}$ (XXXVI)
	$p\text{-(CH}_3)_2\text{NC}_6\text{H}_4\text{CH}=\text{CHCH}=\text{C}(\text{CF}_3)\text{COF}$ (XXXVII)
	 (XXXVIII)
	 (XXXIX)
	 (XL)
	 (XLI)
$\text{N}_2\text{CHCOOC}_2\text{H}_5$	 (XLII)

(VII) with excess methanol gave the expected $\text{CH}_3\text{OCF}_2\text{CFHCOOCH}_3$, but with (VII) in excess in addition to this major product considerable $\text{CH}_3\text{OCF}_2\text{CFHCOF}$ and minor amounts of $\text{F}_2\text{C}=\text{CFCOOCH}_3$ and $\text{CF}_3\text{CFHCOOCH}_3$ were obtained. The acrylic esters (XVII) ($X = \text{F}$ or CF_3) have been prepared in quantity by dehydrofluorination of the corresponding α -hydro esters (XVI) ($X = \text{F}$ or CF_3) in the vapor phase over sodium fluoride. The esters (XVI) are available by sulfuric acid hydrolysis of the corresponding ethers¹⁰, (XV) ($X = \text{F}$ and CF_3).



Reactivity of perfluoroacryloyl fluoride and methyl perfluoroacrylate

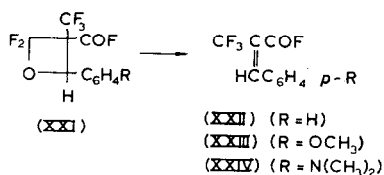
Some differences were noted in the reactivity of the double bond in perfluoroacryloyl fluoride, (VII), and the corresponding ester, methyl perfluoroacrylate, (XVII) ($X = \text{F}$). For example, at 225° it was possible to cyclo-add tetrafluoroethylene to (XVII) ($X = \text{F}$) to give (XVIII). Likewise, hexafluoropropene epoxide and (XVII) ($X = \text{F}$) heated to 225° gave the methyl cyclopropanecarboxylate (XIX). Neither of these two reactions gave any product from (VII) under the same conditions.



The ester (XVII) ($X = \text{F}$) was also dimerized in good yield by the fluoride ion to give $\text{CF}_3\text{CF}(\text{COOCH}_3)\text{CF}=\text{CFCOOCH}_3$ (XX) whereas the acid fluoride (VII) gave a mixture of many products, none of which has been definitely characterized.

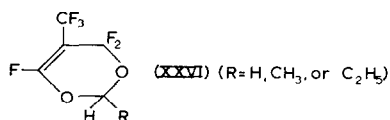
Addition of aldehydes to (III) and (VII)

The type of reaction described above for the acryloyl fluorides (III) and (VII) with dimethylformamide also takes place with other compounds containing the CHO group and appears to involve 1,2 addition of the carbonyl group followed by loss of carbonyl fluoride. For example, the reaction of (III) with benzaldehyde at 100° gave the oxetane (XXI) ($R = \text{H}$) and the products expected from ring cleavage, carbonyl fluoride and the unsaturated acid fluoride (XXII).



Reaction of (III) with anisaldehyde gave (XXIII) and with dimethylaminobenzaldehyde gave (XXIV). Similarly, (VII) gave (XXV) the analog of (XXIV) (F in place of CF_3). Other examples of reactions of aromatic aldehydes with (III) are given in Table I. The acid fluoride (XXIV) was treated with ammonia to give the corresponding amide and with water to give the acid which was decarboxylated by heat.

In contrast to aromatic aldehydes, aliphatic aldehydes react with (III) to give products of the type (XXVI) as a result of 1,4 addition.



Radical reactions

Although it is difficult to homopolymerize the acryloyl fluorides (III) and (VII), they are subject to free-radical catalysis. Benzoyl peroxide-catalyzed addition of cyclohexane gave $\text{C}_6\text{H}_{11}\text{CF}_2\text{C(X)HCOF}$ ($\text{X} = \text{F}$, (XXVII), and $\text{X} = \text{CF}_3$, (XXVIII)) and formation of copolymers with such monomers as ethylene occurred readily.

Reaction of diazoacetic ester

Diazoacetic ester reacted with (III) with loss of nitrogen to give a cyclopropane derivative (XLII) (Table 1). Presumably other nucleophilic-type diazo compounds would react similarly.

EXPERIMENTAL

Melting points and boiling points are uncorrected. ^1H NMR spectra were obtained with a Varian A-60 spectrometer operating at 60 MHz; chemical shifts are reported in ppm from tetramethylsilane as external standard with the downfield direction taken as positive. ^{19}F NMR spectra were obtained with a Varian A56/60 spectrometer operating at 56.4 MHz and peak center positions are reported in ppm downfield from CFCl_3 as external standard.

Methyl 1,1,2,3,3,3-hexafluoropropyl ether (XV) ($\text{X} = \text{F}$): reaction of hexafluoropropene with methanol¹⁰

This addition of methanol to hexafluoropropene (HFP) must be catalyzed by base. However, the base also reacts further with the product and is eventually

neutralized so that the reaction stops. Into a 3 l, three-necked flask, equipped with a large Dry Ice condenser, magnetic stirrer, thermometer and gas inlet, were placed 1 l of methanol and 113 g of powdered sodium methoxide. The mixture was stirred and cooled to 10–25° using a Dry Ice–acetone bath, and addition of HFP was started and maintained at a rate which kept the pot temperature at 10–25° while cooling with the Dry Ice–acetone bath. Reaction was complete when the temperature began to drop rapidly. Addition of HFP was then stopped (after 1414 g had been added) and the mixture poured into an equal volume of cold water in a separating funnel. The heavy layer was removed, washed three more times with an equal volume of water, dried and distilled. There was obtained 1218 g (71%) of the methyl hexafluoropropyl ether, b.p. 53–55° and 142 g of material boiling up to 159°. This material was separated by fractionation into CH₃OCCFHCFCF₃ (XVI) (X = F), b.p. 95° (28%); CH₃OCF₂CFHCFC₂OCH₃¹⁴, b.p. 121° (54%); *trans*-β-methoxydifluoroacryloyl fluoride, CH₃OCF=CFCOF, b.p. 142° (8%); and CH₃OCF₂CFHCOOCH₃, b.p. 159° (10%).

For CH₃OCF₂CFHCFC₂OCH₃: ¹H NMR: 3.34 (singlet, 6H), 4.32 (doublet, *J* = 44.0 Hz to quintets, *J* = 6.0 Hz, 1H). ¹⁹F NMR: –83.1 and –85.7 (A₂B₂ pattern to apparent quintets, *J* = 5.4 Hz, 2F), –86.3 and –88.9 (A₂B₂ pattern to apparent quintets, *J* = 5.4 Hz, 2F) and –211.6 (doublet, *J* = 44 Hz, to quintets, *J* = 11.1 Hz, 1F).

For *trans*-CH₃OCF=CFCOF (nc): IR: 5.50μ (COF) and 5.91μ (C=C). ¹H NMR: 3.77 (triplet, *J* = 0.95 Hz, 3H). ¹⁹F NMR: +13.6 (doublet, *J* = 39 Hz, to doublets, *J* = 59 Hz, 1F), –92.4 (doublet, *J* = 113 Hz, to doublets, *J* = 59 Hz, to quartets, *J* = 0.95 Hz, 1F) and –195.7 (doublet, *J* = 113 Hz, to doublets, *J* = 39 Hz, to quartet, *J* = 0.95 Hz, 1F).

Analysis: Found: C, 34.35; H, 2.07; F, 37.71%. C₄H₃F₃O₂ requires C, 34.31; H, 2.16; F, 40.71%.

*Methyl 2,3,3,3-tetrafluoropropionate*¹⁰ (XVI) (X = F)

This ester, b.p. 96°, was readily prepared by the vigorous mixing of ether (XV) (X = F) with an equal volume of concentrated sulfuric acid with *ca.* 1% of water added. The reaction was exothermic and the yield over 90%.

*2,3,3,3-Tetrafluoropropionyl fluoride*⁹ (XIV)

A 900 g ampoule of liquid sulfur trioxide (11.5 mol) was poured into a 3 l three-necked flask fitted with a thermometer, magnetic stirrer and dropping funnel. The flask was then attached to a 75 cm spinning-band still with an ice-water cooled condenser. While stirring the sulfur trioxide, methyl hexafluoropropyl ether (XV) (X = F) (750 ml, 1040 g, 5.7 mol) was added dropwise. The reaction was exothermic and addition was maintained at a rate sufficient to allow a steady distillation of (XIV), b.p. 25°, into an ice-cooled receiver. When addition was complete, heat was applied to the flask to complete the distillation. There was collected 760 g

(90%) of (XIV). After cooling in Dry Ice, the product was washed three times with 50 ml portions of conc. sulfuric acid to remove sulfur trioxide and re-distilled to give 650 g (77%) of purified (XIV).

Tetrafluoropropionyl fluoride (XIV) has also been prepared from the reaction of fluorosulfonic acid with the ether (XV) ($X = F$), but this reaction is less satisfactory because hydrogen fluoride is evolved and yields are somewhat lower.

The methyl hexafluoropropyl ether (XV) ($X = F$) (728 g, 4 mol) was mixed cold (Dry Ice cooling) with 440 ml (8 mol) of fluorosulfonic acid in a 1 l Monel flask fitted with a water-cooled condenser made of Teflon®. The pot was then warmed on a steam bath. Gases passing through the condenser were condensed in a Dry Ice-acetone trap containing sodium fluoride (112 g). When reaction was complete, (XIV) was re-distilled from the sodium fluoride. Yield: 414 g (70%).

*2,3,3,3-Tetrafluoropropionyl chloride*⁹

This acid chloride was prepared from the ether (XV) ($X = F$) by reaction with chlorosulfonic acid. The ether was mixed at -30° with 274 ml (4 mol) of chlorosulfonic acid in a still pot which was then attached to a still and warmed. At about -5° , HCl gas began to be evolved. α -Hydrotetrafluoropropionyl chloride distilled at 47° and some was carried over into a Dry Ice trap by the HCl evolved. It was recovered by allowing the HCl to escape at room temperature. The total yield was 299 g (91%).

*Perfluoroacryloyl fluoride*⁶ (VII)

The dehydrofluorination of tetrafluoropropionyl fluoride (XIV) to (VII) was shown to be rapidly reversible in the vapor phase in the presence of sodium fluoride catalyst, dehydrofluorination being nearly complete at 550° . A mixture of liquid perfluoroacryloyl fluoride (VII) and HF was shown by gas chromatography not to react on standing at room temperature. Neither did they react when passed through an unpacked platinum tube at 580° (at 1 mm Hg pressure). However, when the tube was packed with sodium fluoride pellets, they did react to form tetrafluoropropionyl fluoride (XIV). At elevated temperatures (500 – 600°), the equilibrium is shifted towards complete dehydrofluorination. Since the reverse reaction does not occur in the absence of catalyst (NaF pellets), excellent results have been obtained by simply not having catalyst present as the mixture cools from the optimum reaction temperature over the catalyst. The mixture of (VII) and HF was condensed in the presence of dry sodium fluoride which removed the HF by forming NaHF_2 .

A vertically mounted Monel tube (85 cm \times 6.25 cm) was fitted with a nickel gauze plug in the center and packed from this point up with 700 ml of 3 mm sodium fluoride pellets. The temperature at the bottom of the catalyst bed was controlled. The vacuum applied to about 250 g of (XIV) (cooled in an ice bath) through the tube was maintained at 12 mmHg pressure and the temperature fell

from 560° to 478° during the run (15 min). The products were condensed by liquid-nitrogen cooling in a stainless-steel trap containing 100 g of dry sodium fluoride powder. The crude product was vaporized from NaHF₂ by slightly warming and shaking the trap and condensing the product under vacuum in a second trap. This gave 197 g of a mixture containing 95% (VII) and 5% (XIV) (90% yield, 87% conversion). The solid weighed 127 g and accounted for 27 g of the 34 g of HF expected as NaHF₂.

Methyl perfluoroacrylate (XVII) (X = F) (nc)

This ester has been prepared as described above for (VII) using a platinum tube (2 cm × 35 cm) packed at the top half with 50 cc of sodium fluoride pellets and collecting the product in a metal trap over sodium fluoride powder to form NaHF₂.

A 32 g portion of methyl α -hydroperfluoropropionate was passed in the vapor phase through the tube at 600° (0.7–2 mmHg pressure) in 80 min. There was recovered 27 g of a mixture containing 65% of methyl perfluoroacrylate and 35% of starting material corresponding to 62.5% conversion and 87.5% yield. The product was not easily separated from the starting material by distillation but was easily purified by gas chromatography using a 20% diglyceride on Gas Chrom R column. It boiled at *ca.* 86°, n_D^{25} 1.3556. IR: 5.65 μ (C=O) and 5.72 μ (C=C). ¹H NMR: 3.49 (singlet, 3H). ¹⁹F NMR: -89.4 (doublet, *J* = 35 Hz, to doublets, *J* = 26 Hz, 1F), -99.7 (doublet, *J* = 111 Hz, to doublets, *J* = 26 Hz, 1F) and -187.1 (doublet, *J* = 111 Hz, to doublets, *J* = 35 Hz, 1F). Analysis: Found: C, 34.08; H, 2.08; F, 40.13%. C₄H₃F₃O₂ requires C, 34.31; H, 2.16; F, 40.71%.

Methyl α -hydrohexafluoroisobutyrate¹⁰ (XVI) (X = CF₃)

An immiscible mixture consisting of 121 g of methyl 1,1,3,3,3-pentafluoro-2-(trifluoromethyl)propyl ether (XV) (X = CF₃) and 125 ml of conc. sulfuric acid in a 500 ml round-bottomed flask was brought to reflux for 15 min and then cooled to give a homogeneous solution. This solution was poured into 200 g of ice and the heavy organic layer washed with water to yield 102 g (93%) of crude methyl hexafluoroisobutyrate. The ester may be distilled over P₂O₅ (b.p. 90°).

α -Hydrohexafluoroisobutyryl fluoride and chloride^{11,12}

Chlorosulfonic acid was found to react rapidly with (XV) (X = CF₃) at about 0° with evolution of HCl to yield a mixture of hexafluoroisobutyric acid fluoride and chloride in nearly quantitative yield.

The ether (XV) (X = CF₃) (464 g, 2 mol) was placed in a 2 l round-bottomed flask and cooled to about -40° with a Dry Ice-acetone bath. The chlorosulfonic acid (200 ml, 4 mol) was then added quite rapidly while the mixture was stirred with a magnetic stirrer and kept below -30°. When addition was complete, the flask was fitted with a still head to which was attached a receiver and a Dry Ice-acetone trap vented up the hood. When the temperature reached about 0°, evolution

of HCl began. A moderate evolution of HCl was maintained by control of the pot temperature. When evolution of gas became slow the pot was heated and hexafluoroisobutyryl fluoride, b.p. 30°, collected in the ice-cooled receiver. A second fraction of hexafluoroisobutyryl chloride, b.p. 54°, was then collected and the higher boiling material discarded (after cooling) by careful dilution with water in the hood drain. A considerable amount of the acid fluoride was recovered from the Dry Ice-acetone trap after this was allowed to warm to room temperature, venting off the HCl. The yield was 209 g (53%) of acid fluoride and 169 g (40%) of acid chloride. When equimolar amounts of chlorosulfonic acid and ether were used, much more HF was evolved (glass etching) and slightly more acid fluoride obtained (65%) and less acid chloride (20%). When sulfur trioxide was used in place of chlorosulfonic acid (run analogous to the preparation of (XIV)), the product was the acid fluoride in nearly quantitative yield.

Perfluoromethacryloyl fluoride (III) and bis(trifluoromethyl)ketene (I)³ by the dehydrofluorination of α -hydrohexafluoroisobutyryl fluoride

It is not surprising that dehydrofluorination of α -hydroperfluoroisobutyryl fluoride gives both (I) and (III) since either may be formed directly and since they are known to be in equilibrium with each other in the vapor phase over sodium fluoride catalyst. A 25 g sample of the acid fluoride was passed through a platinum tube (2 cm \times 35 cm) packed at the top half with 50 cc of sodium fluoride pellets. Five minutes was required at 507° (0.4–1.0 mmHg pressure) when there was obtained 7.5 g (35% conversion, 37.5% yield) of the ketene (I) and 10 g (46% conversion, 50% yield) of (III).

Methyl perfluoromethacrylate (XVII) ($X = CF_3$)

This reaction has also been undertaken in the large Monel tube as described above for the preparation of (VII). A 588 g sample of methyl α -hydroperfluoroisobutyrate was passed through the tube at 625° (1–10 mmHg pressure) in 4 h and condensed in a stainless-steel trap over sodium fluoride powder. The condensate was shown to be 52% methyl perfluoromethacrylate and 48% starting material by GLPC analysis. On distillation, 335 g was recovered, and the last 85 g distilled (95°) was over 90% pure product. IR: 5.65 μ (C=O), 5.83 μ (C=C). ¹H NMR: 3.49 (singlet, 3H). ¹⁹F NMR: –60.8 to –63.5 (complex pattern with 20 resolved peaks with a major peak at –61.5).

Methyl perfluoromethacrylate has also been prepared by dechlorination of methyl α,β -dichloropentafluoroisobutyrate¹⁵.

Reaction of hexafluoropropene with sodium methoxide. Cis- and trans-1-methoxy-pentafluoropropene

Perfluoroallyl chloride has been reported to react with sodium methoxide to give the allyl ether which rearranged to 1-methoxypentafluoropropene on

standing. Both of the unsaturated ethers were brominated¹⁶. A more convenient synthesis of 1-methoxy-pentafluoropropene is the following reaction of hexafluoropropene with sodium methoxide in tetrahydrofuran.

A sample (454 g, 6.4 mol) of dry sodium methoxide powder was stirred in 1 l of dry tetrahydrofuran in a flask equipped with a Dry Ice condenser and kept below -50° while adding 1200 g of perfluoropropene as a gas. The mixture was then allowed to warm slowly with stirring to -15° . At this stage it was necessary to cool intermittently with a Dry Ice-acetone bath to keep the temperature at -10° to -15° and to cut down the amount of perfluoropropene refluxing. As the reaction subsided, the mixture was allowed to warm to $25-30^{\circ}$ and stirred at this temperature for 1 h before pouring into ice water. The heavy layer was washed six times with water, dried and distilled. There was obtained 89 g of material b.p. $35-50^{\circ}$, which was largely the linear dimer of perfluoropropene, 700 g (53%) of a material b.p. $50-70^{\circ}$ (mostly $55-60^{\circ}$), which was mostly *cis*- and *trans*-1-methoxy-pentafluoropropene, and about 200 g of a high boiling material. The *trans* ether boiled at a higher temperature than the *cis* and complete separation was accomplished by GLPC.

For the *cis* isomer: ^1H NMR: 3.35 (doublet, $J = 1.3$ Hz, to doublets, $J = 0.6$ Hz, 3H). ^{19}F NMR: -70.0 (doublet, $J = 12.5$ Hz, to doublets, $J = 10.0$ Hz, 3F), -98.1 (doublet, $J = 18.0$ Hz, to quartets, $J = 10.0$ Hz, to quartets, $J = 1.3$ Hz, 1F), -189.0 (doublet, $J = 18.0$ Hz, to quartets, $J = 12.5$ Hz, to quartets, $J = 0.6$ Hz, 1F).

For the *trans* isomer: ^1H NMR: 3.47 (triplet, $J = 1.1$ Hz, 3H). ^{19}F NMR: -69.7 (doublet, $J = 22.8$ Hz, to doublets, $J = 13.0$ Hz, 3F), -114.0 (doublet, $J = 120.0$ Hz, to quartets, $J = 22.8$ Hz, to quartets, $J = 1.1$ Hz, 1F) and -197.3 (doublet, $J = 120.0$ Hz, to quartets, $J = 13.0$ Hz, to quartets, $J = 1.1$ Hz, 1F).

*1-Methoxy-1,2-dibromopentafluoropropane*¹⁴

A mixture of the above-mentioned *cis*- and *trans*-unsaturated ethers (500 g, 2.75 mol) was stirred at -30° and bromine added until an orange-red color persisted (140 ml, 408 g, 2.55 mol). The mixture was then washed with 10% sodium hydroxide to remove excess bromine, with water, dried and distilled to give 760 g (86% on ether used, 93% on bromine used) of dibromide, b.p. $41^{\circ}/20$ mmHg.

*α -Bromotetrafluoropropionyl chloride and bromide*⁹

Chlorosulfonic acid (225 ml, 4.2 mol) was stirred and cooled at 0° to -10° in a flask equipped with a Dry Ice condenser while adding dropwise 653 g (2.03 mol) of the above dibromide. When the reaction was complete, the mixture was stirred at room temperature for 1 h until evolution of hydrogen chloride had stopped. A material which was volatile at the pressure generated by a water pump on warming to *ca.* 50° was then collected in a large Dry Ice trap. It was shaken with

mercury to remove bromine and distilled over mercury. The yield of $\text{CF}_3\text{CFBrCOCl}$, b.p. ca. 70° , was 335 g (69%) and of $\text{CF}_3\text{CFBrCOBr}$, b.p. 88° , was 130 g (21%).

Dehalogenation of α -bromotetrafluoropropionyl chloride in dimethylformamide

To a stirred mixture consisting of 25 ml of dimethylformamide and 12 g amalgamated zinc was added dropwise 24 g (0.1 mol) of the above acid chloride keeping the temperature below 10° . About 1 l of gas, which was identified as carbon dioxide by infrared spectroscopy, was collected. Volatile material was collected in a liquid-nitrogen trap when the reaction vessel was heated with boiling water under vacuum. This material was re-distilled to give 1.6 g (10%) of $\text{CF}_3\text{CF}=\text{CHN}(\text{CH}_3)_2$, (VI), b.p. $56^\circ/110$ mmHg, shown by infrared spectroscopy to be identical to the material prepared from perfluoroacryloyl fluoride (VII) and dimethylformamide (see below).

Dehalogenation of α -bromotetrafluoropropionyl chloride in acetone. α -Fluoro- α -(trifluoromethyl)- β,β -dimethylpropiolactone (nc)

A mixture of 13 g (0.2 mol) of amalgamated zinc in 50 ml of acetone was stirred while 24.5 g (0.1 mol) of α -bromoperfluoropropionyl chloride was added dropwise. The temperature was kept at 30 – 40° by cooling. When addition was complete, the mixture was stirred for 10 min, filtered and the filtrate distilled. After removal of acetone, there was obtained 2.5 g (6%) of α -fluoro- α -(trifluoromethyl)- β,β -dimethylpropiolactone, b.p. $63^\circ/100$ mmHg. It was further purified by gas chromatography. IR: 5.35μ ($\text{C}=\text{O}$). ^1H NMR: 1.35 (doublet, $J = 5.0$ Hz, 3H), 1.40 (broad singlet, 3H). ^{19}F NMR: -76.4 (doublet, $J = 9.5$ Hz, to quartets, $J = 1.5$ Hz, 3F) and -179.7 (quartet, $J = 9.5$ Hz, to quartets, $J = 5.0$ Hz, 1F). Analysis: Found: C, 39.34; H, 3.48; F, 41.06%. $\text{C}_6\text{H}_6\text{F}_4\text{O}_2$ requires C, 38.74; H, 3.25; F, 40.86%.

Dehalogenation of α -bromotetrafluoropropionyl chloride by iron

α -Bromoperfluoropropionyl chloride was passed under vacuum over steel wool packed in a quartz tube heated by an electric furnace. The resulting products were collected in a trap cooled by liquid nitrogen. No reaction occurred at 300° , but at 400° a reaction took place (435° hot-spot) and perfluoroacryloyl fluoride was isolated.

Reaction of perfluoroacryloyl fluoride (VII) with dimethylformamide. 1-Dimethylamino-2,3,3,3-tetrafluoroprop-1-ene (nc) and α -fluoro- β -dimethylaminoacryloyl fluoride (VIII) (nc) (its methyl ester (nc) and N,N-dimethylamide (nc))

Dimethylformamide (7 g) was condensed in a Carius tube with 8 ml (13.5 g) of (VII) at liquid-nitrogen temperature. On warming to room temperature, the mixture turned yellow and became black after 15 min heating on a steam bath.

Both CO_2 and COF_2 were detected in the gas evolved. A fraction, b.p. $38\text{--}40^\circ/60$ mmHg, (1.8 g) was purified by gas chromatography and characterized as $\text{CF}_3\text{CF}=\text{CHN}(\text{CH}_3)_2$, (VI). Another fraction, b.p. $68\text{--}84^\circ/0.6$ mmHg, (2.7 g) solidified, was recrystallized from carbon tetrachloride and characterized as $(\text{CH}_3)_2\text{NCH}=\text{CFCOF}$, (VIII), m.p. $53\text{--}54^\circ$.

For (VI): IR: 5.82μ ($\text{C}=\text{C}$). ^1H NMR: 5.43 (doublet, $J = 30$ Hz, 1H) and 2.50 (multiplet, 6H). ^{19}F NMR: -70.0 (doublet, $J = 15$ Hz, with fine structure, 3F) and -181.0 (doublet, $J = 30$ Hz, to quartets, $J = 15$ Hz, with fine structure, 1F). Analysis: Found: C, 38.05; H, 4.26; F, 48.18; N, 8.80%. $\text{C}_3\text{H}_7\text{F}_4\text{N}$ requires C, 38.25; H, 4.49; F, 48.41; N, 8.92%.

For (VIII): IR: 5.65μ ($\text{C}=\text{O}$), 6.05μ ($\text{C}=\text{C}$). ^1H NMR: 6.84 (doublet, $J = 26$ Hz, 1H) and 3.13 (doublet, $J = 1.5$ Hz, 6H). ^{19}F NMR: -11.8 (doublet, $J = 56$ Hz, 1F) and -180 (doublet, $J = 56$ Hz, to doublets, $J = 26$ Hz, 1F). Analysis: Found: C, 44.66; H, 5.44; N, 10.21; F, 28.00%. $\text{C}_5\text{H}_7\text{F}_2\text{NO}$ requires C, 44.48; H, 5.23; N, 10.38; F, 28.15%.

Only the acid fluoride (VIII) was isolated from the following preparation. A solution of (VII) (52 g, 0.4 mol) in 100 ml of ether was kept by cooling at 0° to -5° while 25 g (0.34 mol) of dimethylformamide was added dropwise. On warming slowly with stirring, COF_2 was evolved at about 20° . Removal of ether gave 22 g of crystalline (VIII) in four crops. Distillation of the residue gave about 8 g of a low-boiling material and an additional 3 g of (VIII). The total yield was 25 g (54%).

A diethylamide, $(\text{CH}_3)_2\text{NCH}=\text{CFCON}(\text{C}_2\text{H}_5)_2$, was prepared from the acid fluoride. To 25 g of diethylamine in 50 ml of ether was added dropwise with stirring of solution consisting of 8.7 g of the acid fluoride in 75 ml of ether. After addition was complete, the mixture was water-washed, dried and distilled to give 9.5 g (78%) of the above amide, b.p. $88^\circ/0.6$ mmHg, n_D^{25} 1.5100. IR: 5.95μ ($\text{C}=\text{O}$) and 6.25μ ($\text{C}=\text{C}$). ^1H NMR: 6.3 (doublet, $J = 39$ Hz, 1H), 3.12 (quartet, $J = 7$ Hz, to doublets, $J = 2$ Hz, 4H), 0.90 (triplet, $J = 7$ Hz, 6H), and 2.7 (doublet, $J = 2$ Hz, 6H). ^{19}F NMR: -164 (doublet, $J = 30$ Hz, with fine structure). Analysis: Found: C, 57.42; H, 8.73; F, 10.16; N, 15.28%. $\text{C}_9\text{H}_{17}\text{FN}_2\text{O}$ requires C, 57.49; H, 9.11; F, 10.11; N, 14.90%.

A methyl ester, $(\text{CH}_3)_2\text{NCH}=\text{CFCOOCH}_3$, was prepared from the acid fluoride. The acid fluoride (22 g, 0.16 mol) was dissolved in 50 ml of methanol and added slowly with stirring to 50 ml (0.36 mol) of triethylamine, keeping the temperature below 55° . The mixture was washed with water, dried and distilled to give 8.4 g (35%) of the ester, b.p. $66^\circ/0.25$ mmHg. It could be recrystallized from carbon tetrachloride with cooling, m.p. $25\text{--}28^\circ$. IR: 5.84μ ($\text{C}=\text{O}$) and 6.02μ ($\text{C}=\text{C}$). ^1H NMR: 6.42 (doublet, $J = 28$ Hz, 1H), 3.43 (singlet, 3H), 2.77 (doublet, $J = 1.5$ Hz, 6H). ^{19}F NMR: -175 (doublet, $J = 28$ Hz, to septets, $J = 1.5$ Hz). Analysis: Found: C, 49.39; H, 6.90; F, 12.63; N, 9.20%. $\text{C}_6\text{H}_{10}\text{FNO}_2$ requires C, 49.02; H, 6.86; F, 12.93; N, 9.53%.

Reaction of perfluoromethacryloyl fluoride (III) with dimethylformamide. α -Trifluoromethyl- β -dimethylaminoacryloyl fluoride (IV) (nc)

To 89.0 g (0.5 mol) of perfluoromethacryloyl fluoride, magnetically stirred in a dry nitrogen atmosphere in a flask immersed in an ice bath, 36.5 g (0.5 mol) of dimethylformamide was added at a rate which maintained the reaction temperature at 12–15° (ca. 1 h). Gas evolution was immediate and continuous during the addition. After the addition was complete (ca. 1 h), the reaction mixture was stirred under a slight stream of nitrogen at room temperature for 2 h and then distilled to give 74.5 g of a pale yellow liquid (81% yield), b.p. 67–68°/0.7 mmHg. NMR spectroscopy indicated a mixture of *cis* and *trans* isomers. IR: 5.64 μ (C=O) and 6.12 μ (C=C). ¹H NMR: 3.25 (two overlapping singlets of the two isomers, 6H) and 7.5 (broad singlet and a doublet, $J = 7$ Hz, 1H). ¹⁹F NMR: For the main isomer (60%): -57.2 (doublet, $J = 14$ Hz, 3F) and +26.1 (quartet, $J = 14$ Hz, to doublets, $J = 7$ Hz, 1F). For the minor (40%) isomer: -49.3 (doublet, $J = 16$ Hz, 3F) and +11.7 (quartet, $J = 16$ Hz, 1F). Analysis: Found: C, 39.42; F, 41.03; H, 3.92; N, 7.53%. C₆H₇F₄NO requires C, 38.92; F, 41.05; H, 3.81; N, 7.57%.

Reaction of bis(trifluoromethyl)ketene with dimethylformamide. Hexafluoroisobutenyldimethylamine (II) and (IV)

This reaction is reported to give the unsaturated amine (II). In the following reaction, (IV) was also formed, probably due to some rearrangement of the ketene to perfluoromethacryloyl fluoride by the dimethylformamide.

Each of two Carius tubes was loaded with 15 g of dimethylformamide and 39 g of bis(trifluoromethyl)ketene at liquid-nitrogen temperature. On thawing, a white solid was rapidly formed in the cold. On standing at room temperature for a short time, the solid was exothermally converted to a two-phase liquid mixture. After heating for 2 h on a steam bath, the mixture was homogeneous at room temperature. After heating overnight on a steam bath, there was recovered 18 g of material volatile below -30° (probably CO₂ + COF₂), 8 g of the ketene and the residue was distilled to give 63 g (74%) of compound (II), b.p. 64°/15 mmHg, n_D^{25} 1.3818 and 15 g (20%) of compound (IV), n_D^{25} 1.4512.

For (II): IR: 6.02 μ (C=C). ¹H NMR: 2.7 (quartet, $J(\text{H-cis-CF}_3) = 4.0$ Hz, to quartets, $J(\text{H-trans-CF}_3) = 0.8$ Hz, 6H), 6.6 (quartet, $J(\text{H-trans-CF}_3) = 1.5$ Hz, to quartets, $J(\text{H-cis-CF}_3) = 0.3$ Hz, 1H). ¹⁹F NMR: -47.1 (quartet, $J(\text{F-F}) = 9.5$ Hz, to septets, $J(\text{H-F}) = 4.0$ Hz, to doublets, $J(\text{H-F}) = 1.5$ Hz, 3F) and -55.0 (quartet, $J(\text{F-F}) = 9.5$ Hz, to septets, $J(\text{H-F}) = 0.8$ Hz, to doublets, $J(\text{H-F}) = 0.3$ Hz, 3F)*.

* We are indebted to Dr. F. J. Weigert for the resolution of this spectrum.

Pyrolysis of α -hydrotetrafluoropropionic acid anhydride. Tetrafluoroethyl tetrafluoropropionate¹⁷ (XII), (XIV) and (VII)

The above anhydride (50 g) was passed under low pressure over quartz in a vertically mounted tube heated to 550°. The gas evolved was passed through a liquid-nitrogen cooled condenser. Evolution of gas (presumably CO) made it difficult to maintain the low pressure. Only a trace of material boiling at room temperature or below was recovered together with 14 g (31%) of tetrafluoroethyl tetrafluoropropionate (XII), b.p. 47°/205 mmHg, and 25 g of a higher boiling material, presumably unchanged anhydride and acid. When the pyrolysis was undertaken at 650°, there was obtained from 50 g of anhydride, 14 g of the above ester, 20 g of a mixture of (VII) (25%) and (XIV) (75%) and 5 g of high boiling material.

Reaction of perfluoroacryloyl fluoride (VII) with methanol

The major product of this reaction was methyl α -fluoro- β,β -difluoro- β -methoxypropionate (nc), $\text{CH}_3\text{OCF}_2\text{CFHCOOCH}_3$, but by using (VII) in excess it was also possible to isolate three other products.

To a stirred mixture consisting of 10 g of sodium fluoride, 10 ml of methylene chloride and 16 ml (25 g, 0.2 mol) of (VII) was added dropwise with stirring a solution of 3.2 g (0.1 mol) of methanol, keeping the temperature below 20°. Distillation gave 2 g of a liquid, b.p. 32–34°/85 mmHg. This was largely $\text{CH}_3\text{-OCF}_2\text{CFHCOF}$ (nc) containing some $\text{F}_2\text{C}=\text{CF-COOCH}_3$, (XVII) ($X = \text{F}$), and $\text{CF}_3\text{CFHCOOCH}_3$, (XVI) ($X = \text{F}$). In addition, there was distilled 5 g of a material of b.p. 62°/25 mmHg which was largely $\text{CH}_3\text{OCF}_2\text{CFHCOOCH}_3$. This methoxy ester was the major product when an excess of methanol was used.

The acryloyl fluoride (VII) (25 g) was added dropwise with cooling to 25 ml of methanol keeping the temperature at 30–40°. The mixture was then poured into cold water and the heavy layer separated, water-washed and distilled to give 23.5 g (70%) of the methoxy ester, b.p. 63°/18 mmHg, n_D^{25} 1.3600. IR: 5.65 μ ($\text{C}=\text{O}$). ^1H NMR: 4.87 (doublet, $J = 45$ Hz, to triplets, $J = 5.7$ Hz, 1H), 3.62 (singlet, 3H) and 3.43 (singlet, 3H). ^{19}F NMR: –205 (doublet, $J = 45$ Hz, to doublets, $J = 13$ Hz, to doublets, $J = 11$ Hz, 1F), –83.7 and –86.4 (half of AB pattern, doublets, $J = 11$ Hz, to doublets, $J = 5.2$ Hz, 1F) and –86.7 and –89.4 (half of AB pattern, doublets, $J = 13$ Hz, to doublets, $J = 5.7$ Hz, 1F). Analysis: Found: C, 35.06; H, 4.31; F, 33.19%. $\text{C}_5\text{H}_7\text{F}_3\text{O}_3$ requires C, 34.91; H, 4.10; F, 33.14%.

For $\text{CH}_3\text{OCF}_2\text{CFHCOF}$: ^{19}F NMR: +29.7 (multiplet, 1F), –205 (multiplet, 1F), –83.1, –85.8, –86.5 and –89.2 (AB multiplets, 2F).

Reaction of perfluoromethacryloyl fluoride (III) with methanol. 2-Trifluoromethyl-3,3-difluoro-3-methoxypropionyl fluoride (XXIX) (nc)

Reaction of (III) with excess methanol gives $\text{CH}_3\text{OCF}_2\text{CH}(\text{CF}_3)\text{COOCH}_3$ ¹³, but by using an equimolar amount of methanol it was possible to prepare the above methoxyacid fluoride.

A flask fitted with a rubber serum cap containing 26.7 g of perfluoromethacryloyl fluoride (0.15 mol) was placed in an ice bath. Methanol (4.8 g, 0.15 mol) was slowly added *via* a syringe through the serum cap at a rate sufficient to cause gentle refluxing. After the addition was completed (*ca.* 30 min), the reaction was left for a further 30 min at room temperature and then distilled to give 21.8 g of product (70%), b.p. 88°. IR: 5.37 μ (C=O). ^1H NMR: 3.75 (singlet, 3H), 4.13 (12 line pattern consistent with quartet, $J = 7.6$ Hz, to triplets, $J = 7.6$ Hz, to doublets, $J = 3.6$ Hz, 1H). ^{19}F NMR: ± 49.2 (multiplet, 1F), -65.1 (multiplet, 37) and -74.4 (multiplet, 2F). Analysis: Found: C, 28.90; H, 2.34; F, 54.20%. $\text{C}_5\text{F}_6\text{H}_4\text{O}_2$ requires C, 28.59; H, 1.92; F, 54.27%.

2-Trifluoromethyl-3,3-difluoro-3-methoxypropionanilide (nc)

To a magnetically stirred solution of 15.4 g (0.163 mol) of aniline in 75 ml of methylene chloride was added 14.6 g (0.075 mol) of the methyl ether prepared from perfluoromethacryloyl fluoride as mentioned above. Immediate precipitation of a white solid occurred and stirring became difficult and remained so after the addition of 15 ml of chloroform. After the addition was complete (1 h), the reaction mixture was stirred for an additional hour and then filtered to give a white solid. The solid was washed with methylene chloride and then with hot water and dried to give 16 g of the above anilide, m.p. 139–141°. This was recrystallized from benzene–hexane and sublimed, m.p. 143–144°. IR: 5.86 μ (C=O). UV: λ_{max} , (EtOH) 244 m μ ($\epsilon = 13\,900$). ^1H NMR: 3.65 (singlet, 3H), 4.25 [sextet (quartet, $J = 8.4$ Hz, to triplets, $J = 8.4$ Hz), 1H], 7.8–7.1 (multiplet, 5H), 0.4 (broad, 1H). ^{19}F NMR: -65.1 (triplet, $J = 9.6$ Hz, to doublets, $J = 8.0$ Hz, 3F), -76.0 (multiplet, 2F). Analysis: Found: C, 46.91; H, 3.64; F, 32.64%. $\text{C}_{11}\text{H}_{10}\text{F}_5\text{NO}_2$ requires C, 46.65; H, 3.57; F, 33.55%.

Reaction of (III) with sodium methoxide. Methyl trifluoromethylmalonate

A suspension of 5.4 g (0.1 mol) of sodium methoxide in 50 ml of tetrahydrofuran was cooled and stirred while 18 g (0.1 mol) of perfluoromethacryloyl fluoride was added dropwise, the temperature being kept below 20°. The resulting solution was poured into water and the heavy layer separated, dried and distilled to give 4.0 g (80% based on 4 mol NaOCH_3 to give 1 mol of product) of methyl trifluoromethylmalonate, b.p. 44°/1.5 mmHg. IR: 5.68 μ (C=O). ^1H NMR: 4.2 (quartet, $J = 8.5$ Hz, 1H), 3.6 (singlet, 6H). ^{19}F NMR: -67.2 (doublet, $J = 8.5$ Hz, 3F). Analysis: Found: C, 36.07; H, 3.41; F, 28.97%. $\text{C}_6\text{H}_7\text{F}_3\text{O}_4$ requires C, 36.00; H, 3.50; F, 28.50%.

Reaction of (III) with phenol. 2-Trifluoromethyl-3,3-difluoro-3-phenoxypropionyl fluoride (XXX) (nc)

A mixture consisting of 14.1 g of phenol (0.15 mol) and 26.7 g of perfluoromethacryloyl fluoride was sealed in a Carius tube and heated overnight on a

steam bath. Distillation gave 20.0 g of (XXX), b.p. 73°/10 mmHg. IR: 5.36 μ (C=O). ^1H NMR: 7.15 (singlet, 5H), 4.13 (quartet, $J = 7$ Hz, to triplets, $J = 7$ Hz, to doublets, $J = 3$ Hz, 1H). Analysis: Found: C, 44.34; F, 41.76; H, 2.39%. $\text{C}_{10}\text{F}_6\text{H}_6\text{O}_2$ requires C, 44.15; F, 41.91; H, 2.22%.

Reaction of (III) with allyl alcohol. 3-Allyloxy-3,3-difluoro-2-trifluoromethylpropionyl fluoride (XXXI) (nc)

To 35.6 g of perfluoromethacryloyl fluoride, magnetically stirred in an ice bath, was added 11.6 g (0.2 mol) of allyl alcohol over 1 h. The reaction mixture was left for 2 h at room temperature and then distilled to give 25 g (53%) of (XXXI), b.p. 68°/120 mmHg. IR: 5.36 μ (C=O). ^1H NMR: 4.5 (multiplet, 2H), 4.05 (multiplet, 1H), 5.13 to 5.5 (multiplet, 2H) and 5.4 to 6.3 (multiplet, 1H). ^{19}F NMR: +49.4 (multiplet, 1F), -64.9 (multiplet, 3F) and -71.1 (multiplet, 2F). Analysis: Found: C, 36.35; H, 3.04; F, 48.17%. $\text{C}_7\text{F}_6\text{H}_6\text{O}_2$ requires C, 35.62; H, 2.56; F, 48.31%.

Reaction of (III) with methyl hydroxyacetate. 2-Trifluoromethyl-3,3-difluoro-3-methoxycarbonylmethylpropionyl fluoride (XXXII) (nc)

To 35.6 g of perfluoromethacryloyl fluoride (0.2 mol) which was magnetically stirred in an ice bath, 18.0 g of methyl hydroxyacetate was slowly added over 1 h. The material was then distilled to give 39.2 g (74%) of (XXXII), b.p. 85–93°/0.35 mmHg. A sample was re-distilled for analysis, b.p. 99–100°/4 mmHg. IR: 5.35 μ (C=O), 5.6–5.7 μ doublet (C=O, ester). ^1H NMR: 3.8 (singlet, 3H), 4.6 (multiplet, 2H), 4.4 (multiplet, 1H). ^{19}F NMR: +49.8 (multiplet, 1F), -64.6 (multiplet, 3F) and -71.9 (multiplet, 2F). Analysis: Found: C, 31.88; H, 2.44; F, 42.20%. $\text{C}_7\text{F}_6\text{H}_6\text{O}_4$ requires C, 31.37; H, 2.26; F, 42.54%.

Reaction of (III) with methyl mercaptoacetate. 2-Trifluoromethyl-3,3-difluoro-3-methoxycarbonylmethylthiopropionyl fluoride (XXXIII) (nc)

A Carius tube was charged with 17.8 g (0.1 mol) of perfluoromethacryloyl fluoride and 10.6 g (0.1 mol) of methyl mercaptoacetate and heated for 3 h on a steam bath and then left overnight at room temperature. The gases were vented and the liquid was distilled to give 17.0 g (61%) of (XXXIII), b.p. 57–60°/0.6 mmHg. A sample was re-distilled for analysis, b.p. 53–55°/0.4 mmHg. IR: 5.38 μ (COF), 5.72 μ (COOCH₃). ^1H NMR: 3.80 (singlet, 3H), 3.82 (singlet, 2H). Analysis: Found: C, 30.04; F, 39.61; H, 1.68; S, 11.12%. $\text{C}_7\text{F}_6\text{H}_6\text{O}_3\text{S}$ requires C, 29.58; F, 40.11; H, 2.12; S, 11.28%.

Reaction of (III) with benzenethiol. 2-Trifluoromethyl-3,3-difluoro-3-phenylthiopropionyl fluoride (XXXIV) (nc)

A Carius tube was charged with 17.8 g (0.1 mol) of perfluoromethacryloyl fluoride and 11.0 g (0.1 mol) of benzenethiol and heated for 4 h on a steam bath

and then left overnight at room temperature. The gases were vented and the liquid was distilled to give 19.2 g (68%) of (XXXIV), b.p. 90–93°/8 mmHg. IR: 5.37 μ (C=O). ^1H NMR: 4.0 (multiplet, 1H), 7.4 (multiplet, 5H). Analysis: Found: C, 42.03; H, 2.30; F, 39.82; S, 11.31%. $\text{C}_{10}\text{F}_6\text{H}_6\text{OS}$ requires C, 41.67; H, 2.10; F, 39.55; S, 11.13%.

Reaction of (III) with β -mercaptoethanol. 3,3-Difluoro-2-trifluoromethyl-7-mercapto-4-oxahexanoyl fluoride (XXXV) (nc) and 2,9-bis(trifluoromethyl)-3,3,8,8-tetrafluoro-4-oxa-7-thiadecandioyl difluoride (XXXVI) (nc)

To a flask, immersed in an ice bath, containing 17.8 g (0.1 mol) of (III), magnetically stirred in a dry-nitrogen atmosphere, 7.8 g of β -mercaptoethanol was added, at a rate (*ca.* 1 h) which maintained the exothermic reaction below 20°. The reaction was left at room temperature for 1 h and then distilled to give 14.7 g (57.5%) of (XXXV), b.p. 29–32°/1.5 mmHg and 3.27 g (15%) of (XXXVI), b.p. 65–73°/0.8 mmHg.

For (XXXV): IR: 5.39 μ (C=O). ^1H NMR: 1.5 μ (triplet, $J = 9$ Hz, 1H), 2.8 (doublet, $J = 9$ Hz, to triplets, $J = 6.5$ Hz, 2H), 4.17 (multiplet, 3H). ^{19}F NMR: –64.8 (multiplet, 3F), –70.9 (multiplet, 2F) and +49.7 (multiplet, 1F). Analysis: Found: C, 28.38; H, 2.73; F, 44.88; S, 12.90%. $\text{C}_6\text{F}_6\text{H}_6\text{O}_2\text{S}$ requires C, 28.13; H, 2.36; F, 44.51; S, 12.52%.

For (XXXVI): IR: 5.38 μ (C=O). ^1H NMR: 3.27 (triplet, $J = 6.5$ Hz, 2H), 4.3 (multiplet, 4H). Analysis: Found: C, 27.85; H, 1.63; F, 52.76; S, 7.66%. $\text{C}_{10}\text{H}_6\text{F}_{12}\text{O}_3\text{S}$ requires C, 27.66; H, 1.39; F, 52.52; S, 7.39%.

Reaction of methyl trifluoroacrylate (XVII) (X = F) with tetrafluoroethylene. Carbomethoxyheptafluorocyclobutane (XVIII) (nc)

Methyl perfluoroacrylate (13 g, 0.009 mol) in a mixture containing methyl tetrafluoropropionate (2 g) was sealed in a Carius tube with 19 g (0.19 mol) of tetrafluoroethylene, 5 drops of limonene and 0.1 g of phenothiazine. The tube was heated to 200° for 1 h and then 225° for 7 h. There was recovered 15 g of material boiling above room temperature. Through the use of preparative gas chromatography, 3 g of (XVIII) was separated from the starting materials. In another run, on heating at 175° for 8 h, no product was isolated. IR: 5.60 μ (C=O). ^1H NMR: 3.63 (singlet, 3H). ^{19}F NMR: –125.6, –129.7, –131.3 and –135.4 (A_2B_2 multiplets, 4F), –133.7 (multiplet, 2F) and –186.7 (multiplet, 1F). Analysis: Found: C, 30.28; H, 1.30; F, 55.18%. $\text{C}_6\text{H}_3\text{F}_7\text{O}_2$ requires C, 30.03; H, 1.26; F, 55.42%.

Attempts to react tetrafluoroethylene with perfluoroacryloyl fluoride (VII) in place of the ester (XVII) (X = F) under similar conditions produced no product.

Addition of difluorocarbene to (XVII) (X = F). Carbomethoxypentafluorocyclopropane (XIX) (nc)

This reaction was undertaken in exactly the same manner as described above using hexafluoropropene epoxide (21 g) in place of tetrafluoroethylene. In the same

way, no product was isolated at 175° but when the reaction was carried out at 225° 15 g of a material boiling above room temperature was isolated. From this, by gas chromatography and recrystallization, was obtained 3 g of crystalline carbomethoxyperfluorocyclopropane, m.p. 41–43°. This material sublimed very readily. IR: 5.65 μ (C=O). ^1H NMR (20% CDCl_3 solution): 3.90 (singlet, 3H). ^{19}F NMR: -148.4, -151.8, -152.2 and -155.6 (A_2B_2 multiplets, 4F) and -208.8 (triplet, $J = 4$ Hz, 1F). Analysis: Found: C, 32.05; H, 2.05; F, 49.68%. $\text{C}_5\text{H}_3\text{F}_5\text{O}_2$ requires C, 31.60; H, 1.59; F, 50.00%.

Similar attempts to react hexafluoropropene epoxide with (VII) gave no product.

Reaction of (VII) initiated by F^- or Cl^- ions

Perfluoroacryloyl fluoride (VII) reacted vigorously when initiated with either fluoride ion (cesium fluoride in glyme) or with chloride ion (tetraethylammonium chloride in methylene chloride). A great many products were formed but none has been characterized.

Dimerization of (XVII) ($X = \text{F}$) with the F^- ion. Methyl 4-carbomethoxy-perfluoro-2-pentenoate (XX) (nc)

A sample of methyl perfluoroacrylate (5 g, 90% purity) was mixed with 0.1 g of cesium fluoride and 1 ml of glyme and allowed to stand overnight. Gas chromatography indicated that the ester had dimerized and the resulting dimer was separated by preparative gas chromatography (1.9 g recovered, n_{D}^{25} 1.3804) and characterized as the above pentenoate. The material boiled at 96°/15 mmHg. IR: 5.57 μ , 5.67 μ and 5.88 μ (C=O and C=C). ^1H NMR: 3.65 (singlet, 3H), 3.57 (singlet, 3H). ^{19}F NMR: -76.6 (doublet, $J = 14$ Hz, to doublets, $J = 9$ Hz, to doublets, $J = 5$ Hz, 3F), -145.2 and -147.6 (half of AB pattern, doublets, $J = 21$ Hz, to quartets, $J = 10$ Hz, 1F), -152.3 and -154.7 (half of AB pattern, doublets, $J = 15$ Hz, to doublets, $J = 5$ Hz) and -147.6 (multiplet, 1F). Analysis: Found: C, 34.08; H, 1.92; F, 40.50%. $(\text{C}_4\text{H}_3\text{F}_3\text{O}_3)_2$ requires C, 34.31; H, 2.16; F, 40.71%.

Reaction of (VII) with cyclohexane. 2,3,3-Trifluoro-3-cyclohexyl-propionyl fluoride (XXVII) (nc)

A mixture consisting of 16 g (0.125 mol) of (VII), 20 ml of cyclohexane and 1.0 g of benzoyl peroxide was sealed in a Carius tube and heated overnight on a steam bath. Distillation gave 14.8 g (55.5%) of the above product, b.p. 59°/4.5 mmHg, and 4.2 g of a higher boiling mixture. IR: 5.34 μ (C=O). ^1H NMR: 5.00 (multiplet, 1H), 1.33 (multiplet, 11H). ^{19}F NMR: +33.5 (multiplet, 1F), -203.1 (multiplet, 1F), -110.4 and -118.2 (AB multiplets, $J = 265$ Hz, 2F). Analysis: Found: C, 51.06; H, 5.53; F, 35.84%. $\text{C}_9\text{H}_{12}\text{F}_4\text{O}_2$ requires C, 50.99; H, 5.71; F, 35.85%.

Reaction of (III) with cyclohexane. 2-Trifluoromethyl-3,3-difluoro-3-cyclohexylpropionyl fluoride (XXVIII) (nc)

A mixture consisting of 18 g of perfluoromethacryloyl fluoride, 10 g of cyclohexane and 2.5 g of benzoyl peroxide was sealed in a Carius tube and heated overnight on a steam bath. The resulting mixture was distilled to give 17 g (64%) of the above acid fluoride, b.p. 70°/10 mmHg, n_D^{25} 1.3805. IR: 5.38 μ (C=O). ^1H NMR: 3.9 (multiplet, 1H), 1.5 (multiplet, 11H). Analysis: Found: C, 46.14; H, 4.57; F, 43.47%. $\text{C}_{10}\text{H}_{12}\text{F}_6\text{O}$ requires C, 45.84; H, 4.62; F, 43.51%.

Reaction of (VII) with p-dimethylaminobenzaldehyde. p-Dimethylamino- α -fluorocinnamoyl fluoride (XXV) (nc)

To a solution of 15 g (0.1 mol) of *p*-dimethylaminobenzaldehyde in 25 ml of ether frozen in a Carius tube was added 15 g of (VII) by distillation. Reaction occurred readily on thawing and mixing, and crystals separated. After standing overnight, the tube was opened and COF_2 detected in the gas evolved by infrared spectroscopy. The residue was recrystallized from chloroform to give 12.7 g (57%) of the above acid fluoride, m.p. 152–158°. Another recrystallization gave 10.2 g, m.p. 155–160°. IR: 5.57 μ (C=O). ^1H NMR (*ca.* 5% in deuterioacetone): 7.22, 7.08, 6.36 and 6.22 (AB pattern, 4H), centered 6.67 (doublet, $J = 35$ Hz, 1H), 2.53 (singlet, 6H). ^{19}F NMR: +4.38 (doublet, $J = 27$ Hz, 1F), -137.6 (doublet, $J = 35$ Hz, to doublets, $J = 27$ Hz, 1F). Analysis: Found: C, 62.63; H, 5.57; F, 19.00; N, 6.97%. $\text{C}_{11}\text{H}_{11}\text{F}_2\text{NO}$ requires C, 62.61; H, 5.25; F, 18.01; N, 6.64%.

Reaction of (III) with benzaldehyde. 2-Difluoro-4-phenyl-3-(trifluoromethyl)-3-oxetanecarbonyl fluoride (XXI) (R = H) (nc), its methyl ester (nc), cis- and trans- α -trifluoromethylcinnamoyl fluoride (XXII) (nc)

The initial product of this reaction is believed to be (XXI) (R = H). Because it is difficult to separate from benzaldehyde even by GLPC, it has only been characterized by NMR spectroscopy. However, its methyl ester was isolated. Reactions run at higher temperatures and for longer times gave less of (XXI) (R = H) and more of its expected cleavage products, (XXII), COF_2 and benzal fluoride (from the reaction of benzaldehyde with COF_2).

Compound (III) (41 g, 0.23 mol) was distilled into an acid-washed Carius tube containing 21 g (0.2 mol) of benzaldehyde. The mixture was sealed and heated on a steam bath overnight. After distillation, 11.6 g of a material of b.p. 42–53°/2.3 mmHg was obtained. This material was reacted with methanol, water-washed and distilled to give 5 g of the impure methyl ester of (XXI) (R = H). A sample was purified by GLPC for characterization. IR: 5.65 μ (C=O). ^1H NMR: 6.98 (singlet, 5H), 5.36 (doublet, $J = 8.0$ Hz, 1H), 2.90 (singlet, 3H). ^{19}F NMR: centered -58.1 (AB doublet, $J = 107$ Hz, quartets, $J = 4$ Hz, to doublets, $J = 8$ Hz, 1F), centered -66.8 (AB doublet, $J = 107$ Hz, quartets, $J = 15.2$ Hz, with fine structure, 1F) and -70.2 (doublet, $J = 15.2$ Hz, to doublets, $J = 4.0$ Hz,

3F). Analysis: Found: C, 49.17; H, 3.31; F, 31.86%. $C_{12}H_9F_5O_3$ requires C, 48.69; H, 3.07; F, 32.09%.

In another run, the crude distilled product was separated by preparative gas chromatography instead of reacting with methanol. Using a fluorosilicone-on-firebrick column, three fractions were obtained. The first was benzal fluoride, the second was (XXI) ($R = H$) mixed with benzaldehyde (they eluted together) and the third was (XXII).

For (XXI) ($R = H$): IR: 5.50μ ($C=O$). 1H NMR: 5.40 (multiplet, 1H). ^{19}F NMR: centered -57.5 (AB doublet, $J = 105$ Hz, to multiplets, 1F), centered -66.7 (AB doublet, $J = 105$ Hz, to multiplets, 1F), -69.5 (multiplet, 3F) and $+49.3$ (multiplet, 1F).

Another run was made at 150° for 40 h using 42 g (0.4 mol) of benzaldehyde and 36 g (0.2 mol) of (III). From the resulting mixture was distilled 14 g of product of b.p. $110-125^\circ/18$ mmHg which was mostly (XXII). It was possible to separate *cis* and *trans* isomers by preparative GLPC using a silicone-703-on-firebrick column.

For one isomer: IR: 5.50μ ($C=O$). 1H NMR: 7.45 (singlet, 5H), 7.77 (doublet, $J = 5.4$ Hz, to quartets, $J = 1.6$ Hz, 1H). ^{19}F NMR: -65.1 (doublet, $J = 9.4$ Hz, to doublets, $J = 1.6$ Hz, 3F), $+41.6$ (quartet, $J = 9.5$ Hz, to doublets, $J = 5.4$ Hz, 1F). Analysis: Found: C, 55.36; H, 2.84; F, 34.88%. $C_{10}H_6OF_4$ requires C, 55.06; H, 2.77; F, 34.84%.

For the other isomer: IR: 5.50μ ($C=O$). 1H NMR: 7.45 (singlet, 5H), 8.30 (multiplet, 1H). ^{19}F NMR ($CDCl_3$ soln.): -59.0 (doublet, $J = 11.0$ Hz, 3F), $+24.6$ (quartet, $J = 11.0$ Hz, 1F).

Reaction of (III) with anisaldehyde. 3-(p-Methoxyphenyl)-2-(trifluoromethyl)-acryloyl fluoride (XXIII) (nc)

Anisaldehyde (13 g, 0.1 mol) and (III) (18 g, 0.1 mol) were mixed (exothermic reaction) in a still pot and distilled. There was obtained 17.9 g (60%) of (XXIII) which boiled mostly at $88^\circ/1$ mmHg, n_D^{25} 1.5364. It was washed with water and re-distilled, b.p. $83^\circ/0.75$ mmHg, n_D^{25} 1.5370. IR: 5.50μ ($C=O$). 1H NMR: centered 7.07 (A_2B_2 doublet, $J = 8.8$ Hz, 7H), 6.32 (AB doublet, $J = 8.8$ Hz, 2H), 3.22 (singlet, 3H). Analysis: Found: C, 53.56; H, 3.28; F, 30.13%. $C_{11}H_8F_4O_2$ requires C, 53.27; H, 3.25; F, 30.65%.

Reaction of (III) with p-dimethylaminobenzaldehyde. p-Dimethylamino- α -trifluoromethylcinnamoyl fluoride (XXIV) (nc)

To a magnetically stirred suspension of 14.9 g (0.1 mol) of *p*-dimethylaminobenzaldehyde in 80 ml of ether in a dry-nitrogen atmosphere, 19.0 g (0.106 mol) of (III) was added. The rate of addition was adjusted to give a steady evolution of gas (COF_2) and to maintain the reaction temperature between $25-30^\circ$. After the addition was completed (total time *ca.* 2 h), all solids had dissolved and the

solution was dark green in color. The solvent was removed with a rotary evaporator *in vacuo* to give 26.0 g of (XXIV) (theoretical yield = 26.1 g). This material was sublimed at 65°/0.15 mmHg to give 24.0 g (92%) of an analytically pure yellow solid, m.p. 62–69°. ¹⁹F NMR spectroscopy indicated a *cis-trans* isomer mixture of about 79:21. IR: 5.56 μ (C=O). ¹H NMR: 3.08 (singlet, 6H), 6.6 (A₂B₂ doublet, *J* = 10 Hz, 2H), 7.7 (A₂B₂ doublet, *J* = 10 Hz, 2H) overlapped with multiplet (1H). ¹⁹F NMR for main isomer: -61.0 (doublet, *J* = 13.6 Hz, to doublets, *J*(H-F) = 1.3 Hz, 3F), +37.6 (quartet, *J* = 13.6 Hz, to doublets, *J*(H-F) = 7.2 Hz, 1F). Minor isomer: -57.3 (doublet, *J* = 13.8 Hz, 3F) and +20.7 (quartet, *J* = 13.8 Hz, to doublets, *J*(H-F) = 2.2 Hz, 1F). Analysis: Found: C, 55.28; F, 29.12; H, 4.37; N, 5.71%. C₁₂F₄H₁₁NO requires C, 55.18; F, 29.10; H, 4.25; N, 5.37%.

p-Dimethylamino- α -(trifluoromethyl)cinnamide (*nc*)

To a magnetically stirred solution of the above acid fluoride (20.0 g) in 150 ml of methanol plus 150 ml of ether, 30 ml of conc. ammonia was added at ice-bath temperature. After the addition was completed, the reaction was left at 50° on a water bath overnight. The product was concentrated *in vacuo*, washed with water and recrystallized from methanol-water to give 16.2 g (80%) of yellow crystals, m.p. 181–185°. IR: 5.95 μ (C=O). UV: λ_{\max} . (EtOH) 336 m μ (ϵ 23 000), 234 m μ (ϵ 9 700). ¹H NMR: ((CD₃)₂SO): 7.0 (singlet, 6H), 6.72 (A₂B₂ doublet, *J* = 9.2 Hz, 2H), 7.5 (A₂B₂ doublet, *J* = 9.2 Hz, 2H), 7.0 (quartet, *J* = 1.6 Hz, 1H), 7.9 (multiplet, 2H) exchangeable with D₂O. ¹⁹F NMR: -61.4 (quartet, *J* = 1.6 Hz, 3F). Analysis: Found: C, 56.20; H, 5.23; F, 21.26; N, 10.56%. C₁₂H₁₃F₃N₂O requires C, 55.82; H, 5.08; F, 22.07; N, 10.85%.

p-Dimethylamino- α -(trifluoromethyl)cinnamic acid (*nc*)

To a magnetically stirred solution of 20.0 g of *p*-dimethylamino- α -(trifluoromethyl)cinnamoyl fluoride in 150 ml of dimethylformamide, 6 g of potassium hydroxide in 40 ml of distilled water was added. The solution was stirred overnight at 60°. Acidification gave 11 g of an acid. A sample was recrystallized from cyclohexane for analysis, m.p. 123–125°. IR: 5.9 μ (C=O). ¹H NMR (CD₃CN soln.): 3.0 (singlet, 6H), 6.73 (A₂B₂ doublet, *J* = 9 Hz, 2H), 7.6 (A₂B₂ doublet, *J* = 9 Hz, 2H, overlapping multiplet 1H). ¹⁹F NMR: -61.9 (doublet, *J* = 1.7 Hz, 3F). Analysis: Found: C, 55.46; H, 4.71; F, 21.88; N, 5.59%. C₁₂H₁₂F₃NO₂ requires C, 55.64; H, 4.67; F, 22.01; N, 5.41%.

Decarboxylation of p-dimethylamino- α -(trifluoromethyl)cinnamic acid. *p*-Dimethylamino- β -(trifluoromethyl)styrene (*nc*)

The above acid (12.5 g) was sublimed at 90–100° to give 7.5 g (73%) of a yellow solid, m.p. 122–125°, which was shown to be the above styrene. IR: 6.05 μ (C=C). UV: λ_{\max} . (EtOH) 327 m μ (ϵ 20 600). ¹H NMR: 7.02 (singlet, 6H),

5.95 (AB doublet, $J = 16.6$ Hz, to quartets, $J(\text{H-F}) = 6.5$ Hz, 1H), 7.07 (AB doublet, $J = 16.6$ Hz, to quartets, $J(\text{H-F}) = 2.0$ Hz, 1H), 6.67 (A_2B_2 doublet, $J = 9.3$ Hz, 2H), 7.3 (A_2B_2 doublet, $J = 9.3$ Hz, 2H). ^{19}F NMR (CDCl_3 soln.): -62.8 (doublet, $J = 6.5$ Hz, to doublets, $J = 2.0$ Hz, 3F). Analysis: Found: C, 61.49; H, 5.61; F, 25.77; N, 6.17%. $\text{C}_{11}\text{H}_{12}\text{F}_3\text{N}$ requires C, 61.39; H, 5.63; F, 26.49; N, 6.51%.

Reaction of (III) with p-dimethylaminocinnamaldehyde. 5-(p-Dimethylamino-phenyl)-2-trifluoromethyl-2,4-pentadienoyl fluoride (XXXVII) (nc)

To a magnetically stirred suspension of *p*-dimethylaminocinnamaldehyde (17.0 g, 0.097 mol) in 80 ml of ether in a dry-nitrogen atmosphere, 18.0 g (0.101 mol) of (III) was added at a rate sufficient to keep the reaction temperature between $25\text{--}30^\circ$ (no cooling was necessary). After the addition was completed, the reaction mixture consisted of a deep red solution containing some yellow solid indicating unreacted aldehyde. An additional 30 ml of ether and 25 ml of benzene effected solution. After refluxing for 2 h, the mixture was concentrated *in vacuo* to give 28.0 g of a violet solid (slightly pasty) m.p. $95\text{--}105^\circ$ (yield of crude product quantitative). One recrystallization from ether-hexane (5 l) gave a material of m.p. $119\text{--}121^\circ$. This material was recrystallized from ether to give an analytical sample of (XXXVII), m.p. $122\text{--}124^\circ$. IR: $5.57\ \mu$ (C=O). UV: λ_{max} . (cyclohexane) $435\ \mu$ (ϵ 34 500); λ_{max} . (EtOH) $465\ \mu$ (ϵ 38 500). ^1H NMR: 3.1 (singlet, 6H), 6.7 (A_2B_2 doublet, $J = 9.5$ Hz, 2H), 7.55 (A_2B_2 doublet, $J = 9.5$ Hz, 2H) which overlapped a multiplet (3H). ^{19}F NMR: -61.5 (doublet, $J = 13.6$ Hz, 3F), $+36.0$ (multiplet, 1F). Analysis: Found: C, 58.43; F, 26.47; H, 4.99; N 4.84%. $\text{C}_{14}\text{H}_{13}\text{F}_4\text{ON}$ requires C, 58.52; F, 26.45; H, 4.57; N, 4.88%.

Reaction of (III) with furfuraldehyde. 2-Trifluoromethyl-3-(2-furyl)acryloyl fluoride (XXXVIII) (nc)

A Carius tube was charged at Dry Ice temperature with 35.6 g (0.2 mol) of (III) and 19.2 g (0.2 mol) of furfural. After warming to room temperature, the reaction mixture consisted of a red homogeneous solution. This was left overnight at room temperature and then heated on a steam bath for 3 h. The tube was cooled in Dry Ice and opened to a liquid-nitrogen trap to collect 13.0 g (98%) of carbonyl fluoride (IR, $5.1\ \mu$). The liquid remaining was distilled to give 24.0 g (58%) of a pale green mobile liquid, b.p. $74\text{--}78^\circ/15$ mmHg. IR: $5.50\ \mu$ (C=O). UV: λ_{max} . (cyclohexane) $328\ \mu$ (ϵ 20 700), λ_{max} . (EtOH) $332\ \mu$ (ϵ 18 100). ^1H NMR: 6.7 (doublet, $J = 3.8$ Hz, to doublets, $J = 1.8$ Hz, to doublets, $J = 0.6$ Hz, 1H), 7.8 (multiplet, 3H). ^{19}F NMR: Two isomers in a 96:4 ratio. Main isomer: -63.1 (doublet, $J = 13.6$ Hz, 3F), $+36.1$ (quartet, $J = 13.6$ Hz, to doublets, $J = 7.0$ Hz, to doublets, $J = 0.7$ Hz, 1F). Minor isomer: -60.0 (doublet, $J = 13.4$ Hz, 3F), $+21.0$ (quartet, $J = 13.4$ Hz, to doublets, $J = 1.8$ Hz, 1F). Analysis: Found: C, 46.46; H, 2.09; F, 36.57%. $\text{C}_8\text{H}_4\text{F}_4\text{O}_2$ requires C, 46.17; H, 1.94; F, 36.52%.

Reaction of (III) with N-methylpyrrole-2-carboxaldehyde. α -(Trifluoromethyl)- β -(1-methyl-2-pyrrole)acryloyl fluoride (XXXIX) (nc)

To 40.0 g (0.225 mol) of (III) which was magnetically stirred in a dry-nitrogen atmosphere in a flask immersed in an ice bath, 21.8 g (0.20 mol) of *N*-methylpyrrole-2-carboxaldehyde was added at a rate which maintained the reaction temperature below 25° (*ca.* 1 h). A gentle stream of nitrogen was passed through the flask during the course of the reaction to remove COF₂ as it was formed. The reaction mixture was concentrated and the crude product was washed with hexane to give 32 g (73%) of a purple solid which was sublimed twice (50°/0.5 mmHg) to give a yellow solid, m.p. 58–63°. ¹⁹F NMR indicated an isomer mixture (*ca.* 76:24). IR: 5.62 μ (C=O), 6.3 μ (C=C). UV: λ_{\max} . (EtOH) 371 m μ (ϵ 31 200); λ_{\max} . (cyclohexane) 365 m μ (ϵ 28 500), 355 m μ (ϵ 27 400). ¹H NMR (CDCl₃ soln.): 3.75 (singlet, 3H), 6.35 (doublet, J = 4.8 Hz, to doublets, J = 2.6 Hz, to doublets, J = 0.6 Hz, 1H), 7–8 (multiplet, 3H). ¹⁹F NMR: Main isomer: –62.1 (doublet, J = 15.2 Hz, to doublets, J = 1.4 Hz, 3F), +33.4 (quartet, J = 15.2 Hz, to doublets, J = 7.4 Hz, to doublets, J = 1.2 Hz, 1F). Minor isomer: –60.6 (doublet, J = 14.6 Hz, to doublets, J = 1.8 Hz, to doublets, J = 0.7 Hz, 3F), +18.3 (quartet, J = 14.6 Hz, to doublets, J = 2.4 Hz, 1F). Analysis: Found: C, 49.52; H, 3.27; F, 34.18; N, 6.59%. C₉H₇F₄NO requires C, 48.88; H, 3.19; F, 34.37; N, 6.34%.

Reaction of (III) with indole-3-carboxaldehyde. Methyl α -(trifluoromethyl)- β -(3-indole)acrylate (XL) (nc)

To a magnetically stirred suspension of indole-3-carboxaldehyde (14.5 g, 0.1 mol) in 60 ml of ether in a dry-nitrogen atmosphere in a flask immersed in an ice bath, 19.0 g (0.107 mol) of (III) was added at a rate sufficient to keep the temperature between 15–20° and to maintain a steady evolution of gas. After the addition was complete, the reaction was stirred for 2 h on a water bath at 40° and then concentrated *in vacuo* to give 28.3 g of a yellow solid. The infrared spectrum (Nujol) showed absorption at 3.0 μ (–NH), 5.6 μ (COF). This product rapidly darkened and fumed and was therefore converted to the methyl ester by dissolving the total crude product in 50 ml of methanol, adding 20 ml of pyridine and stirring overnight. The reaction mixture was diluted with 100 ml of methylene chloride and then washed consecutively with water, 10% HCl, water, saturated sodium bicarbonate and brine. The methylene chloride solution was dried over MgSO₄, filtered and concentrated *in vacuo* to give 23.2 g of an orange solid. A sample was recrystallized four times from cyclohexane–benzene and sublimed to give an analytical sample, m.p. 144.5–145.5°. ¹⁹F NMR spectroscopy indicated an isomer mixture (*ca.* 86:14). IR: 5.85 μ (C=O). UV: λ_{\max} . (EtOH) 351 m μ (ϵ 16 600), 275 m μ (ϵ 7 440), 264 m μ (ϵ 8 440), 218 m μ (ϵ 24 700). ¹H NMR: 3.87 (singlet, 3H), 7.2 to 7.9 (multiplet, 4H), 8.0 (multiplet, 1H), 8.63 (doublet, J = 3 Hz, 1H), 12.25 (broad, 1H). ¹⁹F NMR: Main isomer: –60.6 (doublet, J = 1 Hz, 3F).

Minor isomer: -59.0 (doublet, $J = 1$ Hz, 3F). Analysis: Found: C, 58.33; H, 3.83; F, 20.88; N, 5.49%. $C_{13}H_{10}F_3NO_2$ requires C, 58.00; H, 3.75; F, 21.17; N, 5.21%.

Reaction of (III) with 2,6-dimethyl- γ -pyrone. α -(Trifluoromethyl)-2,6-dimethyl- Δ^4 , α -pyranacetyl fluoride (XLI) (nc)

To a magnetically stirred suspension of 25.0 g of 2,6-dimethyl- γ -pyrone (0.201 mol) in 120 ml of ether, 38.0 g (0.215 mol) of (III) was slowly added over 1 h. Gas was evolved immediately on addition of the acid fluoride. The reaction was heated to reflux for 1 h after the addition and then concentrated *in vacuo* to give 46 g of a crude brown product which after subliming, triturating with carbon tetrachloride and re-subliming gave 37.0 g of light tan crystals. A sample was sublimed three times to give an analytical sample, m.p. 87.5 – 90.0° . IR: 5.70μ (C=O). UV: λ_{\max} . (cyclohexane) $330 m\mu$ (ϵ 21 300), $243 m\mu$ (ϵ 6 060). λ_{\max} . (EtOH) $335 m\mu$ (ϵ 24 100), $250 m\mu$ (ϵ 6 660). 1H NMR: 3.3 (singlet, 6H), 6.7 (multiplet, 1H), 7.7 (multiplet, 1H). ^{19}F NMR: -54.2 (doublet, $J = 26$ Hz, 3F), $+33.4$ (quartet, $J = 26$ Hz, 1F). Analysis: Found: C, 51.17; H, 3.52; F, 32.14%. $C_{10}H_8F_4O_2$ requires C, 50.90; H, 3.42; F, 32.20%.

Reaction of (I) with formaldehyde. 4,4,6-Trifluoro-5-(trifluoromethyl)-m-dioxin (XXVI) (R = H) (nc)

A mixture consisting of 5 g of alkaform (polyformaldehyde), 36 g of (I) and 0.25 g of phosphorus pentoxide was sealed in a Carius tube and heated to 150° for 4 h. There was recovered 17 g of (I), 11.6 g of a material of b.p. 48 – $58^\circ/90$ mmHg and 3.4 g of a higher boiling oil. A second tube with an identical charge, except that 0.5 g of phosphorus pentoxide was used, gave almost the same products: 17 g of recovered ketene, 10.8 g of a material of b.p. 46 – $52^\circ/75$ mmHg and 5.6 g of higher boiling material. The lower boiling products from both runs were combined and fractionated twice to give 12.5 g (10%) of a material boiling mostly at $62^\circ/105$ mmHg, n_D^{25} 1.3313, characterized as (XXVI) (R = H). IR: 5.85μ (C=C). 1H NMR: 5.3 (doublet, $J = 1.4$ Hz, 2H). ^{19}F NMR: -59.1 (doublet, $J = 16$ Hz, to triplet, $J = 6.5$ Hz, 3F), -70.0 (doublet, $J = 15$ Hz, to quartet, $J = 6.5$ Hz, 2F), -73.2 (quartet, $J = 16$ Hz, to triplet, $J = 15$ Hz, 1F). Analysis: Found: C, 29.11; H, 0.94; F, 54.67%. $C_5H_2F_6O_2$ requires C, 28.87; H, 0.97; F, 54.81%.

Reaction of (III) with acetaldehyde. 4,4,6-Trifluoro-2-methyl-5-(trifluoromethyl)-m-dioxin (XXVI) (R = CH₃) (nc)

A mixture consisting of 4 g of acetaldehyde, 18.5 g of (III) and 15 ml of 1,1,2-trichlorotrifluoroethane was distilled into an acid-washed Carius tube at liquid-nitrogen temperature, sealed, mixed well on melting and allowed to stand overnight. Distillation of the product gave 12.6 g (62%) of crude (XXVI)

($R = CH_3$), b.p. $55^\circ/60$ mmHg. This material was further purified by gas chromatography. IR: 5.85μ ($C=C$). 1H NMR: 5.40 (quartet, $J = 5.2$ Hz, to doublets, $J = 1.3$ Hz, 1H), 1.40 (doublet, $J = 5.2$ Hz, to triplet, $J = 0.7$ Hz, 3H). ^{19}F NMR: -54.4 and -57.2 (AB doublet to doublets, $J = 17$ Hz, to quartets, $J = 6$ Hz, 1F), -79.2 and -82.0 (AB doublet to doublets, $J = 13$ Hz, to quartets, $J = 6.5$ Hz, 1F), -58.7 (doublet, $J = 16$ Hz, to triplets, $J = 6.5$ Hz, 3F), -73.1 (quartet, $J = 16$ Hz, to doublets, $J = 17$ Hz, to doublets, $J = 13$ Hz, 1F). Analysis: Found: C, 32.53; H, 1.65; F, 50.75%. $C_6H_4F_6O_2$ requires C, 32.46; H, 1.82; F, 51.35%.

Reaction of (III) with propionaldehyde. 4,4,6-Trifluoro-2-ethyl-5-(trifluoromethyl)-m-dioxin (XXVI) ($R = C_2H_5$) (nc)

A mixture consisting of 5.3 g of propionaldehyde and 17.3 g of (III) was distilled into an acid-washed Carius tube at liquid-nitrogen temperature, sealed and mixed well on melting. An exothermic reaction occurred and gave a dark colored liquid which was distilled. There was recovered 10.6 g (41%) of crude (XXVI) ($R = C_2H_5$), b.p. $61^\circ/50$ mmHg. This was further purified by gas chromatography. IR: 5.85μ ($C=C$). 1H NMR: 0.84 (triplet, $J = 7.2$ Hz, 3H), 1.77 (doublet, $J = 5$ Hz, to quartets, $J = 7.2$ Hz, 2H), 5.23 (triplet, $J = 5$ Hz, to doublets, $J = 1.2$ Hz, 1H). ^{19}F NMR: -58.6 (doublet, $J = 15.5$ Hz, to triplet, $J = 6.5$ Hz, 3F), -54.5 and -57.3 (AB doublet to doublet, $J = 16.5$ Hz, to quartets, $J = 6.5$ Hz, 1F), -79.4 and -82.2 (AB doublet to doublet, $J = 12.5$ Hz, to quartet, $J = 6.5$ Hz, 1F), -73.3 (quartet, $J = 15.5$ Hz, to doublet, $J = 12.5$ Hz, to doublet, $J = 16.5$ Hz, 1F). Analysis: Found: C, 36.03; H, 2.83; F, 47.90%. $C_7H_6F_6O_2$ requires C, 35.62; H, 2.56; F, 48.31%.

Reaction of (III) with ethyl diazoacetate. 1-Trifluoromethyl-2-ethoxycarbonyl-3,3-difluorocyclopropanecarbonyl fluoride (XLII) (nc)

To a magnetically stirred solution consisting of 17.8 g (0.1 mol) of (III) and 12 ml of ether in a flask immersed in an ice bath, 11.4 g (0.1 mol) of ethyl diazoacetate was slowly added. There was an immediate evolution of gas. The rate of addition was adjusted to keep the temperature below 15° and after 2 h an additional 2 g of (III) was added. Distillation gave 13 g (50%) of a pale yellow liquid, b.p. $31-32^\circ/0.4$ mmHg. A sample was re-distilled for analysis, b.p. $59^\circ/10$ mmHg. IR: 5.4μ (COF), 5.68μ ($COOC_2H_5$). 1H NMR: 1.3 (triplet, $J = 7.3$ Hz, 3H), 4.3 (quartet, $J = 7.3$ Hz, 2H), centered 3.67 (multiplet, 1H). The latter area was resolved as consisting of approximately equal amounts of two protons from two isomers, one at 3.85 (doublets, $J = 12.4$ Hz, to doublets, $J = 5.6$ Hz) and one at 3.55 (doublets, $J = 12.2$ Hz, to doublets, $J = 5.2$ Hz, to doublets, $J = 1.8$ Hz). ^{19}F NMR: In pairs corresponding to approximately equal amounts of two isomers: $+46.7$ and $+36.5$ (multiplets, 1F), -61.2 and -64.6 (multiplets, 3F), -93.3 and -98.8 (multiplets, 2F). Analysis: Found: C, 36.78; F, 42.66; H, 2.60%. $C_8F_6H_6O_3$ requires C, 36.39; F, 43.18; H, 2.29%.

Copolymerization of (III) with ethylene

A solution consisting of 18 g of (III) in 50 ml of $\text{CF}_2\text{ClCFCl}_2$ containing 0.1 g of di-*t*-butyl peroxide was heated at 130° for 1 h under an ethylene pressure which dropped during this time from 600 to 540 atm. The product consisted of a viscous solution which after removal of volatiles under vacuum gave 6 g of a rubbery polymer soluble in CCl_4 . Fluorine analysis indicated 5.5 ethylene units per acid fluoride unit but the carbon analysis was low. IR: 5.4μ (COF). Analysis: Found: C, 49.24; H, 5.81; F, 34.54%. $5.5(\text{C}_2\text{H}_4)(\text{C}_4\text{F}_6\text{O})$ requires C, 54.26; H, 6.68; F, 34.54%.

The polymer reacted vigorously with ethylene diamine to give an insoluble, infusible polymer.

Copolymerization of (VII) with ethylene

A mixture consisting of (VII) (0.2 mol, 55% in CF_3CFHCOF) and 0.05 g of α, α' -azobisisobutyronitrile was heated in a bomb at 65° for 12 h under 3000 atm pressure of ethylene. A polymer was recovered which after air drying weighed 18.9 g and was swollen by acetone.

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