Fluoroketenes. I. Bis(trifluoromethyl)ketene and Its Reactions with Fluoride Ion

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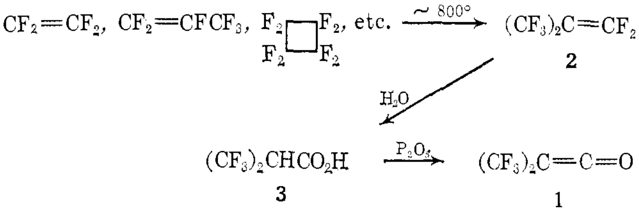
Abstract: Bis(trifluoromethyl)ketene, obtained in two simple steps from octafluoroisobutylene, is a thermally stable gas which is susceptible to nucleophilic attack. Fluoride ion catalysis has been used to isomerize the ketene to pentafluoromethacrylyl fluoride. From the ketene and from the acid fluoride, conditions have also been found to prepare lactones and allenes in high yield. The results are rationalized in terms of discrete anionic intermediates.

Except for the elusive difluoroketene,[1] bis(trifluoromethyl)ketene (**1**) is the only fluoroketene reported in the literature.[2] The synthesis of **1** is best accomplished by hydration and dehydration of octafluoroisobutylene (**2**). Since a number of fluorocarbons can be pyrolyzed to form **2**,[3] the latter fluorocarbon is readily obtained as a principal component of a pyrolysis mixture. Furthermore, isobutylene **2** is the component most readily attacked by nucleophiles; so hydrolysis can be carried out preferentially to give α-H-hexafluoroisobutyric acid (**3**) under the unusually mild conditions of a water–tetrahydrofuran mixture at 25°. Immediate hydrolysis of **2** as it is being formed is desirable to avoid accumulations of this highly toxic compound.[4] A continuous, or hot tube, reactor conveniently allows for generation of octafluoroisobutylene in any amount as an effluent stream which can be treated directly with water–tetrahydrofuran.

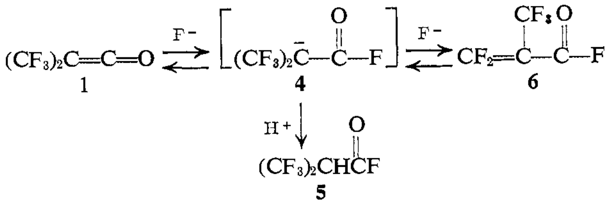


The hydration reaction gives acid **3** in high yield as a water-insoluble complex with tetrahydrofuran.[5] Isolation of **3** is easily accomplished by treatment of the complex with sulfuric acid. Dehydration of acid **3**, the next step, occurs in over 90% yield when **3** is heated with excess phosphorus pentoxide. Gaseous ketene **1**, bp 5°, is formed with unusual ease at reaction temperatures below 250° and removed through a condenser as formed.

Unlike other ketenes, bis(trifluoromethyl)ketene does not spontaneously self-condense; it is, in fact, stable to prolonged exposure to 250° in a neutral nonbasic reactor and does not react at 200° with oxygen under pressure. Other energy sources with negligible effect are X-rays at −196° and ultraviolet light longer than 300 mμ. No difficulty has been experienced with storage and use of large quantities of monomeric **1**.

Ketene **1** has pronounced electrophilic character, a consequence of introducing two electronegative trifluoromethyl groups into the normally electrophilic ketene group. While unreactive toward most electrophiles, **1** combines readily with active hydrogen compounds and electron-donor systems in general. Evidence that **1** is strongly polarized, but in the same manner as ordinary ketenes, is found in the adducts formed with reagents such as water. Hydration proceeds exothermically to re-form the acid **3**, in which the basic oxygen atom of water has become bonded to the electron-deficient central atom of the ketene function. Phenol adds to **1** to form a phenyl ester.

Similarly, attack by fluoride ion occurs at the central atom to generate carbanion **4**,[6] which in the presence of acid can pick up a proton to account for the formation of α-H-hexafluoroisobutyryl fluoride (**5**). Under aprotic conditions, carbanion **4** will lose fluoride ion to regenerate ketene **1** or to give pentafluoromethacrylyl fluoride (**6**), the isomerization product.[7]



$$\underset{\mathbf{1}}{(CF_3)_2C{=}C{=}O} \underset{}{\overset{F^-}{\rightleftharpoons}} \underset{\mathbf{4}}{\left[(CF_3)_2\bar{C}{-}\overset{\overset{O}{\|}}{C}{-}F\right]} \overset{F^-}{\rightleftharpoons} \underset{\mathbf{6}}{CF_2{=}\overset{\overset{CF_3}{|}}{C}{-}\overset{\overset{O}{\|}}{C}{-}F}$$

$$\mathbf{4} \xrightarrow{H^+} \underset{\mathbf{5}}{(CF_3)_2CH\overset{\overset{O}{\|}}{C}F}$$

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[1] (a) N. N. Yarovenko, S. P. Motornyi, and L. I. Kirenskaya, *J. Gen. Chem. USSR*, 27, 2832 (1957); (b) R. E. Banks, R. N. Haszeldine, and D. R. Taylor, *J. Chem. Soc.*, 5602 (1965) refer to some unpublished work by J. M. Birchall, R. N. Haszeldine, and M. Jefferies who were unable to repeat this synthesis of difluoroketene.

[2] (a) D. C. England and C. G. Krespan, *J. Am. Chem. Soc.*, 87, 4019 (1965), provided a preliminary account of our results. (b) I. L. Knunyants, Y. A. Cheburkov, and M. D. Bargamova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1389, 1393 (1963), have independently prepared bis(trifluoromethyl)ketene and pentafluoromethacrylyl fluoride by less attractive routes. In particular, they found that the preparation and dehydrohalogenation of α-H-hexafluoroisobutyryl halides, which we also examined briefly, give relatively low yields of the ketene whereas dehalogenation of the more difficultly accessible α-halohexafluoroisobutyryl halides gives better yields as part of a mixture of products.

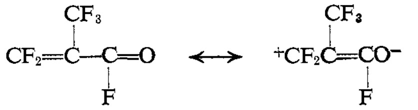
[3] Octafluoroisobutylene has been obtained (a) from octafluorocyclobutane by W. H. Pearlson and L. J. Hals, U. S. Patent 2,617,836 (1952); (b) from hexafluoropropylene by M. Hauptschein, A. H. Fainberg, and M. Braid, *J. Am. Chem. Soc.*, 80, 842 (1958); and (c) from tetrafluoroethylene or chlorodifluoromethane as described by J. M. Hamilton, Jr., *Advan. Fluorine Chem.*, 3, 153 (1963).

[4] (a) J. M. Hamilton, Jr., *ibid.*, 3, 146 (1963), reports that octafluoroisobutylene has an LC-50 of 0.5–1.0 ppm by volume toward rats exposed for 4 hr. Other fluoroolefins that were tested are much less toxic. (b) S. L. Danishevchii and M. M. Kochanov, *Gigiena Truda i Prof. Zabolevaniya*, 5, 3 (1961), estimate a lethal dose for rats to be 0.015 mg/l. of air after 2 hr.

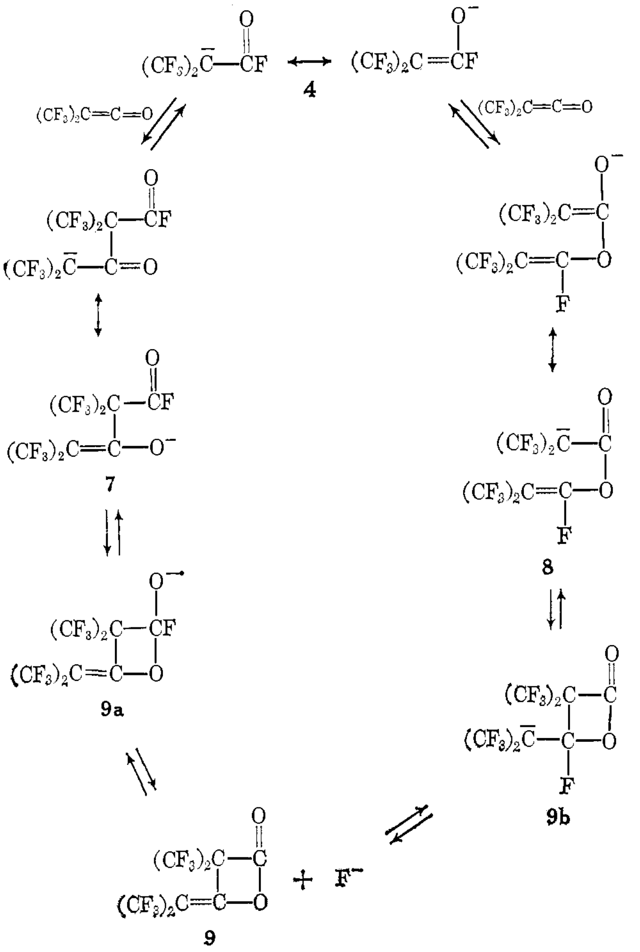
[5] I. L. Knunyants, L. German, and B. Dyatkin, *Bull. Acad. Sci. USSR, Div. Chem. Sci.* (English Transl.), 1387 (1956), describe the first synthesis of α-H-hexafluoroisobutyric acid by prolonged acid hydrolysis of an ether derived from octafluoroisobutene.

[6] Y. A. Cheburkov, M. D. Bargamova, and I. L. Knunyants, *ibid.*, 339 (1964), present evidence that carbanion **4** is present in the complex of α-H-hexafluoroisobutyryl fluoride with triethylamine.

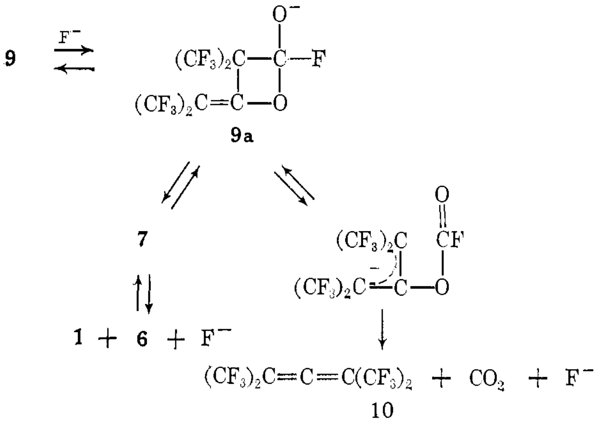
The rearrangement of **1** to **6** occurs cleanly in a flow system at 300° (1 atm) over a bed of sodium fluoride. The equilibrium mixture under these conditions, obtained starting from either **1** or **6**, contains 60% of ketene **1** and only 40% of **6** and reflects the stability of internal unsaturation relative to terminal unsaturation in fluorinated systems. The boiling points of **1** (5°) and **6** (52°) are so widely separated that purification by distillation in the absence of catalyst is easy. The isomerization of ketene **1** is therefore a useful synthetic route to the methacrylyl fluoride **6**. The unusually high boiling point of **6** apparently results from polarization (**6a**) of the molecule with a consequent increase in intermolecular attraction. The corresponding molecule having the double bond saturated by fluorine, $(CF_3)_2CFCOF$, boils at about 0°.[8]


6a

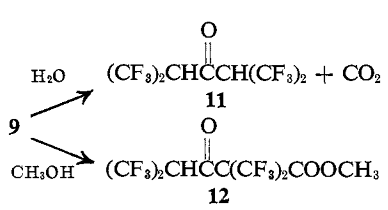
Treatment of ketene **1** with fluoride ion or other anionic catalysts in a condensed phase at 25–40° causes formation of anion **4** in the presence of excess **1**. Anion **4**, presumably stabilized by resonance and relatively long-lived under these conditions, can attack another molecule of **1** before significant isomerization by loss of fluoride ion occurs. Assuming discrete anions as intermediates, two new anions (**7** and **8**) can arise which are also stabilized by an ability to delocalize negative charge. One or both of these anions undergo ring closure and expulsion of fluoride ion to form the product, β-lactone dimer **9**, in 90% yield.[9]



Ring closures to 1,3-dioxetane and 1,3-cyclobutanedione rings are also possible in this system, but such products were not found and are probably unstable relative to β-lactone **9**. Two by-products indicative of two other types of reaction are formed, however, especially with large amounts of catalyst. Tetrakis(trifluoromethyl)allene (**10**)[10] arises from secondary attack of fluoride on β-lactone **9**. This reaction of **9** with fluoride ion was shown in a separate experiment to result in loss of carbon dioxide with formation of allene **10** and also to give the expected products of reversible formation of lactone **9**; both ketene **1** and methacrylyl fluoride **6** were identified. Observations of the latter type lead us to consider these reactions to be at least partially reversible. Since yields of allene **10** from the base-catalyzed reactions of **9** are lowered by formation of by-product, **10** is better obtained (in 95% yield) by pyrolysis of lactone **9** at 600°.



Transformation of **9** to **10** may also proceed through anion **9b**, but the route through **9a** is the one analogous to observed reactions of **9** with the neutral nucleophiles, water and methanol, to form **11** and particularly **12**.



In the dimerization of **1** to **9** with large amounts of catalyst, the side reaction encountered in addition to attack of fluoride on product **9** is isomerization of **1** to acid fluoride **6**. This isomerization, already shown to occur in the vapor phase–solid bed system, was observed indirectly in this case by isolation of a δ-lactone (**13**). The presence of methacrylyl fluoride **6** in solution with excess ketene **1** and fluoride ion could result

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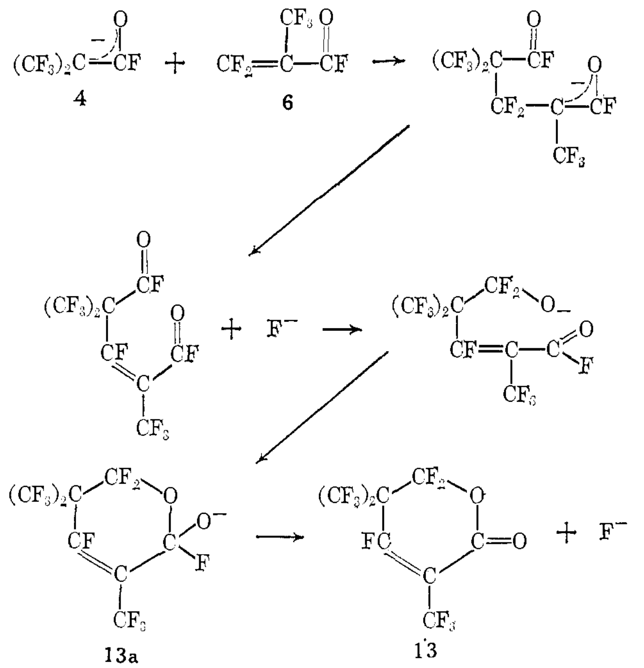
(7) Anionic catalysis of fluoroolefin isomerizations is well known. See, for example, W. T. Miller, Jr., J. H. Fried, and H. Goldwhite, *J. Am. Chem. Soc.*, 82, 3091 (1960).

(8) F. S. Fawcett, C. W. Tullock, and D. D. Coffman, *ibid.*, 84, 4280 (1962).

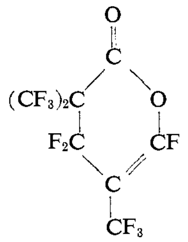
(9) G. A. Cheburkov, G. E. Arnov, N. S. Mirzabekyants, and I. L. Knunyants, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 773 (1966), report this dimer and products of its reaction with water and methanol.

(10) Y. A. Cheburkov, Y. E. Arnov, and I. L. Knunyants, *ibid.*, 582 (1966), report another preparation of this allene and its methanol adduct.

in an adduct of anion **4** with **6** which could in theory cyclize in several ways. The preferred mode leads to lactone **13** as shown below.



This scheme is verified by the course of reaction of fluoride ion with methacrylyl fluoride **6** in solution. Since anion **4** is formed from **6** as well as from ketene **1**, conditions are favorable for formation of lactone **13**, which is obtained as the major (73% yield) product. Two other δ-lactones, **15** and **16**, have been isolated in low yield and are plausibly derivable from anion **14** by direct ring closure in one case and by loss of fluoride followed by cyclization in a direction opposite to that for **13**.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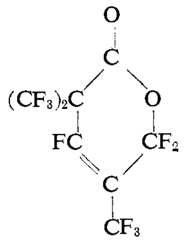
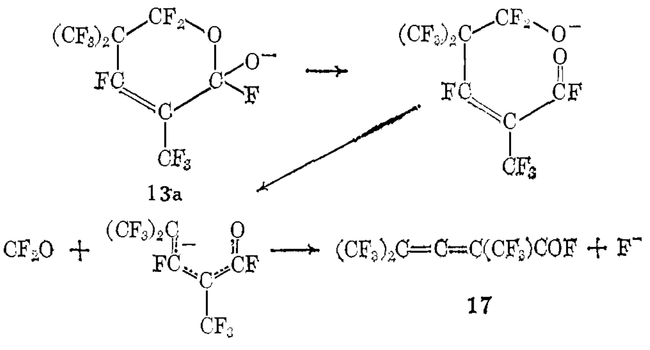
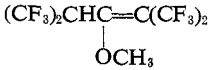
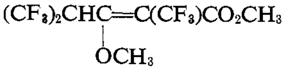

16

In the same manner as postulated for β-lactone **9**, fluoride ion apparently attacks the carbonyl group of δ-lactone **13** to form anion **13a**, which at elevated temperatures will lose carbonyl fluoride to form allenic acid fluoride **17**. Pyrolysis of **13** at 700° affords an even higher yield (78%) of **17**.



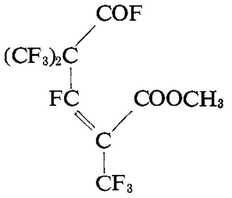
Neither allene **10** nor allenic acid fluoride **17** gave detectable isomerization products when passed over sodium fluoride at 300°, but the allenic system in each could be made to add methanol to afford adducts **18**, **19**, and **20**. In this system, as with the ketene **1**, nucleophilic attack occurs at the central atom.


$(CF_3)_2CHC(OCH_3){=}C(CF_3)_2$
18


$(CF_3)_2CHC(OCH_3){=}C(CF_3)CO_2CH_3$
19


$(CF_3)_2C{=}C(OCH_3)CH(CF_3)CO_2CH_3$
20

In the reaction of δ-lactone **13** with methanol, as with the fluoride ion, attack occurs at the carbonyl group and both the ester–acid fluoride **21** (3%) and the diester **22** (58%) were isolated. However, the lactone **23** was also isolated in appreciable yield (24%), indicating attack at the conjugated double bond as well.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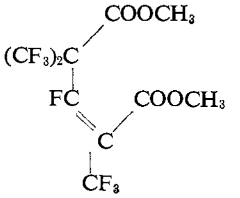
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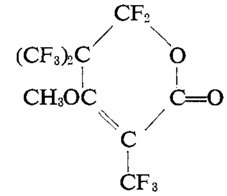
23

The principal product of the reaction of δ-lactone **13** with water is the acid **24**, which is accounted for by attack at the carbonyl group, followed by hydrolysis of the resulting acid fluoride group and decarboxylation. This acid also decarboxylates easily to give the olefin **25** (84%). In addition there was some double bond migration *via* a 1,3 hydrogen shift to give **26** (15%). A very small amount (1%) of the ketone **27** was isolated and can be accounted for by attack at the double bond as well as the carbonyl group, repeated elimination of hydrogen fluoride, hydrolysis, and decarboxylation.

$(CF_3)_2CHCF{=}C(CF_3)COOH$ **24** $(CF_3)_2CHCF{=}CHCF_3$ **25**

$(CF_3)_2C{=}CF{-}CH_2CF_2$ **26** $(CF_3)_2CHCOCH_3$ **27**

Experimental Section[11]

Octafluoroisobutylene (2). The method used for the preparation of **2** was the atmospheric pressure pyrolysis of tetrafluoroethylene dimer (octafluorocyclobutane) which was reported to give this fluoroolefin in 50% yield.[3a] Use of monomeric tetrafluoroethylene gave the same result. In an unpacked nickel tube, ~2.5-in. i.d., heated in an 18-in. split furnace, maximum yields of about 30% were obtained at 815°. The reaction was monitored by gas chromatography of the products through a column packed with Kel-F ester on Chromosorb. The major products were hexafluoropropene and octafluoroisobutylene (**2**,) with minor amounts of tetra-

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[11] Melting points and boiling points are uncorrected. F^{19} nmr spectra are reported in ppm upfield from internal trichlorofluoromethane. H^1 nmr resonances are relative to external tetramethylsilane.

fluoroethylene, tetrafluoromethane, and high boilers, presumably the linear butenes. Fractionation of this mixture gave **2** (bp 5–6°), containing small amounts of isomeric butenes, or the hydrolysis described below could be carried out directly.

Products of the pyrolysis were first passed through an ice-cooled receiver to collect high boilers, and then the gases were passed through two consecutive scrubbing columns. These glass columns were 2.5-in. i.d., 3 ft long, and packed with 0.5-in. Beryl saddles. The gas mixture was introduced into the bottom of the first column and passed upwards while a mixture of tetrahydrofuran–water (50:50 by volume) was passed down over the saddles. At the bottom of the column was a 4-l. separatory funnel where two liquid layers collected. The bottom layer (hexafluoroisobutyric acid–tetrahydrofuran complex) was separated and the top layer discarded. The bottom layer was washed three times with equal volumes of water and then distilled to give a constant-boiling mixture containing about 60% of acid **3**, bp $\sim$70°(30 mm). Because the reaction of **2** with H_2O–tetrahydrofuran is relatively slow, all of **2** may not be consumed in the first scrubbing column. The gas mixture was therefore passed through a second column containing methanol to remove any **2** still present. With this procedure, acid **3** can be obtained in about 10% yield from octafluorocyclobutane.

α-H-Hexafluoroisobutyric Acid (3). The acid is also available by batchwise hydration of pyrolyzate. In one experiment, three gas-scrubbing bottles (fritted glass disks) cooled in ice and connected in series were used. The first two each contained 100 ml of tetrahydrofuran and 100 ml of water and the third 200 ml of methanol. An octafluoroisobutylene (**2**)–octafluorocyclobutane gas mixture (18% of **2**) was bubbled through this scrubbing train. In 5 hr 206 l. of gas was used, which corresponds to about 1.5 moles of **2**. Of this amount, 0.8 mole reacted with water. The first two scrubbing bottles now contained two liquid layers. The bottom layers were combined, treated slowly with an equal volume of concentrated sulfuric acid to wash out tetrahydrofuran and water (exothermic), shaken well, and then continuously extracted with methylene chloride. Distillation of the extract yielded 121 g (77% based on 0.8 mole of **2**) of crystalline hexafluoroisobutyric acid (**3**), bp 95° (200 mm) [130° (1 atm)]; mp 49–50°; pK_a (H_2O) = 2.35; neut equiv 198 (theory 196). This acid rapidly loses F^- in dilute alkali and cannot be back titrated.

Bis(trifluoromethyl)ketene (1). Synthesis. α-Hydrohexafluoroisobutyric acid (196 g, 1.0 mole), which had been ground in a mortar in a drybox, was mixed well with 284 g (2 moles) of phosphorus pentoxide powder in a 2-l., one-necked, round-bottomed flask (glass flasks repeatedly break, but only on cooling at the end of the reaction). The solid mixture was spread evenly over the bottom half of the flask. The flask was then fitted to a water-cooled condenser to which a −80° trap was attached, and it was heated with a mantle. Initial reaction was quite vigorous with the solid turning dark and reflux occurring in the water condenser. After 4 hr of strong heating, refluxing had stopped in the condenser, a solid black foam had nearly filled the flask, and ketene **1** had collected in the trap (110 ml). The material in the trap essentially all distilled through a low-temperature still at 5° (168 g, 94%). Most samples showed, by infrared absorption, a slight contamination with POF_3. The pure material absorbed at 4.54 μ in the infrared and 315 μ in the ultraviolet (ϵ_{max} 6.33). The F^{19} nmr showed a single sharp peak at +58.3 ppm (external reference (ext ref)).

Anal. Calcd for C_4F_6O: F, 64.04; mol wt, 178. Found: F, 64.06, 63.77; mol wt, 177.8 (gas density).

It was also possible to prepare the ketene as described above but using in place of the pure α-hydrohexafluoroisobutyric acid the constant-boiling acid–tetrahydrofuran mixture. When this source of acid was used, it was cooled in a −80° bath in the pot before mixing with the P_2O_5 to avoid the spontaneous reaction which frequently started at room temperature with liberation of ketene. Glass flasks could be used safely without breakage at the end of the reaction when this material was used. Reactions of 392 g of liquid acid–THF mixture (235 g or 1.3 moles of acid **3**) and 568 g of P_2O_5 in a 3-l. flask gave 60–68% yields of crude material. This product was contaminated with about 15% of POF_3 which was easily removed by distillation through a Podbielniak column.

Stability. A sample of ketene 1 was heated for 8 hr at 250° in a sealed Pyrex tube. Nearly all of the ketene was recovered, leaving a trace of oil in the tube.

A 200-ml steel tube charged with 37 g of **1** and 50 ml of $CFCl_2$-CF_2Cl was heated to 200° under 850 psi of oxygen and held there for 80 min. Aside from starting ketene, only a small amount of the isomer, pentafluoromethacrylyl fluoride, was obtained.

Irradiation of **1** in a Pyrex tube with X-rays for 1 hr at −196° gave no detectable reaction aside from slight turbidity in the liquified ketene. Irradiation of a similar sample with an AH-3 ultraviolet lamp for 6 days was without effect.

Addition of ROH. A sample of ketene **1** reacted exothermically and completely with water to regenerate acid **3**, $(CF_3)_2CHCO_2H$, mp 48–50°.

A mixture of 19 g (0.20 mole) of phenol and 39 g (0.22 mole) of **1** sealed in a Carius tube was heated overnight on a steam bath. Distillation afforded 49.1 g (90%) of $(CF_3)_2CHCO_2C_6H_5$, bp 58° (4 mm), n^{25}D 1.4001. The infrared spectrum showed absorption at 5.61 μ (C=O). The proton nmr showed a split phenyl peak at τ 3.35 and a single proton septet (J = 7 cps) at τ 6.30. The F^{19} nmr was a doublet (J = 7 cps) centered at 65.8 ppm.

Anal. Calcd for $C_{10}H_6F_6O_2$: C, 44.15; H, 2.22; F, 41.91. Found: C, 44.32; H, 2.28; F, 42.14.

Pentafluoromethacrylyl Fluoride (6). A glass tube, $\sim$22 in. long, 26 mm in diameter, and having a 5-mm glass thermocouple well down the center, was packed in the center section with 50 ml of $^1/_8$-in. sodium fluoride pellets. The top of the tube was fitted with a gas inlet and dropping funnel. The center 12-in. section was heated by a split furnace, and the bottom exit was fitted with a −80° trap. With the catalyst bed at 300°, bis(trifluoromethyl)ketene was passed over at a rate of about 100 g in 1 hr. The material which collected in the trap from 94 g (0.53 mole) of ketene charged was distilled to give 32 g (34%) of pentafluoromethacrylyl fluoride, bp 52°, and 59 g (63%) of recovered ketene.

The pentafluoromethacrylyl fluoride exhibited infrared absorption at 5.40 (COF) and 5.80 μ (CF_2=C). The F^{19} nmr spectrum consisted of three complex multiplets in the area ratio of 1:3:2 centered, respectively, at −37.5, +50.5, and +60.0 ppm.

Anal. Calcd for C_4F_6O: C, 26.99; F, 64.04. Found: C, 27.37; F, 64.07.

The above reaction was indicated to be an equilibrium because the yield of acid fluoride from the ketene was essentially unchanged by large variations in contact time. The acid fluoride (**6**) was also used as starting material in place of the ketene in the experiment described above. The product was essentially the same mixture of ketene and acid fluoride as was obtained from the pure ketene, thus demonstrating an equilibrium reaction.

The acid fluoride (29 g, 0.16 mole) was added dropwise in a slow current of nitrogen over a bed of sodium fluoride pellets heated at 300°. The product was collected in a cold trap and distilled. There was obtained 10.3 g (40%) of recovered acid fluoride (**6**) and 15.0 g (60%) of **1**. The latter was collected in a trap and characterized by boiling point and infrared absorption. The equilibrium yields were nearly the same from 200 to 400°. At 100° with ketene as starting material less acid fluoride (17%) was obtained and at 500° some decomposition was observed.

β-Lactone of 3-Hydroxy-2,2,4,4-tetrakis(trifluoromethyl)-3-butenoic Acid (9). Low concentrations of either cesium fluoride in diglyme or tetraethylammonium chloride in methylene chloride catalyze the dimerizaton of bis(trifluoromethyl)ketene to the lactone **9**. With higher concentrations of catalyst, carbon dioxide was evolved, and tetrakis(trifluoromethyl)allene (**10**) was also isolated along with a second dimer assigned structure **13**.

A Carius tube containing 34 g (0.19 mole) of ketene **1**, 0.5 g of tetraethylammonium chloride, and 5 ml of methylene chloride (sealed at liquid nitrogen temperature) was shaken gently overnight at room temperature. Distillation gave 31 g (91%) of lactone **9**, bp 93°, n^{25}D 1.3082. It absorbed strongly in the infrared at 5.14 μ (several shoulders) and at 5.77 μ. The F^{19} nmr was in agreement with the assigned structure as it consisted of three general areas at 59.5, 61.2, and 65.5 ppm in the ratio of 1:1:2, quartet (J = 7.5 cps), overlapping quartet (J = 7.5 cps) with septet (J = 7 cps), and quartet (J = 9 cps), corresponding to three types of CF_3 groups undergoing spin–spin splitting except between one of the CF_3 groups and the two like CF_3 groups.

Anal. Calcd for $C_8F_{12}O_2$: C, 26.99; F, 64.04. Found: C, 27.43; F, 64.09.

Similar results are obtained if shaking is continued only 1 hr after the exothermic reaction has set in. In another experiment 77 g (0.43 mole) of bis(trifluoromethyl)ketene was sealed in a Carius tube with a solution of 2 g of tetraethylammonium chloride in 10 ml of methylene chloride. The tube was shaken gently overnight at room temperature, cooled to −80°, poured into a still pot, and distilled. There was recovered 31 g (40%) of ketene (1) in a −80° trap and 12.2 g (18%) of tetrakis(trifluoromethyl)allene (**10**), bp 41°. The F^{19} nmr is a single sharp peak at +64.7 ppm (ext ref). The allene absorbs at 4.95 μ in the infrared.

Anal. Calcd for C_7F_{12}: C, 26.95; F, 73.08. Found: C, 27.08; F, 73.32.

Continued distillation gave 24.5 g (32%) of material, bp 113°, $n^{25}D$ 1.3260. The F^{19} nmr spectrum and analyses are in agreement with structure **13**. Absorptions at 5.50 and 5.89 μ are attributed to the C=O and C=C groups, respectively. The F^{19} nmr consists of four general areas in the ratio of 3:6:2:1, representing a CF_3 group at 60.5 ppm, two equivalent CF_3 groups at 64.3 ppm, a CF_2 group at 71.8 ppm, and CF at 83.0 ppm. By decoupling experiments it was shown that the CF_3 peak (doublet, J = 28 cps) is split by CF. The $(CF_3)_2$ peak is a quadruplet (overlapping doublet, J = 10 cps, and triplet, J = 11 cps) split by CF and CF_2. The CF_2 peak is split by $(CF_3)_2$ into a septet (J = 11 cps) and by CF into doublets (J = 7 cps). The CF multiplet is split correspondingly by all the other groups.

Anal. Calcd for $C_8F_{12}O_2$: C, 26.99; F, 64.04. Found: C, 27.48; F, 63.93.

Bis(α-H-hexafluoroisopropyl) Ketone (11). The dimer **9** (9 g, 0.025 mole) was shaken in a separatory funnel with 25 ml water. It reacted vigorously with evolution of carbon dioxide and crystallized on cooling. About 4 g of the extremely volatile solid ketone **11** was recovered. After recrystallization from carbon tetrachloride only 0.9 g remained. At atmospheric pressure it sublimed rapidly without melting. It melted at 70–71° in a sealed tube. The carbonyl group absorbs at 5.75 μ in the infrared. The H^1 nmr of a 20% solution in deuterioacetone is a septet (J = 7 cps) centered at τ 4.98 and the F^{19} nmr a doublet (J = 7 cps) at 64.7 ppm (ext ref).

Anal. Calcd for $C_7H_2F_{12}O$: F, 69.09. Found: F, 68.66.

Methyl 2,2,4,4-Tetrakis(trifluoromethyl)acetoacetate (12). With stirring and cooling to keep the temperature below 40°, 25 g (0.07 mole) of lactone **9** was added to 25 ml of methanol. The mixture was then distilled, and after removal of methanol there was obtained 27.2 g (86%) of ester **12**, bp 94° (100 mm), $n^{25}D$ 1.3232. Infrared absorption occurred at 5.61 (ketone) and 5.70 μ (ester). The H^1 nmr showed a septet (J = 13 cps) centered at τ 5.37 and a singlet at τ 6.35 with area ratios of 1:3. The F^{19} spectrum centered around 64.5 ppm (ext ref) was not well resolved and appeared to be temperature dependent.

Anal. Calcd for $C_9H_4F_{12}O_3$: C, 27.86; H, 1.04; F, 58.76. Found: C, 28.07; H, 1.16; F, 57.68.

Tetrakis(trifluoromethyl)allene (10). The quartz pyrolysis tube was 22 in. long and 26 mm in diameter, packed in the center section with 0.25-in. lengths of 8-mm quartz tubing. The center section was heated by a split furnace. The top of the tube was fitted with a dropping funnel and the bottom with a trap cooled in liquid nitrogen and connected to a vacuum pump. With the tube heated to ~600° and under a vacuum of 1–5 mm, a total of 50 g (0.14 mole) of lactone **9** was passed through it in 1 hr. The material that collected in the liquid nitrogen-cooled trap, when warmed to room temperature, gave off considerable gas (CO_2), and the remaining tetrakis(trifluoromethyl)allene distilled at ~41°. The yield was 42 g (95%).

Reversal of Lactone 9 Formation. Lactone **9** (10 g, 0.03 mole), 0.1 g of cesium fluoride, and 1 ml of diglyme were sealed together in a glass tube. After standing 2 days at room temperature the tube was cooled and opened. Carbon dioxide was detected in the off gas. Distillation gave 7.2 g of material boiling from 34 to 114° with no pure cuts. There was identified in the products by infrared and gas phase chromatography bis(trifluoromethyl)ketene, pentafluoromethacrylyl fluoride, tetrakis(trifluoromethyl)allene, recovered lactone **9**, and lactone **13**.

Vinyl Ether 18. When allene **10** (15.6 g, 0.05 mole) was added to 10 ml of methanol, there was no evidence of reaction. However, addition of a catalytic amount of sodium methoxide caused an exothermic reaction, and distillation of the mixture gave 14.4 g (84%) of vinyl ether **18**, bp 54° (100 mm) $n^{25}D$ 1.3084. It absorbed in the infrared at 6.09 μ (C=C). Proton nmr showed a single proton as a septet (J = 7 cps) centered at τ 3.90 and a peak for the methyl group at τ 6.20 with unresolved fine structure. The F^{19} nmr consisted of a $(CF_3)_2$ doublet (J = 7 cps) further split into quartets (J = 2 cps) centered at 65.4 ppm and a pair of CF_3 quartets (J = 10 cps) with undefined but different fine structure located at 57.2 and 60.3 ppm.

Anal. Calcd for $C_8H_4F_{12}O$: C, 27.93; H, 1.17; F, 66.28. Found: C, 28.37; H, 1.34; F, 66.01.

Lactone 13 [3,5,5-Trifluoro-5-hydroxy-2,4,4-tris(trifluoromethyl)-2-pentenoic Acid δ-Lactone] and Lactone 16 [3,5,5-Trifluoro-5-hydroxy-2,2,4-tris(trifluoromethyl)-3-pentenoic Acid δ-Lactone]. A solution of 0.5 g of tetramethylammonium chloride in 10 ml of dichloromethane was stirred in a 500-ml, three-necked flask fitted with a reflux condenser, thermometer, and dropping funnel. About 7 g of pentafluoromethacrylyl fluoride (**6**) was added. The temperature began to rise slowly, and when it reached about 35° a solution of 100 g (0.60 mole total) of pentafluoromethacrylyl fluoride in 100 ml of dichloromethane was added rapidly. Stirring was continued and the temperature again rose; in about 10 min refluxing began. Stirring was continued until the temperature had dropped to 25° and then the two-phase mixture was distilled. After removal of methylene chloride (bp 40°) the first fraction collected (3.5 g) boiled up to 103°. Fractions totaling 32.5 g were then collected boiling up to 112°. The final fraction (47 g) boiled mostly at 114° and was essentially pure lactone **13** as judged by gas chromatography. The previous fractions were mostly **13** containing a little lactone **16**. The yields based on gas chromatography were 5 g (5%) of **16** and 78 g (73%) of **13**.

Lactone **16** was separated by gas chromatography. Infrared absorption occurred at 5.48 (C=O) and 5.75 μ (C=CF). The F^{19} nmr consisted of four peaks of relative area 3:2:6:1 centered respectively at +59.3, +60.8, +64.3, and +93.1 ppm. The CF_3 peak was a doublet (J = 20 cps) into triplets (J = 7 cps) with further fine structure, apparently septets (J = 0.5 cps). The CF_2 peak was a doublet (J = 14 cps) into quartets (J = 7 cps). The $(CF_3)_2$ peak was a doublet (J = 13 cps) into quartets (J = 0.5 cps) and the CF peak was a complex multiplet.

Anal. Calcd for $C_8F_{12}O_2$: C, 26.99; F, 64.04. Found: C, 27.27; F, 63.86.

2,4,4-Tris(trifluoromethyl)-2,3-butadienoic Acid Fluoride (17). The above mixture of lactones [estimated 78 g (0.22 mole) of **13** and 5 g (0.24 mole) of **16**] was subjected to the same pyrolysis condition described above for lactone **9** except that a higher temperature was used (~700°). Low-boiling gases formed were characterized by infrared as predominantly COF_2 with some CO_2. There was obtained 52.7 g (78%) of material boiling at 69° and characterized as 2,4,4-tris(trifluoromethyl)-2,3-butadienoic acid fluoride (**17**). Infrared absorption was at 4.99 (C=C=C) and 5.45 μ (C=O). The F^{19} nmr consisted of three peaks of relative areas 1:6:3 centered relative to 1,2-difluorotetrachloroethane respectively at −35.2, 61.0, and 63.2 ppm. The COF peak was a quadruplet (J = 10 cps) and the $(CF_3)_2$ peak a doublet (J = 10 cps).

Anal. Calcd for $C_7F_{10}O$: C, 28.99; F, 65.52. Found: C, 29.27; F, 65.35.

The thermal reaction described above for converting lactone **13** to the allenic acid fluoride could also be accomplished at lower temperature with fluoride ion catalysis.

A mixture of 16.6 g (0.047 mole) of **13**, 0.5 g of cesium fluoride, and 1 ml of diglyme was placed in a still pot attached to a still and heated to reflux. Carbonyl fluoride was evolved, and there was collected a total of 9.1 g (67%) of nearly pure acid fluoride (**17**), bp 68–69°.

3,3,5-Trifluoro-5-hydroxy-2,2,4-tris(trifluoromethyl)-4-pentenoic Acid δ-Lactone (15). When an equimolar mixture of ketene 1 and methacrylyl fluoride **6** was treated with a catalytic amount of tetramethylammonium chloride in methylene chloride, an exothermic reaction occurred and, as expected, the product was a mixture containing lactones **13** and **16** and products derived from them by anionic catalysis. However, there was in addition an appreciable amount of another dimer, lactone **15**, having the structure assigned on the basis of infrared absorption and nmr.

A mixture of 18 g (0.10 mole) of **6**, 18 g (0.10 mole) of **1**, 0.05 g of tetraethylammonium chloride, and 1 ml of methylene chloride was sealed in a Carius tube at liquid nitrogen temperature. On mixing at room temperature an exothermic reaction occurred. After standing overnight, the mixture was distilled. After collection of about 6 g, the boiling point had risen from about 40 to 90°. The remaining fraction (20 g) boiled up to 104°, but the boiling point fluctuated and some low boilers seemed to be evolved. When examined by gas phase chromatography the fractions boiling above 90° showed **13** and **16** and an appreciable amount of another compound, lactone **15**. Judging from gas chromatography the yield was about 7 g (20%). A sample was separated on a preparative scale for analysis.

Infrared absorption occurred at 5.41 (C=O) and 5.74 μ (C=CF). The F^{19} nmr consisted of four peaks of relative area 3:6:1:2 centered relative to 1,2-difluorotetrachloroethane (external) respectively at 57.0, 63.0, 75.6, and 95.5 ppm. The CF_3 peak was a doublet (J = 22 cps) into triplets (J = 8 cps). The $(CF_3)_2$ peak was a triplet (J = 13 cps). The CF peak was a quartet (J = 22 cps) into triplets (J = 14 cps) and the CF_2 peak was a complex multiplet not well resolved.

Anal. Calcd for $C_8F_{12}O_2$: C, 26.99; F, 64.04. Found: C, 27.23; F, 63.69.

Esters 19 and 20. The acid fluoride **17** (14.5 g, 0.05 mole) was added to methanol (10 ml) and stirred. An exothermic reaction occurred and distillation gave 12.2 g (74%) of product, bp 48–53° (5.5 mm). Gas chromatography separated it into two components **19**, n^{25}D 1.3508, and **20**, n^{25}D 1.3520.

Compound **19** absorbed in the infrared at 5.77 (C=O) and 6.12 μ (C=C). Proton nmr showed a septet (J = 7 cps) for hydrogen centered at τ 4.80, a methyl group quartet (J = 0.7 cps) at τ 6.3, and a methyl group singlet at τ 6.48. The F^{19} nmr consisted of the corresponding $(CF_3)_2$ doublet (J = 7 cps) at 65 ppm and quartet (J = 0.7 cps) at 59 ppm.

Anal. Calcd for $C_9H_7O_3F_9$: C, 32.36; H, 2.11; F, 51.20. Found: C, 32.57; H, 2.61; F, 51.07.

Compound **20** absorbed in the infrared at 5.65 (C=O) and 6.09 μ (C=C). The proton nmr consisted of a quartet (J = 7 cps) for hydrogen at τ 5.63, a methyl peak with fine structure at τ 6.30, and a singlet methyl at τ 6.48. The F^{19} nmr consisted of two CF_3 quartets (J = 10 cps) at 57.5 (with ill-defined fine structure) and 60.0 ppm and another pair (J = 7 cps) of identical quartets (J = 2 cps) representing a CF_3 group centered at 65.3 ppm.

Anal. Calcd for $C_9H_7O_3F_9$: C, 32.36; H, 2.11; F, 51.20. Found: C, 32.70; H, 2.07; F, 51.22.

Reaction of Lactone 13 with Methanol. The δ-lactone **13** (20 g) was added dropwise with stirring to 10 ml of methanol at a temperature below 50°. The resulting solution was distilled under vacuum and 18.2 g collected, bp 58–78° (15 mm). Analysis by gas chromatography indicated a 3% yield of 2,2,4-tris(trifluoromethyl)-3-fluoro-4-carbomethoxy-3-butenoic acid fluoride (**21**), a 58% yield of the corresponding methyl ester (**22**), and a 24% yield of 5,5-difluoro-3-methoxy-5-hydroxy-2,4,4-tris(trifluoromethyl)-2-pentenoic acid δ-lactone (**23**). Material boiling at 78° (15 mm) was essentially the pure diester **22**. Pure samples of all three compounds were obtained by preparative gas chromatography of the lower boiling fractions. Compound **21**, n^{25}D 1.3352, absorbed in the infrared at 5.31 and 5.37 (COF), 5.65 and 5.71 ($COOCH_3$), and 5.98 μ (C=C). Proton nmr showed a single sharp peak at τ 6.5. The F^{19} nmr (ext ref) showed the $(CF_3)_2$ peak as an unsymmetrical triplet (overlapping doublets, J = ~10 and 12 cps) centered at 66 ppm, the CF_3 peak as a doublet (J = 28 cps) centered at 61 ppm, the COF peak as a septet (J = 10 cps) with further unresolved splitting centered at −38.5 ppm, and the remaining CF as a broad peak with unresolved splitting centered at 90 ppm.

Anal. Calcd for $C_9H_3F_{11}O_3$: C, 29.37; H, 0.82; F, 56.77. Found: C, 29.58; H, 0.85; F, 56.71.

The diester **22**, n^{25}D 1.3540, absorbed in the infrared at 5.61 and 5.67 ($COOCH_3$) and at 5.96 μ (C=C). The proton nmr consisted of two sharp peaks of equal intensity at τ 6.36 and 6.45. The F^{19} nmr (external reference) consisted of a $(CF_3)_2$ doublet (J = 12 cps) centered at 65.8 ppm, a CF_3 doublet (J = 24 cps) centered at 60.8 ppm, and a CF multiplet centered at 92 ppm for a quartet (J = 24 cps) into septets (J = 12 cps) overlapping with nine of the thirteen expected peaks clearly resolved.

Anal. Calcd for $C_{10}H_6F_{10}O_4$: C, 31.61; H, 1.59; F, 50.00. Found: C, 32.17; H, 1.71; F, 49.94.

The methoxylactone **23** was a solid which could be recrystallized from chloroform, mp 36–38°. It absorbed in the infrared at 5.56 (C=O) and 6.09 μ (C=C). The proton nmr of a 20% solution in deuteriochloroform was a quartet (J = 2 cps) centered at τ 5.77. The F^{19} nmr (ext ref) showed a CF_3 doublet (J = 2 cps) centered at 57.3 ppm, a $(CF_3)_2$ triplet (J = 12 cps) centered at 62.8 ppm, and a CF_2 septet (J = 12 cps) centered at 72.5 ppm.

Anal. Calcd for $C_9H_3F_{11}O_3$: C, 29.37; H, 0.82; F, 56.77. Found: C, 29.00; H, 0.90; F, 56.65.

Reaction of Lactone 13 with Water. A mixture of 25 g of lactone **13** and 5 ml of water was sealed in a Carius tube and heated overnight in a steam bath. When the tube was cooled and opened, carbon dioxide was detected in the off gas by infrared absorption. The crystalline product was dissolved in hot chloroform. The chloroform solution was dried over magnesium sulfate, filtered, and cooled in Dry Ice, and the resulting crystals were filtered and dried. The first crop yield of 2,4,4-tris(trifluoromethyl)-3-fluoro-2-butenoic acid (**24**), mp 52–54°, was 15.5 g (72%). It absorbed in the infrared at 5.80 (C=O) and 6.00 μ (C=C). The proton nmr at 70° showed the acidic proton (exchanges with D_2O) as a sharp peak at τ −1.76 and the other proton as a doublet (J = 29 cps) into septets (J = 7.2 cps) centered at τ 3.94. The F^{19} nmr (ext ref) consisted of a CF_3 peak at 60.9 ppm which was a doublet (J = 31 cps), a $(CF_3)_2$ peak at 65.6 ppm which was a doublet (J = 7.9 cps) into doublets (J = 7.2 cps), and a broad CF peak centered at 80.9 ppm with much undefined splitting.

Anal. Calcd for $C_7H_2F_{10}O_2$: C, 27.30; H, 0.65; F, 61.69. Found: C, 27.70; H, 0.75; F, 62.39.

In another experiment with a higher ratio of water to lactone, olefins were the major products. A mixture of 9 g of lactone **13** and 4 g of water was sealed in a Carius tube and heated overnight on a steam bath. The tube was then cooled and opened. Carbon dioxide was detected by infrared absorption of the off gas. The heavy layer of liquid which was separated (6.7 g) represented a quantitative conversion to the following products separated by gas chromatography: 1,1,3-tris(trifluoromethyl)-2-fluoro-2-propene (**25**, 84%); 1,1,3-tris(trifluoromethyl)-2-fluoro-1-propene (**26**, 15%); and methyl α-hydroperfluoroisopropyl ketone (**27**, 1%). When this reaction was run in the presence of about 20% of glyme in the water, the yield of ketone **27** increased to about 5% at the expense of olefin **25**.

Olefin **25** absorbed in the infrared at 5.82 μ (C=C). The proton nmr consisted of two equal areas, one a doublet (J = 31 cps) into quartets (J = 7 cps) centered at τ 4.85 and the other a doublet (J = 22 cps) into septets (J = 7.5 cps) centered at τ 6.75. The F^{19} nmr (ext ref) consisted of three areas (3:6:1) centered at 62, 67.8, and 97.5 ppm. They were respectively a doublet (J = 18 cps) into doublets (7 cps), a triplet (overlapping doublets of J = 7.5 cps), and a complex multiplet.

Anal. Calcd for $C_6H_2F_{10}$: C, 27.30; H, 0.76; F, 71.97. Found: C, 27.47; H, 0.98; F, 71.91.

Olefin **26** absorbed in the infrared at 5.86 μ (C=C). The proton nmr consisted of a doublet (J = 23 cps) into quartets (J = 9 cps) centered at τ 7.08. The F^{19} nmr (ext ref) consisted of four separate areas (3:3:3:1) centered at 60.5, 61.5, 66.1, and 75.9 ppm. All of the peaks contained fine structure which was not well defined.

Anal. Calcd for $C_6H_2F_{10}$: C, 27.30; H, 0.76; F, 71.97. Found: C, 27.42; H, 1.03; F, 71.96.

The ketone **27** absorbed in the infrared at 5.71 μ. The proton nmr consisted of a septet (J = 8 cps, area 1) centered at τ 6.15 and a singlet (area 3) at τ 8.09. The F^{19} nmr (ext ref) was a doublet (J = 8 cps) centered at 65.9 ppm.

Anal. Calcd for $C_5H_4F_6O$: C, 30.95; H, 2.08; F, 58.76. Found: C, 31.54; H, 2.18; F, 59.89.