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FLUOROKETENES
VIII.* ADDUCTS OF PERFLUOROMETHACRYLOYL FLUORIDE WITH UNSATURATED MOLECULES. *N*-ALKYL-BIS(TRIFLUOROMETHYL)KETENIMINES

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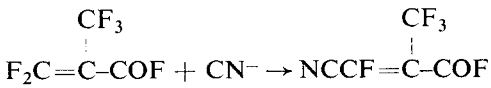
SUMMARY

Perfluoromethacryloyl fluoride has been found to yield predominantly 1,4 cyclo-adducts with olefins, isocyanates, nitriles and ketenes. With olefins and isocyanates, 1,2 cyclo-adducts and open-chain adducts are also formed, and evidence is presented to indicate that such adducts are obtained *via* dipolar intermediates. A new synthesis of *N*-alkyl-bis(trifluoromethyl)ketenimines is also reported.

INTRODUCTION

Anionic attack on perfluoromethacryloyl fluoride (I) by both the fluoride ion and a carbanion has been shown to occur preferentially at the terminal CF_2 group[2]. Similarly, the cyanide ion will attack the terminal position of (I) to form a nitrile, (II)



$$F_2C{=}\overset{CF_3}{\overset{|}{C}}{-}COF + CN^- \rightarrow NCCF{=}\overset{CF_3}{\overset{|}{C}}{-}COF$$

(I) (II)

This terminal position is, in fact, sufficiently electrophilic that uncharged nucleophiles such as methanol may add exothermically with little attack at the carbonyl carbon[1]. Aldehydes containing a group capable of stabilizing a positive charge also appear to attack (I) at the terminal carbon atom to form a dipolar intermediate which subsequently closes to an unstable oxetane ring. In the case of

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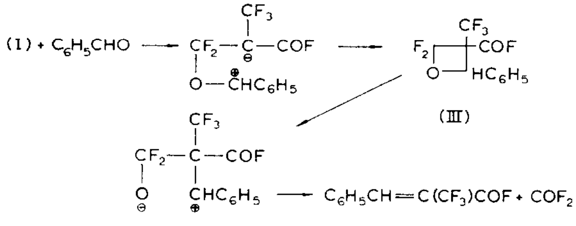
* For Part VII, see ref. 1.

benzaldehyde, oxetane (III) has been isolated as a moderately stable 1,2 cyclo-adduct which will thermolyze to an olefin with loss of carbonyl fluoride[1].



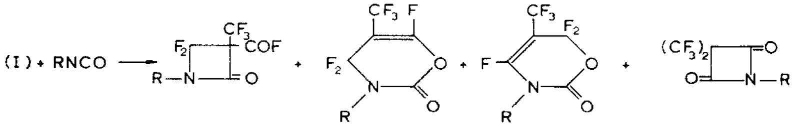
(III)

(*cis* and *trans*)

Other aldehydes tended to form an olefin with (I) even more readily, with the exception of aliphatic aldehydes and formaldehyde. Presumably the stabilization available to a positive charge in the latter cases is insufficient to direct the reaction through a dipolar intermediate, so that 1,4 cyclo-addition occurs instead[1]. Compound (I) is known to undergo the 1,4 mode of cyclo-addition in one other case, namely reaction with propylene[3]. This paper reports on the reaction of (I) with various unsaturated compounds and describes an unusual synthesis of *N*-alkyl-bis(trifluoromethyl)ketenimines from the 1,4 adducts of (I) with isocyanates.

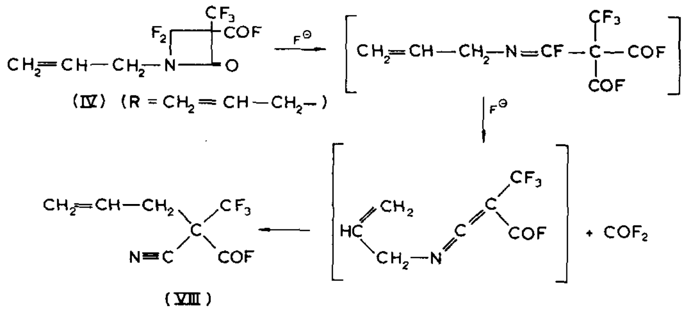
SYNTHESIS AND CHEMISTRY OF ISOCYANATE ADDUCTS

The reaction of (I) with cyclohexyl isocyanate gave as products of 1,2 cyclo-addition (IV) (R = C_6H_{11}), of 1,4 cyclo-addition (V) (R = C_6H_{11}), of 1,4 cyclo-addition followed by a 1,3-fluoride shift (VI) (R = C_6H_{11}) together with the cyclic imide (VII) (R = C_6H_{11}). The latter compound is formed in high yield from bis(trifluoromethyl)ketene and cyclohexyl isocyanate, so that its isolation may be due to some isomerization of (I) to ketene under the reaction conditions employed. Compound (V) was converted to (VI) (1,3-fluoride shift) by heating in glyme, indicating that compounds (IV) and (V) are the primary reaction products of (I) with cyclohexyl isocyanate. In most cases of 1,4 addition to (I), only the rearranged product of the type (VI) was isolated.



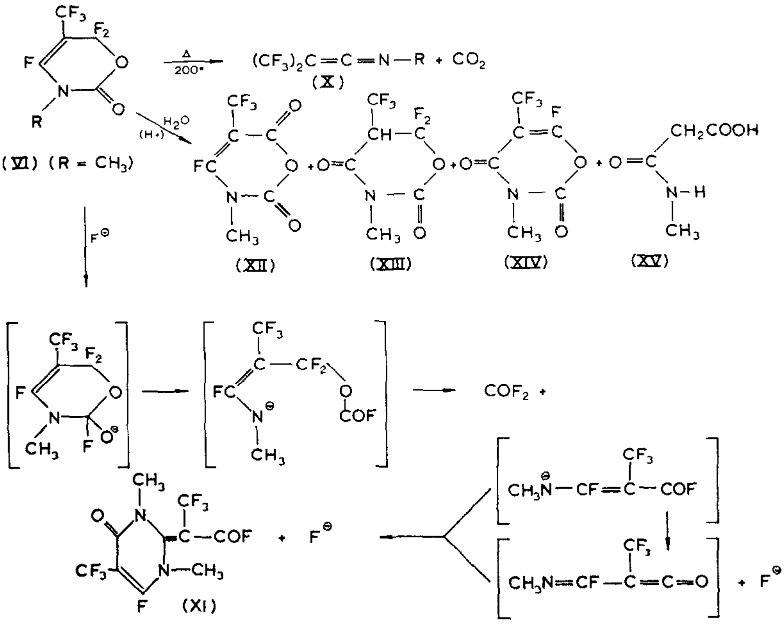
(IV) (V) (VI) (VII)

Allyl isocyanate reacted with (I) to give 1,2 and 1,4 adducts corresponding to (IV) and (VI) above, as well as some of the ketene adduct corresponding to (VII). The adduct (IV) (R = allyl) when heated to 100° in the presence of fluoride ion rearranged (including an allylic rearrangement) to (VIII) with loss of COF_2.



Pyrolysis of the 1,2-cyclo-adduct (IV) (R = CH_3) regenerated (I) and methyl isocyanate. Similarly, (IX), the methyl ester prepared by treatment of (IV) (R = CH_3) with methanol, pyrolyzed to (I) and methyl perfluoromethacrylate. Adducts of (I) corresponding to (VI) having *N*-methyl and *N*-butyl groups, however, lost carbon dioxide and were cleanly rearranged to the *N*-alkyl-bis(trifluoromethyl)ketenimines (X) (R = CH_3 and C_4H_9) by heating to 200°. *N*-Alkyl-bis(trifluoromethyl)ketenimines have been reported from the reaction of bis(trifluoromethyl)thioketene with *N,N'*-dialkylsulfurdi-imide[4], and *N*-phenyl-bis(trifluoromethyl)ketenimine from perfluoroisobutylene with *N*-phenyltriphenylphosphinimine[5].

The *N*-methyl compound (VI) (R = CH_3) on treatment with the fluoride ion in refluxing methylene chloride gave a good yield of (XI) with loss of carbonyl fluoride. A reasonable mechanism involving anionic intermediates may be formu-



lated as shown below. Acid hydrolysis of (VI) (R $= CH_3$) gave (XII), (XIII), (XIV) and (XV). Methanolysis of (VI) (R $= CH_3$) gave methyl α-trifluoromethylacetate and dimethyl trifluoromethylmalonate.

The *N*-methyl compound corresponding to (IV) was hydrolyzed to $CF_3CH_2CONHCH_3$, and reacted with dimethylamine to give the corresponding amide and with methanol to give the ester. The ester was pyrolyzed to methyl isocyanate and methyl perfluoroacrylate.

In an attempt to control the ratio of the two types of cyclo-adducts corresponding to (IV) (4-ring) and (VI) (6-ring), (I) was treated with butyl isocyanate without solvent and with three solvents of different polarity. The results (Table 1) indicate that some control is exercised and suggest that different amounts of charge are developed during the two cyclo-addition reactions. Formation of the 1,2 cyclo-adduct, which may well proceed *via* a dipolar intermediate, is favored in polar media.

TABLE 1

PRODUCTS FROM THE REACTION OF BUTYL ISOCYANATE AND PERFLUOROMETHACRYLOYL FLUORIDE*

Solvent	Product isolated (% yield)	
	4-Ring	6-Ring
–	37	45.5
Hexane	32.5	50.5
Methylene chloride	34.6	43.2
Nitromethane	53.2	22.4

* Carried out in sealed tubes for 88 h at 100° using 0.1 mol of each reactant in 25 ml of solvent.

Adducts of olefins with (I)

Perfluoromethacryloyl fluoride, (I), reacted with a number of other compounds, as is shown in Table 2 together with the structures of the products isolated. Many products were easily hydrolyzed. Details of these experiments are given in the experimental section.

Products of the reaction of (I) with olefins could be accounted for by a mechanism involving nucleophilic attack of the olefin at the terminal CF_2 group. The resulting intermediate zwitterion could then ring-close (*i.e.* (XVI) from propylene), undergo proton migration (*i.e.* (XIX) from isobutylene) or fluoride migration (*i.e.* (XX) from isobutylene).

The cyclic product from vinyl acetate (XXV) could be hydrolyzed with loss of acetic acid to give the pyrone structures (XXVI) and (XXVII).

Adducts of nitriles with (I)

The reaction of (I) with nitriles involved 1,4 cyclo-addition and the products were easily hydrolyzed. Several examples are listed in Table 2.

TABLE 2

REACTIONS OF PERFLUOROMETHACRYLOYL FLUORIDE

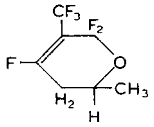
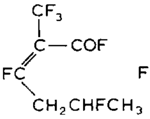
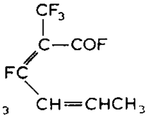
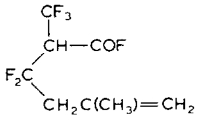
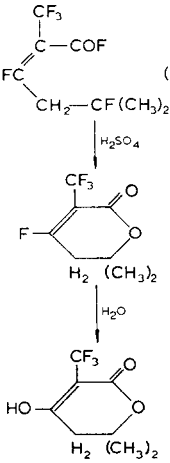
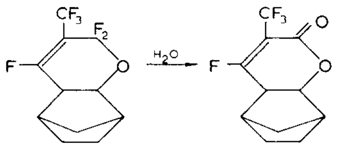
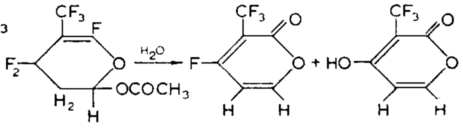
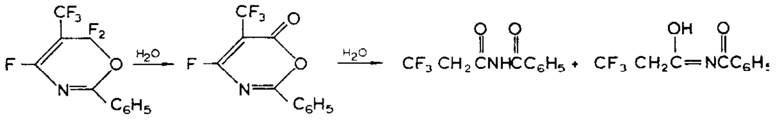
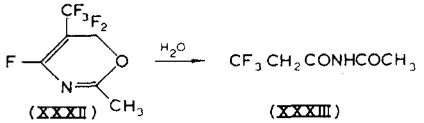
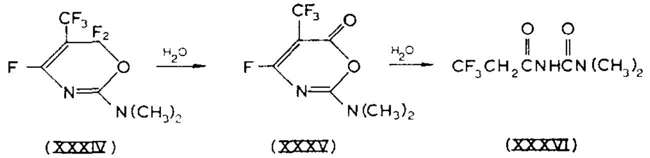
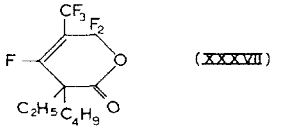
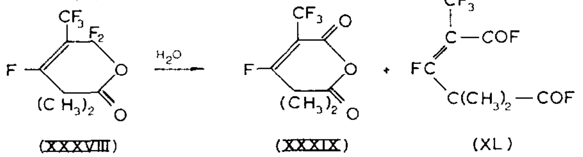
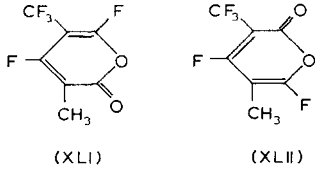
Reactants	Products
$CH_2{=}CH{-}CH_3$	 (XVI)  (XVII)  (XVIII)
$CH_2{=}C(CH_3)_2$	 (XIX)  (XX) (XXI) (XXII)
	 (XXIII) (XXIV)
$CH_2{=}CHOCOCH_3$	 (XXV) (XXVI) (XXVII)
C_6H_5CN	 (XXVIII) (XXIX) (XXX) (XXXI)

TABLE 2 *(continued)*

Reactants	Products
CH_3CN	 (XXXII) $CF_3CH_2CONHCOCH_3$ (XXXIII)
$(CH_3)_2NCN$	 (XXXIV) (XXXV) (XXXVI)
$(C_2H_5)(C_4H_9)C{=}C{=}O$	 (XXXVII)
$(CH_3)_2C{=}C{=}O$	 (XXXVIII) (XXXIX) (XL)
$CH_3CH{=}C{=}O$	 (XLI) (XLII)

Adducts of ketenes with (I)

Reaction of (I) with ketenes involved 1,4 cyclo-addition to the C=C bond of the ketene. In the case of methylketene, the presumed initial product easily lost hydrogen fluoride to form (XLI) and (XLII).

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 an 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 an external standard.

*Reaction of (I) with cyclohexyl isocyanate. 1-Cyclohexyl-2,2-difluoro-4-oxo-3-(trifluoromethyl)-3-azetidinecarbonyl fluoride (IV) (R = C_6H_{11}) (nc), 4,4,6-trifluoro-3,4-dihydro-3-cyclohexyl-5-(trifluoromethyl)-2*H*-1,3-oxazin-2-one (V) (R = C_6H_{11}) (nc), 4,6,6-trifluoro-3,6-dihydro-3-cyclohexyl-5-trifluoromethyl-2*H*-1,3-oxazin-2-one (VI) (R = C_6H_{11}) (nc) and 2,2-bis (trifluoromethyl)-*N*-cyclohexylmalonimide (VII) (R = C_6H_{11}) (nc)*

It appears that the primary products of the reaction of (I) with cyclohexyl isocyanate are (IV) and (V) above. In one reaction using commercial isocyanate (not distilled), all four of the above products were isolated. Compound (V) readily isomerized to (VI) by heating in a polar solvent (glyme) indicating that isolation of (V) is favored by non-polar conditions. Compound (VII) has been prepared in high yield from bis(trifluoromethyl)ketene and cyclohexyl isocyanate and is probably formed through base-catalyzed isomerization of (I) to the ketene. Using re-distilled isocyanate, compounds (IV) and (VI) have been isolated in high yield. Attempted pyrolysis of (VI) to *N*-cyclohexyl-bis(trifluoromethyl)ketenimine gave only tar.

A mixture consisting of 44 ml (0.4 mol) of (I) and 50 g (0.4 mol) of freshly distilled cyclohexyl isocyanate was sealed in a glass tube and heated for 40 h on a steam bath. There was isolated 49 g (40.5%) of (IV), b.p. 42°/0.1 mmHg, 4 g of an intermediate cut and 44 g (36.4%) of (VI), b.p. 72°/0.1 mmHg, m.p. 45–46° (from petroleum ether). When this reaction was repeated (on a 0.05 mol scale) at 175° for 8 h, only compound (IV) plus tar and none of (VI) was isolated. Likewise heating of compound (VI) in a sealed tube to 175° for 8 h gave a tar. When the reaction was repeated (on a 0.05 mol scale) in an acid-washed tube overnight on a steam bath, again about equal amounts of (IV) and higher boiling material were obtained. In this case the high boiling material was not pure (VI), but was separated by partial crystallization (petroleum ether) into 3.4 g of compound (V), m.p. 70–71°, and 3.0 g of compound (VI), m.p. 46°.

A 0.5 g sample of (V), m.p. 71°, in 5 ml of glyme was heated in a sealed tube on a steam bath for 60 h. It was then water-washed, recrystallized from petroleum ether and characterized by mixed melting point determinations (45–46°) as (VI).

A mixture consisting of 0.2 mol each of (III) and cyclohexyl isocyanate which had not been freshly distilled was sealed in a Carius tube and heated for 60 h on a steam bath. There was recovered 40 g of material, b.p. 55–60°/1.5 mmHg, which was a mixture of (IV) and (VII) (separable by GLPC), about 4 g of (V) and 8 g of (VI).

For (IV) (R = C_6H_{11}): IR: 5.36 μ and 5.46 μ (C=O). ^1H NMR: 3.5 (broad, 1H), centered 1.5 (multiplet, 10H). ^{19}F NMR: +42.7 (doublet, $J = 9$ Hz, to quartets, $J = 9$ Hz, to doublets, $J = 3$ Hz, 1F), −68.6 (doublet, $J = 12$ Hz, to doublets, $J = 9$ Hz, to doublets, $J = 4$ Hz, 3F), −87.5 and −90.2 (AB doublet to doublets, $J = 9$ Hz, to quartets, $J = 4$ Hz, 1F), −92.7 and −95.4 (AB doublet to quartets, $J = 12$ Hz, to doublets, $J = 3$ Hz, 1F). Analysis: Found: C, 42.93; H, 3.84; F, 37.48; N, 4.54%. $C_{11}H_{11}F_6NO_2$ requires C, 43.60; H, 3.66; F, 37.62; N, 4.62%.

For (V) ($R = C_6H_{11}$): IR: 5.52 μ (C=O) and 5.73 μ (C=C). ^1H NMR: 3.8 (broad, 1H), centered 1.83 (multiplet, 10H). ^{19}F NMR: −57.0 (doublet, $J = 17$ Hz, to triplets, $J = 8$ Hz, 3F), −60.7 (doublet, $J = 11$ Hz, to quartets, $J = 8$ Hz, 2F), −76.3 (quartet, $J = 17$ Hz, to triplets, $J = 11$ Hz, 1F). Analysis: Found: C, 43.25; H, 3.45; F, 37.60; N, 4.69%. $C_{11}H_{11}F_6NO_2$ requires C, 43.60; H, 3.66; F, 37.62; N, 4.62%.

For (VI) ($R = C_6H_{11}$): IR: 5.59 μ (C=O) and 5.82 μ (C=C). ^1H NMR: 4.20 (broad, 1H), centered 1.50 (multiplet, 10H). ^{19}F NMR: −57.3 (doublet, $J = 18$ Hz, to triplets, $J = 7$ Hz, 3F), −51.3 (doublet, $J = 13$ Hz, to quartets, $J = 7$ Hz, 2F), −94.9 (quartet, $J = 18$ Hz, to triplets, $J = 13$ Hz, 1F). Analysis: Found: C, 44.98; H, 4.48; F, 34.90; N, 4.86%. $C_{11}H_{11}F_6NO_2$ requires C, 43.60; H, 3.66; F, 37.62; N, 4.62%.

*Reaction of (I) with cyclohexyl isocyanate. 2,2-Bis(trifluoromethyl)-*N*-cyclohexylmalonimide (VII) ($R = C_6H_{11}$)*

A mixture consisting of 8 g (0.045 mol) of (I) and 6 g (0.48 mol) cyclohexyl isocyanate when heated in a sealed tube on a steam bath for 16 h gave 13 g (95%) of (VII). IR: 5.64 μ (C=O). ^1H NMR: 3.7 (broad, 1H), centered 1.6 (multiplet, 10H). ^{19}F NMR: −66.7 (singlet, 6F). Analysis: Found: C, 43.54; H, 3.86; F, 37.54; N, 4.45%. $C_{11}H_{11}F_6NO_2$ requires C, 43.60; H, 3.66; F, 37.62; N, 4.62%.

*Reaction of (I) with allyl isocyanate. 1-Allyl-2,2-difluoro-4-oxo-3-(trifluoromethyl)-3-azetidinecarbonyl fluoride (IV) ($R = H_2C{=}CH{-}CH_2{-}$) (nc) and 4,6,6-trifluoro-3,6-dihydro-3-allyl-5-(trifluoromethyl)-2*H*-1,3-oxazin-2-one (VI) ($R = H_2C{=}CH{-}CH_2{-}$) (nc)*

The reaction of (I) with allyl isocyanate gave good yields of a mixture of (IV) and (VI) ($R = H_2C{=}CH{-}CH_2{-}$). In some runs (IV) was contaminated with (VII) ($R = H_2C{=}CH{-}CH_2{-}$) which could be prepared in nearly quantitative yield from allyl isocyanate and bis(trifluoromethyl)ketene.

A mixture consisting of 22 ml (0.2 mol) of (I) and 16.6 g (0.2 mol) of allyl isocyanate contained in a sealed tube was heated overnight on a steam bath. There was recovered 19.1 g (36.5%) of (IV), b.p. 60°/21 mmHg, n_D^{25} 1.3658, and 19.5 g (37.5%) of (VI), b.p. 96°/23 mmHg, n_D^{25} 1.4010.

For (IV) ($R = H_2C{=}CH{-}CH_2{-}$): IR: 5.36 μ, 5.44 μ (COF), 5.60 μ (C=O), 6.06 μ (C=C). ^1H NMR: centered 5.1 (multiplet, 3H), 3.61 (doublet, $J = 5$ Hz, 2H). ^{19}F NMR: +42.7 (quartet, $J = 9$ Hz, to doublets, $J = 9$ Hz, to doublets, $J = 3$ Hz, 1F), −68.6 (doublet, $J = 12$ Hz, to doublets, $J = 9$ Hz, to doublets, $J = 4$ Hz, 3F), −90.7 and −93.4 (AB doublet to doublets, $J = 9$ Hz, to quartets, $J = 4$ Hz, 1F), −95.8 and −98.5 (AB doublet to quartets, $J = 12$ Hz, to doublets, $J = 3$ Hz, 1F). Analysis: Found: C, 36.81; H, 2.09; F, 43.50; N, 5.24%. $C_8H_5F_6NO_2$ requires C, 36.81; H, 1.93; F, 43.68; N, 5.37%.

For (VI) ($R = H_2C{=}CH{-}CH_2{-}$): IR: 5.57 μ (C=O), 5.81 μ (FC=C), 6.07 μ (C=C). ^{1}H NMR: 5.1 (multiplet, 3H), 4.1 (multiplet, 2H). ^{19}F NMR: −50.4 (doublet, $J = 13$ Hz, to quartets, $J = 7$ Hz, 2F), −57.7 (doublet, $J = 18$ Hz, to triplets, $J = 7$ Hz, 3F), −95.9 (multiplet, 1F). Analysis: Found: C, 36.78; H, 1.97; F, 43.60; N, 5.41%. $C_8H_5F_6NO_2$ requires C, 36.81; H, 1.93; F, 43.68; N, 5.37%.

Reaction of (IV) ($R = H_2C{=}CH{-}CH_2{-}$) with the fluoride ion. 2-Cyano-2-(trifluoromethyl)-4-pentenoyl fluoride (VIII) (nc)

The acid fluoride (11.2 g), 0.1 g of cesium fluoride, 0.1 g of tetraethylammonium chloride and 5 ml of methylene chloride were heated together in a sealed tube on a steam bath for 60 h. There was recovered 2 g of (VIII), b.p. 30°/17 mmHg, 3 g of starting material and some tar. IR: 5.37 μ (C=O), 4.35 μ (C≡N), 6.05 μ (C=C). ^{1}H NMR: 5.2 (multiplet, 3H), 2.63 (multiplet, 2H). ^{19}F NMR: +38.8 (quartet, $J = 9.5$ Hz), −71.0 (doublet, $J = 9.5$ Hz, 3F). Analysis: Found: C, 43.29; H, 3.06; F, 38.70; N, 7.13%. $C_7H_5F_4NO$ requires C, 43.11; H, 2.58; F, 38.97; N, 7.18%.

*Reaction of bis(trifluoromethyl)ketene with allyl isocyanate. 2,2-Bis(trifluoromethyl)-*N*-allylmalonimide (VII) ($R = H_2C{=}CH{-}CH_2{-}$) (nc)*

A mixture consisting of allyl isocyanate (8.5 g, 0.1 mol) and the ketene (34 g, 0.19 mol) in a sealed tube was heated for 60 h on a steam bath. There was recovered 16 g of the ketene and 25.3 g (97%) of (VII), b.p. 55°/20 mmHg. IR: 5.63 μ (C=O), 6.06 μ (C=C). ^{1}H NMR: centered 5.10 (multiplet, 3H), 3.70 (doublet, $J = 5$ Hz, with fine structure, 2H). ^{19}F NMR: −68.0 (singlet, 6F). Analysis: Found: C, 36.81; H, 1.89; F, 43.99; N, 5.07%. $C_8H_5F_6NO_2$ requires C, 36.81; H, 1.93; F, 43.68; N, 5.37%.

*Reaction of (I) with butyl isocyanate. 1-Butyl-2,2-difluoro-4-oxo-3-(trifluoromethyl)-3-azetidinecarbonyl fluoride (IV) ($R = C_4H_9$) (nc) and 4,6,6-trifluoro-3,6-dihydro-3-butyl-5-(trifluoromethyl)-2*H*-1,3-oxazin-2-one (VI) ($R = C_4H_9$) (nc)*

A mixture consisting of 36 g (0.2 mol) of (I) and 20 g (0.2 mol) of butyl isocyanate contained in a sealed tube was heated for 90 h on a steam bath. There was recovered 21.8 g (39%) of (IV), b.p. 70°/20 mmHg, n_D^{25} 1.3650, 4.4 g of an intermediate cut and 26.6 g (48%) of (VI), b.p. 62°/0.8 mmHg, n_D^{25} 1.3972.

For (IV) ($R = C_4H_9$): IR: 5.37 μ (COF), 5.45 μ (C=O). ^{1}H NMR: 3.11 (triplet, $J = 7$ Hz, 2H), 0.65 (triplet, $J = 7$ Hz, 3H), 1.3 (multiplet, 4H). ^{19}F NMR: +42.7 (quartet, $J = 9$ Hz, to doublets, $J = 9$ Hz, to doublets, $J = 3$ Hz, 1F), −68.6 (doublet, $J = 12$ Hz, to doublets, $J = 9$ Hz, to doublets, $J = 4$ Hz, 3F), −90.9 and −93.6 (AB doublet to doublets, $J = 9$ Hz, to quartets, $J = 4$ Hz, 1F), −96.1 and −98.8 (AB doublet to quartets, $J = 12$ Hz, to doublets, $J = 3$ Hz, 1F). Analysis: Found: C, 39.01; H, 3.20; F, 41.01; N, 4.98%. $C_9H_9F_6NO_2$ requires C, 39.02; H, 3.28; F, 41.16; N, 5.06%.

For (VI) (R = C_4H_9): IR: 5.57 μ (C=O), 5.80 μ (C=C). ^{1}H NMR: 3.65 (triplet, J = 7 Hz, 2H), 0.78 (triplet, J = 6 Hz, 3H), 1.35 (multiplet, 4). ^{19}F NMR: −57.6 (doublet, J = 18 Hz, to triplets, J = 7 Hz, 3F), −50.1 (doublet, J = 14 Hz, to quartets, J = 7 Hz, 2F), −96.3 (multiplet, 1F). Analysis: Found: C, 39.03; H, 3.31; F, 41.20; N, 4.97%. $C_9H_9F_6NO_2$ requires C, 39.02; H, 3.28; F, 41.16; N, 5.06%.

Pyrolysis of (VI) (R = C_4H_9). N-*Butyl-bis(trifluoromethyl)ketenimine (X) (R = C_4H_9)*

Compound (VI) (R = C_4H_9) (19.9 g) was heated for 4 h at 200° in a sealed tube. There was recovered 11.2 g (67%) of (X) (R = C_4H_9), b.p. 65°/40 mmHg, n_D^{25} 1.3628. IR: 4.74 μ (C=C=N). ^{1}H NMR: 3.44 (triplet, J = 7 Hz, 2H), 0.67 (triplet, J = 7 Hz, 3H), centered 1.30 (multiplet, 4H). ^{19}F NMR: −57.0 (singlet, 6F). Analysis: Found: C, 41.46; H, 3.86; F, 48.88; N, 5.90%. $C_8H_9F_6N$ requires C, 41.24; H, 3.89; F, 48.93; N, 6.01%.

*Reaction of (I) with methyl isocyanate. 2,2-Difluoro-1-methyl-4-oxo-3-(trifluoromethyl)-3-azetidinecarbonyl fluoride (IV) (R = CH_3) (nc) and 4,6,6-trifluoro-3,6-dihydro-3-methyl-5-(trifluoromethyl)-2*H-*1,3-oxazin-2-one (VI) (R=CH_3) (nc)*

Into each of three Carius tubes was placed 33 ml (0.3 mol) of (I) and 30 ml of methyl isocyanate and the mixture heated on a steam bath for 40 h. There was obtained by distillation 96.5 g (46%) of (IV), b.p. 78°/100 mmHg, n_D^{25} 1.3470 and 96.5 g (46%) of (VI), b.p. 57°/0.8 mmHg, n_D^{25} 1.3865. Compound (VI) solidified and could be recrystallized from petroleum ether, m.p. 36–37°.

For (IV) (R = CH_3); IR: 5.35 μ and 5.40 μ (COF), 5.60 μ (C=O). ^{1}H NMR: 2.7 (triplet, J = 1 Hz, 3H). ^{19}F NMR: −68.8 (doublet, J = 12 Hz, to doublets, J = 9 Hz, to doublets, J = 4 Hz, 3F), −94.2 and −97.2 (AB doublet to doublets, J = 9 Hz, to quartets, J = 4 Hz, 1F), −99.0 and −102.0 (AB doublet to quartets, J = 12 Hz, to doublets, J = 3 Hz, 1F), +42.5 (quartet, J = 9 Hz, to doublets, J = 9 Hz, to doublets, J = 3 Hz, 1F). Analysis: Found: C, 30.83; H, 1.35; F, 48.11; N, 5.94%. $C_6H_3NF_6O_2$ requires C, 30.66; H, 1.29; F, 48.51; N, 5.96%.

For (VI) (R = CH_3): IR: 5.58 μ (C=O), 5.80 μ (C=C). ^{1}H NMR: 3.14 (doublet, J = 3 Hz, 3H). ^{19}F NMR: −58.0 (doublet, J = 19 Hz, to triplets, J = 7 Hz, 3F), −50.0 (doublet, J = 13 Hz, to quartets, J = 7 Hz, 2F), −94.3 (quartet, J = 19 Hz, to triplet, J = 13 Hz, to quartet, J = 3 Hz, 1F). Analysis: Found: C, 31.13; H, 1.5; F, 47.93; N, 6.07%. $C_6H_3NF_6O_2$ requires C, 30.66; H, 1.29; F, 48.51; N, 5.96%.

Hydrolysis of (IV) (R = CH_3). N-*Methyl-β-trifluoromethylacetamide*

The acid fluoride (50 g) and 10 ml of water contained in an open polythene bottle were warmed on a steam bath. When reaction began it became very vigorous with much evolution of gas. The residue was taken up in chloroform, distilled and recrystallized from chloroform to give the above amide (4.4 g, 14.6%), m.p. 72°. IR: 6.01 μ (C=O), 6.34 μ (secondary amide band). ^1H NMR (20% in $CDCl_3$ soln.): 2.82 (doublet, $J = 5$ Hz, 3H), 3.17 (quartet, $J = 10.5$ Hz, 2H), 7.6 (broad, 1H). ^{19}F NMR: −63.2 (triplet, $J = 10.5$ Hz, 3F). Analysis: Found: C, 33.63; H, 4.42; F, 40.09; N, 9.76%. $C_4H_6F_3NO$ requires C, 34.07; H, 4.29; F, 40.43; N, 9.93%.

Reaction of (IV) (R = CH_3) with diethylamine. 2,2-Difluoro-1-methyl-4-oxo-3-(trifluoromethyl)-3-azetidine-diethylcarboxamide (nc)

The acid fluoride (IV) (R = CH_3) (30 g) was added dropwise with stirring to 130 ml (10-fold excess) of diethylamine in 200 ml ether. Gentle refluxing was continued for 0.5 h after addition. The mixture was then washed well with water, dried and distilled to give 25 g of the above amide, b.p. 98°/2.5 mmHg, n_D^{25} 1.4164. IR: 5.44 μ and 5.52 μ (ring C=O), 6.00 μ (amide C=O). ^1H NMR: 1.93 (triplet, $J = 6$ Hz, 6H), 3.24 (quartet, $J = 6$ Hz, 4H), 2.79 (singlet, 3H). ^{19}F NMR: −66.6 (singlet, 3F), −90.3 and −92.9 (AB doublet), −101.5 and −104.1 (AB doublet with fine structure). Analysis: Found: C, 41.69; H, 4.70; F, 32.60; N, 9.68%. $C_{10}H_{13}F_5N_2O_2$ requires C, 41.70; H, 4.55; F, 32.99; N, 9.73%.

Reaction of (IV) (R = CH_3) with methanol. 2,2-Difluoro-1-methyl-4-oxo-3-(trifluoromethyl)-3-azetidinecarboxymethylate (IX) (nc)

The acid fluoride (IV) (R = CH_3) (30 g) was added dropwise with stirring to 50 ml of methanol keeping the temperature below 60°. When addition was complete, the mixture was refluxed for 15 min, cooled, poured into water, washed three times with water, dried and distilled. There was obtained 24 g (76.5%) of (IX), b.p. 55°/3 mmHg, n_D^{25} 1.3734. IR: 5.42 μ (ring C=O), 5.71 μ (ester C=O). ^1H NMR: 2.67 (triplet, $J = 1$ Hz, 3H), 3.62 (singlet, 3H). ^{19}F NMR: −68.3 (doublet, $J = 10.5$ Hz, to doublets, $J = 2.5$ Hz, 3F), −95.6 and −98.2 (AB doublet to quartets, $J = 2.5$ Hz, 1F), −100.4 and −103.0 (AB doublet to quartets, $J = 10.5$ Hz, 1F). Analysis: Found: C, 34.35; H, 2.50; F, 38.05; N, 5.88%. $C_7H_6F_5NO_3$ requires C, 34.04; H, 2.45; F, 38.46; N, 5.67%.

Pyrolysis of (XI). Methyl perfluoroacrylate and methyl isocyanate

A sample (25 g) of the above ester was pyrolyzed under vacuum over quartz chips at 700°. The material which collected in a liquid-nitrogen trap was distilled to give about 15 g of a mixture containing about 2 g of methyl isocyanate and 3 g of impure methyl perfluoromethacrylate, b.p. 85–90°, which was purified by gas chromatography. The sample was identical (IR and NMR) with one prepared by dehydrofluorinating $(CF_3)_2CH{-}COOCH_3$.

*Acid hydrolysis of (IV) ($R = CH_3$). 4-Fluoro-3-methyl-5-(trifluoromethyl)-2*H*-1,3-oxazin-2,6(3*H*)-dione (XII) (nc), 6,6-difluoro-dihydro-3-methyl-5-(trifluoromethyl)-2*H*-1,3-oxazin-2,4(3*H*)-dione (XIII) (nc), 6-fluoro-3-methyl-5-(trifluoromethyl)-2*H*-1,3-oxazin-2,4(3*H*)-dione (XIV) (nc) and* N*-methylmalonamic acid (XV)*

Compound (IV) ($R = CH_3$) (40 g) was added dropwise to 40 ml of conc. sulfuric acid with stirring and cooling in order to keep the temperature below 30°. When addition was complete, the solution was poured on to ice giving a mixture of solid and oil. The solid after being recrystallized twice from benzene gave 1.5 g of compound (XII), m.p. 105° (gas). On standing overnight in moist air, it was converted to compound (XV) which was formed directly from another run and recrystallized from nitromethane, m.p. 94–108°. The oil was distilled and compound (XIII) isolated, *ca.* 5 g, b.p. 39°/0.015 mmHg, n_D^{25} 1.3921, as well as compound (XIV), b.p. *ca.* 70°/1 mmHg, which solidified and could be recrystallized from benzene, m.p. 90–93°.

For (XII): IR: 5.54 μ and 5.75 μ (C=O), 5.98 μ (C=C). ^1H NMR (20% in deuteroacetone): 3.0 (doublet, $J = 3.4$ Hz, 3H). ^{19}F NMR: −59.4 (doublet, $J = 23$ Hz, 3F), −79.4 (quartet, $J = 23$ Hz, to quartets, $J = 3.4$ Hz, 1F). Analysis: Found: C, 34.19; H, 1.58; F, 35.32; N, 6.79%. $C_6H_3F_4NO_3$ requires C, 33.83; H, 1.42; F, 35.68; N, 6.58%.

For (XIII): IR: 5.53 μ and 5.76 μ (C=O). ^1H NMR: 3.1 (singlet, 3H), 4.25 (quartet, $J = 7$ Hz, to doublets, $J = 5$ Hz, to doublets, $J = 14$ Hz, 1H). ^{19}F NMR: −65.2 (triplet, $J = 10$ Hz, to doublets, $J = 7$ Hz, 3F), −69.6 and −72.2 (AB doublet to quartets, $J = 10$ Hz, to doublets, $J = 5$ Hz, 1F), −74.3 and −76.9 (AB doublet to quartets, $J = 10$ Hz, to doublets, $J = 14$ Hz, 1F). Analysis: Found: C, 31.39; H, 1.86; F, 40.53; N, 6.00%. $C_6H_4F_5NO_3$ requires C, 30.93; H, 1.73; F, 40.77; N, 6.01%.

For (XIV): IR: 5.51 μ and 5.89 μ (C=O). ^1H NMR (20% in deuteroacetone): 2.77 (singlet, 3H). ^{19}F NMR: −60.8 (doublet, $J = 23$ Hz, 3F), −69.4 (quartet, $J = 23$ Hz, 1F). Analysis: Found: C, 33.72; H, 1.95; F, 34.98; N, 6.63%. $C_6H_3F_4NO_3$ requires C, 33.83; H, 1.42; F, 35.68; N, 6.58%.

For (XV): IR: 5.76 μ (COOH), 6.14 μ (C=O). ^1H NMR (20% in D_2O): 2.71 (singlet, 3H) (other protons exchangeable). Analysis: Found: C, 40.22; H, 5.40; N, 11.84%. $C_4H_7NO_3$ requires C, 41.06; H, 6.03; N, 11.97%.

Reaction of (VI) ($R = CH_3$) with methanol. Methyl trifluoromethylacetate and dimethyl trifluoromethylmalonate

A mixture consisting of 15 g of (VI), 25 ml of methanol and 0.5 g of sodium methoxide was sealed in a Carius tube and heated overnight on a steam bath. There was some etching. The mixture was poured into water, extracted with methylene chloride, dried and distilled. There was obtained about 2.2 g (24%) of methyl trifluoroacetate, b.p. 54°/150 mmHg, and 7.1 g (55%) of dimethyl trifluoromethylmalonate, b.p. 99°/50 mmHg, identical with the sample described earlier.

For methyl trifluoromethylacetate: IR: 5.69 μ (C=O). ^{1}H NMR: 3.41 (singlet, 3H), 2.93 (quartet, $J = 10.5$ Hz, 2H). ^{19}F NMR: -65.7 (triplet, $J = 10.5$ Hz, 3F). Analysis: Found: C, 33.75; H, 3.82; F, 35.42%. $C_4H_5F_3O_2$ requires C, 33.83; H, 3.55; F, 40.15%.

Pyrolysis of (VI) ($R = CH_3$). N-*Methyl-bis(trifluoromethyl)ketenimine (X) ($R = CH_3$)*

Compound (VI) (9.5 g) was heated for 8 h in a Carius tube at 200°. After venting off the carbon monoxide, there was distilled 6 g (78%) of *N*-methyl-bis-(trifluoromethyl)ketenimine, b.p. 44°/1.0 mmHg, n_D^{25} 1.3355. IR: 4.75 μ (C=C=N). ^{1}H NMR: 3.06 (singlet, 3H). ^{19}F NMR: -57.5 (singlet, 6F). Analysis: Found: C, 31.70; H, 1.73; F, 59.98; N, 7.30%. $C_5H_3F_6N$ requires C, 31.44; H, 1.58; F, 59.69; N, 7.33%.

Reaction of (VI) ($R = CH_3$) with the F^- ion. 1,3-Dimethyl-3,6-dihydro-6-oxo-α,5-bis(trifluoromethyl)-$\Delta^{2(1H),\alpha}$-pyrimidineacetyl fluoride, (XI) (nc)

A mixture consisting of (VI) ($R = CH_3$) (30 g, 0.13 mol), *ca.* 0.1 g of cesium fluoride, *ca.* 0.1 g of tetraethylammonium chloride and 10 ml of methylene chloride was refluxed overnight. The product was filtered off and washed with methylene chloride to give 16 g (74.5%) of yellow crystalline (XI). Recrystallization from toluene gave 9.6 g of product, m.p. 170–171°. IR: 5.65 μ, 5.75 μ, 5.80 μ, 5.94 μ (C=O and C=C). ^{1}H NMR: 3.58 (doublet, $J = 5.5$ Hz, 3H), 3.33 (singlet, 3H). ^{19}F NMR: $+13$ (quartet, $J = 14$ Hz, 1F), -53.4 (doublet, $J = 14$ Hz, 3F), -60.8 (doublet, $J = 27$ Hz, 3F), -77.8 (quartet, $J = 27$ Hz, to quartets, $J = 5.5$ Hz, 1F). Analysis: Found: C, 35.19; H, 1.99; F, 45.07; N, 7.94%. $C_{10}H_6F_8N_2O_2$ requires C, 35.53; H, 1.79; F, 44.97; N, 8.29%.

*Reaction of (I) with propylene. 4,6,6-Trifluoro-3,6-dihydro-2-methyl-5-(trifluoromethyl)-2*H*-pyran (XVI), 3,5-difluoro-2-(trifluoromethyl)-2-hexenoyl fluoride (XVII) (nc) and 3-fluoro-2-(trifluoromethyl)-2,4-hexadienoyl fluoride (XVIII) (nc)*

Products (XVI), (XVII) and (XVIII) above were formed at 100°. The amount of product (XVIII) (formed by loss of HF from (XVII)) increased when the reaction temperature was raised to 150°. We have previously reported the formation of (XVI) as a by-product from the reaction of propylene with bis(trifluoromethyl)-ketene[3].

A mixture consisting of 8 g (0.19 mol) of propylene and 21.2 g (0.12 mol) of (I) was distilled into an acid-washed Carius tube at liquid-nitrogen temperature, sealed and heated on a steam bath for 60 h. Subsequent distillation gave 5.2 g of product, b.p. 68–86°/50 mmHg, which by gas chromatographic analysis was shown to consist of *ca.* 48% of (XVI), 43% of (XVII) and 8% of (XVIII). Another fraction, (2.5 g), b.p. 86°/50 mmHg, was nearly pure (XVI).

In another reaction run at 150° for 8 h, a mixture of 10 g of propylene and

28 ml of (I) gave 13 g of product, b.p. 62–86°/45 mmHg. This material consisted of *ca.* 70% of (XVII) and 15% of (XVIII) along with minor amounts of (XVI) and other unknown products. In addition, 5 g of higher boiling mixture was distilled. Products (XVI), (XVII) and (XVIII) were all separated by preparative gas chromatography for characterization.

For (XVI): IR: 5.90 μ (C=C). ^{1}H NMR: 4.15 (quartet, $J = 7$ Hz, 1H), 2.3 (multiplet, 2H), 1.2 (doublet, $J = 7$ Hz, 3H). ^{19}F NMR: −84.5 (quartet, $J = 17$ Hz, 1F), −59.5 (multiplet including doublet, $J = 17$ Hz, 3F), −56.4 and −59.5 (AB doublet to multiplet, 1F), −71.0 and −74.1 (AB doublet to multiplet, 1F). Analysis: Found: C, 38.86; H, 2.95; F, 51.66%. $C_7H_6F_6O$ requires C, 38.21; H, 2.75; F, 51.82%.

For (XVII): IR: 5.46 μ (C=O), 6.05 μ (C=C). ^{1}H NMR: centered 4.68 (doublet, $J = 48$ Hz, 1H with different fine structures in each half of the doublet due to second-order effects of close chemical shift and coupling with the adjacent non-equivalent protons of the CH_2 group. At 100 MHz the fine structure was still different, but at 220 MHz it was the same), centered 2.8 (multiplet, 2H), 1.1 (doublet, $J = 24$ Hz, to doublets, $J = 6$ Hz, 3H). ^{19}F NMR: +40.1 (doublet, $J = 36$ Hz, to quartets, $J = 16$ Hz, 1F), −60.1 (doublet, $J = 28$ Hz, to doublets, $J = 16$ Hz, 3F), −57.5 (doublet, $J = 36$ Hz, to quartets, $J = 28$ Hz, 1F), −174 (doublet, $J = 48$ Hz, to quartets, $J = 24$ Hz, 1F). Analysis: Found: C, 38.71; H, 2.86; F, 51.75%. $C_7H_6F_6O$ requires C, 38.21; H, 2.75; F, 51.82%.

For (XVIII): IR: 5.49 μ (C=O), 6.05 μ and 6.22 μ (C=C). ^{1}H NMR: 6.6 (multiplet, 2H), 1.6 (doublet, $J = 6$ Hz, 3H). ^{19}F NMR: +39.6 (doublet, $J = 34$ Hz, to quartets, $J = 17$ Hz, 1F), −59.2 (doublet, $J = 29$ Hz, to doublets, $J = 17$ Hz, 3F), −84.6 (multiplet, 1F). Analysis: Found: C, 42.54; H, 2.65; F, 47.18%. $C_7H_5F_5O$ requires C, 42.00; H, 2.50; F, 47.50%.

Reaction of (I) with isobutylene. 3,3-Difluoro-5-methyl-2-(trifluoromethyl)-5-hexenoyl fluoride (XIX) (nc) and 3,5-difluoro-5-methyl-2-(trifluoromethyl)-2-hexenoyl fluoride (XX) (nc)

A mixture consisting of 12 g (0.21 mol) of isobutylene and 38 g (0.21 mol) of (I) was sealed in an acid-washed Carius tube and heated for 3 h on a steam bath. There was recovered 15 g of a low boiling material and the residue was distilled to give 9.5 g of a product b.p. 52–65°/40 mmHg. By gas chromatographic analysis this material was shown to consist of 80% of compound (XIX), 15% of compound (XX) together with a small amount of an unidentified third product. Distillation also yielded 23 g of a material boiling mostly at 40°/7 mmHg which was virtually pure compound (XX). The yield of (XIX) was therefore *ca.* 16% and that of (XX) *ca.* 51%.

For (XIX): IR: 5.37 μ (C=O), 6.05 μ (C=C). ^{1}H NMR: 4.79 (singlet, 1H), 4.63 (singlet, 1H), centered 3.78 (multiplet, 1H), 2.49 (triplet, $J = 18$ Hz, 2H), 1.49 (singlet, 3H). ^{19}F NMR: +50.5 (triplet, $J = 9$ Hz, to quartet, $J = 9$ Hz, to doublets, $J = 4$ Hz, 1F), −65.0 (multiplet, 3F), −91.0 and −95.6 (AB multiplet to multiplets, 1F), −96.9 and −101.5 (AB multiplets to multiplets, 1F). Analysis: Found: C, 41.38; H, 3.40; F, 48.77%. $C_8H_8F_6O$ requires C, 41.06; H, 3.45; F, 48.72%.

For (XX): IR: 5.47 μ (C=O), 6.05 μ (C=C). ^1H NMR: 1.16 (doublet, $J = 21$ Hz, 6H), 2.85 (doublet, $J = 27.6$ Hz, to doublets, $J = 19.2$ Hz, 2H). ^{19}F NMR: −54.7 (triplet, $J = 27.6$ Hz, to multiplet, 1F), −60.1 (doublet, $J = 28$ Hz, to doublets, $J = 15$ Hz, 3F), −137.0 (triplet, $J = 19.2$ Hz, to multiplet, 1F), +40.7 (doublet, $J = 34$ Hz, to quartets, $J = 15$ Hz, to doublets, $J = 2$ Hz, 1F). Analysis: Found: C, 41.42; H, 3.60; F, 48.75%. $C_8H_8F_6O$ requires C, 41.06; H, 3.45; F, 48.72%.

*Hydrolysis of (XX) to (XXI). 4-Fluoro-5,6-dihydro-6,6-dimethyl-3-(trifluoromethyl)-2*H*-pyran-2-one (XXI) (nc)*

Compound (XX) on standing for several weeks in glass vials appeared to have reacted with the glass and SiF_4 was evolved. The residue (20.5 g) was poured into water and warmed but did not appear to react. Distillation gave recovered (XX) (8.8 g) and compound (XXI) (5.8 g) which was a solid. Recrystallization from carbon tetrachloride gave 2.7 g of (XXI), m.p. 49–50°. The recovered (XX) was dissolved in 10 ml of conc. sulfuric acid and poured on to 50 g of ice to give (XXI) (6 g) which recrystallized from CCl_4, m.p. 45–47°. IR: 5.81 μ (C=O), 5.92 μ (C=C). ^1H NMR: 1.56 (doublet, $J = 0.6$ Hz, 6H), 2.87 (doublet, $J = 5$ Hz, to quartets, $J = 2$ Hz, 2H). ^{19}F NMR: −59.4 (doublet, $J = 26$ Hz, to multiplet, 3F), −68.3 (quartet, $J = 26$ Hz, to multiplet, 1F). Analysis: Found: C, 45.69; H, 3.88; F, 35.85%. $C_8H_8F_4O_2$ requires C, 45.32; H, 3.80; F, 35.85%.

*Hydrolysis of (XXI) to (XXII). 4-Hydroxy-5,6-dihydro-6,6-dimethyl-3-(trifluoromethyl)-2*H*-pyran-2-one (XXII) (nc)*

Compound (XXI) after standing about 3 months in a glass vial was largely converted to compound (XXII), a strong acid (vinyl analog of COOH). Unlike (XXI), this material was not very soluble in carbon tetrachloride but could be recrystallized from nitromethane and acetonitrile. Thus, a 6 g sample of (XXI) after standing for 3 months yielded 0.9 g of (XXII), which after recrystallization from nitromethane and acetonitrile exhibited a melting point of 145–146° (dec.). IR: 6.15 μ [5.88 μ (sh), 6.02 μ (sh)] (C=O and C=C). ^1H NMR (20% in deuteroacetone): 0.98 (singlet, 6H), 2.43 (quartet, $J = 1.7$ Hz, 2H). ^{19}F NMR: −58.5 (triplet, $J = 1.7$ Hz, 3F). Analysis: Found: C, 46.10; H, 4.16; F, 25.95%. $C_8H_9F_3O_3$ requires C, 45.75; H, 4.32; F, 27.14%.

*Reaction of (I) with norbornene. 2,2,4-Trifluoro-4*a*,5,6,7,8,8*a*-hexahydro-3-(trifluoromethyl)-5,8-methano-2*H*-1-benzopyran (XXIII) (nc)*

A mixture of 9.4 g (0.1 mol) of norbornene and 29 g (0.16 mol) of (I) was sealed in a Carius tube and heated overnight on a steam bath. The resulting product distilled to yield 18.7 g (68%) of (XXIII), b.p. 62°/1 mmHg, n_D^{25} 1.4175. IR: 5.86 μ (C=C). ^{1}H NMR: 4.25 (doublet, $J = 7$ Hz, 1H), 2.45 (multiplet, 3H), centered 1.4 (multiplet, 6H). ^{19}F NMR: −88.1 (multiplet, 1F), −56.2 and −59.3 (AB multiplet to multiplets, 1F), −70.7 and −73.8 (AB multiplet to multiplets, 1F), −59.3 (multiplet, 3F). Analysis: Found: C, 48.99; H, 3.77; F, 41.45%. $C_{11}H_{10}F_6O$ requires C, 48.57; H, 3.20; F, 41.91%.

*Hydrolysis of (XXIII) to (XXIV). 4-Fluoro-4*a*,5,6,7,8,8*a*-hexahydro-3-(trifluoromethyl)-5,8-methano-2*H*-1-benzopyran-2-one (XXIV) (nc)*

Compound (XXIII) did not hydrolyze in water when warmed on a steam bath. A sample (13 g) was dissolved in 10 ml of conc. sulfuric acid at room temperature and poured on to ice. The resulting crystals of (XXIV) were filtered and recrystallized from hexane using Darco, 5.5 g (46%), m.p. 79–81°. IR: 5.84 μ (C=O and C=C). ^{1}H NMR: 4.3 (doublet, $J = 8$ Hz, 1H), 2.6 (multiplet, 1H), 2.21 (multiplet, 1H), 2.03 (multiplet, 1H), centered 1.0 (multiplet, 6H). ^{19}F NMR: −59.6 (doublet, $J = 29$ Hz, to doublet, $J = 28$ Hz, 3F), −73.3 (quartet, $J = 29$ Hz, to doublets, $J = 8$ Hz, to doublets, $J = 4$ Hz, 1F). Analysis: Found: C, 53.18; H, 4.07; F, 30.34%. $C_{11}H_{10}F_4O_2$ requires C, 52.84; H, 4.02; F, 30.40%.

*Reaction of (I) with vinyl acetate. 4,4,6-Trifluoro-3,4-dihydro-5-(trifluoromethyl)-2*H*-pyran-2-ol acetate (XXV) (nc)*

A mixture consisting of 17.2 g (0.2 mol) of vinyl acetate, 23 ml (0.2 mol) of (I) and 0.1 g of phenothiazine was sealed in a Carius tube and heated overnight on a steam bath. There was obtained 33 g (62%) of (XXV), b.p. 56°/0.2 mmHg, n_D^{25} 1.3834. IR: 5.62 μ (C=O), 5.87 μ (C=C). ^{1}H NMR: 6.42 (broad singlet, 1H), 2.45 (triplet, $J = 13$ Hz, to doublets, $J = 4$ Hz, 2H), 1.88 (singlet, 3H). ^{19}F NMR: −89.9 (multiplet, 2F), −57.7 (doublet, $J = 17$ Hz, to triplets, $J = 7$ Hz, 3F), −73.9 (quartet, $J = 17$ Hz, to triplets, $J = 16$ Hz, 1F). Analysis: Found: C, 36.65; H, 2.33; F, 42.96%. $C_8H_6F_6O_2$ requires C, 36.39; H, 2.29; F, 43.18%.

*Hydrolysis of (XXV) to (XXVII). 4-Hydroxy-3-(trifluoromethyl)-2*H*-pyran-2-one (XXVII) (nc)*

Part of product (XXV) (15 g) was dissolved by slow addition to 15 ml of conc. sulfuric acid at a temperature of 30°. After stirring for about 15 min, the product was poured on to ice when a solid separated. After two recrystallizations from nitromethane, there was recovered 1.8 g of (XXVII), m.p. 165° (dec.). IR: 6.12 μ (C=O), 6.30 μ and 6.44 μ (C=C). ^{1}H NMR: 10.1 (broad, 1H), 7.26 (doublet, $J = 6$ Hz, 1H), 5.91 (doublet, $J = 6$ Hz, 1H). ^{19}F NMR: −59.2 (singlet, 3F). Analysis: Found: C, 39.99; H, 1.78; F, 31.42%. $C_6H_3F_3O_3$ requires C, 40.03; H, 1.68; F, 31.67%.

*Hydrolysis of (XXV) to (XXVI). 4-Fluoro-3-(trifluoromethyl)-2*H*-pyran-2-one (XXVI) (nc)*

Product (XXV) (18.6 g) from another preparation was treated similarly with 15 ml of conc. sulfuric acid, the resulting solution kept cold and finally poured on to ice. In this experiment no crystals were obtained but rather an oil which was distilled to give 3 g of (XXVI), b.p. 75°/1.5 mmHg. IR: 5.72 μ (C=O), 6.05 μ and 6.32 μ (C=C). ^{1}H NMR: 7.55 (doublet, $J = 8$ Hz, to doublets, $J = 6$ Hz, 1H), 6.18 (doublet, $J = 8.6$ Hz, to doublets, $J = 6$ Hz, 1H). ^{19}F NMR: −61.5 (doublet, $J = 25$ Hz, 3F), −83.7 (quartet, $J = 25$ Hz, to triplets, $J = 8$ Hz, 1F). Analysis: Found: C, 39.14; H, 1.22; F, 42.22%. $C_6H_2F_4O_2$ requires C, 39.59; H, 1.11; F, 41.76%.

*Reaction of (I) with benzonitrile. 4,6,6-Trifluoro-2-phenyl-5-(trifluoromethyl)-6*H*-1,3-oxazine (XXVIII) (nc)*

A mixture consisting of 20 g (0.2 mol) of benzonitrile and 22.5 ml (0.2 mol) of (I) sealed in a Carius tube was heated for 60 h on a steam bath when 26 g (46%) of (XXVIII) were isolated, b.p. 63°/0.75 mmHg, n_D^{25} 1.4903. This product was also formed in 35% conversion from benzonitrile and bis(trifluoromethyl)ketene at 200° (no reaction at 100°). IR: 6.00 μ, 6.22 μ, 6.35 μ, 6.69 μ (C=C and C=N). ^{1}H NMR: 7.3 (multiplet, 5H). ^{19}F NMR: −58.3 (doublet, $J = 16$ Hz, to triplets, $J = 7$ Hz, 3F), −46.2 (doublet, $J = 14$ Hz, to quartets, $J = 7$ Hz, 2F), −74.0 (quartet, $J = 16$ Hz, to triplet, $J = 14$ Hz, 1F). Analysis: Found: C, 47.45; H, 1.87; F, 40.69%. $C_{11}H_5F_6NO$ requires C, 47.01; H, 1.80; F, 40.57%.

*Hydrolysis of (XXVIII) to (XXIX). 4-Fluoro-2-phenyl-5-(trifluoromethyl-6*H*-1,3-oxazin-6-one (XXIX) (nc)*

Compound (XXVIII) (5 g) was added slowly to 50 ml of conc. sulfuric acid. The resulting solution was poured on to ice and the solid (XXIX) obtained recrystallized from carbon tetrachloride as long white needles, m.p. 138–140° (sealed tube). IR: 5.65 μ (C=O). ^{1}H NMR: 7.5 (multiplet, 5H). ^{19}F NMR: −60.6 (doublet, $J = 22$ Hz, 3F), −58.3 (quartet, $J = 22$ Hz, 1F). Analysis: Found: C, 50.79; H, 2.25; F, 29.47; N, 5.56%. $C_{11}H_5F_4NO_2$ requires C, 51.01; H, 1.95; F, 29.34; N, 5.41%.

Hydrolysis of (XXVIII) to (XXX) and (XXXI). N-*(3,3,3-Trifluoropropionyl)-benzamide (XXX) and* N-*benzoyl-3,3,3-trifluoropropionimidic acid (XXXI)*

A 10 g sample of (XXVIII) was refluxed overnight in 28 ml of water. On cooling, a mixture of oil and crystals separated, and the latter were filtered off and recrystallized twice from carbon tetrachloride (0.8 g), m.p. mostly 77–78° with a little melting higher. This material was characterized as being an impure mixture of the tautomers (XXX) and (XXXI). IR: Multiple bands in the 3 μ region (–OH and NH), 5.82 μ, 5.92 μ, 6.03 μ, 6.10 μ (C=O, C=C, C=N). ^{1}H NMR

(20% in deuteroacetone): centered 7.3 (multiplet, 5H), 10 (broad exchangeable, 1H), 3.54 (quartet, $J = 10.0$ Hz), 2.92 (quartet, $J = 10.5$ Hz). The two quartets were in the approximate ratio of 1:3. ^{19}F NMR: −64.0 (triplet, $J = 10.0$ Hz), −64.8 (triplet, $J = 10.5$ Hz). The two triplets were also in the approximate ratio of 1:3. Analysis: Found: C, 51.94; H, 4.68; F, 20.08; N, 6.87%. $C_{10}H_8F_3NO_2$ requires C, 51.99; H, 3.49; F, 24.68; N, 6.06%.

*Reaction of (I) with acetonitrile. 4,6,6-Trifluoro-2-methyl-5-(trifluoromethyl)-6*H*-1,3-oxazine (XXXII) (nc)*

A mixture consisting of 22.5 ml (0.2 mol) of (I) and 20 ml of acetonitrile contained in each of two Carius tubes was heated at 125° for 8 h. On work-up there was recovered 20 g of (I) and 26.2 g (41.4%, based on the amount of (I) consumed) of (XXXII), b.p. 48°/30 mmHg. IR: 5.94 μ, 6.07 μ (C=C and C=N). ^{1}H NMR: 2.13 (broad singlet, 3H). ^{19}F NMR: −58.7 (doublet, $J = 17$ Hz, to triplets, $J = 7.5$ Hz, 3F), −39.2 (doublet, $J = 14$ Hz, to quartets, $J = 7.5$ Hz, 2F), −75.2 (quartets, $J = 17$ Hz, to triplets, $J = 14$ Hz, 1F). Analysis: Found: C, 32.94; H, 1.69; F, 52.27; N, 6.55%. $C_6H_3F_6NO$ requires C, 32.90; H, 1.38; F, 52.05; N, 6.40%.

Hydrolysis of (XXXII) to (XXXIII). N-*Acetyl-3,3,3-trifluoropropionamide (XXXIII)*

Compound (XXXII) was hydrolyzed even in moist air giving eventually (XXXIII), m.p. 133–134° (*ex* chloroform). Intermediate impure hydrolysis products melting with loss of gas between 80° and 130° were also isolated from the material left after standing in moist air. Hydrolysis to (XXXIII) was rapid in warm water. IR: 3.07 μ, 3.14 μ (N–H), 5.73 μ (C=O), 6.45 μ and 6.58 μ (secondary amide). ^{1}H NMR (20% in deuteroacetone): 1.67 (singlet, 3H), 3.17 (quartet, $J = 10.5$ Hz, 2H). ^{19}F NMR: −64.0 (triplet, $J = 10.5$ Hz, 3F). Analysis: Found: C, 35.64; H, 3.89; F, 33.55; N, 8.08%. $C_5H_6NO_2$ requires C, 35.53; H, 3.58; F, 33.73; N, 8.29%.

*Reaction of (I) with dimethylcyanamide. 2-(Dimethylamino)-4,6,6-trifluoro-5-(trifluoromethyl)-6*H*-1,3-oxazine (XXXIV) (nc)*

A solution consisting of 14 g (0.2 mol) of dimethylcyanamide in 50 ml of ether was stirred and 22.5 ml (0.2 mol) of (I) added dropwise with stirring. Ether was allowed to reflux during the addition. Distillation of the product gave 43.5 g (87%) of (XXXIV), b.p. 52°/0.1 mmHg, n_D^{25} 1.4230. IR: 6.11 μ, 6.04 μ (sh) (C=C, C=N). ^{1}H NMR: 2.9 (singlet, 6H). ^{19}F NMR: −56.0 (doublet, $J = 16$ Hz, to triplet, $J = 8$ Hz, 3F), −43.2 (doublet, $J = 15$ Hz, to quartets, $J = 8$ Hz, 2F), −71.2 (quartet, $J = 16$ Hz, to triplet, $J = 15$ Hz, 1F). Analysis: Found: C, 33.88; H, 2.59; F, 46.08; N, 11.02%. $C_2H_6N_2F_6O$ requires C, 33.90; H, 2.44; F, 45.97; N, 11.30%.

*Hydrolysis of (XXXIV) to (XXXV). 2-(Dimethylamino)-4-fluoro-5-(trifluoromethyl)-6*H*-1,3-oxazin-6-one (XXXV) (nc)*

About 0.5 g of the above material was warmed in water in a test tube and allowed to stand overnight. Crystals of (XXXV) formed and were filtered and recrystallized from carbon tetrachloride, m.p. 77–78°. A larger sample of these crystals was obtained from a sample of (XXXIV) which had been standing for about two years in a glass vial. After separating from ether-insoluble material, the product was recrystallized from carbon tetrachloride, m.p. 76–78°. IR: 5.62 μ (C=O), 6.08 μ, 6.30 μ, 6.65 μ (C=C, C=N). ^{1}H NMR (20% in $CDCl_3$): 3.22 (singlet, 6H). ^{19}F NMR: −56.9 (doublet, $J = 21$ Hz, 3F), −51.6 (quartet, $J = 21$ Hz, 1F). Analysis: Found: C, 37.24; H, 3.14; F, 32.78; N, 12.14%. $C_7H_6F_4N_2O_2$ requires C, 37.20; H, 2.68; F, 33.63; N, 12.40%.

Hydrolysis of (XXXIV) to (XXXVI). N*-(Dimethylcarbamoyl)-3,3,3-trifluoropropionamide (XXXVI)*

A sample of (XXXIV) was dissolved in an equal volume of cold conc. sulfuric acid and an equal weight of ice added to produce crystals of (XXXVI) which were recrystallized from acetonitrile, m.p. 122–124°. IR: 3.10 μ (NH), 5.83 μ, 6.05 μ (C=O), 6.52 μ (secondary amide). ^{1}H NMR (20% in deuteroacetone): 2.5 (singlet, 6H), 3.27 (quartet, $J = 11$ Hz, 2H). ^{19}F NMR: −63.6 (triplet, $J = 11$ Hz, 3F). Analysis: Found: C, 36.09; H, 4.35; F, 28.05; N, 13.95%. $C_6H_9F_3N_2O_2$ requires C, 36.39; H, 4.58; F, 28.79; N, 14.15%.

Reaction of (I) with NaCN in HCN. 3-Cyano-3-fluoro-2-(trifluoromethyl)acryloyl fluoride (II)

A mixture consisting of 35.6 g of (I), 20 ml of hydrogen cyanide and 0.1 g of sodium cyanide was stirred at room temperature for 60 h. After recovery of some starting material, there was distilled about 10 g of a higher boiling material. From a 4 g sample, b.p. *ca.* 80°, the above compound (II), n_D^{25} 1.3552, was isolated by preparative gas chromatography. IR: 4.45 μ ($C{\equiv}N$), 5.45 μ (C=O), 6.04 μ (C=C). ^{19}F NMR: −83.0 (doublet, $J = 28.5$ Hz, to doublets, $J = 27$ Hz, 1F), +36.6 (doublet, $J = 27$ Hz, to quartets, $J = 13$ Hz, 1F), −61.8 (doublet, $J = 28.5$ Hz, to doublet, $J = 13$ Hz, 3F). Analysis: Found: C, 32.71; F, 50.32; N, 7.44%. C_5F_5NO requires C, 32.46; F, 51.35; N, 7.57%.

*Reaction of (I) with butylethylketene. 3-Butyl-3-ethyl-4,6,6-trifluoro-3,6-dihydro-5-(trifluoromethyl)-2*H*-pyran-2-one (XXXVII)*

A 20% hexane solution of butylethylketene (65 g) (*ca.* 0.1 mol of the ketene) was frozen at liquid-nitrogen temperature in a Carius tube and 12 ml (0.1 mol) of (I) condensed with it and the tube sealed. The contents were warmed to room temperature and mixed well. After standing overnight at room temperature, the yellow color of the ketene had disappeared and the solution was colorless. After removal of solvent, there was distilled 24.5 g (80%) of (XXXVII), b.p. 101°/20 mmHg, n_D^{25} 1.3975. IR: 5.46 μ (C=O), 5.79 μ (C=C). ^{1}H NMR: 2–0.7 (multiplet, 18H). ^{19}F NMR: −58.4 (doublet, $J = 22$ Hz, to triplets, $J = 7.5$ Hz, 3F), −99.1 (doublet, $J = 15$ Hz, to quartets, $J = 7.5$ Hz, 2F), −78.1 (quartet, $J = 22$ Hz, to triplet, $J = 15$ Hz, 1F). Analysis: Found: C, 47.48; H, 4.61; F, 37.45%. $C_{12}H_{14}F_6O_2$ requires C, 47.41; H, 4.64; F, 37.50.

*Reaction of (I) with dimethylketene. 3,3-Dimethyl-4,6,6-trifluoro-3,6-dihydro-5-(trifluoromethyl)-2*H*-pyran-2-one (XXXVIII) (nc), 4-fluoro-3,3-dimethyl-5-(trifluoromethyl)-2*H*-pyran-2,6(3*H*)-dione (XXXIX) (nc) and 3-fluoro-5,5-dimethyl-2-(trifluoromethyl)glutaconyl fluoride (XL) (nc)*

Dimethylketene was prepared by the pyrolysis of isobutyric acid anhydride at *ca.* 600° (1 mmHg pressure) in a quartz tube packed with quartz chips. The product gases were first passed through a −30° trap and then a liquid-nitrogen trap which collected most of the dimethylketene. In the liquid-nitrogen trap before pyrolysis was placed 22 ml (0.2 mol) of (I) and 25 ml of hexane. After pyrolyzing 50 ml of isobutyric acid anhydride, the liquid-nitrogen-cooled trap, which now contained both (I) and dimethylketene, was allowed to warm in a Dry Ice–acetone bath and react. About 10 g was distilled, boiling mostly at 75°/50 mmHg. This product was separated by gas chromatography into one main cut ((XL)) and one minor cut ((XXXVIII)). There was also distilled 14 g of (XXXIX), b.p. 85°/0.3 mmHg, which solidified and could be recrystallized from carbon tetrachloride, m.p. 76–78°. The initial product of this reaction is probably the rearranged Diels–Alder adduct (XXXVIII), which was isolated in very small amounts and characterized by IR and NMR spectroscopy only, which compared favorably with the above product from butylethylketene. Product (XL), the ring-opened isomer of (XXXVIII), was isolated in larger amounts, but the major product isolated was (XXXIX), the hydrolysis product of (XXXVIII).

For (XXXVIII): IR: 5.60 μ (C=O), 5.85 μ (C=C). ^{1}H NMR: 1.36 (singlet, 6H). ^{19}F NMR: −98.1 (quartet, $J = 18$ Hz, 1F), centered −59.3 (multiplet, 5F).

For (XXXIX): IR: 5.54 μ and 5.69 μ (C=O), 5.94 μ (C=C). ^{1}H NMR: 1.25 (doublet, $J = 1.1$ Hz, 6H). ^{19}F NMR: −61.1 (doublet, $J = 27$ Hz, 3F), −85.3 (quartet, $J = 27$ Hz, to septets, $J = 1.1$ Hz, 1F). Analysis: Found: C, 42.64; H, 2.71; F, 33.65%. $C_8H_6F_4O_3$ requires C, 42.51; H, 2.68; F, 33.63%.

For (XL): IR: 5.45 μ and 5.51 μ (C=O), 6.15 μ (C=C). ^{1}H NMR: 1.32 (doublet, $J = 3$ Hz, 6H). ^{19}F NMR: +25.2 (doublet, $J = 6$ Hz, 1F), +41.4 (doublet, $J = 38$ Hz, to quartets, $J = 17$ Hz, 1F), −60.1 (doublet, $J = 29$ Hz, to doublets, $J = 17$ Hz, 3F), −67.1 (doublet, $J = 38$ Hz, to quartets, $J = 29$ Hz, to doublets, $J = 6$ Hz, to septets, $J = 3$ Hz, 1F). Analysis: Found: C, 39.72; H, 3.11; F, 42.40%. $C_8H_6F_6O_2$ requires C, 38.74; H, 2.44; F, 45.97%.

*Reaction of (I) with methylketene. 4,6-Difluoro-3-methyl-5-(trifluoromethyl)-2*H*-pyran-2-one (XLI) (nc) and 4,6-difluoro-5-methyl-3-(trifluoromethyl)-2*H*-pyran-2-one (XLII) (nc)*

Methylketene, prepared from 50 g of propionic anhydride as described above for dimethylketene, was condensed with liquid nitrogen in a trap containing 22 ml (0.2 mol) of (I) and 25 ml of hexane. Reaction occurred on warming the mixture in a Dry Ice–acetone bath. Distillation gave 11 g of product boiling mainly at *ca.* 80°/50 mmHg with a refractive index varying from 1.349 to 1.407. Separation of the major cut by gas chromatography gave a material, n_D^{25} 1.4148, characterized as a mixture of (XLI) (71%) and (XLII) (29%) above. Apparently, dehydrofluorination occurred during chromatography. IR: 5.56 μ (C=O), 5.87 μ and 6.17 μ (C=C). ^{1}H NMR: 1.68 (doublet, J = 3.2 Hz, to doublets, J = 1.2 Hz, 3H). ^{19}F NMR for (XLI): −59.4 (doublet, J = 24 Hz, to doublets, J = 15 Hz, 3F), −68.5 (quartet, J = 24 Hz, to doublets, J = 14 Hz, 1F), −99.5 (quartet, J = 15 Hz, to doublets, J = 14 Hz, 1F). ^{19}F NMR for (XLII): −61.4 (doublet, J = 25 Hz, 3F), −69.5 (doublet, J = 27 Hz, 1F), −82.3 (doublet, J = 27 Hz, to quartets, J = 25 Hz, 1F). Analysis: Found: C, 39.41; H, 1.61; F, 42.71%. $C_7H_3F_5O_2$ requires C, 39.29; H, 1.41; F, 44.39%.

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