Anal. Calcd for $C_{13}H_{10}F_2O_2$: C, 66.10; H, 4.27. Found: C, 66.31; H, 4.23.

3,4-Difluoro-6-(*p*-isopropylphenyl)-2*H*-pyran-2-one (6l) and 1-Phenyl-3,3,4-trifluoro-1-cyclobutene-4-carboxylic Acid (8, X = *p*-(*i*-C_3H_7)C_6H_4). (*p*-Isopropylphenyl)acetylene (26.43 g, 0.18 mol) and 23.6 g (0.18 mol) of 1 were heated to 100° C for 24 h. Distillation of the resultant black liquid produced 30 g of pale yellow crystals, bp 84 °C (0.5 mm). These crystals were stirred for 10 h with 200 mL of saturated aqueous sodium bicarbonate solution, filtered, washed with water, and dried. The crystals weighed 26 g (58%). Acidification of the bicarbonate filtrate with dilute hydrochloric acid and extraction with carbon tetrachloride yielded crystalline acid. Both samples were recrystallized from cyclohexane: α-pyrone, 12 g (27%), mp 86–87.5 °C; cyclobutene acid, 3.55 g (7%), mp 121–124 °C.

Anal. Calcd for $C_{14}H_{12}F_2O_2$ (6l): C, 67.19; H, 4.83. Found: C, 67.36, 67.30; H, 4.72, 4.58. Calcd for $C_{14}H_{13}F_3O_2$ [8 (X = *p*-(*i*-C_3H_7)C_6H_4)]: C, 62.22; H, 4.85. Found: C, 62.60, 62.50; H, 4.70, 4.73.

2-[1-(Acetyloxy)cyclohexyl]-1,4,4-trifluoro-2-cyclobutene-1-carboxylic Acid (12). A mixture of 27.6 g (0.166 mol) of 1-acetoxy-1-ethynylcyclohexane and 18 mL (0.2 mol) of 1 were heated to 140 °C for 4 h. The yellow distillate [bp 114 °C (0.7 mm)] was stirred with a saturated aqueous sodium bicarbonate solution. Extraction of the alkaline solution with ether failed to yield the expected pyrone. The aqueous solution was acidified with hydrochloric acid and extracted with ether. Evaporation of the dried, neutralized ether layer yielded a brown oil which crystallized in 4 days. Recrystallization from nitromethane yielded 3.38 g (7%) of the cyclobutene 12, mp 152–153 °C.

Anal. Calcd for $C_{13}H_{15}F_3O_4$: C, 53.42; H, 5.18; F, 19.50. Found: C, 53.95, 53.56; H, 5.34, 5.18; F, 19.60.

2-Phenyl-1,4,4-trifluoro-3-chloro-2-cyclobutene-1-carboxylic Acid (11). A mixture of 13.6 g (0.1 mol) β-chlorophenylacetylene and 15.3 g (0.12 mol) of 1 in a sealed tube was heated on a steam bath for 4 h. After removal of 4.1 g of a low boiler, the black liquid was distilled, yielding 7.7 g of product at 59 °C (0.50 mm). This liquid was stirred into 50 mL of saturated sodium bicarbonate. The small amount of insoluble precipitate was filtered and discarded. The filtrate was acidified and continuously extracted with ether for 72 h. The semisolid obtained upon the evaporation of the ether was sublimed and recrystallized from cyclohexane, yielding 3.32 g of 11, mp 92–93 °C.

Anal. Calcd for $C_{11}H_6O_2F_3Cl$: C, 50.31; H, 2.31; F, 21.70; Cl, 13.50. Found: C, 50.24; H, 2.47; F, 21.71; Cl, 13.29.

4-[(Phenylmethyl)amino]-3-fluoro-6-phenyl-2*H*-pyran-2-one (13a). Benzylamine (2.62 g, 0.024 mol) was added dropwise to a solution of 2 g (0.01 mol) of **6b** in methanol. After the mixture was stirred at room temperature for 48 h, the solvent was evaporated. The resultant white solid was washed with dilute hydrochloric acid and distilled water and was recrystallized from chloroform–hexane: yield 2.3 g (70%); mp 137–140 °C; ^1H NMR ($CDCl_3$, Me_4Si) 4.55 (d, 2, J = 6 Hz), 5.72 (br s, 1), 6.47 (d, 1, J = 5.0 Hz), 7.21–7.74 ppm (m, 10); ^{19}F NMR ($CDCl_3$/CCl_3F) −177 ppm (t, 1, J = 4.0 Hz); ^{19}F NMR ($CDCl_3$/CCl_3F, D_2O, pyridine) (d, 1, J = 5.0 Hz).

Anal. Calcd for $C_{18}H_{14}NO_2F$: C, 73.21; H, 4.78; N, 4.74. Found: C, 72.72, 72.37; H, 4.52, 4.70; N, 4.65, 4.64.

4-(Phenylamino)-3-fluoro-6-phenyl-2*H*-pyran-2-one (13b). A mixture of 1.0 g (0.005 mol) of **6b** and 1.0 g (0.015 mol) of aniline in methanol was stirred at room temperature for 24 h. The solid remaining after evaporation of the solvent was washed with dilute hydrochloric acid and then distilled water. Recrystallization from dimethyl sulfoxide–water yielded 1.0 g (70%) of pale yellow brightly fluorescing solid: mp 224–229 °C; ^1H NMR [$(CD_3)_2SO$, Me_4Si] 6.7 (d, 1, J = 5.0 Hz), 7.40 (m, 10), 9.40 ppm (br s, <1 H due to exchange); ^{19}F NMR [$(CD_3)_2SO$/CCl_3F] −168 ppm (t, 1; with D_2O, d, J = 5.50 Hz).

Anal. Calcd for $C_{17}H_{20}FNO_2$: C, 72.59; H, 4.30; N, 4.98. Found: C, 71.71; H, 4.37; N, 4.91.

4-(3-Chlorophenoxy)-3-fluoro-6-phenyl-2*H*-pyran-2-one (13c). A solution of 2.08 g (0.01 mol) of **6b**, 1.28 g (0.01 mol) of *m*-chlorophenol, and 2.76 g (0.02 m) of potassium carbonate was refluxed in acetone for 24 h. Evaporation of the cooled filtered solution and recrystallization of the resultant solid from carbon tetrachloride yielded 2.2 g (70%) of white crystals, mp 115.5–116.5 °C.

Anal. Calcd for $C_{17}H_{10}ClFO_3$: C, 64.47; H, 3.19. Found: C, 63.76; H, 3.23.

Registry No. 1, 667-49-2; 2, 684-36-6; 4c, 75599-84-7; 4d, 75599-85-8; 5a, 75599-86-9; 6a, 75599-87-0; 6b, 75599-88-1; 6c, 41255-02-1; 6d, 75599-89-2; 6e, 75599-90-5; 6f, 41255-03-2; 6g, 41392-38-5; 6h, 41255-04-3; 6i, 41255-06-5; 6j, 41255-05-4; 6k, 75599-91-6; 6l, 75599-92-7; 7, 25631-78-1; 8 (X = C_6H_5), 75599-93-8; 8 (X = C_6H_5)$_2$ acid fluoride, 54376-62-4; 8 (X = *p*-ClC_6H_4), 75599-94-9; 8 (X = *p*-(*i*-C_3H_7)C_6H_4), 75599-95-0; 9, 75599-96-1; 10, 75599-97-2; 11, 75599-98-3; 12, 75599-99-4; 13a, 75600-00-9; 13b, 75600-01-0; 13c, 75600-02-1; acetone, 67-64-1; acetophenone, 98-86-2; phenylacetylene, 536-74-3; dimethyl acetylenedicarboxylate, 762-42-5; $(CF_3)_2CHCOF$, 382-22-9; (*p*-fluorophenyl)acetylene, 766-98-3; (*p*-chlorophenyl)acetylene, 873-73-4; (*p*-bromophenyl)acetylene, 766-96-1; *p*-tolylacetylene, 766-97-2; *p*-anisylacetylene, 768-60-5; (2,4-dimethylphenyl)acetylene, 16017-30-4; (*p*-ethylphenyl)acetylene, 40307-11-7; (*p*-isopropylphenyl)acetylene, 23152-99-0; 1-acetoxy-1-ethynylcyclohexane, 3742-81-2; β-chlorophenylacetylene, 1483-82-5; benzylamine, 100-46-9; aniline, 62-53-3; *m*-chlorophenol, 108-43-0.

Fluoroketenes. 10.[1] Synthesis and Chemistry of a Perfluoroacylketene and a Related Perfluorovinyl Ketone

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The synthesis and chemistry of a perfluoroacylketene (12) and a related perfluorovinyl ketone (5) are described. Both are prepared in good yields from a dimer of hexafluoropropene (2). They are thermally stable but very reactive. No acylketene has previously been isolated. Both compounds give the same hydrolysis product and the same product from dimethylformamide. The vinyl ketone, like previously reported[3] perfluoroacryloyl fluorides, is subject to nucleophilic attack at the terminal unsaturated carbon and reacts as a diene in Diels–Alder additions to C=C, C≡C, C=N, C≡N, and C=O unsaturation. The acylketene also reacts as a diene to give adducts that are hydrolysis products of the vinyl ketone adducts.

Perfluoromethylpropionylketene (12), the first acylketene to be isolated,[4] and the vinyl ketone perfluoro-2-methyl-1-penten-3-one (5) have been prepared in quantity from a readily available dimer of hexafluoropropene[5] (2)

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and their chemistry studied. Although vinyl ketones are known to act as dienes in Diels–Alder reactions,[6] **5** is exceptionally reactive. Acylketenes have not been isolated previously, but some have been trapped as Diels–Alder adducts,[7] indicating that even nonfluorinated acylketenes are potent dienes in this reaction. The electron-withdrawing fluorine atoms activate **5** and **12** toward electron-rich dienophiles and other nucleophiles.

The variety of new products isolated in this work have been characterized by NMR, infrared, and elemental analyses.

Results and Discussion

Synthesis of the Vinyl Ketone 5. Hexafluoropropene (HFP) catalyzed by cesium fluoride in acetonitrile at 0 °C gives the kinetic dimer **1**. Heating the resulting mixture in a sealed vessel to 150 °C converts this dimer to the thermodynamic dimer **2**[8] (eq 1)

$$\underset{\mathbf{1}}{(F_3C)_2CFCF{=}CFCF_3} \xrightarrow{F^-} \underset{\mathbf{2}}{(F_3C)_2C{=}CFC_2F_5} \quad (1)$$

Methanol was added to **2** with a catalytic amount of potassium hydroxide to give **3**[9] in >80% yield (eq 2), and **3** was reacted with sulfur trioxide to give the ketone **4**[10] in 83% yield (eq 3). Dehydrofluorination of **4** in the vapor phase at 450 °C over sodium fluoride pellets gave the vinyl ketone **5** in 76% yield (eq 4).

$$\mathbf{2} + CH_3OH \rightarrow \underset{\mathbf{3}}{F_3CCH(CF_3)CF(OCH_3)C_2F_5} \quad (2)$$

$$\mathbf{3} + SO_3 \rightarrow \underset{\mathbf{4}}{F_3CCH(CF_3)COC_2F_5} + CH_3OSO_2F \quad (3)$$

$$\mathbf{4} \xrightarrow[NaF]{450\ °C} \underset{\mathbf{5}}{F_2C{=}C(CF_3)COC_2F_5} + HF \quad (4)$$

A minor product was perfluoro-α-methyl-β-ethylacryloyl fluoride (**8**). Apparently, a small amount of the terminally unsaturated isomer of the HFP dimer (**2a**) with methanol gave the vinyl ether **6** which yielded the acid fluoride **7** with sulfur trioxide (aqueous workup) and finally the acryloyl fluoride **8** (eq 5–7). The *E* and *Z* isomers of **8**

$$\underset{\mathbf{2a}}{CF_2{=}C(CF_3)C_3F_7} + CH_3OH \rightarrow \underset{\mathbf{6}}{CH_3OCF{=}C(CF_3)C_3F_7} + HF \quad (5)$$

$$\mathbf{6} \xrightarrow[H_2O]{SO_3} \underset{\mathbf{7}}{FOCCH(CF_3)C_3F_7} \quad (6)$$

$$\mathbf{7} \xrightarrow[450\ °C]{NaF} \underset{\mathbf{8}}{FOCC(CF_3){=}CFC_2F_5} \quad (7)$$

were separable and identified by ^{19}F NMR. The quartet splitting of the CF_2 group by CF_3 was 3.4 Hz when trans (**8a**) and 17.2 Hz when cis (**8b**).

Synthesis of the Acylketene 12. When HFP dimer **2** was reacted in methanol with 2 equiv of sodium methoxide, the product was a mixture of isomers, largely **9** (*E* and *Z*), especially after being refluxed with 15% aqueous potassium hydroxide and distilled[9] or after the product was stirred in bis[2-(2-methoxyethoxy)ethyl] ether (tetraglyme) containing cesium fluoride. However, when this mixture was distilled at reduced pressure from cesium fluoride–tetraglyme, partial equilibration to **10** (*E* and *Z*) occurred (eq 8). These isomers were separated by gas chroma-

$$\underset{\mathbf{9}}{CH_3OCF{=}C(CF_3)CF(OCH_3)C_2F_5} \rightleftharpoons \underset{\mathbf{10}}{CH_3OCF_2C(CF_3){=}C(OCH_3)C_2F_5} \quad (8)$$

tography and characterized by NMR. Isomer mixtures (**9** and **10**) reacted with SO_3 to give the acylketene **12** and methyl fluorosulfate (eq 9). The mixtures were also hydrolyzed by concentrated sulfuric acid to the keto ester **11**. The overall yield of **12** from HFP dimer **2** was 58%.

$$\underset{\mathbf{11}}{F_5C_2COCH(CF_3)COOCH_3} \xleftarrow{H_3O^+} \mathbf{9}\text{ and }\mathbf{10} \xrightarrow{SO_3} \underset{\mathbf{12}}{O{=}C{=}C(CF_3)COC_2F_5} + CH_3OSO_2F \quad (9)$$

Reaction with Water and Dimethylformamide. Both the acylketene **12** and the vinyl ketone **5** are stable to storage but are easily hydrolyzed with decarboxylation to ketone **13** (eq 10 and 11).

$$\mathbf{12} + H_2O \rightarrow \underset{\mathbf{13}}{F_3CCH_2COC_2F_5} + CO_2 \quad (10)$$

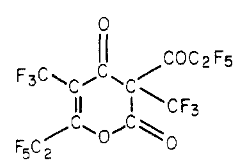
$$\mathbf{5} + 2H_2O \rightarrow \mathbf{13} + CO_2 + 2HF \quad (11)$$

Both the acylketene **12** and the vinyl ketone **5** react with dimethylformamide to give 1-(dimethylamino)-4,4,5,5,5-pentafluoro-2-(trifluoromethyl)-1-penten-3-one (**14**) with loss of carbon dioxide and carbonyl fluoride, respectively (eq 12). These reactions are analogous to those reported for fluoroketenes and fluoroacryloyl fluorides, respectively, with dimethylformamide.[3]

$$\mathbf{5}\text{ or }\mathbf{12} + (CH_3)_2NCHO \rightarrow \underset{\mathbf{14}}{(CH_3)_2NCH{=}C(CF_3)COC_2F_5} + CO_2\text{ or }COF_2 \quad (12)$$

Fluoride Ion Catalyzed Self-Addition. Cesium fluoride catalyst in tetraglyme without heating caused the vinyl ketone **5** to react exothermally, but only the hydrogen fluoride adduct **4** was isolated.

Cesium fluoride catalyst in tetraglyme without heating caused the acylketene **12** to dimerize to **15**. The structure



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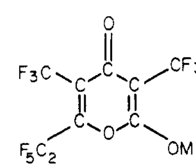

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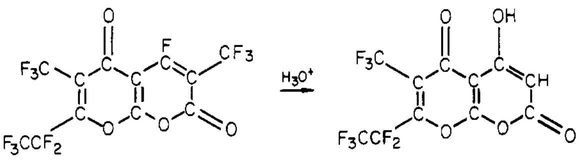
of this dimer corresponds to that of dimers formed in reactions aimed at nonfluorinated acylketenes, i.e., pyrolysis of ethanol from ethyl acetoacetate which gives dehydroacetic acid, a dimer of acylketene.[11] Use of molar amounts of cesium or potassium fluoride gave the salts **16** and C_2F_5COF. When heated with catalytic amounts of cesium fluoride in tetraglyme the acylketene **12** gave the pyronopyrone **17** (from 3 mol of acylketene **12** with loss

(1) Part 9: Krespan, C. G. *J. Fluorine Chem.* **1976**, *8*, 105.
(2) Contribution No. 2771.
(3) England, D. C.; Krespan, C. G. *J. Fluorine Chem.* **1973**, *3*, 63.
(4) England, D. C. "Abstracts of Papers", 169th National Meeting of the American Chemical Society, Philadelphia, PA, Apr 1975; American Chemical Society: Washington, DC, 1975; *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 1023; U.S. Patent 3 825 599, 1974.
(5) Brunskill, W.; Flowers, W. T.; Gregory, R.; Haszeldine, R. N. *J. Chem. Soc., Chem. Commun.* **1970**, 1444.
(6) Needleman, J. B.; Chang Kuo, M. C. *Chem. Rev.* **1962**, *62*, 419.
(7) Jager, G. *Chem. Ber.* **1972**, *105*, 137.
(8) Miller, W. T., Cornell University, private communication.
(9) Ishikawa, N.; Nagashima, A. *Bull. Chem. Soc. Jpn.* **1976**, *49*(2), 502.
(10) Martini, T., Schumann, K. *J. Fluorine Chem.* **1976**, *8*(6), 535.
(11) Berkowitz, W. F.; Ozorio, A. A. *J. Org. Chem.* **1971**, *36*, 3787.

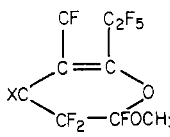
of 2 mol of C_2F_5COF). Hydrolysis of **17** by sulfuric acid gave **18** (eq 13).



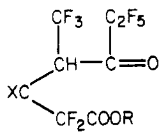
(13)

17 **18**

Additions to Vinyl Ethers. Both the vinyl ketone **5** and the acylketene **12** reacted with methyl trifluorovinyl ether at 100 °C to give the corresponding adducts **19** and **20** which were hydrolyzed to the acids **21** and **23** and/or the methyl esters thereof.

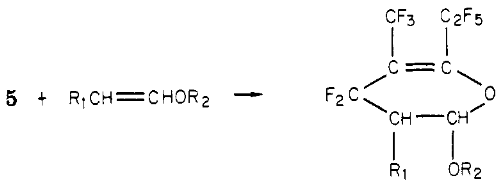


19, X = F_2
20, X = O



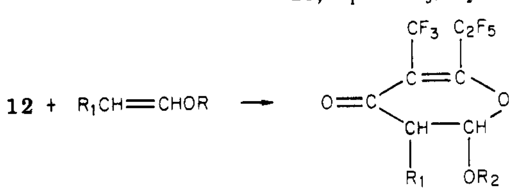
21, X = F_2; R = H
22, X = O; R = CH_3
23, X = O; R = H

Diels–Alder additions of vinyl ketone **5** and acylketene **12** to alkyl vinyl ethers was very exothermic and gave stable liquid adducts. Ethyl vinyl ether gave **24** and **26**, respectively. Propenyl vinyl ether gave **25** and **27** (eq 14 and 15). In the case of propenyl vinyl ether the cis and



(14)

24, R_1 = H; R_2 = C_2H_5
25, R_1 = CH_3; R_2 = C_3H_7

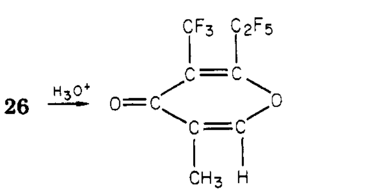


(15)

26, R_1 = H; R_2 = C_2H_5
27, R_1 = CH_3; R_2 = C_3H_7

trans isomers were reacted separately in various solvents and the products examined by ^{1}H NMR. Reactions with the vinyl ketone were stereospecific in both hexane and glyme, indicating a concerted mechanism. Reactions with the acylketene in hexane or chloroform were nonstereospecific, indicating that at least some of the reaction may involve a zwitterionic intermediate.

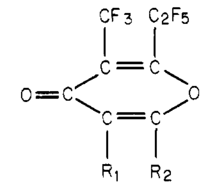
The products **26** on hydrolysis also lost propanol to give the pyrone **28** (eq 16), isomeric with **30**, which is formed from the acylketene and methylacetylene.



(16)

28

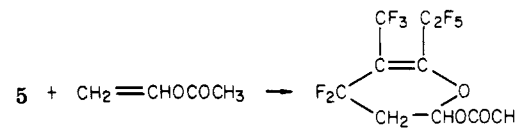
Additions to C≡C and Vinyl Esters. The acylketene **12** reacted with phenylacetylene to give **31**, with butylacetylene to give **32**, and with dimethylacetylene to give **33**. Although acetylene was not reacted with **12**, the



29, R_1 = R_2 = H
30, R_1 = H; R_2 = CH_3
31, R_1 = H; R_2 = C_6H_5
32, R_1 = H; R_2 = C_4H_9
33, R_1 = R_2 = CH_3

corresponding product, **29**, was obtained by reaction with vinyl acetate or with vinyl benzoate with simultaneous loss of acetic or benzoic acid, respectively.

Reaction of the vinyl ketone **5** with vinyl acetate gave the adduct **34** (eq 17).



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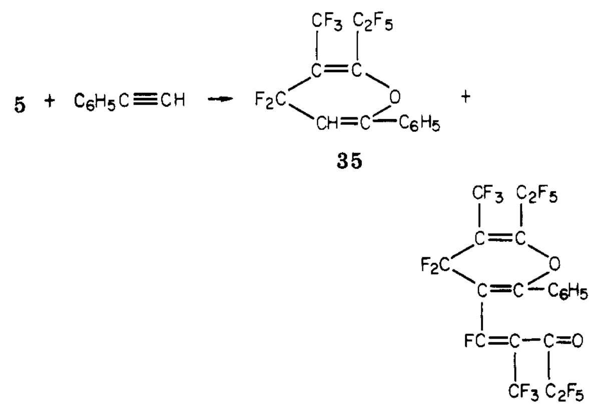
Reactions of the vinyl ketone **5** with acetylenes were not so clean, apparently because of the labile fluorine atoms. In the presence of sodium fluoride, the adduct **35** could be isolated from phenylacetylene along with the hydrolysis product **31** and a third product believed to be **36** (eq 18). Product **36** could be isolated in low yield by reacting **35** with vinyl ketone **5**.



(18)

35 **36**

Additions to C=C. The vinyl ketone **5** gave high yields of 1,4-adducts with the following olefins: propylene (**37**), 2-butene (**38**), isobutylene (**39**), styrene (**40**), cyclohexene (**51**), and norbornene (**48**), especially in the presence of sodium fluoride, which apparently prevented side reactions caused by small amounts of hydrogen fluoride. Isobutylene reacted much faster than *trans*-2-butene which reacted faster than *cis*-2-butene. Longer heating in glass gave the cyclic and acyclic hydrolysis products **43** and **45** (see Chart I) from isobutylene. They were formed directly from the acylketene and isobutylene.

The acylketene with propylene gave the cyclic adduct **41**. With *trans*-2-butene the acylketene gave three products, **42**, **46**, and **50**. *cis*-2-Butene was less reactive and gave only **42** and **46**. Cyclohexene gave the corresponding cyclic (**52**) and acyclic (**53**) products as did cyclopentene (**54** and **55**, respectively). Styrene and norbornene gave only cyclic products **44** and **49**, respectively. α-Methylstyrene gave only the acyclic product **47**. One can postulate zwitterionic

Chart I

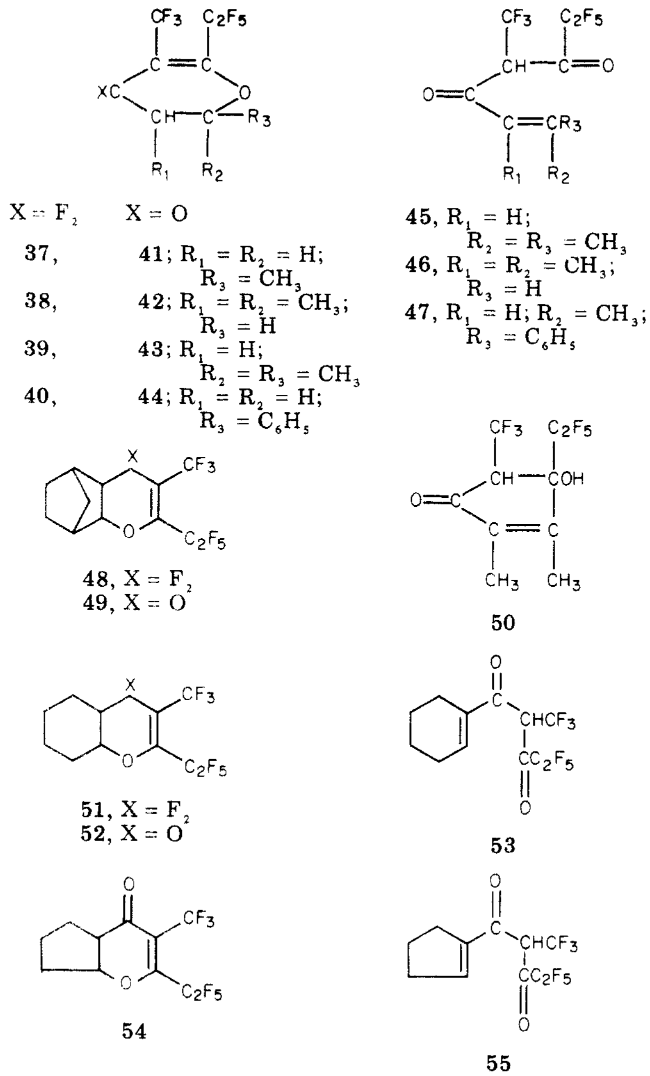


Chart II

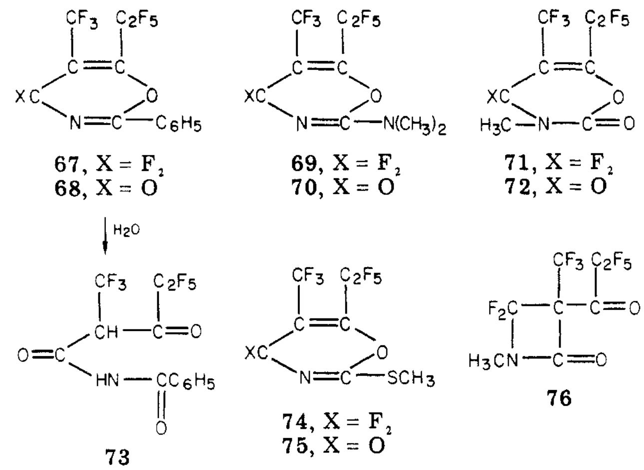
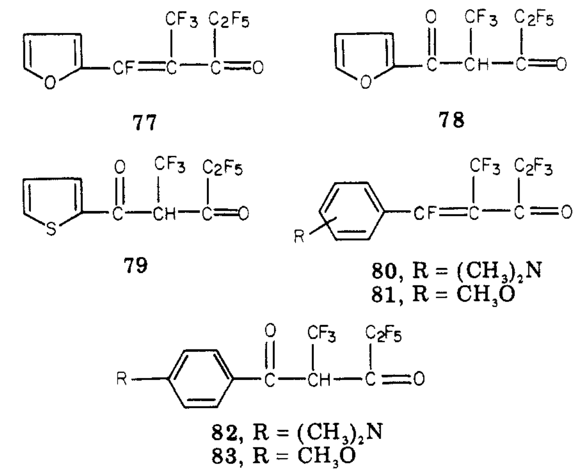
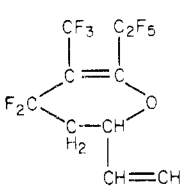


Chart III



intermediates that give the final products by either ring closure or migration of hydrogen.

In other additions to doubly bonded carbon atoms, the vinyl ketone **5** added to one of the double bonds in butadiene, giving **56** and to methyl vinyl ketone to give **57**. The acylketene **12** apparently added to one of the double bonds in bicycloheptadiene to give **58**.



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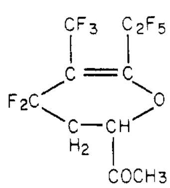

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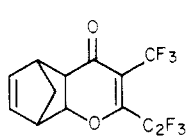

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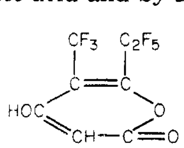
The acylketene **12** added readily to the C=C bond in ketene with proton migration to give a mixture of hydroxypyrone **59** and the acetylated product **60**. These products could be interconverted by hydrolysis of **60** in sulfuric acid and by acetylation of **59** with ketene.



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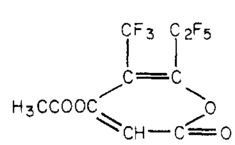
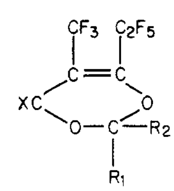


60

Addition to C=O. Both the vinyl ketone **5** and the acylketene **12** reacted exothermally with acetaldehyde, benzaldehyde, and acetone by addition to the carbonyl group to give **61–66**.

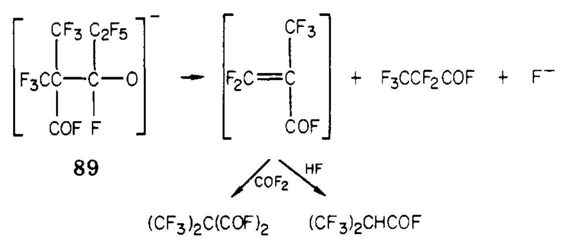


X = F_2	X = O
61,	64; R_1 = H; R_2 = CH_3
62,	65; R_1 = H; R_2 = C_6H_5
63,	66; R_1 = R_2 = CH_3

Addition to C≡N and C=N. The vinyl ketone **5** and the acylketene **12** also added to the carbon–nitrogen bonds in benzonitrile (**67** and **68**), dimethylcyanamide (**69** and **70**), methyl isocyanate (**71** and **72**), and methyl thiocyanate (**74** and **75**; see Chart II). The reaction of the vinyl ketone with methyl isocyanate gave a small amount of [2 + 2] cycloadduct **76** in addition to **71**. Instead of the adduct **68** from **12** with benzonitrile, its hydrolysis product **73** was isolated.

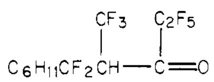
Substitution on Aromatic Rings. The vinyl ketone **5** reacted with furan to give **77** and $(CF_3)_2CHCOC_2F_5$ (from HF eliminated in the reaction). In an analogous reaction with furan, the acylketene **12** gave **78** and with thiophene gave **79** (Chart III). Related products were obtained from both compounds with dimethylaniline (**80** and **82**) and

Scheme I

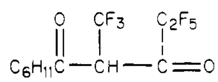


anisole (81 and 83). The reaction of these two compounds with the vinyl ketone 5 gave mixtures of ortho and para isomers. The acylketene 12 gave para isomers.

Addition of Cyclohexane. In another type of reaction, both the vinyl ketone 5 and the acylketene 12 underwent benzoyl peroxide catalyzed additions to cyclohexane, giving 84 and 85, respectively. The 1,3-diene 85 showed chelating ability with cobalt ions.

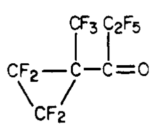


84

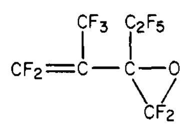


85

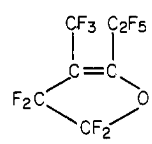
Addition of Difluorocarbene. Reaction of the vinyl ketone 5 with difluorocarbene generated from hexafluoropropene epoxide at 225 °C (the byproduct is CF_3COF) gave the 1,4-adduct 88, probably formed by rearrangement of either 86 or 87.



86



87

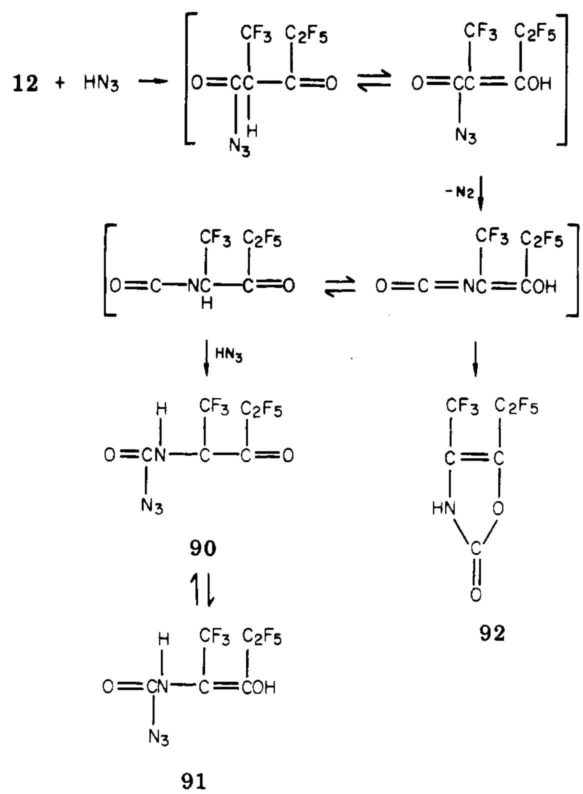


88

Addition of Carbonyl Fluoride. Fluoride ion catalyzed addition of carbonyl fluoride to the vinyl ketone 5 gave perfluoropropionyl fluoride, hexafluoroisobutyroyl fluoride, and perfluoromalonyl fluoride. These products can be explained through intermediate 89 cleaving to perfluoropropionyl fluoride and perfluoromethacryloyl fluoride (Scheme I). The latter is known to add carbonyl fluoride to give perfluorodimethylmalonyl fluoride. Hydrogen fluoride from moisture or reaction with solvent would account for the formation of hexafluoroisobutyroyl fluoride.

Addition of Hydrazoic Acid. Reaction of the acylketene 12 with hydrazoic acid gave the ketocarbamyl azide 90 and the cyclic urethane 92. A sample of 90 on being allowed to stand tautomerized to the enol form 91. The acylketene with hydrazoic acid would be expected to give an acid azide which would undergo Curtius rearrangement to an isocyanate which could then either cyclize or add hydrazoic acid[12] to give the products isolated as in Scheme II.

Scheme II



Experimental Section

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 parts per million from tetramethylsilane as external standard with the downfield direction taken as positive. ^{19}F NMR spectra were obtained with a Varian A56/60 spectrometer operating at 56.4 MHz; chemical shifts are reported in parts per million downfield from $CFCl_3$ as internal standard.

Experimental details leading to the vinyl ketone 5 and the acylketene 12 are given below. Products prepared from them are listed in Table I, with details of their preparation and characterization being available as supplementary material.

2-(Trifluoromethyl)-3-methoxy-1,1,1,3,4,4,5,5,5-nonafluoropentane (3).[9] A mixture of 200 mL of methanol and 0.5 g of powdered KOH was stirred while 500 g of dimer 2 was added dropwise, with the temperature kept about −10 °C with cooling in an acetone bath to which a little dry ice was added occasionally. If the mixture did not remain clear and homogeneous, more KOH was added. Higher temperatures seemed to promote byproduct formation. After the addition, the mixture was washed with water, dried, and distilled to give 453–391 g (90–78%) of 3 (bp 98 °C) along with 10–78 g of $(CF_3)_2CHC_3H_7$, bp 63 °C.

2-(Trifluoromethyl)-1,1,1,4,4,5,5,5-octafluoropentan-3-one (4).[10] The above methoxyfluoropentanone (3, 400 g) was added slowly to 100 mL of SO_3 with stirring (exothermic), and the mixture refluxed for 30 min. It was then cooled and added slowly with stirring to 200 mL of water at a rate to maintain a gentle reflux which ensured hydrolysis of the methyl fluorosulfate. The heavy layer was separated, dried, and distilled to give 297 g (83%) of 4, bp 62 °C.

Perfluoro-2-methyl-1-penten-3-one (5). This reaction was run on a large scale in a Monel tube which had a 3-in. diameter, was 2.5 ft long, and was heated by an 18-in. split-type electric furnace. The tube was packed to the center of the heated portion with 100 mL of 1/8-in. sodium fluoride pellets and below the center with sections of quartz tubing for reaction with hydrogen fluoride. This prevented reverse reaction, which did occur in one case when the products (HF and 5) were allowed to stand in a metal cylinder over sodium fluoride at room temperature for 60 h.

Products of the reaction were directed from the bottom of the tube to a 1-L Monel metal trap containing 100 g of anhydrous magnesium sulfate and 50 cm^3 of quartz tubing sections and cooled with liquid nitrogen. A second small glass trap was used to collect any material passing through the metal trap. The reaction was run at about 450 °C (1 mm), with the starting material being vaporized into the tube from a stirred flask at room temperature.

(12) Smith, P. A. S. "Organic Reactions"; Wiley: New York, 1947; Vol. III, Chapter 9.

Table I

no.	yield, %	bp [mmHg] (mp, °C)	no.	yield, %	bp [mmHg] (mp, °C)
1	95	48-50	**45**	27	78 [15] (43-45)
2	95	48-50	**46**	10	60 [1.8] (45-47)
3	90	98	**47**	59	85 [0.7] (29-31)
4	83	62	**48**	66	66 [0.2]
5	74	63	**49**	67	95 [0.1] (36-38)
6	5	98	**50**	16	60-65 [0.5] (90-93)
7	80	64	**51**	64	56 [1.0]
8a	30	53	**52**	13	68 [0.2]
8b	30	58	**53**	10	88 [20] (70-72)
9 + **10**	70	80 [35]	**54**	21	78 [0.4] (50-51.5)
11	95	121	**55**	33	55 [0.7] (49-50)
12	85	84	**56**	25	70 [18]
13	68	68	**57**	71	60 [28]
14	43	75 [0.7]	**58**	44	80 [0.5] (56-57.5)
15	90	65 [0.2] (40-43)	**59**	20	140 [3.0] (138-140)
16 (M = Cr)	14	(235 dec)	**60**	47	90 [3.0] (61-62)
16 (M = K)	17	(250-252 dec)	**61**	77.5	52 [35]
17	47	(208-210)	**62**	77.3	66 [1.8]
18	64	(138-141)	**63**	76	53 [25]
19	87	56 [35]	**64**	77	(49-54)
20	73	35 [1.0]	**65**	75	(61-62)
21	53.5	106 [22]	**66**	68	(28-29)
22	51	81 [40]	**67**	72	80 [0.6]
23	42	110 [40]	**69**	74.7	65 [0.4]
24	88	43 [0.5]	**70**	44	(72-74)
25	80	60 [2.2]	**71**	75	80 [20]
26	75	60 [0.1] (27-28)	**72**	94	(79-81)
27	65	68 [0.3]	**73**	45	(95-96)
28	94	48 [0.3]	**74**	80	35 [0.4] (35)
29	48	74 [2.0]	**75**	63	84 [0.5]
30	50	130 [50] (64-66)	**76**	12	68 [20]
31	48	(152-154)	**77**	50	84 [27]
32	49	70 [0.2]	**78**	67	105 [38]
33	40	69 [0.8]	**79**	81	122 [33] (47-48)
34	62	110 [35]	**80** (ortho)	29	76 [1.1]
35	8	(57-58)	**80** (para)	18	109 [1.1] (67-71)
36	5	97 [0.5] (92-97)	**81**	27	64 [0.2]
37	97	103 [100]	**82**	33	(125-126)
38	93	80 [20]	**83**	69	90 [0.3] (61-62)
39	97	74 [20]	**84**	62	88 [20]
40	63	67 [0.3]	**85**	65	55 [0.2]
41	20	115 [60]	**88**	46	65
42	47	62 [0.2]	**90**	32	90 [20] (54-55)
43	34	54 [0.4] (34-35)	**91**		(89-90)
44	60	(115-117)	**92**	31	125 [20] (53-55)

When all of the starting material had been passed through the tube, the metal trap was removed from the liquid nitrogen bath, and it was brought to atmospheric pressure by bleeding in nitrogen. It was then allowed to warm to room temperature, and the contents were transferred by vacuum to a large glass trap cooled by liquid nitrogen and then poured into a still pot for distillation.

One run with 250 g of **4** at 421-436 °C (0.6-1.4 mm) required 35 min and gave 212 g of crude product which on distillation gave 178 g (76.5%) of **5** containing about 2% of **4**. For **5**: bp 63 °C; IR 1779 (C=O), 1742 cm^{-1} (C=C); ^{19}F NMR -60.7 (m, 3), -62.2 (m, 2), -84.4 (m, 3), -123.2 ppm (m, 2).

Anal. Calcd for $C_6F_{10}O$: C, 25.92; F, 68.35. Found: C, 26.07; F, 68.57.

***cis*- and *trans*-1,3-Dimethoxy-2-(trifluoromethyl)-1,3,4,4,5,5,5-heptafluoro-1-pentene (9)[9] and *cis*- and *trans*-1,3-Dimethoxy-2-(trifluoromethyl)-1,1,4,4,5,5,5-heptafluoro-2-pentene (10a and 10b).** A mixture of 630 g (2.10 mol) of HFP dimer **2** in 600 mL of methanol was stirred at 0 to -10 °C while a solution of sodium methoxide (0.50 lb, 226 g, 4.2 mol) in 800 mL of methanol was added dropwise. When the addition was complete, the mixture was poured into cold, dilute HCl, washed with water, and dried over $MgSO_4$ to give 660 g of crude product. This mixture has not been completely characterized. It consists predominately of the two isomers of **9** described by Ishikawa and Nagashima[9], apparently the kinetic dimethoxy derivative. However, when the mixture was allowed to stand, other isomers were formed. Distillation of **9** from tetraglyme and a catalytic amount of cesium fluoride caused partial isomerization to lower boiling **10a** and **10b**, and these isomers were sometimes isolated along with **9** simply by distilling the crude product. Isomers **10a** and **10b** (bp ca. 62 and 72 °C, respectively, at 35 mm) can be separated from each other and from **9** [bp ca. 80 °C (35 mm)] by careful fractionation and easily by gas chromatography (fluorosilicone on Gas Chrom R). All of these isomers react with sulfur trioxide to give the acylketene **12**, so the crude mixture was used for its preparation (see below). Yields of distilled isomer mixtures were 60-70%.

For isomer 10a: IR 1675, 1639 cm^{-1} (sh, C=O and C=C); ^{1}H NMR 3.30 (s, 3), 3.66 ppm (s, 3); ^{19}F NMR -61.1 (t, 3, J = 12.0 Hz), -68.4 (m, 2), -82.6 (t, 3, J = 4.4 Hz), -114.0 ppm (t, 2, J = 20.4 Hz).

Anal. Calcd for $C_8H_6F_{10}O_2$: C, 29.65; H, 1.86; F, 58.64. Found: C, 29.97; H, 1.96; F, 58.49.

For isomer 10b: IR 1683, 1650 cm^{-1} (sh, C=O and C=C); ^{1}H NMR 3.35 (s, 3), 3.70 ppm (s, 3); ^{19}F NMR -57.4 (m, 3), -71.7 (q, 2, J = 11.0 Hz), -82.9 (q, 3, J = 3.7 Hz), -115.1 ppm (q, 2, J = 21.0 Hz).

Anal. Calcd for $C_8H_6F_{10}O_2$: C, 29.65; H, 1.86; F, 58.64. Found: C, 29.65; H, 2.01; F, 58.47.

In one isomer all spin-spin splitting was by the CF_2 of the CF_2OCH_3 group, whereas in the other isomer all splitting was by the CF_3 group on doubly bonded carbon.

Perfluoromethylpropionylketene (12). The crude cis-trans isomer mixture of **9** and **10** (660 g, not distilled) prepared above from HFP dimer **2** and sodium methoxide in methanol was added dropwise with stirring to 200 mL of sulfur trioxide with the temperature kept around 40 °C with cooling. When the addition was complete, the mixture was distilled. There was collected 410 g of product, bp 82–85 °C. Analyzed by gas chromatography, this material was 76% perfluoromethylpropionylketene (**12**) and the remainder methyl fluorosulfate, bp 90–92 °C. Thus the yield was 312 g of **12** (58% based on HFP dimer **2**). Precision distillation of the 76% material through a Podbielniak column gave an azeotrope boiling at 84 °C (85% **12** and 15% methyl fluorosulfate). A pure sample of the ketene **12** was obtained by preparative gas chromatography; n^{25}_D 1.3248. On a large scale, the methyl fluorosulfate could be removed by reaction with sodium fluoride at elevated temperature (see below). For **12**: IR 2174 (C=C=O), 1718 cm^{-1} ((C=O); ^{19}F NMR -57.8 (s, 3), -84.7 (t, 3, J = 1.1 Hz), -122.6 ppm (q, 2, J = 1.1 Hz).

Anal. Calcd for $C_6F_8O_2$: C, 28.15; F, 59.37. Found: C, 27.98; F, 59.18.

Removal of methyl fluorosulfate from the azeotrope was accomplished by eq 19 which took place in the vapor phase at 400–500 °C. The ketene **12** was unchanged under these conditions.

$$CH_3OSO_2F + NaF \rightarrow CH_3F + Na_2SO_3F \quad (19)$$

Methyl fluorosulfate (25 g) was passed as vapor (evaporated from liquid) in 25 min over a bed of sodium fluoride pellets in a quartz tube at 550 °C (1.2 mm). There was collected in a liquid nitrogen cooled trap 9 g of material characterized roughly by its boiling point (<-80 °C; bp of CH_3F is -84 °C) and by infrared methods as the methyl fluoride. This represents approximately the theoretical yield based on the above reaction. The sodium fluoride pellets were coated with a white powder, presumably Na_2SO_3F.

An azeotropic mixture (37.9 g) of **12** and methyl fluorosulfate (85:15) was passed in 30 min over 50 mL of sodium fluoride pellets at 445 °C (1.6 mm). There was recovered 33 g of nearly pure ketene **12** after evaporation of methyl fluoride. It was repassed over the sodium fluoride at 600 °C in 35 min, and 29 g of pure ketene **12** was recovered.

The yields (not optimized) and boiling points (melting points) of products reported in this work are listed in Table I. Due to the high volatilities involved, most reactions were carried out in heavy-walled glass tubes which were necked-down and annealed before loading (no more than half full). They were sealed under vacuum at liquid nitrogen temperature, heated in steel pipes, and recooled in liquid nitrogen before opening. After the workup the products were characterized by NMR, infrared, and elemental analyses. Details are available as supplementary material.

Registry No. **1**, 2070-70-4; **2**, 1584-03-8; **3**, 54376-60-2; **4**, 61637-91-0; **5**, 54376-59-9; **6**, 75732-70-6; **7**, 75732-71-7; **8a**, 75732-72-8; **8b**, 75732-73-9; **9** (isomer 1), 59754-88-0; **9** (isomer 2), 59736-18-4; **10** (isomer 1), 53352-87-7; **10** (isomer 2), 53434-60-9; **11**, 75732-74-0; **12**, 53352-88-8; **13**, 61637-92-1; **14**, 75732-75-1; **15**, 53352-89-9; **16** (M = Cs), 53352-90-2; **17**, 53609-34-0; **18**, 75732-76-2; **19**, 75751-07-4; **20**, 75732-77-3; **21**, 75732-78-4; **22**, 75732-79-5; **23**, 75732-80-8; **24**, 75732-81-9; *cis*-**25**, 75732-82-0; *trans*-**25**, 75733-44-7; **26**, 75732-83-1; *cis*-**27**, 75732-84-2; *trans*-**27**, 75733-45-8; **28**, 75732-85-3; **29**, 75732-86-4; **30**, 75732-87-5; **31**, 75732-88-6; **32**, 75732-89-7; **33**, 75732-90-0; **34**, 75732-91-1; **35**, 75732-92-2; **36**, 75751-08-5; **37**, 75732-93-3; *cis*-**38**, 75732-94-4; *trans*-**38**, 75733-46-9; **39**, 75732-95-5; **40**, 75732-96-6; **41**, 75732-97-7; **42**, 75732-98-8; **43**, 75732-99-9; **44**, 75733-00-5; **45**, 75733-01-6; **46**, 75733-02-7; **47**, 75733-03-8; **48**, 75733-04-9; **49**, 75733-05-0; **50**, 75733-06-1; **51**, 75733-07-2; **52**, 75733-08-3; **53**, 75733-09-4; **54**, 75733-10-7; **55**, 75733-11-8; **56**, 75733-12-9; **57**, 75733-13-0; **58**, 75733-14-1; **59**, 75733-15-2; **60**, 75751-09-6; **61**, 75733-16-3; **62**, 75733-18-5; **63**, 75733-17-4; **64**, 75733-19-6; **65**, 75733-20-9; **66**, 75733-21-0; **67**, 75733-22-1; **68**, 75733-23-2; **69**, 75733-24-3; **70**, 75733-25-4; **71**, 75751-10-9; **72**, 75751-11-0; **73**, 75733-26-5; **74**, 75733-27-6; **75**, 75733-28-7; **76**, 75733-29-8; **77**, 75751-12-1; **78**, 75733-30-1; **79**, 75733-31-2; *o*-**80**, 75733-32-3; *p*-**80**, 75733-33-4; *o*-**81**, 75733-34-5; *p*-**81**, 75733-43-6; **82**, 75733-35-6; **83**, 75733-36-7; **84**, 75733-37-8; **85**, 75733-38-9; **88**, 75733-39-0; **90**, 75733-40-3; **91**, 75733-41-4; **92**, 75733-42-5; methyl fluorosulfate, 421-20-5; perfluoropropionyl fluoride, 422-61-7; dimethylformamide, 68-12-2; *cis*-propenyl propyl ether, 14360-78-2; methyl trifluorovinyl ether, 3823-94-7; phenyl acetylene, 536-74-3; propylene, 115-07-1; *trans*-2-butene, 624-64-6; *cis*-2-butene, 590-18-1; isobutylene, 115-11-7; styrene, 100-42-5; α-methylstyrene, 98-83-9; norbornene, 498-66-8; cyclohexene, 110-83-8; cyclopentene, 142-29-0; butadiene, 106-99-0; bicycloheptadiene, 121-46-0; vinyl acetate, 108-05-4; vinyl benzoate, 769-78-8; methyl vinyl ketone, 78-94-4; acetaldehyde, 75-07-0; benzaldehyde, 100-52-7; acetone, 67-64-1; benzonitrile, 100-47-0; dimethylcyanamide, 16703-51-8; methyl isocyanate, 624-83-9; anisole, 100-66-3; dimethylaniline, 121-69-7; furan, 110-00-9; thiophene, 110-02-1; cyclohexane, 110-82-7; carbonyl fluoride, 353-50-4; hexafluoropropene epoxide, 428-59-1; diketene, 674-82-8; hydrazoic acid, 7782-79-8; ethyl vinyl ether, 109-92-2; methylacetylene, 74-99-7; butylacetylene, 693-02-7; dimethylacetylene, 503-17-3; *trans*-propenyl propyl ether, 21087-24-1.

Supplementary Material Available: Experimental details concerning compounds reported in this work, including their preparation and infrared, NMR, and analytical data (66 pages). Ordering information is given on any current masthead page.

Fluoroketenes. 11.[1] Synthesis and Chemistry of a Perfluoroacylketene and Related Compounds Containing a Perfluoroisopropyl Sulfide Group

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Received June 16, 1980

The dimer of hexafluorothioacetone (**4**) and the perfluorovinyl sulfide **7** have been prepared in good yield from hexafluoropropene (HFP) and sulfur in standard laboratory equipment slightly below atmospheric pressure. Compound **7** is structurally similar to a dimer of HFP from which a vinyl ketone and an acylketene were prepared.[1] Preparation of the related vinyl ketone **13** and acylketene **14** containing the perfluoroisopropyl sulfide group are reported here as well as some chemistry of the acylketene **14**. This chemistry is analogous to that of a previously prepared acylketene (**15**) in its reactions with water, benzamide, and hydrazoic acid, in Diels–Alder addition reactions to dienophiles containing C=C, C≡C, C=N, C≡N, and C=O unsaturation, and in electrophilic substitution reactions with aromatic compounds. However, different behavior was observed in reactions involving fluoride ion, dimethylformamide, dimethylacetamide, and tetramethylurea.

Following discovery of the reaction of perfluoroisobutylene with potassium fluoride and sulfur in dimethylformamide (DMF),[3] the behavior of other fluoro olefins under these mild conditions was examined. The results with HFP reported here differ somewhat from those reported elsewhere[4] under different conditions. A reactive perfluorovinyl sulfide (**7**) became readily available, and

(1) Part 10: England, D. C., *J. Org. Chem.*, previous paper in this issue.
(2) Contribution No. 2785.
(3) Krespan, C. G.; England, D. C. *J. Org. Chem.* **1968**, *33*, 1853.
(4) Dyatkin, B. L.; Sterlin, S. R.; Zhuravkova, L. G.; Martynov, B. I.; Mysov, E. I.; Knunyants, I. L. *Tetrahedron* **1973**, *29*, 2759.

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