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FLUOROKETENES IX.*
FUNCTIONALITY α TO THE KETENE GROUP

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SUMMARY

Three new fluoroketenes have been prepared having the acid fluoride, sulfonyl fluoride and ester functions, respectively, α to the ketene group. The synthesis and characterization of these ketenes is described, along with a convenient synthesis of trifluoromethylmalonyl fluoride.

INTRODUCTION

Aside from vinyl fluoroketenes postulated as intermediates from fluorocyclobutenone pyrolyses [2], the stable α-ketofluoroketenes of England [3] appear to be the only known fluoroketenes bearing an unsaturated function α to the ketene group. The synthesis and characterization of other fluoroketenes with α-functionality was therefore of interest. This paper describes three such ketenes, I, II, and III, as well as a useful synthesis of trifluoromethylmalonyl fluoride (IV).

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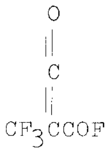
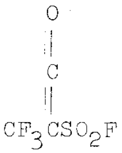
[*] For Part VIII, see Ref. 1.



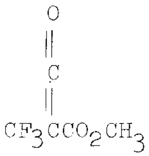
$CF_3\overset{\overset{O}{\|}}{\overset{C}{\|}}COF$

I



$CF_3\overset{\overset{O}{\|}}{\overset{C}{\|}}SO_2F$

II



$CF_3\overset{\overset{O}{\|}}{\overset{C}{\|}}CO_2CH_3$

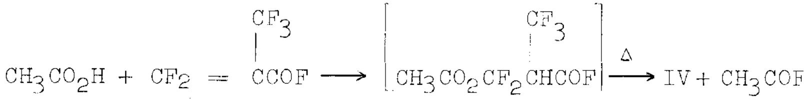
III

$CF_3CH(COF)_2$

IV

RESULTS AND DISCUSSION

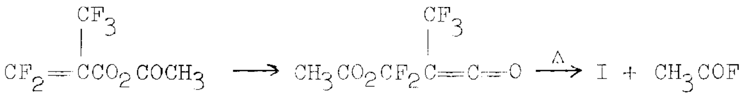
Weak bases attack perfluoromethacryloyl fluoride preferentially at the terminal difluoromethylene group[4], and acetic acid behaves similarly. The addition of acetic acid to perfluoromethacryloyl fluoride is exothermic, and an unstable adduct is obtained if the temperature is kept below 50°. This adduct is presumed to be predominantly V, since mild thermolysis cracks it to acetyl fluoride and IV in good yield.



$$CH_3CO_2H + CF_2 = \overset{\overset{CF_3}{|}}{C}COF \longrightarrow \left[CH_3CO_2CF_2\overset{\overset{CF_3}{|}}{C}HCOF \right] \xrightarrow{\Delta} IV + CH_3COF$$

V

Malonyl fluoride IV as distilled is accompanied by a few per cent of ketene I formed in the reaction. This latter product can be visualized as the result of reaction to a minor extent at the acid fluoride group of perfluoromethacryloyl fluoride, followed by a 1,3-isomerization of the acetoxy group as shown below.



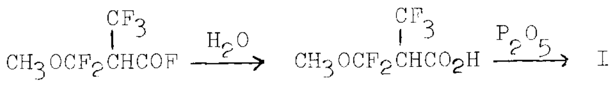
$$CF_2=\overset{\overset{CF_3}{|}}{C}CO_2COCH_3 \longrightarrow CH_3CO_2CF_2\overset{\overset{CF_3}{|}}{C}=C=O \xrightarrow{\Delta} I + CH_3COF$$

Pure I can be obtained from the dehydrofluorination of IV with sulfur trioxide. Acid fluorides are known to react more or less readily with sulfur trioxide to form acyl fluorosulfates [5,6]. In one other case, that of

α-H-hexa-fluoroisobutyroyl fluoride, the adduct with sulfur trioxide has been shown to pyrolyze with dehydrofluorination to a ketene as well as with regeneration of starting carboxylic acid fluoride [5]. Treatment of IV with sulfur trioxide followed by distillation gave a mixture of I and pyrosulfuryl fluoride from which was isolated 17% of I after fractionation. Pure fluorocarbonyltrifluoromethyl ketene, I, is a colorless, fuming liquid, bp 58-59°, which is only moderately stable to storage. A reddish-orange precipitate tends to form after a few weeks at 25°. The precipitate is reminiscent of byproduct high-boilers formed during preparations of I and probably results from self-condensation reactions.

$$\text{IV} + SO_3 \longrightarrow \text{I} + FSO_2OSO_2F$$

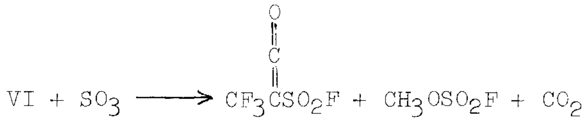
A different and less direct synthesis of I starts from the 1:1 methanol/perfluoromethacryloyl fluoride adduct. This adduct [4] is hydrolyzed to the acid VI, which gives with phosphorus pentoxide a modest overall yield of I. Acid-catalyzed ether cleavage as well as dehydration are thus observed.



$$CH_3OCF_2\overset{\overset{CF_3}{|}}{C}HCOF \xrightarrow{H_2O} CH_3OCF_2\overset{\overset{CF_3}{|}}{C}HCO_2H \xrightarrow{P_2O_5} \text{I}$$

VI

Cleavage of such ether groups can often be efficiently accomplished with sulfur trioxide [2], so that if dehydration also occurred, sulfur trioxide and VI could lead to ketene I. Treatment of acid VI with sulfur trioxide, however, results in a vigorous reaction, evolution of carbon dioxide, and formation of II along with methyl fluorosulfate. The new ketene II, isolated in 18-26% yield, is a fuming distillable liquid with good stability. A sample stored in glass at 25° for one month showed little change.

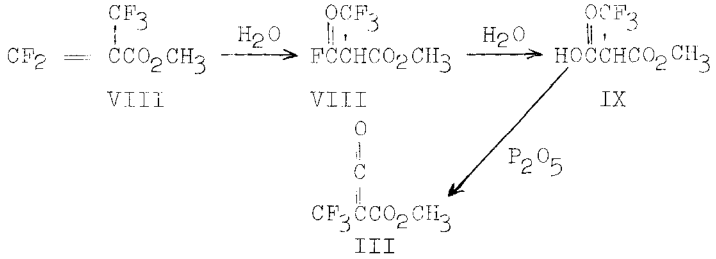


$$VI + SO_3 \longrightarrow CF_3\overset{\overset{\displaystyle O}{\|}\atop{\overset{\displaystyle C}{\|}}}{C}SO_2F + CH_3OSO_2F + CO_2$$

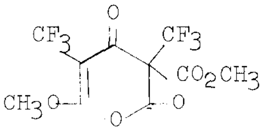
II

The probable source of II is reaction of ketene I, formed as expected, with the excess of sulfur trioxide. More than one mechanism can be postulated.

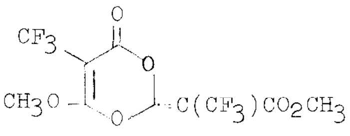
Methyl perfluoromethacrylate, VII, obtained from perfluoromethacryloyl fluoride by a new route [5], was observed to react on long storage in glass. Analysis by ^{19}F NMR indicated hydrolysis of the difluoromethylene group had occurred, leading to a mixture of acid fluoride VIII and acid IX. The crude mixture was reacted with sufficient water to convert it completely to IX, and the resulting product was treated with phosphorus pentoxide. Distillation afforded 38% of ketene ester III.



Of the three new α-functionalized fluoroketenes, III proved to be least stable toward self-condensation. Monomeric III slowly gave a dimer on standing at 25°; after 3 weeks, the mixture was composed of approximately equal amounts of monomer and dimer. Previous work [3a] with fluorinated α-ketoketenes revealed a tendency to form 1,4-cycloadducts involving addition to the keto oxygen as one terminus. The dimer X from III shows no IR bands compatible with carbonyl in a four-membered ring, so that a six-membered ring with 1,4-cycloaddition is presumed present in X also.



X



XI

Of the two most likely dimeric structures, X and XI, X is preferred on the basis that the observed ^{19}F chemical shift for one of the trifluoromethyl groups (-67.2 ppm) is most compatible with a trifluoromethyl on saturated carbon and that two isomers might well be detectable for structure XI whereas only one was observed.

EXPERIMENTAL

Melting points and boiling points are uncorrected. ^{1}H NMR spectra were obtained with a Varian A-60 spectrometer operating at 60 MHz; chemical shifts are reported in ppm from tetramethylsilane as internal 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 ppm downfield from $CFCl_3$ as internal standard.

Trifluoromethylmalonyl Fluoride (IV)(nc)

Dropwise addition of 6.6 g (0.11 mol) of acetic acid to 19 g (0.11 mol) of perfluoromethacryloyl fluoride resulted in an exothermic reaction, so cooling was applied to keep the temperature below 50°. Acetyl fluoride, bp 20-25°, was removed by heating the adduct above 70°

for 2 hr. Distillation of the product gave fractions with bp 58-64°, 15.1 g (78% calculated as $CF_3CH(COF)_2$). ^{19}F NMR indicated a 17:1 mixture of trifluoromethylmalonyl fluoride and ketene I. IR (CCl_4): 3.38 (CH), 5.38 and 5.42 μ (C=O) for $CF_3CH(COF)_2$ with weak bands at 4.57 (C=C=O) and 5.47 μ (sh, C=O) for $CF_3C(=C=O)COF$. NMR (CCl_4): ^{19}F at 46.4 (q, J_{FF} = 10 Hz, 2, $\mathrm{CO}\underset{\sim}{\mathrm{F}}$) and -66.0 ppm (t, J_{FF} = 10 Hz, into d. J_{HF} = 7 Hz, 3, $\underset{\sim}{\mathrm{CF_3}}$) with previously assigned peaks for $CF_3C(=C=O)COF$ also present in 5.5% amount.

Anal. Calcd for $C_4HF_5O_2$: C, 27.29; H, 0.57; F, 53.96
Found: C, 27.75; H, 0.79; F, 54.34

Reaction carried out on a one-mole scale gave 92% of IV containing a small percentage of I, bp 60-63°.

Fluorocarbonyltrifluoromethylketene (I)(nc)

A mixture of 17.6 g (0.10 mol) of trifluoromethylmalonyl fluoride (containing ca.5% of the ketene) and 24 g (0.3 mol) of SO_3 was heated and crude distillate was redistilled to afford 11.9 g (40%) of pyrosulfuryl fluoride, bp 51-54°, and 2.4 g (15%) of fluorocarbonyltrifluoromethylketene, bp 58-59.5°. Pyrosulfuryl fluoride was identified by comparison of bp, infrared spectrum and NMR spectrum with those reported for authentic samples. The ketene was shown by infrared to be the same as that prepared below.

Anal. Calcd for $C_4F_4O_2$: C, 30.79; F, 48.71
Found: C, 29.95; F, 48.50

A lesser proportion of SO_3 resulted in a lower yield. A combination of SO_3/P_2O_5 appeared to give a better yield of product, but in a mixture difficult to separate by distillation. P_2O_5 at 25-60° gave little reaction with trifluoromethylmalonyl fluoride. KF at 150° (100 mm) in a hot tube gave essentially no reaction with trifluoromethylmalonyl fluoride, while at 250° (50 mm) partial elimination of HF occurred with formation of considerable orange-red tar. A similar orange-red involatile tar or solid forms in the successful preparations of fluorocarbonyltrifluoromethylketene, and when the latter is stored for long periods (months) in glass. Reaction of trifluoromethylmalonyl fluoride with excess silylating agent ($CF_3C[OSi(CH_3)_3]=NSi(CH_3)_3$) occurred exothermically. The only volatile product formed in major amount and detected by glpc and mass spec. was $(CH_3)_3SiF$; presumably fluorocarbonyltrifluoromethylketene was formed but did not survive the conditions for reaction and isolation. Similarly, sodium acetate reacted vigorously with perfluoromethacryloyl fluoride to give a high yield of acetyl fluoride and orange-red solid.

3-Methoxy-3,3-difluoro-2-trifluoromethylpropionic Acid (VI)(nc) and its Conversion to I

A solution of 50 g (0.28 mol) of perfluoromethacryloyl fluoride in 100 ml of ether was stirred at 0° while 9.0 g (0.28 mol) of methanol was added at a rate sufficient to keep the reaction mixture near 20°. When the addition was complete, 100 g of anhydrous NaF was added, and the mixture was stirred while 5.4 g (0.30 mol) of water was added. The temperature was not allowed to go above 35°. After having stood overnight, the reaction mixture was filtered and distilled. It was necessary to keep the pot temperature below 70° to avoid excessive etching. Product acid VI was obtained as 22.1 g (38%) of distillate, bp 45° (0.5 mm). IR (neat): 3.25 (broad, OH), 5.72 (C=O), 7.5-9 μ (CF, COC). NMR (CCl_4): ^1H at 11.8 (s, 1, OH), 3.83 (sextet(q, J_{HF} = 7.5 Hz, into t, J_{HF} = 7.5 Hz), 1, CH), and 3.67 ppm (s, 3, OCH_3); ^{19}F at -65.1 ppm (t, J_{FF} = 10.5 Hz, into d, J_{HF} = 7.5 Hz, 3, CF_3) and 14 lines from overlapping center lines of an AB pattern at -4233 Hz and -4247 Hz (both q, J_{FF} = 10.5 Hz, into d, J_{HF} = 7.5 Hz, 2, CF_2).

Anal. Calcd for $C_5H_5F_5O_3$: C, 28.86; H, 2.42
Found: C, 29.30; H, 2.57

A mixture of 7.2 g (0.035 mol) of 3-methoxy-3,3-difluoro-2-trifluoromethylpropionic acid and 45 g of P_2O_5 was heated at 120-160° and product was distilled directly from the reaction mass. There was thus obtained 0.93 g (17%) of ketene I as a fuming liquid, bp 58°. IR (CCl_4): 4.56 (C=C=O), 5.47 (COF), and 7.2-8.5 μ (CF). NMR (CCl_4): ^{19}F at 33.3 (q, J_{FF} = 11.5 Hz, 1, COF) and -56.0 ppm (d, J_{FF} = 11.5 Hz, 3, CF_3). Mass spec.: m/e 156 (M^+) 137 (M^+-F), 128 (M^+-CO), and 100 (M^+-2CO); mass measurement gave 155.9861, calcd for $C_4F_4O_2$ is 155.9834.

Fluorosulfonyltrifluoromethylketene (II)(nc)

Crude acid VI was prepared from 50 g (0.28 mol) of perfluoromethacryloyl fluoride, 9.0 g (0.28 mol) of methanol and 6.0 g (0.33 mol) of water as described above. Dropwise addition of VI (47.8 g) to 62 g (0.78 mol) of SO_3 was carried out over 45 min. Cooling was applied to keep the temperature in the bulk of the reaction below 50°, but reaction occurred very exothermically where the drops landed. Evolution of CO_2 was noted. Rough distillation afforded 31 g of fuming liquid, bp 76-90°, and a residue containing suspended orange-red solid with mp > 300°. Fractionation of the distillate gave 15.3 g (48%) of methyl fluorosulfate, bp 91-92°, along with 9.9 g (18%) of fluorosulfonyltrifluoromethylketene, bp 78-80°. IR (CH_2Cl_2): 4.56 (C=C=O), 6.92 (SO_2F), and 8-8.5 μ (C-F, SO_2F). NMR (CCl_4): ^{19}F at +79.6 (q, J_{FF} = 5 Hz, 1, $SO_2\underset{\sim}{F}$) and -54.1 ppm (d, J_{FF} = 5 Hz, 3, $C\underset{\sim}{F_3}$). Mass spec.: m/e 192 (M^+), 173 (M^+-F), 164 (M^+-CO), 109 (M^+-SO_2F); mass measurement gave 191.9542, calcd for $C_3F_4SO_3$ is 191.9504; M^++2 confirms the presence of sulfur.

<u>Anal</u>. Calcd for $C_3F_4O_3S$: C, 18.76; F, 39.56; S, 16.69
Found: C, 18.85; F, 39.86; S, 16.98

A similar reaction at higher temperature gave 13.8 g (26% from perfluoromethacryloyl fluoride) of product, bp 78-82°.

Methoxycarbonyltrifluoromethylketene (III)(nc)

A sample of methyl perfluoroacrylate (23.9 g, 16.5 ml at 25°) had reacted noticeably with glass after standing for about 6 mos., volume now 10.5 ml. Analysis by ^{19}F NMR showed starting material to be gone and indicated the liquid to be chiefly a 2:1 mixture of esters VIII and IX.

This mixture (14.2 g, ~ 0.076 mol) was added to a suspension of 15 g of anhydrous NaF in 50 ml of ether. The resulting solution was treated with 0.90 g (0.050 mol) of water. The mixture was stirred for 3 hr, during which time the initial exothermic reaction subsided. The mixture was then filtered, the filtrate evaporated to give 11.5 g of high-boiling oil, and the oil added dropwise to 28 g of P_2O_5. This reaction mass was slowly heated to

160-180° at 200 mm to distill product, a fuming liquid, bp 66-67° (200 mm), 4.8 g (38% from the mixture of VIII and IX). IR and NMR both indicated the product to be pure as distilled, but rapidly accumulating a second dimeric component on standing at 25°. After 3 weeks, the mixture was about equal amounts of monomer and dimer. IR: 3.30 and 3.35 (satd. CH), 4.59 (C=C=O), 5.73 (ester C=O), 7.5-10 μ (CF, COC); bands at 5.62, 5.89, and 6.18 (C=O, C=C) became prominent with time while those at 4.59 and 5.73 diminished. NMR (CCl_4): ^{19}F at -55.8 ppm (s) with singlets of similar intensity developing at -58.4 and -67.2 ppm; ^1H at 3.80 ppm (s) with singlets of similar intensity developing at 4.26 and 3.87 ppm. Mass spec.: m/e 168 (M^+), 148 (M^+-HF), 137 (M^+-CH_3O) with no higher mass peaks; mass measurement 168.0035, calcd for $C_5H_3O_3F_3$ is 168.0034.

<u>Anal</u>. Calcd for $C_5H_3F_3O_3$: C, 35.73; H, 1.80; F, 33.91
Found: C, 35.72; H, 1.99; F, 33.71

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