Fluorinated Pyrones and Cyclobutenecarboxylates

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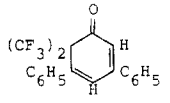
Fluorinated α-pyrones **6** have been prepared from perfluoroacryloyl fluorides **1** and **2** by reaction with arylacetylenes and/or methyl ketones. Cyclobutenecarboxylates **8** have also been obtained from the reactions of **1** with acetylenes. The NMR spectrum of pyrone **6e** shows unusually long-range fluorine–fluorine coupling.

Previous reports on the chemistry of perfluoroacryloyl fluoride[2] (**1**) and perfluoromethacryloyl fluoride[3] **2** have illustrated their activity as dienes in Diels–Alder additions to double bonds. We now report[4] their addition to aromatic acetylenes, which provides a route to the α-pyrones **6** shown in Scheme I. Acetone and acetophenone react with **2**, providing another route to the same 1,2-pyrones. The yields in both routes are moderate.

Results and Discussion

As shown in Scheme I, the arylacetylene route involves a [4 + 2] cycloadduct **3**, followed by a 1,3 fluoride ion shift to **4** and hydrolysis to the pyrone **6**. The methyl ketone route may involve addition of an α-hydrogen to the fluorinated double bond, ring closure through the enol form of the resulting adduct **5**, and loss of hydrogen fluoride. The pyrones **6** are generally stable crystalline solids formed by ready hydrolysis of their liquid precursors **4** and **5**. The compounds have been characterized by elemental analyses and infrared and NMR spectra.

In the reaction of **2** with phenylacetylene, some **7** is isolated, indicating isomerization of **2** to bis(trifluoromethyl)ketene which reacts[5] with phenylacetylene to give **7**. In the reaction of **1** with phenylacetylene, the byproducts isolated were a [2 + 2] cycloadduct, which hydrolyzed to the acid **8** (X = C_6H_5), and difluorodiphenylbenzene **9**, formed by addition of **4** to phenylacetylene followed by loss of carbonyl fluoride. When the reaction was run in excess phenylacetylene for longer times, less **4** and more **9** were isolated. Further evidence for this diene behavior of **4** was provided by its reaction with dimethyl acetylenedicarboxylate to give **10** with loss to carbonyl fluoride.



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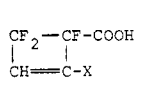

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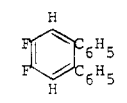

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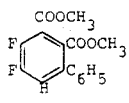
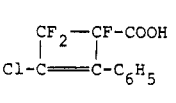


10

The [2 + 2] cycloadduct was only a minor product with most of the phenylacetylenes reacted, but it was the only product isolated (as the acid) with β-chlorophenylacetylene, **11**, and with 1-acetoxy-1-ethynylcyclohexane, **12**.

The β-fluorine of **6c** could be replaced by reactions with benzylamine, giving **13a**, aniline, **13b**, and *m*-chlorophenol, **13c**.

The NMR spectra of **6e** show some unusual long-range coupling constants from which the mechanism of the transmission of spin information can be inferred. The ^1H NMR spectrum of **6e** shows a phenyl multiplet and an eight-line pattern for the vinyl proton, indicating that the vinyl proton is coupled to all three fluorines. The proton-noise-decoupled ^{19}F NMR spectrum consists of three doublets of doublets, showing that all fluorines are coupled to each other. NMR and structural data for **6e** are summarized in Table I. The signs of the F–F couplings were determined by homonuclear INDOR experiments with heteronuclear proton noise decoupling. The two pyrone fluorines are positively identified by comparing the chemical shifts with those of **6a**. The 2.2-Hz coupling between F_a and F_c involves atoms separated by 10 Å and nine bonds and can in no way arise from "through-space" interactions. The corresponding coupling in 4,4′-difluorobiphenyl was not observable.[6] However, in other molecules with intervening substituents which allow the two aromatic rings to be coplanar such as N=N, CH=CH, and CH=CHCH=CH, couplings of 1.0, 0.4, and 0.5 Hz, respectively, were observed between 4,4′-difluorobiphenyl groups.[7] Comparable proton–proton couplings have been observed in polyynes.[8]



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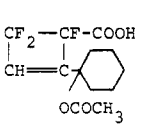

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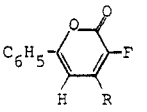
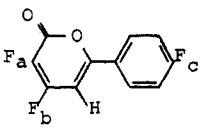


13a R = $NHCH_2C_6H_5$
b R = NHC_6H_5
c R = OC_6H_4Cl-*m*



6e

The large couplings in **6e** may result from the near planarity of the two rings as judged from UV spectra (Table II) and simple steric considerations. A ring oxygen is smaller than a CH bond in the corresponding biphenyl, thus favoring the planar structure.[9] It should be apparent from the couplings in **6e** that any correlation of fluorine–fluorine coupling with internuclear distance has limited application at best and that, in general, coupling cannot be predicted from internuclear distance nor internuclear distance from coupling. Many of the previous examples of "through-space" fluorine–fluorine or proton–fluorine coupling have in common the possibility of transmitting the spin information through a π system.[10] Separating

(1) Contribution No. 2787.
(2) England, D. C.; Solomon, S; Krespan, C. G. *J. Fluorine Chem.* **1973**, *3*, 63.
(3) England, D. C.; Krespan, C. G. *J. Fluorine Chem.* **1973**, *3*, 91.
(4) England, D. C. U.S. Patent 3 723 470, 1973.
(5) England, D. C.; Krespan, C. G. *J. Org. Chem.* **1970**, *35*, 3308.
(6) Cooper, M. A.; Weber, H. E.; Manatt, S. L. *J. Am. Chem. Soc.* **1971**, *93*, 2369.
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(8) Snyder, E. I.; Roberts, J. D. *J. Am. Chem. Soc.* **1962**, *84*, 1582.
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Scheme I

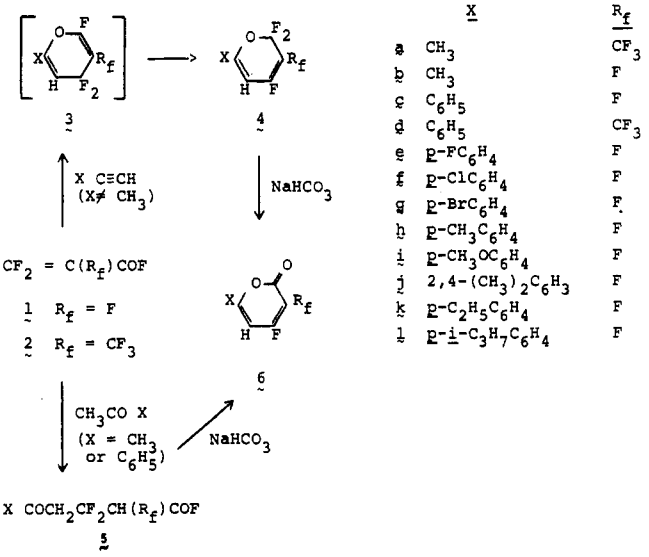
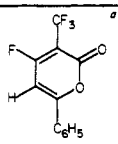
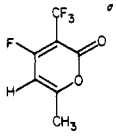


Table I. NMR and Structural Data for Pyrone 6e[a]

	H	F_a	F_b	F_c
H	6.56	4.5	2.6	6.1
F_a	4.6	−164.5	2.7	9.7
F_b	8.6	±16.4	−118.4	8.7
F_c	0.45	±2.2	±0.65	−107.5[b]

[a] The diagonal elements are chemical shifts (^1H in parts per million from Me_4Si and ^{19}F in parts per million from $CFCl_3$); elements above and to the right of the diagonal are internuclear distances (Dreiding models) in nanometers; elements to the left and below the diagonal are coupling constants in hertz. [b] The intraring H-F couplings of F_c are unexceptional.

Table II. UV Data for Pyrones and Model Compounds

compd	λ_{max}	ϵ
 [a]	332	15000
	240	5430
	223	6410
 [a]	292	6220
1,3-cyclohexadiene[b]	257	4360
1-phenyl-1,3-cyclohexadiene[b]	248	8930
biphenyl[b]	247	20000

[a] In ethanol. [b] "Organic Electronic Spectral Data"; Kamlet, M. J., Ed.: Interscience: New York, 1960.

these effects requires the synthesis of saturated compounds with fluorines in analogous positions.

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.

3,3-Difluoro-5-oxo-2-(trifluoromethyl)hexanoyl Fluoride (5a) and 4-Fluoro-6-methyl-3-(trifluoromethyl)-2*H*-pyran-2-one (6a). A mixture of 15.8 g (0.089 mol) of **2** and 5 g (0.086 mol) of acetone was distilled into an acid-washed Carius tube which was sealed and heated overnight on a steam bath. Distillation gave 6 g (29%) of **5a** [bp 72 °C (20 mm)] and 1.8 g (10%) of **6a**, which solidified and could be recrystallized from carbon tetrachloride; mp 77–78 °C. Longer heating (36 h) raised the yields slightly to 36% and 12%, respectively. A sample (8 g) of **5a** shaken in saturated sodium bicarbonate gave 3.6 g (55%) of **6a**.

For **5a**: IR 1859 (COF), 1736 cm^{-1} (C=O); ^1H NMR 1.89 (s, 3), 3.11 (t, 2, J = 16 Hz), 4.61 ppm (m, 1); ^{19}F NMR −65 (d, 3, J = 18 Hz, to t, J = 9 Hz), −94.6 (m, 2), 50.4 ppm (q, 1, J = 9 Hz, to t, J = 9 Hz).

Anal. Calcd for $C_7H_6F_6O_2$: C, 35.62; H, 2.56; F, 48.31. Found: C, 35.89; H, 2.64; F, 47.84.

For **6a**: IR 1733 (C=O), 1653 and 1592 cm^{-1} (C=C); ^1H NMR 1.88 (m, 3), 5.99 ppm (d, 1, J = 9.5 Hz); ^{19}F NMR −60.8 (d, 3, J = 25 Hz), −86.5 ppm (q, 1, J = 25 Hz, to d, J = 9.5 Hz).

Anal. Calcd for $C_7H_4F_4O_2$: C, 42.89; H, 2.06; F, 38.78. Found: C, 42.92; H, 1.94; F, 38.65.

3,4-Difluoro-6-methyl-2*H*-pyran-2-one (6b). A mixture of 34 g of **1** and 50 mL of acetone was heated in a Hasteloy bomb at 175 °C for 8 h. The tarry product was distilled, and the distillate washed with water and redistilled to give 1.2 g of pyrone **6b**, bp 70 °C (2.8 mm). It was 95% pure by GLC but darkened on standing and gave poor analyses. However, the structure was confirmed by IR and NMR comparison with the analogous pyrone **6a** made from perfluoromethacryloyl fluoride above: IR 1754 (C=O), 1689 and 1613 cm^{-1} (C=C); ^1H NMR 5.98 (d, 1, J = 8.7 Hz, to d, J = 4.8 Hz), 1.98 ppm (d, 3, J = 1.5 Hz); ^{19}F NMR −120.6 ppm (d, 1, J = 16.8 Hz, to d, J = 4.8 Hz, to q, J = 1.5 Hz).

3,4-Difluoro-6-phenyl-2*H*-pyran-2-one (6c). A mixture of 50 g of acetophenone and 34 g of **1** was heated to 175 °C for 8 h in a Hasteloy bomb. Distillation of the crude product gave a fraction boiling about 132 °C (2 mm) which was recrystallized from carbon tetrachloride to give 3.7 g (6.7%) of pyrone **6c**, mp 107–118 °C. It was the same material prepared from phenylacetylene by IR and mixed melting point (see below). Apparently hydrolysis of **5c** to **6c** occurred during workup.

2,2,3,4-Tetrafluoro-6-phenyl-2*H*-pyran (4c), 6c (See Above), 1,4,4-Trifluoro-2-phenyl-2-cyclobutene-1-carbonyl Fluoride (8, X = C_6H_5; Acid Fluoride), 1,4,4-Trifluoro-2-phenyl-2-cyclobutene-1-carboxylic Acid (8, X = C_6H_5), and 1,2-Difluoro-4,5-diphenylbenzene (9). A mixture of 20 g (0.196 mL) of phenylacetylene and 18 mL (0.2 mol) of **1** in a sealed tube was heated on a steam bath for 48 h and became black. After removal of 8 g of low boilers there was distilled 22.4 g (49%) of material boiling mostly at 56–66 °C (0.5 mm). It was a mixture of compounds **4c** and **8** (X = C_6H_5) in a ratio of about 2:1 as determined by NMR. Compound **4c** was concentrated in the higher boiling fractions. Continued distillation gave 2 g of material boiling about 140 °C (0.5 mm) which was recrystallized from petroleum ether to give 0.5 g of compound **9**, mp 95–7 °C.

A portion (5 g) of the above distilled mixture of **4c** and **8** (X = C_6H_5) was stirred in 25 mL of 10% aqueous sodium bicarbonate. Filtration gave 3.4 g of insoluble material which when recrystallized from carbon tetrachloride gave 2.1 of compound **6c**, mp 131–132 °C. Acidification of the filtrate gave 1.55 g of oil which crystallized and could be recrystallized from carbon tetrachloride to give 1.2 g of the acid **8** (X = C_6H_5), mp 104–106 °C.

The following experiment is in agreement with compound **9** being formed in a secondary reaction of **4c** with phenylacetylene. With an excess of phenylacetylene (30 g, 0.3 mol) with **1** (8 mL, 0.1 mol) for a longer time (6 days) on a steam bath, nearly all of the compound **4c** was consumed, and 5 g of compound **8** (X = C_6H_5) and 5 g of recrystallized **9** were isolated along with about 1 g of the hydrolysis product **6c**. In one attempt to react compound **4c** (in an isolated mixture with **8**) with phenylacetylene to give **9**, only the hydrolysis product **6c** was isolated, and much decomposition took place. However, this same mixture containing **4c** did react with dimethyl acetylenedicarboxylate to give **10** with loss of COF_2 (see below).

(10) Agranat, I.; Rabinovitz, M.; Gosnay, I.; Weitzer-Dagan, A. *J. Am. Chem. Soc.* **1972**, *94*, 2889. Gribble, G. W.; Douglas, J. R. *Ibid.* **1970**, *92*, 5764. Servis, K. L.; Jerome, F. R. *Ibid.* **1971**, *93*, 1535. Abushanab, E. *Ibid.* **1971**, *93*, 6532. Myhre, P. C.; Edmonds, J. W.; Kruger, J. D. *Ibid.* **1966**, *88*, 2459. Petrakis, L.; Sederholm, C. H. *J. Chem. Phys.* **1961**, *35*, 1243.

Compounds **4c** and **8** (X = C_6H_5; acid fluoride) were characterized in a mixture of the two compounds.

For **4c**: ^1H NMR 5.30 (d, 1, J = Hz, to d, J = 5 Hz), 6.81 ppm (s, 5); ^{19}F NMR −48.4 (d, 2, J = 20 Hz, to d, J = 12 Hz), −175.8 (t, 1, J = 20 Hz, to d, J = 9 Hz, to d, J = 5 Hz), −139.9 ppm [t, 1, J = 12 Hz, to t (overlapping doublets), J = 9 Hz].

For **8** (X = C_6H_5; acid fluoride): IR 1852 cm^{-1} (COF); ^1H NMR 6.09 (d, 1, J = 5.5 Hz, to d, J = 2.0 Hz), 6.81 ppm (s, 5); ^{19}F NMR 30.5 (d, 1, J = 18.0 Hz, to d, J = 9 Hz, to d, J = 2.0 Hz), −162.5 [t, 1, J = 18 Hz (overlapping d's, J = 18 Hz), to d, J = 9.5 Hz, to d, J = 5.5 Hz), AB pattern at −100.7 and −104.2 (d, 1, J = 18 Hz, to d, J = 9 Hz, to d, J = 2.0 Hz), −106.0 and −109.5 ppm (d, 1, J = 9.5 Hz, with fine structure).

Anal. Calcd for $C_{11}H_6F_4O$: C, 57.44; H, 2.63; F, 33.04. Found for the mixture: C, 57.70; H, 2.58; F, 33.04.

For **6c**: IR 1724 cm^{-1} (C=O); ^1H NMR 6.58 (d, 1, J = 5.0 Hz, to d, J = 9.0 Hz), 7.10 ppm (m, 5); ^{19}F NMR −167.6 (d, 1, J = 16.0 Hz, to d, J = 5.0 Hz), −121.8 ppm (d, 1, J = 16.0 Hz, to d, J = 9.0 Hz).

Anal. Calcd for $C_{11}H_6F_2O_2$: C, 63.51; H, 2.91; F, 18.27. Found: C, 63.44; H, 3.01; F, 18.13.

For **8** (X = C_6H_5): IR 1733 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) 11 (s, 1), 7.42 (s, 5), 6.75 ppm (d, 1, J = 5.5 Hz, to t, J = 1.5 Hz); ^{19}F NMR −163.1 (d, 1, J = 18.0 Hz, to d, J = 8.0 Hz, to d, J = 5.5 Hz), AB pattern at −101.1 and −104.5 (d, 1, J = 18 Hz, to d, J = 1.5 Hz), −105.8 and −109.2 ppm (d, 1, J = 8 Hz, b).

Anal. Calcd for $C_{11}H_7F_3O_2$: C, 57.94; H, 3.09; F, 25.00. Found: C, 57.90; H, 3.15; F, 24.07.

For **9**: ^1H NMR 6.92 (m, 10), 7.01 ppm (t, 2, J = 9.3 Hz); ^{19}F NMR −139.3 ppm (t, 2, J = 9.3 Hz).

Anal. Calcd for $C_{18}H_{12}F_2$: C, 81.27; H, 4.55; F, 14.29; mol wt 266. Found: C, 81.35; H, 4.46; F, 14.28; mol wt 266 (mass spectrum).

Dimethyl 3,4-Difluoro-6-phenyl-1,2-benzenedicarboxylate (10). A mixture of 5.6 g (0.04 mL) of dimethyl acetylenedicarboxylate and 9 g of a mixture of **4c** and **8** (X = C_6H_5; acid fluoride) (about 67% **4c**; 6.0 g, 0.026 mol) was sealed in a Carius tube and heated 60 h on a steam bath. Considerable decomposition occurred, but distillation gave 1.4 g of product [bp 120 °C (0.6)] which solidified and could be recrystallized from carbon tetrachloride to give 0.4 g of **6c**. In addition, a fraction [bp 120–160 °C (0.6 mm)] solidified and was recrystallized from hexane three times and washed with cold alkali to give finally 1.6 g of **10**: mp 92–93 °C; IR 1745 and 1721 cm^{-1} (C=O); ^1H NMR 2.99 (s, 3), 3.32 (s, 3), 6.85 (s, 5), 7.00 ppm (d, 1, J = 11.0 Hz, to d, J = 8.0 Hz); ^{19}F NMR −135.5 (d, 1, J = 21.0 Hz, to d, J = 11.0 Hz), −141.6 ppm (d, 1, J = 21.0 Hz, to d, J = 8.0 Hz).

Anal. Calcd for $C_{16}H_{12}F_2O_4$: C, 62.80; H, 3.95; F, 12.42. Found: C, 62.63; H, 3.89; F, 12.27.

2,2,4-Trifluoro-3-(trifluoromethyl)-6-phenyl-2*H*-pyran (4d) and 4-Fluoro-6-phenyl-3-(trifluoromethyl)-2*H*-pyran-2-one (6d). A mixture of 22.5 mL (0.2 mol) of **2** and 21 g (0.2 mol) of phenylacetylene was sealed in a Carius tube and heated overnight on a steam bath. Six grams of $(CF_3)_2CHCOF$ (bp 30 °C) was recovered and characterized by gas chromatography and infrared spectroscopy. Most of the product (35 g, 62%) boiled at 78 °C (0.5 mm) and solidified. It could be recrystallized from petroleum ether (mp 48–50 °C) and was characterized as **4d**. Lower boiling fractions contained several components by gas chromatography, and higher boiling material crystallized and could be recrystallized from hexane to give 0.8 g of **7** (mp 100–108 °C), identical with a sample isolated from the reaction of $(CF_3)_2C$=C=O with phenylacetylene.[5] The filtrate from recrystallization of compound **4d** warmed in an open beaker overnight on a steam bath yielded compound **6d** which when recrystallized from acetonitrile melted at 149–151 °C. Compound **4d** in the lower boiling fractions (ca. 20 g) was also hydrolyzed to **6d** (8 g) by being warmed in water on a steam bath.

For **4d**: 1689 and 1626 cm^{-1} (C=C); ^1H NMR 6.10 (d, 1, J = 9.50 Hz), 7.50 ppm (m, 5); ^{19}F NMR −58.0 (d, 3, J = 37.0 Hz, to t, J = 16.0 Hz), −38.9 (d, 2, J = 26.0 Hz, to q, J = 16.0 Hz), −102 ppm (m, 1).

Anal. Calcd for $C_{12}H_6F_6O$: C, 51.47; H, 2.16; F, 40.71. Found: C, 51.87; H, 2.36; F, 40.74.

For **6d**: IR 1751 cm^{-1} (C=O); ^1H NMR 7.45 (m, 2), 7.07 (m, 3), 6.65 ppm (d, 1, J = 10.4 Hz, to q, J = 0.60 Hz); ^{19}F NMR −60.3 (d, 3, J = 25.0 Hz, to d, J = 0.6 Hz), −85.7 ppm (q, 1, J = 25.0 Hz, to d, J = 10.4 Hz).

Anal. Calcd for $C_{12}H_6F_4O_2$: C, 55.86; H, 2.34; F, 29.46. Found: C, 55.73; H, 2.39; F, 28.80.

3,4-Difluoro-6-(*p*-fluorophenyl)-2*H*-pyran-2-one (6e). (*p*-Fluorophenyl)acetylene (25 g) and **1** (27 g) were heated in a Hasteloy bomb at 140 °C for 4 h. After distillation at 78 °C (3 mm), the crude product was stirred with 250 mL of saturated sodium bicarbonate, extracted with chloroform, and recrystallized from cyclohexane to give **6e**: 10 g (37%); mp 79–81 °C.

Anal. Calcd for $C_{11}H_5F_3O_2$: C, 58.42; H, 2.23. Found: C, 58.95; H, 2.30.

3,4-Difluoro-6-(*p*-chlorophenyl)-2*H*-pyran-2-one (6f). (*p*-Chlorophenyl)acetylene (13.6 g, 0.1 mol) and **1** (15.3 g, 0.12 mol) were heated in a Carius tube at 140 °C for 3 h. After recovery of 5 g of **1** and distillation at 74–82 °C (0.7 mm), the crude product was stirred in 30 mL of 10% aqueous $NaHCO_3$. Filtration gave 2.85 g of solid which was purified by chromatography and sublimation to give 0.45 g (2%) of **6f**: mp 123–125 °C; ^1H NMR ($CDCl_3$, Me_4Si) 7.72 (q, 4), 6.74 ppm (d, 1, J = 5 Hz, to d, J = 9 Hz); ^{19}F NMR ($CDCl_3/CCl_3F$) −118 (d, 1, J = 9 Hz, to d, J = 16 Hz), −164 ppm (d, 1, J = 5 Hz, to d, J = 16 Hz).

Anal. Calcd for $C_{11}H_5O_2F_2Cl$: C, 54.47; H, 2.07; Cl, 14.61; F, 15.66. Found: C, 54.16; H, 2.34; Cl, 14.94; F, 15.48.

Acidification of the sodium bicarbonate extract yielded impure **8** (X = *p*-ClC_6H_4) which after sublimation and recrystallization from cyclohexane–benzene melted at 94.5–105 °C (1.35 g, 5%).

3,4-Difluoro-6-(*p*-bromophenyl)-2*H*-pyran-2-one (6g). (*p*-Bromophenyl)acetylene (18.1 g, 0.1 mol) and **1** (15.3 g, 0.12 mol) were heated in a Carius tube to 150 °C for 3 h. There was recovered 9.3 g of **1** and, by sublimation of the remaining material at 100 °C (0.25 mm), 4.3 g of semisolid. This was stirred in 25 mL of 10% $NaHCO_3$. The filtered solid (3.55 g) was recrystallized from 50 mL of CCl_4 to give 1.58 g (5%) of **6g**: mp 130.5–137 °C; ^1H NMR [$(CD_3)_2CO$, Me_4Si] 7.62 ppm (m, 5); ^{19}F NMR [$(CD_3)_2CO/CCl_3F$] −164 (d, 1, J = 9 Hz, to d, J = 16 Hz), −123 ppm (d, 1, J = 5 Hz, to d, J = 16 Hz).

Anal. Calcd for $C_{11}H_5BrF_2O_2$: C, 46.02; H, 1.75; F, 13.23. Found: C, 46.85; H, 2.04; F, 12.05.

3,4-Difluoro-6-(*p*-tolyl)-2*H*-pyran-2-one (6h). *p*-Tolylacetylene (11.6 g, 0.1 mol) and **1** (15.3 g, 0.12 mol) were heated in a Carius tube on a steam bath for 12 h. Workup as above gave 6 g of **1** and 8.8 g of distilled semisolid which after $NaHCO_3$ treatment was sublimed [90 °C (1 mm)] and recrystallized from benzene to give 4.3 g (10%) of **6h**: mp 106–107 °C; ^1H NMR [$(CD_3)_2CO$, Me_4Si] 7.27, 7.40, 7.71, and 7.84 (AB pattern, 4), 7.05 (d, 1, J = 4 Hz, to d, J = 9 Hz), 2.37 ppm (s, 3); ^{19}F NMR [$(CD_3)_2CO/CCl_3F$] −125 ppm (d, 1, J = 4.0 Hz, to d, J = 17.0 Hz).

Anal. Calcd for $C_{12}H_8F_2O_2$: C, 64.86; H, 3.63; F, 17.11. Found: C, 65.28; H, 3.85; F, 17.54.

3,4-Difluoro-6-(*p*-anisyl)-2*H*-pyran-2-one (6i). *p*-Anisylacetylene (10.1 g, 0.75 mol) and 12.8 g (0.1 mol) of **1** were heated to 140 °C for 4 h in a sealed tube. After removal of low boilers, the tarry residue was treated with $NaHCO_3$ and extracted with ether. The ether extract was purified by chromatography and recrystallized from $CHCl_3$ to give 1.5 g of **6i**, mp 134.5–135.5 °C.

Anal. Calcd for $C_{12}H_8F_2O_3$: C, 60.51; H, 3.39. Found: C, 60.57; H, 3.41.

3,4-Difluoro-6-(2,4-dimethylphenyl)-2*H*-pyran-2-one (6j). (2,4-Dimethylphenyl)acetylene (20.49 g, 0.16 mol, 75%) and 20.25 g (0.16 mol) of **1** were heated in a sealed tube on a steam bath for 48 h. Distillation at 88 °C (0.9 mm) gave a clear yellow liquid which was stirred with saturated $NaHCO_3$ solution and extracted with $CHCl_3$. The dried extract after removal of solvent and recrystallization of the residue from cyclohexane gave 8.5 g of **6j**, mp 83–84.5 °C.

Anal. Calcd for $C_{13}H_{10}F_2O_2$: C, 66.11; H, 4.27. Found: C, 66.13; H, 4.25.

3,4-Difluoro-6-(*p*-ethylphenyl)-2*H*-pyran-2-one (6k). (*p*-Ethylphenyl)acetylene (19.5 g, 0.15 mol) and 21.8 g (0.17 mol) of **1** were heated in a Carius tube at 120 °C for 4 h. After removal of low boilers, the residue was stirred in saturated $NaHCO_3$ solution for 24 h and extracted with ether. After removal of the ether, the tarry residue was purified by chromatography to give 6.4 g of **6k**, mp 94–97 °C.

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 $C_{13}H_{16}F_3O_4$: 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; ^{1}H 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; ^{1}H 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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