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.

0022-3263/81/1946-0153$01.00/0

Scheme I

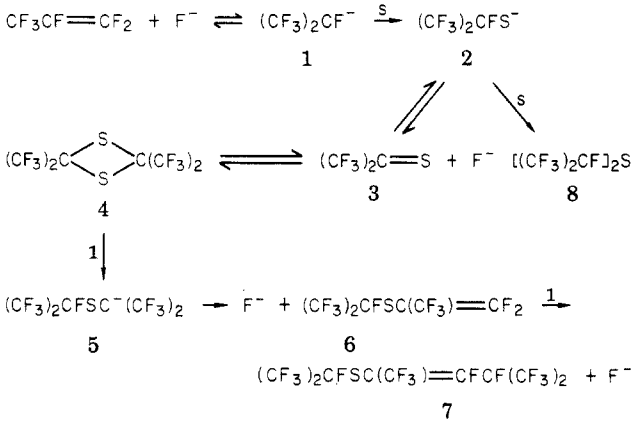
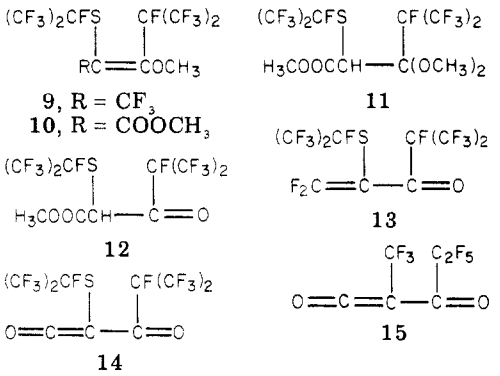


Chart I



from it, many new compounds were prepared, including a vinyl ketone (13) and an acylketene (14). Ready availability of the latter made it of interest to compare its chemistry to that of the first acylketene (15) to be isolated.[1]

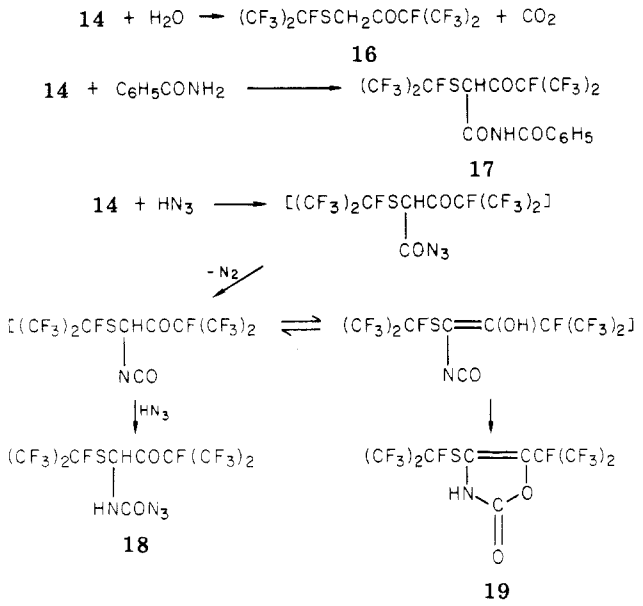
Results and Discussion

Preparation of Perfluorovinyl Sulfide 7. The reaction of HFP with sulfur and potassium fluoride in DMF was carried out conveniently in a glass vessel slightly below atmospheric pressure. It could be controlled to give good yields of the dimer of hexafluorothioacetone (4), or this product could be made to react further to give *E* and *Z* isomers of 7.[5] Two minor products were HFP dimer and perfluoroisopropyl sulfide (8).[6] Our interpretation of the reaction is shown in Scheme I.

The perfluoroisopropyl anion 1 formed from HFP and fluoride ion attacks sulfur to give anion 2 which can lose fluoride ion to form hexafluorothioacetone (3) which dimerizes to 4. We have been able to stop the reaction at this point with good yields of 4 or to continue it in the same or a separate step, with anion 1 attacking 4 to give, through the probable intermediates 5 and 6, good yields of the vinyl sulfide 7. The sulfide 8 must be formed through oxidation of the anion 2 by sulfur.

Preparation of Vinyl Ketone 13 and Acylketene 14. The four compounds 9–12 (Chart I) have been isolated as products from the reaction of the vinyl sulfide 7 with potassium hydroxide in methanol. The acylketene 14 was

Scheme II

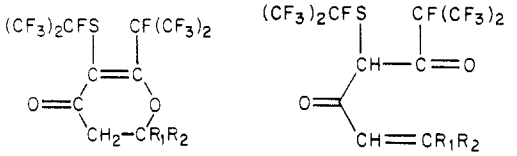


the product of reactions of 10, 11, or 12 with sulfur trioxide. The reaction of 9 with sulfur trioxide gave the vinyl ketone 13 which was partially hydrolyzed to the acylketene 14 on workup.

The chemistry of compound 14 is like that reported[1] for the first acylketene 15 in reactions summarized below with water, benzamide, hydrazoic acid, dienophiles, and aromatic compounds. Differences were observed in reactions involving fluoride ion, dimethylformamide, dimethylacetamide, and tetramethylurea.

Reactions with Water, Hydrazoic Acid, and Benzamide. Hydrolysis of 14 was accompanied by decarboxylation to give the ketone 16 (Scheme II). Reaction of 14 with benzamide gave 17. Reaction of 14 with hydrazoic acid gave 18 and 19. The initial product expected could be an acid azide which would undergo Curtius rearrangement to an isocyanate which could then either cyclize to give 19 or add hydrazoic acid to give 18.

Diels–Alder Additions to C=C. Reaction of 14 with isobutylene gave the cyclic adduct 20 along with some of the acyclic adduct 21. Reaction with styrene gave the cyclic adduct 22 or, under acid conditions, the acyclic adduct 23. Compound 22 was ring opened to 23 by hot sulfuric acid.



Diels–Alder addition of 14 to vinyl acetate was accompanied by loss of acetic acid to give the parent pyrone 24 of addition to acetylenes.

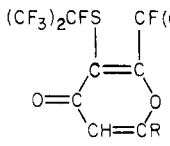
Diels–Alder Additions to C≡C. The reaction of 14 with phenylacetylene gave 25 and with butylacetylene gave 26.

Diels–Alder Additions to C=O. Adducts of 14 with propionaldehyde (27) and benzaldehyde (28) could be isolated, but the former reverted to starting materials on attempted distillation. No acetone adduct could be isolated.

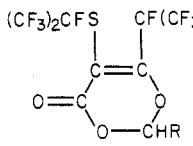
Diels–Alder Additions to C≡N and C=N. The adducts of 14 with dimethylcyanamide (29), methyl thio-

(5) Our product 7 is undoubtedly the same product isolated by the above authors[4] and postulated by them to have the structure $(CF_3)_2CFSCF{=}C(CF_3)CF_2CF_2CF_3$ formed by attack of anion 2 on the terminally unsaturated dimer of HFP, $CF_2{=}C(CF_3)CF_2CF_2CF_3$. This structure is ruled out for our product by NMR and by its chemical reactions reported here.

(6) Dyatkin et al.[4] report $(CF_3)_2CFSSCF(CF_3)_2$. Analyses rule out this structure for our product.

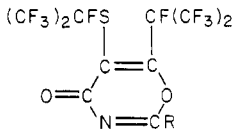


24, R = H
25, R = C_6H_5
26, R = C_4H_9

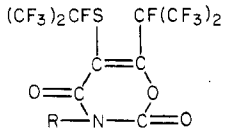


27, R = C_2H_5
28, R = C_6H_5

cyanate (30), and isocyanates 31–33 were prepared. The adducts from acetonitrile and benzonitrile were not stable to distillation, reverting to starting materials.

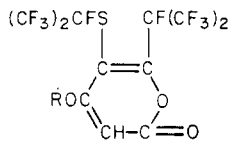


29, R = $N(CH_3)_2$
30, R = SCH_3

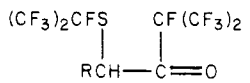


31, R = CH_3
32, R = C_2H_5
33, R = C_6H_5

Diels-Alder Addition to Ketene. Addition of 14 to the C=C bond of ketene was accompanied by a 1,3 hydrogen shift to give the hydroxy pyrone 34 and its acetylated product 35.



34, R = H
35, R = CH_3CO



36, R = *p*-$(CH_3)_2NC_6H_4CO$

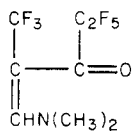
37, R = 

38, R = 

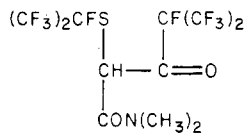
Electrophilic Substitution on Aromatic Rings. Reaction of 14 with dimethylaniline gave 36, with furan gave 37, and with thiophene gave 38.

Fluoride Ion. Under conditions of fluoride ion catalysis that gave a dimer and other products from acylketene 15,[1] acylketene 14 remained unchanged.

Dimethylformamide. The reactions of the two acylketenes follow different courses. Whereas acylketene 15 is subject to nucleophilic attack by the oxygen of DMF, resulting in loss of CO_2 to give 39,[1] acylketene 14 is subject to nucleophilic attack by the nitrogen of DMF, resulting in loss of CO to give 40.



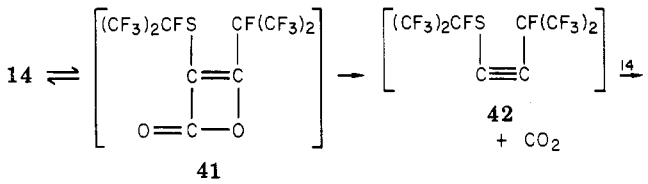
39



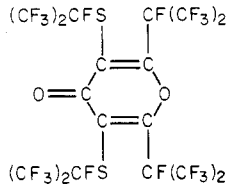
40

Self-Condensation. In the presence of a weak base such as dimethylacetamide or dimethylpropionamide, 14 underwent a self-condensation reaction with loss of CO_2 to give the pyrone 43. One can postulate the existence of an equilibrium amount of the unsaturated lactone 41 which loses CO_2 to give the acetylene 42 which adds to the acylketene, giving 43 (eq 1). The structure of 43 was confirmed by X-ray analysis.[7] This reaction was not observed with acylketene 15.

Reaction with Tetramethylurea. Tetramethylurea reacted with acylketene 15 at room temperature, evolving CO_2 and C_2F_5COF. However, no other product could be isolated. Under the same conditions acylketene 14 gave

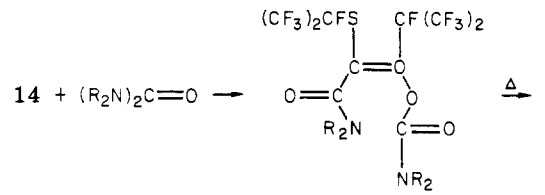


41 42 + CO_2



43 (1)

the amide–urethane 44 by cleavage of a C–N bond of the urea. Heating this compound gave 31 which had been prepared from 14 and methyl isocyanate (eq 2).



44, R = CH_3
45, R = C_2H_5

R_3N + 31 (R = CH_3) or 32 (R = C_2H_5) (2)

The fluorine magnetic resonance of 44 in acetone shows nonequivalence of the CF_3 groups, indicating that the compound must be held in a conformation which lacks a plane of symmetry. In dimethyl sulfoxide this structure is apparently destroyed by solvation because the CF_3 groups become equivalent. The phenomenon is reversible by removal of dimethyl sulfoxide and replacement of it with acetone. In addition, all of the methyl groups are nonequivalent because of restricted rotation around nitrogen[8] at room temperature. When the mixture is warmed, the methyl groups on the urethane nitrogen became equivalent before those on the amide nitrogen.

Reaction of 14 with tetraethylurea was apparently similar, but 45 did not crystallize. Attempted distillation caused decomposition and gave some of 32.

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 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; chemical shifts are reported in parts per million downfield from $CFCl_3$ as internal standard.

Experimental details leading to the acylketene 14 are given below. Products prepared from it are listed in Table I, with details of their preparation and characterization being available as supplementary material.

2,2,4,4-Tetrakis(trifluoromethyl)-1,3-dithietane (4), *cis*- and *trans*-2-[[1-(Trifluoromethyl)-1,2,2,2-tetrafluoroethyl]thio]-4-(trifluoromethyl)-1,1,1,3,4,5,5,5-octafluoro-2-pentene (7), and Bis(heptafluoroisopropyl) Sulfide (8). Potassium fluoride (25 g) was vacuum dried in a 3-L, three-necked flask by being heated with a hot-air gun under vacuum. After the flask was cooled and flushed with nitrogen, 64 g (2 mol) of sulfur (vacuum dried) and 200 mL of purified DMF were added, the flask was tared, evacuated, and pressured with HFP (maintained automatically at ca. 740 mm), and the mixture was vig-

(7) Schmutzler, R; Schomburg, D. Lehrstuhl B für Inorganische Chemie, Technische Universität, Braunschweig, West Germany, private communication.

(8) Phillips, W. D., *J. Chem. Phys.* **1955**, *23*, 1363.

Table I

no.	yield, %	bp [mmHg] (mp, °C)
4	80	110 (25)
7	75	130-134
8		80
9	8.5	30-35 [1.5]
10	18	77 [5] (56-57)
11	21	105 [5]
12	16	45 [5.5]
13	15	40 [10]
14	94	70 [40]
16	97	101
17	54	(83-86)
18	21	(53-54)
19	5	89-98 [1] (68-69)
20 + 21	63	65-70 [0.2]
22	32.5	(81-83)
23	44	(70-71)
24	35	(64-65)
25	15	(119-120)
26	31	105 [0.5]
27	100	reversible
28	83.5	(52-53)
29	76	(148-150)
30	48	(99-101)
31	75	(95-97)
32		(76-78)
33	63	(102-104)
34	28	(125-126)
35	41	90 [0.2]
36	56	(88-90)
37	90	78 [1.4]
38	77	75 [0.16]
40	76	80 [0.5]
43	65	(106-108)
44	88	(76-80)

orously stirred. After the mixture was heated to 75 °C to start the reaction, it was exothermic to 83 °C. It was stopped while still reacting (856 g of HFP absorbed) and started again the next morning after addition of 25 g of fresh catalyst. This addition was not always necessary, but it did reactivate the reaction in case absorption of HFP stopped before the desired amount had been added. If the dimer of hexafluorothioacetone, **4**, was the desired product, the reaction was stopped when the sulfur had been consumed (ca. an equivalent amount of HFP absorbed). Yields of **4** were >80% along with minor amounts of HFP dimer and the sulfide **8**. The respective boiling points were 110, 50, and 80 °C.

This reaction was continued until an additional 151 g of HFP had been absorbed, making a total of 1007 g (6.7 mol). The mixture was then washed three times each with water and then concentrated H_2SO_4. After 181 g of a mixture of HFP dimer and trimer and sulfide **8** was distilled off, 707 g (75%) of **7** (cis and trans isomers, bp 130–134 °C) was obtained. Compound **7** could also be prepared in a similar reaction by starting with **4** instead of sulfur. The sulfide **8** could be purified by distillation: bp 80 °C; ^{19}F NMR −78.2 (d, 6, J = 2 Hz), −166.1 ppm (septet, 1, J = 2 Hz).

Anal. Calcd for $C_6F_{14}S$: F, 71.89; S, 8.65. Found: F, 71.90; S, 7.90.

The cis and trans isomers of **7** were separated by preparative gas chromatography (Fluorosilicone on Gas Chrom R). Although the fluorine magnetic resonance was not clearly resolved, strong doublet splitting (40 Hz) for the CF_3 group would indicate that it is cis to the vinyl fluorine in **7b**. For **7a** (trans): IR 1647 (C=C), 812, 763, 744, 726 cm^{-1}; ^{19}F NMR −62.3 (m, 3), −76.3 (m, 13), −159.4 (m, 1), −178.8 ppm (m, 1). For **7b** (cis): IR 1645 (C=C), 789, 755, 748, 737 cm^{-1}; ^{19}F NMR −55.4 (m with doublet splitting, 3, J = 40.0 Hz), −73.2 (m, 1), −76.0 (m, 6), −77.0 (m, 6), −159.8 (m, 1), −186.3 ppm (m, 1).

Anal. Calcd for $C_8F_{18}S$: C, 22.43; F, 70.95; S, 6.65. Found for **7a**: C, 22.79; F, 69.47; S, 6.69. Found for **7b**: C, 22.78; F, 69.37; S, 6.75.

1,1,1,4,5,5,5-Heptafluoro-2-[[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]thio]-4-(trifluoromethyl)-3-methoxy-2-pentene (9), Methyl 4,5,5,5-Tetrafluoro-3-methoxy-2-[[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]thio]-4-(trifluoromethyl)-2-pentenoate (10), Methyl 4,5,5,5-Tetrafluoro-3,3-dimethoxy-2-[[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]thio]-4-(trifluoromethyl)pentenoate (11), and Methyl 4,5,5,5-Tetrafluoro-3-oxo-2-[[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]thio]-4-(trifluoromethyl)pentanoate (12). A solution of 132 g of 85% KOH (2 mol) in 500 mL of methanol was cooled to −30 °C and 250 g (0.5 mol) of the vinyl sulfide **7** added slowly. When the addition was complete, cooling was stopped and stirring continued. The exothermic reaction was cooled if necessary to keep the temperature below 50 °C. After being stirred for 1 h at room temperature, the mixture was poured into cold water, and the heavy layer was washed with water, dried, and distilled. There was obtained 37 g [16%; bp 47–63 °C (8.5 mm)] largely of **12**, 21 g [8.5%; bp 65–70 °C (8.5 mm)] largely of **9**, 43 g [18%; bp 75–95 °C (8.5 mm)] largely of **10**, and 53 g [21%; bp 100–112 °C (8.5 mm)] largely of **11**.

More refined boiling points, refractive indices, and other data for these compounds are given below.

For **9** (first isomer): bp 30 °C (1.5 mm); n^{25}_D 1.3385; IR 1600 cm^{-1} (C=C); ^1H NMR 3.80 ppm (s, 3); ^{19}F NMR −60.4 (d, 3, J = 13.8 Hz), −75.2 (d, 6, J = 6.0 Hz), −75.7 (t, 6, J = 8.0 Hz), −158.9 (m, 1), −170.0 ppm (m, 1).

For **9** (second isomer): bp 35 °C (1.5 mm); n^{25}_D 1.3380; IR 1600 cm^{-1} (C=C); ^1H NMR 3.90 ppm (s, 3); ^{19}F NMR −54.6 (d, 3, J = 45.0 Hz), −74.6 (br, 6), −77.0 (d, 6, J = 10.0 Hz), −162.7 (m, 1), −180.3 ppm (q, 1, J = 45.0 Hz, to septet, J = 4.9 Hz).

Anal. Calcd for $C_{10}H_3F_{17}SO$: C, 24.31; H, 0.61; F, 65.38; S, 6.49. Found for first isomer: C, 24.08; H, 0.58; F, 65.35; S, 6.66. Found for second isomer: C, 24.25; H, 0.64; F, 64.94; S, 6.66.

Mass measurement gave mol wt 493.9566 for both isomers (calcd mol wt 493.9632).

For **10** (liquid isomer purified by GLC): bp 77 °C (5 mm); n^{25}_D 1.3650; IR 1754 (C=O), 1613 cm^{-1} (C=C); ^1H NMR 4.13 (s, 3), 3.80 ppm (s, 3); ^{19}F NMR −74.0 (d, 6, J = 6.0 Hz), −74.8 (d, 6, J = 10.5 Hz), −177.0 (s, 1, J = 6.0 Hz), −173.3 ppm (s, 1, J = 10.5 Hz).

For **10** (solid isomer): mp 56–57 °C; IR 1745 (C=O), 1605 cm^{-1} (C=C); ^1H NMR (20% $CDCl_3$) 3.87 ppm (s, 6); ^{19}F NMR −73.8 (d, 6, J = 6.7 Hz), −74.9 (d, 6, J = 10.8 Hz, to d, J = 7.0 Hz), −162.7 (septet, 1, J = 10.8 Hz), −173.9 ppm (septet, 1, J = 6.7 Hz, to septet, J = 7.0 Hz).

Anal. Calcd for $C_{11}H_6F_{14}SO_3$: C, 27.27; H, 1.23; F, 54.96; S, 6.61. Found for **10** (liquid isomer): C, 27.48; H, 1.41; F, 54.14; S, 6.18. Found for **10** (solid isomer): C, 26.69; H, 1.29; F, 54.00; S, 6.41.

For **11**: bp 105 °C (5 mm); n^{25}_D 1.3730; IR 1760 (C=O); ^1H NMR 4.0 (s, 3), 3.78 (s, 3), 3.46 (s, 3), overlapping peaks (1 H); ^{19}F NMR −71.46 (m, 6), −74.85 (m, 3), −75.42 (m, 3), −180.9 (m, 1), −164.3 ppm (m, 1).

Anal. Calcd for $C_{12}H_{20}F_{14}SO_4$: C, 27.92; H, 1.95; F, 51.52; S, 6.21. Found: C, 27.56; H, 1.69; F, 54.26; S, 5.59.

For **12**: bp 45 °C (5.5 mm); n^{25}_D 1.3408; IR 1767 (C=O); ^1H NMR 4.97 (d, 1, J = 2.5), 3.22 ppm (s, 3); ^{19}F NMR −75.3, −75.6, −76.0 and −77.3 (m, 12), −162.0 and −163.5 (m, 1), −177.0 and −184.1 ppm (m, 1); mass spectrum, calcd m/e 469.9657, found m/e 469.9619.

Anal. Calcd for $C_{10}H_4F_{14}SO_3$: C, 25.53; H, 0.85; F, 56.60; S, 6.80. Found: C, 25.64; H, 0.94; F, 56.39; S, 6.06.

2-[[1-(Trifluoromethyl)-1,2,2,2-tetrafluoroethyl]thio]-4-(trifluoromethyl)-1,1,4,5,5,5-hexafluoro-1-penten-3-one (13). This reaction required heating, and the vinyl ketone product **13** apparently formed a loose complex with SO_3 which was decomposed by heat or cold water. The vinyl ketone was rather easily hydrolyzed to the acylketene **14**.

A mixture of 28 g of the vinyl sulfide **9** and 5 mL of SO_3 was distilled, and starting materials were recovered. The recovered **9** and 5 mL of fresh SO_3 were sealed in a Carius tube and heated in a steam bath overnight. It now separated into two layers. The top layer was mostly CH_3OSO_2F. After the mixture was washed with cold water, there was obtained 15.5 g of product boiling at 38–53 °C (10 mm). The vinyl ketone **13** was separated from acylketene **14** and starting material by preparative GLC. Another run gave a nearly pure cut: bp 40 °C (10 mm); n^{25}_D 1.326. Direct distillation of a crude reaction product at reduced pressure gave

13 complexed with SO_3; bp ca 80 °C (50 mm). Redistillation at atmospheric pressure gave 13 mixed with the acylketene 14, bp 140–147 °C. For 13: IR 1754 (C=O), 1681 cm^{-1} (C=C); ^{19}F NMR −73.06 (p, 6, J = 3.8 Hz), −75.26 (d, 6, J = 10.0 Hz), −53.08 (d, 1, J = 44.0 Hz, to d, J = 22.0 Hz, to s, J = 3.8 Hz), −55.54 (d, 1, J = 44.0 Hz, to m), −159.26 (m, 1), −181.11 ppm (d, 1, J = 22.0 Hz, to m); mass spectrum, calcd m/e 459.9414, found m/e 459.9452.

Anal. Calcd for $C_9F_{16}SO$: C, 23.49; F, 66.06; S, 6.97. Found: C, 23.70; F, 64.90; S, 7.42.

2-[[1-(Trifluoromethyl)-1,2,2,2-tetrafluoroethyl]thio]-4-(trifluoromethyl)-4,5,5,5-tetrafluoro-1-pentene-1,3-dione (14). From 12. Sulfur trioxide (20 mL) was stirred while 57.9 g of material which was largely compound 12 was added dropwise. The exothermic reaction was kept at about 50 °C by the rate of addition and cooling. When the addition was complete, the mixture separated into two layers. Distillation of the bottom layer gave 35 g (65%) of the acylketene 14. Some codistilled SO_3 was removed by washing with a little dioxane, separating, and distilling: bp 70 °C (40 mm); $n^{25}D$ 1.3472; IR 2179 (C=C=O), 1724 cm^{-1} (C=O); ^{19}F NMR −74.64 (d, 6, J = 6.6 Hz), −75.10 (d, 6, J = 10.0 Hz), −162.0 (s, 1, J = 10.0 Hz), −180.8 ppm (s, 1, J = 6.6 Hz); mass spectrum, calcd m/e 437.9395, found m/e 437.9430.

Anal. Calcd for $C_9F_{14}SO_2$: C, 24.67; F, 60.71; S, 7.32. Found: C, 24.63; F, 60.60; S, 7.77.

From 10. The ether ester 10 (60 g) was added dropwise with stirring to 14 mL of SO_3, and the exothermic reaction was kept below 65 °C. The bottom layer (60 g) was separated from the top layer (26 g) and distilled to give 51 g (94%) of 14.

From 11. The ketal ester 11 (100 g) was added dropwise with stirring to 40 mL of SO_3 with the exothermic reaction kept below 75 °C. The bottom layer (89 g) was separated from the top layer (75 g) and distilled to give 71.7 g (85%) of 14.

The yields, boiling points and/or melting points for compounds prepared in this work are listed in Table I. Details concerning their preparation and characterization, including infrared, NMR, and analytical data, are available as supplementary material.

Registry No. 4, 791-50-4; 7a, 75781-86-1; 7b, 75781-87-2; 8, 756-89-8; 9 (isomer 1), 75781-88-3; 9 (isomer 2), 75782-19-3; 10 (isomer 1), 75781-89-4; 10 (isomer 2), 75782-20-6; 11, 75781-90-7; 12, 75781-91-8; 13, 75781-92-9; 14, 75790-42-0; 16, 75781-93-0; 17, 75781-94-1; 18, 75781-95-2; 19, 75781-96-3; 20, 75781-97-4; 21, 75781-98-5; 22, 75781-99-6; 23, 75782-00-2; 24, 75782-01-3; 25, 75782-02-4; 26, 75782-03-5; 27, 75782-04-6; 28, 75782-05-7; 29, 75782-06-8; 30, 75782-07-9; 31, 75782-08-0; 32, 75782-09-1; 33, 75782-10-4; 34, 75782-11-5; 35, 75782-12-6; 36, 75782-13-7; 37, 75782-14-8; 38, 75782-15-9; 40, 75782-16-0; 43, 75782-17-1; 44, 75782-18-2; 45, 75790-43-1; isobutylene, 115-11-7; styrene, 100-42-5; vinyl acetate, 108-05-4; phenylacetylene, 536-74-3; butylacetylene, 693-02-7; propionaldehyde, 123-38-6; benzaldehyde, 100-52-7; acetone, 67-64-1; dimethylcyanamide, 1467-79-4; benzonitrile, 100-47-0; methyl isocyanate, 624-83-9; phenyl isocyanate, 103-71-9; methyl thiocyanate, 556-61-6; furan, 110-00-9; thiophene, 110-02-1; benzamide, 55-21-0; ketene, 463-51-4; dimethylformamide, 68-12-2; dimethylacetamide, 127-19-5; dimethylpropionamide, 758-96-3; tetramethylurea, 632-22-4; dimethylaniline, 121-69-7; tetraethylurea, 1187-03-7; hydrazoic acid, 7782-79-8; *N,N*-dimethyl-4,4,5,5,5-pentafluoro-2-(trifluoromethyl)-3-oxopentamide, 75782-21-7.

Supplementary Material Available: Details concerning properties and characterization (IR, NMR, analyses) of compounds reported in this work (21 pages). Ordering information is given on any current masthead page.

Synthesis and Reactions of N-Protected 2-Lithiated Pyrroles and Indoles. The *tert*-Butoxycarbonyl Substituent as a Protecting Group

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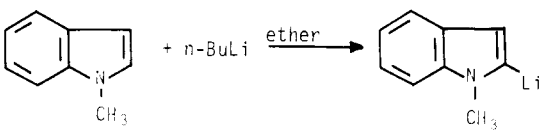
N-(*tert*-Butoxycarbonyl)pyrrole and *N*-(*tert*-butoxycarbonyl)indole have been prepared and lithiated at the 2-position with lithium 2,2,6,6-tetramethylpiperidide and *tert*-butyllithium, respectively. These lithium reagents react with a variety of electrophiles to give the 2-substituted *N*-(*tert*-butoxycarbonyl)pyrroles and *N*-(*tert*-butoxycarbonyl)indoles. The *N*-(*tert*-butoxycarbonyl) substituent may be removed rapidly and in high yield from the pyrrole derivatives under basic conditions. For the indole derivatives, the protecting group may be removed with either acidic or basic conditions.

The directed metalation of aromatic substrates[1] has provided an important synthetic alternative to electrophilic substitution reactions. The rapid expansion of the list of functionalities capable of directing metalations[2] has made this an important strategy for the synthesis of regiospecifically substituted benzenes[3] and heterocycles.[4] The utility of these lithiated derivatives is amply demonstrated by their use as intermediates for the preparation of complex natural products.[5]

Lithioindoles[6] and pyrroles[7] have been useful for the synthesis of regiospecifically substituted derivatives. For example, 2-lithio-*N*-methylindole[6] can be prepared by treatment of *N*-methylindole with *n*-butyllithium in ether (eq 1). Subsequent reaction with electrophiles leads to



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