probe cooled to $-50°$. The nmr spectra were taken after heating at different temperatures for varying times followed by quenching in Dry Ice–acetone. The heating schedules were 0.25, 0.5, 1, and 2 hr at 0° (wet ice bath) and 0.25, 0.5, 1, 2, 4, 8, 16, 20, and 24 hr at 25° (refluxing $CFCl_3$ bath).

2,2-Bis(trifluoromethyl)-3-(p-methoxyphenyl)cyclobutanone (22).—*p*-Methoxystyrene (27.0 g, 0.20 mol), 1 (43.0 g, 0.24 mol), 25 ml of benzene, and 0.1 g of phenothiazine were heated overnight at 100° in a sealed tube. After removal of volatiles, the resulting solid was recrystallized from CCl_4 to give 49 g (79%) of **22**, mp 84–86°. Another recrystallization gave an analytical sample, mp 85–87°. In other experiments, it was found that the reaction goes at 25° and the product can be distilled: bp 96° (1 mm); ir 5.53 μ (ring C=O); nmr [(CD₃)₂CO] ¹H at τ 3.2 (AA'BB', 4, aromatic CH), 6.3 (overlapping multiplets, 3, $CHCH_2$), 6.7 (singlet, 3, CH_3); ¹⁹F at 64.3 (quartet, 1, $J_{F/F}$ = 8.6 Hz, CF₃), 68.6 ppm (quartet, 1, $J_{F/F}$ = 8.6 Hz, CF₃).

Anal. Calcd for $C_{13}H_{10}F_6O_2$: C, 50.04; H, 3.23; F, 36.54. Found: C, 49.82; H, 3.16; F, 36.49.

In hexane at 25°, oxetane 21 was also formed, causing an nmr signal for ¹⁹F at 58.9 ppm (multiplet).

Ethyl 5,5,5-Trifluoro-4-(trifluoromethyl)penta-2,3-dienoate (24).—A sealed tube containing 14 g (0.20 mol) of ethoxyacetylene and 39 g (0.22 mol) of 1 was held at $-80°$ overnight in an attempt to control the exothermic reaction. Distillation gave 19.5 g (39%) of **24**: bp 68° (50 mm); $n^{25}D$ 1.3580; ir 5.03 (C=C=C), 5.77 μ (ester C=O); nmr ¹H at τ 3.77 (septet, 1, $J_{H/F}$ = 2.5 Hz, =CH), 6.12 (quartet, 2, $J_{H/H}$ = 7.2 Hz, CH₂), 9.10 (triplet, 3, $J_{H/H}$ = 7.2 Hz, CH₃); ¹⁹F at 62.6 ppm (doublet, $J_{H/F}$ = 2.5 Hz).

Anal. Calcd for $C_8H_6F_6O_2$: C, 38.74; H, 2.44; F, 45.97. Found: C, 39.10; H, 2.72; F, 46.31.

Evidence for oxete 23 was ¹⁹F nmr signals obtained at *ca.* 57.0 (quartet, 1, $J_{F/F}$ = 7.0 Hz, CF₃), 59.8 ppm (quartet, 1, $J_{F/F}$ = 7.0 Hz, CF₃), along with the doublet at 62.6 ppm when rapidly scanned while warming from $-80°$ in the probe at 30°. These quartets rapidly disappeared as the doublet signal became stronger.

Registry No.—**1**, 684-22-0; **2**, 4233-20-9; **3**, 4141-80-4; **4**, 25636-21-9; **5**, 25636-22-0; **6**, 25631-65-6; **8**, 25636-23-1; **9**, 25631-66-7; **10**, 25631-67-8; **11**, 25636-24-2; **12**, 25636-25-3; **13**, 25636-95-7; **14**, 143360-78-2; **15**, 21087-24-1; **17**, 25631-70-3; **18**, 25679-31-6; **20**, 25631-71-4; **22**, 25636-96-8; **24**, 25636-97-9; difluoromethyl hexafluoroisopropyl ketone, 25636-98-0.

# Fluoroketenes. VI. Cycloadditions of Cumulenes to Bis(trifluoromethyl)ketene[1]

DAVID C. ENGLAND AND CARL G. KRESPAN

Dimethylallene cycloadds to bis(trifluoromethyl)ketene to form both oxetane and cyclobutanone, but tetramethylallene forms only products of an ene reaction because of steric hindrance to ring closure. Cycloadditions of ketene and methylketene to bis(trifluoromethyl)ketene proceed easily and in good yield to form β lactones derived only from addition across the C=C of the nonfluorinated ketene. A dipolar intermediate is proposed for this reaction. Dimethylketene cycloadds to bis(trifluoromethyl)ketene to form both cyclobutanedione and β lactone, a change presumably induced by increased steric hindrance. The direction of this latter reaction is strikingly dependent on solvent polarity.

Allenes.—The reactions of bis(trifluoromethyl)ketene (1) with allenes and with simple olefins are somewhat analogous, indicating that some factors governing the reaction courses are similar. As with ethylene, allene itself has not been made to react with 1 up to 165°. 1,3-Dimethylallene showed reactivity like that of a vinyl ester[1] in that it gave an unusual cycloaddition to 1 (apparently unique for an allene–ketene combination) at 100° to form both cyclic ketone 2 and oxetane 3. The orientation of substituents in the adducts is that expected from bond formation at the central allene carbon atom to form stabilized dipolar intermediates and/or polar transition states.

$$(CF_3)_2C=C=O \ + \ CH_3CH=C=CHCH_3 \ \longrightarrow$$

<div align="center">1</div>
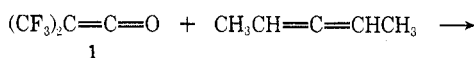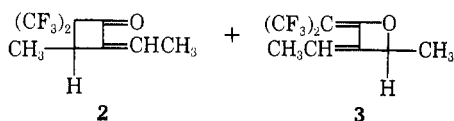
Tetramethylallene resembled isobutylene in its slow reaction with 1 at 25° to form only open-chain products of an ene reaction. Steric hindrance to closure of

either the normally stable cyclobutanone ring or the oxetane ring resulted in preferential formation of products of hydrogen migration. Even when equimolar amounts of reactants were used, the enol ester 5 was the major product (79%). The ketodiene 4 was isolated in only 9% yield and could not be reacted in a separate step with 1 to give 5. This is analogous to the formation of enol esters through intermediates not isolated in the reactions of 1 with butene-1 and with α-methylstyrene.[2]

$$1 \ + \ (CH_3)_2C=C=C(CH_3)_2 \ \longrightarrow$$
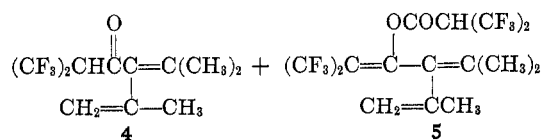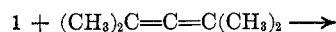
Ketenes.—Mixed ketene dimers have seldom been studied, presumably because of a tendency to form in low yield along with simple dimers.[3] Since ketene 1 does not dimerize thermally but is extremely reactive toward unsaturated nucleophiles, mixed dimers of 1 with various other ketenes form easily and in high yield. Dimers of both the 1,3-dione type 6 and β-lac-

(1) Part V: D. C. England and C. G. Krespan, *J. Org. Chem.*, **35**, 3312 (1970).

(2) D. C. England and C. G. Krespan, *ibid.*, **35**, 3300 (1970).

(3) *Cf.* W. E. Hanford and J. C. Sauer, *Org. React.*, **3**, 129 (1946).

tone type **7** have been observed, but these dimers were derived *only* from cycloaddition to the carbon–carbon double bond and not to the carbon–oxygen double bond of the nonfluorinated ketene.

$$1 \;+\; R^1R^2C{=}C{=}O \;\longrightarrow$$

6a, $R^1 = R^2 = CH_3$
b, $R^1 = C_4H_9; R^2 = C_2H_5$

7a, $R^1 = R^2 = CH_3$
b, $R^1 = R^2 = H$
**c,** $R^1 = H; R^2 = CH_3$
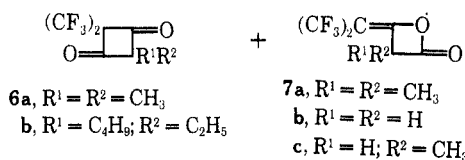
Ketene reacted exothermically with ketene **1** at very low temperature to give lactone **7b** in 89% yield. On pyrolysis this lactone reverted to starting materials in preference to loss of carbon dioxide with allene formation. This behavior is similar to that of ketene alone, which dimerizes solely to the β lactone[4] which in turn pyrolyzes mainly to regenerate ketene.[5] Reaction of **7b** with water gave the keto acid **8a** and with methanol the corresponding ester **8b**. The β lactone was readily dimerized by base to give **9**, a reaction analogous to the formation of dehydroacetic acid from diketene. Lactone **7b** also reacted with another equivalent of ketene **1** in the presence of zinc chloride as catalyst to give the insertion product, **10**. δ-Lactone **10** hydrolyzed in high yield with loss of carbon dioxide to the 1,3-dione **11**, an excellent chelating agent which exists mainly in the enol form. Compound **9** has also been isolated from the reaction of **1** with acetic anhydride, and both **9** and **10** were isolated from a reaction of **1** with acetyl chloride in the presence of zinc chloride. These reactions apparently proceed through the formation of ketene, perhaps with mixed anhydride as a coproduct.

8a, R = H
b, R = CH$_3$

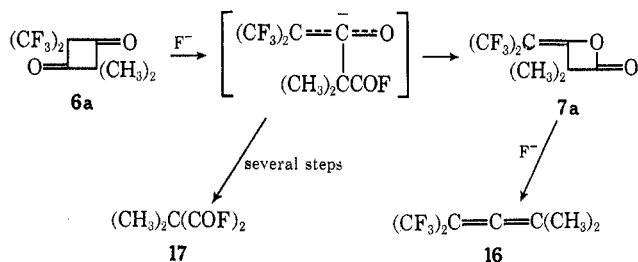**9**   **10**   **11**
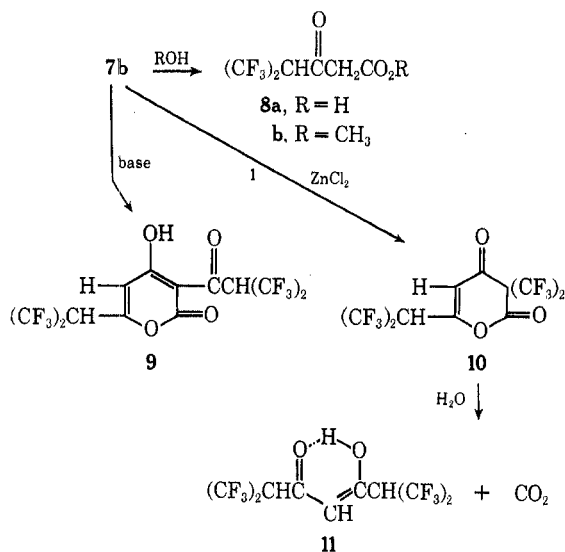
Methylketene, like ketene, reacted with **1** to give a mixed lactone, **7c**, in good yield. Even under conditions found to favor 1,3-dione formation with dimethylketene (see below), no dione or related product derived from cycloaddition of methylketene to the carbon–carbon double bond of **1** was detected. This behavior is unlike that of methylketene alone, which affords both

cyclobutane and oxetane rings on dimerization.[6] Pyrolysis of dimer **7c** proceeded normally, however, giving starting materials in preference to allene formation with loss of carbon dioxide. The mixed dimer which could be hydrolyzed to keto acid **12a**, gave the corresponding methyl ester **12b** with methanol, and polymerized readily with basic catalysts. Attempted reaction of **7c** with another mole of **1** in the presence of zinc chloride did not give a homolog of **10**, but a hydrogen fluoride elimination product believed to be pyranone **13** was isolated. This ring structure is the same as that present in some aldoketene trimers[4,7] and in a derivative prepared from diketene and water.[8] Reaction of pyranone **13** with sodium methoxide replaced two fluorine atoms to give the dimethoxypyranone **14** and with methanol gave the keto diester **15**.

12a, R = H
b, R = CH$_3$

13   **14**

15
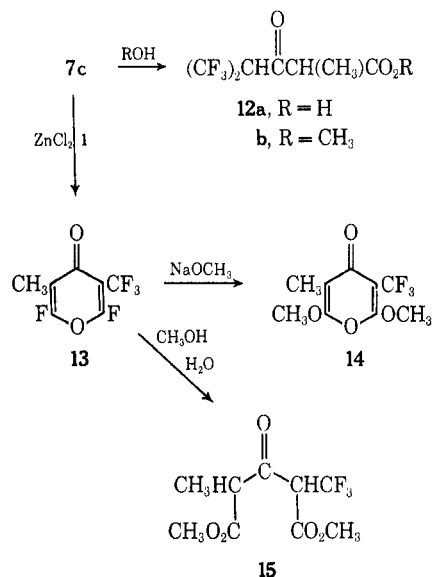
Dimethylketene gave with **1** both dione (**6a**) and lactone (**7a**) as cycloadducts in a reaction which was strikingly solvent dependent. In cyclohexane a high yield of dione was formed, but in a more polar solvent (ethyl acetate) a mixture of the dione and the lactone was produced. Dione **6a** was shown to be stable in polar solvents once formed, but was easily isomerized to lactone **7a** by fluoride ion at room temperature. The isomerization proceeded to completion, indicating the lactone to be the more stable isomer, a reverse order of stability to that observed for the oxetane–cyclobutanone systems.[1] At 200° fluoride ion in glyme promoted formation of allene **16** from the dione **6a** presumably through the lactone **7a** and of dimethylmalonyl fluoride

6a   **7a**

17   **16**

(4) D. G. Farnum, J. R. Johnson, R. E. Hess, T. B. Marshall, and B. Webster, *J. Amer. Chem. Soc.*, **87**, 5191 (1965).

(5) R. N. Lacy, "The Chemistry of Alkenes," S. Patai, Ed., Interscience, New York, N. Y., 1964, p 1171.

(6) Reference 5, p 1183.

(7) E. Wedekind, J. Haussermann, W. Weisswange, and M. Miller, *Justus Liebigs Ann. Chem.*, **378**, 261 (1911).

(8) E. Marcus, J. K. Chan, and C. B. Strow, *J. Org. Chem.*, **31**, 1369 (1966), report 2,6-dimethyl-4H-pyran-4-one as a product of base-catalyzed hydrolysis of diketene.
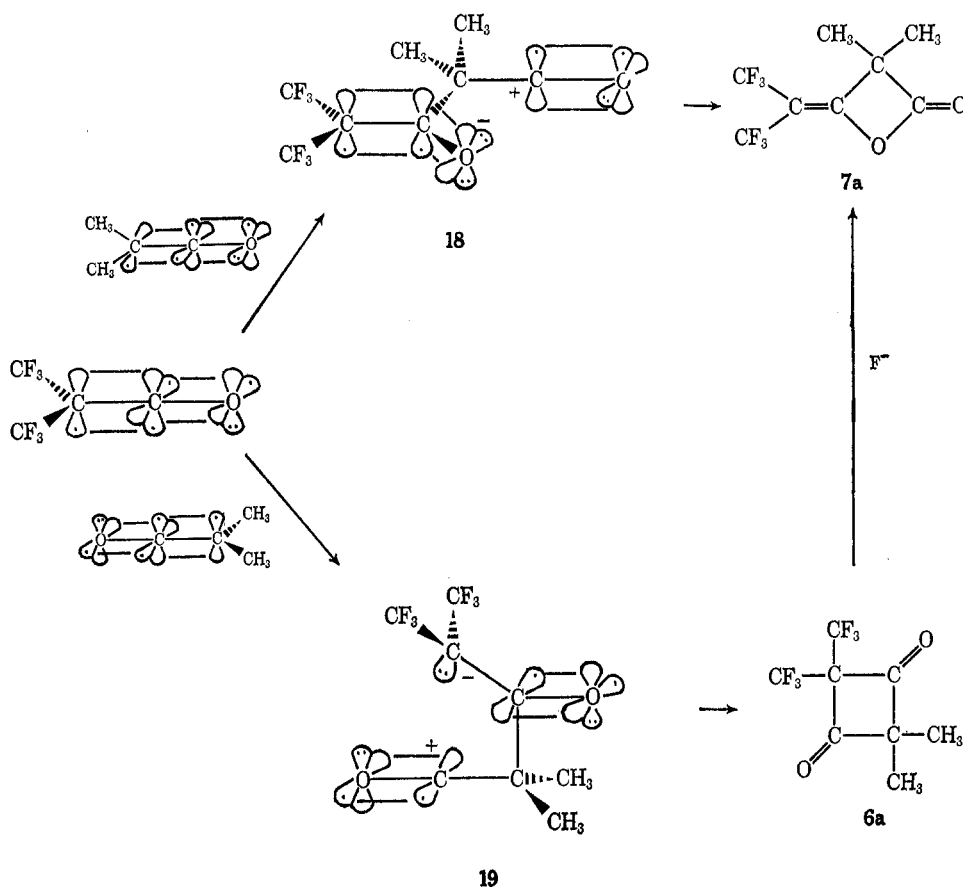
Figure 1.—Proposed intermediates in the cycloaddition of dimethylketene to bis(trifluoromethyl)ketene.

17, the latter probably from a side reaction involving the anionic intermediate. Hydrolysis of **7a** and methanolysis of **6a** gave the expected ring-opened products.

Butylethylketene reacted with **1** in hexane similarly to dimethylketene to give dione **6b** in 87% yield. However, diphenylketene did not react with **1** at 100° over a period of a week.

Discussion

The evidence suggests that cycloadditions of ketenes to the carbonyl group of **1** to form β lactones go through a dipolar intermediate similar to that from **1** and nucleophilic olefins.[1] Reactions are rapid, even at low temperature. They are highly selective, in that only the β lactone derived from the most highly stabilized dipolar intermediate is formed. The second mode of cycloaddition, to the carbon–carbon double bond of **1** with cyclobutanedione formation, is less favored and is not seen except with dialkylketenes. We propose that the results with dimethylketene are explicable on the basis that steric hindrance to the formation of intermediate **18** (Figure 1) allows formation of an intermediate (or unsymmetrical transition state) such as **19** to compete. That **18** has the greater charge separation is indicated by the fact that formation of **7a** is favored by polar solvents. There is no indication of a readily accessible pathway from **18** to possible intermediate **19**; indeed the observed dramatic product shifts with solvent polarity may stem from large differences most likely to be associated with separate reaction paths. Formation of cyclobutanedione **6a** may, of course, proceed by an essentially concerted mechanism rather

than a discrete intermediate, insofar as our evidence can show.

Both types of product (**6** and **7**) are stable under reaction conditions once formed, but dissociate to starting materials at higher temperatures. The preferred path of lactone decomposition is probably by way of the stable polarized species represented by **18**, in a reversal of the original reaction. Loss of CO_2 from the β lactones to form allenes was negligible. Thus, the equilibria seen with **1** and reactive olefins[1] were not observed with **1** and other ketenes, and the reason seems to be the greater stability of the β lactones as compared with the oxetanes.

Allenes are generally considered to cycloadd as 2π systems which follow Woodward–Hoffmann rules.[9] In a stepwise 2 + 2 case, allenes are presumed to be able to stabilize an unpaired electron or positive charge by generating an allyl system. Combined with the negatively charged 3-atom system from **1**, the allylic cation may provide an intermediate uniquely capable of closing to either an oxetane such as **3** or cyclobutanone such as **2**. This system merits detailed study.

Experimental Section[10]

2-Ethylidene-3-methyl-4,4-bis(trifluoromethyl)cyclobutanone (2) and 2-Methyl-3-ethylidene-4-hexafluoroisopropylidenoxetane

(9) *E.g.*, see W. R. Dolbier, Jr., and S.-H. Dai, *J. Amer. Chem. Soc.*, **90** 5028 (1968).

(10) Melting and boiling points are uncorrected. Proton nmr spectra were obtained with a Varian A-60 spectrometer. Peak center positions for ¹H are reported $\tau = 10 - \delta_H$ ppm. Fluorine nmr spectra were obtained with a Varian A56-60 spectrometer using CFCl₃ as an external standard. Peak center positions for ¹⁹F are reported in parts per million upfield from CFCl₃.

(3).—1,3-Dimethylallene, bp 48°, was prepared by pyrolysis of the β-lactone dimer of methylketene under vacuum at 600°. A sample of the allene (4 g, 0.06 mol) was sealed in a Carius tube with 31 g (0.16 mol) of 1. The mixture separated into two layers on cooling to −80°. After being heated 0.5 hr at 100°, the mixture no longer separated on cooling, indicating reaction. After 60 hr at 100° there was recovered 20 g of 1 and 14 g of crude product. The crude material was partially separated by distillation into fractions, bp 56–70° (10 mm) and bp 70–80° (10 mm). Further separation was accomplished by preparative vpc and the purified products were characterized. The lower boiling material was largely a mixture of *cis* and *trans* isomers having the conjugated cyclobutanone structure 2. The conjugated structure is preferred on the basis of uv absorption. The yields were 27 and 38% in the order of increasing boiling point, but *cis* was not distinguished from *trans*. The higher boiling material is largely compound 3, formed in 17% yield. Other higher and lower boiling products isolated amounted to about 8% and were not characterized.

For the more volatile vpc isomer of 2: ir 5.62 (C=O), 5.97 μ (C=C); uv $\lambda_{max}^{isooctane}$ 241 mμ (ϵ 13,100); nmr ^{1}H at τ 4.25 (quartet, 1, $J_{H/H}$ = 7.5 Hz into doublets, $J_{H/H}$ = 2.5 Hz, =CH), 6.85 (broad, 1, ring CH), 8.27 (doublet, 3, $J_{H/H}$ = 7.5 Hz, into doublets, $J_{H/H}$ = 3.0 Hz, =CCH$_3$), 8.88 (doublet, 3, $J_{H/H}$ = 7.5 Hz, into doublets, $J_{H/H}$ = 1.6 Hz, CH$_3$); ^{19}F at 64.1 (quartet into multiplet, 1, $J_{F/F}$ = 9.0 Hz, CF$_3$), 69.2 ppm (quartet,1, $J_{F/F}$ = 9.0 Hz, CF$_3$).

For the second vpc isomer of 2: ir 5.62 (C=O), 5.79 μ (C=C); uv $\lambda_{max}^{isooctane}$ 245 mμ (ϵ 12,300); nmr ^{1}H at τ 3.50 (quartet, 1, $J_{H/H}$ = 7.6 Hz, into doublets, $J_{H/H}$ = 3.2 Hz, =CH), 6.47 (broad, 1, ring CH), 8.32 (doublet, 3, $J_{H/H}$ = 7.6 Hz, into doublets, $J_{H/H}$ = 2.2 Hz, =CCH$_3$), 8.63 (doublet, 3, $J_{H/H}$ = 7.6 Hz, into doublets, $J_{H/H}$ = 1.6 Hz, CH$_3$); ^{19}F at 64.0 (quartet into multiplets, 1, $J_{F/F}$ = 9.1 Hz, CF$_3$), 69.5 ppm (quartet, 1, $J_{F/F}$ = 9.1 Hz, CF$_3$).

For 3: ir 5.86 and 6.01 μ (C=C); uv $\lambda_{max}^{isooctane}$ 256 mμ (ϵ 9850); nmr ^{1}H at τ 3.88 (quartet, 1, $J_{H/H}$ = 7.2 Hz, =CH), 4.65 (quartet, 1, $J_{H/H}$ = 6.6 Hz, ring CH), 8.55 (doublet, 3, $J_{H/H}$ 7.2 Hz, =CCH$_3$), 8.68 (doublet, 3, $J_{H/H}$ = 6.6 Hz, CH$_3$); ^{19}F at 57.8 ppm [complex multiplet, =C(CF$_3$)$_2$].

Anal. Calcd for C$_9$H$_8$F$_6$O: C, 43.94; H, 3.28; F, 46.34. Found for first isomer of 2: C, 44.25; H, 3.47; F, 45.64. Found for second isomer of 2: C, 43.77; H, 3.46; F, 46.47. Found for 3: C, 43.69; H, 2.99; F, 46.50.

Hexafluoroisopropyl 1-Isopropenyl-2-methylpropenyl Ketone (4) and 1,1,1-Trifluoro-2-trifluoromethyl-4-isopropenyl-5-methyl-2,4-hexadien-3-yl Hexafluoroisobutyrate (5).—A mixture of 8.0 g (0.045 mol) of 1 and 25 ml of ether was frozen in a Carius tube at liquid nitrogen temperature and 4.5 g (0.047 mol) of tetramethyallene was added. The tube was sealed, warmed to room temperature with mixing, and allowed to stand overnight. Distillation gave a fraction, bp 83–98° (25 mm), containing 4 and 5. A sample of 4 was purified by vpc. The product with bp 98° (25 mm) was 5 with a minor impurity which could be removed by vpc. Yields based on vpc data were 9% 4 and 79% 5. Purified 4 (50 mg) was sealed in a glass tube with 1.0 g of 1 and heated overnight in a steam bath. Removal of 1 under vacuum gave recovered 4, and no 5 could be detected by ir or glpc.

For 4: ir 3.27 (vinyl CH), 3.39, 3.45 and 3.52 (satd CH), 5.90 (C=O), 6.10 μ (C=C); uv λ_{max}^{hexane} 326 mμ (ϵ 74), 258 (7100); nmr ^{1}H at τ 4.95 (5 lines, 1, $J_{H/H}$ = 1.6 Hz, =CH), 5.35 (broad, 1, =CH), 5.63 [septet, 1, $J_{H/F}$ = 8.0 Hz, (CF$_3$)$_2$CH], 8.35 (singlet, 3, CH$_3$), 8.47 (unresolved structure, 6, CH$_3$); ^{19}F at 64.7 ppm [doublet, $J_{H/F}$ = 8.0 Hz, (CF$_3$)$_2$CH].

Anal. Calcd for C$_{11}$H$_{12}$F$_6$O: C, 48.22; H, 4.41; F, 41.61. Found: C, 48.51; H, 4.63; F, 40.29.

For 5: ir 3.21 (vinyl CH), 3.33, 3.39 and 3.47 (satd CH), 5.55 (vinyl ester C=O), 5.99 (conjd C=O), 6.09 μ (C=C); uv λ_{max}^{hexane} 269 mμ (ϵ 3070); nmr ^{1}H at τ 5.06 (multiplet, 1, =CH), 5.45 (broad, 1, =CH), 6.32 [septet, 1, $J_{H/F}$ = 7.3 Hz, (CF$_3$)$_2$CH], 8.35 (broad, 3, CH$_3$), 8.48 (broad, 3, CH$_3$), 8.53 (broad, 3, CH$_3$); ^{19}F at 61.0 (quartet, 3, $J_{F/F}$ = 8.2 Hz with fine structure, =CCF$_3$), 62.2 (quartet, 3, $J_{F/F}$ = 8.2 Hz, =CCF$_3$), 65.8 ppm [doublet, 6, $J_{H/F}$ = 7.3 Hz with fine structure, (CF$_3$)$_2$CH].

Anal. Calcd for C$_{15}$H$_{12}$F$_{12}$O$_2$: C, 39.86; H, 2.68; F, 50.44. Found: C, 40.42; H, 3.12; F, 49.15.

β-Hexafluoroisopropylidene-β-propiolactone (7b).—Freshly prepared ketene (8.0 g, 0.19 mol, from cracking of the dimer) was vacuum distilled into a Carius tube cooled in liquid nitrogen. Compound 1 (34 g, 0.19 mol) was then condensed into the tube,

and the tube was sealed and placed in a fiber glass sleeve on its side on a mechanical shaker. Reaction was immediate and exothermic on thawing. After the tube had reached room temperature, it was opened and the contents distilled to give 37 g (89%) of 7b: bp 43° (6 mm); n^{25}D 1.3603; ir 5.12 (C=O), 5.74 μ (C=C); nmr ^{1}H at τ 5.63 (multiplet, CH$_2$); ^{19}F at 59.2 (quartet, 1, $J_{F/F}$ = 6.6 Hz with fine structure, CF$_3$), 60.3 ppm (quartet, 1, $J_{F/F}$ = 6.6 Hz with fine structure, CF$_3$).

Anal. Calcd for C$_6$H$_2$F$_6$O$_2$: C, 32.75; H, 0.92; F, 51.82. Found: C, 33.06; H, 1.14; F, 51.35.

The above product (15 g) was pyrolyzed by passing it through a hot tube under vacuum at 558°. Tar was formed and the only distillable material was 3.0 g, bp 38–48°. Infrared showed it to be a mixture of perfluoromethacrylyl fluoride and bis(trifluoromethyl)ketene, which are known to equilibrate under similar conditions. Pyrrolysis apparently reverses the cycloaddition.

Hexafluoroisobutyrylacetic Acid (8a).—Lactone 7b (6 g, 0.027 mol) was placed in a crystallizing dish with 1 ml of water and allowed to stand overnight. The resulting crystals were recrystallized from hexane (2.50 g, 38.5%) and after a second recrystallization melted at 77–78° (2.2 g): ir broad 3–4 (OH), 5.95 (C=O) typical of a carboxylic acid, 6.02 and 6.12 μ (conjd C=O and/or C=C); nmr (CDCl$_3$) ^{1}H at τ 4.55 (singlet, 1, CH), 6.30 [septet, 1, $J_{H/F}$ = 7.7 Hz, (CF$_3$)$_2$CH], two exchangeable (D$_2$O) singlets of equal area (1) at τ −0.9 (enol OH) and −1.8 (COOH); ^{19}F at 64.6 ppm [doublet, $J_{H/F}$ = 7.7 Hz, (CF$_3$)$_2$CH]. The presence of another tautomer in about 0.25 this amount was indicated by a doublet (7.7 Hz) at 63.0 ppm and still another doublet (7.7 Hz) in $^1/_{20}$ this amount at 63.5 ppm. One of the corresponding septets (7.7 Hz) was also visible for ^{1}H at τ 5.55.

Anal. Calcd for C$_6$H$_4$F$_6$O$_3$: C, 30.28; H, 1.69; F, 47.90. Found: C, 30.46; H, 1.95; F, 47.74.

Methyl Hexafluoroisobutyrylacetate (8b).—Methanol (25 ml) was stirred while 19.0 g (0.086 mol) of 7b was added dropwise, keeping the temperature below 10°. The product was distilled directly to give 16.8 g (77.5%) of 8b: bp 47° (8 mm); n^{25}D 1.3626; ir 5.75 and 5.98 (keto and ester C=O), 6.09 μ (enol C=C); nmr (CDCl$_3$) ^{1}H at τ 4.72 (singlet, CH), overlapping peaks for 6.28 (singlet, CH$_3$), 6.40 [septet, $J_{H/F}$ = 7.9 Hz, (CF$_3$)$_2$CH], an exchangeable (D$_2$O) peak at −2.1, a small septet ($J_{H/F}$ = 7.7 Hz) at 5.50 for an isomer; ^{19}F at 65.2 [doublet, $J_{H/F}$ = 7.9 Hz, (CF$_3$)$_2$CH], a second isomer in 40% this amount at 63.6 (doublet, $J_{H/F}$ = 7.7 Hz), a third isomer (6%) at 64.0 ppm (doublet, $J_{H/F}$ = 7.9 Hz).

Anal. Calcd for C$_7$H$_6$F$_6$O$_3$: C, 33.36; H, 2.40; F, 45.24. Found: C, 33.69; H, 2.53; F, 45.32.

3-Hexafluoroisobutyryl-3,4-dihydro-4-keto-6-hexafluoroisopropyl-2H-pyran-2-one (9).—A sample (8.9 g, 0.040 mol) of 7b was sealed in a glass tube and heated overnight on a steam bath. The resulting solid was recrystallized from carbon tetrachloride to give 8.3 g (93%) of 9, mp 76–83°. Three sublimations and another recrystallization from carbon tetrachloride gave 6.5 g of white crystals, mp 84–85°. The following data are in agreement with structure 9: ir 3.23 (vinyl CH), 5.78, 6.01, 6.10 (sh), and 6.40 μ (C=O and C=C); nmr (CDCl$_3$) ^{1}H at τ −5.1 [singlet, 1, exchangeable (D$_2$O)OH], 3.50 (singlet, 1, =CH), 3.80 [septet, 1, $J_{H/F}$ = 7.5 Hz, (CF$_3$)$_2$CH], 5.91 [septet, 1, $J_{H/F}$ = 7.5 Hz, (CF$_3$)$_2$CH]; ^{19}F at 62.9 [doublet, 1, $J_{H/F}$ = 7.5 Hz, (CF$_3$)$_2$CH], 64.5 ppm [doublet, 1, $J_{H/F}$ = 7.5 Hz, (CF$_3$)$_2$CH].

Anal. Calcd for C$_{12}$H$_4$F$_{12}$O$_4$: C, 32.75; H, 0.92; F, 51.82. Found: C, 32.75; H, 0.88; F, 51.47.

The reaction of 1 with acetic ahydride gives a mixture of products. The only one characterized is the same dimer (mp 85°) obtained above from dimerization of the lactone obtained from the reaction of 1 with ketene.

A mixture of 20.4 g (0.20 mol) acetic anhydride and 38 g (0.21 mol) of 1 was sealed in a Carius tube and heated 2 hr on a steam bath. After this time refluxing had ceased, the tube was cooled and opened, and the contents were distilled to give 31.5 g of liquid, bp 49–55° (20 mm), shown by vpc to contain three major components, 4.3 g of forerun mixture, and 10.6 g, bp 82–86° (75 mm). This latter material solidified and was recrystallized from carbon tetrachloride three times to yield 6.2 g, mp 85°. It was identical by mixture melting point and nmr with the material described above for 9.

3,3-Bis(trifluoromethyl)-3,4-dihydro-4-keto-6-hexafluoroisopropyl-2H-pyran-2-one (10) and 1,1,1,7,7,7-Hexafluoro-2,6-bis(trifluoromethyl)heptane-3,5-dione (11).—In the presence of zinc

chloride as catalyst, lactone **7b** reacted slowly with **1** at steam-bath temperature giving a product with structure **10**. This structure is based on analyses, ir, nmr, and reaction with water to give carbon dioxide and 1,3 diketone **11**.

A mixture of **7b** (25.0 g, 0.11 mol), **1** (35.0 g, 0.20 mol), and 1 g of zinc chloride was sealed in a Carius tube and heated 10 days on a steam bath. There was recovered 18 g of **1** and 26.5 g (58.5%) of crystalline product **10**: bp 90° (18 mm); mp 79–80° (from carbon tetrachloride); ir 3.22 (=CH), 3.35 (satd CH), 5.50 and 5.82 (C=O), 5.99 μ (C=C); nmr (CDCl₃) ¹H at τ 3.72 (singlet, 1, =CH), 6.00 [septet, 1, $J_{H/F}$ = 7.2 Hz, (CF₃)₂CH]; ¹⁹F at 64.4 [doublet, 1, $J_{H/F}$ = 7.2 Hz, (CF₃)₂CH], 63.4 ppm [singlet, 1, (CF₃)₂C].

Anal. Calcd for C₁₀H₂F₁₂O₃: C, 30.18; H, 0.50; F, 57.29. Found: C, 29.86; H, 0.66; F, 57.47.

An immiscible mixture of crystalline **10** (10 g, 0.025 mol) and water (10 ml) was sealed in a Carius tube and heated overnight on a steam bath. The tube was cooled, carbon dioxide vented, and the crystalline residue filtered and sublimed to give 7.3 g (82%) of the 1,3 diketone **11** which could be recrystallized from petroleum ether: mp 60–60.5°; ir 6.05 and 6.25 μ (C=O and C=C); nmr (CDCl₃) ¹H at τ 3.95 (singlet, 1, =CH), –3.75 (singlet, 1, acidic H), 6.12 [septet, 2, $J_{H/F}$ = 7.7 Hz, (CF₃)₂CH]; ¹⁹F at 64.1 ppm [doublet, $J_{H/F}$ = 7.7 Hz, (CF₃)₂CH]. The peak at τ –3.75 exchanged with D₂O.

Anal. Calcd for C₉H₄F₁₂O₂: C, 29.06; H, 1.09; F, 61.29. Found: C, 29.04; H, 1.36; F, 61.17.

A number of chelates of **11** were prepared by conventional means. The zinc chelate was prepared from a solution of 4.5 g of zinc acetate dihydrate in 25 ml of water and 5.0 g (0.013 mol) of **11** in 5 ml of methanol. A white oil separated which crystallized to give 6.1 g of crude product. Recrystallization from toluene gave 4.7 g (80%) of white crystals: mp 145–150° dec; ir 6.12 6.51 and 6.79 μ; nmr [(CD₃)₂CO] ¹H at τ 4.84 (singlet, 1, =CH), 6.19 [septet, 2, $J_{H/F}$ = 8.5 Hz, (CF₃)₂CH] [additional singlets at τ 6.56 (area 0.5) and 7.22 (area 1.5) along with analytical data indicated the presence of methanol of crystallization]; ¹⁹F nmr at 65.1 ppm [doublet, $J_{H/F}$ = 8.5 Hz, (CF₃)₂CH].

Anal. Calcd for C₁₈H₆F₂₄O₄Zn·CH₃OH: C, 27.17; H, 1.20; F, 54.30; Zn, 7.78. Found: C, 27.46; H, 1.38; F, 54.46; Zn, 7.65.

α-Methyl-β-hexafluoroisopropylidene-β-propiolactone (7c).—Methylketene was best prepared by pyrolysis of propionic anhydride under vacuum (*ca.* 1 mm) in a vertically mounted quartz tube (1-in. diameter and 22 in. long) packed with quartz chips and heated in the center section to 600° with an electric furnace. The anhydride was added at the top of the tube and the pyrolysis products were passed through two traps connected in series to the bottom of the tube. The first trap was cooled with Dry Ice–acetone and the second with liquid nitrogen. Propionic acid and any unreacted propionic anhydride were collected in the first trap and only methylketene (yellow) passed into the second trap and was condensed there. From 40 g (0.31 mol) of propionic anhydride 10.5 g (60%) of the yellow ketene was collected. Methylketene could be transferred as a gas under vacuum in small amounts. However, even at –80° the liquid ketene dimerized quite rapidly. If the dimerization proceeded at a moderate rate, the product was the solid dione (enol form), mp 138°. However, if the dimerization became very exothermic, the product was the liquid β lactone, bp 61° (25 mm). This β lactone was also the dimer obtained by reaction of propionyl chloride with triethylamine.[4]

The mixed dimer **7c** of methylketene and **1** was best prepared as follows. The fluoroketene (72 g, 0.40 mol) was condensed into the liquid nitrogen trap prior to connecting it to the system described above for generation of methylketene. Methylketene from 50 g (0.38 mol) of propionic anhydride was then condensed on top of the fluoroketene, and the trap was warmed to –80°. After a vigorous reaction there was recovered 27 g (38%) of fluoroketene, indicating that 45 g had reacted (equivalent to 14 g of methylketene). Distillation gave 36 g (61%) of **7c**, bp 43° (10 mm), and 13 g of syrupy polymer: ir 5.20 (C=O), 5.85 μ (C=C); nmr ¹H at τ 5.78 (quartet, 1, $J_{H/H}$ = 7.6 Hz with fine structure, CH), 8.75 (doublet, 3, $J_{H/H}$ = 7.6 Hz, CH₃); ¹⁹F at 59.1 ppm (multiplet, CF₃).

Anal. Calcd for C₇H₄F₆O₂: C, 35.93; H, 1.72; F, 48.72. Found: C, 36.08; H, 2.00; F, 47.37.

7c was rapidly polymerized by base. Samples stored in glass at room temperature usually polymerized within a few days.

Lactone **7c**, like the corresponding β-lactone mixed dimer of ketene and **1**, did not lose carbon dioxide and give the corresponding allene in any appreciable amounts as do nonfluorinated ketene β-lactone dimers. Pyrolysis of **7c** (29 g) in a quartz-packed tube at *ca.* 1 mm pressure and 600° and condensation of the products in a liquid nitrogen trap gave 20 g of liquid. Distillation gave a fraction, 5.3 g, bp <48°, that was mostly perfluoromethacrylyl fluoride (the rearrangement product of **1**), identified by ir. A fraction (6.3 g) boiling about 66° (32 mm) was the β-lactone dimer of methylketene identified by ir; a fraction (7.4 g) boiling about 73° (32 mm) was largely the starting mixed dimer and about 1.1 g of higher boiling oil.

α-(Hexafluoroisobutyryl)propionic Acid (12a).—Lactone **7c** (25 g, 0.11 mol) was dissolved slowly in 25 ml of concentrated sulfuric acid with cooling to keep the temperature near 50°. The resulting solution was poured onto 100 g of ice. The resulting crystals were filtered and recrystallized from hexane to give 19 g (70%) of **12a**. A little color was removed from this material by recrystallizing again from hexane using charcoal to give 16.5 g. This product melted over a wide range (59–80°), and the melting point rose some (*ca.* 65–95°) on standing and was lowered again on sublimation (*ca.* 67–82°), indicating an isomer mixture. Proton and ¹⁹F nmr spectra were in agreement with a keto–enol mixture: ir 3 (broad, H bond), 6.01 and 6.23 μ (C=O, C=C); nmr [(CD₃)₂CO] ¹H at τ 1.79 (broad, 1.45, OH), 5.02 [septet, 0.45, $J_{H/F}$ = 8.4 Hz, (CF₃)₂CH], 5.48 [septet, 0.55 $J_{H/F}$ = 8.4 Hz, (CF₃)₂CH], 6.40 (quartet, 0.55, $J_{H/H}$ = 7.0 Hz, CH₃CH), 8.52 (singlet, 1.35, =CCH₃), 9.10 (doublet, 1.65, $J_{H/H}$ = 7.0 Hz, CH₃CH) [this corresponds to a 55:45 keto–enol mixture]; ¹⁹F nmr at 63.6 [doublet, $J_{H/F}$ = 8.4 Hz, (CF₃)₂CH], 65.1 ppm [doublet, $J_{H/F}$ = 8.4 Hz, (CF₃)₂CH].

Anal. Calcd for C₇H₆F₆O₃: C, 33.36; H, 2.40; F, 45.24. Found: C, 33.71; H, 2.49; F, 45.25.

Methyl α-(Hexafluoroisobutyryl)propionate (12b).—Compound **7c** (22 g, 0.094 mol) was added dropwise to 25 ml of methanol with cooling to maintain 40°. The resulting solution was poured into cold water, extracted with methylene chloride, washed with water, dried, and distilled to give 19.8 g (80%) of **12b**, bp 68° (13 mm), n^{25}D 1.3650. Proton and ¹⁹F nmr data were in agreement with a 65:35 keto–enol mixture: ir 5.68, 5.75, and 5.98 (C=O), 6.10 μ (C=C).

Anal. Calcd for C₈H₈F₆O₃: C, 36.12; H, 3.03; F, 42.86. Found: C, 36.85; H, 3.36; F, 41.78.

2,6-Difluoro-3-(trifluoromethyl)-5-methyl-4H-pyran-4-one (13).—A mixture of 28.5 g (0.12 mol) of **7c**, 1 g of zinc chloride, 25 ml of ether, and 38 g of **1** was sealed in a Carius tube and heated for 12 days on a steam bath. There was recovered 42 g of the low boiler (including ether and ketene) and 41 g of liquid. Distillation gave 1.4 g boiling up to 82° (30 mm), 15.2 g with bp 82–91° (30 mm) which partially solidified, and 7 g boiling higher. The fraction containing solid was recrystallized from carbon tetrachloride to yield 6.6 g (25%) of **13**, mp 81–82°. A second recrystallization gave 5.5 g, mp 81–83°. The crystals were large white plates which changed to needles on standing overnight at room temperature without change in melting point: ir 5.80 (C=O), 5.96 μ (C=C); nmr (CDCl₃) ¹H at τ 8.05 (doublet, $J_{H/F}$ = 2.4 Hz, CH₃); ¹⁹F at 60.8 (doublet, 3, $J_{F/F}$ = 24.4 Hz, CF₃), 72.7 (quartet, 1, $J_{F/F}$ = 24.4 Hz, into doublets, $J_{F/F}$ = 7.4 Hz, CF), 85.4 ppm (doublet, 1, $J_{F/F}$ = 7.4 Hz, into quartets, $J_{H/F}$ = 2.4 Hz, CF).

Anal. Calcd for C₇H₃F₅O₂: C, 39.29; H, 1.41; F, 44.39; mol wt, 214. Found: C, 39.09; H, 1.47; F, 44.40; mol wt, 214 (mass spectrum).

2,6-Dimethoxy-3-(trifluoromethyl)-5-methyl-4H-pyran-4-one (14).—Compound **13** (2.0 g, 0.01 mol) was dissolved in 10 ml of methanol and 0.1 g of sodium methoxide was added, which caused the solution to become warm. The mixture was refluxed 5 hr and poured into cold water. Filtration gave 0.6 g of oily crystals which were recrystallized from methanol, 0.35 g (16%), mp 173–175°, yielding **14**: ir 5.95 (C=O), 6.15 μ (C=C); nmr ¹H at τ 6.20 (singlet, 1, CH₃O), 6.28 (singlet, 1, CH₃O), 8.60 (singlet, 1, CH₃); ¹⁹F at 58.5 ppm (singlet, CF₃).

Anal. Calcd for C₉H₉F₃O₄: C, 45.42; H, 3.81; F, 23.95. Found: C, 45.41; H, 3.86; F, 24.31

Dimethyl 2-Methyl-3-keto-4-(trifluoromethyl)glutarate (15).—Compound **13** (7.0 g, 0.033 mol) was refluxed in 20 ml of methanol for 3 hr to give 7.9 g (95%) of crude compound **15** on dilution with water. Distillation gave 7.2 g (86%): bp 78° (0.5 mm); n^{25}D 1.4050; ir 5.69 and shoulder at 5.76 μ (two C=O); nmr ¹H at τ 5.30 (quartet, 1, $J_{H/F}$ = 8.3 Hz, CHCF₃), 6.34 (quartet,

1, $J_{H/H}$ = 7.0 Hz, into quartets, $J_{H/F}$ = 6.4 Hz, CHCH$_3$), 6.47 (singlet, 3, CH$_3$O), 6.57 (singlet, 3, CH$_3$O), 8.93 (doublet, 3, $J_{H/H}$ = 7.0 Hz, CHCH$_3$); ^{19}F at 65.4 ppm (doublet, $J_{H/F}$ = 8.3 Hz, into doublets, $J_{H/F}$ = 6.4 Hz, CHCF$_3$).

Anal. Calcd for C$_9$H$_{11}$F$_3$O$_5$: C, 42.22; H, 4.33; F, 22.27. Found: C, 42.30; H, 4.38; F, 22.39.

2,2-Dimethyl-4,4-bis(trifluoromethyl)cyclobutane-1,3-dione (6a) and α,α-Dimethyl-β-hexafluoroisopropylidene-β-propiolactone (7a). A.—Ethyl acetate (50 ml) containing 11 g (0.16 mol) of yellow dimethylketene was frozen in liquid nitrogen and 33 g (0.19 mol) of 1 condensed on it. The mixture was allowed to liquify in a Dry Ice–acetone bath, which resulted in a mildly exothermic reaction to give a white solution. On distillation two major fractions were recovered after removal of ethyl acetate: 6a, 7.3 g (19%), bp 52–58° (53 mm), and 7a, 9.5 g (24%), bp mostly at 70° (53 mm).

The β-lactone 7a was essentially pure as obtained from the above distillation, but was further purified by vpc: n^{25}D 1.3633; ir 5.25 (C=O), 5.90 μ (C=C); nmr ^{1}H at τ 8.75 (unresolved fine structure, CH$_3$); ^{19}F at 60.1 ppm (complex multiplet, CF$_3$).

Anal. Calcd for C$_8$H$_6$F$_6$O$_2$: C, 38.74; H, 2.44; F, 45.97. Found: C, 38.83; H, 2.49; F, 45.83.

A sample of 7a (2.0 g) was dissolved in 5 ml of concentrated sulfuric acid and the solution poured onto ice causing crystals to separate. These were filtered, air-dried (1.2 g), and recrystallized from carbon tetrachloride to give 1.05 g of α-hexafluoroisobutyrylisobutyric acid: mp 97–98°; it showed broad absorption in the infrared at 2.8–4 μ characteristic of a carboxylic acid and carbonyl absorption at 5.8 μ; nmr [(CD$_3$)$_2$CO] ^{1}H at τ 0.52 (singlet, 1, CO$_2$H), 5.08 [septet, 1, $J_{H/F}$ = 7.5 Hz, CH(CF$_3$)$_2$], 9.03 (singlet, 6, CH$_3$); ^{19}F at 64.0 ppm [doublet, $J_{H/F}$ = 7.5 Hz, CH(CF$_3$)$_2$].

Anal. Calcd for C$_8$H$_8$F$_6$O$_3$: C, 36.12; H, 3.03; F, 42.86. Found: C, 36.35; H, 3.10; F, 43.34.

B.—Another reaction run as described above but using a cyclohexane solution of dimethylketene gave only the dione 6a in 81% yield: bp 48° (50 mm); n^{25}D 1.3453; ir 5.62 μ (C=O); nmr ^{1}H at τ 8.90 (singlet, CH$_3$); ^{19}F at 64.4 ppm (singlet, CF$_3$).

Anal. Calcd for C$_8$H$_6$F$_6$O$_2$: C, 38.74; H, 2.44; F, 45.97. Found: C, 38.92; H, 2.57; F, 45.44.

In contrast to the behavior of 7a, the dione 6a was not soluble in concentrated sulfuric acid even when heated. However, the ring was cleaved by methanol using base catalysis to give the methyl ester of α-hexafluoroisobutyrylisobutyric acid.

Dione 6a (15 g) in 10 ml of methanol containing 0.5 g of sodium methoxide was refluxed on a steam bath for 15 min, poured into cold, dilute HCl, extracted with methylene chloride, washed with water, dried, and distilled. There was obtained 12 g (70%) of the keto ester: bp 100° (60 mm); n^{25}D 1.3650; ir 5.78 μ (C=O); nmr ^{1}H at τ 4.92 [septet, 1, $J_{H/F}$ = 7.4 Hz, CH(CF$_3$)$_2$], 6.23 (singlet, 3, CH$_3$O), 8.49 (singlet, 6, CH$_3$); ^{19}F at 63.3 ppm (doublet, $J_{H/F}$ = 7.4 Hz, CF$_3$).

Anal. Calcd for C$_9$H$_{10}$F$_6$O$_3$: C, 38.60; H, 3.60; F, 40.71. Found: C, 38.66; H, 3.71; F, 40.67.

Reaction of 6a with Fluoride Ion. A. Isomerization of 6a to 7a.—A mixture of 5 g of 6a, 1 ml of glyme, and 0.1 g of cesium fluoride was allowed to stand overnight at room temperature. It was shown by vpc and by ir that 6a had been completely converted to 7a.

An unsuccessful attempt was made to convert 6a to 7a by aluminum chloride catalysis. The dione (15 g) was added dropwise to 25 ml of benzene containing 1 g of AlCl$_3$. There seemed to be an exothermic reaction at first and the mixture became dark, but later in the addition no heat was evolved and on distillation only starting material was recovered. Similarly, refluxing overnight an ether solution of 6a containing zinc chloride catalyst gave no 7a.

An unsuccessful attempt was also made to isomerize 7a to 6a in refluxing ethyl acetate with zinc chloride. Addition of aluminum chloride was also without effect.

B. 1,1-Dimethyl-3,3-bis(trifluoromethyl)allene (16) and Dimethylmalonyl Fluoride (17).—The reaction with fluoride was carried out using 15 g of 6a, 1 ml of glyme, and 0.1 g of cesium fluoride with heating at 200° for 4 hr to give 7.5 g of impure 7a boiling at ca. 100° (195 mm), and 5.2 g of lower boiling [45–50° (195 mm)] material from which there was obtained by vpc 2.9 g of 16 and 0.6 g of 17. For 16: ir 5.02 μ (C=C=C); nmr ^{1}H at τ 8.59 (singlet, CH$_3$); ^{19}F at 63.2 ppm (singlet, CF$_3$).

Anal. Calcd for C$_7$H$_6$F$_6$: C, 41.21; H, 2.96; F, 55.88. Found: C, 41.10; H, 2.71; F, 55.85.

For 17: ir 5.40 μ (COF); nmr ^{1}H at τ 8.73 (triplet, $J_{H/F}$ = 0.8 Hz, CH$_3$); ^{19}F at −30.3 ppm (septet, $J_{H/F}$ = 0.8 Hz, CF$_3$).

Anal. Calcd for C$_5$H$_6$F$_2$O$_2$: C, 44.15; H, 4.45; F, 27.94. Found: C, 44.25; H, 4.64; F, 28.01.

2-Ethyl-2-butyl-4,4-bis(trifluoromethyl)cyclobutane-1,3-dione (6b).—A mixture of 65 g of 20% hexane solution of butylethylketene (ca. 0.1 mol) and 21 g (0.12 mol) of 1 was sealed in a Carius tube and gave a yellow solution at room temperature. After about 15-min warming on a steam bath it became colorless and on distillation there was obtained 26.6 g (87%) of 6b: bp 32° (0.25 mm); ir 5.66 μ (C=O); nmr ^{1}H was a complex set of peaks at τ 8.1 − 9.6; ^{19}F at 65.0 ppm (singlet, CF$_3$).

Anal. Calcd for C$_{12}$H$_{14}$F$_6$O$_2$: C, 47.41; H, 4.64; F, 37.50. Found: C, 47.50; H, 4.57; F, 37.32.