Fluoroketenes. IV. Cycloadducts of Bis(trifluoromethyl)ketene with Acetylenes[1]

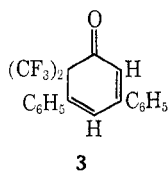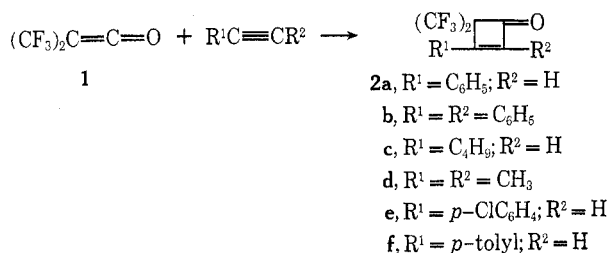DAVID C. ENGLAND AND CARL G. KRESPAN

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Cyclobutenones have been obtained from the reaction of bis(trifluoromethyl)ketene with hexyne-1, butyne-2, phenylacetylene, and diphenylacetylene. Evidence is given for possible mechanisms of these reactions and some unusual chemistry of the products is described. For example, pyrolysis of the cyclobutenone obtained with phenylacetylene has given five products, 10, 11, 12, 13, or 14, depending on conditions.

Cycloaddition of bis(trifluoromethyl)ketene (1) to phenylacetylene was previously shown to give a cyclobutenone directly.[2] This reaction has now been found to have some generality for aryl- and alkyl-substituted acetylenes. Ketene 1 does not react readily with acetylene or ethyl propiolate, probably because of low nucleophilicity of these acetylenes, nor with methylacetylene because of difficulty in obtaining a condensed phase. However, cycloadducts to the carbon–carbon double bond of 1 have been obtained from hexyne-1, butyne-2, phenylacetylene, and diphenylacetylene. Ethoxyacetylene, an exceptionally nucleophilic acetylene, reacts at the carbonyl group of 1 to give a different type of product.[3]

As reported earlier,[2] phenylacetylene with ketene 1 gave 80% cyclobutenone 2a in a slow reaction at 100°. A by-product of this reaction, apparently of structure 3, is formed in good yield by reaction of 2a with phenylacetylene. Characterization of 3 is discussed below.

2a, $R^1 = C_6H_5$; $R^2 = H$
b, $R^1 = R^2 = C_6H_5$
c, $R^1 = C_4H_9$; $R^2 = H$
d, $R^1 = R^2 = CH_3$
e, $R^1 = p\text{-}ClC_6H_4$; $R^2 = H$
f, $R^1 = p\text{-}tolyl$; $R^2 = H$

3

Diphenylacetylene at 200° gave a 95% yield of 2b. Hexyne-1 reacted with 1 at 150° for 8 hr to give a low yield of cyclobutenone 2c. Butyne-2 gave with 1 in 60 hr at 100° a 65% yield of 2d along with a 2:2 adduct of unknown structure.

These cycloadditions with direct formation of cyclobutenones are, with few exceptions, the only such examples known. Previous reactions with other ketenes and various acetylenes have resulted in products of rearrangements.[4] One exception is the additions of ethoxyacetylene which, unlike its reaction with 1, gave

cyclobutenones with diphenylketene[5] and dimethylketene.[6] Also, reactions of a number of diethylaminoacetylenes with arylketenes have recently been shown to give cyclobutenones.[7]

Ring-opening reactions of the new cyclobutenones in every case proceeded by initial scission of the carbon–carbon bond between the carbonyl group and the carbon bearing *gem*-trifluoromethyl groups. Cyclobutenone 2a hydrolyzed readily with warm water to give acid 5 and reacted with fluoride in a liquid phase to form acid fluoride 6. Aqueous alkali followed by acidification resulted in hydrolysis of all fluorine from 2a and formation of the stable acid anhydride 7. Hydrogenation of 2a gave a cyclobutanone 4, identical with that obtained from 1 and styrene.
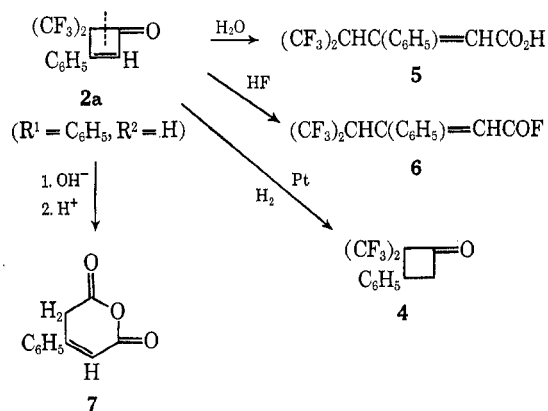

Pyrolysis of 2a might be expected to give an α,β-unsaturated ketene 8 in a reversible isomerization.[8] Ketene 8, a vinylog of ketene 1, could reversibly isomerize to acid fluoride 9 in the same manner as 1 equilibrates with perfluoromethacryloyl fluoride.[9] Products isolated from pyrolyses of 2a in a flow system

(1) Part III: D. C. England and C. G. Krespan, *J. Org. Chem.*, **35**, 3300 (1970).

(2) D. C. England and C. G. Krespan, *J. Amer. Chem. Soc.*, **87**, 4019 (1965).

(3) For details, see part V, *J. Org. Chem.*, **35**, 3312 (1970).

(4) R. N. Lacey in "The Chemistry of Alkenes," S. Patai, Ed., Interscience, New York, N. Y., 1964, p 1161.

(5) J. Druey, E. F. Jenny, K. Schenker, and R. B. Woodward, *Helv. Chim. Acta*, **45**, 600 (1962).

(6) R. H. Hasek and J. C. Martin, *J. Org. Chem.*, **27**, 3743 (1962).

(7) W. E. Truce, R. H. Baury, and P. S. Bailey, Jr., *Tetrahedron Lett.*, 5651 (1968).

(8) (a) E. F. Jenny and J. D. Roberts, *J. Amer. Chem. Soc.*, **78**, 2005 (1956), report evidence for the equilibrium
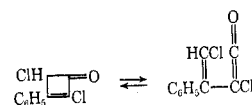
(b) J. E. Baldwin and M. C. McDaniel, *ibid.*, **90**, 6118 (1968); (c) Y. A. Cheburkov, N. Mukhamadaliev, and I. L. Knunyants, *Tetrahedron*, **24**, 1341 (1968), report reaction of 2a with methanol to give 1,2 and 1,4 adducts of methanol to 8 plus a third, uncharacterized product.

(9) D. C. England and C. G. Krespan, *J. Amer. Chem. Soc.*, **88**, 5582 (1966).

corresponded to the two possible modes of ring closure of the proposed common intermediate, **9**. At 350–500°, isomeric ethers **10** and **11** were formed by closure of the six-membered ring,[10] and cyc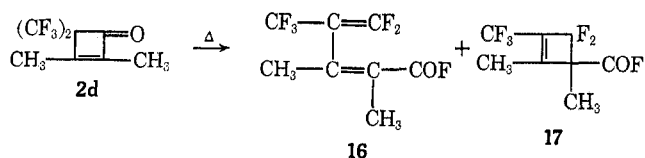lobutenecarbonyl fluoride **12** is also formed by cyclization of **9** as a diene to give a cyclobutene ring. In these experiments, lower pyrolysis temperatures favored ethers **10** and **11** and higher temperatures favored the cyclobutenecarbonyl fluoride **12**.

2a

8 **9**

11 **10** **12**

14 **13**
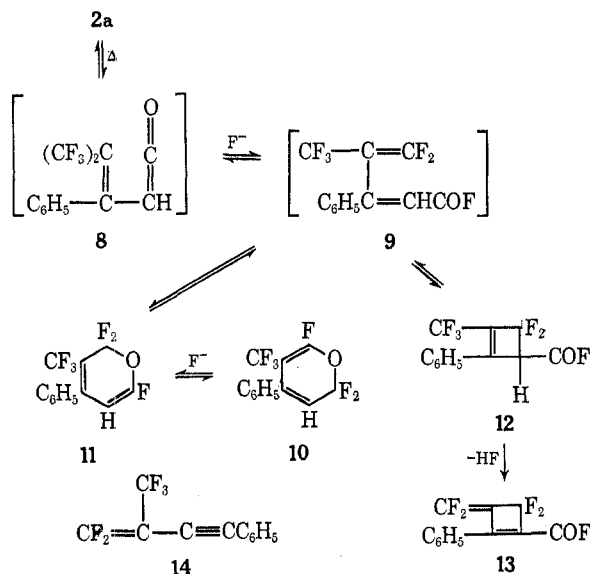
The interrelationship between **10** and **11** on the one hand and **12** on the other through common intermediate **9** was demonstrated by separate pyrolyses of these products. Starting with either a mixture of **10** and **11** or with purified **12**, pyrolysis gave the expected mixture of all three compounds. Higher pyrolysis temperatures (600–650°) with **2a** caused loss of hydrogen fluoride to give **13** and further of carbon monoxide to give rearranged enyne **14**. Loss of hydrogen fluoride may have occurred from **12**, since the proton was shown to be labile on treatment with base, giving a proton shift to form **15**. Simple hydrolysis or methanolysis of **12** gave the unrearranged acid and methyl ester, respectively.
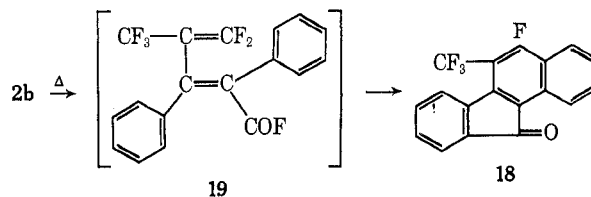
12 $\xrightarrow{\text{base}}$

15
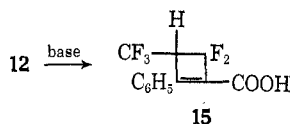
More direct evidence for the presence of **9** was obtained by isolation of the related butadienyl acid fluoride **16** from the pyrolysis of **2d**. Approximately equal amounts of **16** and the corresponding cyclobutene **17** were formed at 500°.

2d $\xrightarrow{\Delta}$

16 **17**

Pyrolysis of **2b** at 515° gave a product (60%) believed to be the aromatic ketone **18**, which could be derived from the expected intermediate **19** by two Friedel–Crafts condensations.

2b $\xrightarrow{\Delta}$

19 **18**

The 2:1 product formed by reaction of **2a** with phenylacetylene is, according to spectral data, a conjugated ketone containing two different vinyl protons having a coupling constant of 1.4 Hz. Almost certainly the reaction proceeds by initial scission of the carbon–carbon bond between the carbonyl groups and the carbon bearing *gem*-trifluoromethyl groups. Products of addition of another mole of phenylacetylene can then be postulated through intermediate **8**. 1,4 Addition could give **20a** or **20b**, but **20a** can be ruled out

20a **20b**

20c $\rightarrow$

20d $\rightarrow$ **3** $\xrightarrow{H_2}$

21
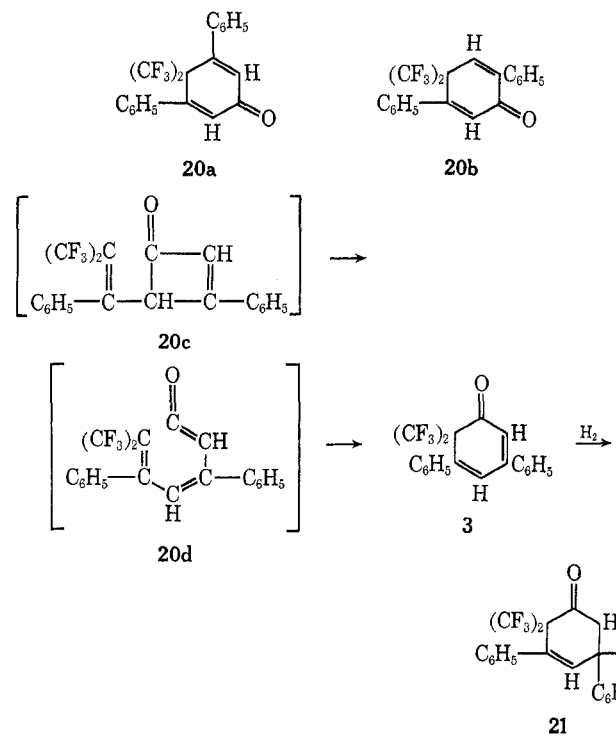
because it contains only one kind of vinyl proton. 1,2 addition of phenylacetylene to **8** in the same manner as addition to **1** would give **20c** which could easily cleave to **20d** and cyclize to **3**. Structure **3** is selected over **20b** because addition of 1 mol of hydrogen gave an unconjugated ketone **21**, whereas addition of 1 mol of hydrogen to **20b** would give a conjugated ketone. By forcing the hydrogenation it was possible to add 1 and 2 more mol, giving saturated ketone and alcohol, respectively (detected by mass spectrometry and infrared).

It was also possible to react **1** with *p*-chlorophenylacetylene to give **2e**, and this cyclobutenone reacted with phenylacetylene to give **22**. An isomer of **22** (**23**)
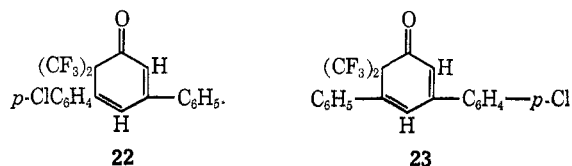
22 **23**

(10) See P. Schiess, H. L. Chia, and C. Suter, *Tetrahedron Lett.*, 5747 (1968), for a discussion of the tendency for dienones such as **9** to exist in the isomeric 2H-pyran form. Although the isomerization **9** → **11** may be uncatalyzed, the formation of **9** from **8** and the interconversion of cyclic ethers **10** and **11** are probably catalyzed by fluoride ion, just as are some analogous reactions starting from ketene **1**.

was prepared by reacting **2a** with *p*-chlorophenyl-acetylene.

Experimental Section[11]

1 and Acetylene.—A bomb charged with 36 g of **1** and 26 g of acetylene was heated at 150° for 12 hr. The pressure reached was 725 atm. Recovered material boiling above room temperature consisted of 4 g of perfluoromethacryloyl fluoride and 4 g of a higher boiling mixture. Ir did not indicate the presence of cyclobutenone.

1 and Methylacetylene.—A mixture of 8.5 g of **1** and 3.5 g of methylacetylene heated in a Carius tube at 175° for 8 hr gave no product.

1 and Ethyl Propiolate.—A mixture of 20 g of **1** and 10 g of ethyl propiolate heated in a Carius tube in a steam bath 13 days at 150° for 12 hr gave no product. Decomposition occurred at 200°.

4,4-Bis(trifluoromethyl)-3-butyl-2-cyclobuten-1-one (2c).—A mixture of 16.5 g (0.20 mol) of hexyne-1 and 37 g (0.21 mol) of **1** was heated in a Carius tube at 150° for 8 hr. There was obtained 6.2 g (11.5%) of the above cyclobutenone: bp 58–59° (5 mm); n^{25}D 1.3778; ir 5.53 (C=O), 6.26 μ (C=C); nmr ^{1}H at τ 3.77 (singlet, 1 =CH), 7.68 (triplet, 2, $J_{\rm H/H}$ = 7.0 Hz, CH$_2$), 8.75 (multiplet, 4, CH$_2$CH$_2$), 9.35 (triplet, 3, $J_{\rm H/H}$ = 6.2 Hz, CH$_3$); ^{19}F at 67.5 ppm (singlet, CF$_3$).

Anal. Calcd for C$_{10}$H$_{10}$F$_6$O: C, 46.19; H, 3.88; F, 43.85. Found: C, 46.53; H, 4.17; F, 44.04.

4,4-Bis(trifluoromethyl)-2,3-dimethyl-2-cyclobuten-1-one (2d).—A mixture of 36 g (0.20 mol) of **1** and 11 g (0.20 mol) of butyne-2 in a Carius tube was heated 60 hr at 100°. Distillation gave 29 g (65%) of the above cyclobutenone, bp 58° (20 mm), n^{25}D 1.3638, and 8 g (17%) of an unknown compound, bp 97° (1.25 mm), which solidified and was recrystallized twice from carbon tetrachloride to give 5.9 g, mp 67°.

For the cyclobutenone: ir 5.57 (C=O), 6.02 with a 6.09 μ shoulder (C=C); nmr ^{1}H at τ 8.11 (singlet, 1, CH$_3$), 8.54 (singlet, 1, CH$_3$); ^{19}F at 68.1 ppm (singlet, CF$_3$).

Anal. Calcd for C$_8$H$_6$F$_6$O: C, 41.41; H, 2.61; F, 49.14. Found: C, 41.38; H, 2.40; F, 49.07.

Pyrolysis of 2d. 5,5-Difluoro-2,3-dimethyl-4-(trifluoromethyl)-2,4-pentadienoyl Fluoride (16) and 4,4-Difluoro-1,2-dimethyl-3-(trifluoromethyl)-2-cyclobutene-1-carbonyl Fluoride (17).—The above cyclobutenone (17.9 g, 0.077 mol, n^{25}D 1.3540) was slowly passed through a quartz-packed tube at 500° (1 mm). There was recovered in a liquid nitrogen trap 17 g, n^{25}D 1.3658, indicating little change. The material was repyrolyzed at 660° (1 mm), and the recovered material (n^{25}D 1.3800) distilled to give 4.2 g, bp 58–72° (60 mm), and 9.3 g boiling mostly at 72–90° (60 mm). The first fraction was separated by vpc into about equal amounts of **16** and **17**. They were characterized by analyses, ir, and nmr.

For the diene **16**: ir 5.49 (conjd COF), 5.74 [CF$_2$=C(CF$_3$)-], 6.11 μ (conjd C=C); nmr ^{1}H at τ 8.10 (multiplet, 1, weak splitting, CH$_3$), 8.35 (multiplet, 1, weak splitting, CH$_3$); ^{19}F at −38.3 (singlet, 1, COF), 60.5 ppm (doublet, 3, $J_{\rm F/F}$ = 18.5 Hz, into doublets, $J_{\rm F/F}$ = 11.5 Hz, CF$_3$), 78.5 ppm (multiplet, 2, CF$_2$).

Anal. Calcd for C$_8$H$_6$F$_6$O: C, 41.41; H, 2.61; F, 49.14. Found: C, 41.89; H, 2.78; F, 49.05.

For the cyclobutene **17**: ir 5.42 (COF), 5.86 μ (C=C); nmr ^{1}H at τ 8.2 (multiplet, 1, CH$_3$), 8.8 (multiplet, 1, CH$_3$); ^{19}F at −36.1 (doublet, 1, $J_{\rm F/F}$ = 6.2 Hz, COF), 64.8 (singlet, 3, CF$_3$), 109.8 and 114.5 ppm (quartet with fine structure, 2, AB, $J_{\rm F/F}$ = 200 Hz, CF$_2$).

Anal. Calcd for C$_8$H$_6$F$_6$O: C, 41.41; H, 2.61; F, 49.14. Found: C, 41.90; H, 2.66; F, 49.14.

4,4-Bis(trifluoromethyl)-3-phenyl-2-cyclobuten-1-one (2a).—Phenylacetylene (5.5 g, 0.054 mol) and the ketene (9.0 g, 0.05 mol) were heated 60 hr in a steam bath to give 11.1 g (79%) of the above cyclobutenone: bp 75° (1 mm); ir 6.40 and 6.69 (aromatic and conjugated C=C), 5.55 μ (C=O); nmr ^{1}H at τ 2.75 (multiplet, 2, aromatic CH), 3.10 (multiplet, 3, aromatic CH), 3.55 (singlet, 1, =CH); ^{19}F at 65.7 ppm (singlet, CF$_3$).

Anal. Calcd for C$_{12}$H$_6$F$_6$O: C, 51.47; H, 2.16; F, 40.71. Found: C, 52.15; H, 2.12; F, 40.37.

(11) Melting points and boiling points are uncorrected. Nmr peak center positions for ^{1}H are reported τ = 10 − $\delta_{\rm H}$ ppm. ^{19}F nmr spectra are reported in parts per million upfield from external trichlorofluoromethane.

3,5-Diphenyl-6,6-bis(trifluoromethyl)-2,4-cyclohexadienone (3). A.—In addition to cyclobutenone **2a** in the above reaction there was distilled 2 g of material, bp 165–180° (1 mm), which partly crystallized. Recrystallization from petroleum ether gave 9 g (9.5%) of yellow crystalline **3**: mp 120–121°; ir 6.01 (conjugated C=O), 6.12, 6.27, 6.34, 6.38, and 6.72 μ (aromatic and conjugated C=C); nmr ^{1}H at τ 2.70 (multiplet 10, aromatic CH), 3.18 (doublet, 1, $J_{\rm H/H}$ = 1.4 Hz, =CH), 3.69 (doublet, 1, $J_{\rm H/H}$ = 1.4 Hz, =CH); ^{19}F at 61.4 ppm [singlet, (CF$_3$)$_2$]; uv $\lambda_{\rm max}^{\rm isooctane}$ 232 mμ (ϵ 14,100), 299 (8300), 329 (8200).

Anal. Calcd for C$_{20}$H$_{12}$F$_6$O: C, 62.88; H, 3.17; F, 29.84. Found: C, 62.84; H, 3.02; F, 29.34.

B.—Compound **3** could be prepared in good yield from phenylacetylene and cyclobutenone **2a**. A mixture of 7.0 g of **2a** and 5.0 g of phenylacetylene in a sealed tube was heated 185 hr in a steam bath. The resulting solid was recrystallized from petroleum ether to give 7.0 g (73%) of **3**, identical with the above by melting point and mixture melting point. The long heating period was subsequently found to be unnecessary.

3,5-Diphenyl-2,2-bis(trifluoromethyl)-3-cyclohexenone (21) from Hydrogenation of 3.—Using a Parr hydrogenator 4.8 g of the conjugated ketone **3**, 50 ml tetrahydrofuran, and 0.1 g PtO$_2$ were shaken for 3 hr at room temperature and 40-psi hydrogen pressure. After removal of tetrahydrofuran by distillation, the residue was recrystallized from petroleum ether to give 2.7 g of colorless crystals and 2 g of oil. After one more recrystallization there was obtained 2.0 g of **21**: mp 101–105°; ir 5.74 μ C=O); nmr ^{1}H (220 MHz) at τ 2.85 (singlet and surrounding multiplet, 10, aromatic CH), 3.83 (doublet, 1, $J_{\rm H/H}$ = 3.0 Hz, =CH), 6.13 [doublet to doublets to doublets, 1, $J_{\rm H/H}$ = 9.0, 6.8 and 3.0 Hz, C(C$_6$H$_5$)H], an AB quartet further split to doublets at 7.05 (1, $J_{\rm H/H}$ = 13.5 and 6.8 Hz, CHH), 7.19 (1, $J_{\rm H/H}$ = 13.5 and 9.0 Hz, CHH); ^{19}F at 60.5 (quartet, 1, $F_{\rm F/F}$ = 9.5 Hz, CF$_3$), 61.5 ppm (quartet, 1, $J_{\rm F/F}$ = 9.5 Hz, CF$_3$); uv $\lambda_{\rm max}^{\rm isooctane}$ 258 mμ (ϵ 620), 264 (470), 288 (70).

Anal. Calcd for C$_{20}$H$_{14}$F$_6$O: C, 62.55; H, 3.68; F, 29.69; mol wt, 384.0948. Found: C, 62.53; H, 3.86; F, 29.81; mol wt, 384.0943 (mass spectrum).

In another hydrogenation carried out in alcohol using Raney nickel catalyst at 100° and 2175 psi, the same product (**21**) was isolated along with a viscous oil which contained hydroxyl by infrared. By mass spectrometry it was possible to determine that the starting material had absorbed 1, 2, and 3 mol of hydrogen. Use of ruthenium-on-carbon catalyst in ethanol–water at 40° and 500 psi gave a syrup which by mass spectrometry appeared to be largely the alcohol resulting from addition of 3 mol of hydrogen.

Neutral Hydrolysis of 2a. 5,5,5-Trifluoro-3-phenyl-4-(trifluoromethyl)-2-pentenoic Acid (5).—An immiscible mixture of the cyclobutenone (25 g, 0.089 mol) and water (13 ml) was warmed on a steam bath for 30 min. Acid **5** crystallized and was recrystallized from chloroform to give 15.5 g of first crop, mp 125–128°, and 5.5 g of second crop: mp 123–125° (total yield 79%); ir 3–4 (carboxylic OH), 5.87 (C=O), 6.15 (conj C=C), 13.45 and 14.43 μ (monosubst aromatic); nmr [(CD$_3$)$_2$CO] ^{1}H at τ 0.00 (broad, 1, COOH), 3.08 (singlet, 5, aromatic CH), 3.86 [septet, 1, $J_{\rm H/F}$ = 9.3 Hz, CH(CF$_3$)$_2$], 4.24 (singlet, 1, =CH); ^{19}F at 62.8 ppm [doublet, $J_{\rm H/F}$ = 9.3 Hz, CH(CF$_3$)$_2$]. Both nmr spectra indicated the presence of a small amount of a second isomer (probably a *cis-trans* mixture).

Anal. Calcd for C$_{12}$H$_8$F$_6$O$_2$: C, 48.36; H, 2.70; F, 38.36. Found: C, 48.66; H, 2.97; F, 38.18.

Basic Hydrolysis of 2a. 3-Phenylglutaconic Anhydride (7).—The cyclobutenone (5.0 g, 0.018 mol) was added dropwise to 10 ml of 10% sodium hydroxide solution and then more alkali was added to make the solution basic. Acidification with aqueous hydrochloric acid gave 1.0 g (30%) of the cyclic anhydride which was recrystallized from chloroform: mp 193–195°; ir 5.59, 5.46 (C=O), 6.12 μ (C=C); nmr ^{1}H at τ 2.70 (multiplet, 5, aromatic CH), 3.65 (triplet, 1, $J_{\rm H/H}$ = 1.5 Hz, =CH), 6.31 (doublet, 2, $J_{\rm H/H}$ = 1.5 Hz, CH$_2$).

Anal. Calcd for C$_{11}$H$_8$O$_3$: C, 70.27; H, 4.29. Found: C, 70.09; H, 4.47.

5,5,5-Trifluoro-3-phenyl-4-(trifluoromethyl)-2-pentenoyl Fluoride (6).—A mixture of 25 g (0.089 mol) of **2a**, 25 ml of glyme, and 1 g of cesium fluoride was refluxed overnight and then poured into cold water, and the heavy layer was washed with cold water and distilled to give 5 g (19% of crude acid fluoride **6**, bp 66° (1.5 mm).

It was purified by preparative glpc to give 3.3 g redistilled at 50° (0.5 mm) to give 2.6 g: n^{25}D 1.4370; ir 5.46 (COF), 610 μ (C=C); nmr indicated a mixture of *cis* and *trans* isomers; nmr for one isomer ¹H at τ 3.14 (singlet, 5, C₆H₅), 4.40 (doublet, 1, $J_{H/F}$ = 4.0 Hz, CHCOF), 4.42 [septet, 1, $J_{H/F}$ = 8.0 Hz, CH(CF₃)₂]; ¹⁹F at −46.0 (doublet, 1, $J_{H/F}$ = 4.0 Hz, CHCOF), 62.9 ppm [doublet, 6, J = 8.0 Hz, CH(CF₃)₂]; nmr for the other isomer ¹H at τ 3.17 (singlet, 5, C₆H₅), 3.99 (broad, 1, CHCOF), 6.40 [septet, 1, $J_{H/F}$ = 7.5 Hz, CH(CF₃)₂]; ¹⁹F at −43.5 (doublet, 1, $J_{H/F}$ = 1.0 Hz, CHCOF), 56.1 ppm [doublet, 6, $J_{H/F}$ = 7.5 Hz, CH(CF₃)₂].

Anal. Calcd for C₁₂H₇F₇O: C, 48.00; H, 2.33; F, 44.33. Found: C, 48.39; H, 2.47; F, 44.04.

Pyrolysis of 2a. 4,4-Difluoro-2-phenyl-3-(trifluoromethyl)-2-cyclobutene-1-carbonyl Fluoride (12).—The cyclobutenone (100 g, 0.36 mol) was metered dropwise under vacuum (1–5 mm) over ¹/₄-in. sections of 8-mm quartz tubing packed in a 1-in.-diameter quartz tube heated by a 12 in. wrap-around electric heater to a maximum of 400° inside temperature. The product was condensed in a trap cooled by liquid nitrogen and then distilled. There was obtained 43 g of starting cyclobutenone, 37 g boiling at 48–52° (0.6 mm) described further below, and 10.5 g (10.5% conversion) of 12, bp 63–64° (0.6 mm), which crystallized and after recrystallization from petroleum ether melted at 38.5°: ir 5.41 (COF), 5.97 μ (C=C); nmr (CCl₄) ¹H at τ 2.55 (singlet, 5, aromatic CH), 5.60 (broad, 1, CH); ¹⁹F at −45.5 (doublet, 1, $J_{F/F}$ = 5.6 Hz, COF), 61.7 ppm (multiplet, 3, CF₃), 5553, 5754, 5977, and 6177 Hz (AB, 2, $J_{F/F}$ = 5.6 Hz, doublets for last two, CF₂).

Anal. Calcd for C₁₂H₆F₆O: C, 51.47; H, 2.16; F, 40.71. Found: C, 51.55; H, 2.18; F, 41.08.

4,4-Difluoro-2-phenyl-3-(trifluoromethyl)-2-cyclobutene-1-carboxylic Acid.—The above acid fluoride 12 (1 g) was warmed on the steam bath in 10 ml of water. It melted and was immiscible, but was soon converted to the white, crystalline acid (1 g, mp 124–125°): ir 3–4 (broad), 5.87 (CO₂H), 6.02 μ (C=C); nmr [(CD₃)₂] ¹H at τ −0.60 (singlet, 1, COOH), 2.83 (multiplet, 5, aromatic CH), and 5.65 (multiplet, 1, CH); ¹⁹F at 62.4 ppm (multiplet, 3, CF₃), 5695, 5893, 6163, and 6361 Hz (AB with fine structure, 2, ring CF₂).

Anal. Calcd for C₁₂H₇F₅O₂: C, 51.84; H, 2.54; F, 34.17. Found: C, 51.64; H, 2.49; F, 34.28.

Methyl 4,4-Difluoro-2-phenyl-3-(trifluoromethyl)-2-cyclobutene-1-carboxylate.—The acid fluoride 12 (2 g) was mixed with methanol giving an exothermic reaction. Evaporation of excess methanol gave 2 g (96%) of crystalline ester which could be recrystallized from petroleum ether: mp 48–50°; ir 5.73 (C=O), 6.00 μ (C=C); nmr (CCl₄) ¹H at τ 2.44 (singlet, 5, aromatic CH), 5.64 (multiplet, 1, ring CH), 6.27 (singlet, 3, CH₃); ¹⁹F at 61.4 ppm (fine structure, 3, CF₃), 5604, 5804, 6089, and 6290 Hz (AB with fine structure, 2, ring CF₂).

Anal. Calcd for C₁₃H₉F₅O₂: C, 53.47; H, 3.11; F, 32.53. Found: C, 53.23; H, 3.15; F, 33.06.

4,4-Difluoro-2-phenyl-3-(trifluoromethyl)-1-cyclobutene-1-carboxylic Acid (15), 2,2,6-Trifluoro-4-phenyl-5-(trifluoromethyl)-2H-pyran (10), and 2,2,6-Trifluoro-4-phenyl-3-(trifluoromethyl)-2H-pyran (11).—The lowest boiling fractions from the above pyrolysis [37 g, bp 48–52° (0.6 mm)] were combined with another 20 g of similar fractions obtained by repyrolyzing the above recovered starting material (43 g) at 400°. This composite was washed twice with 10% sodium hydroxide rapidly. Reaction with acid fluoride 12 was immediate, leaving a base-insoluble (reacting only slowly) oil boiling mostly at 50–54° (0.6 mm) (41.5 g, 41.5% of original). It could be further separated into about equal amounts of the cyclic ethers 10 and 11 by vpc. Compound 10, n^{25}D 1.4545, was obtained quite pure, but 11, n^{25}D 1.4640, was contaminated appreciably with 10. Acidification of the sodium hydroxide solution gave 4.8 g of 15, mp 181–182°. This acid could be prepared quantitatively by dissolving 12 in 10% sodium hydroxide followed by acidification. It could be recrystallized from chloroform.

For 15: ir 3–4 (acidic OH), 5.87 (C=O), 6.17 μ (conjd C=C); nmr [(CD₃)₂CO] ¹H at τ −0.4 (singlet, 1, CO₂H), 2.25 (multiplet, 2, aromatic CH), 2.80 (multiplet, 3, aromatic C–H), 5.50 (multiplet, 1, CH); ¹⁹F at 66.3 (doublet, 3, $J_{F/F}$ = 12.4 Hz, into doublets, $J_{H/F}$ = 7.9 Hz, into doublets, $J_{F/F}$ = 3.4 Hz, CF₃), 5752 and 5963 Hz (doublets, A branch of AB, $J_{H/F}$ = 4.0 Hz, into overlapping quartets, $J_{H/F}$ = 3.4 Hz, CF), 6341 and 6552 Hz (quartets, B branch of AB, $J_{F/F}$ = 12.4 Hz, CF).

Anal. Calcd for C₁₂H₇F₅O₂: C, 51.84; H, 2.54; F, 34.17. Found: C, 51.79; H, 2.59; F, 34.13.

For 10: ir 5.91 μ (C=C); nmr ¹H at τ 3.1 (singlet, 5, aromatic CH), 4.93 (multiplet, 1, =CH); ¹⁹F at 54.3 (doublet with fine structure, 3, $J_{F/F}$ = 26.0 Hz, CF₃), 78.6 (quartet with fine structure, 1, $J_{F/F}$ = 26.0 Hz, =CF), 42.3 ppm (multiplet, 2, CF₂).

Anal. Calcd for C₁₂H₆F₆O: C, 51.47; H, 2.16; F, 40.71. Found: C, 51.81; H, 2.41; F, 41.11.

For 11: ir 5.88 μ (C=C); nmr ¹H at τ 3.10 (singlet, 5, aromatic CH), 5.21 (multiplet, 1, =CH); ¹⁹F at 54.2 (triplet, 3, $J_{F/F}$ = 10.0 Hz, into doublets, $J_{F/F}$ = 1.6 Hz, CF₃), 41.5 (quartet, 2, $J_{F/F}$ = 10.0 Hz, into doublets, $J_{H/F}$ = 1.8 Hz, CF₂), 85.1 ppm (doublet, 1, $J_{H/F}$ = 1.6 Hz into quartets, $J_{F/F}$ = 1.6 Hz, CF).

Anal. Calcd for C₁₂H₆F₆O: C, 51.47; H, 2.16; F, 40.71. Found: C, 51.82; H, 2.29; F, 40.30.

Equilibrium between Pyrolysis Products.—A mixture of 10 and 11 which had been washed with alkali to remove 12 and distilled [14 g, bp 50° (0.6 mm), n^{25}D 1.4565] was pyrolyzed as described above at 400°. Distillation of the product gave 10 g which was largely the same as the starting material by boiling point and refractive index. In addition there was 2 g of higher boiling material. A fraction (1.1 g), bp ~65° (0.5 mm), n^{25}D 1.4602, crystallized on standing and was largely 12.

Similarly a 10-g sample of pure crystalline 12 was pyrolyzed at 400°. The 9 g recovered on distillation of the product was largely unchanged, but infrared and partial insolublity in alkali indicated the presence of 10 and 11 in the first fraction. Recovered 12 (7 g) was repyrolyzed at 500°. Again the 6 g recovered on distillation was largely 12 but the first fraction, 0.7 g, bp 50–54° (0.7 mm), n^{25}D 1.4581, was largely a mixture of 10 and 11, insoluble in alkali.

Pyrolysis of 2a at 500°.—When the pyrolysis of the above cyclobutenone was carried out at 500° instead of 400°, there was less recovered starting material and a higher ratio of cyclobutenyl acid fluoride 12 (47% conversion) to lower boiling cyclic ether 10 and 11 (35% conversion).

Pyrolysis at 650°. 1,1-Difluoro-4-phenyl-2-(trifluoromethyl)-1-buten-3-yne (14) and 4,4-Difluoro-3-(difluoromethylene)-2-phenyl-1-cyclobutene-1-carbonyl Fluoride (13).—Material obtained by pyrolyzing 2a at lower temperatures (66 g) was repyrolyzed at 650° using the apparatus described above. Distilled product amounted to only 31 g. There was obtained 13 g of the vinylacetylene 14, bp 34° (0.75 mm), n^{25}D 1.4749. It redistilled essentially unchanged after washing with concentrated H₂SO₄, dilute sodium hydroxide, and dilute hydrochloric acid and was 97% pure by vpc on a silicone column: ir 3.27 (=CH), 4.50 (C≡C), 5.83 μ (C=C); nmr ¹H at τ 3.2 ppm (multiplet, aromatic CH); ¹⁹F at 62.1 (doublet, 3, $J_{F/F}$ = 21.6 Hz, to doublets, $J_{F/F}$ = 10.6 Hz, CF₃), 69.4 ppm (complex multiplet, 2, CF₂).

Anal. Calcd for C₁₁H₅F₅: C, 56.94; H, 2.17; F, 40.95. Found: C, 57.18; H, 2.77; F, 41.40.

A higher boiling product [5 g, bp 74° (0.75 mm)] solidified and was recrystallized from hexane, mp 84–85°. It appeared to be the acid fluoride 13: ir 3.24 (=CH), 5.66 (conjd COF), 5.72 (exocyclic C=CF₂), 6.10 μ (conjd ring C=C); nmr ¹H at τ 2.2 (multiplet, aromatic CH); ¹⁹F at −35.1 (triplet, 1, $J_{H/F}$ = 2.8 Hz, COF), 78.7 (multiplet, 2, =CF₂), 109.4 ppm (multiplet, 2, CF₂).

Anal. Calcd for C₁₂H₅F₅O: C, 55.43; H, 1.94; F, 36.54. Found: C, 55.58; H, 1.95; F, 36.15.

4,4-Bis(trifluoromethyl)-2,3-diphenyl-2-cyclobuten-1-one (2b).—A mixture of 9.0 g (0.051 mol) of diphenylacetylene and 18 g (0.10 mol) of 1 in a Carius tube remained immiscible after heating 2 hr at 100°. After 8 hr at 200° there was recovered 9 g of low-boiler and 17.0 g (95%) of the above light yellow cyclobutenone, which after two recrystallizations from petroleum ether melted at 52–53° (10.2 g): ir 5.57 (shoulder), 5.65 (C=O), 6.18, 6.27, 6.38, 6.67, and 6.75 μ (C=C and aromatic rings); nmr ¹H at τ 2.2–2.8 (multiplet, aromatic C–H); ¹⁹F at 64.5 ppm (singlet, CF₃).

Anal. Calcd for C₁₈H₁₀F₆O: C, 60.72; H, 2.83; F, 32.02. Found: C, 60.77; H, 2.72; F, 32.15.

5-Fluoro-6-(trifluoromethyl)-11H-benzo[a]fluoren-11-one (18).—2b (20.0 g, 0.056 mol) was recovered unchanged when passed over quartz under vacuum (1 mm) at 400°. However, at 515°, 10.6 g (60%) of crude 18 was recovered in two crops by recrystallization from nitromethane. A second recrystallization of the first crop (6.5 g) from nitromethane gave 5.2 g: mp 195–

196° (further recrystallization from chloroform did not raise the melting point); ir 5.8 μ (C=O); nmr (THF) ¹H at τ 2.4 (broad multiplet, aromatic CH); ¹⁹F at 55.4 (doublet, 3, $J_{F/F}$ = 37.0 Hz, CF₃), 111.2 ppm (quartet, 1, $J_{F/F}$ = 37.0 Hz, CF).

Anal. Calcd for C₁₈H₈F₄O: C, 68.41; H, 2.55; F, 24.05. Found: C, 68.56; H, 2.77; F, 24.36.

An attempt to repeat the reaction over new quartz chips gave a much lower yield, but the yield was improved by pyrolysis over sodium fluoride pellets.

4,4-Bis(trifluoromethyl)-3-(*p*-tolyl)-2-cyclobutenone (2b).—*p*-Tolylacetylene (3.0 g, 0.026 mol) and 1 (8.7 g, 0.049 mol) were heated 16 hr in a steam bath to give, after three crystallizations from petroleum ether, 3.0 g (39.5%) of the cyclobutenone: mp 44.5–45.5°; ir 5.58 (C=O), 6.20, 6.30, 6.42, and 6.64 μ (aromatic and conjugated C=C); nmr (CDCl₃) ¹H at τ 2.27, 2.41, 2.61, and 2.75 (AB quartet, 4, *para*-aromatic C₆H₄), 3.19 (singlet, 1, =CH), 7.60 (singlet, 3, CH₃); ¹⁹F at 64.6 ppm [singlet, (CF₃)₂].

Anal. Calcd for C₁₃H₈F₆O: C, 53.11; H, 2.74; F, 38.78. Found: C, 52.66; H, 2.79; F, 39.11.

4,4-Bis(trifluoromethyl)-3-(*p*-chlorophenyl)-2-cyclobutenone (2e).—*p*-Chlorophenylacetylene (3.5 g, 0.026 mol) and 1 (8.7 g, 0.047 mol) were heated 16 hr in a steam bath to give, after two recrystallizations from petroleum ether, 5.0 g (62%) of 2e: mp 55–60°; ir 5.57 (C=O), 6.25, 6.31, 6.43 and 6.71 μ (aromatic and conjugated C=C); nmr (CDCl₃) ¹H at τ 2.38 (multiplet, 4, aromatic C₆H₄), 3.08 (singlet, 1, =CH); ¹⁹F at 64.5 ppm [singlet, (CF₃)₂].

Anal. Calcd for C₁₂H₅F₆ClO: C, 45.82; H, 1.60; F, 36.25; Cl, 11.28. Found: C, 46.63; H, 1.52; F, 35.10, Cl, 11.49.

3-Phenyl-5-(*p*-chlorophenyl)-6,6-bis(trifluoromethyl)-2,4-cyclohexadienone (22).—Cyclobutenone 2e (2.0 g, 0.0064 mol) and excess phenylacetylene were heated in a steam bath for 60 hr. Distillation up to 160° (45 μ) gave 1.3 g of oil which crystallized in petroleum ether and on recrystallization gave 1.0 g (38%) of

22: mp 105–107°; ir 5.97 (conjd C=O), 6.09, 6.26, 6.36, 6.71, and 6.91 μ (aromatic and conjd C=C); nmr (CDCl₃) ¹H at τ 2.53 (multiplet, 5, C₆H₅), 2.75 (multiplet, 4, C₆H₄), 3.12 (doublet, 1, $J_{H/H}$ = 1.4 Hz, =CH), 3.60 (doublet, 1, $J_{H/H}$ = 1.4 Hz, =CH); ¹⁹F at 61.5 ppm [singlet, (CF₃)₂].

Anal. Calcd for C₂₀H₁₁F₆ClO: C, 57.67; H, 2.66; F, 27.37; Cl, 8.51. Found: C, 57.04; H, 2.72; F, 27.14; Cl, 8.85.

3-(*p*-Chlorophenyl)-5-phenyl-6,6-bis(trifluoromethyl)-2,4-cyclohexadienone (23).—A 7.0-g (0.025 mol) sample of 2a and 3.5 g (0.025 mol) of *p*-chlorophenylacetylene were heated in a steam bath for 50 hr. Rapid distillation gave an oil, bp ~120° (0.4 mm), which solidified. Recrystallization from petroleum ether gave 2.0 g (20%) of crystals, Further crystallization gave 0.6 g of 23, mp 90–94°; ir 5.96 (conjd C=O), 6.09, 6.25, 6.31, 6.40, and 6.66 μ (aromatic and conjd C=C); nmr (CDCl₃) ¹H at τ 2.45 (multiplet, 4, C₆H₄), 2.57 (singlet, 5, C₆H₅), 3.03 (doublet, 1, $J_{H/H}$ = 1.4 Hz, =CH), 3.48 (doublet, 1, $J_{H/H}$ = 1.4 Hz, =CH); ¹¹F at 61.4 ppm [singlet, (CF₃)₂].

Anal. Calcd for C₂₀H₁₁F₆ClO: C, 57.67; H, 2.66; F, 27.37; Cl, 8.51. Found: C, 57.83; H, 2.73; F, 27.43; Cl, 8.33.

Registry No.—2a, 4141-87-1; 2b, 25631-73-6; 2c, 25631-74-7; 2d, 25631-75-8; 2e, 25631-76-9; 2f, 25631-77-0; 3, 25631-78-1; 5, 14203-12-4; 6, *cis*, 25631-80-5; 6, *trans*, 25798-19-0; 7, 25631-82-7; 10, 25631-83-8; 11, 25631-84-9; 12, 25631-85-0; 13, 25631-86-1; 14, 25631-87-2; 15, 25631-88-3; 16, 25631-89-4; 17, 25631-90-7; 18, 25631-91-8; 21, 25631-92-9; 22, 25631-93-0; 23, 25631-94-1; 4,4-difluoro-2-phenyl-3-(trifluoromethyl)-2-cyclobutene-1-carboxylic acid, 25679-32-7; 4,4-difluoro-2-phenyl-3-(trifluoromethyl)-2-cyclobutene-1-carboxylic acid Me ester, 25631-95-2.

Fluoroketenes. V. Cycloadditions to the Bis(trifluoromethyl)ketene Carbonyl Group[1]
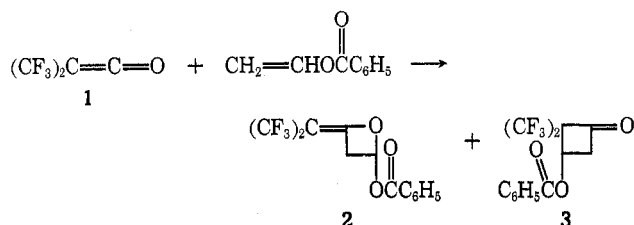
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Cycloadditions of very nucleophilic olefins to bis(trifluoromethyl)ketene tend to occur at the carbonyl group to form oxetanes. The mechanism for this reversible cycloaddition involves a dipolar intermediate, as shown by isomerizations with *cis*- and *trans*-propenyl propyl ethers. Supporting evidence is the increase in rate and in products of proton transfer with increase in solvent polarity, an increasing reactivity with increasing nucleophilicity of olefinic coreactant, the orientation of substituents in product, and a cationic polymerization of vinyl ethers and styrenes as a side reaction. A second mode of cycloaddition to the ketene carbon–carbon double bond also occurs to give thermodynamically more stable cyclobutanones. The latter cycloaddition is also reversible in the vinyl ether case, and evidence that it proceeds through a second type of dipolar intermediate is presented.

Vinyl Esters.—Ketenes normally form cyclobutanones with very reactive olefins as well as with simple alkenes.[2] Aside from the special case of ketene dimerizations to give β-lactones, the only example of a 1,2 cycloaddition to a ketene carbonyl group to form an oxetane seems to be with bis(trifluoromethyl)ketene (1).[3] Reaction of 1 with vinyl benzoate neat at 100° was reported to form 2-benzoyloxy-4-hexafluoroisopropylidenoxetane (2) and 2,2-bis(trifluoromethyl)-3-

benzoyloxycyclobutanone (3) in 34 and 42% yields, respectively.

More extensive work with this system has shown that the ratios of products vary erratically and that the presence of solvent encourages by-product formation. Table I summarizes the results obtained by ¹⁹F nmr for

(1) For parts III and IV on reactions at the double bond of bis(trifluoromethyl)ketene, see D. C. England and C. G. Krespan, *J. Org. Chem.*, **35**, 3300, 3308 (1970).

(2) For a review of the chemistry of ketenes, see R. N. Lacey in "The Chemistry of Alkenes," S. Patai, Ed., Interscience, New York, N. Y., 1964, p 1161.

(3) D. C. England and C. G. Krespan, *J. Amer. Chem. Soc.*, **87**, 4019 (1965).