filtrate was acidified with concentrated hydrochloric acid. On standing a yellow precipitate formed which on filtering amounted to 5–7 g, mp 220° dec. The infrared spectrum contained characteristic peaks at 3150, 1710, 1610, 1320, 1230, and 945 cm^{-1}. The infrared spectrum of the aluminum complex contained broad peaks at 2900–3400, 1100–1200, 840–850, and sharper peaks at 2420, 1950, and 1640 cm^{-1}. Solutions of the complex dissolved silver nitrate without formation of silver chloride. Addition of a sodium chloride solution also failed to cause precipitation indicating that a stable soluble silver complex had formed.

Anal. Calcd for $C_8H_6O_4$: C, 57.8; H, 3.62. Found: C, 56.31; H, 3.83.

Registry No.—V, 10103-12-5; VIa, 10074-64-3; VIb, 10074-65-4; VII, 10074-66-5; VIII, 10074-67-6; X, 10074-68-7; XI, 10074-69-8; XIVa, 10074-70-1; XIVb, 10074-71-2; XVI, 10074-72-3; XVII, 10074-73-4.

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Bicyclobutyl Derivatives. III. Hydrolysis of Fluorinated Cyclobutenes[1,2]

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A series of cyclobutene and bicyclobutyl derivatives was studied with respect to ease of sulfuric acid catalyzed hydrolysis. Evidence is presented in support of a proposed reaction pathway. A number of new ketones are described.

The facility with which 2,2′-dialkoxy-3,3,3′,3′-tetrafluorobicyclobutenyl (I)[4] is hydrolyzed with cold sulfuric acid to diketone II (2,2′-dialkoxy-3,3′-diketobicyclobutenyl)[2a] has led to further investigation of the hydrolysis reactions of fluorinated cyclobutenes.

Acyclic α-difluoro ethers[5] and amines[6] are easily hydrolyzed to the corresponding esters and amides, respectively, in acid. The pathway for the hydrolyses has been quite uncertain.[7]

Also, a series of 2-substituted 1-phenyl-3,3-difluorocyclobutenes has been hydrolyzed to the corresponding 3-ketones by Roberts and his group.[8] Their work reveals no clear-cut influence of 2 substituents on the ease of acid-catalyzed hydrolysis.

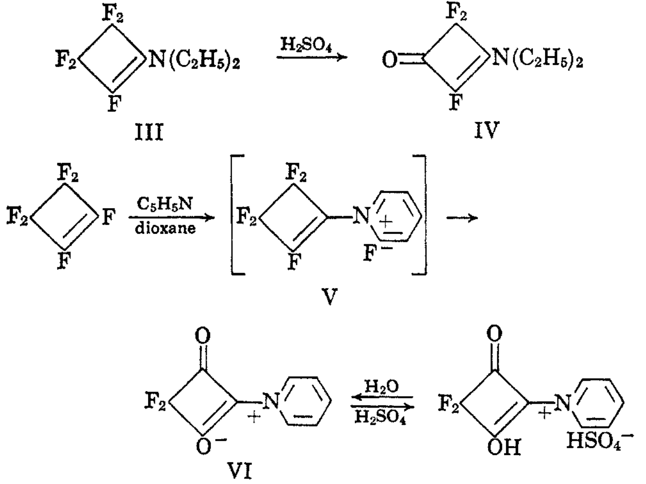
The acid-catalyzed hydrolysis of benzotrifluorides has been reviewed recently[9] and the reaction has been shown to be dependent on the ring substituents. Thus, electron-donating groups *ortho* or *para* to the CF_3 greatly enhance the reaction, while electron-withdrawing groups in these positions have the opposite effect. *meta* substituents show little or no effect on the hydrolysis.

Results

When 1-diethylaminopentafluorocyclobutene (III) was dissolved in cold sulfuric acid, hydrolysis occurred rapidly and a monoketone was obtained in high yield as the sole product. This was shown to be 1-diethylamino-3-keto-2,4,4-trifluorocyclobutene (IV) by its F^{19} nmr spectrum.

On the other hand, perfluorocyclobutene forms an unstable complex (V) with pyridine which reacts with moisture to form 3,3-difluoro-2,4-diketocyclobutylpyridiniumbetaine (VI, see Scheme I). This type of behavior was first observed by Pruett[10] in the reaction of trialkylamines with perfluorocyclobutene. The pyridinium betaine which dissolved in sulfuric acid without further hydrolysis, was recovered unchanged on quenching in water.

SCHEME I
HYDROLYSIS OF PERFLUOROCYCLOBUTENYLAMINES



The effect of 1 substituents on the hydrolysis of 2,3,3-trifluorocyclobutenes was studied and the results

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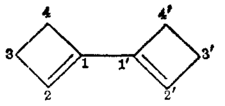
[1] Presented at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965.

[2] Previous papers in this series: (a) J. D. Park and W. C. Frank, *J. Org. Chem.*, **29**, 1445 (1964): (b) *ibid.*, **32**, 1333 (1967).

[3] This paper represents part of a Ph.D. thesis submitted by W. C. Frank to the Graduate School, University of Colorado, 1965.

[4] This structure is more properly written (bi-1,1′-cyclobut-1-enyl) consistent with *Chemical Abstracts* Nomenclature Guide. To permit smoother reading the shortened form will be used throughout the text. The numbering for the bicyclobutenyl structure is as follows.



[5] J. A. Young and P. Tarrant, *J. Am. Chem. Soc.*, **71**, 2432 (1949); **72**, 1860 (1950).

[6] R. L. Pruett, *et al.*, *ibid.*, **72**, 3646 (1950).

[7] E. R. Larson, *J. Org. Chem.*, **28**, 1133 (1963).

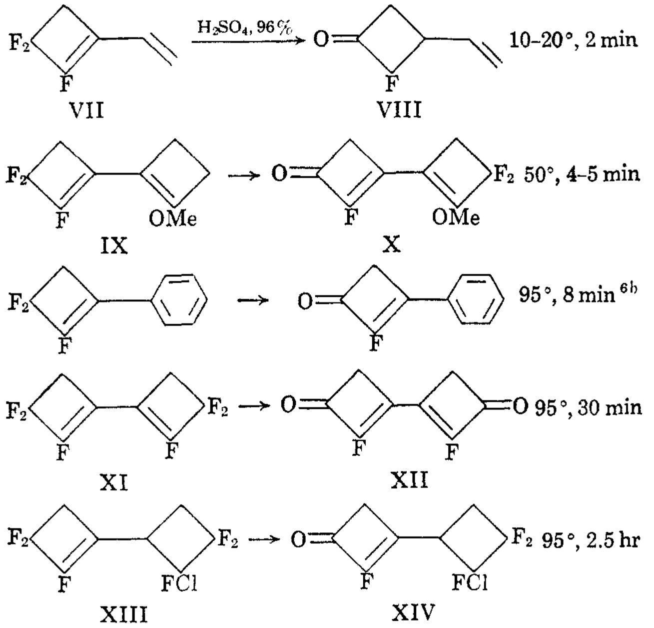
[8] (a) J. D. Roberts, *et al.*, *J. Am. Chem. Soc.*, **80**, 4083 (1958); (b) *ibid.*, **80**, 5840 (1958); (c) *ibid.*, **82**, 3106 (1960); (d) *ibid.*, **86**, 2645 (1964).

[9] R. Fillar and H. Novar, *Chem. Ind.* (London), 1273 (1960).

[10] R. L. Pruett, C. T. Bahner, and H. A. Smith, *J. Am. Chem. Soc.*, **74**, 1633 (1952).

in general showed that ease of hydrolysis by acid is due to the presence of electron-donating groups in the 1 position (see Scheme II).

Scheme II
Hydrolysis of 1-Substituted 2,3,3-Trifluorocyclobutene Derivatives



Thus, 1-vinyl-2,3,3-trifluorocyclobutene[2a] (VII) was easily hydrolyzed in about 2 min in cold, concentrated sulfuric acid to give 1-vinyl-2-fluoro-3-ketocyclobutene (VIII), an acrid-smelling liquid which rapidly and spontaneously polymerized on standing at room temperature.

At 50° 2-methoxy-2,3,3,3′,3′-pentafluorobicyclobutenyl (IX) was easily hydrolyzed in 5 min. The product formed was not the 3-keto derivative, but 3′-keto-2-methoxy-2′,3,3-trifluorobicyclobutenyl (X), whose structural assignment was based on infrared spectral data (see the correlation chart in the Experimental Section.)

Roberts has reported the hydrolysis of 1-phenyl-2,3,3-trifluorocyclobutene. It fits into the middle of the above series, requiring heating for about 8 min at 95° in concentrated sulfuric acid.[8b]

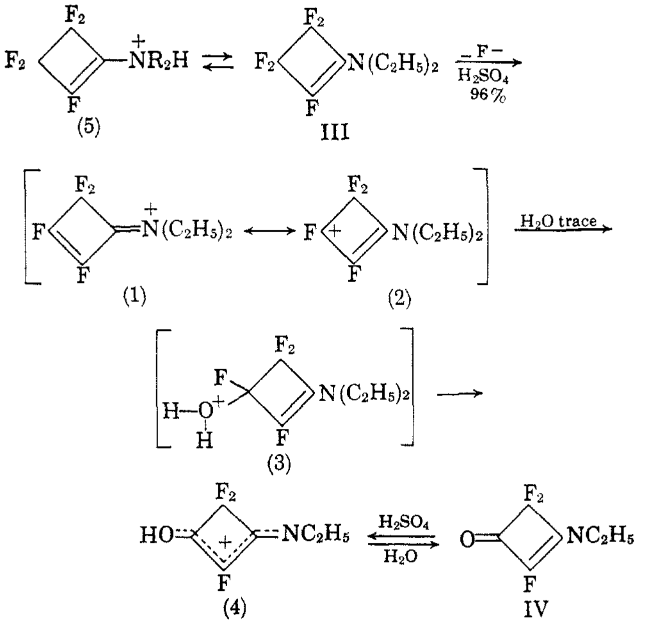
Hydrolysis of 2,2′,3,3,3′,3′-hexafluorobicyclobutenyl (XI) and 2-(2,3,3-trifluoro-2-chlorocyclobutyl)-2,3,3-trifluorocyclobut-1-ene (XIII) proceeded with relative difficulty, requiring long treatment with hot sulfuric acid. With hexafluorobicyclobutenyl, a diketone, 2,2′-difluoro-3,3′-diketobicyclobutenyl (XII) was obtained after heating for about 30 min at 95°. The hydrolysis of the monoolefin required heating at 95° for about 2.5 hr and the product was 1-(2,3,3-trifluoro-2-chlorocyclobutyl)2-fluoro-3-ketocyclobutene (XIV).

Discussion

Using 1,1-diethylaminopentafluorocyclobutene as an example, the pathway shown in Scheme III is being proposed for sulfuric acid hydrolysis of cyclobutenes.

The first step (or series of steps) may be the loss of fluoride ion to give an ammonium ion which is in resonance with an α-fluoroallylic carbonium species (step 2). In 96% sulfuric acid this carbonium ion would be expected to be unstable and react with traces of water to give the hydrated carbonium ion (step 3), which can then lose hydrogen fluoride to give the stable protonated ketone (step 4).

Scheme III
Proposed Hydrolysis Pathway



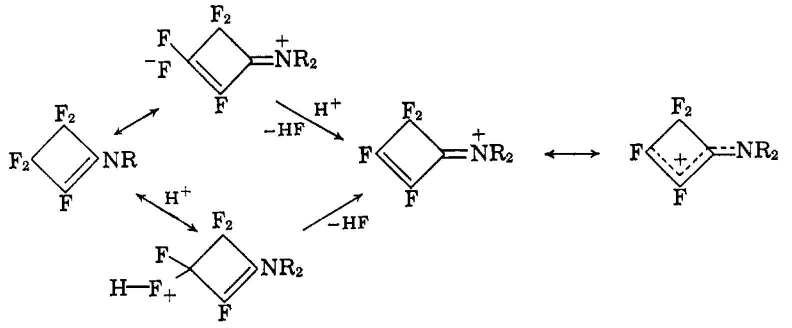
It is possible that the nitrogen atom of the amine may be initially protonated in sulfuric acid. Such a protonated species (step 5), if formed, would not be expected to be an intermediate in the hydrolysis since the $-N^+(C_2H_5)H$ group is strongly electron deficient and deactivates the 3 position to hydrolysis. Such a protonated species would be in very rapid equilibrium with the starting amine (III), the actual species being hydrolyzed.

To test this pathway further, F^{19} nmr spectra were taken, both of the starting material and of the product, alone and in 96% sulfuric acid. It was found that both the starting material and the product formed the same species (step 4) in 96% sulfuric acid. In addition, fluorosulfonic acid was present in the former case. Therefore, the hydrolysis is virtually complete on dissolving the amine in sulfuric acid. There was no nmr evidence of any *other stable* intermediates. In 30% oleum an initial mixture was obtained, which did not include the species present in 96% sulfuric acid. The spectrum could not be interpreted further. After 4 days the F^{19} nmr spectrum of the same oleum solution was obtained. The spectrum was then very simple containing only three peaks roughly in the ratio 2:1:1 in addition to the fluorosulfonic acid peak. It is not possible to assign the peaks with any confidence at this time, but the results are not inconsistent with the assignment of structure $1 \underset{\text{or}}{\leftrightarrow} 2$ for the species.

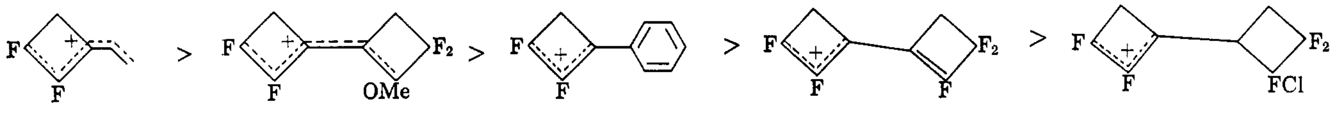
The mode of fluoride ion removal is not clearly known, but it is thought to be intermediate between actual ionization or "no-bond" resonance of the fluorocyclobutene and protonation of a fluorine atom followed by loss of hydrogen fluoride. The resulting cation is conveniently written in the delocalized form as shown in Scheme IV.

From the order of the ease of hydrolysis (Scheme II) it can be qualitatively assumed that the stabilities of

SCHEME IV



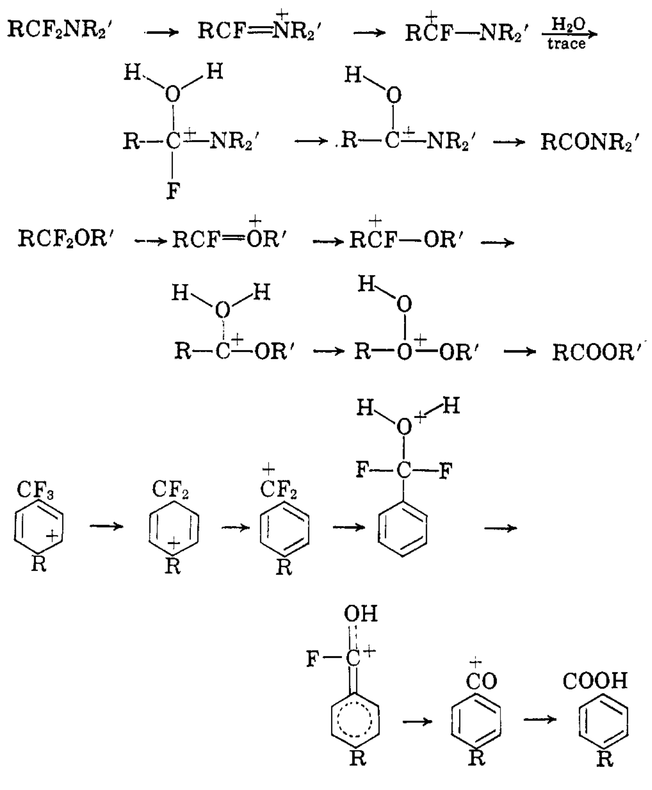
SCHEME V
ORDER OF CATION STABILITIES



the transition states for the formation of the carbonium ion reflects the relative stabilities of those carbonium ions. On this basis, one arrives at the order of cationic stabilities given in Scheme V.

The hydrolysis of the noncyclobutene systems can be considered to go through a similar pathway. This is consistent with observed substituent effects and with autocatalytic hydrolysis, as shown in Scheme VI.

SCHEME VI
ANALOGOUS PATHWAYS PROPOSED FOR
NONCYCLOBUTENE SYSTEMS



Summary.—The presence of electron-donating groups in the 1 position enhances the ease of H_2SO_4 hydrolysis of fluorines in the 3 position. The presence of strong electron-withdrawing groups in the 1 position enhances the base-catalyzed hydrolysis of fluorine in the 2 and 4 positions. The presence of an electron-donating group on the 2 position enhances the ease of H_2SO_4 hydrolysis of fluorines in the 3′ position.

Experimental Section

1,1-Diethylamino-3-keto-2,4,4-trifluorocyclobutene (IV). A.—1,1-Diethylaminopentafluorocyclobutene (III) was prepared by the general method of Pruett, *et al.*[6] Perfluorocyclobutene (63.9 g, 0.394 mole) was bubbled into a solution of diethylamine (73 g, 1.0 mole), in 200 ml of monoglyme at 20–25°. The reaction mixture was quenched in cold water and the crude product was separated and distilled to yield 70.2 g (88% yield) of pure product III: bp 66–72° (24 mm), d^{20}_{20} 1.2330, n^{25}_{D} 1.3919 (lit.[6] n^{25}_{D} 1.3914). The original workers reported a 59% yield using ether as a solvent at 0–25°.

B. Hydrolysis of III to Cyclobutenone IV.—Amino olefin III (41 g, 0.20 mole) was added slowly with stirring and cooling to 200 ml of concentrated sulfuric acid in a 500-ml, three-neck flask, equipped with an addition funnel, mechanical stirrer, thermometer, and reflux condenser. The temperature was kept below 30°. Then 75 ml of water was added cautiously, the temperature being kept below 40°. Foaming was minimized by cooling and decreasing the rate of water addition. After the addition, the mixture was stirred for 5 min, then poured over a large volume of ice with stirring. A white solid separated, and was filtered with suction. *Caution: this material melts at ca. 15°, so it must be kept at ice-water temperature during filtration and washing.* The solid was washed with a large volume of ice water (5°) and quickly transferred to a beaker. The product was then separated from the aqueous phase as an oil and dried over anhydrous magnesium sulfate. A colorless liquid (IV) 24.2 g, 66% yield, d^{20}_{20} 1.2266, n^{25}_{D} 1.4767 was obtained. A sample was distilled giving a single fraction: bp 105° (0.5 mm), n^{25}_{D} 1.4767; no pot residue remaining, indicating that the product was already very pure; infrared peaks at 1840 (sharp, strong) and 1650 cm^{-1} (broad, strong). The F^{19} nmr spectrum showed one strong doublet (=CF_2) at 113.0 and one weaker triplet (=CF) at 134.6. The first-order splitting constant was 26.4 cps, supporting the assignment of the fluorine atoms to positions cross-ring from each other.

Anal. Calcd for $C_8H_{10}F_3NO$: C, 49.7; H, 5.2; F, 29.2. Found: C, 49.5; H, 5.3; F, 29.8.

By a similar procedure, 1-N-morpholino-3-keto-2,4,4-trifluorocyclobutene was prepared from morpholine and perfluorocyclobutene. Colorless crystals from chloroform were obtained melting at 85.7–86.4°. The infrared spectrum contained the expected peaks at 1650 and 1820 cm^{-1}.

2,4-Dioxo-3,3-difluoro-1-cyclobutylpyridiniumbetaine (VI).—A solution of 15 ml of pyridine in 50 ml of moist dioxane was placed in a tall test tube immersed in a cold water bath. About 5 g of perfluorocyclobutene was bubbled through the solution, causing it to become dark orange. After 4 days, a large amount of crystalline material had collected on the walls of the tube. These crystals were separated by filtration. These darkened above 200° without melting and were identified as 2,4-dioxo-3,3-

difluoro-1-cyclobutylpyridiniumbetaine by virtue of their close similarity to the corresponding trimethylammoniumbetaine prepared by Pruett:[10] infrared peaks at 1790, 1640 (broad), 1478, 1255, 833, and 786 cm^{-1}.

Anal. Calcd for $C_9H_5F_2NO_2$: C, 54.7; H, 2.54; F, 19.3; N, 7.11; mol wt, 197. Found: C, 54.3; H, 2.48; F, 19.6; N, 6.92; mol wt (acetone), 197.

This material was found to be soluble without further hydrolysis in concentrated sulfuric acid, the solutions yielding colorless needles of VI on dilution with water. The betaine dissolved in acetonitrile containing a little potassium hydroxide and water, to give a dark green solution. In dimethyl sulfoxide containing potassium *t*-butoxide, a dark crimson color was observed. A dark red-orange solution was obtained on dissolving it in aqueous potassium hydroxide. The nature of these complexes was not further investigated.

1-Vinyl-2-fluorocyclobut-1-en-3-one (VIII).—Sulfuric acid (50 ml) was placed in a 200-ml beaker and cooled to 5° in an ice bath. To this was added with cooling and stirring, 20 g (0.15 mole) of 1-vinyl-2,3,3-trifluorocyclobutene (VII).[3] The reaction was very exothermic and copious quantities of hydrogen fluoride were evolved (*wear gloves!*). After the addition, 10 ml of ice was cautiously added with stirring. Five minutes later, the mixture was poured over 200 ml of ice and a dark brown oil slowly settled to the bottom. The oil was separated and washed with cold water to remove excess acid. Steam distillation gave a colorless liquid with a piercing odor, which quickly darkened on standing and became progressively more viscous during the day. The freshly steam-distilled product had the following properties: $n^{26}D$ 1.4814; infrared peaks at 1770, 1650, 1200, 740 cm^{-1}. The residue from the steam distillation was a tan-white solid with infrared peaks at 1775, 1655, 1300, and 1170 cm^{-1}, and is suspected to be a polymer of (VIII). Distillation under reduced pressure gave 50% recovery of colorless oil, bp 64° (30 mm). Considerable polymerization occurred during the distillation. The only satisfactory means for storing the monomer was at −75°.

2-Methoxy-2′,3,3-trifluoro-3′-ketobicyclobutenyl (X).—Sulfuric acid (100 ml) and 2-methoxy-2′,3,3,3′,3′-pentafluorobicyclobutenyl[11] (IX, 39.0 g, 0.174 mole) were stirred together for about 5 min until a single phase was obtained. The reaction was slightly exothermic. The mixture was poured over ice and extracted with methylene chloride. The extract was dried over magnesium sulfate. The solvent was stripped *in vacuo* to yield 20 g of a crude, dark fluid. On distillation, a yellowish fluid was obtained: bp 92–96° (0.4–0.5 mm); $n^{28}D$ 1.4866; infrared peaks at 1770, 1650, 1605, 1440, and 1320 cm^{-1} in agreement with the proposed structure. Hydrolysis at higher temperatures resulted in destruction of the material.

2,2′-Difluoro-3,3′-diketobicyclobutenyl (XII).—In a test tube containing 20 ml of concentrated sulfuric acid was placed 1.0 g of 2,2′,3,3,3′,3′-hexafluorobicyclobutenyl[2] (XI). The mixture was heated with stirring over a steam bath until homogeneous (25–30 min) and then poured over 100 ml of ice with stirring; no solid separated for about 10 min. Crystallization began after 10 min and was complete after the solution was chilled for several hours. On recrystallization from Skellysolve C the product (XII) was obtained as colorless needles: mp 96.5–97.0°; infrared peaks at 1775, 1610, 1422, 1260, and 925 cm^{-1}, in accord with the proposed structure.

Anal. Calcd for $C_8H_4F_2O_2$: C, 56.5; H, 2.36; F, 22.4. Found: C, 56.46; H, 2.50; F, 22.60.

1-(2,3,3-Trifluoro-2-chlorocyclobutyl)-2-fluoro-3-ketocyclobutene (XIV).—In a test tube containing 60 ml of concentrated sulfuric acid was placed 10.0 g of 1-(2,3,3-trifluoro-2-chlorocyclobutyl)-2,3,3-trifluorocyclobutene[2] (XIII). The mixture was heated with stirring over a steam bath until homogenous. The solution was then poured over ice and extracted with methylene chloride. The extract was dried over magnesium sulfate and filtered. The solvent was stripped off over a steam bath, leaving a brownish fluid with a piercing odor. This was purified further by vacuum distillation: bp 44–46° (0.2 mm); $n^{25}D$ 1.4441; infrared peaks at 1775, 1660, 1420 cm^{-1}, in accord with the proposed structure.

Anal. Calcd for $C_8H_5ClF_4O$: C, 42.3; H, 1.76; F, 33.4. Found: C, 42.28; H, 2.31; F, 33.59.

Registry No.—III, 432-76-8; IV, 10181-49-4; VI, 6508-58-3; VIII, 10181-51-8; X, 10181-52-9; XII, 10181-53-0; XIV, 10181-54-1; 1-N-morpholino-3-keto-2,4,4-trifluorocyclobutene, 10181-55-2.

Acknowledgment.—The authors wish to express their appreciation to the Minnesota Mining and Manufacturing Co., St. Paul, Minn., and the U. S. Army Natick Laboratories, Natick, Mass., under Scientific Project Officer, Dr. Malcolm C. Henry, for their partial support of this work.

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[11] See part II of this series for preparation.