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ARIZONA UNIV TUCSON DEPT OF CHEMISTRY  
SYNTHESIS AND POLYMERIZATION OF FLUOROBICYCLOBUTANES TO CHEMICALS--ETC(U)  
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A novel cyclopropane synthesis was found in the cycloaddition of bromoketene acetal to acrylonitrile or methyl alpha-cyanoacrylate.

Three publications have been based on this work.

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Abstract of AFOSR Program 73-2426

"Synthesis and Polymerization of Fluorobicyclobutanes  
to Chemically, Dimensionally, and Thermally  
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Final Scientific Report to the  
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Grant 73-2426

October 1, 1977

Synthesis and Polymerization of Fluorobicyclobutanes to  
Chemically, Thermally, and Dimensionally Stable Polymers

by

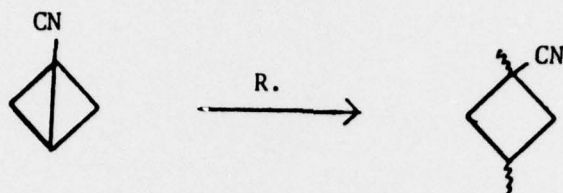
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Introduction

Fluoropolymers have been extensively studied because of their outstanding thermal stability and low adhesion. However, creep behavior remains a problem. Gaskets and other shaped articles kept under pressure for some time tend to flow to conform to the applied stress, and this limits their usefulness in some applications.

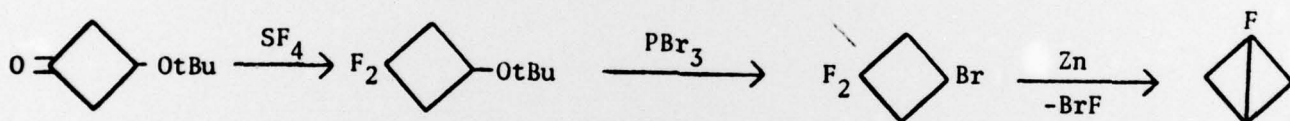
We have published a series of articles dealing with the synthesis and polymerization of a new family of monomers, the bicyclobutanes.

Their polymerization is exemplified by:



The high molecular weight polymers had many outstanding properties as regards thermal and chemical stability. Very high bulk viscosities were found, owing to the presence of rings in the main polymer chains.

During this work, a small amount of 1-fluorobicyclobutane was prepared as follows:



In preliminary work it appeared to polymerize readily.

We proposed to synthesize and polymerize a variety of fluorinated bicyclobutanes in hopes of obtaining novel new materials possessing high thermal stability, low adhesion, and low creep properties.

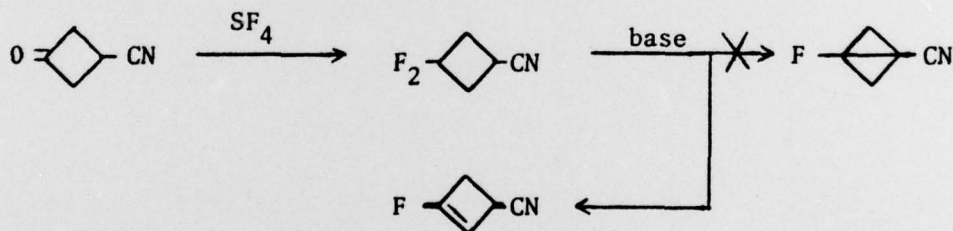
## Results

### I. Attempted Fluorinated Bicyclobutane Syntheses

The problem is to synthesize the appropriate 1,3-disubstituted cyclobutane precursors of the bicyclobutane monomers. We took two approaches:

- (1) fluorinate available cyclobutane intermediates;
- (2) use  $\pi^2 + \pi^2$  cycloadditions of fluoro-olefins.

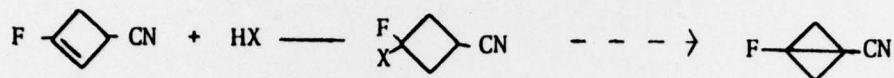
#### (1) Fluorination of Cyclobutane Intermediates



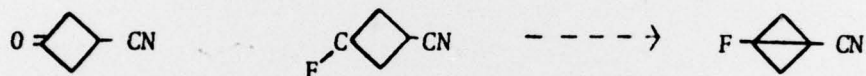
Sulfur tetrafluoride converted the available 3-cyanocyclobutanone to a mixture containing some of the desired 3,3-difluorocyclobutanecarbonitrile. However, treatment of this with base gave none of the desired bicyclobutane but gave 1,2-elimination instead. This may be due to the strong acidifying influence of the fluorine and cyano groups on the CH<sub>2</sub> group.



We tried various experiments to: (a) readd HCl or HBr to this olefin and then do a 1,3-elimination.

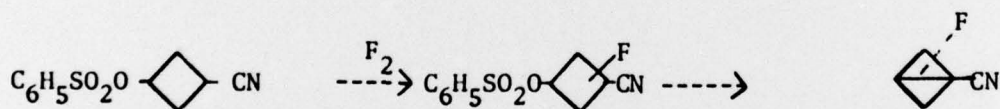


(b) Replace O=C with BrFC or ClFC:



We could not find a reagent to accomplish this task.

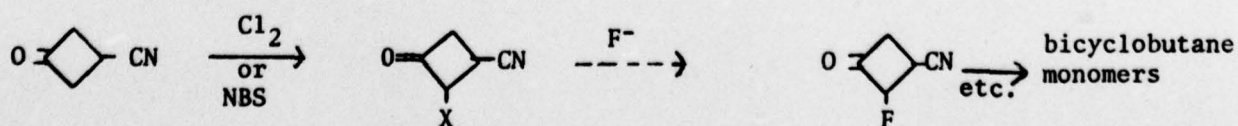
We abandoned an original idea of photofluorination of 3-benzenesulfonyloxycyclobutane-Carbonitrile:



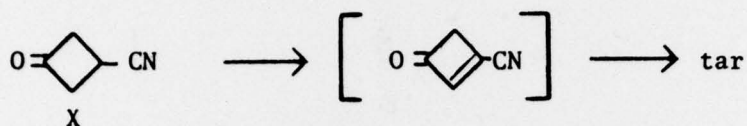
after discussion with Dr. J. Kollonitsch and Prof. D. H. R. Barton.

Successful fluorinations require a special Kel-F photoreactor and electron-rich molecules.

Chlorination or bromination, followed by fluoride replacement was tried:

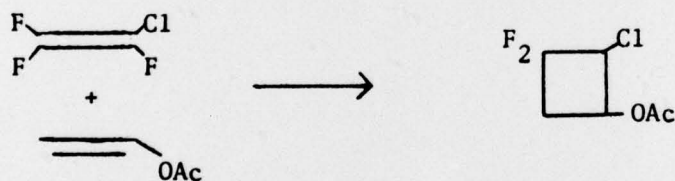


Halogenation of 3-cyanocyclobutanone gave exceptionally unstable halides which rapidly resinified by loss of HX:

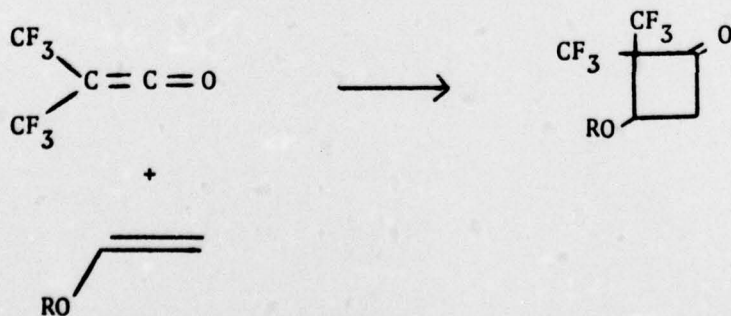


This was shown by halogenating the  $\alpha$ -methyl nitrile to stable halides (which cannot lose HX).

(2) No authentic cycloadditions giving 1,3-disubstituted cyclobutanes were found in the literature, only 1,2-disubstituted products being formed instead. One case had been reported in the reaction of vinyl acetate with chlorotrifluoroethylene. However this was later reported to be a 1,2- adduct, and we independently confirmed this:

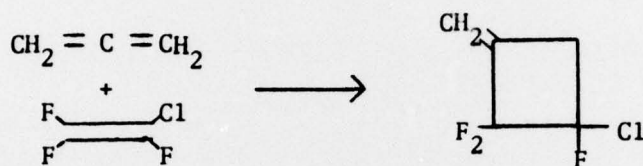


The only cycloadditions giving 1,3- difunctional cyclobutanes are those of bis(trifluoromethyl)ketene, according to Krespan and England.



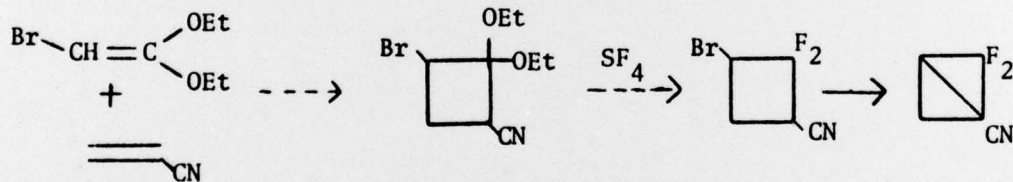
However, only lengthy, impractical schemes could be devised to convert these to bicyclobutanes. Also, the ketene is toxic itself, and its precursor, perfluoroisobutylene, is exceptionally so.

Allene has also been reported to cycloadd to chlorotrifluoroethylene to give a 1,3-difunctional compound:

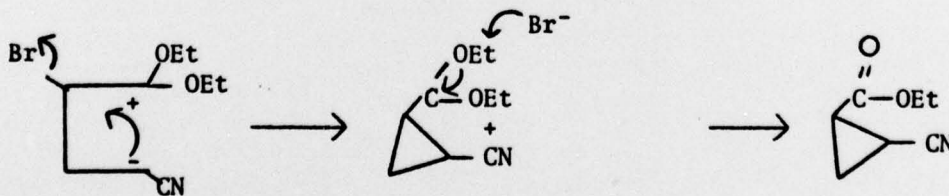


We reinvestigated this reaction and found that, under all conditions we tried, only trace yields are obtained. This compound is not a useful synthesis intermediate.

An attempt was made to carry out the following synthesis scheme:



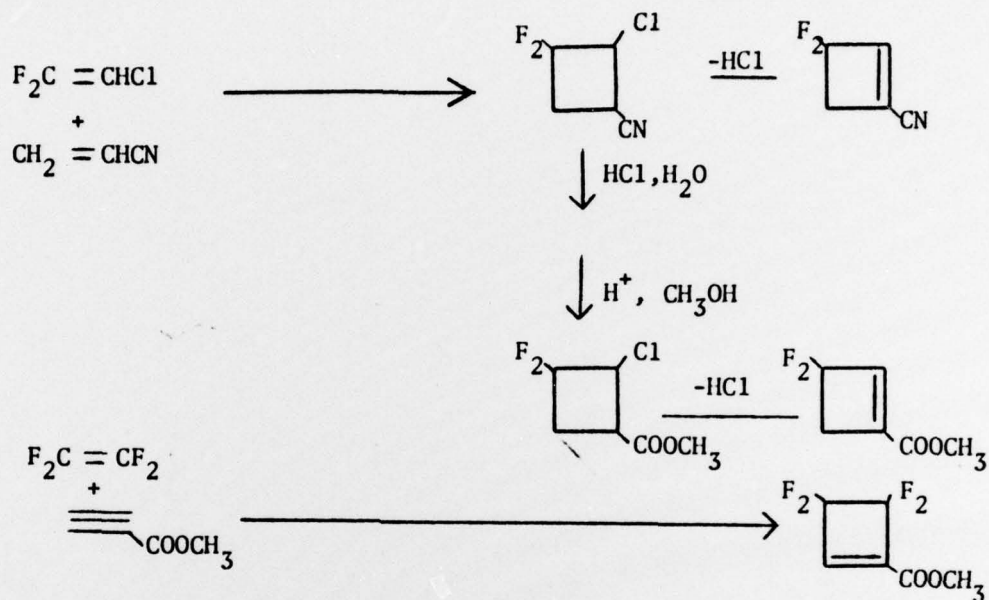
However, this scheme was frustrated by an interesting alternative course of reaction displayed by the zwitterionic intermediate:



The cyclopropane ester-nitrile was the only product isolated. (A manuscript has been submitted to Tetrahedron Letters).

## II. Fluorocyclobutene Monomers and Polymers.

Thwarted in finding 1,3-cycloadditions, we decided to make use of the available 1,2-cycloadducts. Three fluorocyclobutene monomers were synthesized as follows:

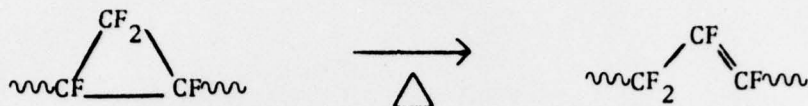


Of these, only the difluoroester gave homopolymer, but in low yield. All of these monomers copolymerized readily with electron-rich vinyl monomers. The polymers were not alternating, but possessed varying composition ratios. The copolymers displayed decomposition exotherms ranging from  $250^\circ$  to  $400^\circ$  by differential scanning calorimetry. They have not as yet displayed the high thermal stability we are seeking, in part because of the presence of the required comonomers (Attached reprint; a manuscript describing the fluoroesters has been submitted to J. Polymer Sci.)

## III. Fluorocyclopropenes

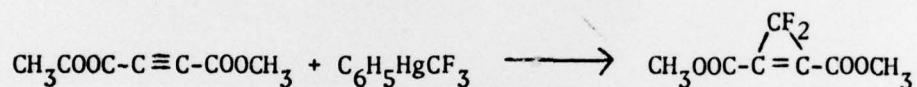
Another fluorinated small-ring system we have investigated is the difluorocyclopropene group. Perfluorocyclopropene has been synthesized and polymerized by Krespan and Sargeant. The polymers were not as

thermally stable as expected, owing to an unexpected thermal isomerization:



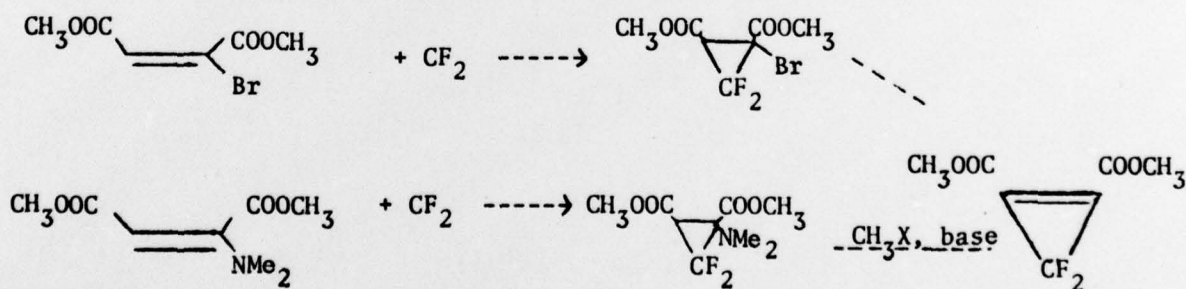
We speculated that electron-attracting carbomethoxy or cyano groups might slow this isomerization. More, once in hand, the fluorocyclopropenes might react with carbenes to form fluorinated bicyclobutane monomers.

Difluorocarbene, generated by the Seyferth reagent phenyltrifluoromethylmercury, added to acetylenedicarboxylic ester in very low yield.



All attempts to generate  $\text{CF}_2$  from a variety of other sources failed in this reaction. The difluorocyclopropene did not homopolymerize, but it copolymerized with *p*-methoxystyrene.

As an alternate possibility, we attempted to carry out the following reactions:

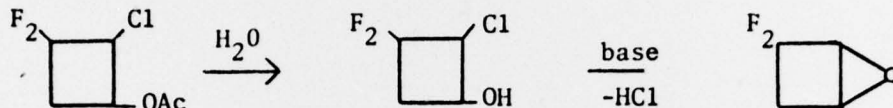


Only negative results were obtained.



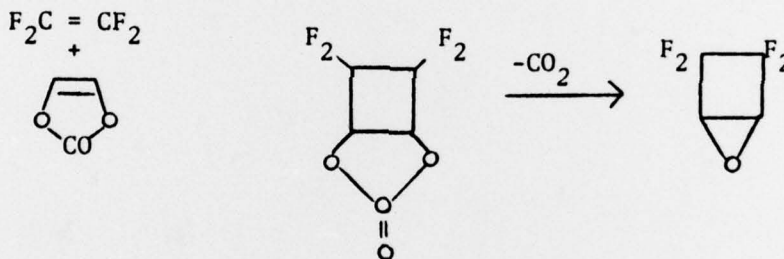
#### IV. Fluoroepoxides

From the 1,2-cycloadduct of chlorotrifluoroethylene with vinyl acetate (described above) we attempted to synthesize a new fluorinated epoxide as follows:



The fluoroalcohol was made, but could not be converted to epoxide.

A second proposed scheme involved a possible cycloaddition of vinylencarbonate to tetrafluoroethylene:



However, even at 210° for 16 hours, these compounds did not cycloadd.

#### Conclusions and Recommendations

A search for new small-ring fluoromonomers has found several fluorinated cyclobutanes to be suitable for synthesis and polymerization. Further work with other substituents and degrees of fluorination on the cyclobutane nucleus appears warranted.

We were not successful in finding new fluorinated bicyclobutane, cyclopropane, or epoxide monomers, owing to synthesis difficulties. Future progress must await the appearance of new intermediates or synthesis procedures.

### Publications

1. H. K. Hall, Jr., and Y. Okamoto, "Synthesis and Copolymerization of 3,3-Difluorocyclobutene-1-Carbonitrile", J. Polymer Sci., Polymer Chem. Ed., 12, 1443 (1974).
2. H. K. Hall, Jr., Y. Okamoto, A. B. Padias, A. Deutschman, Jr., and J. W. Berry, "Synthesis and Polymerizations of Methyl 3,3-Difluorocyclobutene-1-carboxylate and Methyl 3,3,4,4-Tetrafluorocyclobutene-1-carboxylate", submitted to J. Polymer Science.
3. H. K. Hall, Jr., A. B. Padias, A. Deutschman, Jr., and I. J. Westerman, "Cyclopropane formation from a 3-Halo-1,4-dipole", submitted to Tetrahedron Letters.



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