

## Fluorochlorocyclobutenes 와 염화알루미늄과의 반응<sup>1</sup>

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 (1973. 1. 18 접수)

## Reactions of Aluminum Chloride with Fluorocyclobutenes<sup>1</sup>

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(Received Jan. 18, 1973)

요 약. 이 논문은 플루오르의 치환, 분자내의 전위, 분자간의 전이등을 포함하는 fluorochlorocyclobutenes 와 염화 알루미늄과의 반응들을 총괄하여 놓았다.

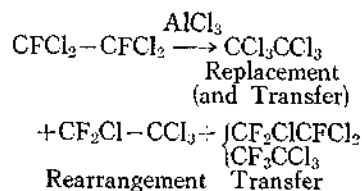
**Abstract.** The present paper represents a summary of the reactions of  $AlCl_3$  with fluorochlorocyclobutenes involving fluorine replacement, and intermolecular transfer.

### Introduction

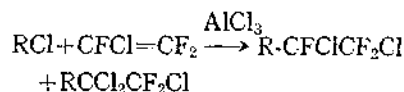
In this limited work reported on reactions of anhydrous aluminum chloride with fluorocarbons, three types of reactions are seen: fluorine atom replacement, intramolecular rearrangement, and intermolecular transfer. An observation made during our study<sup>3</sup> of allylic rearrangements of fluorohalocyclobutenes prompted this extension of the aluminum of chloride reactions to fluorocyclobutenes.

Fluoroalkanes, -alkenes, and  $\alpha$ -fluoroethers react with aluminum chloride to give the corresponding chlorocarbons. This reaction was discovered by Henne and Newman<sup>1</sup> while attempting Friedel-Crafts alkylations with fluorochloromethanes. Higher fluoroalkanes undergo

fluorine atom replacement in competition with rearrangement and transfer. Hudlicky<sup>5</sup> found that increases in reaction times, temperature, and amount of aluminum chloride favor fluorine replacement. Barr et al.<sup>6</sup> encountered considerable fluorine replacement in the products of the



Prins reactions of chlorotrifluoroethylene with *n*-propyl and *t*-butyl chlorides.

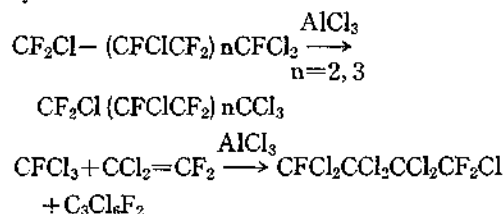


telomers of chlorotrifluoroethylene suffer replacement of the isolated fluorine atom.<sup>7</sup> A similar reaction occurred during the Prins reaction of fluorotrichloromethane with chlorotrifluoro-

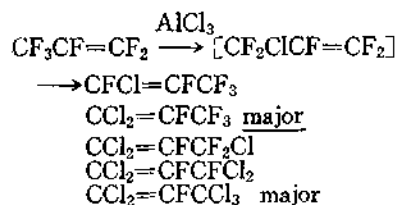
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ethylene.<sup>8,9</sup>

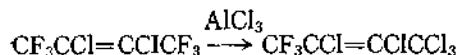


Park and coworkers<sup>10</sup> studied the reaction of perfluoropropene with aluminum chloride, proposing the initial replacement of allylic fluoride and subsequent fluoride rearrangement to the 1-chloro-derivative.

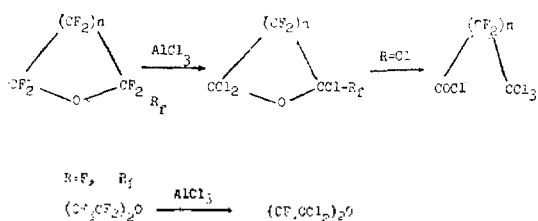


This suggestion is consistent with the inertness of the vinylic fluorine atom at C-2 and of aryl fluoride toward aluminum aluminum chloride.<sup>11</sup>

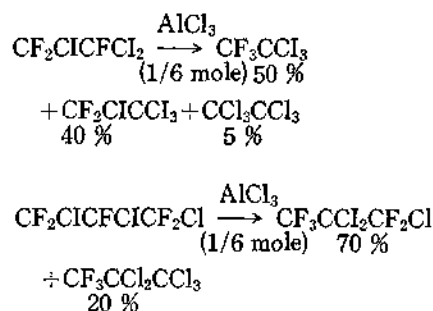
Knunyants<sup>12</sup> later reported the reactions of 2-hydropentafluoropropene and perfluoropropene with aluminum chloride to give the corresponding 2-substituted pentachloroprenes. The reaction of 2,3-dichlorohexafluorobutene-2 with aluminum chloride provides a synthesis of 1,1,1-trifluoropentachlorobutene-2.<sup>13</sup>



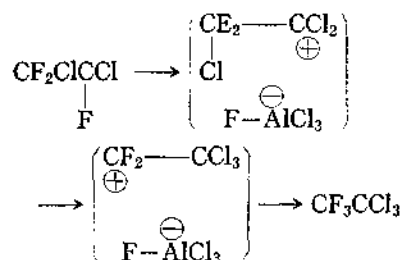
Tiers<sup>14</sup> has found  $\alpha$ -fluoroethers to be susceptible to replacement of  $\alpha$ -fluorine atoms by chlorine when treated with aluminum chloride. Both cyclic and acyclic ethers were completely  $\alpha$ -chlorinated.



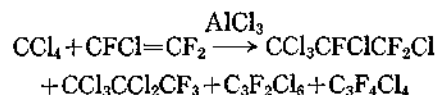
The rearrangement is actually the simplest case of halide transfer and few clearly intramolecular transformations have been reported. Miller<sup>15</sup> showed aluminum chloride to induce rearrangement as well as replacement of fluorine atoms on fluorochloroalkanes.



The order of stability to aluminum chloride was formulated as  $\text{CF}_3 > \text{CF}_2\text{Cl} > \text{CFCl}_2$  and  $\text{R}_1\text{CF}_3 > \text{PhCF}_3$ . Rearrangement of 1,1,2-trichloro-1,2,2-trifluoroethane by labelled aluminum chloride was accompanied by no incorporation of radioactive chloride, thus proving the reaction to proceed *via* aluminum-fluorine coordination.

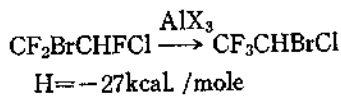


Henne and Kraus<sup>16</sup> encountered extensive rearrangement in the reaction between carbon tetrachloride and chl rotrifluoroethylene, isolating in addition products of halide transfer. Hudlicky<sup>5</sup> used such a rearrangement as a source of  $\text{CF}_2\text{CICCl}_3$ . Probably the most

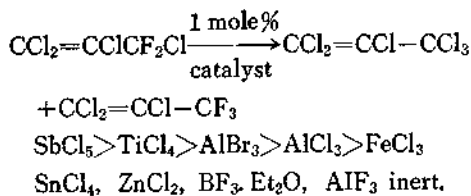


prominent example of the rearrangement is the synthesis of 1,1,1,-trifluoro-2-bromo-2-chloro-

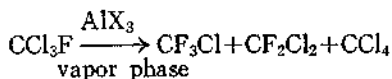
ethane (Halothane).<sup>17</sup>



Aluminum bromide caused isomerization faster and without external heating, being more soluble and a more active Lewis acid. Hudlicky<sup>18</sup> found first-order kinetics in fluorocarbon and (less clearly) in aluminum halide. The driving force in such rearrangements seems to be the formation of the more highly fluorinated (or chlorinated) carbon atoms. In support of this, refluxing 3,3-difluoro-1,1,2,3-tetrachloropropene underwent halide transfer in the presence of a Lewis acid to give perchloropropene and 1,1,2-trichloro-3,3,3-trifluoropropene.<sup>19</sup>

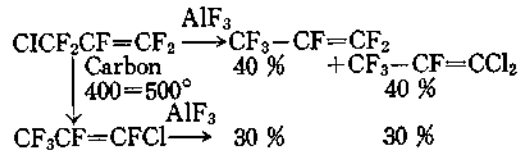


Whaley and Davis<sup>20</sup> had earlier reported allylic rearrangement during the fluorination of 3-hydropentachloropropene-1 by antimony fluorine atom migration. Examples of the transfer between chloromethanes exist in the patent literature, catalysed both by aluminum.



chloride<sup>21</sup> and by extremely fine aluminum fluoride (radius 500Å°, from HF-Al<sub>2</sub>O<sub>3</sub> interaction).<sup>22,23</sup>

This later reagent causes halide transfer in both perfluoroallylchloride and 1-chloropentafluoropropene, each giving 1,1-dichlorotetrafluoropropene and hexafluoropropene.<sup>24</sup> Further, activated charcoal served to rearrange perfluoroallylchloride exactly as hypothesized by Park earlier.



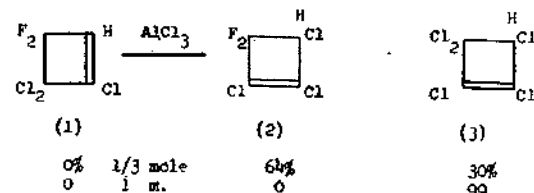
In summary, aluminum halides attack fluorocarbons generally with competition between all three modes of reaction.

### Results

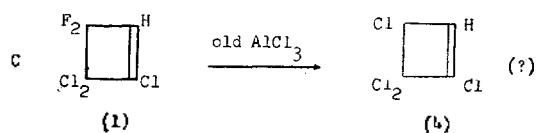
During the study<sup>3</sup> of nucleophile-catalyzed allylic rearrangements of halocyclobutenes, we noted that aluminum chloride exothermically rearranged 2,3,3-trichloro-4,4-difluorocyclobutene (1) to 1,2,3-trichloro-4,4-difluorocyclobutene (2) far more readily than any nucleophile. This rearrangement was accompanied by extensive defluorination to 3-hydropentachlorocyclobutene (3).

The liquid cyclobutenes were treated slowly with aluminum chloride and the usually violent exotherm thus partially controlled. Under those conditions, ca. 1.2 to 1.3 Cl atoms were required for each F replaced. Unless otherwise noted, percentages refer to the g. i. c. composition of the product mixtures.

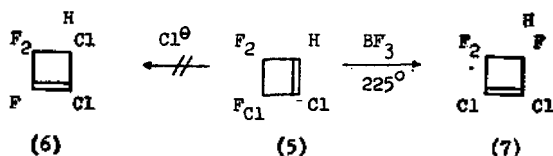
Cyclobutene (2) was identified by comparison with authentic material. Of the four possible isomers of C<sub>4</sub>HCl<sub>5</sub> (1-hydropentachlorocyclobutene, (3), and 1- or 2-hydropentachlorobutadiene, structure (3) is favored by the IR (1,630 cm<sup>-1</sup> absorption, characteristic of Cl-C=C-Cl in cyclobutenes) and nmr spectra (singlet at 4.59τ, characteristic of allylic hydrogen). This was confirmed by complete thermal ring opening during distillation to 1-hydropentachlorobutadiene-1,3.



For a listing of various double bond absorption frequencies<sup>25</sup> in halocyclobutenes, cyclobutene 3 may have formed by defluorination of 2 and/or defluorination of 1 followed by rearrangement. The absence of 1 in the partially reaceted mixture (Expt. A) suggests prior rearrangement to 2. An irreproducible experiment (Expt. C) gave mainly what is thought to be 2, 3, 4-trichloro-4-fluorocyclobutene (4), on the basis of microanalyses and the IR spectrum (3100 and 1580<sup>cm-1</sup>, characteristic of H-C=C-Cl. However, the presence of only a singlet at T in the H-nmr spectrum argues for the absence of fluorine. Distillation caused apparent isomerization to a diene. In view of the spectral anomalies and the high reactivity of the =CFCl= group (as discussed below), little weight should be assigned this result.

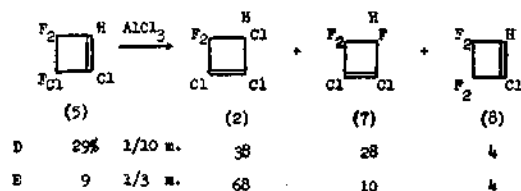


Although 2, 3-dichloro-3, 4, 4-trifluorocyclobutene (5) failed to rearrange to 6 under chloride ion attack (due to the instability of 1, 4, 4-trifluoro-2, 3-dichlorocyclobutene (6) Park and Kjeldgaard<sup>26</sup> have caused allylic fluorine migration to 1, 2-dichloro-3, 4, 4-trifluorocyclobutene (7) by heating with boron trifluoride.

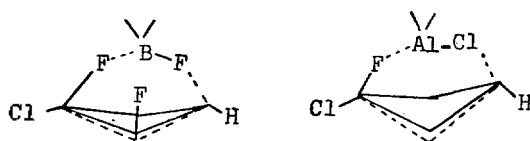


Treatment of 5 with aluminum chloride afforded three major products: 2, by rearrangement/defluorination; 7, by apparent intramolecular fluorine rearrangement; and 2-chloro-3, 3, 4, 4-tetrafluorocyclobutene (8); by intermolecular transfer. Cyclobutene (8) was identified by comparison with an authentic IR spectrum and

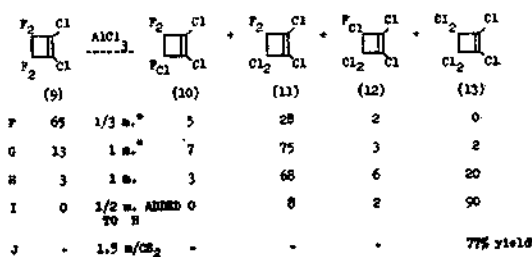
(7) by microanalysis, IR spectrum (1630 cm<sup>-1</sup>, characteristic of Cl-C=C-Cl) H-nmr (quartet at 4.56 T, J=60.7, 1.7 cps) and F-nmr ( ). Thus cyclobutene 5 enjoys all three modes of reaction previously listed. The increase in the amount of 2 at greater extent of reaction (Expt. E vs. D) suggests defluorination of 7 to 2.



It should be noted that a bridged pathway sterically similar to that suggested<sup>27</sup> for the BF<sub>3</sub> reaction is not necessarily favored by the absence of unrearranged 1, since 1 readily gives 2 under these conditions. The formation of 8 argues against exclusive operation of a bridged path, since a new carbon-fluorine bond is formed without rearrangement.



Replacement of the allylic fluorine atoms on 1, 2-dichlorotetrafluorocyclobutene (9) proceeded stepwise, the quality of the aluminum chloride affecting only the extent of reaction. The major products were 1, 2, 3, 3-tetrachloro-4, 4-difluorocyclobutene (11) and hexachlorocyclobutene (13). Hexachlobutene is the first crys-

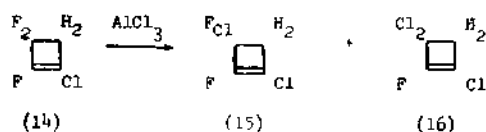


\* old sample of AlCl<sub>3</sub>, partially deteriorated.

line halocyclobutene, a pungent-smelling material. The structure was confirmed by elemental analysis, IR, spectrum (1640  $\text{cm}^{-1}$ ,  $\text{Cl}-\text{C}=\text{CCl}$ ) and thermal isomerization to perchlorobutadiene during determination of the microboiling point. The identities of (10) and (11) were confirmed by comparison of physical data and IR spectra with authentic values. Structure 12, 3-fluoropentachlorocyclobutene, is inferred from the IR spectrum (1,630  $\text{cm}^{-1}$ ,  $\text{Cl}-\text{C}=\text{C}-\text{Cl}$ ) and the relative g.l.c. retention time.<sup>27</sup>

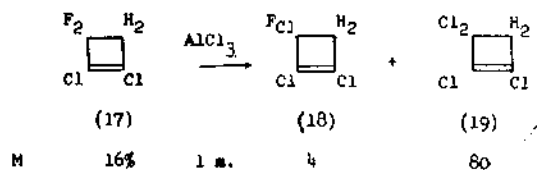
The higher reactivity of the *gem*- $\text{CFCl}$  group relative to that of the *gem*- $\text{CF}_2$  group is evident, 10 and 12 being present only in trace amount at any stage of the reaction. An attempt to limit the chlorination of 9 was carried out by refluxing it under a cooled tube of aluminum chloride. It was hoped that after the initial reaction 1,2,3-trichloro-3,4,4-difluorocyclobutene 10 would concentrate in the boiling flask, while its more volatile precursor 9 would continue to react. After several days, a low conversion to a 1:2 mixture of 10 and 11 had occurred, demonstrating this procedure to have some synthetic potential.

The low reactivity of vinylic fluoride was evinced in the reaction of 1-chloro-2,3,3-trifluorocyclobutene (14) with aluminum chloride. The main product proved to be 2-fluoro-1,3,3-trichlorocyclobutene (16), with no 1,2,3,3-tetrachlorocyclobutene (19) found and but traces



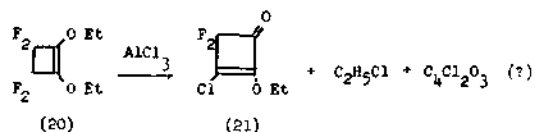
|   |        |       |    |
|---|--------|-------|----|
| K | 1/3 m. | trace | 29 |
| L | 1 m.   | 4     | 56 |

of the *gem*- $\text{CFCl}$  derivative 15. Cyclobutene 19 was the major product obtained from 1,2-dichloro-3,3-difluorocyclobutene (17), again with a small amount of the product of mono-chlorina-

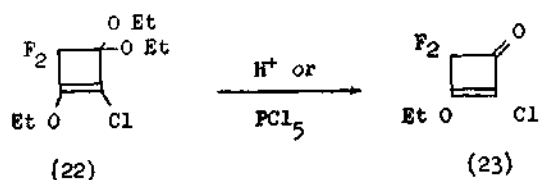


tion (18). Cyclobutene (16) exhibited a doublet in the H-nmr at 6.83  $\tau$  ( $J=12.0$  cps) and (19) a singlet at 6.51 $\tau$ , both absorbing at 1,630  $\text{cm}^{-1}$  in the IR. Structures (15) and (18) are inferred from g.l.c. retention times and IR spectra.

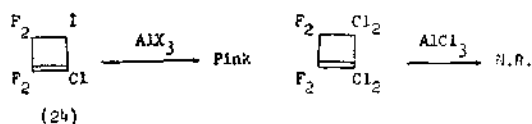
Cyclobutenyl alkyl ethers are readily available as a result of Park's<sup>28</sup> extensive study of nucleophilic substitution by alkoxides on halocyclobutenes. Since aryl alkyl ethers are known to be cleaved to phenols and alkyl chlorides by aluminum chloride,<sup>29</sup> the reaction of 1,2-diethoxytetrafluorocyclobutene (20) with aluminum chloride was undertaken with the hope of finding a new synthetic application for this class of ether. The major products were ethyl chloride and 1-chloro-2-ethoxy-4,4-difluorocyclobuten-3-one (21). More extensive reaction gave an unstable yellow solid, best analyzing as  $\text{C}_4\text{Cl}_2\text{O}_2$ . Structure 21 is supported by the n. m. r. pattern of the ethoxy group (triplet 9.17 $\tau$ , quartet 5.58 $\tau$ ), it being well established that the  $\text{CH}_2$ -vinylic ethoxy gives rise to a quartet at 5.58 $\tau$ , while the corresponding absorption of allylic ethoxy in halocyclobutenes is found at 5.89 $\tau$ .<sup>28</sup> The identification of compound 21 was completed by comparison with the isomeric 1-chloro-2-ethoxy-3,3-difluorocyclobuten-4-one (23), prepared from 2-chloro-1,3,3-tri-



ethoxy-4, -difluorocyclobutene (22) by Park and coworkers.<sup>30</sup>



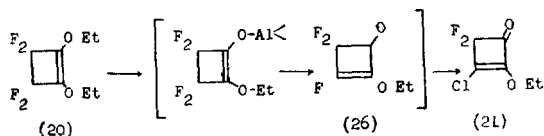
In brief experiments, 1-iodo-2-chlorotetrafluorocyclobutene<sup>24</sup> gave a deep pink color when treated with aluminum chloride or aluminum bromide. Antimony chloride 1,2-dichlorotetrafluorocyclobutene to hexachlorocyclobutene. The saturated halocarbon 1,1:2,2-tetrachlorotetrafluorocyclobutane<sup>25</sup> failed to react with aluminum chloride in methylene chloride.



Aluminum bromide has been found quite reactive and will be the subject of a future report.

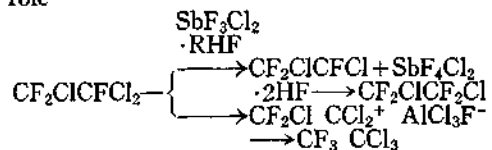
### Discussion

The order of reactivity toward aluminum chloride of the halocyclobutene substituents is as expected from previous work:<sup>10,15</sup> allyl CFCI > allyl CF<sub>2</sub> > vinyl CF. The high reactivity of the gem CFCI group makes the procedure seem poor as a synthesis of such halocyclobutenes, but the partial success in controlling the chlorination of 1,2-dichlorotetrafluorocyclobutene (9) supports hope for a practical synthetic process. The combination of alkyl-oxygen cleavage and fluoride replacement on diether 20 probably proceeds as follows:



The principle of vinylogy, successfully applied elsewhere<sup>30</sup> to halocyclobutenones, would predict that 26 behave as an acid fluoride. Acid fluorides are known to give the corresponding acid chlorides when treated with aluminum chloride.<sup>31</sup> This mechanistic concept places the reactivity of vinyl-OEt above that of allyl-CF<sub>2</sub>; i.e.  $-\text{CO}-\text{C}=\text{C}-\text{F} > \text{C}=\text{C}-\text{OEt} > \text{CF}_2$ .

Little can be said of the mechanism of fluoride replacement. From Miller's work,<sup>15</sup> aluminum-III has a greater affinity for bonded fluoride than for chloride, making it surprising that the intermediate carbonium ion can abstract fluoride (giving rearrangement or unobserved internal return) as well as chloride (to give chlorination) from the intermediate aluminum tetrahalide complex. The low reactivities of alkyl and vinylic fluorides as compared with allylic fluoride are consistent with the proposed cationic pathway. However, the superficially similar antimony-catalysed fluorination of fluoroalkanes does not lead to rearranged structures, indicating that the cationic species (if involved) are not of equal freedom or lifetime. That the cyclobutene skeleton also plays a role

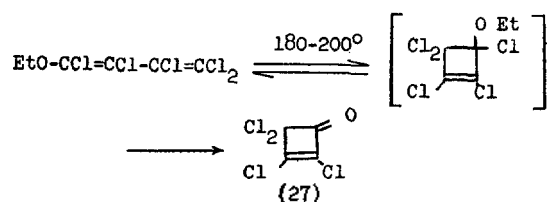


is evinced by the exothermic nature of these of these reactions relative to the sluggishness of cyclic fluoroolefins and 1,2-dichlorohexafluorocyclopentene,<sup>33</sup>

The formation of products of intramolecular (compound 7) and intermolecular (8) fluoride migration from (5) is explicable in terms of reactive aluminum fluoride formed as colloidal particles in the chlorination step. Such particulate aluminum fluoride is active in fluorination of chlorocarbons.<sup>22,23</sup> Thus no intramolecular

or bimolecular transfers are required.

The synthetic utility of this procedure is obvious. The two general syntheses of halocyclobutenes require the presence of at least two fluorine atoms. These methods are olefin cyclo-dimerizations<sup>34</sup> and cyclization of 1,3 dienes.<sup>35</sup> The only exception to this prerequisite of fluorine atoms is the formation of perchlorocyclobutenone (27) from 1-ethoxypentachlorobutadiene,<sup>36</sup> in which the loss of ethyl chloride provides a driving force. No indication of cyclization of chlorinated butadienes exists in the literature, and the thermal instability of the chlorocyclobutenes **3** and **13** indicates this to be unfavored under equilibrium conditions.

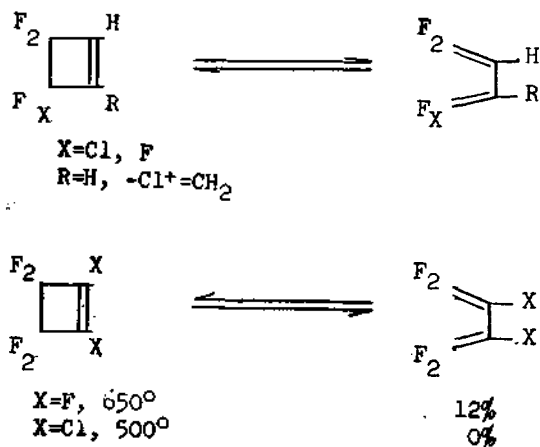


Removal of the ubiquitous fluorine atoms has thus far been accomplished by amine and alkoxide displacements, which lead away from halocyclobutenes. Halide ions are incapable of nucleophilically displacing fluoride from halocyclobutenes under useful conditions.<sup>3</sup> Thus, aluminum chloride reactions provide a route to mono- and non-fluorinated chloro-cyclobutenes, previously inaccessible compounds.

In addition, new and easy syntheses of known compounds have been found. Thus, 1,2,3,3-tetrachloro-4,4-difluorocyclobutene was previously prepared in good overall yield from 1,1-dichloro-2,2-difluoroethylene by J. R. Dick,<sup>37</sup> but involved a difficult codimerization and separation, risk of rearrangement of the dehydrochlorinated product (1) to the inert isomer (2) and slow chlorination of (1). The new synthesis requires a simple homodimerization, dechlorination to a stable product (9) and a simple distillation of the aluminum chloride

reaction product.

The thermal ring cleavage of **3** and **13** is of interest. Du Pont workers have shown 1,2-dihydrotetrafluorocyclobutene and related 1-hydroderivatives to be favored in high temperature equilibrium with the tetrafluorobutadienes.<sup>38</sup> On the other hand perfluorocyclobutene<sup>39</sup> and 1,2-dichlorocyclobutene<sup>40</sup> are highly favored under similar conditions.



The well-known instability of perchloroalkanes (only themethane, ethane, and propane are known) makes it attractive to attribute the thermal instability of **3** and **13** to steric interaction. Indeed, it is surprising to find these compounds to be at all stable, since each suffers from the eclipsing of vicinal chlorine atoms. (An x-ray study of **13** would reveal the extent to which the cyclobutene skeleton can deform to relieve *cis*-eclipsing). Since *cis*-1,2-dihaloolefins are more stable than *trans*, 1,2-dichlorocyclobutenes may enjoy some kind of positive stabilization.

#### Acknowledgment

We are grateful to AFOSR and to the 3M Co., St. Paul, Minn. for their support of this work.<sup>17</sup>

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