K-762
Chemistry

REACTIONS OF TERTIARY AMINES WITH POLYFLUOROOLEFINS

Part A: ALIPHATIC TERTIARY AMINES

Part B: AROMATIC TERTIARY AMINES

AUTHOR:

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K-25 PLANT
CARBIDE AND CARBON CHEMICALS COMPANY
A DIVISION OF UNION CARBIDE AND CARBON CORPORATION
OAK RIDGE, TENNESSEE

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Roy L. Pruett

This report is a dissertation presented to the Graduate Council of the University of Tennessee. The work was done in the Research Laboratories of the K-25 Plant.

CARBIDE AND CARBON CHEMICALS COMPANY
K-25 Plant
Oak Ridge, Tennessee

II

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PART A

CHAPTER I

HISTORICAL

The recent development of wholly or partially fluorinated organic compounds in commercial quantities has made several of the unsaturated polyfluoroolefins available for wide investigation. For example, chlorotrifluoroethylene and subsequently hexafluorocyclobutene can be prepared from Freon-113 (1,1,2-trichloro-1,2,2-trifluoroethane) easily and in excellent yields.

There have been many articles and patents concerned with the action of nucleophilic reagents on these unsaturated compounds. Among the first was a patent by Hanford and Rigby[1], which described the reactions of alcohols and compounds containing the -OH group with polyfluoroethylenes to produce ethers. The catalysts used were sodium alkoxides, sodium hydroxide and potassium cyanide. Other workers[2,3,4,5] also have produced polyfluoroethers by the action of alcohols on polyfluoroethylenes in the

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(1) Hanford, W. E. and Rigby, G. W., U. S. Patent 2,409,274 (1946).

(2) Barr, J. T., Rapp, K. E., Pruett, R. L., Bahner, C. T., Gibson, J. D. and Lafferty, R. H., Jr., *J. Am. Chem. Soc.*, *72*, 4480 (1950).

(3) Hurwitz, M. D. and Miller, W. T., Jr., *Abstracts of Papers*, 114th Meeting of American Chemical Society, Washington, D. C., August, 1948, p. 4L.

(4) Miller, W. T., Jr., Fager, E. W. and Griswold, P. H., *J. Am. Chem. Soc.*, *70*, 431 (1948).

(5) Park, J. D., Vail, D. K., Lea, K. R. and Lacher, J. R., *ibid.*, *70*, 1550 (1948).

presence of basic catalysts, both organic and inorganic. Rapp, et al.[6] produced the corresponding sulfides by using mercaptans rather than alcohols.

Rigby and Schroeder[7] described the reaction of primary and secondary amines with polyfluoroethylenes in the presence of borax. The products obtained were mono- and disubstituted fluoro- and chlorofluoroacetamides. Huskins and Tarrant[8] also prepared substituted amines by this method. In all cases sufficient borax was used to furnish the necessary water for the reaction. The latter workers presented proof for the fact that only one mode of addition occurred at lower temperatures.

$$CClF = CF_2 + HNR_2 \longrightarrow [CHClFCF_2NR_2] \xrightarrow{H_2O} CHClFCONR_2$$

No substituted difluoroacetamides were found in the reaction products.

Hurwitz and Miller[9] investigated the reactions of anionic reagents with polyfluoroethylenes. With secondary amines they obtained "saturated products having exclusively the α, α-difluoro structures." With alcohols and polyfluoroethylenes they obtained saturated ethers but reported that the reactions with fluoropropenes and butenes were complicated by elimination of halogen.

---

(6) Rapp, K. E., Pruett, R. L., Barr, J. T., Bahner, C. T., Gibson, J. D. and Lafferty, R. H., Jr., J. Am. Chem. Soc., 72, 3642 (1950).

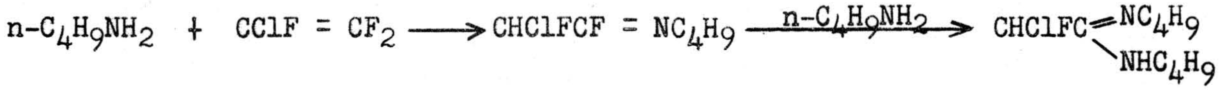
(7) Rigby, G. W. and Schroeder, H. E., U. S. Patent 2,409,315 (1946).

(8) Huskins, C. W. and Tarrant, P., "Preparations and Reactions of Certain Fluorochloroethylenes," Report to Office of Naval Research Under Contract N8onr503, June 15, 1949.

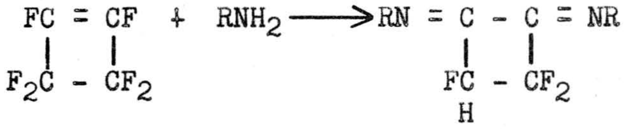
(9) Hurwitz, M. D. and Miller, W. T., Jr., Abstract of Papers, 114th Meeting of American Chemical Society, Washington, D. C., August, 1948, p. 4L.

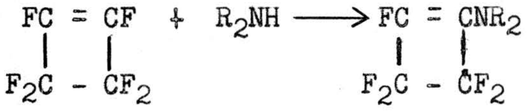
$$CX_3CX = CX_2 + ROH \longrightarrow [CX_3CXHCX_2OR] \longrightarrow CX_2 = CXCX_2OR + HX$$

Pruett, *et al.*[10] reported the reactions of primary and secondary amines with chlorotrifluoroethylene and with hexafluorocyclobutene. In the case of primary aliphatic amines, the products were imino- or imido-type compounds, while secondary amines gave substituted tertiary amines.

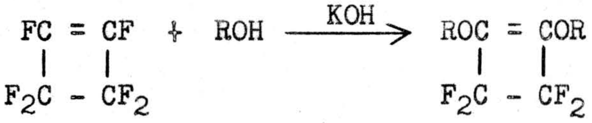


$$n\text{-}C_4H_9NH_2 + CClF = CF_2 \longrightarrow CHClFCF = NC_4H_9 \xrightarrow{n\text{-}C_4H_9NH_2} CHClFC\genfrac{}{}{0pt}{}{=NC_4H_9}{\diagdown NHC_4H_9}$$





Park, Sharrah and Lacher[11] described the action of alcohols on hexafluorocyclobutene. They reported the formation of dialkoxy compounds and proposed a substitution mechanism:



Rapp, *et al.*[12] investigated the reactions of mercaptans with this olefin and isolated three types of compounds:

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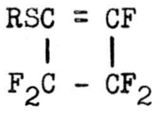
[10] Pruett, R. L., Barr, J. T., Rapp, K. E., Bahner, C. T., Gibson, J. D. and Lafferty, R. H., Jr., *J. Am. Chem. Soc.*, *72*, 3646 (1950).

[11] Park, J. D., Sharrah, M. L. and Lacher, J. R., *ibid.*, *71*, 2337 (1949).

[12] Rapp, K. E., Pruett, R. L., Barr, J. T., Bahner, C. T., Gibson, J. D. and Lafferty, R. H., Jr., *ibid.*, *72*, 3642 (1950).



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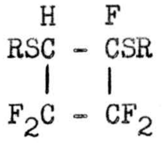

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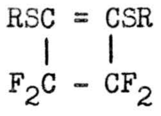


III

They proposed that the reaction proceeded by step-wise addition followed by loss of hydrogen fluoride. Barr, et al[13] found that monoalkoxy butenes could be produced also in the reaction of alcohols with hexafluorocyclobutene. They also presented evidence that the reaction was one of addition rather than substitution.

During the investigation of the action of mercaptans on hexafluorocyclobutene, in the particular case where triethylamine was used as the basic catalyst, a crystalline material was discovered during the purification process[14]. Analysis proved that this solid contained no sulfur but did contain nitrogen. A subsequent investigation in which triethylamine was mixed with hexafluorocyclobutene showed that these components did react easily with each other. The initial product produced was a solid which was very reactive with water or alcohols. When mixed with dilute hydrochloric acid, this solid hydrolyzed vigorously to produce a solid identical with that produced during the reaction of mercaptans with hexafluorocyclobutene in the presence of triethylamine.

Analysis of the initial product indicated that it was a quaternary salt formed from the two components. Analysis of the stable hydrolytic

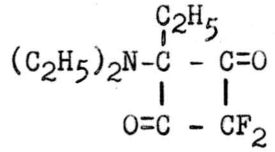
---

(13) Barr, J. T., Rapp, K. E., Pruett, R. L., Bahner, C. T., Gibson, J. D. and Lafferty, R. H., Jr., J. Am. Chem. Soc., 72, 4480 (1950).

(14) Rapp, K. E., Unpublished work.

product gave the empirical formula $(C_{10}H_{15}NO_2F_2)_x$. Molecular weight determinations by the boiling point elevation method showed that the compound was monomolecular, or that x was equal to one.

The structure of the hydrolysis product was not determined, but the following was assigned as a possible structure:

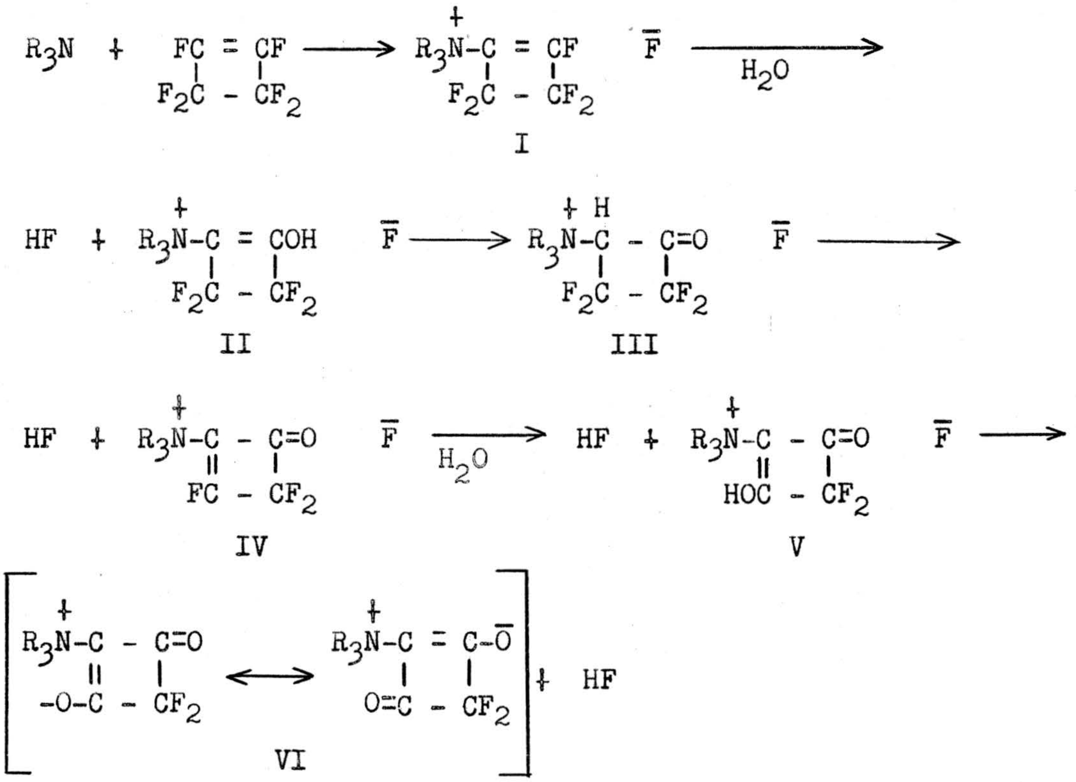


Tests for the carbonyl group, such as attempted reaction with p-nitrophenylhydrazine, hydroxylamine and semicarbazide, were all negative. No explanation could be offered for this inertness. Also, if the above formula were correct, there must have been a shift of an ethyl group from the tertiary nitrogen to the adjacent carbon. No further work has been done to elucidate the structure of the hydrolyzed product.

CHAPTER II

DISCUSSION

As has been stated in Chapter I, triethylamine reacts with hexafluorocyclobutene to produce a reactive quaternary salt, which in turn reacts vigorously with water to produce a stable hydrolytic product. The proposed structure for this product contained two carbonyl groups but the presence of these groups was not detected by chemical means. On the basis of the results of this investigation, the following is given as more probable series of reactions for the quaternary salt formation and the final hydrolysis:



Two compounds of type I were characterized. They were tri-n-butyl (2,3,3,4,4-pentafluorocyclobutenyl) ammonium fluoride (IA) and triethyl (2,3,3,4,4-

pentafluorocyclobutenyl) ammonium fluoride (IB). Due to the reactivity of these intermediates, no other analogs were isolated.

Although the intermediates (II, III, IV and V) were so unstable and transitory that they could not be isolated, a derivative of II was prepared. This was accomplished by alcoholizing the initial product of the reaction of triethylamine with hexafluorocyclobutene in absolute ethanol, then adding a solution of picric acid in absolute ethanol. This produced (2-ethoxy-3,3,4,4-tetrafluorocyclobutenyl)triethylammonium picrate.

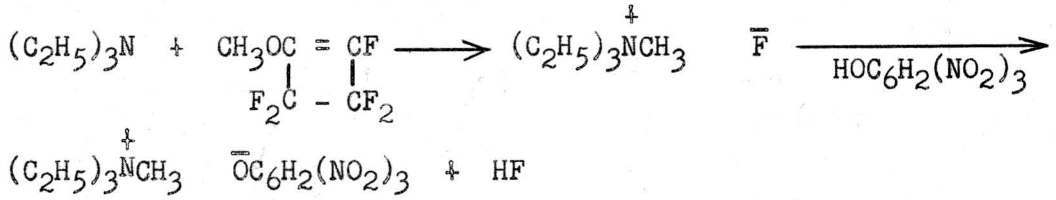
In order to determine whether or not this reaction is general among aliphatic tertiary amines, eight amines, ranging in carbon content from trimethylamine to tributylamine, were used to prepare compounds of type VI. In addition, two of these amines contained cyclic groups (1-ethylpiperidine and 4-methylmorpholine). Several trends were noted in this series of compounds. Although they were all insoluble in benzene, ether and other non-polar solvents, the lower alkyl members [for example: (3,3-difluoro-2,4-dioxocyclobutyl)trimethylammonium betaine] were water soluble and only slightly soluble in alcohol while the higher members [for example: tri-n-butyl(3,3-difluoro-2,4-dioxocyclobutyl)ammonium betaine] were insoluble in water and soluble in alcohol. The melting point increased as the carbon content decreased. However, when the original amine contained three alkyl groups which were not the same, for example N-methyldiethylamine, the hydrolyzed product had a low melting point and high solubility in alcohol.

The rate of hydrolysis of the original quaternary salt varied with the size of the alkyl group. The lower members hydrolyzed instantaneously while in the case of tri-*n*-butyl(2,3,3,4,4-pentafluorocyclobutenyl)ammonium fluoride it was necessary to heat with a dilute basic solution. The rate of formation also varied inversely with the size of the alkyl group.

In at least one case, the quaternary salt was found to decompose to the original reactants. When tri-n-butyl(2,3,3,4,4-pentafluorocyclobutenyl)ammonium fluoride was dissolved in benzene-dibutyl ether solution and heated to 85-90°, hexafluorocyclobutene was evolved.

A synthesis in which triethylamine and 1-chloropentafluorocyclobutene were used showed that this type of reaction is not limited to hexafluorocyclobutene. Hydrolysis of the initial product gave the same betaine as that formed by hydrolysis of the quaternary salt of triethylamine and hexafluorocyclobutene, although the yield was considerably lower. However, triethylamine did not react with octafluorobutene-2, even upon heating for long periods of time.

Aliphatic tertiary amines did react with monoalkoxy- and monoalkylthiopentafluorocyclobutenes[1]. In every case a tarry product resulted and the only compound identified was methyltrialkylammonium fluoride, which was isolated as the picrate salt. For example:



$$(C_2H_5)_3N + \underset{F_2C - CF_2}{CH_3OC = CF} \longrightarrow (C_2H_5)_3\overset{+}{N}CH_3 \quad \bar{F} \xrightarrow[HOC_6H_2(NO_2)_3]{} (C_2H_5)_3\overset{+}{N}CH_3 \quad \bar{O}C_6H_2(NO_2)_3 + HF$$

---

(1) The preparations of monoalkoxy- and monoalkylthiopentafluorocyclobutenes are described in the following references, respectively: Barr, J. T., Rapp, K. E., Pruett, R. L., Bahner, C. T., Gibson, J. D. and Lafferty, R. H., Jr., *J. Am. Chem. Soc.*, *72*, 4480 (1950); Rapp, K. E., Pruett, R. L., Barr, J. T., Bahner, C. T., Gibson, J. D. and Lafferty, R. H., Jr., *ibid.*, *72*, 3642 (1950).

The means by which the quaternary fluoride was obtained have not been established.

1,2-Bis(butylthio)-3,3,4,4-tetrafluorocyclobutene did not react with 4-methylmorpholine. This was expected since the olefin did not contain a fluorine atom on either carbon of the double bond.

4-Methylmorpholine did not react appreciably with 1,2-dichloro-3,3,4,4,5,5-hexafluorocyclopentene, even upon heating.

The hydrolyzed products from the reactions of aliphatic tertiary amines with hexafluorocyclobutene (VI) were found to be very stable and inert to the usual carbonyl reactions. The fact that they did not form p-nitrophenylhydrazones, oximes or semicarbazones was verified. This is not surprising in view of the conjugated nature of the carbonyl groups present in the proposed structure.

Gustafsson[2] has reported a compound which is somewhat similar in structure, 1,1-dimethyl-3,5-dioxopiperidinium betaine. This compound formed addition complexes with acids and inorganic salts. However, he stated that the substitution of bromine for hydrogen in the four position of the piperidine ring decreased the tendency toward addition reactions. Therefore the relative inertness of the difluoro betaines should not be surprising. (3,3-Difluoro-2,4-dioxocyclobutyl)triethylammonium betaine showed no tendency to react with inorganic acids or salts. It did not decolorize solutions of bromine or potassium permanganate. However, (3,3-difluoro-2,4-dioxocyclobutyl)trimethylammonium betaine formed an

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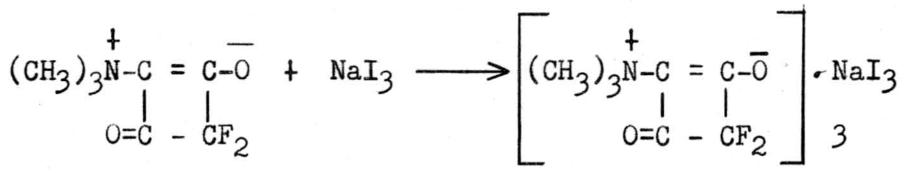
(2) Gustafsson, C., Ber., 70B, 1591 (1937).

addition complex with NaI_3 in water which was quite stable and contained a molar ratio of three moles of betaine to one of inorganic salt (VII).

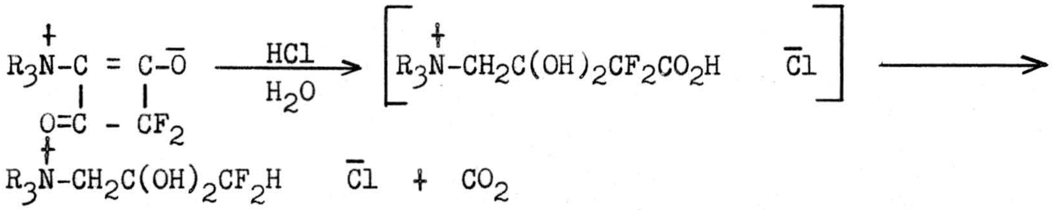


$$(CH_3)_3\overset{+}{N}-\underset{\substack{| \\ O=C}}{C}=\underset{\substack{| \\ -\ CF_2}}{C}-\bar{O} + NaI_3 \longrightarrow \left[(CH_3)_3\overset{+}{N}-\underset{\substack{| \\ O=C}}{C}=\underset{\substack{| \\ -\ CF_2}}{C}-\bar{O}\right]_3 \cdot NaI_3$$

VII

This betaine also formed an unstable complex with concentrated sulfuric acid which reverted to the original components when recrystallization from methanol was attempted.

All the betaines containing small alkyl groups (those from N-methyldiethylamine, 4-methylmorpholine, N,N-dimethylethylamine and trimethylamine), reacted with boiling 3 N hydrochloric acid, splitting the ring and forming trialkyl(3,3-difluoro-2-oxopropyl)ammonium chloride monohydrates, together with carbon dioxide.



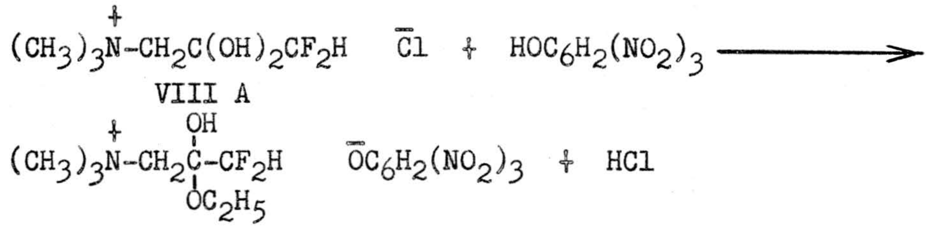
$$R_3\overset{+}{N}-\underset{\substack{| \\ O=C}}{C}=\underset{\substack{| \\ -\ CF_2}}{C}-\bar{O} \xrightarrow[H_2O]{HCl} \left[R_3\overset{+}{N}-CH_2C(OH)_2CF_2CO_2H \quad \bar{Cl}\right] \longrightarrow$$

$$R_3\overset{+}{N}-CH_2C(OH)_2CF_2H \quad \bar{Cl} + CO_2$$

VIII

The velocity of splitting was dependent on the size of the alkyl groups which were present. (3,3-Difluoro-2,4-dioxocyclobutyl)triethylammonium betaine failed to react with boiling 3 N hydrochloric acid, whereas with the dimethylethyl- and trimethylammonium betaines the reaction was complete in four hours. The methyldiethylammonium betaine assumed an intermediate position. After refluxing with 3 N hydrochloric acid for four hours, the betaine was only partially converted to the ionic chloride; after twenty hours the reaction was essentially complete. The progress of the reaction was determined by testing for the evolution of carbon dioxide.

(3,3-Difluoro-2-oxopropyl)trimethylammonium chloride monohydrate (VIII A) was found to undergo the usual reactions. It formed a picrate with picric acid in absolute ethanol which, instead of being a hydrate, contained one mole of ethanol.



$$(CH_3)_3\overset{+}{N}\text{-}CH_2C(OH)_2CF_2H\quad \bar{Cl} + HOC_6H_2(NO_2)_3 \longrightarrow$$

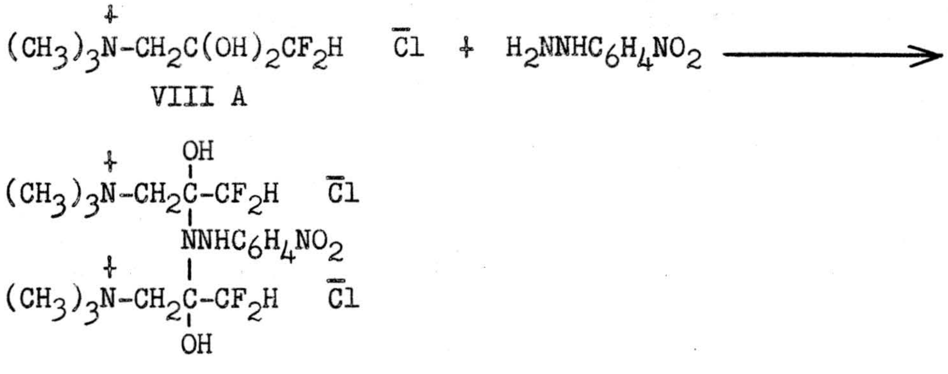
VIII A

$$(CH_3)_3\overset{+}{N}\text{-}CH_2\underset{OC_2H_5}{\overset{OH}{C}}\text{-}CF_2H\quad \bar{O}C_6H_2(NO_2)_3 + HCl$$

IX

The ethanol was removed by heating at 100° under reduced pressure for six hours.

(3,3-Difluoro-2-oxopropyl)trimethylammonium chloride monohydrate (VIII A) reacted with p-nitrophenylhydrazine to form an anomolous hydrazone (X) which contained two moles of ionic chloride to one of p-nitrophenylhydrazine.



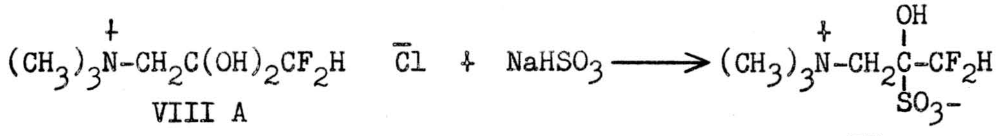
$$(CH_3)_3\overset{+}{N}\text{-}CH_2C(OH)_2CF_2H\quad \bar{Cl} + H_2NNHC_6H_4NO_2 \longrightarrow$$

VIII A

$$\begin{array}{l} (CH_3)_3\overset{+}{N}\text{-}CH_2\overset{OH}{C}\text{-}CF_2H\quad \bar{Cl} \\ \qquad\qquad\quad NNHC_6H_4NO_2 \\ (CH_3)_3\overset{+}{N}\text{-}CH_2\underset{OH}{C}\text{-}CF_2H\quad \bar{Cl} \end{array}$$

X

It also reacted with sodium bisulfite to form a zwitterion (XI)



$$(CH_3)_3\overset{+}{N}\text{-}CH_2C(OH)_2CF_2H \quad \overline{Cl} + NaHSO_3 \longrightarrow (CH_3)_3\overset{+}{N}\text{-}CH_2\overset{\overset{OH}{|}}{\underset{\underset{SO_3^-}{|}}{C}}\text{-}CF_2H$$

VIII A

XI

With hot concentrated potassium hydroxide it split to form trimethylamine.

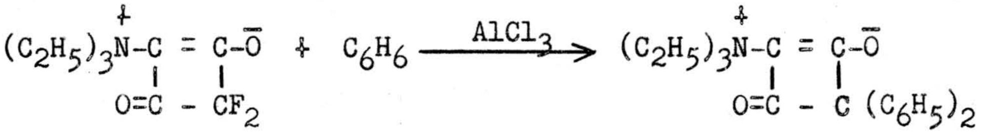
$$(CH_3)_3\overset{+}{N}\text{-}CH_2C(OH)_2CF_2H \quad \overline{Cl} + H_2O \xrightarrow{KOH} (CH_3)_4\overset{+}{N} \quad \overline{OH} \longrightarrow$$

VIII A

$(CH_3)_3N$

The latter is in line with the observation of Kroehnke[3,4], who found that the action of alkali on 1-(2-oxoalkyl)pyridinium salts produced 1-methylpyridinium hydroxide.

The fluorine atoms in the trialkyl(3,3-difluoro-2,4-dioxocyclobutyl)ammonium betaines (VI) were found to be susceptible toward Friedel-Crafts type reactions. (3,3-Difluoro-2,4-dioxocyclobutyl)triethylammonium betaine (VI A) reacted easily with benzene in the presence of anhydrous aluminum chloride to produce (2,4-dioxo-3,3-diphenylcyclobutyl)triethylammonium betaine (XII).



$$\begin{array}{l}(C_2H_5)_3\overset{+}{N}\text{-}C = C\text{-}\overline{O} \\ \qquad\quad\;\; | \quad\;\; | \\ \qquad\;\; O{=}C - CF_2\end{array} + C_6H_6 \xrightarrow{AlCl_3} \begin{array}{l}(C_2H_5)_3\overset{+}{N}\text{-}C = C\text{-}\overline{O} \\ \qquad\quad\;\; | \quad\;\; | \\ \qquad\;\; O{=}C - C(C_6H_5)_2\end{array}$$

VI A

XII

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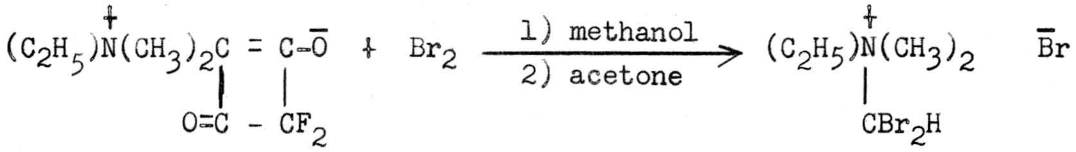
(3) Kroehnke, F., Ber., 68B, 1177 (1935).

(4) Kroehnke, F. and Heffe, W., ibid., 70B, 864 (1937).

Whereas all the difluoro betaines (VI) had failed to react with acids, the diphenyl compound (XII) produced a hydrobromide easily and in good yield.

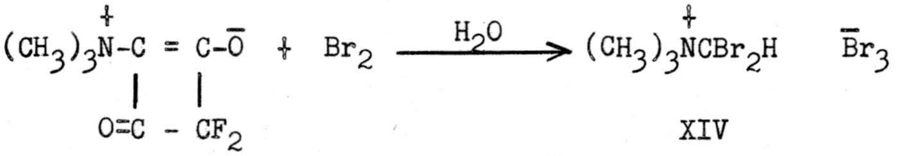
Bromine caused extensive degradation of the difluoro betaines (VI), either in methanol or in aqueous solution. When the reaction was carried out in methanol and the product isolated by the addition of acetone, dibromomethyltrialkylammonium bromide (XIII) was isolated.



VI B

XIII A

When the reaction was performed by the use of bromine in aqueous solution, dibromomethyltrimethylammonium tribromide (XIV) precipitated from the solution.



XIV

VI C

The dibromomethyltrimethylammonium tribromide (XIV) was converted to dibromethyltrimethylammonium bromide by treatment with acetone. After this operation, the acetone had a lachrymatory odor similar to that of brominated acetone.

The structure of the betaines which has been proposed is based on the following evidence: elemental analysis and the negative test with potassium permanganate showed that, if the compound is monomolecular, a ring structure is necessary to fulfill the necessary valences. Molecular weight determinations proved that the compounds were monomolecular.

This, together with the fact that a ring structure was present in one of the starting materials, was taken as sufficient evidence for the presence of a ring in the final product. The identification of trimethylamine as one of the splitting products when (3,3-difluoro-2-oxopropyl)trimethylammonium chloride monohydrate (VIII A) was heated with alkali and the production of dibromomethyl trimethylammonium bromide by the action of bromine on the corresponding betaine proved that there had been no migration of alkyl groups from the original trialkyl nitrogen grouping to the adjacent carbon. The solubility characteristics of the compounds also were indicative of a quaternary salt-type structure.

Thus it has been determined that a four-membered ring is present, and that a trialkylammonium group is attached to one of the ring carbons. The proven presence of a carbonyl group in the ionic chloride product (VIII) obtained when the betaines (VI) were treated with dilute hydrochloric acid showed that at least one carbonyl group was present in the original betaine and the evolution of carbon dioxide was evidence for a second. These facts point to a structure of type VI, and this structure is produced by a mechanism which is entirely reasonable in light of the known tendency of the reaction products of hexafluorocyclobutene to split out hydrogen fluoride[5,6,7].

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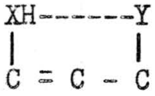
(5) Pruett, R. L., Barr, J. T., Rapp, K. E., Bahner, C. T., Gibson, J. D. and Lafferty, R. H., Jr., _J. Am. Chem. Soc._, _72_, 3646 (1950).

(6) Rapp, K. E., Pruett, R. L., Barr, J. T., Bahner, C. T., Gibson, J. D. and Lafferty, R. H., Jr., _ibid._, _72_, 3642 (1950).

(7) Barr, J. T., Rapp, K. E., Pruett, R. L., Bahner, C. T., Gibson, J. D. and Lafferty, R. H., Jr., _ibid._, _72_, 4480 (1950).

The infrared and ultraviolet spectra of these compounds also add support to this type of structure. The infrared spectra of (3,3-difluoro-2,4-dioxocyclobutyl)triethylammonium betaine, (3,3-difluoro-2,4-dioxocyclobutyl)diethylmethylammonium betaine and (2,4-dioxo-3,3-diphenyl)-triethylammonium betaine were obtained over the range of 2-15 μ, and they all showed strong absorption in the region 6.0-6.2 μ. Strongly conjugated carbonyl structures are known to cause absorption in this region[8]. Rasmussin, Tunnicliff and Brattain[9] examined the spectrum of acetyl acetone and found a tremendously strong band at 6.1-6.3 μ which they attributed to the system



$$\begin{array}{ccccc} \mathrm{XH} & - & - & - & \mathrm{Y} \\ | & & & & | \\ \mathrm{C} & = & \mathrm{C} & - & \mathrm{C} \end{array}$$

where XH and Y are participating as a hydrogen bond donor-acceptor system. This system is electronically similar to the one present in the betaines (VI).

The ultraviolet absorption spectra of these three compounds were obtained over the range 220-400 mμ. (3,3-Difluoro-2,4-dioxocyclobutyl)-triethylammonium betaine and (3,3-difluoro-2,4-dioxocyclobutyl)diethyl-methylammonium betaine showed strong absorption maxima at 230 mμ, which indicates conjugated unsaturation[10]. The substitution of phenyl groups

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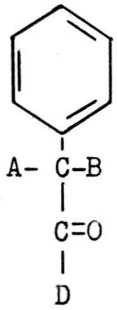
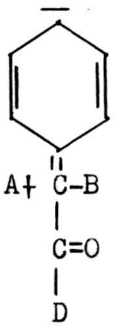
[8] Randall, H. M., Fowler, R. G., Fuson, M. and Dangl, J. R., "Infrared Determination of Organic Structure," D. van Nostrand Co., New York, N. Y., 1949.

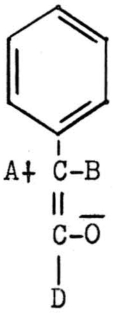
[9] Rasmussen, R. S., Tunnicliff, D. D. and Brattain, R. R., *J. Am. Chem. Soc.*, *71*, 1068 (1949).

[10] Braude, E. A., *Ann. Repts. Progress Chem.*, *42*, 105 (1945).

for fluorine atoms caused the maximum to shift to 251 $m\mu$, indicating that the phenyl groups change the characteristics of the resonating structure. It is possible that these groups undergo the type of resonance postulated by Kumlet, Strait and Alpen for α-phenyl ketones[11,12]. They assumed that in this type of compound no bond resonance or hyperconjugation occurred, giving rise to the following forms:







As an alternative explanation, it might be that the phenyl groups change the absorption frequency by changing the strain present in the cyclic system.

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(11) Kumler, W. D., Strait, L. A. and Alpen, E. L., *J. Am. Chem. Soc.*, *72*, 1463 (1950).

(12) Alpen, E. L., Kumler, W. D. and Strait, L. A., *ibid.*, *72*, 4558 (1950).

CHAPTER III

EXPERIMENTAL

A. Materials

1. Amines

a. Commercial amines. Trimethylamine, triethylamine, tri-*n*-butylamine and 1-ethylpiperidine were obtained from Eastman Kodak Company, and 4-methylmorpholine from Paragon Division of the Matheson Company, Inc. These amines were used without further purification.

b. Trialkyl amines containing different alkyl groups. N,N-Dimethylethylamine, N-methyldiethylamine and N-methyldi-*n*-butylamine were prepared by the method of Clarke, Gillespie and Weisshaus[1].

Either two moles of diethylamine or di-*n*-butylamine was added with cooling to five moles of 90 per cent formic acid. After all the amine had been added, two and two-tenths moles of 35 per cent formaldehyde was added and the resulting solution was allowed to stand at room temperature for eighteen hours, after which the solution was heated on a water bath for four hours. After cooling to room temperature, slightly more than one mole of concentrated hydrochloric acid was added and the solution was distilled under reduced pressure until the amine salt began to separate. The solid was dissolved in water and the resulting solution was made basic with concentrated potassium hydroxide. This was then extracted with

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(1) Clarke, H. T., Gillespie, H. B. and Weisshaus, S. Z., *J. Am. Chem. Soc.*, *55*, 4571 (1933).

ether. The ether solution was dried over anhydrous sodium carbonate, the ether was distilled from the amine, and the amine was distilled from sodium.

For the preparation of N,N-dimethylethylamine, the following modification of the above procedure was used. In the original reaction mixture, two moles of 33 per cent aqueous ethylamine was used. After the reaction mixture had been made basic with concentrated potassium hydroxide, the amine was distilled from the aqueous solution, rather than extracting with ether. The amine was dried over anhydrous sodium carbonate, then distilled from sodium.

2. Hexafluorocyclobutene

The preparation of this butene has been described by Rapp, et al.[2] This procedure involved the dechlorination of 1,2-dichlorohexafluorocyclobutane, which was prepared by the thermal dimerization of chlorotrifluoroethylene. Almost quantitative conversion of chlorotrifluoroethylene to the cyclic dimer was obtained by heating about 1200 g. of the former in a 1-liter high-pressure reactor for eighteen hours at 200°. The product, b.p. 59°, was obtained by direct distillation of the reaction mixture.

Dechlorination was carried out most conveniently by placing 300 g. of 1,2-dichlorohexafluorocyclobutane, 300 ml. of absolute ethanol and 175 g. of 30-mesh zinc in a flask equipped with a reflux condenser and

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(2) Rapp, K. E., Pruett, R. L., Barr, J. T., Bahner, C. T., Gibson, J. D. and Lafferty, R. H., Jr., J. Am. Chem. Soc., 72, 3646 (1950).

connected through a calcium chloride tube to a metal trap chilled in Dry Ice to condense and hold the product. The flask was heated to 45-50° to initiate the reaction, which caused spontaneous refluxing for about one hour. Refluxing was continued for three hours by external heating. The yields obtained were about 90 per cent.

3. Other Polyfluoro Olefins

a. Octafluorobutene-2. This was prepared by dechlorination of 2,3-dichlorooctafluorobutane, which was obtained from Hooker Electrochemical Company. The dechlorination was carried out in a manner similar to that described for the dechlorination of 1,2-dichlorohexafluorocyclobutane. A 76 per cent yield was obtained.

b. 1-Methoxy- and 1-phenoxy-2,3,3,4,4-pentafluorocyclobutene. These compounds were made in the K-25 Chemistry Laboratories in work which was completed previous to this investigation[3]. Their preparation has been described by Barr, *et al.*[4]

c. 1-Butylthio-2,3,3,4,4-pentafluorocyclobutene and 1,2-bis(butylthio)-3,3,4,4-tetrafluorocyclobutene. These compounds were made in the K-25 Laboratories in work which was completed previous to this investigation[5]. Their preparation has been described by Rapp, *et al.*[6]

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(3) The writer is indebted to John T. Barr, who furnished the 1-methoxy-2,3,3,4,4-pentafluorocyclobutene.

(4) Barr, J. T., Rapp, K. E., Pruett, R. L., Bahner, C. T., Gibson, J. D. and Lafferty, R. H., Jr., *J. Am. Chem. Soc.*, *72*, 4480 (1950).

(5) The writer is indebted to Karl E. Rapp, who furnished both these compounds.

(6) Rapp, K. E., Pruett, R. L., Barr, J. T., Bahner, C. T., Gibson, J. D. and Lafferty, R. H., Jr., *ibid.*, *72*, 3642 (1950).

d. <u>1-Chloropentafluorocyclobutene.</u> For the synthesis of 1-chloropentafluorocyclobutene, 1,1-dichloro-2,2-difluoroethylene was codimerized with chlorotrifluoroethylene, and the codimer was then dechlorinated. The preparation of the codimer has been reported by Kropa and Padbury[7], but the exact experimental conditions were not available.

Three hundred fifty-seven grams of 1,1-dichloro-2,2-difluoroethylene and 440 g. of chlorotrifluoroethylene were heated to 200° for twenty-four hours in a 1-liter high-pressure reactor. The reactor was cooled and the excess gases vented. The contents were distilled with the following fractions being collected: 75 ml. distilling below 58.5°, 50 ml. of 1,2-dichlorohexafluorocyclobutane distilling at 58.5-59.6°, 21 ml. distilling 59.6-93.7° and 123 ml. of 1,2,2-trichloropentafluorocyclobutane distilling at 93.8-94.0°. This codimer weighed 200 g. which represents a 30 per cent yield based on the dichlorodifluoroethylene. It had a melting point of 31-32°.

The codimer was dechlorinated by the use of zinc and 1-butanol. Three hundred milliliters of 1-butanol and 180 g. of 30-mesh zinc were placed in a 1-liter three-necked flask. To this was attached an upright condenser through which water at 40° was circulated. To the upright condenser was attached a downward condenser through which water at 3-8° was circulated. This in turn was connected to an Erlenmeyer flask which was cooled in a Dry Ice-trichloroethylene bath and which had an outlet to air protected from moisture by means of a calcium chloride drying tube.

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(7) Kropa, E. L. and Padbury, J. J., Canadian Patent 453,791 (1949); <u>C</u>. <u>A</u>. <u>44</u>, 2019 (1950).

The 1-butanol was heated to reflux and a solution of 200 g. of codimer in 1-butanol was added slowly from a dropping funnel over a period of two hours. During this operation external heat was supplied to maintain boiling at a brisk rate. After all the codimer had been added, the mixture was refluxed for one-half hour, then cooled.

The distillate which collected in the Erlenmeyer flask weighed 122 g. Fractional distillation gave 99 g. of 1-chloropentafluorocyclobutene distilling at 32.0-32.2°, n_D^{25} 1.3201, d_{20}^{25} 1.505. The yield was 69 per cent and the atomic refraction of fluorine, calculated from the experimental values obtained, was 1.13.

B. Quaternary Salt Formation

1. From Aliphatic Tertiary Amines and Hexafluorocyclobutene

a. *Tri-n-butyl(2,3,3,4,4-pentafluorocyclobutenyl)ammonium fluoride (IA).* Eighteen and one-half grams of tri-*n*-butylamine was placed in a thick-walled glass reactor tube. The tube and contents were placed in a liquid nitrogen bath and the tube was evacuated. Thirty grams of hexafluorocyclobutene was then distilled into the tube. The tube was sealed and the tube and contents were warmed to room temperature and allowed to remain at that temperature for six days. The tube was then opened, the excess butene was allowed to escape, and the liquid was decanted from the solid. The solid was macerated with *n*-heptane and the mixture was filtered. The solid was washed with *n*-heptane and dried. The brown solid produced by this method weighed 19 g. and decomposed with evolution of gas above 82°[8]. This represents a 55 per cent yield. Two recrystallizations from benzene gave pure white crystals which were hygroscopic.

Anal. Calcd. for $C_{16}H_{27}NF_6$: C, 55.31; H, 7.83; N, 4.03. Found: C, 55.08; H, 8.09; N, 4.06.

The formation of this quaternary fluoride was found to be reversible. Seventy-five grams was dissolved in a mixture of 85 ml. of dibutyl ether and 400 ml. of benzene. The solution was heated to boiling and the gaseous product was collected in a cold trap surrounded by a Dry Ice-trichloroethylene bath. The gas solidified in the trap and after warming boiled at 2°. The yield of hexafluorocyclobutene was 28 g. (59 per cent).

b. Triethyl(2,3,3,4,4-pentafluorocyclobutenyl)ammonium fluoride (IB)[9]. A stainless-steel reaction vessel was charged at Dry Ice temperature with equimolar quantities of triethylamine (86 g.) and hexafluorocyclobutene (138 g.). After standing at room temperature for six hours the cylinder was shaken at 40° for sixteen hours. The liquid portion of the reaction mixture was then removed by decantation, after which approximately 75 g. of crystalline solid remained.

The reactive crystalline product thus obtained was soluble in benzene but separated, upon the addition of n-heptane, as a red oil from which crystals precipitated when cooled below 0°. After centrifugation,

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(8) The melting points listed in this paper were taken using a 0-360° thermometer with 76 mm. immersion. An insulated aluminum melting point block was used for all melting points.

(9) This method was originated by Karl E. Rapp.

the liquid was decanted from the solid which was then washed twice with n-heptane and finally recovered by suction filtration upon fritted glass under an atmosphere of dry nitrogen in an effort to remove the occluded heptane. The solid was transferred to a drying tube and the residual heptane was removed by evacuation for sixteen hours at room temperature and for four hours at 50°.

Anal. Calcd. for $C_{10}H_{15}NF_6$: C, 45.63; H, 5.74; N, 5.32. Found: C, 45.72; H, 6.05; N, 6.35.

In the present investigation this method was modified since it was found that the heating was not necessary. The best conditions consisted of allowing the two components to stand at room temperature for eighteen hours, then removing the solid. Longer periods of time accompanied by heating caused the formation of an oil, as noted above, which was not identified due to instability.

c. Triethyl(2-ethoxy-3,3,4,4-tetrafluorocyclobutenyl)ammonium picrate. A small amount of triethyl(2,3,3,4,4-pentafluorocyclobutenyl)-ammonium fluoride was added to absolute ethanol. The resulting solution was treated with a solution of picric acid in ethanol. Thorough cooling gave yellow crystals which after filtration and drying melted at 69-71°. Two recrystallizations from absolute ethanol resulted in a melting point of 78-79° with sintering at 76°.

Anal. Calcd. for $C_{18}H_{22}N_4O_8F_4$: C, 43.38; H, 4.45; N, 11.25; F, 15.25. Found: C, 43.90; H, 4.75; N, 11.66; F, 14.63.

d. Others. All of the initial quaternary salts, with the exception of the one formed from tri-n-butylamine and hexafluorocyclobutene, were extremely reactive. Therefore, in general, they were not isolated but were immediately hydrolyzed after formation.

2. From Aliphatic Tertiary Amines and Monoethers or Monothioethers of Hexafluorocyclobutene

None of these was isolated as the quaternary fluoride but all were isolated as the picrate salt, formed by the substitution of the picrate ion for the fluoride ion. In all cases the yield of picrate was quite low, which probably means that the reaction did not proceed to any appreciable extent. The quaternary salt which was formed was not one which would be formed from the two components, as triethyl(3,3,4,4-tetrafluoro-2-methoxycyclobutenyl)ammonium fluoride from triethylamine and 1-methoxypentafluorocyclobutene, but was a degradation product, methyltriethylammonium fluoride.

Due to the fact that these experiments had no material significance in the paper as a whole, no further work was done to determine optimum conditions or exact yields. The preparation is presented since two of the compounds are new.

a. Methyltriethylammonium picrate. Ten milliliters of 1-methoxypentafluorocyclobutene and 20 ml. of triethylamine were mixed. The resulting solution was heated at 70-90° for two hours. During this time a black lower layer formed, which had a volume of about 10 ml. This lower layer was separated and placed under vacuum to remove the residual triethylamine. The remainder could not be distilled, even in a molecular still using a temperature of 70° and a pressure of 0.05 mm. It was dissolved in a saturated solution of picric acid in ethanol and a yellow precipitate formed immediately. The mixture was filtered and the yellow crystals were dried, after which they melted at 270.5-272° with decomposition. Recrystallization from absolute ethanol gave a melting point of 273-274° dec. (Lossen[10] gives 267-268°).

Anal. Calcd. for $C_{13}H_{20}N_4O_7$: C, 45.34; H, 5.85; N, 16.28. Found: C, 45.39; H, 5.68; N, 16.32.

b. Methylethylpiperidinium picrate. Two milliliters of 1-methoxypentafluorocyclobutene and 3 ml. of 1-ethylpiperidine were heated on a water bath for one-half hour. The lower layer formed was separated and mixed with water. This gave an immediate reaction with evolution of heat, and a lower layer formed. This was washed with water and with ethanol, then dissolved in absolute ethanol. This solution was mixed with a saturated solution of picric acid in ethanol. An immediate precipitate of yellow crystals formed. The mixture was filtered and the crystals were dried, after which they weighed 0.5 g. and melted at 254-256° dec. Several recrystallizations from absolute ethanol gave a final m. p. of 261-262° dec.

Anal. Calcd. for $C_{14}H_{20}N_4O_7$: C, 47.18; H, 5.66; N, 15.73: Found: C, 47.53; H, 5.66; N, 15.59.

c. 4,4-Dimethylmorpholinium picrate. Five grams of 4-methylmorpholine and 5 g. of 1-phenoxypentafluorocyclobutene were mixed and

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(10) Lossen, von W., Ann., 181, 364 (1876).

heated on a water bath for eight hours. During this time a black solid precipitated from the solution. The liquid was decanted from the solid and the solid was dissolved in absolute ethanol. To this was added a saturated solution of picric acid in ethanol. The crystals produced by this method were removed by filtration and dried, after which they weighed 2-3 g. and melted at 284-285° with decomposition. Two recrystallizations from cyclohexanone gave a final product of fine yellow needles, m. p. 287-288° dec.

Anal. Calcd. for $C_{12}H_{16}N_4O_8$: C, 41.86; H, 4.68; N, 16.28. Found: C, 42.19; H, 4.56; N, 16.09.

This same picrate was also produced by the reaction of 1-methylmorpholine with 1-butylthiopentafluorocyclobutene. Two grams of 1-butylthiopentafluorocyclobutene and 2 g. of 4-methylmorpholine were mixed and allowed to stand together at room temperature for five days, then heated on a water bath for two hours. The reaction mixture was placed in a molecular still and the volatile material was removed by warming under reduced pressure. The residue was dissolved in 5 ml. of absolute ethanol and mixed with 20 ml. of a saturated solution of picric acid in ethanol. The resulting mixture was filtered and the yellow crystals retained were dried after which they weighed 1.5 g. After recrystallization from cyclohexanone this solid had a melting point of 285-286° dec. A mixed melting point with the picrate produced from the reaction of 4-methylmorpholine with 1-phenoxypentafluorocyclobutene resulted in a value of 286-287° dec.

3. Others Which Did Not Form Quaternary Fluorides

a. 4-Methylmorpholine with 1,2-bis(butylthio)-3,3,4,4-tetrafluorocyclobutene. One milliliter of 1,2-bis(butylthio)-3,3,4,4-tetrafluorocyclobutene and 2 ml. of 4-methylmorpholine were heated together at 90° for six hours. At the end of this time there were no indications of reaction.

b. 4-Methylmorpholine with 1,2-dichloro-3,3,4,4,5,5-hexafluorocyclopentene. Five grams of 4-methylmorpholine and 12.2 g. of 1,2-dichlorohexafluorocyclopentene were placed in a glass tube, the tube was sealed and the tube and contents were heated at 60° for one day, then at 122° for fifteen days. The product was removed from the tube, washed with dilute hydrochloric acid, dried over anhydrous sodium carbonate, and distilled. All but a few drops distilled at 85-88° and the distillate had n_D^{24} 1.3675 (for the original cyclopentene: b. p. 89° and n_D^{23} 1.3678).

c. Triethylamine with octafluorobutene-2. Fifty milliliters of triethylamine was placed in a pressure vessel and the vessel and the contents were cooled in liquid nitrogen. Seventy-two grams of octafluorobutene-2 was then added by gaseous transfer. The mixture was heated at 50-55° for five hours and then at 85° for twenty-five hours. After this time, during which the pressure in the vessel had remained constant at about 80 psi., the gaseous contents were allowed to escape and the vessel was opened. Practically all the contents were soluble in dilute hydrochloric acid, indicating that no appreciable reaction had occurred.

C. Hydrolysis of Trialkyl(2,3,3,4,4-pentafluorocyclobutenyl)ammonium Fluorides

In all cases except one (that of tri-n-butylamine with hexafluorocyclobutene), the intermediate quaternary fluorides were hydrolyzed directly without complete isolation and purification. Therefore, unless otherwise specified, all yields given are based on the original tertiary amine.

1. (3,3-Difluoro-2,4-dioxocyclobutyl)trimethylammonium Betaine

Sixteen grams of trimethylamine and 94 g. of hexafluorocyclobutene were distilled into a reaction vessel cooled in liquid nitrogen. The vessel and contents were warmed to room temperature and allowed to remain at this temperature for three days.

The excess butene was vented from the container and the remaining white solid was placed cautiously in approximately 200 ml. of water. During this operation the temperature was maintained below 30° with the use of an ice bath. After all the solid had been added, the solution was made basic with concentrated sodium hydroxide, again maintaining a temperature of less than 30°. During the neutralization a white solid precipitated. After thorough cooling, the white solid was removed by filtration and dried. The filtrate was set aside to evaporate to dryness.

The solid was placed in a Soxhlet extractor and extracted for eight hours with acetone. The extract was cooled in an ice bath and the resulting mixture was filtered. The white solid thus obtained weighed 21.3 g. after drying, m. p. 232.5-234°.

After the original filtrate had evaporated to dryness, there remained a solid. This was also extracted with acetone by the same procedure, by means of which an additional 5.5 g. of the betaine was produced, m. p. 231-233°. Evaporating the combined acetone residues to dryness and recrystallizing the residue from methanol gave an additional 8.3 g., m. p. 227-230°. The combined yield was 73 per cent of the theoretical. Further purification by recrystallization from methanol gave a final melting point of 233-234°.

Anal. Calcd. for $C_7H_9NO_2F_2$: C, 47.46; H, 5.12; N, 7.91; M. W., 177[11]. Found: C, 47.42; H, 4.91; N, 7.98; M. W., 174.

2. (3,3-Difluoro-2,4-dioxocyclobutyl)ethyldimethylammonium Betaine

Fourteen and six-tenths grams of N,N-dimethylethylamine was placed in a stainless-steel reaction vessel, the vessel and contents were cooled in liquid nitrogen, the vessel was evacuated, and 40 g. of hexafluorocyclobutene was distilled into it. The vessel and contents were then warmed to room temperature and allowed to stand at this temperature for eighteen hours.

The excess gas was vented and the vessel was opened. The solid contents were poured into water cooled by an ice bath. The resulting solution was made basic with concentrated potassium hydroxide. During this addition it was stirred in an ice bath to avoid excessive tempera-

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(11) All molecular weights, unless otherwise specified, were determined by means of the boiling point elevation method. A Menzies-Wright apparatus was used, together with a differential thermometer. Absolute ethanol was used as the solvent.

tures. After all the potassium hydroxide had been added, the mixture was cooled thoroughly, and the resulting crystals were removed by filtration. The solid produced by this method weighed 31 g. but did not melt sharply due to the presence of a small amount of inorganic salt. Cooling the filtrate to 0° produced a second crop of crystals, which weighed 2 g. after filtering and drying. The total yield of crude product was 87 per cent. The combined solids were recrystallized from ethyl acetate. This gave a white solid, m. p. 145-147°, wt. 24 g. (63%).

Two additional recrystallizations from ethyl acetate gave shiny white plates, which melted at 153-154°.

Anal. Calcd. for $C_8H_{11}NO_2F_2$: C, 50.26; H, 5.80;, N, 7.33; F, 19.88. Found: C, 50.17; H, 5.71; N, 7.23; F, 19.10.

3. (3,3,-Difluoro-2,4-dioxocyclobutyl)diethylmethylammonium Betaine

Twenty-three and one-half grams of N-methyldiethylamine was placed in a stainless-steel reaction vessel and the vessel and contents were cooled in a liquid nitrogen bath. Then 51 g. of hexafluorocyclobutene was distilled into the vessel. The vessel and contents were warmed to room temperature and kept at this temperature for four days.

The excess gas was vented and the solid was added cautiously to cold water. After all the solid had been added, the cold water solution was made basic with concentrated potassium hydroxide solution. The resulting mixture of liquid and solid was cooled to 5° and filtered. The solid thus obtained was washed with a little cold water and dried, after which it weighed 50.0 g. and melted at 103-107°. The filtrate was cooled again, and the resulting crystals were removed by filtration and dried. The weight was 1.0 g., m. p. 102-105°. The total yield was 92 per cent.

One recrystallization from ethyl acetate gave 43.4 g. (78 per cent) of nearly white solid, m. p. 117-119°. Further recrystallization from ethyl acetate gave as final product a snowy-white solid, m. p. 126-127°.

Anal. Calcd. for $C_9H_{13}NO_2F_2$: C, 52.67; H, 6.39; N, 6.83; M. W., 205. Found: C, 53.20; H, 6.47; N, 6.92; M. W., 202.

4. (3,3-Difluoro-2,4-dioxocyclobutyl)triethylammonium Betaine[12]

Ten and one-tenth grams of triethylamine was placed in a thick-walled glass tube. The tube was cooled in a liquid nitrogen bath, evacuated, and 23 g. of hexafluorocyclobutene was added by gaseous transfer. The tube was then sealed and warmed to room temperature.

After two days at this temperature the tube was opened. The solid was added cautiously to 150 ml. of water with cooling. The resulting mixture was filtered and the crystals thus obtained were washed with cold water and dried, after which they weighed 17.4 g. and melted at 160-162°.

The aqueous filtrate was neutralized with concentrated potassium hydroxide solution, cooled and filtered. This produced 2.8 g. of ad-

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(12) The original method for producing this compound was developed by Karl E. Rapp, who purified it and obtained analyses for it.

ditional solid, m. p. 157-160°. The total yield was 92 per cent of the theoretical. Recrystallization from methanol raised the melting point to 166-167°.

Anal. Calcd. for $C_{10}H_{15}NO_2F_2$: C, 54.79; H, 6.90; N, 6.39; F, 17.33; M. W., 219. Found: C, 54.95; H, 6.87; N, 6.59; F, 17.10; M. W., 226.

This same betaine was produced by the reaction of triethylamine with 1-chloropentafluorocyclobutene. Three grams of the amine and 5.4 g. of the butene were mixed together. Within one-half hour nearly all the liquid had turned to a slightly orange solid. After eighteen hours the solid was placed in water. The water solution became acidic, but no crystals appeared; instead an oil separated from the solution. The mixture was made basic with concentrated potassium hydroxide, after which crystals formed, although some of the liquid still remained. The mixture was filtered and the crystals were dried. The yield was 2.0 g. (30 per cent) of betaine melting at 163-165°. Recrystallization from methanol raised the melting point to 165-166°.

5. Di-n-butyl(3,3-difluoro-2,4-dioxocyclobutyl)methylammonium Betaine

Thirty-six grams of N-methyldi-*n*-butylamine was placed in the vessel. After cooling and evacuating, 41 g. of hexafluorocyclobutene was added. The vessel and contents were then maintained at room temperature for four days.

The solid quaternary fluoride was added in portions to water, during which process a lower layer formed. This lower layer was separated and shaken with a solution of potassium hydroxide until it solidified. The mixture was then filtered, the solid was washed with water and dried, m. p. 42-45°. The 61 g. obtained represents a yield of 81 per cent of the theoretical.

The material was recrystallized by dissolving in a small amount of methanol and cooling for a long period of time in a Dry Ice-trichloroethylene bath. After this recrystallization the white solid melted at 60-63°. It was recrystallized an additional three times; the final melting point obtained was 68-70°.

Anal. Calcd. for $C_{13}H_{21}NO_2F_2$: C, 59.75; H, 8.10; N, 5.36. Found: C, 59.65; H, 8.04; N, 5.63.

6. Tri-n-butyl(3,3-difluoro-2,4-dioxocyclobutyl)ammonium Betaine

As stated in Section B, Page 22, tri-*n*-butylamine reacted slowly with hexafluorocyclobutene to give after six days a 55 per cent conversion to the quaternary salt. Two and two-tenths grams of this salt was heated with 50 ml. of 5 per cent potassium hydroxide solution for ten minutes. The resulting mixture was filtered and the solid was dried, m. p. 106.5-107.5°. The 1.9 g. obtained represents a quantitative yield based on the quaternary salt. The solid was recrystallized by dissolving in warm methanol, adding water until precipitation barely began, and then cooling. This did not change the melting point.

Anal. Calcd. for $C_{16}H_{27}NO_2F_2$: C, 63.34; H, 8.97; N, 4.62. Found: C, 63.47; H, 8.95; N, 4.63.

7. (3,3-Difluoro-2,4-dioxocyclobutyl)ethylpiperidinium Betaine

Twelve grams of 1-ethylpiperidine and 16 g. of hexafluorocyclobutene were sealed together in a glass tube and allowed to remain at room temperature for eighteen hours.

The solid thus produced was added to water. A small amount of a black lower liquid layer was formed. The aqueous solution was separated from this lower layer and evaporated by means of an air blast. This caused a solid consisting of fine needles to separate from the solution. The mixture was filtered after partial evaporation had taken place, and the solid thus obtained weighed 7.0 g., m. p. 167-170°. Additional solid was obtained by further concentration.

The solid was purified by dissolving in methanol at room temperature, then cooling to -78° to cause precipitation. Two such recrystallizations gave a pure white solid, m. p. 174-175°.

Anal. Calcd. for $C_{11}H_{15}NO_2F_2$: C, 57.13; H, 6.54; N, 6.07. Found: C, 56.85; H, 6.40; N, 6.05.

8. (3,3-Difluoro-2,4-dioxocyclobutyl)methylmorpholinium Betaine

Ten and six-tenths grams of 4-methylmorpholine and 19 g. of hexafluorocyclobutene were sealed together in a glass tube, then allowed to remain at room temperature for four days.

The solid product was added to water, after which the aqueous solution was neutralized with concentrated potassium hydroxide, cooled and filtered. After drying the solid, it weighed 14 g., which represents a 63 per cent yield. The solid was purified by two recrystallizations from methanol, after which it melted at 215-216°.

Anal. Calcd. for $C_9H_{11}NO_3F_2$: C, 49.31; H, 5.06; N, 6.39. Found: C, 48.91; H, 4.83; N, 6.57.

D. Trialkyl(3,3-difluoro-2-oxopropyl)ammonium Chloride Monohydrates (VIII).

1. (3,3-Difluoro-2-oxopropyl)trimethylammonium Chloride Monohydrate (VIII A).

Ten grams of (3,3-difluoro-2,4-dioxocyclobutyl)trimethylammonium betaine was dissolved in 60 ml. of water and 20 ml. of concentrated hydrochloric acid was added. This mixture was refluxed for three hours and then set aside to evaporate to dryness under an air blast.

The crystals produced by evaporation were macerated with 50 ml. of acetone and filtered. The white solid thus produced weighed 11.2 g. and melted at 135-137° with decomposition. This product represents a 97 per cent yield. The crystals were purified by dissolving in a small amount of methanol, filtering, and adding excess ethyl acetate. Two recrystallizations carried out in this manner produced glistening white platelets, m. p. 134.5-135.5° dec.

Anal. Calcd. for $C_6H_{14}NO_2F_2Cl$: C, 35.04; H, 6.86; N, 6.81; F, 18.48; Cl, 17.24. Found: C, 34.79; H, 6.77; N, 6.81; F, 18.60; Cl, 17.26.

a. Picrate (IX). One gram of the chloride (VIII A) dissolved in 10 ml. of absolute ethanol was heated for twenty minutes with 20 ml. of a saturated solution of picric acid in ethanol. Thorough cooling of this solution produced slow crystallization of a slightly yellow solid which, after being filtered and dried, weighed 1.3 g. (68 per cent) and melted at 133-135°. Two recrystallizations from absolute ethanol gave a final melting point of 137-138°.

Anal. Calcd. for $C_{14}H_{20}N_4O_9F_2$: C, 39.43; H, 4.73; N, 13.14; F, 9.54. Found: C, 39.39; H, 4.77; N, 13.23; F, 9.76.

In order to remove the ethanol which was bound in the molecule, this alcoholated picrate was heated in a drying pistol at 100° and 0.1 mm. for six hours.

Anal. Calcd. for $C_{12}H_{14}N_4O_8F_2$: C, 37.90; H, 3.71. Found: C, 38.24; H, 3.83.

b. p-Nitrophenylhydrazine derivative (X). Two grams of the chloride (VIII A) was heated with 2.0 g. of p-nitrophenylhydrazine in 15 ml. of absolute ethanol. The solids dissolved and after about five minutes yellow crystals began to form. After twenty minutes the mixture was cooled and filtered. The solid produced by this method was purified by dissolving in methanol and precipitating with ether. The purified solid did not have a reproducible melting point; the melting points obtained ranged from 120-121° to 127-128°.

Anal. Calcd. for $C_{18}H_{31}N_5O_4F_4Cl_2$: C, 40.91; H, 5.91; N, 13.26; F, 14.38. Found: C, 40.78; H, 5.75; N, 13.58; F, 14.04.

c. Sodium bisulfite derivative (XI). One gram of the chloride (VIII A) was dissolved in 2 ml. of water and the resulting solution was treated with 5 ml. of a saturated solution of sodium bisulfite in water. A heavy precipitate formed immediately. This precipitate, after being removed by filtration and dried, weighed 1.8 g. but contained some inorganic material as indicated by the ash which remained after ignition. Recrystallization from a minimum amount of water gave 0.9 g. (82 per cent of α-hydroxy-α-difluoromethyl-β-trimethylammonoethanesulfonate, dec. 190-192°. Another recrystallization from water gave glistening white crystals, dec. 190-191.5°.

Anal. Calcd. for $C_6H_{13}NO_4SF_2$: C, 30.90; H, 5.62; N, 6.01. Found: C, 30.98; H, 5.65; N, 5.99.

d. Reaction with concentrated potassium hydroxide. Two grams of the chloride (VIII A) was heated with 6 ml. of 40 per cent potassium hydroxide solution. The volatile amine was carried into a solution of picric acid in absolute ethanol. A precipitate began to form when the potassium hydroxide solution reached the boiling point. After ten minutes the refluxing was stopped. The alcoholic solution was filtered and the picrate dried, m. p. 214-217°. Recrystallization from absolute ethanol gave a melting point of 219-220°. A mixed melting point with an authentic sample of trimethylamine picrate having a melting point of 220-221° gave a value at 219-220°.

2. (3,3-Difluoro-2-oxopropyl)ethyldimethylammonium Chloride Monohydrate

Ten grams of (3,3-difluoro-2,4-dioxocyclobutyl)ethyldimethylammonium betaine was dissolved in a solution of 60 ml. of water and 20 ml. of concentrated hydrochloric acid. The resulting solution was refluxed for four hours, then set aside to evaporate to dryness.

The residue was treated with 50 ml. of acetone and the resulting solid was removed by filtration. This gave 4.5 g. of solid, m. p. 102-105°. The filtrate was evaporated to dryness under reduced pressure and the residue was dissolved in absolute ethanol. This solution gave a precipitate when treated with ethyl acetate. The mixture was filtered and the solid thus produced weighed 2.0 g. after drying, m. p. 98-101°. The combined solids represent a yield of 57 per cent. The chloride was purified by dissolving in ethanol, filtering, and adding ether to produce crystallization. Four recrystallizations conducted in this manner gave shiny white platelets, m. p. 102-103°.

Anal. Calcd. for $C_7H_{16}NO_2F_2Cl$: C, 38.27; H, 7.34; N, 6.38; F, 17.38. Found: C, 38.46; H, 6.99; N, 6.13; F, 16.73.

3. (3,3-Difluoro-2-oxopropyl)diethylmethylammonium Chloride Monohydrate

Ten grams of (3,3-difluoro-2,4-dioxocyclobutyl)diethylmethylammonium betaine, 60 ml. of water and 20 ml. of concentrated hydrochloric acid were refluxed together for four hours. The resulting solution was distilled on a water bath at 15 mm. until only a solid residue remained. This was dissolved in hot acetone, cooled and treated with excess ether. The solid thus formed weighed 10.4 g. after drying and melted over a long range (60-90°). Recrystallization from the same solvents reduced the weight to 8.0 g., but the melting range was not materially improved.

The 8.0 g. was recrystallized from water. This produced 2.9 g. of white solid which, after thorough drying, melted at 126-127°, the melting point of the original betaine. It is evident that for this compound refluxing for four hours was not sufficient to complete the reaction as a mixture was produced.

The same experiment was repeated with the quantities of materials being changed to 15 g. of betaine, 90 ml. of water and 30 ml. of concentrated hydrochloric acid. This time the condenser of the reflux apparatus was attached to a tube dipped in a saturated solution of calcium hydroxide. A slow evolution of carbon dioxide was proved by the precipitation of calcium carbonate from the solution. The evolution of carbon dioxide proceeded for more than thirteen hours. At the end of twenty hours the heat was removed and the solution was distilled at reduced pressure until only a very thick syrup remained. It was found to be necessary to distill until only this syrup remained; otherwise the next step would not be successful.

The syrup was treated with acetone, a process which produced white crystals, m. p. 90-95°. The actual yield should be larger than the 6.0 g. actually obtained as some mechanical loss occurred during the operations. The solid was purified by dissolving in warm acetic acid and precipitating with ethyl acetate. Four such recrystallizations gave a final product consisting of glistening white needles, m. p. 97-98°.

<u>Anal</u>. Calcd. for $C_8H_{18}NO_2F_2Cl$: C, 41.11; H, 7.76; N, 5.99; F, 16.26; Cl, 15.17. Found: C, 41.15; H, 7.82; N, 5.49; F, 17.03; Cl, 15.81.

4. (3,3-Difluoro-2-oxopropyl)methylmorpholinium Chloride Monohydrate

Ten grams of (3,3-difluoro-2,4-dioxocyclobutyl)methylmorpholinium betaine was dissolved in 60 ml. of water. Twenty milliliters of concentrated hydrochloric acid was added and the solution was refluxed for four hours. It was then set aside to evaporate to dryness under an air blast.

The residue from the evaporation was macerated with 50 ml. of acetone and the resulting mixture was filtered. The solid produced by this procedure was separated by filtration and dried, after which it weighed 5.0 g. An additional 3.0 g. was recovered by adding ether to the acetone filtrate and filtering the mixture produced. The combined yield was 70 per cent of the theoretical. The product was recrystallized by dissolving in methanol and then precipitating with ether. Four purifications conducted in this manner resulted in fine white crystals, m. p. 142-143° with sintering about 5° below the melting point.

Anal. Calcd. for $C_8H_{16}NO_3F_2Cl$: C, 38.79; H, 6.51; N, 5.66. Found: C, 39.15; H, 6.51; N, 5.75.

E. Reactions of Trialkyl(3,3-difluoro-2,4-dioxocyclobutyl)ammonium Betaines (VI).

1. Trialkyl(3,3-difluoro-2-oxopropyl)ammonium Chloride Monohydrates (VIII).

The reactions of trialkyl(3,3-difluoro-2,4-dioxocyclobutyl)-ammonium betaines (VI) with dilute hydrochloric acid, in which trialkyl (3,3-difluoro-2-oxopropyl)ammonium chloride monohydrates (VIII) are produced, have been described in section D of this chapter.

2. Tris[(3,3-difluoro-2,4-dioxocyclobutyl)trimethylammonium Betaine] Sodium Triodide (VII)

A solution of 10 g. of iodine and 25 g. of sodium iodide in 100 ml. of water was added with stirring to a solution of 5 g. of (3,3-difluoro-2,4-dioxocyclobutyl)trimethylammonium betaine in 20 ml. of water until the dark color of the sodium iodide-iodine solution remained. The mixture was allowed to stand for ten minutes, then the red-brown crystals were separated by filtration and dried. The yield of crude material was 8.0 g. (91 per cent calculated for three moles of betaine to one of sodium iodide-iodine). This material decomposed at 232-235° with the liberation of iodine vapors. Two recrystallizations from glacial acetic acid gave a final product of red-brown crystals which decomposed at 233-235°.

Anal. Calcd. for $C_{21}H_{27}N_3O_6F_6NaI_3$: C, 26.97; H, 2.91; N, 4.49; I, 40.71; Na (as sulfate), 7.60. Found: C, 27.12; H, 2.72; N, 4.24; I, 41.22; Na (as sulfate), 7.59.

3. (3,3-Difluoro-2,4-dioxocyclobutyl)trimethylammonium Betaine-Sulfuric Acid Complex

One and one-half grams of the trimethylammonium betaine was dissolved by warming in 3 ml. of concentrated sulfuric acid. The solution was cooled and added with stirring to 50 ml. of absolute ether. Continued stirring caused a white solid to separate from the solution. The mixture was filtered under an atmosphere of nitrogen and the solid was dried under this atmosphere. This extremely hygroscopic solid weighed 2.0 g. and melted at 103-108°. One recrystallization from methanol gave a melting point of 207-210°. A second recrystallization by the same method gave 0.9 g. of white, non-hygroscopic solid melting at 231-233° which was identical with the starting material.

4. (2,4-Dioxo-3,3-diphenylcyclobutyl)triethylammonium Betaine (XII)

A mixture of 10.0 g. of (3,3-difluoro-2,4-dioxocyclobutyl)triethylammonium betaine, 200 ml. of benzene and 30.0 g. of anhydrous aluminum chloride was placed in a 3-necked flask fitted with a mechanical stirrer, reflux condenser and drying tube. The mixture was refluxed for one hour with vigorous stirring. During this time most of the solids dissolved, a considerable amount of hydrogen chloride was evolved, and the solution turned black. The solution was then cooled and poured with stirring into a dilute hydrochloric acid-ice mixture. The black color disappeared and slightly yellow crystals began to separate. After standing for one hour, the solution was filtered and the solid was dried. This produced 10.5 g. (69 per cent) of crude material, m. p. 122-132°. This solid was dissolved in 50 ml. of glacial acetic acid and the small amount of insoluble material was removed by centrifuging. The supernatant acetic acid solution was poured with stirring into 400 ml. of water and allowed to stand for thirty minutes, then filtered. The dried white solid weighed 7.0 g. (46 per cent) and melted at 180-183°. Several recrystallizations from methyl acetate raised the melting point to 188-189°.

<u>Anal.</u> Calcd. for $C_{22}H_{25}NO_2$: C, 78.77; H, 7.51; N, 4.18. Found: C, 78.49; H, 7.10; N, 4.21.

In order to form the hydrobromide of this diphenylammonium betaine, 1 g. was heated with 15 ml. of 48 per cent hydrobromic acid for ten minutes. During this time a white precipitate formed. The mixture was cooled and filtered. The yield was 1.3 g. (95 per cent) of white solid, m. p. 168-170°. Two recrystallizations from glacial acetic acid gave a final melting point of 166-167°.

Anal. Calcd. for $C_{22}H_{26}NO_2Br$: C, 63.46; H, 6.29; N, 3.36. Found: C, 63.52; H, 6.40; N, 3.32.

When a sample of this bromide was heated for a few minutes with water and then filtered and dried, it was found to have reverted to the original (2,4-dioxo-3,3-diphenylcyclobutyl)triethylammonium betaine.

5. Dibromomethyltrimethylammonium Tribromide (XIV)

Five grams of (3,3-difluoro-2,4-dioxocyclobutyl)trimethylammonium betaine was dissolved in 100 ml. of water and 4 ml. of bromine was added with stirring over a period of two hours. During this time a red-orange precipitate began to form. The mixture was stirred two hours longer and then cooled and filtered. The red solid which was produced by this procedure was dried, after which it weighed 7.5 g. and melted at 65-70° with decomposition. This represents a yield of 56 per cent.

The solid was purified by recrystallization from glacial acetic acid. Two recrystallizations from this solvent gave a final melting point of 70-72° dec.

Anal. Calcd. for $C_4H_{10}NBr_5$: C, 10.18; H, 2.14; N, 2.97; Br, 84.70. Found: C, 10.92; H, 2.21; N, 2.56; Br, 83.93.

6. Trialkyldibromomethylammonium Bromides (XIII)

a. Dibromomethyltrimethylammonium Bromide. Two grams of dibromomethyltrimethylammonium tribromide was dissolved in 5 ml. of acetone and ether was then added to the resulting solution. A white precipitate formed which, after filtration, weighed 1.3 g. (100 per cent). This was purified by four recrystallizations from 95 per cent ethanol. The final product consisted of long flat needles of white crystals, decomposing at 154-155° with the evolution of a gas.

Anal. Calcd. for $C_4H_{10}NBr_3$: C, 15.40; H, 3.23; N, 4.49; Br, 76.87. Found: C, 15.73; H, 3.33; N, 3.72; Br, 76.18.

b. Dibromomethylethyldimethylammonium Bromide. Five and one-half grams of (3,3-difluoro-2,4-dioxocyclobutyl)ethyldimethylammonium betaine was dissolved in 15 ml. of methanol and 3.5 ml. of liquid bromine was added. The resulting solution was allowed to stand at room temperature for eighteen hours.

The solution was poured into 100 ml. of acetone. Thorough cooling and stirring caused a white precipitate to separate from the solution. The mixture was filtered and the solid was washed with acetone and dried, after which it weighed 5.5 g. and melted at 118.5-120° with the evolution of a gas. This solid represents a 59 per cent yield. It was recrystallized by dissolving in methanol and precipitating with butyl acetate. The solid produced by this recrystallization melted at 119.5-121° with decomposition. Recrystallization from isopropanol raised the melting point to 123.5-124.5° dec. A second recrystallization from this solvent gave a melting point of 124.0-124.5° dec.

Anal. Calcd. for $C_5H_{12}NBr_3$: C, 18.43; H, 3.71; N, 4.30; Br, 73.56. Found: C, 18.60; H, 3.63; N, 3.70; Br, 74.08.

The picrate of this bromide was prepared by dissolving 1.0 g. of it in 10 ml. of boiling 95 per cent ethanol and adding a solution of 1.0 g. of picric acid in boiling ethanol. The resulting yellow solution was boiled for one minute and then cooled in an ice-bath. Filtering and drying the yellow crystals obtained gave 1.4 g., m. p. 132-135° dec. The yield was 97 per cent of the theoretical. Four recrystallizations from 95 per cent ethanol gave a final melting point of 159-160° with decomposition. The melting point obtained varied greatly with the rate of heating.

Anal. Calcd. for $C_{11}H_{14}N_4O_7Br_2$: C, 27.86; H, 2.98; N, 11.82; Br, 33.71. Found: C, 28.18; H, 3.04; N, 11.42; Br, 33.62.

c. Dibromomethyldiethylmethylammonium Bromide. Two grams of (3,3-difluoro-2,4-dioxocyclobutyl)diethylmethylammonium betaine was dissolved in 5 ml. of methanol and 1 ml. of liquid bromine was added. This solution was maintained at room temperature for eighteen hours. After this time, 15 ml. of acetone was added, and the mixture was cooled, then filtered. The white solid obtained weighed 1.0 g. after drying (30 per cent yield) and melted at 130-131° with decomposition. Three recrystallizations from absolute ethanol gave a pure product having a melting point of 133-134° dec.

Anal. Calcd. for $C_6H_{14}NBr_3$: C, 21.20; H, 4.15; N, 4.12. Found: C, 21.74; H, 4.14; N, 3.54.

F. Absorption Spectra

1. Infrared

The infrared absorption spectra of (3,3-difluoro-2,4-dioxocyclobutyl)triethylammonium betaine, (3,3-difluoro-2,4-dioxocyclobutyl)-diethylmethylammonium betaine and (2,4-dioxo-3,3-diphenylcyclobutyl)-triethylammonium betaine were obtained over the range 2-15μ. The measurements were obtained using a Perkin-Elmer model 21 double-beam spectrophotometer with a rock-salt prism. The sample was prepared by evaporation of either a methanol or acetone solution on rock-salt plates. The spectra are recorded in Figure 1 and the wave lengths of the maxima are given in Table I.

In addition, the spectrum of (3,3-difluoro-2,4-dioxocyclobutyl)-triethylammonium betaine was obtained over the range of 15-38μ. The spectrum from 15 to 25μ was obtained with the use of a Perkin-Elmer model 12-A spectrophotometer with a potassium bromide prism. The spectrum from 25 to 38μ was obtained with the use of a Perkin-Elmer model 12-C spectrophotometer with a KRS-5 prism. In both cases the sample was prepared in a nujol paste. The spectra are recorded in Figures 2 and 3 and are corrected for the nujol absorption. The wave lengths of the important maxima are recorded in Table II.

2. Ultraviolet

The ultraviolet absorption spectra of (3,3-difluoro-2,4-dioxocyclobutyl)triethylammonium betaine, (3,3-difluoro-2,4-dioxocyclobutyl)-diethylmethylammonium betaine and of (2,4-dioxo-3,3-diphenylcyclobutyl)-

triethylammonium betaine were obtained over the range of 220-400 mμ. A Beckman model DU spectrophotometer was used with quartz prism and hydrogen discharge lamp. The quartz absorption cells were of 1.000 ± 0.001 cm. length. The samples were dissolved in absolute ethanol and diluted to the required concentration in volumetric flasks. Readings were taken every 5 mμ, except in the regions of maximum absorption, in which case they were taken every 2 mμ. The spectra are recorded in Figures 4 and 5 and the principal absorption regions are tabulated in Table III.

G. Analyses[13].

Carbon, hydrogen and nitrogen were determined by combustion. Halogens, with the exception of fluorine, were determined by the Carius tube method. Fluorine was determined by the method of Rickard, Ball and Harris[14].

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(13) Analyses were performed by Clark Microanalytical Laboratory, Urbana, Illinois; Galbraith Laboratories, Knoxville, Tennessee; and Frances Ball and R. R. Rickard of the Microchemical Group of the Analytical Research Section.

(14) Rickard, Ball and Harris, Unpublished Work.

TABLE I

INFRARED ABSORPTION DATA, TWO TO FIFTEEN MICRONS

(3,3-Difluoro-2,4-dioxocyclobutyl)triethylammonium Betaine		(3,3-Difluoro-2,4-dioxocyclobutyl)diethylmethylammonium Betaine		(2,4-Dioxo-3,3-diphenylcyclobutyl)-triethylammonium Betaine	
$\lambda(\mu)$	Intensity[a]	$\lambda(\mu)$	Intensity[a]	$\lambda(\mu)$	Intensity[a]
				2.75	w
		2.94	w	2.94	w
3.35	w	3.37	w	3.36	w
		4.39	w		
5.60	m	5.60	m	5.60	w
				5.68	w
				5.83	w
6.02	s	6.10	s	6.19	vs
6.76	m	6.78	m	6.72	w
6.92	m	6.96	m	6.94	m
7.25	w	7.25	w	7.21	w
7.51	w			7.62	w
7.99	s	7.99	s	7.99	w

---

[a] The abbreviations are as follows: w, weak; m, medium; s, strong; vs, very strong.

INFRARED ABSORPTION DATA, TWO TO FIFTEEN MICRONS (Continued)

(3,3-Difluoro-2,4-dioxocyclobutyl)triethylammonium Betaine		(3,3-Difluoro-2,4-dioxocyclobutyl)diethylmethylammonium Betaine		(2,4-Dioxo-3,3-diphenylcyclobutyl)-triethylammonium Betaine	
$\lambda(\mu)$	Intensity[a]	$\lambda(\mu)$	Intensity[a]	$\lambda(\mu)$	Intensity[a]
		8.18	m	8.29	w
8.49	w			8.47	w
8.82	m	8.76	m	8.71	w
9.15	w			9.29	m
9.58	s	9.62	s	9.42	w
				9.76	w
9.93	w			9.99	w
10.16	w	10.20	w		
		10.36	m	10.34	w
10.85	m				
11.07	w	11.20	s		
12.17	s	12.24	s	12.30	w
				12.52	w
12.90	m			13.02	m
13.21	m	13.19	s		

[a] The abbreviations are as follows: w, weak; m, medium; s, strong; vs, very strong.

INFRARED ABSORPTION DATA, TWO TO FIFTEEN MICRONS (Continued)

(3,3-Difluoro-2,4-dioxocyclobutyl)triethylammonium Betaine		(3,3-Difluoro-2,4-dioxocyclobutyl)diethylmethylammonium Betaine		(2,4-Dioxo-3,3-diphenylcyclobutyl)-triethylammonium Betaine	
$\lambda(\mu)$	Intensity[a]	$\lambda(\mu)$	Intensity[a]	$\lambda(\mu)$	Intensity[a]
				13.49	m
				13.84	w
				14.09	w
				14.36	m

[a] The abbreviations are as follows: w, weak; m, medium; s, strong; vs, very strong.

TABLE II

INFRARED ABSORPTION FOR (3,3-DIFLUORO-2,4-DIOXOCYCLOBUTYL)TRIETHYLAMMONIUM BETAINE, FIFTEEN TO THIRTY-EIGHT MICRONS

Region	(μ)
15-25	15.24
	17.36
	19.02
	22.45
	23.95
25-38	26.87
	28.79
	32.30

TABLE III

ULTRAVIOLET ABSORPTION DATA

(3,3-Difluoro-2,4-dioxocyclobutyl)triethylammonium Betaine		(3,3-Difluoro-2,4-dioxocyclobutyl)diethylmethylammonium Betaine		(2,4-Dioxo-3,3-diphenylcyclobutyl-triethylammonium Betaine	
$\lambda (m\mu)$[a]	ϵ[b]	$\lambda (m\mu)$[a]	ϵ[b]	$\lambda (m\mu)$[a]	ϵ[b]
230	21,000 23,000	230	20,000	251	10,000
263-274	88 98	263-274	53 59	274-294	1,500 1,500

[a] Single values represent an absorption maximum; ranges represent the limits of the plateaus observed.

[b] Double values represent those values determined at two different concentrations.

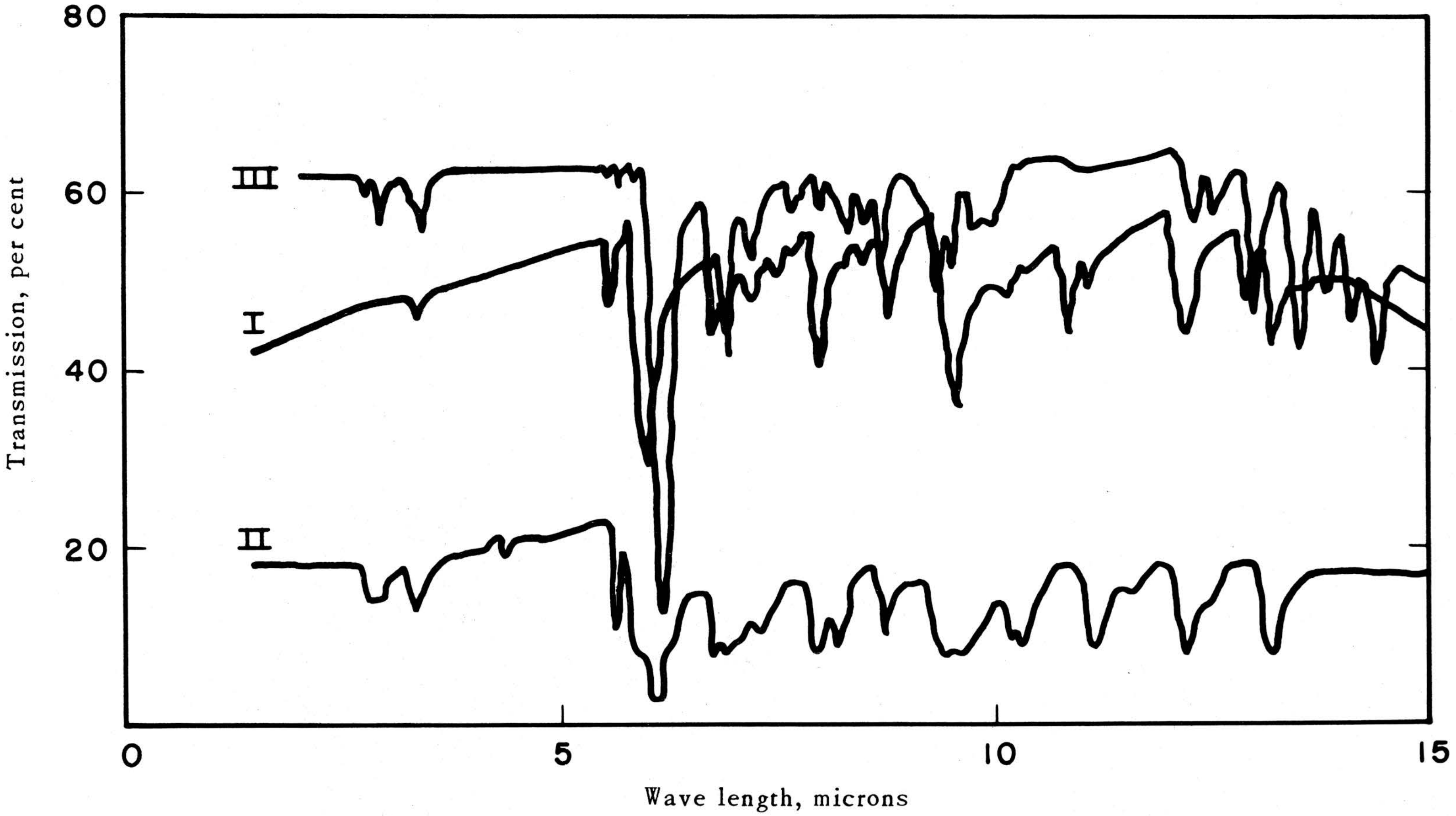

Figure 1. - Infrared absorption spectra of: I, (3,3-difluoro-2,4-dioxocyclobutyl)- triethylammonium betaine; II, (3,3-difluoro-2,4-dioxocyclobutyl) diethylmethylammonium betaine; III, (2,4-dioxo-3,3-diphenylcyclobutyl)triethylammonium betaine. Range: 2 to 15 microns. Preparation: deposited from methanol or acetone.

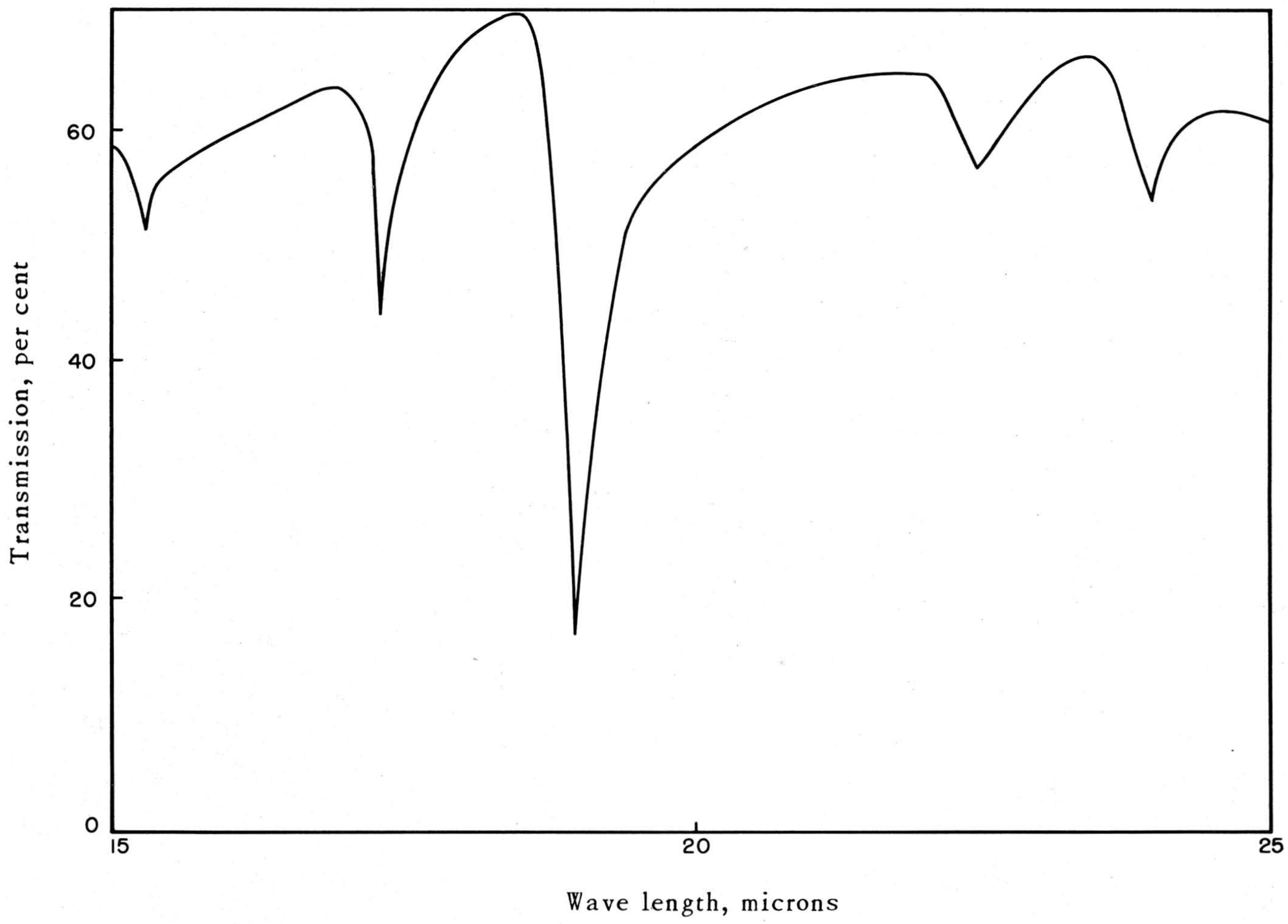

Figure 2.- Infrared absorption spectrum of (3,3-difluoro-2,4-dioxocyclobutyl)-triethylammonium betaine, 15 to 25 microns. Preparation: nujol paste. The spectrum is corrected for the nujol absorption.

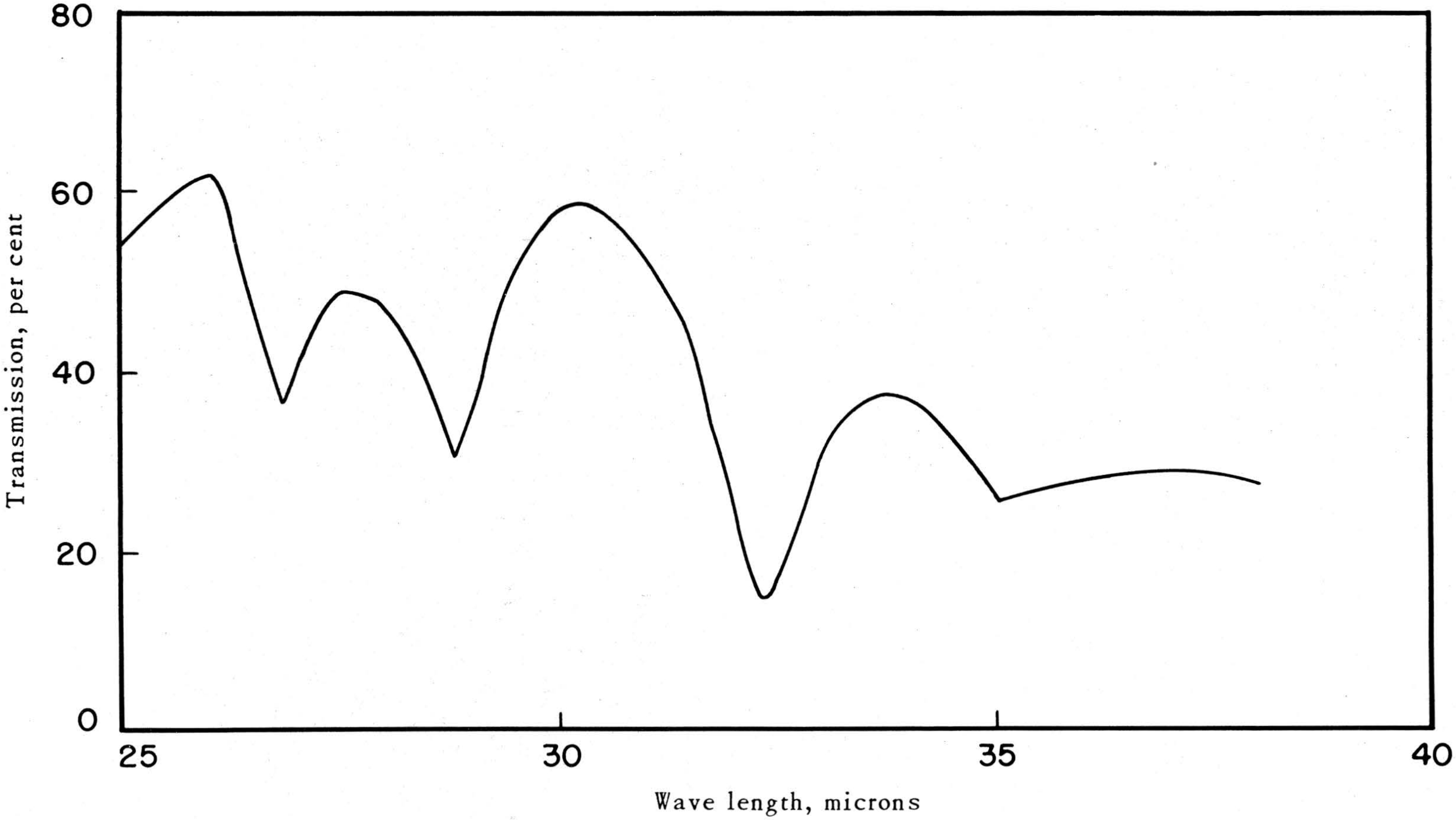

Figure 3.- Infrared absorption spectrum of (3,3-difluoro-2,4-dioxocyclobutyl)-triethylammonium betaine, 25 to 38 microns. Preparation: nujol paste. The spectrum is corrected for the nujol absorption.

Figure 4.- Ultraviolet absorption spectra of: ——, (3,3-difluoro-2,4-dioxocyclobutyl)-triethylammonium betaine, c = 1.69 x 10^{-3} moles/liter; ----, (3,3-difluoro-2,4-dioxocyclobutyl) diethylmethylammonium betaine, c = 1.98 x 10^{-3} moles/liter; — . —, (2,4-dioxo-3,3-diphenylcyclobutyl) triethylammonium betaine, c = 2.19 x 10^{-4} moles/liter.

58

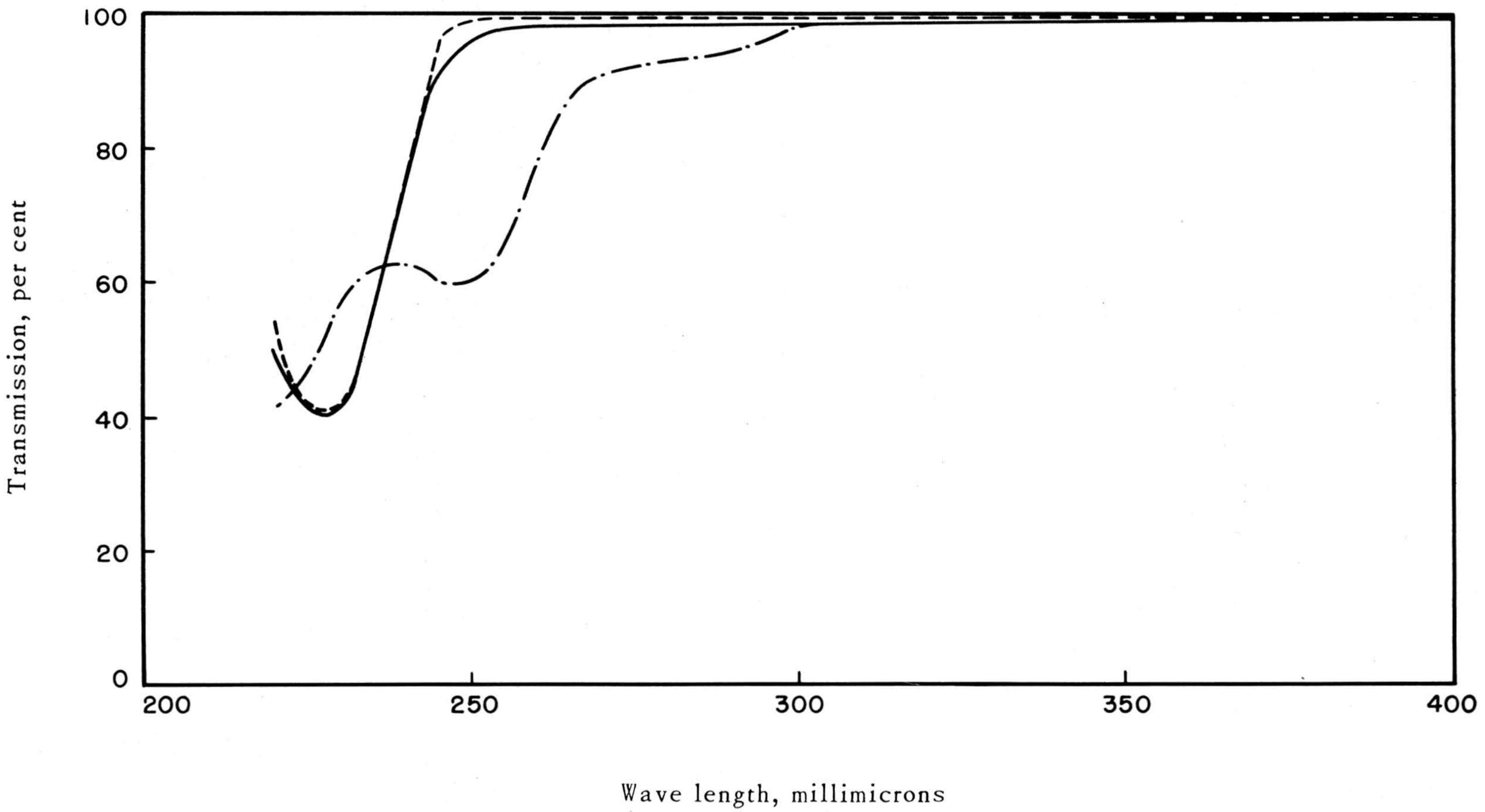

Figure 5.- Ultraviolet absorption spectra of: —, (3,3-difluoro-2,4-dioxocyclobutyl)-triethylammonium betaine, c = 1.69 x 10^{-5} moles/liter; ----, (3,3-difluoro-2,4-dioxocyclobutyl) diethylmethylammonium betaine, c = 1.98 x 10^{-5} moles/liter; — . —, (2,4-dioxo-3,3-diphenylcyclobutyl) triethylammonium betaine, c = 2.19 x 10^{-5} moles/liter.

CHAPTER IV

CONCLUSIONS

From the results of this investigation it would appear that the four-membered ring, which is remarkably stable in compounds of the polyfluoro type, is also stable in compounds which contain less than 20 per cent fluorine. The compounds of the betaine structure produced in this work were very stable solids and decomposed only above their melting points, which in some cases were above 200°. However, the resonance which is postulated may increase the stability above that which would normally be expected. The stability is of a chemical as well as thermal nature. This is especially true of those betaines containing a relatively large trialkylammonium grouping, as, for example, (3,3-difluoro-2,4-dioxocyclobutyl)triethylammonium betaine.

A trialkylammonium group in the 1 position greatly enhances the reactivity of a fluorine atom attached to the 2 position of the cyclobutene ring. In previous work[1], it had been found that 1-diethylamino-2,3,3,4,4-pentafluorocyclobutene was quite stable to reactions which would normally affect the fluorine, such as hydrolysis and alcoholysis. In this investigation it was found that in compounds of the type trialkyl(2,3,3,4,4-pentafluorocyclobutenyl)ammonium fluoride, especially in the case where the alkyl groups were small, hydrol-

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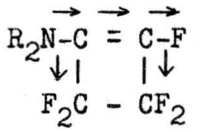
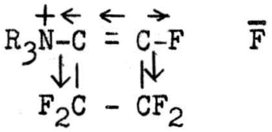
(1) Pruett, R. L., Barr, J. T., Rapp, K. E., Bahner, C. T., Gibson, J. D. and Lafferty, R. H., Jr., *J. Am. Chem. Soc.*, *72*, 3646 (1950).

ysis and alcoholysis occurred readily. The explanation for this may be found in the following electronic interpretation:





The arrows represent the direction of electron drift. The difference between the electron donor character of the dialkylamino groups and the electron attracting character of the trialkylammonium groups makes a large difference in the electrophilic nature of the double-bonded carbon carrying the fluorine. This difference in electrophilic nature would account for the difference in reactivity with anionic reagents.

The reactivity of polyfluoroolefins with tertiary amines is associated in some manner with the presence of the ring. This is proved by the fact that octafluorobutene-2 failed to react with tertiary amines.

The reactivity of tertiary amines with hexafluorocyclobutene is greatly influenced by the size of the alkyl groups present in the amine. It was found that tri-n-butylamine reacted much slower than did trimethylamine. This phenomenon is assumed to be the result of steric hindrance.

CHAPTER V

SUMMARY

Aliphatic tertiary amines, particularly those which contain small alkyl groups, have been found to react readily at room temperature with hexafluorocyclobutene. The initial quaternary salts obtained were very reactive toward water, alcohols and primary or secondary amines. Hydrolysis gave a series of stable compounds which, on the basis of chemical degradation, method of preparation and spectral data, are thought to be trialkyl(3,3-difluoro-2,4-dioxocyclobutyl)ammonium betaines.

The betaines which contain small alkyl groups were found to react with dilute hydrochloric acid, producing trialkyl(3,3-difluoro-2-oxopropyl)ammonium chloride monohydrates. Four of these salts were prepared, together with various derivatives.

Reactions of tertiary amines with the monoalkoxy-, monoaryloxy- and monothioalkyl-2,3,3,4,4-pentafluorocyclobutenes produced trialkylmethylammonium fluorides, which were isolated as the picrates.

Octafluorobutene-2 failed to react with tertiary amines.

The fluorine atoms in (3,3-difluoro-2,4-dioxocyclobutyl)triethylammonium betaine were replaced by phenyl groups when this compound was treated with benzene in the presence of anhydrous aluminum chloride.

The trialkyl(3,3-difluoro-2,4-dioxocyclobutyl)ammonium betaines reacted with bromine in methanol solution to produce trialkyldibromomethylammonium bromides. When (3,3-difluoro-2,4-dioxocyclobutyl)trimethylammonium betaine was treated with bromine in aqueous solution, dibromomethyltrimethylammonium tribromide was produced. This was converted to the bromide by acetone.

(3,3-Difluoro-2,4-dioxocyclobutyl)trimethylammonium betaine formed a complex with sodium iodide and iodine, consisting of three moles of betaine to one mole of NaI_3.

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PART B

CHAPTER I

HISTORICAL

A general discussion of the work which has been done on the reactions of polyfluoroolefins with various reagents may be found in Part A, Chapter I of this paper.

The discovery of the reaction of triethylamine with hexafluorocyclobutene led to an investigation of the reactions of other types of tertiary amines with hexafluorocyclobutene[1]. Pyridine was mixed with hexafluorocyclobutene. Although the two substances were not miscible, a reaction occurred when the two substances were allowed to stand together overnight. However, this reaction was found to be entirely different than that of triethylamine with the butene. A black liquid mixture was produced which, when distilled at reduced pressure, was found to consist of two liquid layers. The upper layer was mostly pyridine, while the lower layer was a mobile liquid having a low refractive index and high density, a fact which indicated a fluorocarbon. This liquid gave a distillation curve characteristic of a single compound. Analysis proved that the compound consisted of only carbon and fluorine, and gave an empirical formula $(C_4F_6)_x$. A molecular weight determination by the vapor density method gave a value of 476 (calculated for $C_{12}F_{18}$: 486). Thus it appeared that trimerization of the butene had occurred in the presence of pyridine. No other compound was isolated from the reaction mixture.

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(1) Pruett, R. L., Unpublished Work.

Isoquinoline has been found to react easily with hexafluorocyclobutene. The product obtained was a tarry solid from which a small amount of crystalline material was isolated. No empirical formula was obtained from the analysis.

CHAPTER II

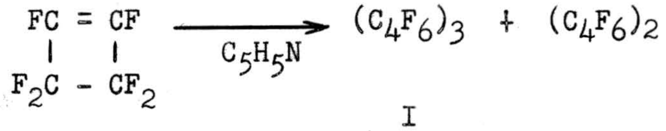
DISCUSSION

Aromatic tertiary amines* might be expected to react differently from aliphatic tertiary amines due to either or both of two reasons: (a) the resonance possible because of the aromatic character of the amine, (b) the decreased basicity of the aromatic amine.

The first reaction investigated was that of pyridine with hexafluorocyclobutene. When allowed to stand together overnight, the two compounds did react. The initial product obtained was a black liquid mixture. This mixture was separated into the following components: recovered pyridine, a tar, and a mobile liquid of high density and low refractive index. This liquid analyzed for the molecular formula $(C_4F_6)_x$ and a molecular weight determination showed that the compound was a trimer of hexafluorocyclobutene.

This trimer was the only compound isolated, other than pyridine, when the ratio of pyridine to butene was comparatively high (approximately 1:1 molar). When only a small amount of pyridine was used, the product was a mixture of recovered pyridine, recovered butene, trimer and also a small amount of a mixture of dimers. In all cases separation was difficult due to the formation of black tars.

The overall reaction may be written as:



$$\begin{array}{c} FC = CF \\ | \qquad | \\ F_2C - CF_2 \end{array} \xrightarrow[C_5H_5N]{} (C_4F_6)_3 + (C_4F_6)_2$$

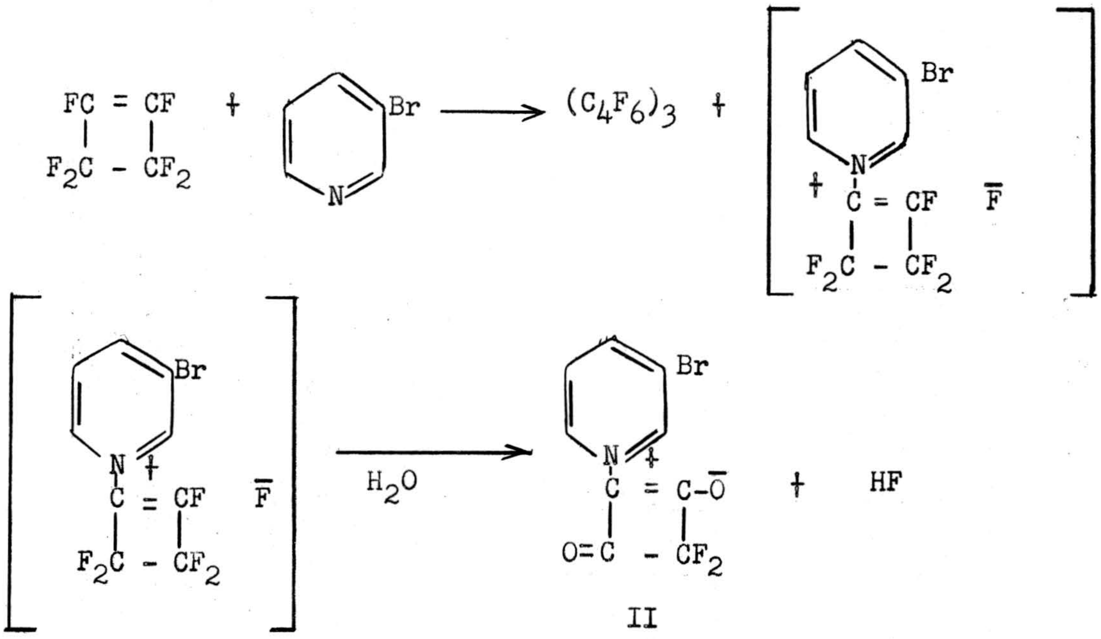
I

---

*In this paper, the term aromatic tertiary amines refers only to aromatic heterocyclic amines.

2-Chloropyridine failed to react with this butene when shaken with it on a mechanical shaker for ten days at room temperature. This may have been due either to the deactivating influence of the chlorine or to the steric hindrance of the chlorine in the 2-position. 2-Methylpyridine reacted vigorously with the butene but the tar formation was so great that no product was identified. 2,2'-Dipyridyl failed to react.

3-Bromopyridine also produced the trimer, but in this case the tar formation was not so great and another product was isolated. This product, a solid, was obtained after treatment with dilute hydrochloric acid and appeared to be a betaine[1]. The probable reaction is:



II

Ethyl nicotinate produced trimer, some dimers, and a solid product. Analysis of this solid gave the formula $C_{16}H_9NO_2F_{12}$, which is

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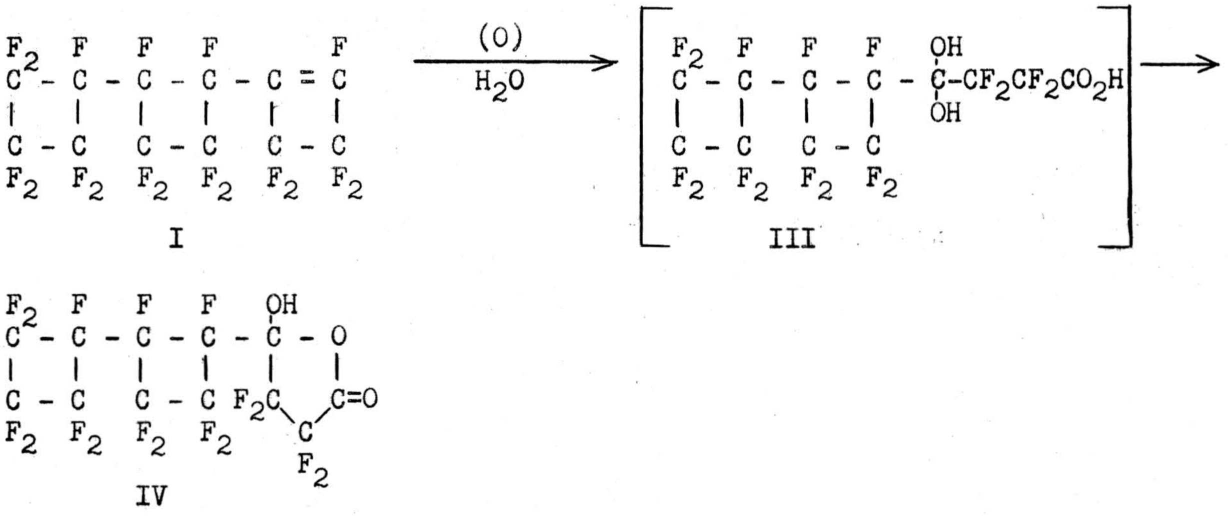
(1) See Part A.

the formula obtained by the addition of ethyl nicotinate to the dimer of hexafluorocyclobutene. Ethyl isonicotinate gave a compound having this same empirical formula as the major product; only a small amount of the trimer was produced and no dimer.

Oxidation of the trimer gave a liquid of composition $C_{12}F_{17}O_3H$. This liquid was soluble in cold sodium hydroxide solution, and slowly soluble in sodium bicarbonate solution. A compound having these properties could be produced if the double bond in the trimer were located on a carbon still carrying a fluorine atom.

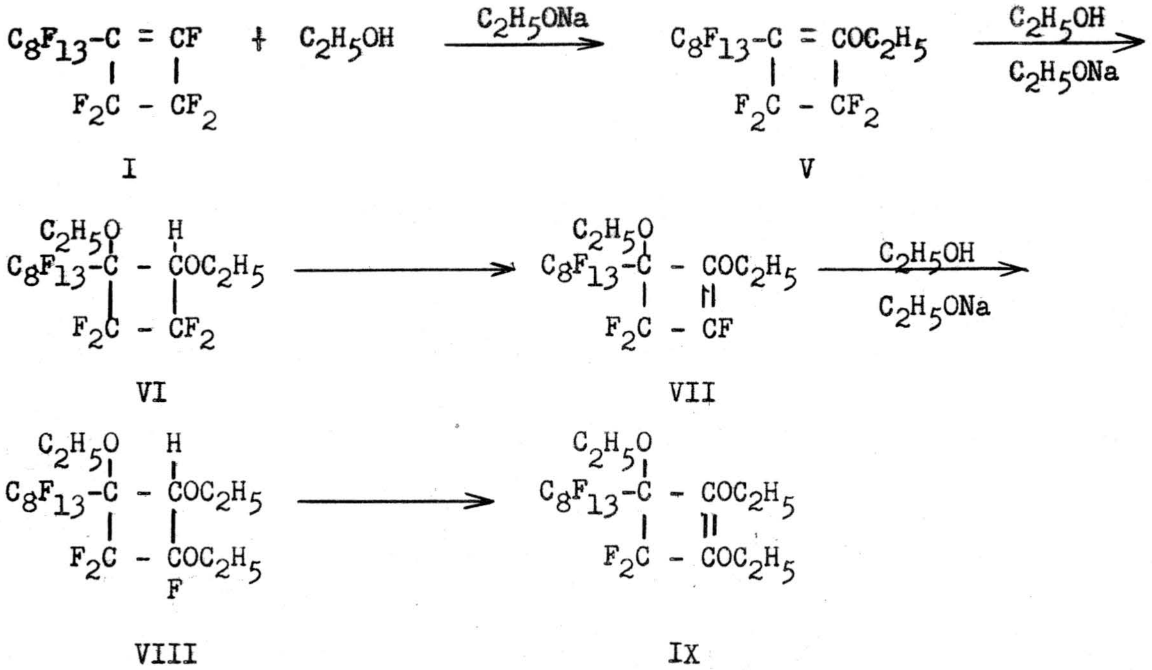


I

III

IV

Additional evidence for this structure of the trimer has been found. When the trimer was treated with a boiling solution of sodium ethoxide in ethanol, a product of composition $C_{18}H_{15}O_3F_{15}$ resulted. This is consistent with the following reaction, which would be expected if the double bond were on a carbon still carrying a fluorine atom.



The addition mechanism, as has been proposed[2,3,4,5], would account for this type of reaction.

A mechanism has been formulated which will account for all the products which have been obtained and for the structure of the dimer as given above. This mechanism consists of three steps which are outlined below, ethyl isonicotinate being used as the amine.

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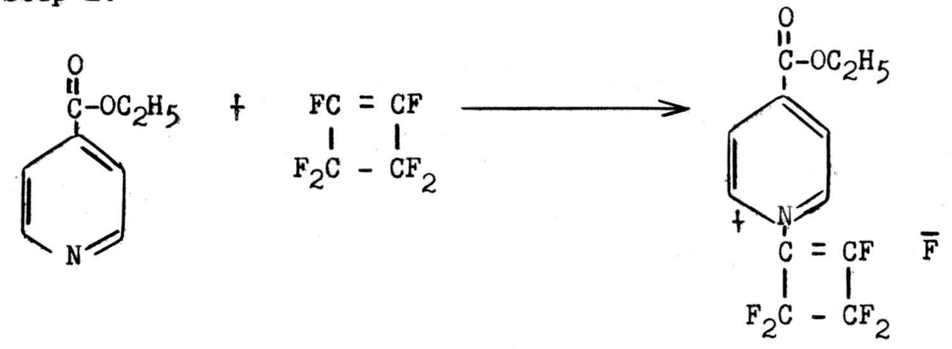
(2) Rapp, K. E., Pruett, R. L., Barr, J. T., Bahner, C. T., Gibson, J. D. and Lafferty, R. H., Jr., J. Am. Chem. Soc., 72, 3642 (1950).

(3) Pruett, R. L., Barr, J. T., Rapp, K. E., Bahner, C. T., Gibson, J. D. and Lafferty, R. H., Jr., ibid., 72, 3646 (1950).

(4) Barr, J. T., Rapp, K. E., Pruett, R. L., Bahner, C. T., Gibson, J. D. and Lafferty, R. H., Jr., ibid., 72, 4480 (1950.

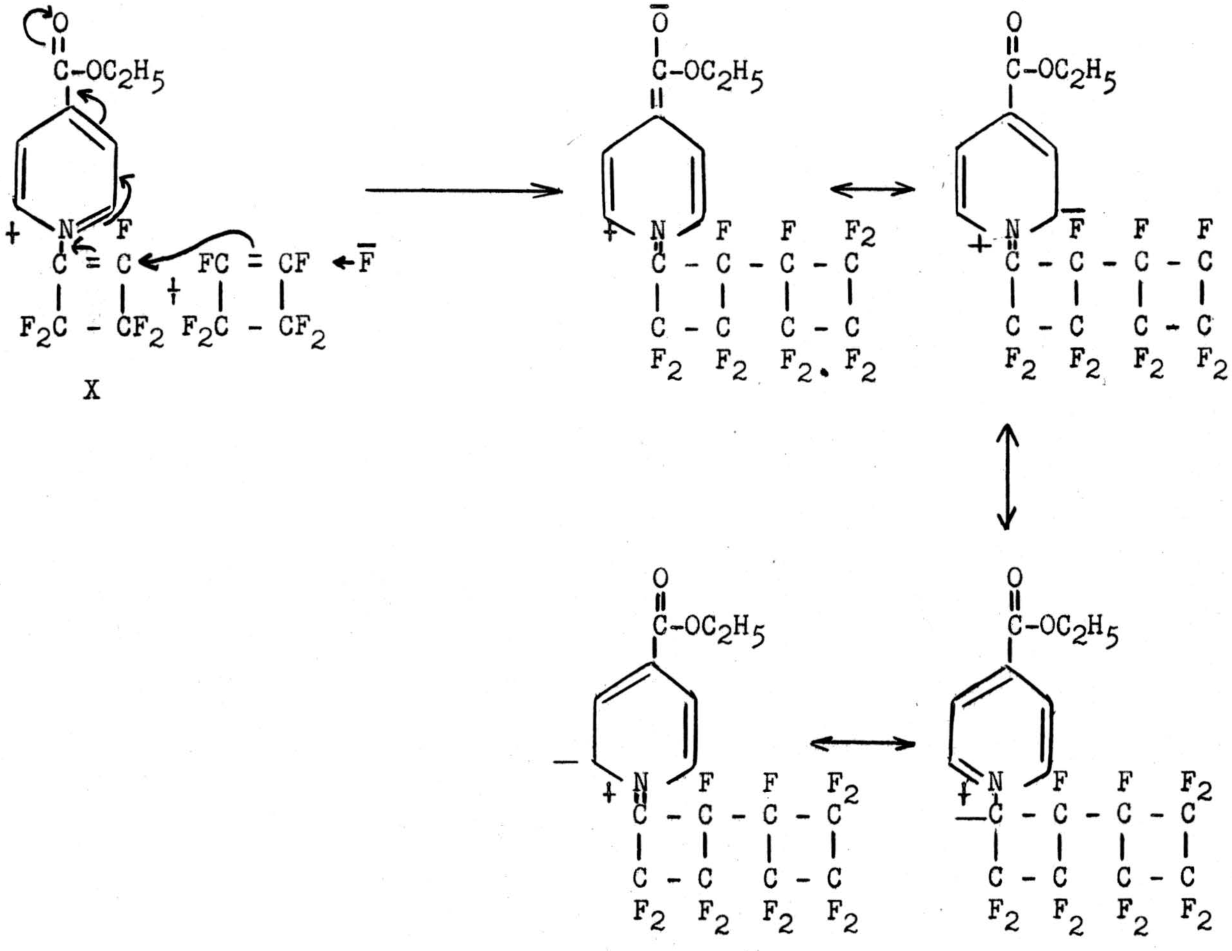
(5) Part A, Chapter I, p. 5.

Step 1.



X

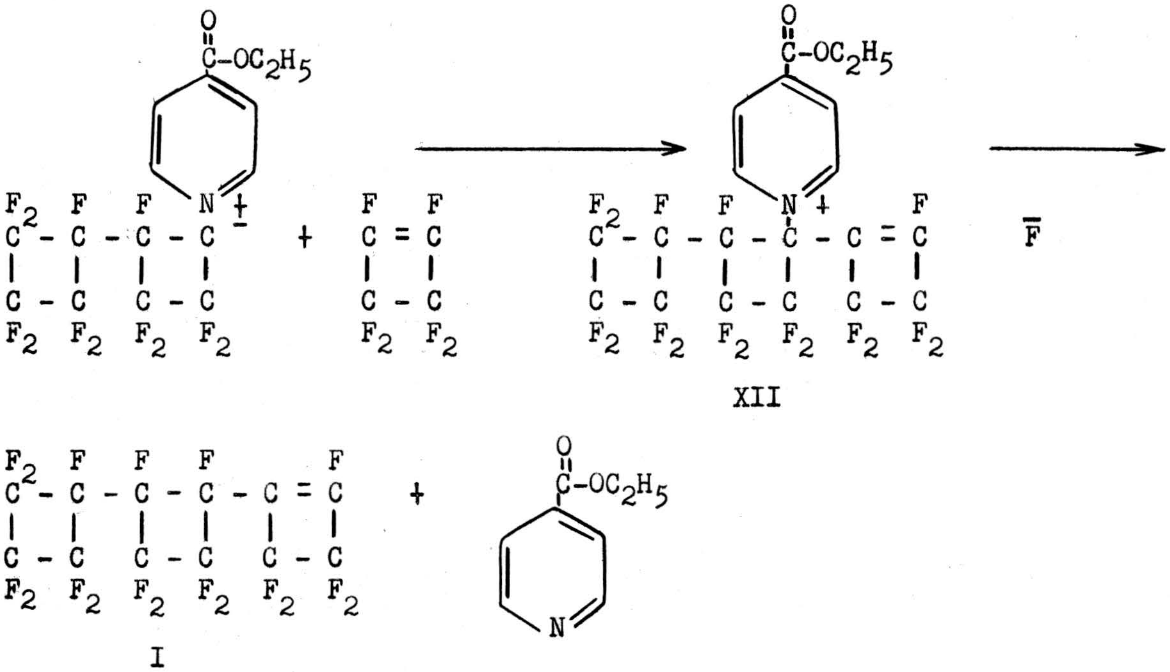
Step 2.



X

XI

Step 3.

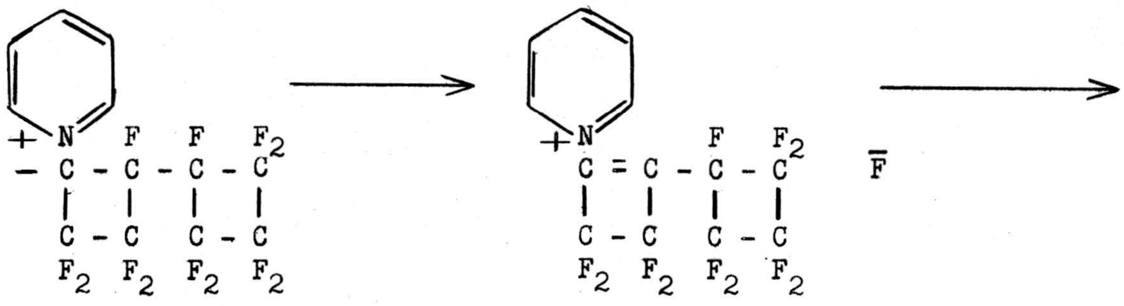


XII

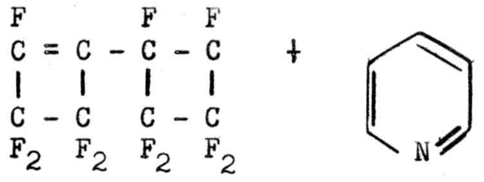
I

When pyridine was used as the amine, a similar resonance structure for the compound produced in step 2 (XI) would place the negative charge on the number four carbon atom in the pyridine ring rather than on the oxygen.

A side reaction involving the product of step 2 would account for the formation of dimer. For example, using pyridine rather than ethyl isonicotinate:



XIII



XIV

Evidence has been obtained for each step in the above mechanism. (3,3-Difluoro-2,4-dioxocyclobutyl)-3-bromopyridinium betaine (II), obtained from the reaction of 3-bromopyridine with hexafluorocyclobutene, must result from hydrolysis of the intermediate quaternary fluoride. The product of step 2 (XI) was isolated when the amine was either ethyl nicotinate or ethyl isonicotinate. The product of step 3, the trimer (I), was isolated in every case in which a pyridine derivative was used as the amine, except where no reaction at all occurred or where only a tar was formed.

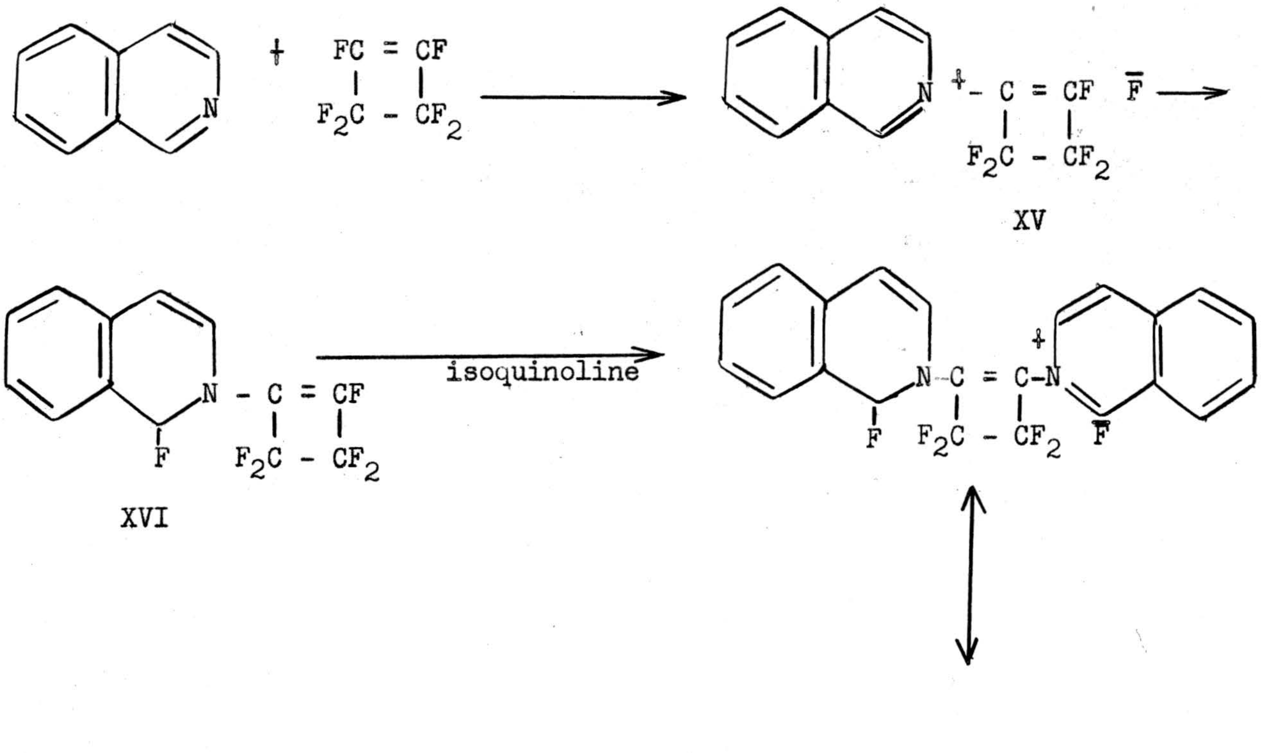
Qualitative predictions concerning the relative resonance ability agree with the findings. Ethyl isonicotinate was the only amine from which the product of step 2 was isolated in good yields. This was also the only amine used which contained an electron-accepting group in the two or four position of the pyridine ring. It appears that resonance is necessary for both the formation and the stabilization of this type of compound.

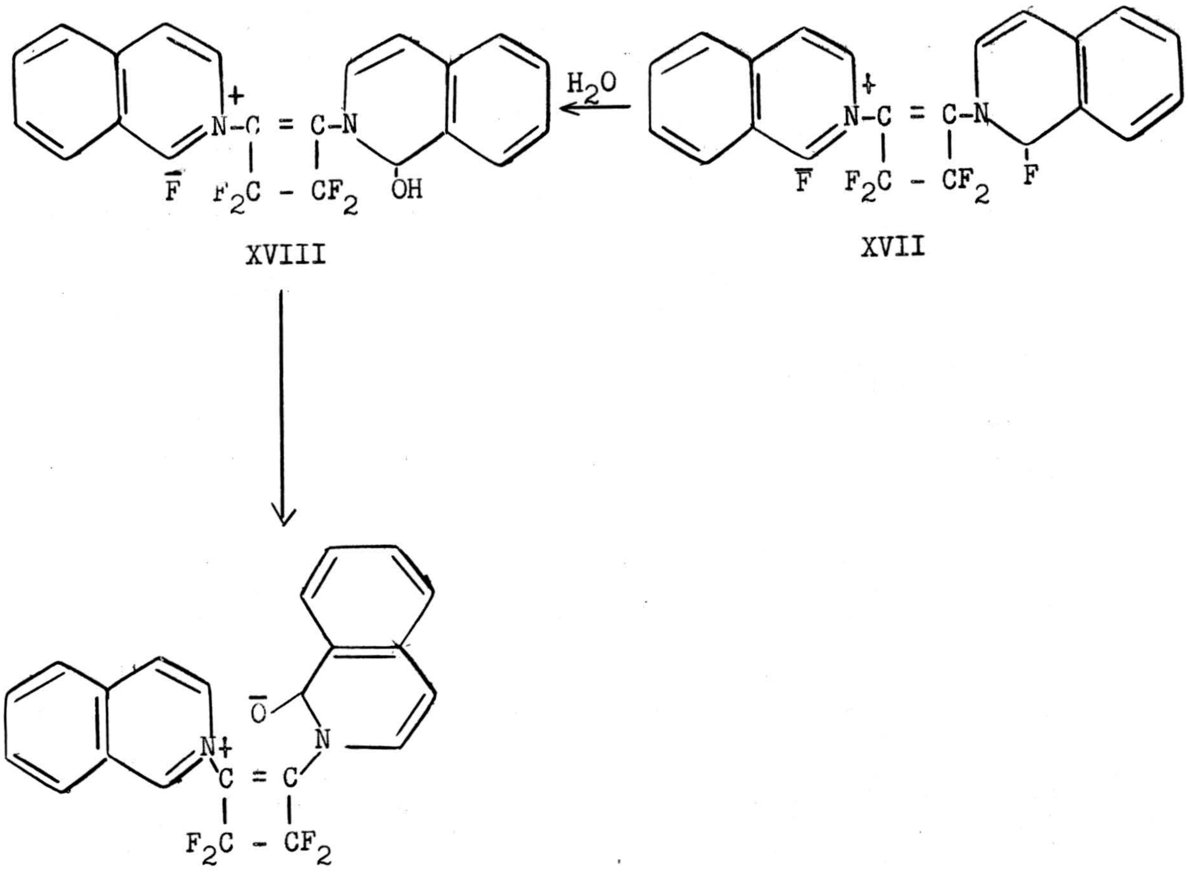
Isoquinoline and its derivatives produced several different types of products. Quinoline did not react with the butene appreciably, except with the application of heat.

3-Methylisoquinoline reacted slowly with hexafluorocyclobutene to give, in short periods of time, a compound which hydrolyzed to give the betaine structure. With longer periods of time this compound was also produced, but the major product was a solid which could not be purified.

Isoquinoline reacted easily with hexafluorocyclobutene in ether solution. Two products were isolated from the reaction mixture. One of these proved to be 2-[2-(heptafluorocyclobutyl)-2,3,3,4,4-pentafluorocyclobutyl]isoquinolinium carbeniate, an analog of the type of product which was isolated in the cases of ethyl nicotinate and ethyl isonicotinate. The other was isolated after hydrolysis, and analysis and molecular weight determinations indicated the formula $C_{22}H_{14}N_2OF_4$. The exact structure of this product has not been determined. There are several ways that a compound of this formula could be produced; these are outlined below.

Method 1.



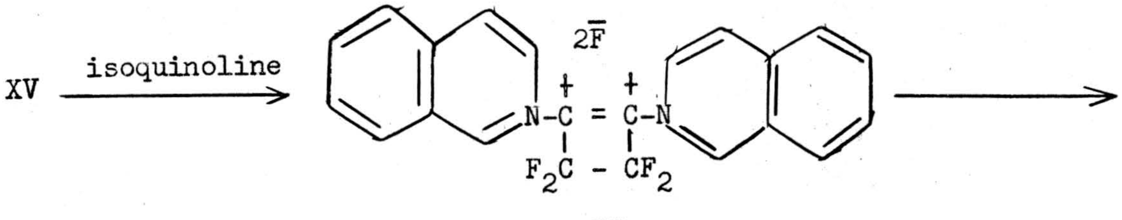


XVIII

XVII

XIX

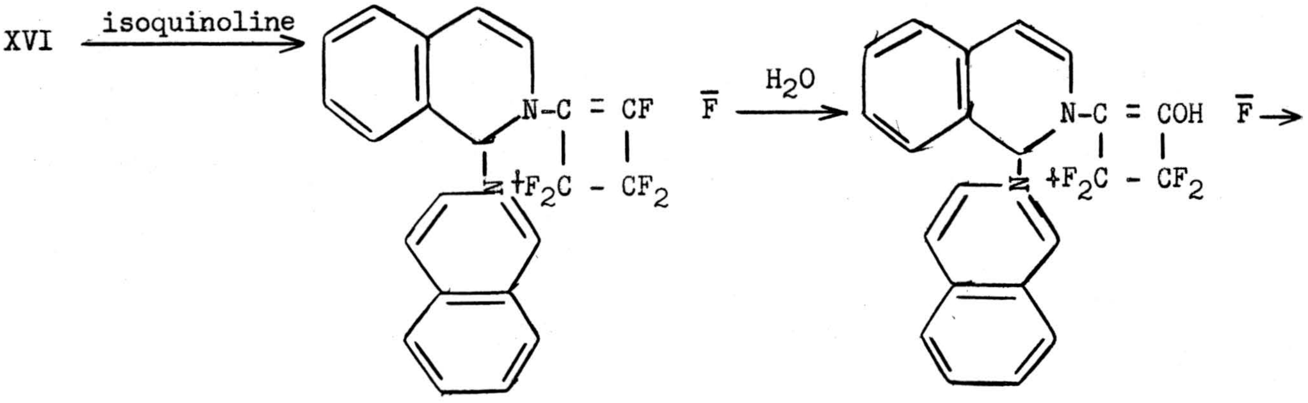
Method 2.



XX

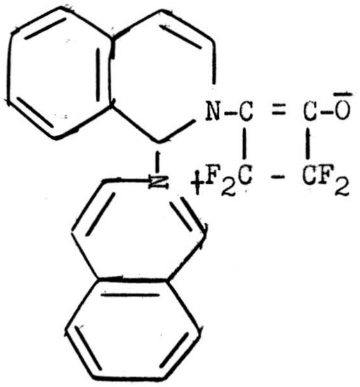
$$\text{XVII} \xrightarrow{H_2O} \text{XVIII} \longrightarrow \text{XIX}$$

Method 3.



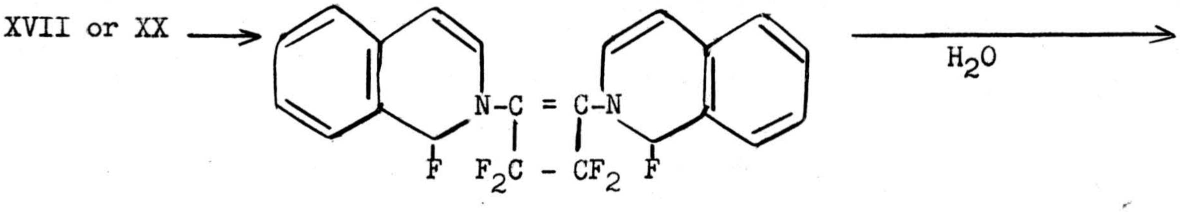
XXI

XXII

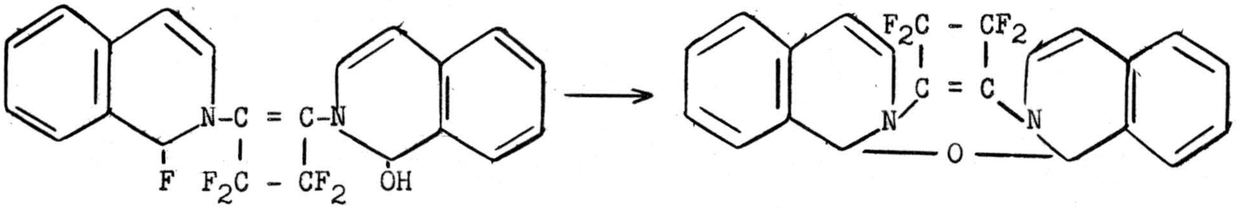


XXIII

Method 4.



XXIV



XXV XXVI

There are several objections which may be raised for each of the proposed mechanisms. In method 1, the reaction of XVI with isoquinoline to produce XVII may be questioned. In previous work[6], it was found that (2,3,3,4,4-pentafluorocyclobutenyl)diethylamine did not react with amines, alcohol or water. However, the difference between the alkyl groups and the aromatic group may be sufficient to allow the reaction to proceed as indicated.

In method 2, it is difficult to see why the shift of the fluorine atom to the number one position of the isoquinoline ring would not occur when only one ring is attached, if it does occur later when two rings are attached. It is probably true that the shift, if it occurs, would be an equilibrium process with only a small amount of the fluorine attached covalently to the number one carbon atom. If this reasoning is true, then method 2 may actually apply.

In method 3, the reaction of XXI with water to give XXII probably would not take place, as the former compound also contains a tertiary nitrogen in the beta position to the fluorine atom.

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(6) Pruett, R. L., Barr, J. T., Rapp, K. E., Bahner, C. T., Gibson, J. D. and Lafferty, R. H., Jr., J. Am. Chem. Soc., 72, 3646 (1950).

In method 4, the existence of a seven-membered ring in compound XXVI makes this mechanism somewhat unlikely.

The final product reacted easily with acidic substances. With concentrated hydrobromic acid, it formed (2-bromo-3,3,4,4-tetrafluorocyclobutenyl isoquinolinium bromide. This bromide hydrolyzed easily in boiling water to produce (3,3-difluoro-2,4-dioxocyclobutyl)isoquinolinium)betaine. With concentrated hydrochloric acid, the intermediate chloride could not be isolated, probably due to its greater reactivity with water.

The ultraviolet spectra of each type of compound containing nitrogen was obtained in the region 220-400 mμ. The absorption in the region of 230 mμ cannot be taken as an indication of the betaine structure in the cases where an isoquinoline ring was present, since this ring itself would be expected to absorb at this wave length[7]. This was confirmed by measuring the absorption of isoquinoline ethiodide, which was found to absorb at this wave length.

Isoquinoline and pyridine were found to react readily with 1-chloropentafluorocyclobutene, but in neither case was the product successfully purified.

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(7) Braude, E. A., <u>Ann</u>. <u>Repts</u>. <u>Progress</u> <u>Chem</u>., <u>42</u>, 105 (1945).

CHAPTER III

EXPERIMENTAL

A. Materials

1. Aromatic Amines

All the aromatic amines, with the exception of pyridine and ethyl isonicotinate, were obtained from Eastman Kodak Company. Pyridine was obtained from the Fisher Scientific Company. All these commercial amines were used without further purification.

Ethyl isonicotinate was prepared by the method of Gilman and Broadbent[1]. A three-necked flask was fitted with a mechanical stirrer and a thermometer. In this, two and one-half liters of water was heated by means of a water bath to a temperature of 70°. Two hundred and ten grams of 4-methylpyridine was added, then 700 g. of potassium permanganate in ten portions over a period of three hours. The temperature was maintained in the range 65-75°. After all the permanganate had been added, the temperature was raised to 90° and maintained at this temperature for one hour, after which all the permanganate had been reduced. The mixture was filtered while hot and the precipitate was washed with one liter of hot water. The combined filtrates were cooled and acidifed to a pH of approximately 4. This produced a heavy white precipitate which was removed by filtration and air-dried. The oxidation of 1 kg. of amine in this manner produced 714 g. (54 per cent) of isonicotinic acid.

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(1) Gilman, H. and Broadbent, H. S., J. Am. Chem. Soc., 70, 2755 (1948).

One hundred and forty grams of isonicotinic acid was suspended in 950 ml. of absolute ethanol. While this mixture was stirred and cooled in an ice bath, dry hydrogen chloride was introduced. The temperature was maintained below 25° during this operation. After three hours the alcohol was saturated at 10°. The bath was then removed and heat applied. The solution was refluxed for four hours, during which time the solid dissolved. The major part of the alcohol and hydrogen chloride was then removed by distillation at 30-50° under reduced pressure. The residue was cooled and dissolved in water. A saturated sodium carbonate solution was added until the solution became basic; this resulted in the formation of two layers. The upper layer was separated and the water layer was extracted with three successive 100 ml. portions of ether. The upper layer and the combined extracts were distilled at atmospheric pressure until the excess solvents were removed, then the pressure was reduced. The ester distilled at 111° at 23 mm. The total yield was 141 g. (82 per cent).

2. Polyfluoroolefins

The preparations of all the olefins used in this investigation have been described in Part A, Chapter III, Section A.

B. Reactions of Pyridine and Its Derivatives with Hexafluorocyclobutene

1. Pyridine[2]

Eighty milliliters of pyridine was placed in a stainless-steel reaction vessel and the vessel and contents were cooled in liquid nitrogen.

After evacuation, 127 g. of hexafluorocyclobutene was added by gaseous transfer. The mixture was warmed to 0° and then allowed to stand at this temperature for eighteen hours.

The vessel was opened and the black liquid product was distilled at 40° and 1 mm. pressure until no more liquid distilled. For this operation, Dry Ice was used to cool the receiver and a liquid-nitrogen cold trap was placed in the vacuum line. A small amount of tarry residue remained after the distillation. The distillate separated into two layers and the lower layer was separated, washed once with dilute hydrochloric acid, twice with water, dried over anhydrous sodium carbonate and distilled. The pressure obtained with the use of a water aspirator was used for the distillation and a trap cooled in Dry Ice was placed in the line. The trimer, 1-[2-(heptafluorocyclobutyl)hexafluorocyclobutyl]-2,3,3,4,4-pentafluorocyclobutene (I), distilled at 51-52° at 17 mm. pressure; the yield was 36 per cent of the theoretical. No dimer was obtained in this reaction. The purified trimer had the following physical properties: n_D^{25} 1.3246, d_4^{25} 1.7767. From these physical data, the atomic refraction of fluorine was found to be 1.21.

<u>Anal</u>. Calcd. for $C_{12}F_{18}$: C, 29.65; M. W., 486. Found: C, 29.48; M. W. (vapor density method), 476.

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(2) The initial work on this reaction was completed prior to the present investigation. See Chapter I.

Another reaction was carried out in which all the conditions were the same as above, except for the quantities of reactants. Ten milliliters of anhydrous pyridine and 137 g. of hexafluorocyclobutene were used. This gave 11 per cent of recovered hexafluorocyclobutene, 50 per cent of trimer and a liquid which collected in the cold trap. This liquid (dimer) distilled at 80-85.5° at atmospheric pressure and represented a 15 per cent yield. The refractive index at 26° was 1.3045.

Anal. Calcd. for C_8F_{12}: C, 29.65. Found: C, 29.42.

2. 2-Chloropyridine

Twenty-four grams of 2-chloropyridine was placed in a thick-walled glass tube. The tube and contents were cooled in liquid nitrogen and 33 g. of hexafluorocyclobutene was added by gaseous transfer. The tube was then sealed, warmed to room temperature and placed on a mechanical shaker.

After shaking for twenty-four days, the tube was opened. All the lower layer distilled below room temperature. The amine layer was completely soluble in dilute hydrochloric acid, a fact which indicated that no reaction had occurred.

3. 2-Methylpyridine

Six milliliters of 2-methylpyridine was placed in a glass tube. The tube was cooled in liquid nitrogen and 37 g. of hexafluorocyclobutene was added. The tube was then sealed and warmed to room temperature. Immediately upon reaching room temperature the contents of the tube became black.

After standing for five days, the tube was opened. After the unreacted butene had escaped, there remained only a black tar, from which no products were isolated.

4. 2,2'-Dipyridyl

One gram of 2,2'-dipyridyl was dissolved in 15 ml. of absolute ether and the resulting solution was placed in a glass tube. The tube and contents were cooled in liquid nitrogen and 6 g. of hexafluorocyclobutene was added, after which the tube was sealed. The resulting solution was heated to 60° in an oven and maintained at that temperature for five days.

The solution was still clear and colorless. The tube was cooled, opened, and the ether solution was evaporated to dryness. This produced 1.0 g. of solid, m. p. 60-63°. Recrystallization from n-heptane gave a melting point of 68-69° (Lange[3] gives 69.5° for 2,2'-dipyridyl).

5. 3-Bromopyridine

Fifty-two grams of 3-bromopyridine was placed in a glass tube and the tube and contents were cooled in liquid nitrogen. Thirty-nine grams of hexafluorocyclobutene was added, the tube sealed, and then shaken on a mechanical shaker at room temperature for ten days.

The product was a black liquid mixture consisting of two layers. The lower layer was separated, washed with dilute hydrochloric acid and

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(3) Lange, N. A., "Handbook of Chemistry," 5th Ed., Handbook Publishers, Inc., Sandusky, Ohio, 1944, p. 465.

then washed with water. After drying over anhydrous sodium carbonate, it was distilled at reduced pressure. The yield was 12 g. (31 per cent) of trimer.

The upper layer from the original reaction mixture was mixed with dilute hydrochloric acid. The liquid dissolved after which a brown solid began to separate. After cooling thoroughly, the mixture was filtered. The dried brown solid weighed 8.8 g. and melted at 195-205° dec. The yield of this crude (3,3-difluoro-2,4-dioxocyclobutyl)-3-bromopyridinium betaine (II) was 13 per cent.

The following purification procedure was used. The brown solid was dissolved in acetone and the solution was boiled with activated charcoal for a few minutes. The mixture was filtered to remove the bulk of the charcoal and the filtrate was centrifuged to remove the last traces of this contaminant. The acetone solution was then diluted with n-heptane and evaporated nearly to dryness. The resulting mixture was filtered to remove the white crystals. These were recrystallized twice by dissolving in acetone, adding an equal volume of absolute ethanol, and cooling to -78° in a Dry Ice-trichloroethylene bath. The final product was snow-white and melted at 223-224°.

Anal. Calcd. for $C_9H_4NO_2F_2Br$: C, 39.16; H, 1.46; N, 5.09; Br, 28.95; F, 13.77. Found: C, 38.72; H, 1.66; N, 4.69; Br, 28.20; F, 13.77.

In another experiment 12 g. of 3-bromopyridine and 45 g. of the butene were shaken together for twelve days. This produced only a small amount of trimer and 3.0 g. of the crude betaine.

6. Ethyl Nicotinate

Ten grams of ethyl nicotinate and 42 g. of hexafluorocyclobutene were shaken together in a sealed tube for ten days. The product was distilled at 60° and 1 mm. until no more liquid distilled. For this operation a Dry Ice-cooled receiver was used, together with a cold trap cooled by liquid nitrogen. The cold trap contained 7 g. (17 per cent) of recovered hexafluorocyclobutene. Redistillation at 12 mm. gave 14.5 g. (35 per cent) of trimer and less than 2 per cent dimer.

The dark residue from the original distillation was shaken with 1:1 hydrochloric acid solution. This gave a black lower layer which slowly solidified. This lower layer was shaken with dilute sodium hydroxide and then washed with water. The yield of crude product, which slowly melted above 50°, was 9.5 g. This was recrystallized by dissolving in acetone at room temperature and cooling to -78°. The product obtained by this method was slightly yellow and melted at 71-74°. Another recrystallization by the same method gave a melting point of 76-78°. The yellow solid was then sublimed at 70° and 0.06 mm., but the melting point was not changed.

Anal. Calcd. for $C_{16}H_9NO_2F_{12}$: C, 40.43; H, 1.91; N, 2.95. Found: C, 40.54; H, 2.06; N, 3.14.

7. Ethyl Isonicotinate

Thirty-two grams of hexafluorocyclobutene and 21.5 g. of ethyl isonicotinate were shaken together for ten days. The product was distilled at 65° and 1 mm. until no more liquid distilled. The receiver was cooled in Dry Ice and a liquid nitrogen-cooled cold trap was used in the vacuum line. No hexafluorocyclobutene collected in the trap. A small amount of liquid collected in the receiver which, after redistillation, gave 2 g. (6 per cent) of trimer and 2 g. (6 per cent) of dimer.

The black residue from the original distillation was washed once with 1:1 hydrochloric acid solution and once with water, after which there remained 22 ml. of a very viscous liquid which weighed 32.7 g. Six milliliters of this black liquid was dissolved in about 20 ml. of dry ether. After decantation from the few black particles, the ether solution was cooled to -78°. After about two hours, a brown precipitate separated. The mixture was filtered; the dried solid weighed 5.0 g. and melted at 54-56°. This 5.0 g. of 1-[2-(heptafluorocyclobutyl)-2,3,3,4,4-pentafluorocyclobutyl]-4-carbethoxypyridinium carbeniate (XI) is equivalent to a 39 per cent yield based on the hexafluorocyclobutene.

Further recrystallization from ether removed the color from the solid but did not change the melting point. This solid was distilled in a sublimation apparatus at 60° and 0.02 mm., after which the solid still melted at 64-66°.

Anal. Calcd. for $C_{16}H_9NO_2F_{12}$: C, 40.43; H, 1.91; N, 2.95. Found: C, 40.34; H, 1.88; N, 3.08.

C. Reaction of Isoquinoline with Hexafluorocyclobutene

1. Compound $C_{22}H_{14}N_2OF_4$ (XIX, XXIII or XXVI)[4]

Forty-one grams of isoquinoline was dissolved in 300 ml. of absolute ether and the solution was placed in a stainless-steel reaction vessel. The vessel and contents were cooled in liquid nitrogen and 37 g. of hexafluorocyclobutene was added by distillation. After all the butene had been added, the vessel was closed and allowed to warm to room temperature.

After standing at room temperature for forty hours, the reactor was opened. The ether solution was mixed with about 200 ml. of water and, after the reaction had subsided, the water layer was separated. The ether layer was evaporated nearly to dryness and the residue was mixed with methanol and the mixture filtered. This produced 37 g. of solid, m. p. 158-161° dec. The yield was 59 per cent calculated from isoquinoline or 41 per cent calculated from the butene. Purification by recrystallization from chloroform gave a final melting point of 168-169° dec.

<u>Anal</u>. Calcd. for $C_{22}H_{14}N_2OF_4$: C, 66.16; H, 3.53; N, 7.02, F, 19.0, M. W. 398. Found: C, 65.82, 65.88, 65.93; H, 3.70, 3.59, 3.58; N, 7.05, 6.59, 6.32; F, 17.4, 17.6, 18.8; M. W., 397, 433[5].

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(4) The isolation and purification of this compound was accomplished prior to the present investigation. See Chapter I.

(5) This molecular weight was obtained by the boiling point elevation method with the use of a Menzies-Wright apparatus, together with a differential thermometer. Acetone was used as the solvent.

a. (2-Bromo-3,3,4,4-tetrafluorocyclobutenyl)isoquinolinium bromide. Three grams of Compound $C_{22}H_{14}N_2OF_4$ was heated with 10 ml. of 48 per cent hydrobromic acid for five minutes. During that time the solid dissolved; then a precipitate formed. The mixture was cooled and filtered. This produced 2.7 g. of an orange-yellow solid, dec. 176-178°. The yield was 87 per cent of the theoretical. Purification was accomplished by recrystallization from glacial acetic acid. Two recrystallizations from this solvent gave golden-yellow crystals, dec. 176-178°.

Anal. Calcd. for $C_{13}H_7NF_4Br_2$: C, 37.80; H, 1.71; N, 3.39; F, 18.4. Found: C, 38.09; H, 1.94; N, 3.40; F, 18.5.

b. (3,3,4,4-Tetrafluoro-2-iodocyclobutenyl)isoquinolinium iodide. Three grams of compound $C_{22}H_{14}N_2OF_4$ was heated for five minutes at 90° with 10 ml. of 57 per cent hydriodic acid. During this time the crystal form appeared to change and the mixture became blood red. It was cooled and filtered, and the resulting crystals were dried. The red crystals thus obtained weighed 3.5 g. (92 per cent) and melted at 145-148° with decomposition. No method was found for further purification of this solid due to its tendency to decompose in solution.

c. (3,3-Difluoro-2,4-dioxocyclobutyl)isoquinolinium betaine. Twenty-one grams of (3,3,4,4-tetrafluoro-2-bromocyclobutenyl)isoquinolinium bromide was dissolved in 35 ml. of boiling glacial acetic acid. This solution was added with stirring to 200 ml. of boiling water. After heating the mixture for one minute, excess ice was added. The cooled mixture was allowed to stand for one-half hour and then the water solution was decanted from the lower layer of semi-solid. The residue was macerated with methanol and the mixture was filtered. Recrystallization of this solid from methanol gave 4.5 g. (36 per cent) of (3,3-difluoro-2,4-dioxocyclobutyl)isoquinolinium betaine, m. p. 248-249° dec.

Anal. Calcd. for $C_{13}H_7NO_2F_2$: C, 63.16; H, 2.85; N, 5.67. Found: C, 63.67; H, 3.02; N, 5.77.

This betaine could also be produced directly from the original $C_{22}H_{14}N_2OF_4$ by the use of hydrochloric acid. Sixteen grams of this original compound was dissolved in 40 ml. of boiling concentrated hydrochloric acid. Eighty milliliters of boiling water was then added and the resulting solution was boiled for a few minutes. Eighty milliliters of boiling water was again added and the solution boiled for a short time. Cooling caused a yellow solid to separate. This was removed by filtration. The dried solid weighed 4.5 g. (45 per cent) and melted at 240-243° with decomposition. Recrystallization from ethanol raised the melting point to 248-249° dec.

2. 2-/2-(Heptafluorocyclobutyl)-2,3,3,4,4-pentafluorocyclobutyl/-isoquinolinium Carbeniate

Forty-one grams of isoquinoline, 300 ml. of ether and 40 g. of hexafluorocyclobutene were sealed together in a reaction vessel and allowed to stand at room temperature for forty hours. One hundred milliliters of the resulting ether solution was mixed with 50 ml. of methanol. After standing overnight at room temperature, the solution was distilled at room temperature and reduced pressure to a volume of 30 ml. Continued cooling at -78° caused crystals to appear in the concentrate. After filtering the solution and drying the retained crystals, the product weighed 4.0 g. and melted slowly above 60°. The yield of this crude material was 10 per cent calculated from isoquinoline or 24 per cent calculated from hexafluorocyclobutene.

The yellow crystals were purified by dissolving in methanol at room temperature and cooling this solution in a Dry Ice-trichloroethylene bath. Three recrystallizations conducted in this manner gave a snowy-white solid, m. p. 68-69°.

Anal. Calcd. for $C_{17}H_7NF_{12}$: C, 45.04; H, 1.56; N, 3.09. Found: C, 45.23; H, 1.52; N, 3.24.

D. Reaction of 3-Methylisoquinoline with Hexafluorocyclobutene

1. Short Reaction Time

Twenty-eight and six-tenths grams of 3-methylisoquinoline was dissolved in 150 ml. of absolute ether. This solution was placed in a stainless-steel reaction vessel. The vessel and contents were cooled in liquid nitrogen and 40 g. of hexafluorocyclobutene was then added by distillation. The vessel and contents were warmed to room temperature and maintained at this temperature for three days. The ether solution was then shaken with water, separated and evaporated to dryness. The brown solid which was produced by this method was treated with dilute (1:1) hydrochloric acid. The solid dissolved and then reprecipitated. The solution was filtered and the solid was dried, after which it weighed 8.0 g. (15 per cent). This (3,3-difluoro-2,4-dioxocyclobutyl)-3-methylisoquinolinium betaine was purified by recrystallization from absolute ethanol. The final product was yellow and had a decomposition point of 240-243°.

Anal. Calcd. for $C_{14}H_9NO_2F_2$: C, 64.37; H, 3.47; N, 5.36; F, 14.6. Found: C, 64.85; H, 3.48; N, 5.46; F, 15.3.

2. Long Reaction Time

When 40 g. of 3-methylisoquinoline, 85 ml. of ether and 34 g. of hexafluorocyclobutene were allowed to stand together for about one month, the predominant product was a dark solid which was not purified. As before, a small amount of the betaine was isolated.

E. Quinoline with Hexafluorocyclobutene

Thirty-one milliliters of quinoline was dissolved in 300 ml. of ether and the solution was placed in a stainless-steel reaction vessel. The vessel and contents were cooled in liquid nitrogen, evacuated, and 23 g. of hexafluorocyclobutene was added by gaseous transfer. The vessel and contents were then allowed to stand at room temperature for seven days. During this time the gaseous pressure did not decrease.

After this period of time, the vessel was opened. The contents were clear and only slightly colored. The ether solution gave no reaction when shaken with water.

In another experiment, 26 g. of quinoline and 20 g. of the butene were heated together in a sealed tube for eighteen hours at 55°. This produced a black tar which could not be purified.

F. Reactions of Aromatic Amines with Other Olefins

1. Pyridine with 1-Chloropentafluorocyclobutene

When one milliliter of pyridine was added to 10 ml. of 1-chloropentafluorocyclobutene, a purple color immediately appeared and a few crystals formed. An additional 9 ml. of pyridine was added. The mixture became very hot and the color became black. No identifiable product was isolated from the tarry product. This same experiment was repeated with the use of benzene as solvent. This allowed the temperature to be controlled, but again only a tar was obtained.

2. Isoquinoline with 1-Chloropentafluorocyclobutene

A three-necked flask was fitted with a stirrer and a thermometer. In this was placed 150 ml. of benzene and, after cooling to 10°, 10 ml. of 1-chloropentafluorocyclobutene. To this was added 20 ml. of isoquinoline while the mixture was being cooled by an ice bath. This addition caused a sharp temperature rise and in five minutes a precipitate began to form. After thirty minutes the precipitation was complete. The mixture was allowed to warm to room temperature over a period of one and one-half hours. Water was then added and the mixture was shaken. The solid dissolved and the benzene layer turned black. The benzene was separated and set aside to evaporate to dryness.

The benzene residue consisted of a plastic-like solid which started to crystallize when the surface was scratched. It was dissolved in hot ethanol and precipitated by the addition of water. This produced 19 g. of a red-brown solid which melted at 77-85°. The filtrate was heated and more water was added. This gave a second crop of yellow orange crystals which, after filtration and drying, melted at 80-90°. The weight of this second crop was 7 g.

No means was found for purifying this solid to a stage where analysis would be feasible.

G. Reactions of Trimer

1. Oxidation

Thirty-five and one-half grams of the trimer was dissolved in 300 ml. of acetone and the resulting solution was cooled to 5°. A solution of 18 g. of potassium permanganate in 100 ml. of hot water was added in small portions with stirring over a period of one hour. The temperature was maintained in the range 10-20° with the use of an ice bath. After all the permanganate had been added, the mixture was stirred at 10° for one hour, then the ice bath was removed and the mixture was stirred for an additional hour.

The mixture was filtered and the manganese dioxide was washed with acetone and with 50 ml. of water. The combined filtrates were concentrated to about 150 ml. and then acidifed with concentrated hydrochloric acid. After adding sodium bisulfite to destroy the color, the concentrate was extracted with one 100 ml. portion, then two 50 ml. portions of ether. The combined ether extracts were distilled at 15 mm. until most of the ether had been removed. The residue was placed in a Hickman alembic molecular still. The product (IV, 14.5 g., 39 per cent,

n_D^{22} 1.3602) distilled at approximately 50° at 0.05-0.10 mm. Much degassing occurred during the distillation.

The distillate was redistilled in a similar manner, with only a trace of residue remaining. Distillation of the oxidized trimer in a 2-foot Vigreux column gave a constant boiling point of 45.5-46.5° at 0.5-0.7 mm., even though successive fractions had different refractive indices. For fraction 1, n_D^{22} = 1.3332; for fraction 2, n_D^{22} = 1.3418.

Anal. Calcd. for $C_{12}F_{17}O_3H$: C, 27.92; H, 0.20; F, 62.58. Found: (fraction 1) C, 27.48; H, 0.54; F, 61.95; (fraction 2) C, 27.71; H, 0.77; F, 63.43.

2. With Ethanol

Twenty-one grams of trimer was added to a solution which resulted from the addition of 2 g. of sodium to 100 ml. of absolute ethanol. The trimer formed a lower layer. Shaking caused a sharp rise in temperature and the solution became cloudy. An additional 100 ml. of ethanol was added but the trimer still existed as a lower layer. The mixture was heated to reflux temperature, at which point the trimer dissolved. The mixture was refluxed for two hours. After cooling, two volumes of water was added, and the resulting lower layer was separated and washed three times with water. Distillation gave 3 g. (14 per cent) of recovered trimer and a small fraction distilling at 39-42° at 0.4 mm. After this, the temperature rose sharply and the distillation was discontinued. Cooling the residue gave 11 g. of 3-[2-(heptafluorocyclobutyl)hexafluorocyclobutyl]-1,2,3-triethoxy-4,4-difluorocyclobutene (IX)

(67 per cent based on sodium). This material was purified by recrystallization from methanol at -78°. Three recrystallizations by this procedure gave a final melting point of 51.5-52.5°.

Anal. Calcd. for $C_{18}H_{15}O_3F_{15}$: C, 38.31; H, 2.68; F, 50.50. Found: C, 38.64; H, 2.98; F, 50.38.

H. Ultraviolet Absorption Spectra

The ultraviolet absorption spectra of the compounds produced in this investigation were obtained by means of a Beckman Model DU spectrophotometer. A quartz prism and a hydrogen discharge lamp were used. The quartz absorption cells were of 1.000 ± 0.001 mm. length. The samples were dissolved in absolute ethanol and then diluted to the required concentrations. Readings were taken every 5 mμ, except in the regions of maximum absorption, in which case they were taken every 2 mμ. The spectra are recorded in Figures 1, 2 and 3 and the important data are summarized in Table I.

I. Analyses[6]

Carbon, hydrogen and nitrogen were determined by combustion. Halogens, with the exception of fluorine, were determined by the Carius tube method. Fluorine, in the presence of nitrogen, was determined by

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(6) Analyses were performed by Clark Microanalytical Laboratory, Urbana, Illinois; Galbraith Laboratories, Knoxville, Tennessee; and Frances Ball and R. R. Rickard of the Microchemical Group of the Analytical Research Section.

the method of Rickard, Ball and Harris[7]. Fluorine, in the absence of nitrogen, was determined by the method of Clark[8].

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(7) Rickard, Ball and Harris, Unpublished Work.

(8) Clarke, H. S., *Anal. Chem.*, *23*, 659 (1951).

TABLE I

ULTRAVIOLET ABSORPTION DATA

Compound	λ(mμ)	ε
(3,3-Difluoro-2,4-dioxocyclobutyl)isoquinolinium Betaine	227	41,000
	290	9,000
	357	18,000
(3,3-Difluoro-2,4-dioxocyclobutyl)-3-methylisoquinolinium Betaine	229	60,000
	286	8,000
	350	13,000
(3,3-Difluoro-2,4-dioxocyclobutyl)-3-bromopyridinium Betaine	230	31,500
	345	16,000
$C_{22}H_{14}N_2OF_4$	264	16,000
	295	19,000
	347	17,000
1-[2-(Heptafluorocyclobutyl)2,3,3,4,4-pentafluorocyclobutyl]-4-carbethoxypyridinium Carbeniate	335	1,500
2-[2-(Heptafluorocyclobutyl)-2,3,3,4,4-pentafluorocyclobutyl]isoquinolinium Carbeniate	228	12,500
	296	8,000

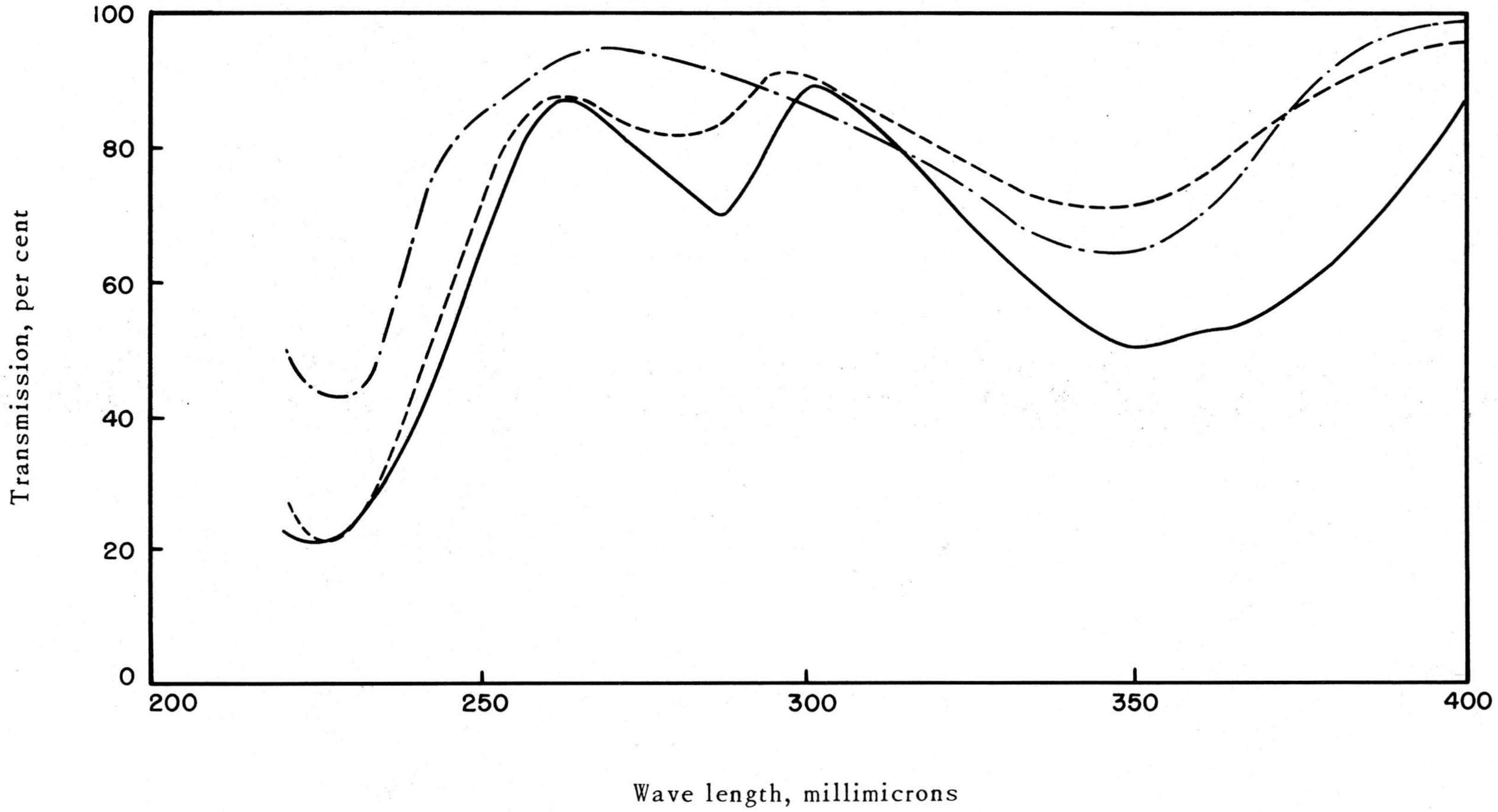

Figure 1.- Ultraviolet absorption spectra of : ——, (3, 3-difluoro-2, 4-dioxocyclobutyl)- isoquinolinium betaine, c = 1.66 x 10^{-5} moles/liter; ----, (3,3-difluoro-2,4-dioxocyclobutyl) -3- methylisoquinolinium betaine, c = 1.12 x 10^{-5} moles/liter; —— . ——, (3,3-difluoro-2,4-dioxocyclobutyl) -3- bromopyridinium betaine, c = 1.17 x 10^{-5} moles/liter.

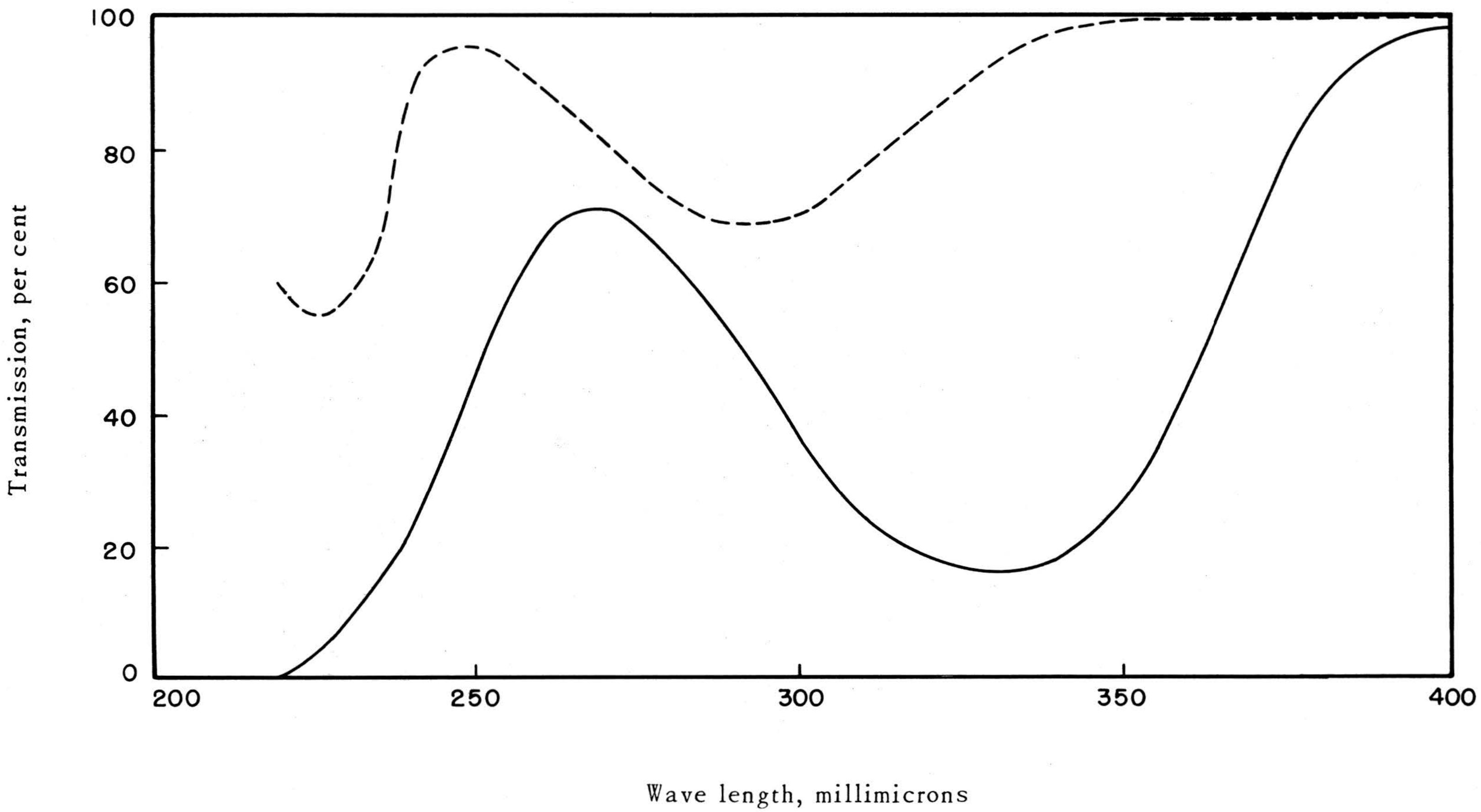

Figure 2.- Ultraviolet absorption spectra of: ——, 1-[2-(heptafluorocyclobutyl)-2,3,3,4,4-pentafluorocyclobutyl]-4-carbethoxypyridinium carbeniate, c = 4.61×10^{-4} moles/liter; ----, 2- [2-(heptafluorocyclobutyl)-2,3,3,4,4-pentafluorocyclobutyl]- isoquinolinium carbeniate, c = 2.10×10^{-5} moles/liter.

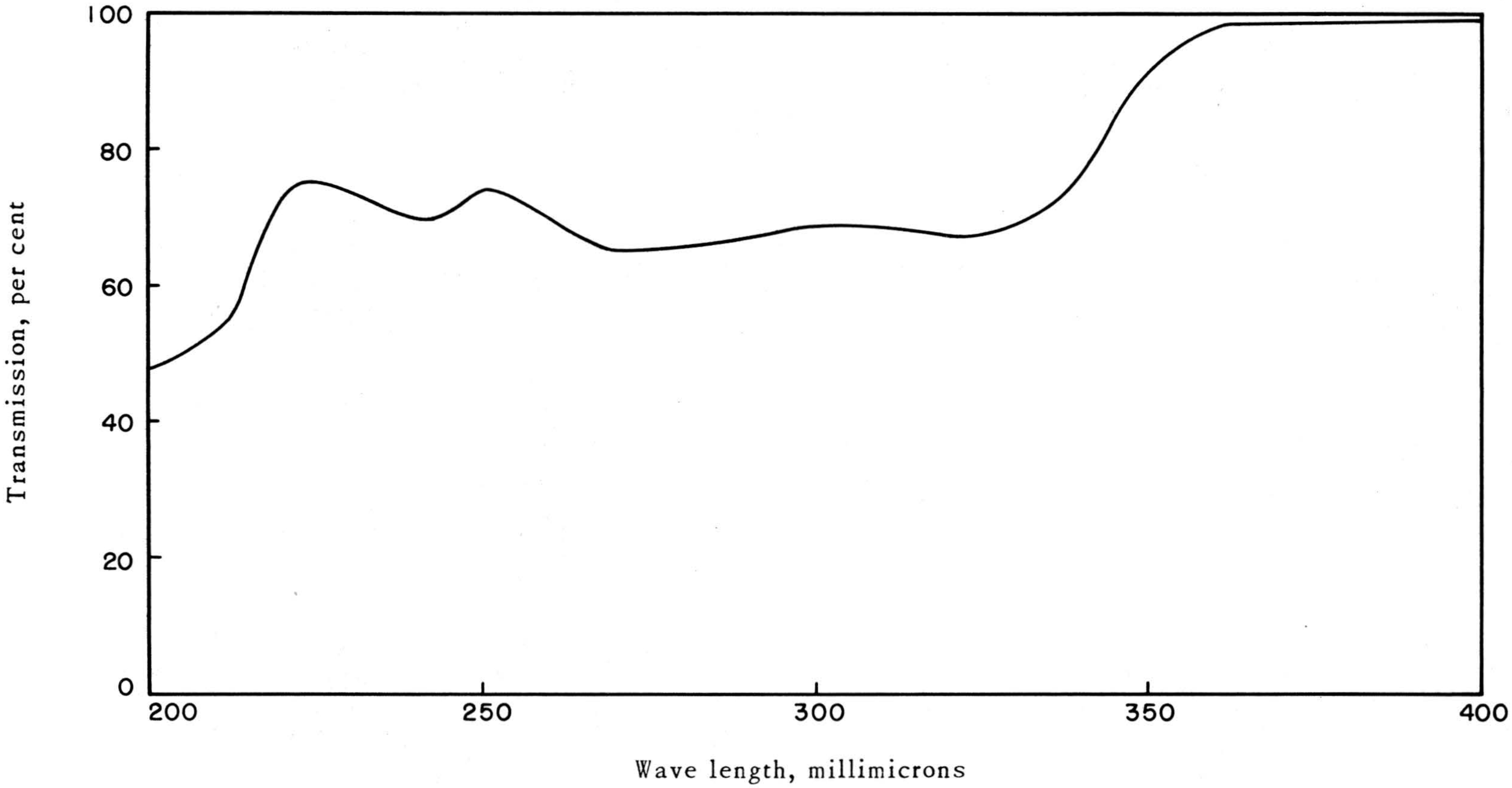

Figure 3.- Ultraviolet absorption spectrum of unidentified compound obtained from the reaction of isoquinoline with hexafluorocyclobutene ($C_{22}H_{14}N_2OF_4$), c = 1.01 x 10^{-5} moles/liter.

CHAPTER IV

CONCLUSIONS

It may be seen that the nature of the products obtained from the reactions of tertiary amines with polyfluoroolefins varies greatly with the type of amine. There is little similarity between the products obtained from aliphatic tertiary amines and polyfluoroolefins and those obtained from aromatic tertiary amines with polyfluoroolefins. The types of products are not altogether the same with different types of aromatic amines as is shown by the difference between the results with pyridine and isoquinoline. However, it appears that the types of products remain constant within a given family, such as pyridine and its analogs or isoquinoline and its analogs.

From the results of this investigation, it may be concluded that a highly fluorinated group exerts a very strong attraction for electrons. It is known that in tris(nonafluorobutyl)amine the presence of the unshared electrons of the nitrogen atom cannot be detected by ordinary means, such as reaction with acids, methiodide formation, picrate formation, etc. Also the powerful electrophilic character of boron trifluoride is due to the electron pull of the fluorine atoms. In this investigation the stability of 1-[2-(heptafluorocyclobutyl)-2,3,3,4,4-pentafluorocyclobutyl]-4-ethoxypyridinium carbeniate and its analogs is due greatly to the ability of the fluorinated cyclobutyl rings to absorb the unshared electrons of the trivalent carbon atom. Since this type of compound did not form with aliphatic tertiary amines and is formed in greatest quantity when the attached amine also contains an electron-attracting group, it appears that both the fluorinated alkyl groups and the pyridinium or isoquinolinium radicals are necessary for complete stabilization.

CHAPTER V

SUMMARY

Aromatic tertiary amines have been found to react with hexafluorocyclobutene at room temperature. The time required for these reactions varied from several hours to a period of weeks. The betaine type compounds which were produced exclusively upon hydrolysis of the reaction products of aliphatic tertiary amines with the cyclobutene were produced only to a small extent when aromatic amines were used. The main product obtained in the latter case varied with the nature of the aromatic amine, but whenever pyridine derivatives were used a trimer of hexafluorocyclobutene was produced to some degree. Usually this was the major product. The structural formula of this trimer has been proved and a mechanism is proposed which will account for it. An intermediate in the proposed mechanism has been isolated as the major product in one case.

Isoquinoline gave two products with hexafluorocyclobutene. One of these was an analog of the compounds produced by pyridine derivatives; the other was isolated after hydrolysis and was not completely identified. 3-Methylisoquinoline also produced two products. One of these, isolated after hydrolysis, was a typical betaine; the other was not identified.

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