

THE PREPARATION AND REACTIONS
OF SOME FLUOROCARBON
ACYLAMINO COMPOUNDS

By

WILLIAM SANDFORD DURRELL

A DISSERTATION PRESENTED TO THE GRADUATE COUNCIL OF
THE UNIVERSITY OF FLORIDA
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

June, 1961

UNIVERSITY OF FLORIDA



3 1262 08552 2976

ACKNOWLEDGMENTS

The author wishes to express his deep appreciation to Dr. John A. Young, his research director, for his constant interest and encouragement throughout this investigation.

The members of the entire staff of Reed Laboratory are also due thanks for their many timely and helpful suggestions.

The success of this work is due in no small part to the author's wife who was a constant source of inspiration and encouragement.

TABLE OF CONTENTS

	Page
ACKNOWLEDGMENTS	ii
LIST OF TABLES	v
LIST OF FIGURES	vi
CHAPTER	
I. INTRODUCTION	1
II. DISCUSSION	4
A. Synthesis of Diamides	4
B. Some Reactions of Amides, Diamides, and Their Derivatives	22
1. The thermal decomposition of their metal salts	22
2. Reactions with perfluoropropene	24
3. Reactions with acyl halides	26
4. Reactions of metal salts of di- amides with bromine and iodine	29
5. Indirect fluorination with silver difluoride	31
6. Some reactions of N-bromoper- fluoroglutaramide	33
C. The Reactions of Bis-(perfluorodi- methylamino)mercury	40
III. EXPERIMENTAL	43
A. General	43
B. Synthesis of Diamides	54

TABLE OF CONTENTS (continued)

	Page
1. Reactions of acids and nitriles.....	54
2. Reaction of anhydrides and amides	61
C. Some Reactions of Amides, Diamides, and Their Derivatives	62
1. The thermal decomposition of some of their metal salts	62
2. Reactions with perfluoropropene	64
3. Reactions with acyl halides	66
4. Reactions of metal salts of diamides with bromine and iodine	71
5. Indirect fluorinations of amides and diamides	72
6. Some reactions of N-bromoperfluoro- glutarimide	74
D. The Reactions of Bis-(perfluoro- dimethylamino)mercury	80
IV. SUMMARY	82
BIBLIOGRAPHY	85
BIOGRAPHICAL SKETCH	89

LIST OF TABLES

	Page
TABLE	
1. Relative Rates and Equilibria in the Reaction, $\text{RCOOH} + \text{R}'\text{CN} \rightleftharpoons \text{RCONHCOR}'$	6
2. Nuclear Magnetic Resonance Spectra	46
3. Infrared Spectra Used in this Work	48
4. Reactions of Acids and Nitriles	56

LIST OF FIGURES

Figure	Page
1. Yield of diacetamide at 150°.	7
2. Yield of N-acetyltrifluoroacetamide at 150°.	8
3. Yield of bis-(trifluoroacet)amide at 150°.	9
4. Yield of N-acetyltrifluoroacetamide from the reaction of acetic acid and trifluoroacetonitrile at 150°.	10

CHAPTER I
INTRODUCTION

Even though Moissan³⁹ first isolated elemental fluorine in 1886, it is hardly likely that fluorine chemistry could have developed into a significant area of chemistry had it not been for the discovery by Swarts of the usefulness of antimony fluorides in replacing halogens with fluorine.²⁶ The later work of Henne led ultimately to the commercial production of fluorine compounds for the first time,²⁶ and still accounts for the greatest proportion of fluorocarbon derivatives commercially produced.

The discovery of the electrochemical process²⁷ by Simons has been of great significance in producing classes of fluorocarbons generally obtainable only with difficulty, if at all, from the Swarts process. Indeed, most of the fluorocarbon derivatives used in this work are derived from products of this process.

War-time development of nuclear weapons created the need for materials stable to the volatile, corrosive, highly toxic uranium hexafluoride used in the gaseous diffusion process in the separation of the desired uranium²³⁵ from the much more common isotope of mass number 238. The ensuing crash program

developed a tremendous amount of data concerning fluorocarbons and their derivatives. Probably most important, the direct use of elemental fluorine, in conjunction with silver⁸ or copper¹³ as catalysts, gave practical yields of usable products for the first time. In addition, the indirect method of fluorination, using a powerful fluorinating agent such as cobaltic fluoride,¹² was found to be useful.

Besides their chemical and oxidative stability, fluorocarbons have demonstrated great thermal stability. The combination of these factors has aroused interest in the practical applications of these unusual materials. The theoretical implications of these properties have no less interest among theorists.

Chemical development of an area requires that the materials under study undergo convenient chemical reactions. These properties which arouse great interest in fluorocarbons therefore hamper development of knowledge concerning them. In fluorocarbon chemistry a "handle" or functional group present in the molecule is much more important than in hydrocarbon chemistry because of the much lesser reactivity of the C-F bond. Of the various possibilities acyl derivatives are of great utility and of these fluorocarbon acylamino compounds seem particularly worthy of study since relatively little work has been described utilizing these materials. For instance, almost the only interest in fluorocarbon amides has been as intermediates in the synthesis of nitriles³²

and/or N-bromo amides.³¹ The N-bromo amides have been of interest largely in regard to their ability to brominate or as intermediates in the Hofmann reaction.^{3,4}

This study was, therefore, undertaken to elucidate further the chemistry of these species.

The long-known reaction of acids and nitriles to give diamides³⁷ was extended to fluorocarbon acids and nitriles and the reaction studied in considerable detail.

Acylation of fluorocarbon amides is reported only for the trifluoroacetylation of trifluoroacetamide⁴² and the base-catalyzed addition to fluoroolefins is unknown, although the addition of other amides to fluoroolefins¹¹ was described after the work reported herein was complete.

The indirect fluorination of fluorocarbon amides and their derivatives is not described in the literature although Bigelow and coworkers^{1,2} have carried out the direct fluorination of several hydrocarbon amides.

The syntheses and several interesting reactions of fluorocarbon N-bromo amides were studied, and new methods for preparing amides substituted on the nitrogen by per-fluoralkyl groups were sought.

CHAPTER II

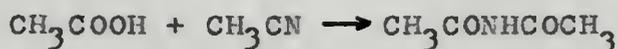
DISCUSSION

A. Synthesis of Diamides

Reactions of acids and nitriles

In the early stages of this work it was necessary to prepare bis-(trifluoroacet)amide, $(CF_3CO)_2NH$, in quantity. Earlier work in this laboratory had shown that trifluoroacetic acid and trifluoroacetonitrile react quantitatively at 150° to give the desired compound in an essentially pure state. Attempts to scale the reaction up from several gram quantities to larger amounts, in an autoclave, resulted in much poorer yields and extensive decomposition. Smith⁴² had reported the synthesis of this compound in good yields from the trifluoroacetylation of trifluoroacetamide with trifluoroacetic anhydride. Sufficient quantities were obtained in this manner to achieve the desired synthetic objectives. Nevertheless, it seemed desirable to study the acid-nitrile reaction because of its potential synthetic utility and the intrinsic value of a more detailed knowledge of its mechanism.

The reaction of nitriles with organic acids was first studied before the turn of the century³⁷ and, in the case of acetic acid and acetonitrile at 200° , gave principally the diamide:



This early study led to the following generalizations:

- (1) Fatty nitriles react with fatty acids to give secondary amides.
- (2) Fatty nitriles react with aromatic acids to exchange their cyano and carboxyl groups to give fatty acids and aromatic nitriles.
- (3) Aromatic nitriles and fatty acids give mixed secondary amides.
- (4) Aromatic nitriles and aromatic acids give secondary amides.

There are numerous exceptions to the above as might be expected from a reaction which is carried out in the 150-200° temperature range.

No further work was reported until Wiley and Guerrant⁴⁷ reported that the reactions of phenylacetic acid and nitrile, and p-nitrophenylacetic acid and nitrile, give an equilibrium yield of about 40% of the diamides at 175-190°.

In the present work acetic and trifluoroacetic acids were reacted with aceto- and trifluoroacetonitriles. Equimolar quantities of the appropriate acid and nitrile were heated together in glass ampoules at 150 and 200°. The reactions of acetonitrile were followed by removing the ampoule after the desired period and evaporating under vacuum the unreacted acid and nitrile. The nonvolatile residue was shown to be fairly pure diamide by comparison of its infrared spectrum with that of a pure sample. However, after reaction

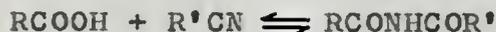
at 200° and long periods at 150° decomposition had occurred to varying extents.

The reactions of trifluoroacetonitrile were followed by measuring the change in vapor pressure of the volatile nitrile before and after reaction. The diamide and unreacted acid were separated by distillation in large scale runs and in small scale runs the nonvolatile residue was examined spectroscopically. It was determined in this manner that the reaction was basically straightforward since there were no absorptions of consequence in the infrared spectra which were not due to the acid or diamide. To test the reverse reaction pure samples of the appropriate diamide were treated in the same manner as the acid and nitrile and the conversions calculated as above.

The experimental results are summarized in Table 1.

TABLE 1

Relative Rates and Equilibria in the Reaction,



System:	Equil. Conv.	Hours for rxn. to reach 50% completion	Effect of Catalysis	
			Acid	Base
R=CH ₃ , R'=CF ₃	97%*	2	++	++
R=CF ₃ , R'=CH ₃	72%	3	+	0
R=CF ₃ , R'=CF ₃	96%	8	+++	+++
R=CH ₃ , R'=CH ₃	60%	96	++	0

*Apparent equilibrium, see text.

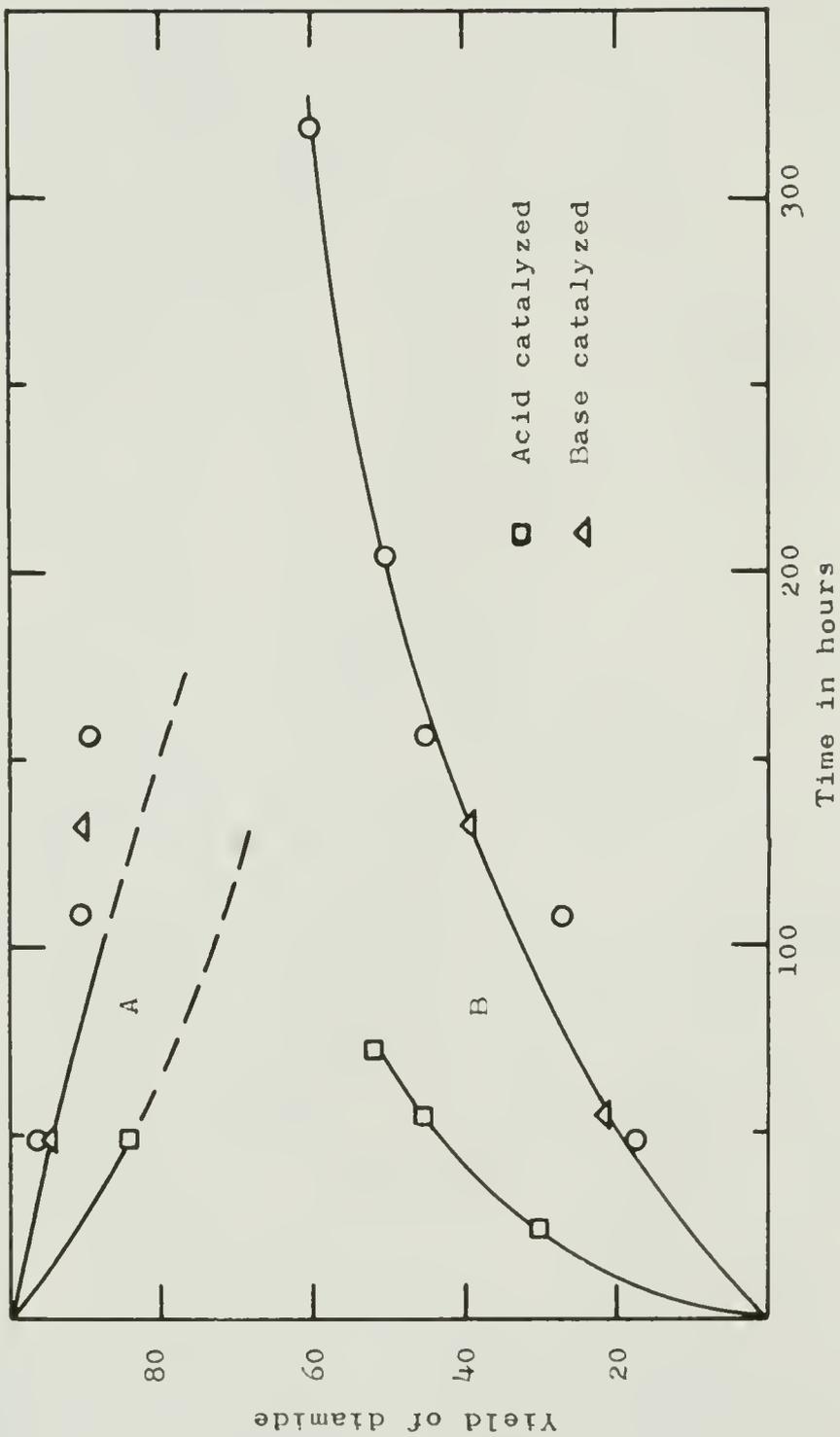


Fig. 1.- Yield of diacetamide at 150°. A. From the equilibration of diacetamide. B. From acetic acid and acetonitrile.

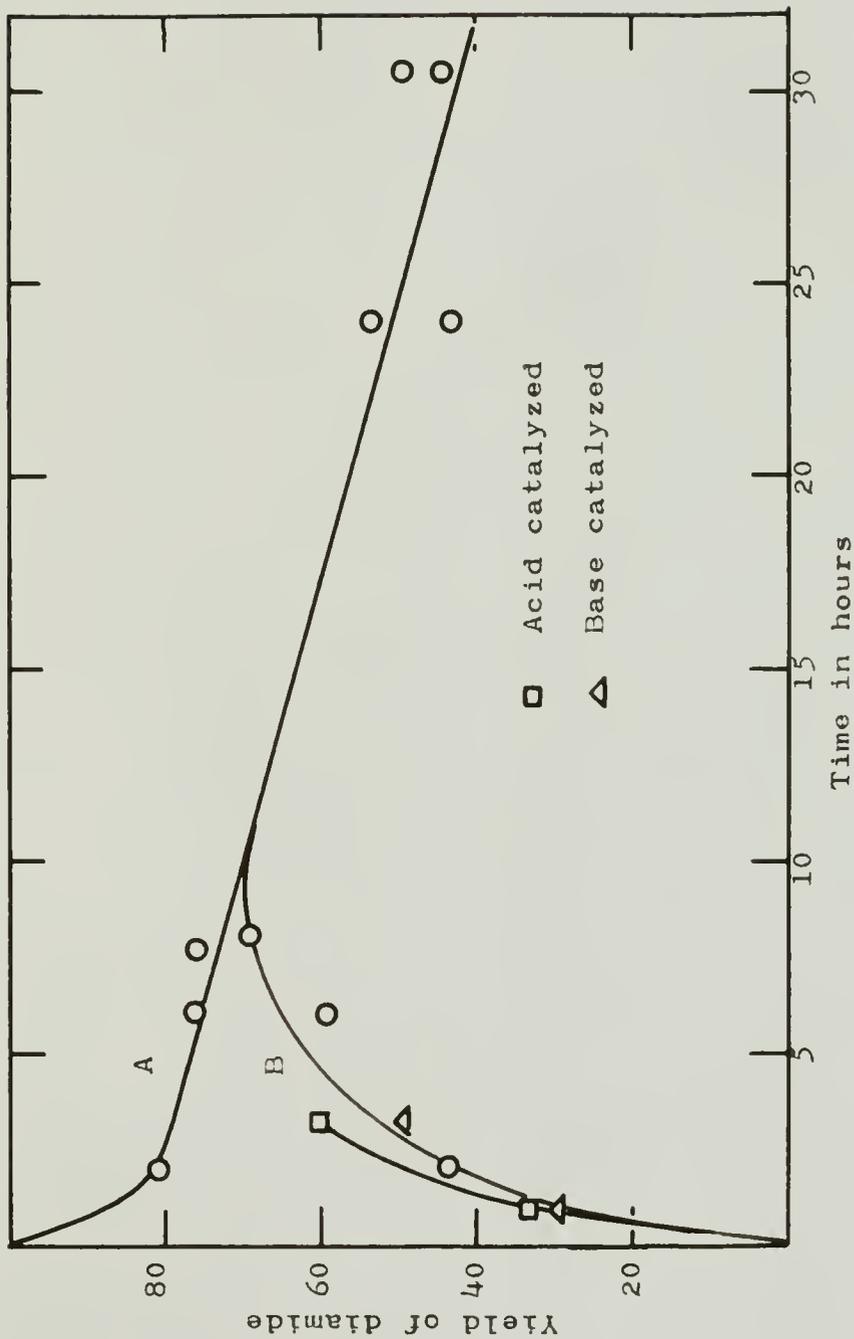


Fig. 2.-Yield of N-acetyltrifluoroacetamide at 150°.

A. From the equilibration of N-acetyltrifluoroacetamide.

B. From trifluoroacetic acid and acetonitrile.

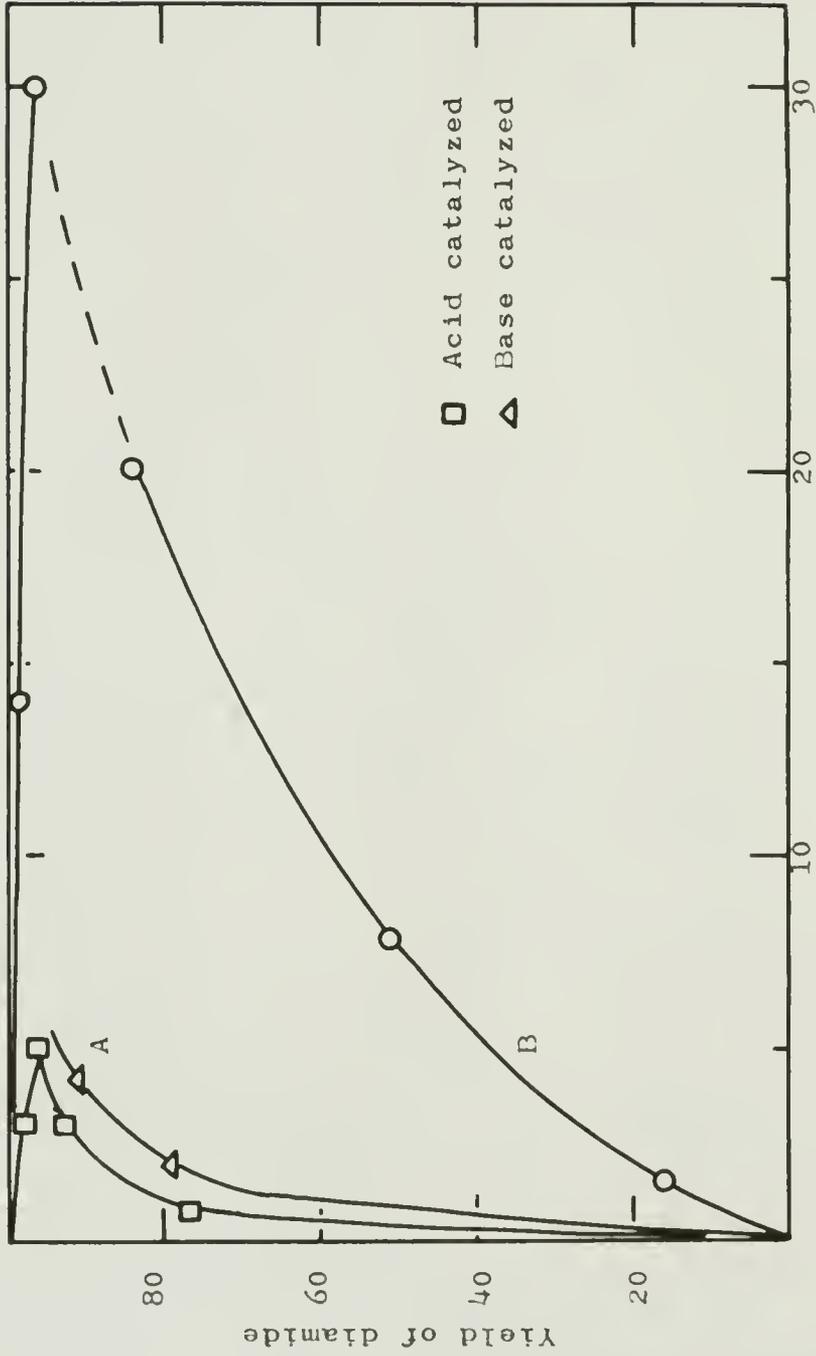


Fig. 3.-Yield of bis-(trifluoroacet)amide at 150°
A. From the equilibration of bis-(trifluoroacet)amide.
B. From trifluoroacetic acid and trifluoroacetonitrile.

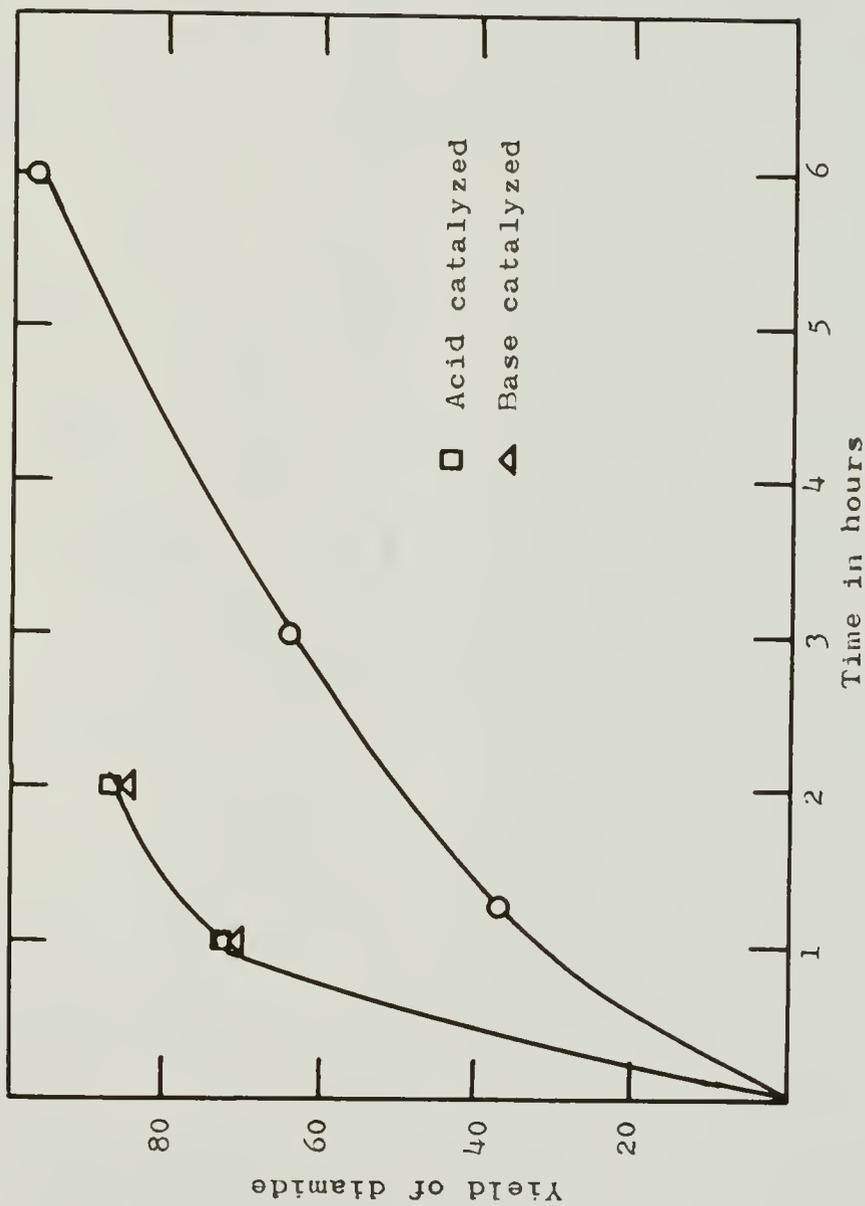


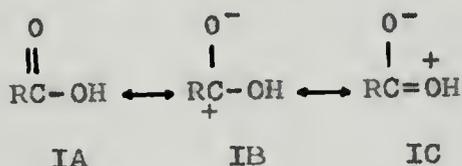
Fig. 4.- Yield of N-acetyltrifluoroacetamide from the reaction of acetic acid and trifluoroacetoneitrile at 150°.

While Wiley and Guerrant⁴⁷ had established that the extent of reaction in the aromatic acid-nitrile systems are controlled by equilibrium, it remained to be shown that an equilibrium would obtain in the present cases. In this work equilibrium was shown by approaching it from either direction. That is, the pure diamides were heated under the same conditions as an equimolar solution of the starting acid and nitrile. In the slow reacting acetic acid-acetonitrile system equilibrium was somewhat difficult to establish since tar formation and other side reactions became important after long reaction periods. This problem was of less consequence in the much faster reacting trifluoroacetic acid-acetonitrile system, and of no consequence in the trifluoroacetonitrile systems. In the systems where acetonitrile was present the unreacted, recovered acid-nitrile mixture was shown by its infrared spectrum to contain a smaller proportion of nitrile than the starting mixture. This indicates, as is well known,³⁶ that nitriles undergo various reactions, in the presence of proton acids, which would account for the tar formation in these cases. Trifluoroacetonitrile with its lower basicity, due to the electron withdrawing fluorine substituents, is much less susceptible to attack by proton acids and, therefore, is less likely to be destroyed in such side reactions.

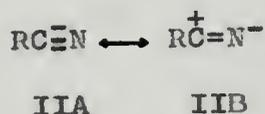
The position of equilibrium in the systems studied presents an interesting situation. Wiley and Guerrant⁴⁷

noted that electronegative substituents cause greater conversions to diamide, but offer no explanation. Our data substantiate this fact, increasing substitution of fluorine for hydrogen bringing about increasingly greater equilibrium conversions, and suggest that these facts might be explained on the basis of relative resonance stabilization of the various reactants and products in their ground states.

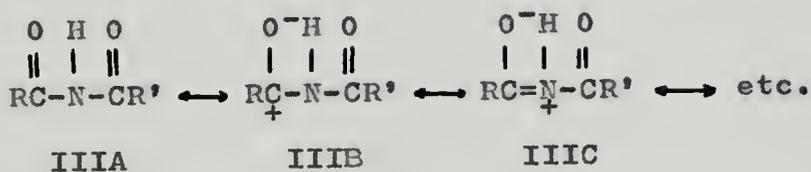
An organic acid is a hybrid of the following structures:



For a nitrile we may write:



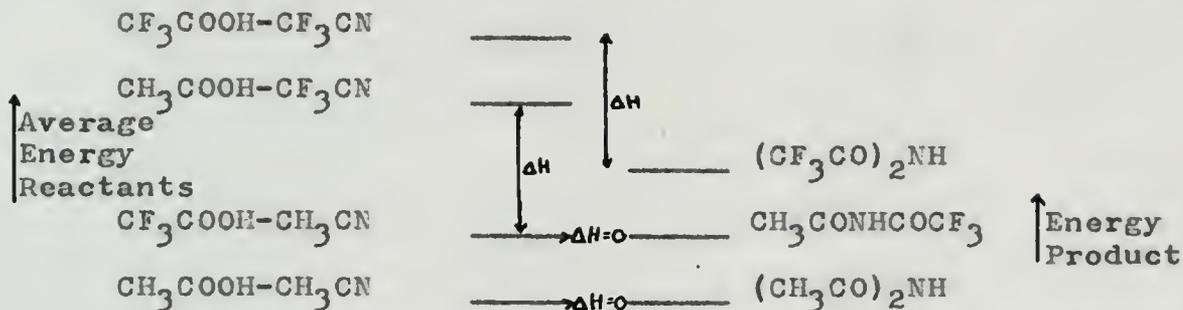
And for a secondary amide:



If R is an alkyl group, the energies of the B structures may be lowered by either inductive or hyperconjugative effects, while if it were a trifluoromethyl group the B structures would be of higher energy relative to A or C structures, in which there is no positive charge adjacent to the trifluoromethyl group. Since a nitrile has no available form of the

C type, it should follow that electronegative substituents destabilize a nitrile to greater extent than either an acid or a diamide, assuming resonance structures of the C type make a real contribution.

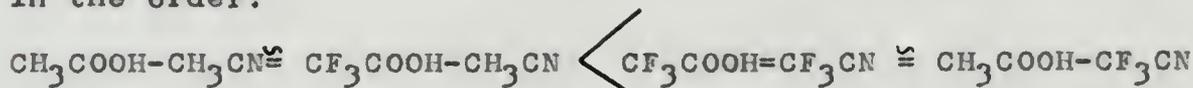
A concise illustration of the situation just described:



The difference in energies of products and reactants is a rough estimate for the value of $-H$ for the reaction, and since entropy change should be about constant for any of the acid-nitrile systems, we may use the familiar relationship:

$$\Delta H \cong \Delta F = -RT \ln K$$

Thus, the greater the value of $-\Delta H$, the greater should be the conversion to diamide. The order of increasing conversions can be estimated from the preceding discussion to be in the order:



This corresponds approximately to the order of increasing conversion found experimentally.

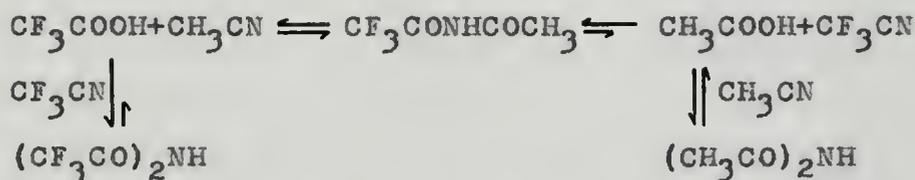
Care must be taken to differentiate between apparent equilibrium and actual equilibrium in the $\text{CH}_3\text{COOH}-\text{CF}_3\text{CN}$ system.

The equation involved in this case is:



The reaction proceeds rapidly to give an apparent equilibrium mixture composed of 97% of the mixed diamide. As time passes the actual equilibrium mixture consisting of mixed diamide, acetonitrile, trifluoroacetic acid, and small but unknown amounts of acetic acid and trifluoroacetonitrile will obtain.

In one experiment the $\text{CF}_3\text{COOH} - \text{CH}_3\text{CN}$ mixture was allowed to react at 200° for eight hours. Fractionation of the product gave a small amount of bis-(trifluoroacet)amide in the most volatile fraction of the diamide cut, and because of its considerably higher boiling point, diacetamide was easily isolated from the high boiling residue. Finding these diamides is to be expected from the total equilibrium in this system:



There is another reaction which can occur but which is only of consequence in hydrocarbon systems. That is the reaction of the diamide with acid:



Davidson showed¹⁰ that an equilibrium of this type exists in the case of dipropionamide and propionic acid and the reaction

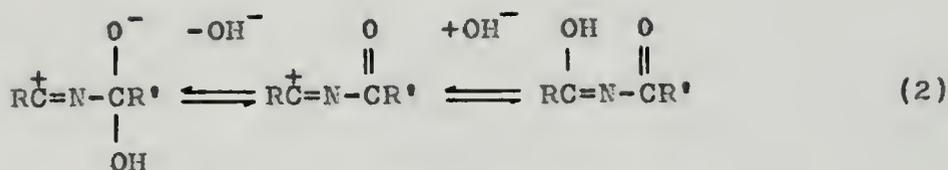
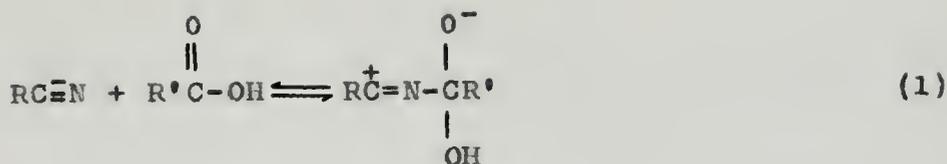
of diacetamide and acetic acid was reported¹⁹ even earlier. Even if this reaction were important in the $\text{CH}_3\text{COOH}-\text{CH}_3\text{CN}$ system, it would not change any of the conclusions reached but would only serve to emphasize them since the correction of the results for the formation of any acetamide, boiling point 222° , would decrease the yield of nonvolatile materials and therefore decrease the equilibrium conversion even more. In none of the fluorocarbon systems was any of the amide found except as discussed later in the thermal decomposition of the sodium salt of the mixed diamide, $\text{CH}_3\text{CONHCOCF}_3$.

To explain the results of the earlier workers³⁷ in the same manner is tempting. Thus, in a typical fatty acid-aromatic nitrile system the following equilibrium would exist:



Since the equilibrium lies to the right, it is obvious that the fatty acid-aromatic nitrile pair are the more stable. If it is assumed that, as in the previous cases, the relative stabilities of the nitriles are the most important single factor, then the obvious rationalization is that the aromatic ring's pi electrons are more available for lowering the energy of the resonance structure IIB than those of an alkyl group, which is wholly expected on the basis of modern electronic theory.

An explanation for the relative rates of reaction of the various systems studied is less obvious. At first sight the most obvious sequence of steps is:



Tautomerization would then give the product.

If the first step were slow and the subsequent steps fast, the most important factor should be the nucleophilicity of the nitrile and the electrophilicity of the acid or, in other words, the ability of the pair of unshared electrons on the nitrogen to attack the carbonyl carbon of the acid. Thus, the fastest reaction might be expected to be that between the nitrile with the most available electrons and the acid with the most electron deficient carbonyl carbon. Using these criteria, the relative rates of the systems studied should be:



Instead it was found that the reaction between acetic acid and trifluoroacetonitrile is the most rapid and that between acetic acid and acetonitrile the slowest. Therefore, either the simple mechanism given is not followed, or an alternative pathway is available.

It should also be noted that acids should catalyze the reaction by enhancing the reactivity of the carbonyl group

of the acid unless the unshared nitrile electrons effectively scavenge the system of acid.

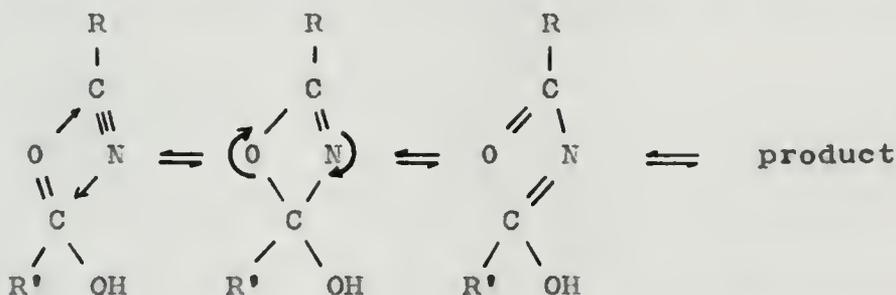
The major requirements of an alternative mechanism are that it must explain:

(1) The higher than anticipated reactivity of trifluoroacetonitrile.

(2) The enhancement of rate in all cases by the addition of small amounts of acid.

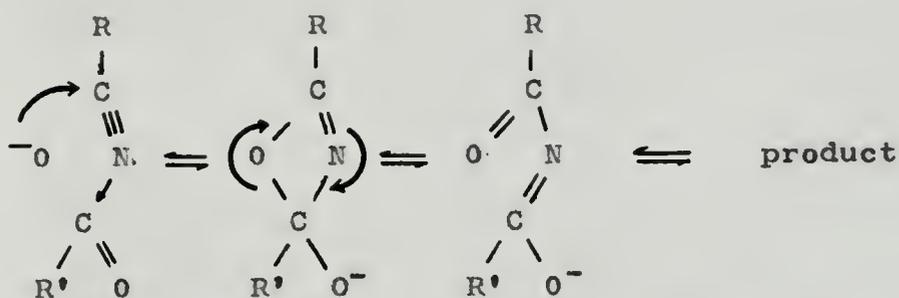
(3) The enhancement in rate, in systems containing trifluoroacetonitrile, by addition of small amounts of base.

The above requirements are met if it is assumed that the oxygen atom of the carbonyl group might participate by simultaneously attacking the nitrile carbon in the following manner:



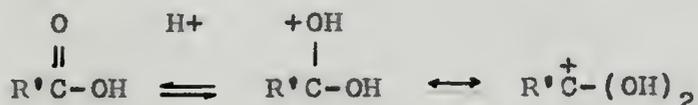
Using this mechanism as an alternative pathway in systems containing trifluoroacetonitrile, all of the experimental results may be rationalized. Considering only these systems, it can be seen that acetic acid would react more rapidly than trifluoroacetic acid because of the greater availability of the carbonyl oxygen for participation, overcoming the lower reactivity of its carbonyl carbon in comparison with trifluoroacetic acid. In view of this it is not surprising that

these systems are catalyzed by base. The carboxylate anion is less electrophilic than the unionized species but, more important, has an increased capability for attack on the nitrile carbon, thus resulting in a higher reaction rate in the presence of base:



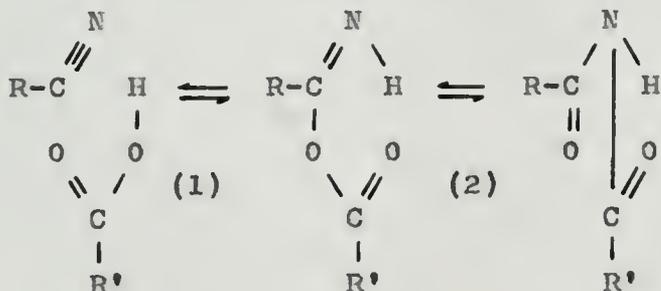
This mechanism might be expected to be followed only in systems in which the nitrile has an abnormally electron deficient carbon atom and is particularly susceptible to nucleophilic attack⁶ such as in trifluoroacetonitrile, as shown above. It is, therefore, likely that in the systems containing acetonitrile the simple mechanism given originally is followed. There is no catalysis by base in these systems and trifluoroacetic acid reacts much more rapidly than acetic acid by virtue of its more electron deficient carbonyl carbon.

All the systems studied are catalyzed to varying degrees by sulfuric acid. Apparently, then in both mechanisms the rate is increased as the concentration of the protonated, highly electrophilic species increases:



This result is compatible with the simple mechanism but is not wholly expected in the participation mechanism since the effect here should be to lower the availability of the electrons on the oxygens adjacent to a formal charge. Apparently the effect of increasing the electrophilicity of the carbonyl carbon more than makes up for the former effect. When acetonitrile was the nitrile constituent acid catalysis was less effective. In these cases the nitrile probably competes with acid for protons. As mentioned previously, acetonitrile is known to react with proton acids.

A third possible mechanism, which Davidson¹⁰ assumes, is the preliminary formation of the isoimide, IV, which then decomposes to the imide or diamide in the following manner:



IV

Using this mechanism it is difficult to account for the experimental results. First, since the reactions involving acetonitrile are not base catalyzed, (2) must be the rate-determining step in these cases. Conversely, (1) must be the rate-determining step in systems containing trifluoroacetonitrile since they are base catalyzed. Since the overall rates are about the same in the reactions of these two

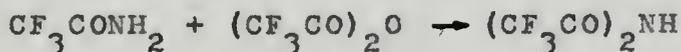
nitriles with trifluoroacetic acid, we are saying, in effect, that acetonitrile is more electrophilic than trifluoroacetonitrile in their reactions with trifluoroacetic acid. This is obviously false; trifluoroacetonitrile is well known to be more susceptible to reactions with nucleophiles, as has been previously discussed.

There is some possibility that the isoimide mechanism is a special case, such as postulated for the participation mechanism. There is a resemblance in these two mechanisms, particularly in the decomposition of the isoimide to diamide. The important difference is that in the isoimide case the attack of oxygen on carbon occurs prior to, rather than simultaneously with, attack of nitrogen on carbon. Thus, in the trifluoroacetonitrile systems the fact that they are base catalyzed might be explained but a rationalization of the enhancement of rate by acid becomes more difficult.

The case for any of the mechanisms is certainly neither proved nor disproved, but on the basis of present information a combination of the simple and participation mechanisms seems most reasonable.

Reactions of anhydrides and amides

Smith's^{1,2} method of synthesis was used to prepare sufficient quantities of bis-(trifluoroacet)amide for use as an intermediate. This reaction may be written:



Attempted trifluoroacetylation of N-methyltrifluoroacetamide in the same manner gave the desired N-methyl-bis-(trifluoroacet)amide only in low yield. It was found that the N-methyl diamide reacted with trifluoroacetic acid to give trifluoroacetic anhydride and the starting amide. Again we have an equilibrium situation:



In this case the equilibrium lies to the left, whereas in the trifluoroacetamide-trifluoroacetic anhydride reaction it lay far to the right (since it was not detectable under the conditions used). It seems doubtful that any arguments on an electronic basis can be brought forward which would explain the large effect of substituting a methyl group for hydrogen. A methyl group in place of the hydrogen in structure IIIC on page 12 would, if anything, lower its energy due to the greater electron donating capacity of methyl over hydrogen. The actual explanation would seem, therefore, to be involved with steric or entropic considerations.

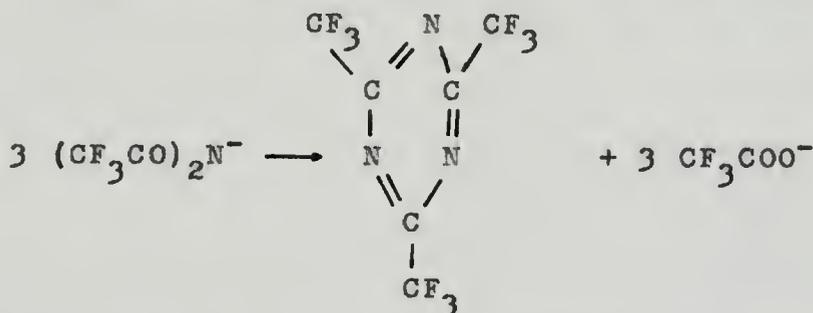
It is interesting to contrast the absence of any formation of nitrile in the trifluoroacetamide-trifluoroacetic anhydride system with results reported by Davidson¹⁰ in the benzamide-benzoic anhydride system in which an equilibrium mixture containing 90% benzonitrile and only 2.7% dibenzamide is reached by refluxing at 224-243° for an hour. The reason for the difference in ease of formation of nitrile in the two systems may be related to the relative thermodynamic

stabilities of the nitriles (in this case trifluoroacetoneitrile and benzonitrile) or may be strictly kinetic since we have no good evidence that the fluorocarbon system is at equilibrium with respect to the formation of nitrile.

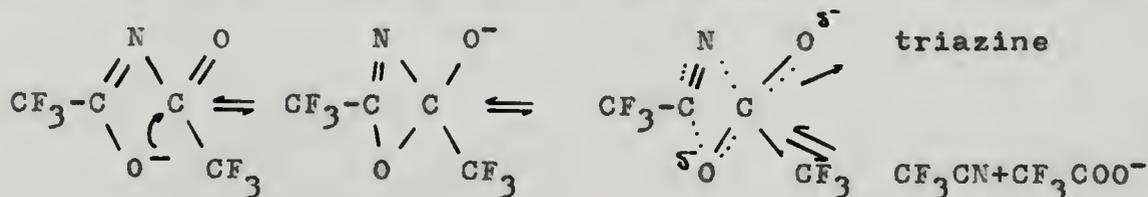
B. Some Reactions of Amides, Diamides,
and Their Derivatives

1. The thermal decomposition of their metal salts

The thermal decomposition of the sodium salt of bis-(trifluoroacet)amide gave a fair yield of 2,4,6-tris-(trifluoromethyl)-1,3,5-triazine, presumably by the reaction:



Although the mechanism for this transformation was not studied, it is certain that it is not due to the base catalyzed trimerization of trifluoroacetoneitrile,⁵ because none of the highly volatile trifluoroacetoneitrile was evolved into a cold trap, which certainly would be expected if it were an intermediate. It might seem possible that an "activated" form trimerizes before it can proceed to nitrile.



This mechanism demands that in the base catalyzed reaction of acid and nitrile, which seems to go through the same intermediate, the trimer should be formed to the exclusion of diamide. Since this was shown earlier not to be the case, the mechanism must involve either a series of additions or some other form of simultaneous reaction of two or more imide anions.

Similar treatment of the mixed diamide resulted in the following transformation:



A 70% yield of trifluoroacetamide was obtained based on diamide, and 140% based on sodium. The exact nature of this reaction remains unknown, however, in particular the relationship with the related reaction of bis-(trifluoroacet)amide.

Sodium perfluoroglutarimide decomposed to a carbonaceous mass from which no identifiable products could be isolated.

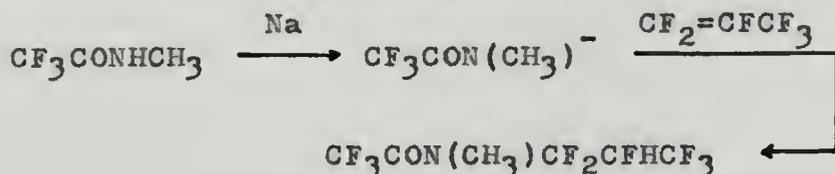
The thermal decomposition of the mercury salt of bis-(trifluoroacet)amide did not give any identifiable products, except metallic mercury, and traces of expected pyrolysis products, trifluoroacetic acid, trifluoroacetonitrile, and fluoroform. The mercury salt of perfluoroglutarimide was

considerably more thermally stable than that of bis-(trifluoroacet)amide, a portion subliming at 470° rather than entirely decomposing.

2. Reactions with perfluoropropene

Additions of nucleophiles to fluoroolefins have been known since 1946 when Hanford and Rigby¹⁵ reported the reaction of alcoholates with several fluoroolefins. The reaction has been of considerable synthetic utility. Among the nucleophiles used, as well as various alcohols,²⁹ have been amines,³⁰ mercaptans,³³ organometallic compounds²⁹ and, while this work was in progress, amides.¹¹

Addition has not been reported, however, of fluorine substituted amides or diamides to fluoroolefins. Additions of four of these materials to perfluoropropene were attempted, trifluoroacetamide, N-methyltrifluoroacetamide, perfluoroglutaramide, and bis-(trifluoroacet)amide. Of these only N-methyltrifluoroacetamide gave the desired addition product:



The anion of the amide was made by adding sodium to the molten amide and heating gently until evolution of hydrogen was complete. The addition was carried out in an autoclave and gave a 75% yield after 40 hours at 80°. The distilled product was shown to be 98-99% pure by vapor phase

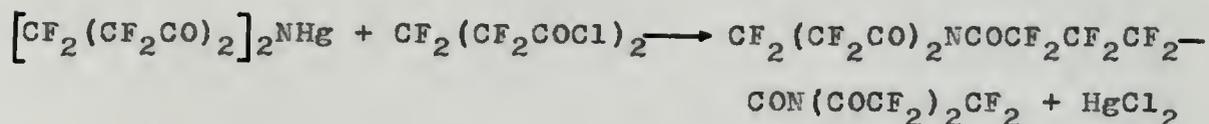
chromatography. The structure of the adduct was shown unequivocally by means of the proton magnetic resonance spectrum which showed, besides an absorption associated with the N-methyl protons, a proton peak which exhibited a complicated fine structure, a complete interpretation of which is incomplete* but which is undoubtedly due to a proton in the position, X-CF₂CFHCF₃. The product slowly evolved HF, but an attempt to isolate the dibromide of the olefinic product was unsuccessful.

Attempted additions using identical conditions were totally unsuccessful with the other amides mentioned previously. The sodium salts of all these materials were rather unstable compared to the sodium salt of N-methyltrifluoroacetamide. The sodium salt of perfluoroglutarimide was most readily prepared by an exchange reaction with sodium methylate, methanol being removed under vacuum until the dry imide salt remained. The sodium salt prepared in this manner was totally inert to perfluoropropene at 100° and decomposed at slightly higher temperatures. When sodamide was added to perfluoroglutarimide the mixture sparked and burned. The attempted reaction of the sodium salt of bis-(trifluoroacet)amide with perfluoropropene resulted only in decomposition to give the triazine discussed previously.

*A complete description of the nuclear magnetic resonance spectra of this compound will be reported on by Dr. W. S. Brey and coworkers.

3. Reactions of acyl halides

As with perfluoropropene, only N-methyltrifluoroacetamide underwent reaction with acyl halides. Attempted reactions of the sodium, mercury, and silver salts of perfluoroglutarimide; and of the sodium and mercury salts of bis-(trifluoroacet)amide with trifluoroacetyl and/or perfluoroglutaryl chloride were unsuccessful. With perfluoroglutaryl chloride and the mercury salt of perfluoroglutarimide the desired reaction was:



While none of the desired N,N,N',N'-bis(perfluoroglutaryl) perfluoroglutardiamide was formed in this reaction, a successful and interesting synthesis was eventually found which is described later.

The sodium salt of N-trifluoromethylacetamide, prepared from sodium sand in ether or tetrahydrofuran, reacted with trifluoroacetyl chloride to give the desired N-methyl-bis-(trifluoroacet)amide. This compound could also be prepared from the amide and acyl chloride in the presence of pyridine, as described by Thompson.⁴³

The sodium salts of both the imide and the diamide gave precipitates with trifluoroacetyl chloride but no triacyl nitrogen compounds were obtained. The only volatile products were the diethyl etherate (when diethyl ether was used as the

solvent) and the tetrahydrofuranate (when tetrahydrofuran was used as the solvent) of trifluoroacetic acid. Addition compounds of this type were originally reported by Hauptschein and Grosse.¹⁶ The diethyl etherate had the same physical constants given by these workers and measurement of the relative intensities of the proton absorptions in the proton resonance spectrum confirmed the formula proposed originally for the etherate, $3 \text{CF}_3\text{COOH} \cdot 2 (\text{C}_2\text{H}_5)_2\text{O}$. The formula of the unreported tetrahydrofuranate was shown by the same means to be $2 \text{CF}_3\text{COOH} \cdot \text{C}_4\text{H}_8\text{O}$.

Trifluoroacetyl chloride must have been the source of the acid found in the product since it was the common reactant in both systems. Since neither of the etherates were found in the reaction with the N-methyl amide, the imide and the diamide must play a role in the formation of acid, but there is insufficient information to draw any conclusions.

It was thought that the mercury salts of the imide and the diamide might be more likely to react with acyl chlorides in the desired manner since the mercury salt of N,N'-bis-(trifluoroacetyl)hydrazine reacts fairly readily with trifluoroacetyl and perfluoroglutaryl chlorides.⁴⁸

The mercury salts of the imide and the diamide were synthesized by means of their exchange reaction with mercuric acetate in anhydrous media. The mercury salts were completely unreactive toward the acyl halides in any system

tried at temperatures up to 100°. Use of trifluoroacetic acid or FC 102 (an inert fluorocarbon ether mixture) as solvents was also ineffective.

It is well known⁴¹ that the silver salt of perfluoroglutaramide is reactive toward bromine in trifluoroacetic acid. Trifluoroacetyl chloride was reacted with silver salt under identical conditions but instead of N-trifluoroacetylperfluoroglutaramide, trifluoroacetic anhydride was formed, evidently from the reaction of the acyl halide with the silver salt of trifluoroacetic acid. It is to be expected that the trifluoroacetate and perfluoroglutaramide anions exist in an equilibrium:



but whether either would actually exist as the free, uncomplexed anion is difficult to say. It is likely that silver plays a more important role than the above equilibrium would suggest. At any rate, trifluoroacetyl chloride reacts preferentially with trifluoroacetate anion (or a complex silver salt), and bromine reacts preferentially with the anion of perfluoroglutaramide (or its complex silver salt). The silver salt of perfluoroglutaramide was prepared free of trifluoroacetic acid but, using excess imide as solvent, no reaction occurred with the acyl chloride.

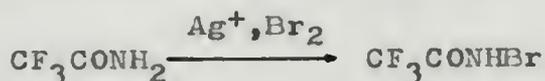
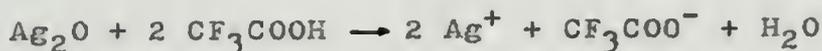
The nonreactivity of the imide and diamide anions toward electrophiles, such as acyl halides and fluoroolefins, is

probably due to resonance stabilization of the anion by the electronegative substituents. Thus, the anion of N-methyltrifluoroacetamide, being less stabilized by the electron donating methyl group, undergoes reactions with both trifluoroacetyl chloride and perfluoropropene.

4. Reactions of metal salts of diamides with bromine and iodine

Either the silver¹⁸ or the mercury salts of perfluoroglutarimide could be brominated readily in trifluoroacetic acid to give N-bromoperfluoroglutarimide. Iodine reacted slowly with the silver salt of perfluoroglutarimide but the product was too unstable to isolate.

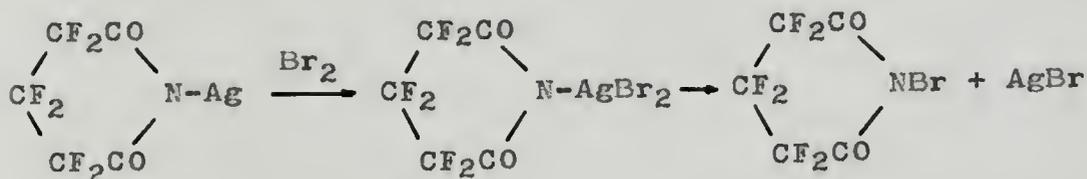
Bis-(trifluoroacet)amide did not react with bromine under the above conditions, however. The bromine which was absorbed when added to the silver salt of the diamide in trifluoroacetic acid reacted according to the equations below to give N-bromotrifluoroacetamide.⁴¹



When the residue which remained after evaporating the trifluoroacetic acid from the brominated mixture was treated with dry HBr the immediate formation of bromine was noted.

Both trifluoroacetamide and bis-(trifluoroacet)amide were present in this product. Under anhydrous conditions, achieved by adding a slight excess of trifluoroacetic anhydride to the reaction mixture, neither the silver, sodium, nor the mercury salts reacted with bromine. It may be concluded, therefore, that any reaction in the original bromination was due to trifluoroacetamide being present.

The difference in reactivities of perfluoroglutarimide and bis-(trifluoroacet)amide toward bromine is remarkable. Since both compounds should have similar electronic environments about their nitrogen atoms, the reason for this great difference must lie elsewhere. This might be attributed to the stabilities of the metal complexes. It could well be that perfluoroglutarimide forms a stable silver complex in solution and that the first step in bromination is complexing of bromine with silver followed by intramolecular transfer of bromine. Such sequences for complex ion reactions have been demonstrated in numerous cases.²⁵ This conjectural mechanism might be written:

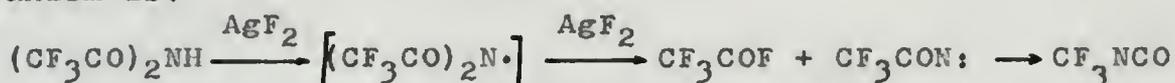


In the bis-(trifluoroacet)amide case a lower stability of the complex, compared to the free anion and silver ion,

would explain its lesser reactivity toward bromine. Further evidence for this point will be given in the next section.

5. Indirect fluorination with silver difluoride

Bis-(trifluoroacet)amide reacts with silver difluoride at 60° and atmospheric pressure to give trifluoroacetyl chloride and trifluoromethyl isocyanate. A plausible mechanism is:

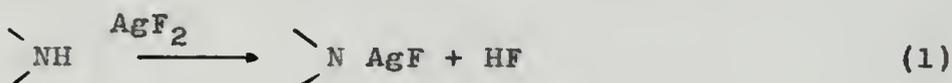


The parenthesized radical may or may not have an independent existence; that is, it may actually be a complex of divalent silver which is rapidly attacked by nascent fluorine or decomposes to give the transitory radical which is then attacked. In either case the attack occurs to break the carbon-nitrogen bond to form trifluoroacetyl fluoride and the electron deficient nitrogen compound which rearranges, as in the Hofmann reaction, to the isocyanate. Both the acyl fluoride and isocyanate volatilize as formed out of the reaction vessel into a cold trap.

Perfluoroglutarimide might be expected to react similarly but under the same conditions gives no volatile products after an initial evolution of HF. Even at much higher temperatures in an inert diluent only a silver salt can be isolated.

Formation of a complex is indicated in both cases, in the diamide case as an intermediate and in the imide reaction as a stable product. Earlier work⁴⁹ has shown that silver

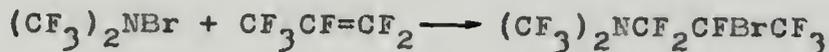
difluoride gives more specific reactions with compounds containing carbon-nitrogen unsaturation than other strong fluorinating agents. This specificity might well be attributed to preliminary formation of a complex, thus lowering the activation energy and allowing the fluorination to be carried out under relatively mild conditions:



In the case of bis-(trifluoroacet)amide the equilibrium in (2) lies far to the right and further fluorination occurs rapidly. With perfluoroglutarimide the equilibrium lies to the left and further fluorination does not occur under the conditions used. As in the attempted bromination, the relative stabilities of the complexes allow a reasonable mechanism to be offered and rationalizes seemingly anomalous behavior. Further, it was previously noted that the mercury salt of the diamide is considerably less stable thermally than that of the imide.

Attempted fluorination of perfluoroglutarimide with iodine pentafluoride failed to give any fluorinated product, only perfluoroglutarimide being identifiable in the product.

reported the facile addition of bis-(trifluoromethyl)nitrogen bromide to perfluoropropene:



It seemed feasible to carry out the analogous addition of N-bromoperfluoroglutarimide to perfluoropropene. When these two were allowed to stand together in the dark no reaction occurred, but if exposed to sunlight or heated in the presence of peroxide a rearrangement of the N-bromo compound occurred rather than bromination of, or addition to, olefin. It was shown that the reaction occurred in the presence of perfluoropropene or chlorotrifluoroethylene, but not in the presence of trifluoroaceticanhydride or in the compound by itself.

The product was found to be ω -bromoperfluorobutyryl isocyanate, $\text{Br}(\text{CF}_2)_3\text{CONCO}$. The following evidence is offered:

(a) The product gave a band in the infrared spectrum at 4.39 microns, indicating either nitrile or isocyanate, and a negatively substituted carbonyl band at 5.5 microns. It reacted violently with water, but gave no precipitate with AgNO_3 and did not oxidize iodide ion.

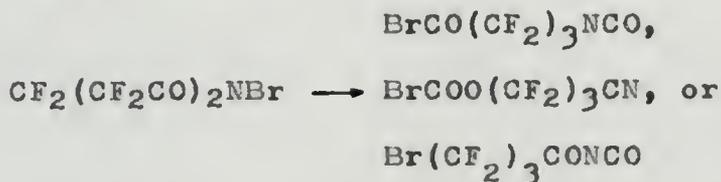
(b) It had a nuclear magnetic resonance spectrum, as did its hydrolysis product, which conclusively showed an open chain structure of the type $\text{X}-\text{CF}_2\text{CF}_2\text{CF}_2-\text{Y}$.

(c) Hydrolysis gave ω -bromoperfluorobutyramide, which was identified by its infrared and nuclear magnetic resonance

spectra, as well as elemental analyses. Unfortunately, as noted in the experimental section, the analytical result for bromine on the amide was slightly low.

(d) The reaction with benzyl alcohol gave a product which, according to the infrared spectrum and elemental analyses, was $\text{Br}(\text{CF}_2)_3 \text{CONHCOOCH}_2\text{C}_6\text{H}_5$.

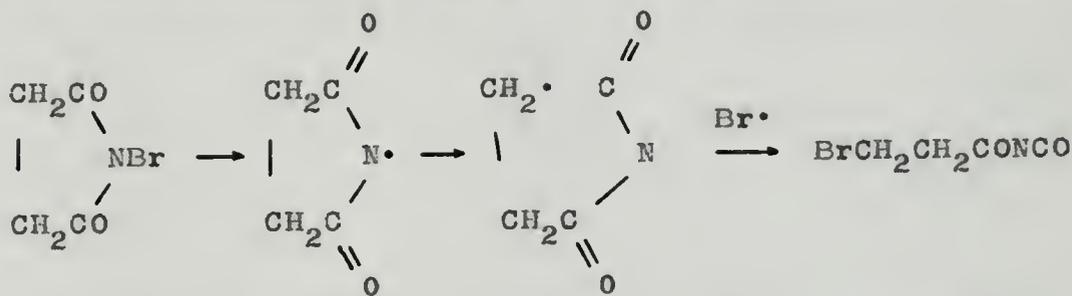
Because of the cleanness of the rearrangement reaction, good yields of a relatively pure product were obtained. Perfluoroglutarimide, present as a contaminant in the N-bromo compound, was the only detectable impurity, along with the unreacted olefin. It was immediately obvious that all the elements of the starting material were present in the product and that it actually was a rearrangement that was being dealt with. There are only three possible products which contain the $-(\text{CF}_2)_3-$ chain:



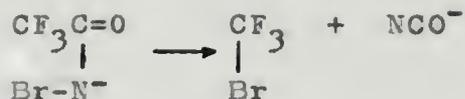
The first product may be eliminated since its hydrolysis should give a succinic acid derivative and bromide ion. The second possible product should give a glutaric acid derivative and positive bromine which would oxidize iodide to free iodine. It did neither of these. The third possibility must, therefore, be the actual product.

Also important, a similar rearrangement has been reported for N-bromosuccinimide^{34,22,23} to give α -bromopropionyl isocyanate.

Martin and Bartlett³⁴ propose a mechanism which simply involves rearrangement of the succinimide radical:



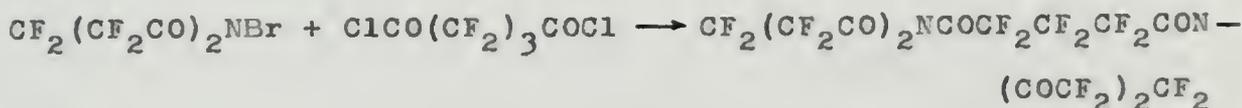
Johnson and Bublitz,²³ in a systematic study, showed that the mechanism was more complex. In addition to chloroform or bromoform as solvent, a terminal olefin containing a 2° or 3° allylic hydrogen was required to be present. Under these conditions addition rather than abstraction of allylic hydrogen, the usual reaction of the succinimide radical,^{14,46} might be expected to be favored. Since the rearrangement of N-bromoperfluoroglutarimide occurs under somewhat similar conditions, it might be surmised that the first step is addition, but rearrangement of either the adduct radical or a subsequent intermediate occurs to give the observed product. Unfortunately, no reactions of this type have been reported to this writer's knowledge. The rearrangement bears a formal resemblance to the reactions of trifluoroacetamide^{3,4} and α -nitroacetamide⁷ with aqueous hypobromite which Barr and Haszeldine^{3,4} formulate as follows:



In anhydrous media the sodium salt of N-bromotrifluoroacetamide decomposes in a normal Hofmann fashion to give sodium bromide and trifluoromethyl isocyanate. The analogy is almost certainly only formal since in the trifluoromethylacetamide case an ionic mechanism is followed, whereas the light and peroxide catalyzed decomposition of N-bromoperfluoroglutarimide is certainly free radical in nature.

The exact mechanism must remain in doubt until a more thorough study of both systems is possible.

The most unusual finding in this study was that N-bromoperfluoroglutarimide reacts, with increasing difficulty, with hydrogen bromide, benzoyl bromide, and perfluoroglutaryl chloride to give bromine and the corresponding N-H or N-acyl compound:

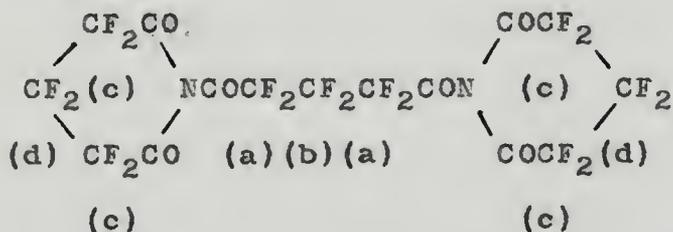


The reactions of hydrogen and benzoyl bromides were rapid and essentially quantitative. The N-benzoyl compound was identified by its infrared and nuclear magnetic resonance

spectra which agreed with the proposed structure in every detail. The nuclear magnetic resonance spectrum was particularly useful, showing absorptions similar to those of the imide itself, but slightly shifted, and since only two types of fluorine were present the benzoyl group must be substituted on the nitrogen, instead of on the carbonyl oxygen, which could be considered a possibility.

It was noted that the N-benzoyl compound picked up moisture from the atmosphere extremely rapidly.

The reaction with perfluoroglutaryl chloride gave a 25% yield of N,N,N',N'-bis-(perfluoroglutaryl)perfluoroglutardiamide. It appeared that bromine was formed but the fate of the chlorine is not known. About half the N-bromo compound was recovered. Once again nuclear magnetic resonance was important in the proof of structure, showing four types of fluorine in the area ratios of 4:2:8:4, as expected from the structure:



In addition, the fine structures of the assigned peaks were identical to those in the parent systems, perfluoroglutaramide and perfluoroglutaryl chloride, and the chemical

shifts were similar but, as expected, not identical. Although this compound is probably sensitive to water, it was not tested because of the small amount on hand.

The reaction failed with trifluoroacetyl bromide and perfluorooctanoyl bromide, perhaps due to the impossibility of removing bromine from the reaction mixture in the first case and the difficulty of separating perfluorooctanoic acid from any of the expected product which might have been formed in the second case. In both reactions an initial, rapid formation of bromine occurred which was undoubtedly due to reaction of the N-bromo compound with dissolved HBr. As mentioned before, this is a very rapid reaction. After this initial surge, evolution of bromine was very slow, evidently slower than the inevitable picking up of moisture, which occurred even though every normal precaution was taken.

In less unusual reactions, the N-bromo compound oxidized mercury to mercuric bromide and formed the mercuric salt of the imide; it also reacted with bis-(1,2,2,2-tetrafluoroethyl)mercury to give the previously unknown 1,1,1,2-tetrafluoro-2-bromoethane in 50% yield.

It appears that all of the reactions of the N-bromo compound which were studied, with the possible exception of its rearrangement to ω -bromoperfluorobutyryl isocyanate, depend in some way on the highly positive nature of the bromine and its oxidizing power.

The driving force behind the reaction with acyl halides is not clear unless the positive bromine functions as a Lewis acid, similarly to a Friedel-Crafts catalyst, to form an acylium ion which may then react with the weakly nucleophilic imide anion:



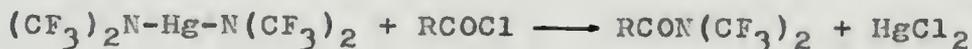
The fact that hydrogen and benzoyl bromides react much more rapidly than trifluoroacetyl and perfluorooctanoyl bromides favors this mechanism since the positively charged ions formed in the first and second cases should be much more stable.

Thermodynamically speaking, there is a net gain of stability of about 20 kcal due almost wholly to the very weak N-Br bond.⁴⁵

C. The Reactions of Bis-(perfluorodimethylamino)mercury

Bis-(perfluorodimethylamino)mercury has been found to react readily with several acyl halides to give the fluorocarbon amides. This is the first reported general synthesis of compounds of the type: $\text{RCO}(\text{CF}_3)_2$. The compounds where

R = CF₃, CH₃, and C₆H₅ were made from the respective acyl chloride in essentially quantitative yields:

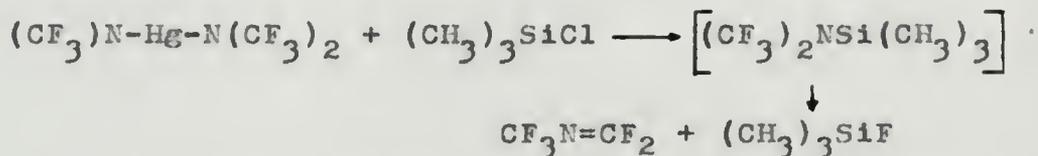


The trifluoromethyl derivative had already been prepared in low yield from the electrochemical process.⁵¹

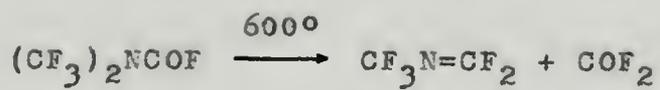
While the properties of these materials were not studied in detail, except for the previously described indirect fluorination of perfluoro-N,N-dimethylacetamide, the benzoyl compound appeared to be quite stable to water while the perfluoro derivative seemed to be very easily hydrolyzed.

The mercurial, surprisingly, failed to react with phosgene, except slowly to form perfluoro-2-azapropene. Although the other reactions occurred at or below room temperature, this one had not proceeded to a substantial extent even after five days at 100°.

The mercurial reacted readily with trimethylchlorosilane to form, not the expected silazane, but the azomethine, as above, and trimethylfluorosilane. It would seem likely that the silazane is formed as an intermediate:



The decomposition of the silazane is analogous to the following pyrolysis, used to synthesize the azomethine:⁵¹



Mao^{33a} observed the formation of azomethine in an attempted reaction of the mercurial with phosphonitrilic chloride trimer.

CHAPTER III
EXPERIMENTAL

A. General

All temperatures are given in degrees centigrade and are uncorrected. The elemental analyses are by Schwarzkopf Microanalytical Laboratory, Woodside, New York.

The fractionations described herein were carried out on standard columns, the size and type of packing depending upon the degree of difficulty of the desired separation and the amount of material available.

The vapor phase chromatography was carried out on a Perkin-Elmer Vapor Fractometer, Model 154-B. The column was packed with the ethyl ester of Kel-F Acid 8114 supported on Celite. The infrared spectra were taken on a Perkin-Elmer Model 137B double beam "Infracord" Spectrophotometer, equipped with sodium chloride optics. Nuclear magnetic resonance spectra were obtained with a 60 mc Varian NMR Spectrophotometer, using CF_3COOH as a reference standard.

The following chemicals were commercial products and were used as received without further purification:

<u>Chemical</u>	<u>Source</u>
Ethyl trifluoroacetate	Peninsular ChemResearch
Perfluoropropene	Peninsular ChemResearch
Trifluoroacetonitrile	Peninsular ChemResearch
Trimethylchlorosilane	Peninsular ChemResearch
Perfluoroglutaryl chloride	Hooker Electrochemical Co.

The fluorocarbon solvents, FC 102 (a mixture of fluorocarbon ether) and FCN-43, $(C_4F_9)_3N$, are products of the Minnesota Mining and Manufacturing Company.

The following compounds were synthesized for this work by the literature method given:

CF_3COCl - This compound was prepared by the method of Henne¹⁷ from CF_3COOH and benzoyl chloride.

CF_3COBr - As above, this compound was prepared from the appropriate benzoyl halide, as described by Tinker.⁴⁴

$(CF_3CO)_2O$ - This compound was prepared in the manner of Clark and Simons,⁹ from CF_3COOH and P_2O_5 .

$(CF_3)_2N-Hg-N(CF_3)_2$ - This mercurial was prepared by the method described by Young⁵⁰ from the reaction of HgF_2 and perfluoro-2-azapropene, $CF_3N=CF_2$.

$CF_2(CF_2CO)_2NH$ - Perfluoroglutarimide was synthesized by the method of McBee³⁵ from perfluoroglutardiamide.

The following compounds were commercial products that were further purified prior to use by the means given:

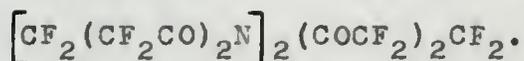
Acetonitrile was dried over calcium chloride and fractionated, the fraction boiling from 81.6-82.0° was used.

Acetic acid was fractionated, the cut boiling from 118-118.5° was taken.

Trifluoroacetic acid was fractionated from a small amount of P₂O₅, the cut boiling from 72-72.5° was used.

Most of the materials used and made in this work displayed varying degrees of ease of hydrolysis by atmospheric moisture. In general, all the materials were protected from moisture by carrying out the appropriate manipulations in a dry-box, or rapidly in the open room. Some of the materials were so hygroscopic, or reactive toward moisture, that extreme care had to be taken to insure good results.

Among these were: (CF₃)₂N-Hg-(CF₃)₂, (CF₃CO)₂NH,
BrCF₂CF₂CF₂CONCO, CF₂(CF₂CO)₂NCOC₆H₅, and probably



Volatile materials were handled as a matter of course in a glass vacuum system, using standard techniques.

TABLE 2

Nuclear Magnetic Resonance Spectra

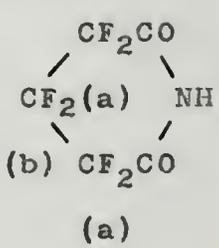
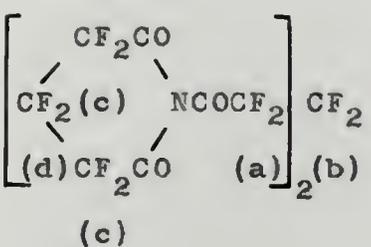
Compound	Nuclei	Peak	Area	Chemical Shift	Fine Structure
1. 	F	a b	4 2	47.0 ppm 60.6	triplet pentet
2. $\text{CF}_2(\text{CF}_2\text{COCl})_2$ (b) (a)	F	a b	4 2	35.7 45.9	singlet singlet
3. $\text{CF}_2(\text{CF}_2\text{CO})_2\text{NCOC}_6\text{H}_5$ (b) (a)	F	a b	4 2	42.1 57.1	triplet pentet
4. $\text{BrCF}_2\text{CF}_2\text{CF}_2\text{CONH}_2$ (a) (b) (c)	F	a b c	2 2 2	-15.1 42.1 42.2	triple triplet triplet triplet
5. $\text{BrCF}_2\text{CF}_2\text{CF}_2\text{CONCO}$ (a) (b) (c)	F	a b c	2 2 2	-14.2 40.1 38.7	triple triplet triplet triplet
6. 	F	a b c d	4 2 8 4	41.7 46.7 49.0 55.6	singlet singlet triplet pentet

TABLE 2 (continued)

<u>Compound</u>	<u>Nuclei</u>	<u>Peak</u>	<u>Area</u>	<u>Chemical Shift</u>	<u>Fine Structure</u>
7. $(CF_3CO)_2NCH_3$	F			5.57 ppm	*
	H			3.44	heptet (barely resolved)
8. $CH_3CON(CF_3)_2$	F			-21.3	singlet
9. $C_6H_5CON(CF_3)_2$	F			-21.5	singlet
10. $CF_3CON(CH_3)CF_2CFHCF_3$	F	**			
	H	**			
11. $2 CF_3COOH \cdot C_4H_8O$	H	a	1		
(a) (b)		b	4		
12. $3 CF_3COOH \cdot 2 (C_2H_5)_2O$	H	a	1		
(a) (b)		b	3.3		

* Two slightly nonequivalent quartets.

** Complex spectrum; a full interpretation is not yet complete but all evidence presently available fits structure given.

TABLE 3

Infrared Spectra Used in this Work

Compound (Phase)	Principal Absorptions (Microns)
1. $(\text{CF}_3\text{CO})_2\text{NH}$ (CCl_4 soln.)	2.86(m), 3.1-3.2(m), 4.28(w), 5.64(s), 5.74(s), 6.25(m), 6.75(w), 8.15(s), 8.25(s), 10.0-10.1(w), 14.30(m).
2. $\text{CF}_3\text{CONHCOCH}_3^*$ (melt)	3.0-3.1(m), 3.33(w), 5.60(s), 5.79(s), 6.6(m), 7.05(w), 7.27(m), 7.60(m), 8.22(s), 8.65(s), 9.79(m), 10.85(w), 11.16(w), 13.62(m).
3. $(\text{CH}_3\text{CO})_2\text{NH}$ (melt)	3.00(s), 3.38(m), 5.79(s), 5.95(s), 6.7(s), 7.05(m), 7.30(s), 8.38(s), 9.70(s), 10.90(w).
4. $\text{CF}_3\text{CONHCH}_3^*$ (melt)	3.02(s), 3.22(w), 3.40(w), 5.78(s), 6.35(m), 7.05(m), 7.40(w), 7.60(w), 8.50(s), 11.36(w), 13.33(w), 13.82(m).
5. $(\text{CF}_3\text{CO})_2\text{NCH}_3^*$ (plates)	3.4-3.5(w), 5.68(s), 5.74(s), 6.83(m), 7.30(s), 7.55(m), 8.60(s), 9.38(s), 9.92(m), 11.80(w), 13.05(m), 13.29(w), 13.93(s).

TABLE 3 (continued)

Compound (Phase)	Principal Absorptions (Microns)
6. $\text{CF}_3\text{CON}(\text{CH}_3)\text{CF}_2-$ CFHCF_3^* (plates)	3.35(w), 5.73(s), 6.73(w), 7.18(m), 7.27(s), 7.41(m), 7.72(s), 7.93(s), 8.25(s), 8.60(s), 8.93(m), 9.28(s), 11.30(m), 11.72(m), 12.60(w), 13.10(w), 13.90(s), 14.35(s).
7. $\text{CF}_2(\text{CF}_2\text{CO})_2\text{NH}$ (melt)	3.02(m), 3.50(w), 5.59(m), 5.70(s), 7.07(w), 7.50(m), 8.00(s), 8.13(s), 8.60(s), 8.95(s), 9.55(s), 10.41(m), 12.5-13.0(w).
8. $[\text{CF}_2(\text{CF}_2\text{CO})_2\text{N}]_2\text{Hg}^*$ (plates)	6.0(s), 6.38(w), 7.20(m), 7.30(w), 7.55(w), 7.75(m), 8.05(w), 8.30(m), 8.70(s), 9.18(w), 9.54(s), 10.22(s), 10.58(w), 10.00(w), 10.23(w), 13.30(m).
9. $\text{CF}_2(\text{CF}_2\text{CO})_2\text{NAg}^*$ (plates)	5.90(s), 6.20(s), 6.55(m), 7.50(m), 7.80(s), 8.2-8.7(s), 9.1(s), 9.65(s), 10.2(s), 11.13(w), 12.20(m), 13.20(m).

TABLE 3 (continued)

Compound (Phase)	Principal Absorptions (Microns)
10. $[(CF_3CO)_2N]_2-Hg^*$ (Nujol mull)	4.80(m), 5.8(m), 6.00(s), 6.87(m), 7.29(m), 8.3-8.7(s), 11.8(w), 12.47(w).
11. 2 $CF_3COOH \cdot C_4H_8O^*$ (plates)	2.80(w), 3.35-3.45(s), 3.7(m), 4.0(s), 5.1(m), 5.64(s), 6.89(w), 7.35(m), 7.55(m), 8.25-8.6(s), 9.62(s), 10.90(w), 11.40(m), 12.3(m), 12.82(m), 14.30(s).
12. 3 $CF_3COOH \cdot$ 2 $(C_2H_5)_2O$ (plates)	3.4(m), 3.72(w), 4.0(m), 5.1- 5.2(w), 5.60(s), 6.92(w), 7.21(w), 7.7(w), 8.22(s), 8.58(s), 9.14(m), 9.4(m), 10.3-10.4(w), 12.0(w), 12.3(w), 12.7(w), 14.32(m).
13. $(CF_3CN)_3$ (gas)	6.35(s), 7.06(s), 7.55(m), 7.70(m), 7.80(m), 8.00(s), 8.39(s), 11.60(s), 14.15(s).
14. $(CF_3)_2NF$ (gas)	7.60(s), 7.87(s), 8.02(s), 8.15(s), 10.25(m), 14.05(m).
15. $(CF_3)_2NN(CF_3)_2$ (gas)	7.46(m), 7.70(s), 8.10(s), 8.40(s), 11.26(m), 13.45(m), 13.85(s).

TABLE 3 (continued)

Compound (Phase)	Principal Absorptions (Microns)
16. $(CF_3)_2NH$ (gas)	2.85(m), 6.63(s), 7.40(s), 7.90(s), 8.30(s), 8.72(s), 10.5(m), 11.32(w), 13.50(w), 14.7(m).
17. $(CF_3)_2NCOF$ (gas)	5.30(s), 7.27(s), 7.60(s), 8.10(s), 8.20(m), 9.68(m), 10.05(s), 13.5-14.0(m).
18. $(CF_3)_2NCOCF_3$ (gas)	5.55(m), 7.35(s), 7.65(s), 7.90(s), 8.10(s), 8.35(m), 8.55(m), 8.80(m), 9.96(m), 11.25(m), 13.6(m).
19. $CF_3N=CF_2$ (gas)	5.51(m), 7.50(s), 7.71(s), 7.90(s), 8.31(s), 9.9-10.0(s), 13.9(m).
20. CF_3NCO (gas)	4.39(m), 6.89(m), 8.30(s), 8.70(s), 9.7(m), 13.9(m).
21. $CF_2(CF_2CO)_2NBr$ (plates)	5.90(s), 6.09(s), 7.19(m), 7.53(m), 7.78(s), 8.16(m), 8.27(m), 8.65(s), 9.6(m), 10.13(s), 12.11(m), 13.20(m), 13.71(w).
22. $Br(CF_2)_3CONCO^*$ (plates)	4.39(s), 5.50(s), 6.5-6.6(m), 6.98(m), 8.35(s), 8.85(m), 9.35(m), 10.1(m), 12.4-12.6(m), 14.25(m).

TABLE 3 (continued)

Compound (Phase)	Principal Absorptions (Microns)
23. $\text{Br}(\text{CF}_2)_3\text{CONHCOO}-$ $-\text{CH}_2\text{C}_6\text{H}_5^*$ (melt)	2.85(w), 2.96(m), 3.23(w), 3.32(w), 5.50(s), 5.69(s), 6.28(w), 6.05(s), 6.33(m), 6.71(m), 7.6-9.0(s), 9.55(m), 9.70(m), 9.92(m), 10.3(m), 10.8(w), 11.2(m), 11.73(m), 12.01(m), 12.43(s), 12.93(m), 13.3-13.5(m), 14.32(s).
24. $\text{Br}(\text{CF}_2)_3\text{CONH}_2^*$ (Nujol mull)	2.97(m), 3.12(m), 5.90(s), 6.20(w), 7.87(m), 8.5(s), 8.75(s), 9.03(s), 9.86(w), 12.21(w), 13.08(w), 14.55(w).
25. $\text{CF}_2(\text{CF}_2\text{CO})_2\text{NCOC}_6\text{H}_5^*$ (melt)	3.22(w), 5.56(s), 5.83(s), 6.25(m), 6.70(m), 6.90(m), 7.5(s), 7.9- 8.8(s), 9.6(s), 10.05(s), 10.5(s), 11.67(m), 12.1(m), 12.95(s), 13.4(m), 14.2(m), 14.6-14.8(s).
26. $\text{CF}_2(\text{CF}_2\text{CO})_2\text{NCOCF}_2-$ $\text{CF}_2\text{CF}_2\text{CON}(\text{COCF}_2)_2-$ CF_2^* (plates)	5.45(s), 5.78(s), 7.5(s), 8.1- 9.0(s), 9.5-9.6(s), 10.0(s), 10.44(m), 9.4-9.6(m), 12.9-14.0(m).

TABLE 3 (continued)

Compound (Phase)	Principal Absorptions (Microns)
27. $\text{CF}_3\text{CHFBr}^*$ (gas)	7.32(m), 7.79(s), 8.30(s), 8.70(s), 9.10(s), 11.5(m), 13.2(m), 14.4- 14.6(m).
28. $\text{CH}_3\text{CON}(\text{CF}_3)_2^*$ (gas)	3.22(w), 5.60(s), 7.3-7.7(s), 8.0-8.7(s), 9.9-10.0(s), 9.67(m), 13.9(m).
29. $\text{C}_6\text{H}_5\text{CON}(\text{CF}_3)_2^*$ (plates)	3.23(w), 5.50(s), 5.77(s), 6.25(m), 6.90(m), 7.5-7.7(s), 7.93(s), 8.3-8.5(s), 9.33(w), 9.64(m), 9.86(m), 10.03(s), 10.7(w), 11.32(s), 12.53(m), 12.99(m), 13.70(m), 14.2-14.5(s).
30. $(\text{CH}_3)_3\text{SiF}$ (gas) ²⁴	3.34(w), 7.70(w), 7.90(s), 10.92(s), 11.70(m), 13.1-13.2(m).

*Compound previously unknown.

B. Synthesis of Diamides

1. Reactions of acids and nitriles

Both CH_3COOH and CF_3COOH were reacted with CH_3CN and CF_3CN at 150 and 200°. The reactions involving the higher boiling CH_3CN were carried out in ordinary glass ampoules, while heavy-walled ampoules were used for the low-boiling (-64°) CF_3CN . The volume of the ampoules was 7-10 ml.

For the reactions with CH_3CN a solution of equimolar quantities of the nitrile and the appropriate acid was prepared. One gram (± 0.02) quantities of this solution were weighed into the ampoule, the ampoule frozen in liquid air, evacuated, degassed, and sealed. The ampoule was allowed to come to room temperature and then completely immersed in a constant temperature bath maintained at $150 \pm 0.5^\circ$ for the desired period. Upon removal the tubes were cooled to room temperature, the tip of the tube broken open, and the tube weighed. The volatile unreacted starting materials were removed at 1 mm. Hg and the contents reweighed. The method was checked by repeating one run using 19 g. of the $\text{CF}_3\text{COOH}-\text{CH}_3\text{CN}$ solution. The conversion of the small scale run was 68% and that obtained by distillation of the 19 g. run was 69%.

$\text{CF}_3\text{CONHCOCH}_3$, b.p. 90° at 60 mm. Hg

Anal. calcd. for $\text{C}_4\text{H}_4\text{F}_3\text{NO}$: C, 31.0%; H, 2.58%;
N, 9.03%. Found: C, 31.2%; H, 2.76%; N, 8.58%

In the reactions involving CF_3CN care was taken that the ampoules used were strain free. Whether this precaution was important is not known, although there were no losses of samples due to failure of the ampoules. The acid, or a solution of catalyst in the acid, was weighed into the ampoule and then a known amount of nitrile condensed into the ampoule. The ampoule was degassed, evacuated, and sealed. While still cold the ampoule was placed in a wire screen cage and after warming to room temperature the ampoule, in its cage, was placed in a furnace maintained at $150 \pm 1^\circ$ for the desired reaction period. Upon removal the ampoule was frozen in liquid air, removed from its cage, and opened into the vacuum system. The change in pressure from the starting amount of nitrile was used to calculate conversion.

The measurements of the reversion of diamide to nitrile and acid in experiments starting with pure diamide were made in similar fashion.

TABLE 4

Reactions of Acids and Nitriles

Reaction of acetic acid and acetonitrile^a at 150±0.5°

<u>time (hrs.)</u>	<u>% conversion^b</u>	<u>catalyst</u>
48	17.5	-
108	27	-
156	45	-
204	50	-
318	60	-
24	30	5% H ₂ SO ₄ by wt.
54	45	5% H ₂ SO ₄ by wt.
70.5	52	5% H ₂ SO ₄ by wt.
54	22	5% NaOAc by wt.
132	38	5% NaOAc by wt.

Reaction of diacetamide at 150±0.5°

<u>time (hrs.)</u>	<u>% unreacted^b</u>	<u>catalyst</u>
48	96	-
108	90	-
156	89 ^c	-
204	87 ^c	-
54	84	5% H ₂ SO ₄ by wt.
132	d	5% H ₂ SO ₄ by wt.
54	94	5% NaOAc by wt.
132	90	5% NaOAc by wt.

TABLE 4 (continued)

Reaction of trifluoroacetic acid and acetonitrile at $150 \pm 0.5^\circ$

<u>time (hrs.)</u>	<u>% conversion^b</u>	<u>catalyst</u>
2	43	-
6	59	-
8	69	-
24	43 ^c	-
30.5	44 ^{c,e}	-
0.92	33	5% H ₂ SO ₄ by wt.
3.2	60	5% H ₂ SO ₄ by wt.
0.92	30	5% KOCCF ₃ by wt.
3.2	48	5% KOCCF ₃ by wt.

Reaction of N-acetyltrifluoroacetamide at $150 \pm 0.5^\circ$

<u>time (hrs.)</u>	<u>% unreacted^b</u>	<u>catalyst</u>
2	80.5	-
6	76	-
8.2	76	-
24	53 ^c	-
30.5	49 ^{c,e}	-
1	87 ^c	5% H ₂ SO ₄ by wt.
3.25	77 ^c	5% H ₂ SO ₄ by wt.
1	94	5% KOCCF ₃ by wt.

TABLE 4 (continued)

Reaction of trifluoroacetic acid and trifluoroacetonitrile
at $150 \pm 0.5^\circ$

<u>time (hrs.)</u>	<u>% conversion^f</u>	<u>catalyst</u>
1.5	16	-
7.92	51	-
20	84	-
0.75	77	5% H ₂ SO ₄ by wt.
3	93	5% H ₂ SO ₄ by wt.
2	79	5% KOCCF ₃ by wt.
4.25	91	5% KOCCF ₃ by wt.

Reaction of bis-(trifluoroacet)amide at $150 \pm 0.5^\circ$

<u>time (hrs.)</u>	<u>% unreacted^f</u>	<u>catalyst</u>
14	98	-
30	96	-
3	98	5% H ₂ SO ₄ by wt.
5	96	5% H ₂ SO ₄ by wt.

TABLE 4 (continued)

Reaction of acetic acid and trifluoroacetonitrile at $150 \pm 0.5^\circ$

<u>time (hrs.)</u>	<u>% conversion^f</u>	<u>catalyst</u>
1.25	37	-
3	64	-
6	97	-
1	73	10% H ₂ SO ₄ by wt.
2	87 ^c	10% H ₂ SO ₄ by wt.
1	71	10% NaOAc by wt.
2	85	10% NaOAc by wt.

Acid:nitrile reactions at 200°

<u>system</u>	<u>time (hrs.)</u>	<u>% conversion^g</u>
CH ₃ COOH:CH ₃ CN	24	45
CF ₃ COOH:CH ₃ CN	8	50 ^h
CF ₃ COOH:CF ₃ CN	8	50

-
- a. The isolated diacetamide fractions were combined and re-crystallized from hexane to give fluffy white crystals, m.p. $69.5-70.5^\circ$ (lit. m.p. 59°).³⁸
- b. Corresponds to per cent nonvolatile at 1 mm. Hg.
- c. Product partially decomposed and insoluble in acetone.
- d. Product largely decomposed and insoluble in acetone.
- e. Infrared spectrum of recovered, unreacted starting material showed greater concentration of acid than in starting mixture.

TABLE 4 (continued)

- f. Based on unrecovered trifluoroacetonitrile.
- g. Conversions are only approximate as decomposition was extensive at this temperature.
- h. Fractionation of the product obtained by reacting 38 g. of an equimolar mixture under these conditions gave 16 g. of recovered starting materials, 18 g. of a cut boiling from 80-90° at 60 mm. Hg, which, from its infrared spectrum, was shown to contain some $(CF_3CO)_2NH$ boiling at about 100° at 1-2 mm. Hg; and several grams of tarry residue.

2. Reaction of anhydrides and amides

Reaction of $(CF_3CO)_2O$ and CF_3CONH_2 . Essentially the method described by Smith⁴² was used. Careful fractionation of the mixture of CF_3COOH and $(CF_3CO)_2NH$ gave a 76% yield of the diamide boiling at 145° and having a melting point of around 70° . The imide when pure was a very hygroscopic solid melting at $84.5-85.5^\circ$.

Reaction of $(CF_3CO)_2O$ and $CF_3CONHCH_3$. Using the method of Smith,⁴² as above, 25 g. (0.2 moles) of $CF_3CONHCH_3$ and 42 g. (0.2 moles) of anhydride were heated together under a fractionation column on total reflux. After several days the pot temperature had risen only from 51 to 75° . The contents were cooled and sealed together in a glass ampoule. After heating at 120° for two days the ampoule was cooled and opened. Careful fractionation gave largely recovered starting materials, but 8 g. of impure material boiling around 100° was obtained which was shown to be largely the desired product, $(CF_3CO)_2NCH_3$, by comparison with an authentic sample prepared by a different method described later. Two grams (0.009 moles) of the pure material and one gram (0.009 moles) of CF_3COOH were sealed together in a glass ampoule. After heating at 150° for 36 hours the ampoule was cooled and opened into the vacuum system. An infrared spectrum showed almost complete reversion to anhydride and N-methyl amide.

C. Some Reactions of Amides, Diamides,
and their Derivatives

1. The thermal decomposition of some of their metal salts

Thermal decomposition of salts of $(CF_3CO)_2NH$. The salts were made and decomposed in the following manner:

(a) A slurry of sodium sand was prepared by shaking molten sodium vigorously in xylene in a stoppered Erlenmeyer flask. When the finely divided sodium had cooled it was washed repeatedly with dry tetrahydrofuran. To such a mixture, containing 2.3 g. (0.1 g. atom) of sodium in 300 ml. of tetrahydrofuran, was added 21 g. (0.1 moles) of $(CH_3CO)_2NH$ in 50 ml. of tetrahydrofuran. Evaporation of the solvent left a clear, yellowish-brown syrup. This material was gradually heated at 150° over a 12-hour period. Charring began at 80° . After three days at 130° there was obtained 2 g. of CF_3H condensed in a cold trap. Distillation of the charred, partially solid residue gave 5 g. of the triazine, $(CF_3CN)_3$. b.p. 95° , n_D^{25} 1.3195. Known values²⁰ for $(CF_3CN)_3$ are b.p. 95° , n_D^{25} 1.3161. Comparison of the infrared spectrum with that of a known sample confirmed the identification.

(b) The Hg salt of $(CF_3CO)_2NH$ was prepared by refluxing under a fractionation column a mixture of 166 g. (0.88 moles) of mercuric acetate at 120 mm.Hg. The CH_3COOH was slowly taken off, eventually 27 g. (theory, 24 g.) including

an intercut being removed. After taking off the excess $(CF_3CO)_2NH$ and finally drying at 100° at 0.5 mm.Hg, the pure salt remained.

Anal. Calcd. for $C_8F_{12}HgN_2O_4$: Hg, 32.4. Found: Hg, 31.4
 The dry Hg salt was heated at $200-340^\circ$. The only volatile materials were small amounts of CF_3COOH , CF_3CN , and some CF_3H . The residue consisted of metallic Hg and carbonaceous material.

Thermal decomposition of salts of perfluoroglutarimide.

(a) The sodium salt of perfluoroglutarimide was prepared by mixing, with cooling, equimolar quantities of the imide and sodium methylate, in methanol solution, then removing the methanol by evaporation under reduced pressure. It was stable at 120° but decomposed rapidly at 140° to a carbonaceous mass.

(b) The Hg salt of perfluoroglutarimide was prepared in the same manner as described for the synthesis of the mercury salt of $(CF_3CO)_2NH$.

Anal. Calcd. for $C_{10}F_{12}HgN_2O_4$: Hg, 31.2. Found: Hg, 31.06
 The dry mercury salt was heated for six days at 470° . Of 5 g., 3 g. remained as residue, a portion of which was metallic Hg, the remainder a charred mass. One g. of imide had distilled into a receiver and 1 g. of the Hg salt had sublimed out of the heated portion of the apparatus.

Thermal decomposition of the sodium salt of $\text{CF}_3\text{CONHCOCH}_3$. A solution of 1.2 g. (0.05 g. atom) of Na in 15.5 g. (0.1 moles) of the diamide was heated at 130-135° for 72 hours with little effect. After 36 hours at 160° the solution had darkened considerably and a small amount of CF_3H evolved into a cold trap. Distillation gave 8 g. of CF_3CONH_2 . This represents a 70% yield based on diamide, or 140% based on sodium. The residue was an intractable material having the consistency of asphalt.

2. Reactions with perfluoropropene

$\text{CF}_3\text{CONH}(\text{CH}_3)$. An excess of CH_3NH_2 was bubbled into $\text{CF}_3\text{CO}_2\text{C}_2\text{H}_5$ at room temperature. The $\text{C}_2\text{H}_5\text{OH}$ which was formed was fractionated off and the product distilled over at 157-160°. Yields in the neighborhood of 80% were easily obtained. The product solidified in the flask as it distilled, m.p. 60.5-62.0°.

Anal. Calcd. for $\text{C}_3\text{H}_4\text{F}_3\text{NO}$: C, 28.4%; H, 3.15%; N, 11.03%. Found: C, 28.6%; H, 3.38%; N, 10.86%.

$\text{CF}_3\text{CON}(\text{CH}_3)\text{CF}_2\text{CFHCF}_3$. One hundred and sixty-eight grams (1.3 moles) of $\text{CF}_3\text{CONH}(\text{CH}_3)$ was heated with 4 g. (0.17 g. atom) of metallic sodium until it had dissolved. The solution of sodium salt was reacted with 40 g. (0.25 moles) of $\text{CF}_3\text{CF}=\text{CF}_2$ in a rocking autoclave at 80° for 40 hours. Upon cooling and opening the bomb into the vacuum system essentially no olefin was recovered. Fractionation gave 52 g. (75%) of

adduct boiling at 115-116°, n_D^{28} 1.3170, 98-99% pure by vapor phase chromatography. Upon standing HF was evolved and both the infrared and nuclear magnetic resonance spectra indicated the formation of an unsaturated material. The adduct was allowed to stand six months, then a small amount of Br₂ in CCl₄ was added but no decolorization occurred.

Attempted reaction with CF₃CONH₂. Twenty-eight grams (0.25 moles) of CF₃CONH₂, 1.2 g. (0.05 g. atom) of sodium were heated and rocked at 80° in an autoclave overnight. After cooling, 25 g. (0.16 moles) of CF₃C=CF₂ was added and the mixture rocked and heated at 80° for 18 hours. Upon cooling and opening the autoclave into the vacuum system, all the olefin was recovered unchanged. The residue in the autoclave was considerably decomposed. Repeating the reaction using 6 g. (0.25 g. atom) of sodium made no difference in the results.

Attempted reaction with perfluoroglutarimide. Forty grams (0.18 moles) of perfluoroglutarimide and 2 g. (0.09 g. atom) of sodium were heated together at 120° but before solution was complete extensive decomposition and carbonation occurred. When a gram or so of sodamide was added to the imide the mixture sparked and burned. The sodium salt was best prepared by reacting the imide with sodium methylate and removing methyl alcohol until only the dry salt remained. In this way 8.8 g. (0.04 moles) of imide was mixed with 0.01

moles of methylate in 2.5 cc of methyl alcohol. After removal of the alcohol by evaporating under reduced pressure the sodium salt was sealed in a glass ampoule with 3 g. (0.02 moles) of $\text{CF}_3\text{CF}=\text{CF}_2$. The ampoule was heated and rocked at $85-100^\circ$ for 12 hours. On cooling and opening the ampoule into the vacuum system the olefin was recovered unchanged. The clear, syrupy residue in the ampoule was soluble in water.

Attempted reaction with $(\text{CF}_3\text{CO})_2\text{NH}$. Thirty grams (0.14 moles) of $(\text{CF}_3\text{CO})_2\text{NH}$, 1.5 g. (0.06 g. atom) of sodium, and 6 g. (0.04 moles) of $\text{CF}_3\text{CF}=\text{CF}_2$ were reacted in an autoclave in the same manner as in the synthesis of $\text{CF}_3\text{CON}(\text{CH}_3)\text{CF}_2\text{CFHCF}_3$. The $\text{CF}_2\text{CF}=\text{CF}_2$ was recovered unchanged and fractionation of the residue gave 7 g. of the triazine, $(\text{CF}_3\text{CN})_3$.

3. Reactions with acyl halides

$(\text{CF}_3\text{CO})_2\text{NCH}_3$

(a) In tetrahydrofuran- A slurry of sodium sand was prepared by shaking molten sodium vigorously in xylene in a stoppered Erlenmeyer flask. When the finely divided sodium had cooled it was washed repeatedly with dry tetrahydrofuran. To such a mixture, containing 2.3 g. (0.1 g. atom) of sodium in 300 ml. of tetrahydrofuran, was added, with stirring and cooling, 13.7 g. (0.1 moles) of $\text{CF}_3\text{CONH}(\text{CH}_3)$ dissolved in a small amount of tetrahydrofuran. Then 13.2 g. of CF_3COCl (0.1 moles) was condensed into the cooled solution which was

stirred overnight and then brought to reflux. Filtration and fractionation gave, after the solvent was removed, 5 g. (25%) of $(CF_3CO)_2NCH_3$, b.p. 118° .

Anal. Calcd. for $C_5H_3F_6NO_2$: C, 26.9%; H, 1.34%; N, 6.28%. Found: C, 27.2%; H, 1.52%; N, 5.99%.

(b) In excess $CF_3CONH(CH_3)$ -

Sixty-eight grams (0.5 moles) of $CF_3CONH(CH_3)$, 2.3 g. (0.1 g. atom) of sodium, and 15 g. (0.11 moles) of CF_3COCl were reacted in an autoclave in the same manner as in the synthesis of $CF_3CON(CH_3)CF_2CFHCF_3$, except that CF_3COCl replaced the $CF_3CF=CF_2$. Fractionation of the semi-solid product gave 7 g. (25%) of $(CF_3CO)_2NCH_3$, b.p. $116-118^\circ$. Fifty grams of $CF_3CONH(CH_3)$ were recovered. Since no CF_3COCl was recovered, it is likely that it had leaked from the autoclave during the reaction period.

(c) In pyridine- Six and six-tenths grams (0.05 moles) of $CF_3CONH(CH_3)$, 4.0 g. (0.05 moles) of pyridine, and 6.6 g. (0.05 moles) of CF_3COCl in 25 ml. of tetrahydrofuran were sealed in a glass ampoule. Upon warming to room temperature a precipitate formed. After standing overnight the ampoule was cooled and opened, then filtered and fractionated. After the solvent was removed 3 g. (30%) b.p. $115-125^\circ$ was obtained which was largely $(CF_3CO)_2NCH_3$, as shown by comparison of the infrared spectrum with that of an authentic sample.

Attempted reactions of CF_3COCl with metal salts of $(\text{CF}_3\text{CO})_2\text{NH}$.

(a) Using the procedure that was successful previously in the synthesis of $(\text{CF}_3\text{CO})_2\text{NCH}_3$, 4.6 g. (0.2 g.atom) of sodium sand, 500 ml. of tetrahydrofuran, 42 g. (0.2 moles) of $(\text{CF}_3\text{CO})_2\text{NH}$, and 26.4 g. (0.2 moles) of CF_3COCl were reacted. Subsequent filtration and fractionation gave 30 g. b.p. 123.5-124.5. As shown by infrared and nuclear magnetic resonance, this was the tetrahydrofuranoate of CF_3COOH . The empirical formula is $2 \text{CF}_3\text{COOH} \cdot \text{C}_4\text{H}_8\text{O}$, according to relative absorptions of the protons in the nuclear magnetic resonance spectrum.

(b) The mercury salt was finely powdered and 30 g. (0.05 moles) was heated with 6.6 g. (0.05 moles) of CF_3COCl along with 75 g. of $(\text{CF}_3\text{CO})_2\text{O}$ in a rocking autoclave at 80° for 24 hours. After cooling the autoclave and opening it into the vacuum system, the volatile product was removed. The bomb was evacuated for 12 hours, any additional volatile material being trapped in a liquid air-cooled trap. Distillation of the combined volatiles gave only recovered starting materials.

Attempted reactions of CF_3COCl with perfluoroglutarimide and several of its metal salts.

(a) Forty-four grams (0.2 moles) of the sodium salt of perfluoroglutarimide, prepared by evaporation of methyl

alcohol under vacuum from a solution of equimolar amounts of the imide and sodium methylate, was taken up in dry ether. This solution was cooled while reacted with 26.4 g. (0.2 moles) of CF_3COCl . A gelatinous precipitate of NaCl formed rapidly. Stirring was continued for three hours and after filtration the solution was fractionated. A product boiling at $105-108^\circ$, 6 g., was obtained and after 10 g. of an inter-cut 30 g. of recovered imide was taken over at 90° mm. Hg. The $105-108^\circ$ product was subsequently shown to be the etherate of CF_3COOH , reported b. p. 102° .¹⁶ The empirical formula, also previously reported, $3 \text{CF}_3\text{COOH} \cdot 2 (\text{C}_2\text{H}_5)_2\text{O}$ was confirmed according to the relative proton absorptions in the nuclear magnetic resonance spectrum.

(b) Repetition of the above reaction using tetrahydrofuran as solvent resulted in the formation of the previously described tetrahydrofuranate of CF_3COOH .

(c) Eleven grams (0.05 moles) of perfluoroglutarimide was dissolved in a solution of 5.8 g. of Ag_2O in 100 cc of CF_3COOH . After condensing 6.6 g. (0.05 moles) of CF_3COCl into the above solution it was allowed to stand for several days at $10-20^\circ$. The solution was filtered from the voluminous precipitate which had formed and distilled to give only several grams of $(\text{CF}_3\text{CO})_2\text{O}$, CF_3COOH , and most of the starting perfluoroglutarimide.

The above quantities of Ag_2O , CF_3COOH , and imide were mixed as above and then the CF_3COOH fractionated off, the

last traces under reduced pressure. Twenty-two grams of additional imide were added to its dry silver salt to form a thick slurry which was reacted with 6.6 g. (0.05 moles) of CF_3COCl in a rocking autoclave for two days at 50° . Distillation of the product gave only starting materials in addition to some CF_3COOH .

Attempted reactions of perfluoroglutaryl chloride with the mercury salt of perfluoroglutarimide.

(a) Twenty-five and six-tenths grams (0.04 moles) of the mercury salt, 9.1 g. (0.04 moles) of perfluoroglutaryl chloride, and 50 ml. of FC 102 were stirred together vigorously in a creased flask at reflux (ca. 100°). After three days the solvent was fractionated off, along with unreacted chloride from which separation was impractical, and the residue sublimed onto a cold finger at 1 mm. Hg. This sublimate consisted only of the mercury salt and some perfluoroglutarimide.

(b) In trifluoroacetic acid- Sixteen grams (0.025 moles) of the mercury salt and 6 g. (0.025 moles) of perfluoroglutaryl chloride were heated at reflux temperature in 75 g. of CF_3COOH . The mercury salt was slightly soluble at this temperature and, upon cooling, the salt recrystallized. After three days of refluxing the mixture was cooled and filtered. Fractionation gave recovered CF_3COOH , 5 g. of perfluoroglutarimide and 1 g. of dark residue which was discarded.

4. Reactions of metal salts of diamides with bromine and iodine

N-bromoperfluoroglutarimide. Bromination of the silver salt of perfluoroglutarimide in CF_3COOH by the method of Henne,¹⁸ gave yields of 70% when carried out in the cold. The product could be distilled at 50° at 2 mm. Hg into a cooled receiver in which it would solidify. The purity was determined by titrating with thiosulfate the I_2 formed from addition of the N-bromo compound to aqueous KI. The purity varied from 85-95%, the only identifiable impurity being unreacted perfluoroglutarimide. The mercury salt could be added to CF_3COOH and brominated to give comparable results.

Attempted brominations of metal salts of $(\text{CF}_3\text{CO})_2\text{NH}$.

Using the procedure of Henne, two volatile products were obtained. The first was an easily sublimed solid and the second, secured in much lesser amounts, was a liquid boiling at $50-60^\circ$ at 2 mm. Hg. Titration of the iodine liberated from iodide gave the following results for positive Br:

Calcd. for $(\text{CF}_3\text{CO})_2\text{NBr}$: 27.8%

Calcd. for CF_3CONHBr : 42.1%

Found: solid, 33.1%; liquid, 22.8%

The solid product gave CF_3CONH_2 , along with a small amount of $(\text{CF}_3\text{CO})_2\text{NH}$, on reaction with anhydrous HBr. A slurry of the dry Hg salt of $(\text{CF}_3\text{CO})_2\text{NH}$ in CF_3COOH did not absorb Br_2 , nor was any absorbed in the above method if sufficient

$(\text{CF}_3\text{CO})_2\text{O}$ was added to insure that no water was present.

Substitution of metallic sodium for Ag_2O had no effect either.

Attempted synthesis of N-iodoperfluoroglutarimide. Substitution of I_2 for Br_2 in the above reaction resulted in a much slower reaction, as evidenced by the lesser rate of formation of silver halide as the reaction proceeded. Even after four days of stirring in the dark only 50% of the theoretical amount of AgI had formed. Filtration and evaporation under vacuum resulted in the removal of CF_3COOH and I_2 , which seemed to be constantly formed. Finally, 10% of theory of material which boiled at $80-90^\circ$ at 2 mm. Hg was obtained. Even in the dark this material rapidly decomposed, I_2 being formed. The only identifiable substance left after removal of the I_2 was perfluoroglutarimide.

5. Indirect fluorinations of amides and diamides

Fluorination of $(\text{CF}_3\text{CO})_2\text{NH}$. Thirty grams (0.21 moles) of AgF_2 was suspended in 60 ml. of FC 102 and stirred while 10 g. (0.05 moles) of $(\text{CF}_3\text{CO})_2\text{NH}$ was added slowly, out of contact with the atmosphere, gaseous products being collected in a liquid air-cooled trap. The reaction temperature was maintained at 60° by adjusting the rate of addition, then raised to reflux (ca. 100°) for a short period of time. The condensate in the trap amounted to 5 g. and had a mol. wt. of 103-122. Its infrared spectrum showed all the lines for CF_3COF and CF_3NCO , plus traces of unidentified products.

Attempted fluorination of perfluoroglutarimide. Sixty-five grams (0.45 moles) of AgF_2 was suspended in 100 ml. of $(\text{C}_4\text{F}_9)_3\text{N}$ and stirred while 35 g. (0.15 moles) of imide was added at reflux (ca. 160°). Extensive etching of the glass vessel indicated the formation of HF. The reaction of the black AgF_2 to form a tan product was also evident, as was the evolution of heat. No volatile products were obtained. Since there was excess AgF_2 present, no attempt was made to isolate the solid product except for enough to obtain an infrared spectrum. Two grams (0.009 moles) of perfluoroglutarimide and 1 g. (0.0045 moles) of IF_5 were heated at reflux for six hours. Iodine was formed on the walls of the vessel but no volatiles were obtained. The rather viscous residue was quite clear and only slightly colored. An infrared spectrum showed no bands not attributable to the starting materials.

Fluorination of $(\text{CF}_3)_2\text{NCOF}$. Thirty grams (0.2 moles) of AgF_2 and 20 grams (0.1 moles) of $(\text{CF}_3)_2\text{NCOF}$ were rocked in an autoclave at 100° for 18 hours. The volatile contents were then fractionated to give 7.5 g. of overhead at Dry Ice temperature, mol. wt. 68.5-81.6, largely COF_2 , mol. wt. 66; 10 g. (60%) of $(\text{CF}_3)_2\text{NF}$, b.p. -37° ; and 4 g. of column holdup which was shown from its infrared spectrum to be a mixture of $(\text{CF}_3)_2\text{NCOF}$ and $(\text{CF}_3)_2\text{NN}(\text{CF}_3)_2$. Passing through aqueous alkali gave 2 g. of relatively pure hydrazine.

Fluorination of $(CF_3)_2NCOCF_3$. Fifteen grams (0.1 moles) of AgF_2 and 10 g. (0.04 moles) of $(CF_3)_2NCOCF_3$ were rocked in an autoclave at 100° for 24 hours. Fractionation of the volatile product was only partially successful because of the small amount, but the following amounts of products were estimated from the infrared spectra of the various cuts: 3.5 g. of CF_3COF , 2 g. (30%) of $(CF_3)_2NF$, 3 g. (45%) of $(CF_3)_2NN(CF_3)_2$, and 1.5 g. of $(CF_3)_2NH$ which was probably present as an impurity in the starting material.

6. Some reactions of N-bromoperfluoroglutarimide

The free-radical rearrangement of N-bromoperfluoroglutarimide. Fifteen grams (0.05 moles) of N-bromo compound and 5 g. (0.033 moles) of $CF_3CF=CF_2$ were sealed together in a heavy-walled ampoule and left in direct sunlight for four days. The original yellowish color disappeared after the first day and there was no further change. Distillation of the product resulted in recovery of all the olefin and a quantitative yield of $BrCF_2CF_2CF_2CONCO$, b.p. 42° at 30 mm. Hg. This material reacted almost explosively with water and a drop placed on a watchglass exposed to the atmosphere turned solid in just a few seconds. The aqueous solution gave no precipitate with $AgNO_3$.

The above quantities were reacted in the presence of 1 g. of benzoyl peroxide in an autoclave at 100° to give comparable results.

When 5 g. (0.011 moles) of the N-bromo compound and 2.5 g. (0.02 moles) of $\text{CF}_2=\text{CFCl}$ were sealed in a heavy-walled ampoule and placed in direct sunlight for several hours the yellow color disappeared. The ampoule was cooled and opened into the vacuum system to recover the olefin quantitatively and give 5 g. of the acyl isocyanate obtained previously.

When $(\text{CF}_3\text{CO})_2\text{O}$ was substituted for the $\text{CF}_2=\text{CFCl}$ in the above experiment no reaction occurred even after two days in direct sunlight except for the formation of some Br_2 . The only other identifiable material was the unchanged N-bromo compound.

Fifteen grams of the N-bromo compound was sealed by itself in an ampoule and left in direct sunlight for three days, after which time what seemed a considerable amount of Br_2 had formed, but fractionation after removal of the Br_2 gave only the N-bromo compound, 80% being recovered along with some of the perfluoroglutarimide.

$\text{BrCF}_2\text{CF}_2\text{CF}_2\text{CONHCOCH}_2\text{C}_6\text{H}_5$. The isocyanate from above was allowed to stand two weeks in an ether solution of benzyl alcohol. Evaporation of the solvent left a solid residue which gave, upon recrystallization from cyclohexane, fluffy crystals, m.p. 76.5-78.5°.

Anal. Calcd. for $\text{C}_{12}\text{H}_8\text{BrF}_6\text{NO}_3$: C, 35.2%; H, 2.0%; N, 3.4%. Found: C, 35.7%; H, 2.3%; N, 3.0%.

BrCF₂CF₂CF₂CONH₂. The isocyanate, 3 g., was added dropwise to an excess of water with which it reacted violently. The white solid which formed was filtered, washed thoroughly with dilute NaHCO₃, then water. After drying and recrystallizing from benzene, 1.5 g. of solid melting at 98-100° was obtained.

Anal. Calcd. for C₄H₂BrF₆NO: N, 5.11%; Br, 29.2%.
Found: N, 5.00%; Br, 26.90, 26.78%.*

Reaction with HBr. Two grams of the N-bromo compound and 1 g. of HBr were sealed together in a glass ampoule and allowed to warm to room temperature. Bromine was formed immediately and after an hour the ampoule was opened into the vacuum system. Perfluoroglutarimide remained after the volatiles were removed.

C₆H₅CON(COCF₂)₂CF₂. Thirteen grams (0.043 moles) of the N-bromo compound and 7.5 g. (0.043 moles) of C₆H₅COBr were mixed together in a distilling flask. The mixture warmed immediately and Br₂ was formed. After heating at 90° under about 45 mm. Hg for four hours, the evolution of Br₂ seemed complete and the resulting clear solution was fractionated. After 5 g. of forerun there was obtained 8 g. (60%) of product boiling from 85-86° at 2.5 mm. Hg. This

* While the reason for the low bromine analysis is not known, sometimes complete decomposition of fluorocarbon bromides is quite difficult. The NMR evidence, and all else, is so conclusive that there can be little doubt that the structure is that given.

material eventually solidified in the receiver and after recrystallization from n-pentane melted at 39-41°. It was quite hygroscopic and upon solution in water gave no precipitate with aqueous AgNO_3 .

Addition of small amounts of AlBr_3 had no effect upon the course of the reaction, nor did the N-bromo compound react appreciably with AlBr_3 alone.

Anal. Calcd. for $\text{C}_{12}\text{H}_5\text{F}_6\text{NO}_3$: N, 4.30%.

Found: 4.55%.

Reaction with CF_3COBr . Fifteen grams (0.05 moles) of the N-bromo compound and 9 g. (0.052 moles) of CF_3COBr were sealed together in an ampoule and allowed to warm to room temperature. Even before the contents had completely melted a considerable amount of Br_2 had formed. After standing overnight the ampoule was opened into the vacuum system and the volatiles removed. Since an obvious color of Br_2 remained, a few ml. of Hg were added but the mixture immediately became quite hot and additional Br_2 was formed which subsequently reacted with the Hg. After several hours the solid contents were extracted with about 50 ml. of tetrahydrofuran. After filtering off the greyish solid and excess Hg, the solution was evaporated. An infrared spectrum of the non-volatile residue showed only the presence of perfluoroglutarimide and its Hg salt. This residue

weighed 18 g. and appeared to be about 80% Hg salt. The volatile product previously obtained was distilled but only Br_2 and recovered CF_3COBr were obtained.

Reaction with $\text{C}_7\text{F}_{15}\text{COBr}$. The bromide was prepared by the reaction of $\text{C}_7\text{F}_{15}\text{COOH}$ with $\text{C}_6\text{H}_5\text{COBr}$ in 55% yield, b.p. 125° .

Anal. Calcd. for $\text{C}_8\text{F}_{15}\text{OBr}$: Br, 16.8%. Found: 16.3%.

Ten grams (0.35 moles) of the N-bromo compound and 17 g. (0.035 moles) of $\text{C}_7\text{F}_{15}\text{COBr}$ were mixed together. Some Br_2 was formed immediately but even on heating under reduced pressure little more was formed. Subsequent distillation gave starting materials, along with some perfluoroglutarimide, as the only identifiable products.

$\text{CF}_2(\text{CF}_2\text{CO})_2\text{NCO}(\text{CF}_2)_3\text{CON}(\text{COCF}_2)_2\text{CF}_2$. Twenty-one grams (0.07 moles) of the N-bromo compound and 9 g. (0.033 moles) of $\text{ClCO}(\text{CF}_2)_3\text{COCl}$ were heated together at 100° . When the color of Br_2 became noticeable, a slight vacuum was applied so as to remove that which had formed. After three days Br_2 was no longer being formed and the slightly yellow solution was distilled under vacuum. There was obtained a cut boiling at $35-45^\circ$ at 60 mm. Hg. which was largely recovered N-bromo compound. The product was taken at $95-100^\circ$ at 1.5 mm. Hg. The yield was 6 g., or 28%.

Anal. Calcd. for $\text{C}_{15}\text{F}_{18}\text{N}_2\text{O}_6$: N, 4.34%.

Found: 4.74%.

Reaction with Hg. Thirteen grams (0.043 moles) of the N-bromo compound and 50 g. of Hg were sealed together in a glass ampoule and allowed to warm to room temperature. As Br₂ was formed initially, considerable heat was evolved. Eventually the Br₂ had all reacted with the Hg and the ampoule had cooled. It was then opened into the vacuum system and heated gently. About a half a gram of perfluoroglutaramide was obtained. The residue was extracted with tetrahydrofuran, filtered and evaporated to obtain a nearly quantitative yield of the Hg salt, identified by means of its infrared spectrum.

Reaction with Hg(CHFCF₃)₂. Four grams (0.013 moles) of the N-bromo compound and 3 g. (0.0075 moles) of the mercurial* were heated at 110° for 24 hours, at which time about 1 g. had collected as overhead in a cold trap. This material had a mol. wt. of 171 (calcd. for CF₃CHFBr, 181) and an infrared spectrum consistent with this structure. Repetition of the reaction in a sealed tube exposed to sunlight gave similar results. Sunlight had no effect on the reaction residue, even after several weeks.

* Furnished by D. E. O'Conner, Department of Chemistry, University of Florida.

D. The Reactions of Bis-(perfluoro-
dimethylamino)mercury

CF₃CON(CF₃)₂. Fourteen grams (0.026 moles) of (CF₃)₂N-Hg-N(CF₃)₂ were sealed in a glass ampoule with 8 g. (0.06 moles) of CF₃COCl and allowed to warm to room temperature. At this time a considerable amount of a white precipitate had formed. Heating the ampoule at 40° for an additional hour caused no further noticeable change so the ampoule was cooled and opened into the vacuum system. Approximately 10 g. (80%) of CF₃CON(CF₃) was obtained in a relatively pure state out of 13.5 g. of condensate. The infrared spectrum matched that of a sample obtained previously from the electrochemical process.⁵¹ The remainder, which was more volatile on distillation, was mainly unreacted CF₃COCl and (CF₃)₂NH.

CH₃CON(CF₃)₂. Twelve grams (0.022 moles) of (CF₃)₂NHg-N(CF₃)₂ and 3.1 g. (0.04 moles) of acetyl chloride were reacted and distilled as in the synthesis of CF₃CON(CF₃)₂. There was obtained 5 g. (62%) of product boiling at 66°, mol. wt. 195, found 194.

Anal. Calcd. for C₄H₃S₆NO: N, 7.22%

Found: 7.41%.

C₆H₅CON(CF₃)₂. Ten grams (0.02 moles) of (CF₃)₂N-Hg-N(CF₃)₂ and 5.4 g. (0.04 moles) of benzoyl chloride were allowed to warm to room temperature together in a distilling

flask. Subsequent distillation gave 10 g. (95%) of product boiling at 95° at 90 mm. Hg.

Anal. Calcd. for $C_9H_5F_6NO$: N, 5.40%.

Found: 5.72%.

Reaction of $(CF_3)_2N-Hg-N(CF_3)_2$ with $COCl_2$. Twelve grams (0.022 moles) of $(CF_3)_2N-Hg-N(CF_3)_2$ and 2 g. of $COCl_2$ were sealed together in a glass ampoule and allowed to warm to room temperature. There was no change in appearance of the contents and after several hours without a precipitate being formed, the ampoule was heated at 100° . After five days the ampoule was allowed to cool to room temperature and then opened into the vacuum system. About 6 g. of volatile products were obtained but these were shown, from the infrared spectrum, to be a mixture of $CF_3N=CF_2$, $COCl_2$, and some $(CF_3)_2NH$. The relatively non-volatile residue was unreacted mercurial.

Reaction of $(CF_3)_2N-Hg-N(CF_3)_2$ with $(CH_3)_3SiCl$. Twenty-one grams (0.041 moles) of $(CF_3)_2N-Hg-N(CF_3)_2$ and 8.7 g. (0.08 moles) of $(CH_3)_3SiCl$ were allowed to warm to room temperature together in a distilling flask. A solid precipitate formed, as in previous reactions, but the products were gaseous, passing through the distilling column and being condensed in a trap cooled in dry ice-acetone. Eighteen grams were obtained that were shown by their infrared spectrum to be a mixture of $CF_3N=CF_2$ and $(CH_3)_3SiF$.

CHAPTER IV

SUMMARY

The syntheses and reactions of some fluorocarbon acyl-amino compounds and their derivatives have been studied.

The reactions of acetic and trifluoroacetic acid with aceto- and trifluoroacetonitrile to give the diamides, N-acetyltrifluoroacetamide and bis-(trifluoroacet)amide, were carried out and the relative rates of reaction of the various systems determined at 150°C. Two mechanisms appear to be followed, the actual choice being dependent upon the nitrile used. The reactions of the acids with acetonitrile were catalyzed by acid and those with trifluoroacetonitrile were both acid and base catalyzed. These reactions were shown to reach equilibria which were studied by approaching them from the opposite direction, i.e., reversion of the diamides to the appropriate acid and nitrile. The effect of substituting methyl for trifluoromethyl groups on the position of equilibrium is discussed.

The reactions of trifluoroacetamide and N-methyltrifluoroacetamide with trifluoroacetic anhydride were studied but only in the former case were good yields obtained of the trifluoroacetylated product.

The reactions of metal salts of trifluoroacetamide, N-methyltrifluoroacetamide, bis-(trifluoroacet)amide, and perfluoroglutarimide with perfluoropropene were studied; only N-methyltrifluoroacetamide giving an addition product, $\text{CF}_3\text{CON}(\text{CH}_3)\text{CF}_2\text{CFHCF}_3$. The metal salts of bis-(trifluoroacet)amide and perfluoroglutarimide failed to react with acyl chlorides, but again the N-methyl compound reacted in the desired manner to give N-methyl-bis-(trifluoroacet)amide. The sodium salt of bis-(trifluoroacet)amide decomposed at 100°C to give 2,4,6-tris(trifluoromethyl)-1,3,5-triazine.

N-bromo-bis-(trifluoroacet)amide could not be made by means of the bromination of the silver salt in trifluoroacetic acid, although N-bromoperfluoroglutarimide could be so obtained.

Fluorination of fluorocarbon acylamino compounds with silver difluoride proceeds in such a manner as to:

- (1) Abstract the hydrogen atom(s) from the nitrogen.
 - (2) Cleave the carbonyl-nitrogen bond to give the acyl fluoride and a nitrogen species which may either rearrange, dimerize, or react with fluorine to form an N-F compound.
- Thus, bis-(trifluoroacet)amide, perfluoro-N,N -dimethylcarbonyl fluoride, and perfluoro-N,N -dimethylacetamide were fluorinated. Attempted fluorination of perfluoroglutarimide stopped after evolution of hydrogen fluoride and the formation of a silver salt.

N-bromoperfluoroglutarimide rearranges under free radical conditions, in the presence of perfluoropropene or chlorotrifluoroethylene, to give ω -bromoperfluorobutyl isocyanate.

The first fluorocarbon triacyl-nitrogen compound, N,N,N',N'-bis(perfluoroglutaryl)perfluoroglutardiamide, has been made from the reaction of perfluoroglutaryl chloride and N-bromoperfluoroglutarimide. The N-bromo compound reacts readily with benzoyl bromide to give N-benzoylperfluoroglutarimide, and with hydrogen bromide to give perfluoroglutarimide. No triacyl compounds were isolated from the reactions with trifluoroacetyl bromide or perfluorooctanoyl bromide.

A new synthesis of N,N-bis-(trifluoromethyl) amides by means of the reaction of bis-(perfluorodimethylamino)-mercury with acyl chlorides is reported. The acyl chlorides used were trifluoroacetyl, acetyl, and benzoyl. Neither phosgene nor trimethylchlorosilane gave the desired amino derivative.

BIBLIOGRAPHY

1. Attaway, J. A., Groth, R. H., and Bigelow, L. A., J. Am. Chem. Soc., 81, 3599 (1959).
2. Avonda, F. P., Gervasi, J. A., and Bigelow, L. A., ibid., 78, 2798 (1956).
3. Barr, D. A., and Haszeldine, R. N., Chem. and Ind., 1050 (1956).
4. Barr, D. A., and Haszeldine, R. N., J. Chem. Soc., 30, (1957).
5. Brown, H. C., and Reilly, W. L., 128th Meeting A.C.S., Minneapolis, Minn., September 11-16, 1955.
6. Brown, H. C., and Reilly, W. L., J. Am. Chem. Soc., 78, 6032 (1956).
7. Brownstein, S. K., J. Org. Chem., 23, 113 (1958).
8. Cady, G. H., et al., Ind. Eng. Chem., 39, 290 (1947).
9. Clark, R. F., and Simons, J. H., J. Am. Chem. Soc., 75, 6305 (1953).
10. Davidson, D., and Skovronek, H., ibid., 80, 376 (1958).
11. England, D. C., et al., ibid., 82, 5116 (1960).
12. Fowler, R. D., et al., Ind. Eng. Chem., 39, 292 (1947).
13. Fukuhara, N. and Bigelow, L. A., J. Am. Chem. Soc., 63, 2792 (1941).
14. Gould, E. S., "Mechanism and Structure in Organic Chemistry," Henry Holt and Company, New York, 1959, p. 700.
15. Hanford, W. E., and Rigby, G. W., U.S. Patent 2,409,274 (1946).

16. Hauptschein, M., and Grosse, A. V., J. Am. Chem. Soc., 73, 5139 (1951).
17. Henne, A. L., Alm, R. M., and Smook, M., ibid., 70, 1968 (1948).
18. Henne, A. L., and Zimmer, W. F., ibid., 73, 1103 (1951).
19. Hentschel, W., Ber., 2395 (1890).
20. Hine, Jack, "Physical Organic Chemistry," McGraw Hill Book Company, New York, 1956, p. 317.
21. Horner, L., and Windelmann, E. H., Angew. Chem., 71, 349 (1959).
22. Johnson, H. W., and Bublitz, D. E., ibid., 72, 753 (1957).
23. Johnson, H. W., and Bublitz, D. E., ibid., 80, 3150 (1958).
24. Kriegsmann, H., Z. anorg. u. allgem. Chem., 294, 113 (1958).
25. Lewis, J., and Wilkins, R. G., "Modern Coordination Chemistry," Interscience Publishers, New York, 1960.
26. Lovelace, A. M., Rausch, D. A., and Postelnek, W., "Aliphatic Fluorine Compounds," Reinhold Publishing Corp., New York, 1958, p. 7.
27. Lovelace, A. M., Rausch, D. A., and Postelnek, W., ibid., p. 17.
28. Lovelace, A. M., Rausch, D. A., and Postelnek, W., ibid., p. 109.
29. Lovelace, A. M., Rausch, D. A., and Postelnek, W., ibid., p. 156.
30. Lovelace, A. M., Rausch, D. A., and Postelnek, W., ibid., p. 262.
31. Lovelace, A. M., Rausch, D. A., and Postelnek, W., ibid., p. 263.
32. Lovelace, A. M., Rausch, D. A., and Postelnek, W., ibid., p. 265.

33. Lovelace, A. M., Rausch, D. A., and Postelnek, W., ibid., p. 333.
- 33a. Mao, T. J., Ph.D. Dissertation, University of Florida, 1960.
34. Martin, J. C., and Bartlett, P. D., J. Am. Chem. Soc., 78, 2553 (1957).
35. McBee, E. T., Ind. Eng. Chem., 39, 415 (1947).
36. Migridichian, V., "The Chemistry of the Organic Cyanogen Compounds," Reinhold Publishing Corp., New York, 1947, p. 56.
37. Migridichian, V., ibid., p. 61.
38. Migridichian, V., ibid., p. 62.
39. Moissan, H., Compt. rend., 102, 1543 (1886).
40. Park, J. D., et al., J. Am. Chem. Soc., 74, 2189 (1952).
41. Simons, J. H., Editor, "Fluorine Chemistry," Vol. II, Academic Press, New York, 1955, p. 389.
42. Smith, G. H., U.S. Patent 2,701,814 (1955).
43. Thompson, Q. E., J. Am. Chem. Soc., 73, 5841 (1951).
44. Tinker, J. M., U.S. Patent 2,255,868 (1941).
45. Walling, C., "Free Radicals in Solution," John Wiley and Sons, Inc., New York, 1957, p. 48.
46. Walling, C., ibid., p. 381.
47. Wiley, R. H., and Guerrant, W. B., J. Am. Chem. Soc., 71, 981 (1949).
48. Young, J. A., unpublished results.
49. Young, J. A., Durrell, W. S., and Dresdner, R. D., J. Am. Chem. Soc., 81, 1587 (1959).
50. Young, J. A., Tsoukalas, S. N., and Dresdner, R. D., ibid., 80, 3604 (1958).

51. Young, J. A., Simmons, T. C., and Hoffmann, F. W., ibid.,
78, 5637 (1956).
52. Ziegler, K., et al., Ann., 551, 80 (1942).

BIOGRAPHICAL SKETCH

William Sandford Durrell was born October 14, 1931, in Miami, Florida. He was graduated from Ft. Lauderdale High School in June, 1949. In August, 1953, he received the degree of Bachelor of Science in Chemistry from the University of Florida. From that time until February, 1956, he worked as a research chemist at Peninsular Chem-Research, Gainesville, Florida, and at the Ethyl Corporation in Baton Rouge, Louisiana. He was then called into active duty in the United States Air Force and was stationed at Wright Air Development Center, Wright-Patterson Air Force Base, Dayton, Ohio. In January, 1958, he enrolled in the Graduate School of the University of Florida and has held the position of Research Assistant until the present time, while pursuing his work toward the degree Doctor of Philosophy.

William Sandford Durrell is married to the former Mary Jane Kusbel and is the father of twin daughters. He is a Captain in the United States Air Force Reserve and is a member of the American Chemical Society, Alpha Chi Sigma, Phi Beta Kappa, and Sigma Xi.

This dissertation was prepared under the direction of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

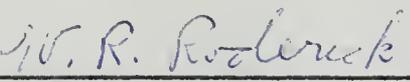
June 5, 1961



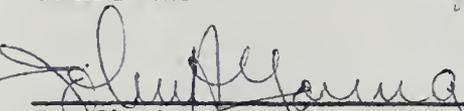
Dean, College of Arts and Sciences

Dean, Graduate School

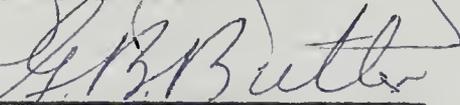
Supervisory Committee:

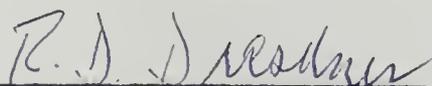
 for P. Tarrant

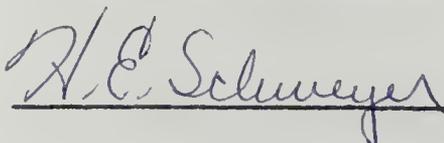
Chairman



Co-Chairman







32506