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ML-TDR-64-142
PART V
AD0842832

THERMALLY STABLE PERFLUORINATED POLYMERS

Henry C. Brown
University of Florida

TECHNICAL REPORT ML-TDR-64-142, PART V

July, 1968

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ML-TDR-64-142
Part V

THERMALLY STABLE PERFLUORINATED POLYMERS

Henry C. Brown
University of Florida

FOREWORD

This report was prepared by the University of Florida under USAF Contract AF-33(615)-3782. The contract was initiated under Project No. 7340, "Nonmetallic and Composite Materials," Task No. 734004, "New Organic and Inorganic Polymers." The work was administered under the direction of the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, with Dr. Christ Tamborski as Project Engineer.

This report covers work performed during the period 1 March 1967 through 29 February 1968, under the direction of Dr. Henry C. Brown, Principal Investigator. Other personnel employed during the period include Dr. Anthony Palmer, Research Associate, Mr. John Turnbull and Mr. Gerald McNeely, Research Assistants.

The report was submitted by the author in May 1968.

This technical report has been reviewed and is approved.

William E. Gibbs

WILLIAM E. GIBBS
Chief, Polymer Branch
Nonmetallic Materials Division
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ABSTRACT

Studies of the poly(perfluoroalkylene-1,2,4-oxadiazole system have been continued; incorporation of bi-oxadiazole linkages in the polymer structure has led to significant changes in the polymer properties.

New monomers for the acyl chloride-tetrazole polymerization reaction have been developed; these monomers have, as a part of their structure, triazole or bioxadiazole linkages which thus become incorporated in the final polymer.

Attempts have been made to synthesize new four and six membered heterocylic systems which have perfluoroalkyl substituents on the ring.

Limited further investigation of the metallic derivatives of perfluoroalkyl-substituted-1,2,4-triazoles has been carried out.

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I. INTRODUCTION

The objective of this research is the synthesis of fluorinated polymers that are stable at high temperatures and are chemically inert. Emphasis has been placed on polymers which have heterocyclic units connected by perfluoroalkylene groups as the backbone chain.

During the present contract period the synthesis of poly(perfluoroalkylene-1,3,4-oxadiazoles) has been extended to include polymers which have both oxadiazole and bioxadiazole linkages in the chain by a terpolymerization reaction using 1,3 bis(5-tetrazolyl)perfluoropropane, bitetrazole and perfluorosebacoyl chloride.

The preparation of several new monomers which contain bioxadiazole or 1,2,4-triazole groups has been carried out; these materials will be used in the typical polymerization reaction developed for polyoxadiazole formation.

A limited amount of further effort has been devoted to the study of the metallic derivatives of the perfluoroalkyl-substituted -1,2,4-triazoles.

Attempts have been made to synthesize new heterocyclic systems from the reactions of hexafluoroacetone or hexafluoropropane imine with perfluorobutyronitrile, perfluorobutyramidine and N(perfluorobutyrimidoyl)perfluoroamidine.

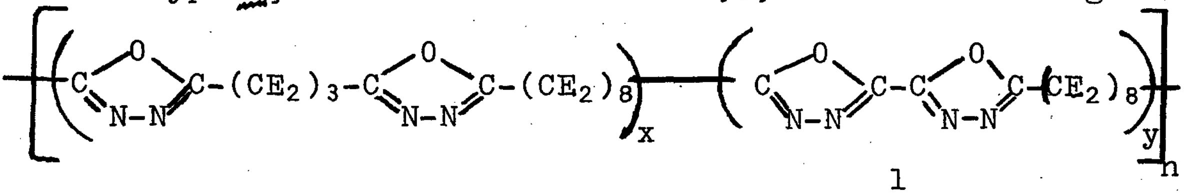
II. DISCUSSION

A. Poly(perfluoroalkylene-1,3,4-oxadiazoles)

1. Reaction of 1,3 *bis*(5-tetrazolyl)perfluoropropane, bitetrazole and perfluorosebacoyl chloride.

The previous report (ML-TDR-64-142 Pt. IV) described the preparation of poly(perfluoroalkylene-1,3,4-oxadiazoles) from the reaction of perfluorosebacoyl chloride and 1,3-*bis*(5-tetrazolyl)perfluoropropane. Elastomeric materials that were relatively stable at elevated temperatures and resistant to solvents were obtained; these polymers, however, had a rather low melting point and slowly crystallized at room temperature.

During the present period polymerizations of a similar type have been carried out using a mixture of 1,3-*bis*(5-tetrazolyl)perfluoropropane and bitetrazole with perfluorosebacoyl chloride in an effort to introduce the less flexible bioxadiazole unit in the chain. The polymers that have been produced apparently have a random structure of the type 1, which contains both 1,3,4-oxadiazole rings and 1,3,4-bioxadiazole rings. These polymers have a much higher softening point than those previously made with only the 1,3,4-oxadiazole units. Films have been pressed from samples at 180°-200°. They appear to be insoluble and stable in air at 300°. We do not yet know the ratio of oxadiazole and bioxadiazole rings actually incorporated in the polymer, though the presence of both can be seen by examination of the infrared spectra.



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In the early reactions of 1,3-*bis*(5-tetrazolyl)-perfluoropropane, bitetrazole and perfluorosebacoyl chloride in xylene, some elastomeric materials were obtained. Several subsequent attempts to repeat this reaction failed, leading to a further investigation of the bis-tetrazole monomer and the reaction itself. A later reaction then led to the successful preparation of an elastomer. Details of these efforts are given below.

A typical reaction was run wherein a 7 to 3 molar ratio of the bis-and bi-tetrazoles, respectively, were reacted with a xylene solution of perfluorosebacoyl chloride. A distillation head was attached to the reaction flask and the system was protected from atmostpheric moisture by dry-ice traps. After the stirring slurry was heated at 85-90° for 12 hours, the temperature was raised and the xylere was removed by distillation. Then over a one hour period, the remaining cream-colored residue was heated to 215°, where it melted, became very dark and evolved a gas. After 12 hours at 215°, 3.5 hours at 22° and 7 hours at 240° no further gas evolution was noted. The product on cooling was dark amber and very brittle, having no elastomeric properties.

Lower molecular weight products were removed with ethyl acetate. The remaining portion softened at 220°C and melted at 270°C with decomposition. An infrared spectrum indicated the presence of both oxadiazole and bioxadiazole groups. The strength of -COOH carbonyl peak relative to the strongest oxadiazole peak (7.1μ) was approximately 2:5.

A similar reaction in dry ethyl acetate, wherein the same reactants were heated at reflux for 82 hours, at 220-225° for 21 hours and at 322-4° for 2 hours yielded a similar dark amber, brittle product having no elastomeric properties.

It was concluded that the temperature had been raised too rapidly, causing decomposition of the tetrazole end-groups rather than promoting oxadiazole formation. Thus the extent of the reaction under milder conditions was examined in order that ideal conditions could be more closely attained.

To this end, a 7 to 3 molar ratio of bis-and bi-tetrazole, respectively, was reacted with a dry xylene solution of perfluorosebacoyl chloride. The stirring slurry, protected from atmostpheric moisture by dry-ice traps, was heated at 90-92° for 32 hours and at 100-130° for 14.5 hours. At this time a white slurry was still present. The mixture was filtered and the white, solid product recovered and dried under reduced pressure.

An infrared spectrum of this crude product showed the presence of both oxadiazole and bioxadiazole peaks. Absorptions were also present which could be attributed to unreacted tetrazole groups. The relative strengths of the -C=0 to the oxadiazole peaks indicated that the product was of very low molecular weight. This fact was also evidenced by the product's solubility in hot ethyl acetate, tetrahydrofuran and diglyme.

The xylene filtrate was evaporated and yielded a tan solid, identified by its infrared spectrum and melting point as perfluorosebacic acid. The amount recovered represented approximately 10% of the starting acid chloride.

These results show that under the above conditions oxadiazole formation occurs. However, there is still 10% of the starting acid chloride that is unreacted. No evidence of tetrazole decomposition under these conditions was noted.

In order to gain an insight as to proper conditions for the polymerization reaction the thermal stability of the 1,3-bis(1,5-tetrazolyl) perfluoropropane was investigated.

The bis-tetrazole which had been used in the polymerization reactions to this point, and had been prepared according to teh method previously reported (Technical Report ML-TDR-64-142 Part III, August 1966), was examined. Its infrared spectrum indicated a pure product and its melting point of 158-160° seemed to be satisfactory. (H. C. Brown and Robert J. Kassal, J. Org. Chem. 32, 1871(1967), report a melting point of 159.8-160-5°). However, when heated to its melting point rapid decomposition (gas evolution) occurred and a dark yellow melt resulted.

In an attempt to obtain pure bis-tetrazole the preparation referred to above was repeated with modifications. The crude bis-tetrazole obtained from the reaction was found to be contaminated with its mono- or disodium salt. The normal method of obtaining the free tetrazole, that is by treatment with concentrated HCl, was abandoned since the bis-tetrazole was found to form strong hydrates. In order to avoid the presence of water as much as possible, a slurry of the product mixture in anhydrous diethyl ether was treated with a large excess of gaseous HCl. The insoluble NaCl was discarded and the solvent was removed under reduced pressure, leaving white, solid bis-tetrazole. The product was washed with bezene to remove any traces of acetic acid, and dried under reduced pressure (0.01-0.02 mm Hg) at 90° for 3 days. Still, the product melted at 157-9°C and decomposed rapidly.

Further purification is normally accomplished by recrystallization from heptafluorobutyric acid. This is not satisfactory however, since traces of this acid are difficult to remove unless higher temperatures are used where slow tetrazole decomposition can also occur. As a result the lower homolog was used. The bis-tetrazole which recrystallized from pentafluoropropionic acid was recovered and dried under reduced pressure at 80°C for 2 days. The best melting point which could be obtained, even after numerous recrystallizations, was 160-161.5°C. With this product however, the melt was clear and colorless. Only slow decomposition (gas evolution) was noted at 173°C. Even at 185°C the rate of decomposition did not increase greatly and the melt remained clear and colorless.

Thus, although the melting point had not been raised much, a marked effect was noted on the stability of the compound. This increased stability is especially important in the polymerization reaction where tetrazole decomposition can compete with polymerization.

After the preceding efforts, a reaction was run from which an elastomeric product was obtained.

A mixture of dry bis- and bitetrazoles (8:2) was reacted with a xylene solution of freshly distilled perfluorosebacoyl chloride. Neither on mixing the slurry at room temperature, nor after heating at 80° for 40 hours was there any sign of reaction occurring. However, at 90° first signs of gas evolution were noted. During the following 25 hour heating period at 90° some spattering of solids to the upper part of the flask occurred, presumably due to stirring which became too rapid as the solids of the slurry began to cling to the walls of the flask. Heating was continued at 98° for 23.5 hours, 116° for 29 hours and at 140° for 19 hours. During this time the spattered solids had become very dark, but the product in the bottom of the flask, in contact with the xylene-acid chloride solution, was still cream-colored. When no further gas evolution was noted and prior to further heating, a 10% excess (0.5333 gms., 1.01×10^{-3}m) of acid chloride was added so that the final product would have the more stable -COOH end-groups. The pressure was then lowered to 431 mm. Hg and the xylene was distilled from the reaction flask. The reaction mixture was then heated at 186° for 23.5 hours, and at 197° for 46 hours. The product turned dark amber but no further gas evolution was noted.

The pressure was then reduced and all volatile products were collected. On evaporation of the solvent 0.26 gms. of tan solid, identified by its infrared spectrum and melting point as perfluorosebacic acid remained.

The amber polymer remaining in the flask was not tacky, did not adhere to the glass, was flexible and had strength. All of the xylene, tetrahydrofluran and ethyl acetate soluble materials were washed from the crude product. The insoluble portion was pressed to a transparant elastomeric film at 180°. Its infrared spectra showed the expected oxadiazole and bioxadiazole peaks. The -C=0 absorption due to the -COOH end-groups was 2:7 in intensity relative to the strongest oxadiazole peak (7.1μ).

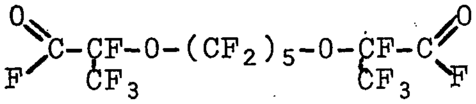
A 2 mil sample of the film was heated in air. After 31 hours at 200-210° there was no apparent change. At 240° the film softened and grew slightly darker. After heating at 240-242° for 19 hours, 300° for 22 hours, 325° for 2.5 hours, and 350° for 6 hours the product was still soft, flexible, light amber and transparent. After heating over night (12 hours) at 350° however, the film had become very dark amber, curled and brittle.

The product was highly insoluble. Among the many solvents tried were boiling ethyl acetate, $C_7F_{15}CO_2CH_3$, diglyme, pyridine, nitrobenzene, dimethyl sulfoxide, Sulfolane A and ethyl cellosolve. The polymer seemed to be slightly soluble in dimethyl formamide and dimethylacetamide. However, no precipitate could be recovered on addition of water to the solutions. This leads to the conclusion that on extensive boiling amine base must have been liberated which then attacked the oxadiazole ring, leading to hydrolysis.

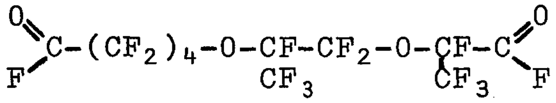
The product was stable to boiling concentrated nitric and heptafluorobutyric acids. Boiling, concentrated sulfuric acid slowly degraded the polymer. Likewise, as expected, aqueous base slowly hydrolyzed the product.

2. Reaction of the perfluoroether-diazyl chloride with 1,3 bis(5-tetrazolyl)perfluoropropane.

The perfluoro-ether diacyl fluoride as originally obtained was a liquid mixture:



(75%)



(25%)

An infrared spectrum of the neat liquid showed the characteristic C=0 of an acyl fluoride at 5.3μ.

The diacyl-fluorides were quantitatively hydrolyzed in refluxing distilled water to the respective dicid. The clear liquid product was identified by its infrared spectrum which showed a C=0 absorption at 5.6μ and the accompanying -0-H absorptions at 3.0-3.5μ expected for the acid function.

Two methods of preparing the diacyl chlorides were attempted. Both thionyl chloride and phosphorous pentachloride were employed as reagents. The preparation utilizing thionyl chloride was not satisfactory as the reaction product was contaminated with sulphur and decomposition products which could not be effectively separated. A sample of the diacyl chloride was obtained however after refluxing the acid in a large excess of phosphorous pentachloride overnight. The clear, colorless liquid product that was recovered was identified as the diacyl chloride by its infrared spectrum. A single acyl chloride C=O peak was present at 5.5µ. In addition, no absorption due to -O-H was present.

Due to the small amount, 2.5 gms., of material available, further characterization and purification were impractical. From the infrared spectrum it is apparent that any impurities possibly present (as H_3PO_4 or its derivatives) are in very small amounts.

Due to the possible presence of contaminate in the diacyl chloride prepared above, a slight excess (1.13 to 1.00) was reacted with 1,3-bis(5-tetrazolyl) perfluoropropane in a dry xylene slurry. The reactants were mixed under a dry nitrogen atmosphere at room temperature. No visible changes occurred until the mixture was heated to reflux (140°C), where an insoluble gum appeared and gaseous HCl evolution was noted. After 132 hours at 142-5°C, a light tan viscous product was recovered. Infrared spectra showed the presence of the oxadiazole function by its characteristic absorptions at 6.4 and 7.1µ. A weak absorption due to C=O was present at 5.5µ. The product was insoluble in diethyl ether, chloroform, hot diglyme, hot acetonitrile and hot alcohol. Very slight solubility was noted in hot tetrahydrofuran and acetone. The product was soluble in ethyl acetate, the methyl ester of trifluoroacetic acid and hot dimethylformamide.

A small portion of the crude polymer was heated under reduced pressure; after 2 hours at 110°C a clear, light-tan melt was present. Further heating, 18.5 hours at 153°C, 19.5 hours at 220°C, 20 hours at 270°C and 20.5 hours at 338°C, caused the product to become dark brown, tacky and opaque. The material had not carbonized, however. Its infrared spectrum showed no change from that of the original product. Solubility was noted only in hot ethyl acetate.

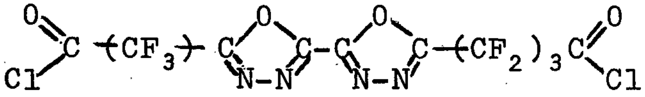
A portion of the dark brown sample, treated as above, was left standing in concentrated nitric acid for 3 days at room temperature and for 3-1/2 hours at 100°C. The remaining light-tan viscous product was washed with water, extracted with hot ethyl acetate and dried. Its infrared spectrum was identical to that of the material before treatment.

Although the product obtained was more like a heavy fluid, as might be expected due to the flexibility of the ether chain of the diacyl chloride monomer, the purpose of the experiment was accomplished in that the reaction was shown to proceed successfully yielding the expected polymer. Also, since small amounts of the reagents were used, as well as a known slight excess of the diacyl chloride, a lower molecular weight product would be expected.

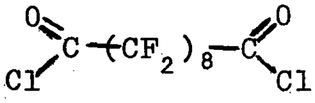
3. Reaction of the bioxadiazole monomer

The use of the bioxadiazole monomer (described in Sect. III B-2) in the preparation of poly(perfluoroalkylene-1, 3,4-oxadiazole) polymers was viewed as advantageous since (a) it should provide a more regular distribution of bioxadiazole units in the polymer and (b) it forms miscible suspensions in common organic solvents. A reaction utilizing this monomer is described below.

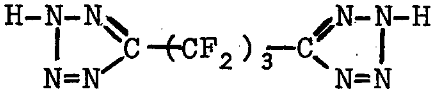
Under a dry nitrogen atmosphere, at room temperature the reactants were added to a round bottom flask with 60 mls. of dry ethyl acetate. The reactants were:



4.0710g 7.23×10^{-3} m



7.6085g 14.43×10^{-3} m



6.2199g 21.60×10^{-3} m

Protected from atmospheric moisture by two Dry Ice traps and a dry nitrogen sweep, the suspension was stirred and refluxed (77°C) for 46 hours. No apparent change occurred except that the suspension had become light tan.

Approximately 25 mls. of dry xylene was added to the reaction flask, and the reflux condenser was replaced with a distillation head. Heating was resumed and the ethyl acetate was distilled from the reaction flask as the temperature rose to that of refluxing xylene. In the xylene, an insoluble, tacky, light tan residue was present. After 41 hours at reflux (140°) no apparent change had occurred. The xylene was then decanted and the residue was heated in an oil bath under reduced pressure (0.01-0.02 mm Hg). At 120° the product, as a melt, could be stirred. Over a three hour period the temperature was raised to 248°C, during which time the product became darker and more viscous as slow gas evolution was noted. After 19 hours at 248°, no further gas evolution occurred and a very dark amber product was present.

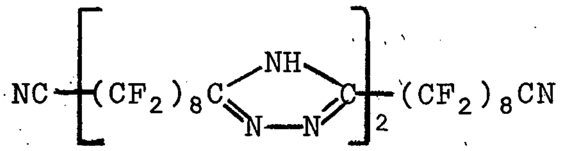
The product was pressed to a thick film. Although it was flexible above room temperature it did not possess any strength, and softened at 195-205°. Insolubility was noted in acetone, boiling ethyl acetate and tetrahydrofuran, and in concentrated nitric acid at 100°. An infrared spectrum indicated the presence of both oxadiazole and bioxadiazole groups as well as -COOH. The strength of the -C-O peak relative to the strongest oxadiazole peak (7.1μ) indicates the product to be of low molecular weight.

It also appeared from the spectrum that some C-H may have been incorporated into the product. Since the bioxadiazole monomer was successfully prepared in ethyl acetate it does not seem likely that the solvent would interfere with oxadiazole formation here. However, under conditions where tetrazole end-groups would decompose we might then expect solvent to be incorporated.

Results of the reaction indicate that oxadiazole formation occurred to an extent. It now appears that the reaction temperature was raised too rapidly. At elevated temperatures, 140°C or greater, decomposition of tetrazole competes with oxadiazole formation. The reaction will be repeated with necessary modifications.

B. Preparation of New Monomers

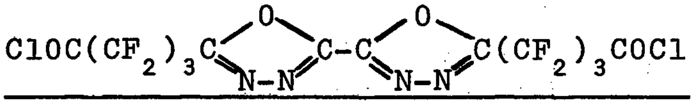
1.



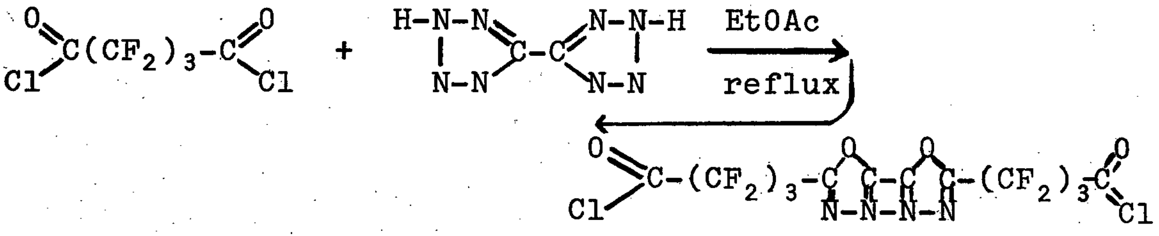
During this period a new monomer was prepared which contained two triazole ring and nitrile end-groups. This compound was prepared by adding a dilute solution of perfluorosebachydrazide to a large excess of perfluorosebaconitrile at room temperature. The product obtained from the initial addition was a white solid whose structure was determined from its infrared spectra. The spectra contained peaks at 2.86, 3.02, and 3.14μ which are due to N-H stretching or possibily O-H stretching for the 2.86μ peak, a peak at 4.4μ due to C≡N, a peak at 5.82μ due to C=O, a peak at 6.01μ due to C=N, a peak at 6.1μ which could be due to C=N or N-H deformation, and a peak at 6.44μ due to N-H deformation. Each of these peaks, with the exception of the 4.4μ peak is also present in the spectra of the intermediate model compound obtained from perfluorobutyronitrile and perfluorobutyrhydrazide.

Two methods were used to split out water from this compound to obtain the triazole structure. A sample of the compound was heated at 280°C under reduced pressure in a sublimation apparatus for one hour. This resulted in approximately one half of the compound decomposing while the other half was dehydrated and sublimed as the triazole. Another sample was heated in refluxing $POCl_3$ for two hours and this treatment resulted in only partial ring closure. The latter method of ring closure appears to be the best since the partial ring closure is probably the result of insufficient reation time. The work done with this monomer was limited due to the lack of starting materials. However, the above type of reaction was repeated using perfluoroglutaronitrile and perfluoroglutarohydrazide as starting materials (See Sect II B 5 and III B 5). This type of monomer offers a very attractive way to obtain a linear polymer which has both triazole and oxadiazole rings in the polymer chain. This type polymer could be obtained by converting the nitrile end-groups of the above monomer to tetrazole groups then reacting this monomer with a diacyl chloride.

2.



In order to incorporate the bioxadiazole linkage into the poly(perfluoroalkylene-1,3,4-oxadiazole) polymer system, it was desirable to prepare a monomer having the bioxadiazole function with acyl chloride groups. This monomer would be expected to have nearly the same reactivity as the parent perfluorodiacyl chlorides and thus would provide a more regular distribution of bioxadiazole units in the polyoxadiazole polymers.



Eq. 1

The reaction shown in Eq. 1 was first attempted by adding solid bitetrazole to an 8 to 1 excess of perfluoroglutaryl chloride. When no reaction occurred at room temperature the mixture was refluxed for 4 days. Although some of the expected product was recovered, due to accompanying hydrolysis the yield was low and contamination with glutaric acid, from which separation is difficult, was high.

In order to eliminate the extensive hydrolysis of the acyl chloride encountered initially, the use of a dry, water immiscible reaction medium was called for; reagent grade ethyl acetate, which was dried by distillation from P_2O_5, was chosen.

A solution of freshly purified and distilled perfluoroglutaryl chloride (9.7×10^{-2}m) in 25 mls. of ethyl acetate was added, under a dry nitrogen atmosphere, to solid bitetrazole (2.18×10^{-2}m) at room temperature. Anhydrous conditions were maintained throughout the experiment to prevent hydrolysis of the 4.4 to 1.0 excess of acyl chloride. After refluxing for 41.5 hours a white suspension was present. The volatile starting materials and products were removed from the reaction mixture leaving a quantitative yield of white solid (flakes) product.

Thatthe expected product was indeed obtained was confirmed by its infrared spectrum. Peaks attributable to the bioxadiazole function (6.4, 6.8 and 7.3μ) and to the acyl chloride (-C=O) function (5.55μ) were present. Absence of any hydrolysis to -COOH was further confirmed by the absence of any accompanying -O-H stretching absorptions. As might be expected for such a product the solubility behavior was unusual. In the common organic solvents and water, a cloudy suspension (miscible, however) was obtained. In larger amounts of the polar, hot solvents complete solution could be obtained. The crude product melted slowly from 188-193°.

3. Reaction of perfluoroglutaric anhydride with hydrazine.

If the end-groups of the monomer described in Sect. II B-1 or II B 4 were converted to either acid chloride or tetrazole, this monomer could possibly be incorporated into a polymer having the arrangement of triazole and oxadiazole groups shown in Fig. 1:

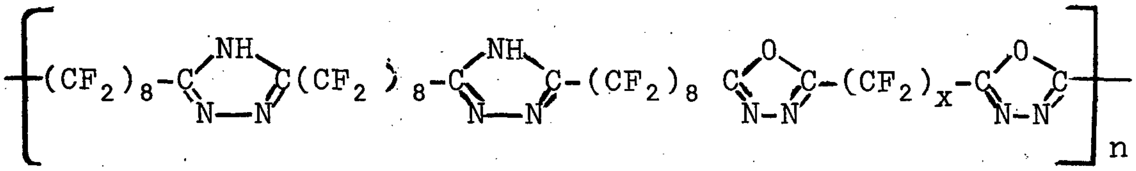


Fig. 1

Alternatively, a monomer containing only one triazole group would allow the incorporation of this type of linkage into a polymer structure one unit at a time to give the polymer shown in Fig. 2:

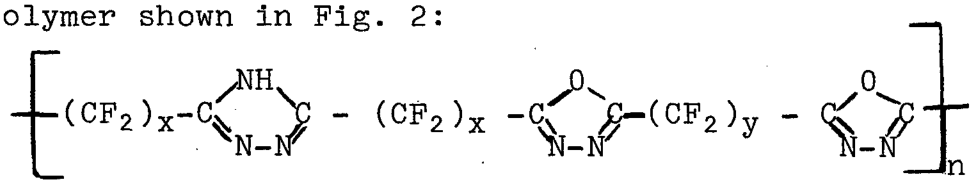


Fig. 2

The simplest approach to such a monomer appeared to be the addition of hydrazine to a large excess of perfluoroglutaronitrile followed by ring closure of the intermediate to give the triazole ring. However this reaction resulted in the formation of a cyclic 1:1 nitrile-hydrazine adduct.

Another approach to the monomer is the addition of hydrazine to a large excess of perfluoroglutaryl chloride to get a diacylhydrazine with acyl end-groups. This compound could then be converted to the desired monomer via the oxadiazole. A reaction between excess perfluoroglutaryl chloride and hydrazine gave a quantitative yield of hydrazine hydrochloride.

Still another approach to the monomer is the use of perfluoroglutaric anhydride in the place of perfluoroglutaryl chloride. Perfluoroglutaric anhydride was prepared in two steps from the acid chloride and several reactions were carried out between the anhydride and hydrazine. The hydrazine was added slowly to a large excess of the anhydride which was cooled to -40°. During the addition of the hydrazine a white solid precipitated continuously. This solid dissolved in the excess anhydride when the contents of the flash were heated to reflux and reprecipitated when the solution was cooled to room temperature. The anhydride was removed under reduced pressure and a very hygroscopic white solid was obtained. This white solid melted between 75-95° and its infrared spectra was very similar to the spectra of perfluoroglutaric acid. The major difference in the two spectra was the appearance of a weak peak at 6.5μ in the spectra of the white solid which was not in the spectra of perfluoroglutaric acid.

Attempts to separate the perfluoroglutaric acid from any diacylhydrazine derivative present by fractional precipitation were unsuccessful. Since these attempts were unsuccessful, the white solid was mixed with P_2O_5 and heated. This treatment should convert the perfluoroglutaric acid to the anhydride which could be removed easily by distillation while the diacylhydrazine derivative was dehydrated to the oxadiazole. During the distillation of the anhydride a small amount of white solid sublimed from the reaction flask. This solid was ether-soluble but no additional ether-soluble product was obtained by treating the reaction mixture with ether and then evaporating the ether to dryness.

By treating the diacylhydrazine derivative with P_2O_5 it was possible that a polyanhydride was formed by splitting out water between the acid end-groups of the diacylhydrazine derivative. A small amount of water was added to the reaction mixture and the aqueous solution was shaken with ether. However no additional ether soluble product was obtained when the ether was evaporated to dryness. The white sublimate obtained from this reaction represented 12% of the expected yield of oxadiazole.

Since the diacylhydrazine derivative was not obtained free of perfluoroglutaric acid, the cause of the low yield could not be determined from the above procedures. It was possible that the diacylhydrazine derivative or the oxadiazole was partially decomposed by the heating in the presence of the polyphosphoric acid formed in the reaction. Another possibility is that the amount of diacylhydrazine derivative formed in the reaction between the anhydride and hydrazine was very low and that the treatment with P_2O_5 had no degradative effect.

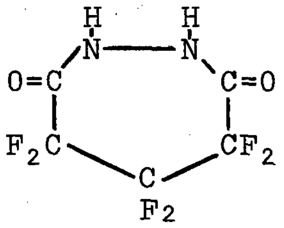
In order to determine the cause of the low yield of the ether soluble product obtained from the above series of reactions, the reaction between perfluoroglutaric anhydride and hydrazine was repeated. This time the anhydride-insoluble white solid was removed by filtration and identified as perfluoroglutaric acid from its infrared spectra and melting point. The excess anhydride was removed from the filtrate under reduced pressure and a small amount of white residue was obtained. This residue was heated carefully in a sublimation apparatus under reduced pressure between 100 and 110° and additional perfluoroglutaric acid was collected on the cold finger. Approximately 5 grams of pale white residue could not be sublimed at this temperature. This 5 grams of solid which represented 10.5% of the expected yield of the diacylhydiazine derivative softened at 145° and slowly melted to a very viscous liquid between 145 and 175°.

In order to rule out the possibility of the low yield of the diacylhydrazine derivative resulting from the presence of hydrogen chloride in the perfluoroglutaric anhydride, another reaction between the anhydride and hydrazine was carried out. The anhydride used in this reaction was tested and found to be free of chloride ion. However the yield of this reaction was also very low.

The infrared spectra of the white solid obtained from the initial anhydride-hydrazine reaction and the white sublimate obtained from the P_2O_5 reaction were very similar. Both contained peaks at 3.0 - 3.3µ, 5.55 - 5.8µ, 6.45 - 6.7µ, and 7.4µ. These peaks could be assigned to the diacylhydrazine derivative expected from the above reactions but not to oxadiazole. The infrared spectra of oxadiazole contains a very strong peak at 7.1 - 7.15µ; therefore it must be concluded that heating of the initial adduct above with P_2O_5 did not give oxadiazole.

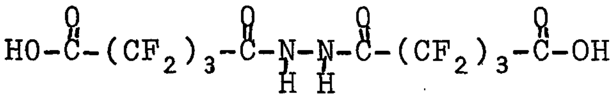
When the two solids (initial adduct and sublimate from P_2O_5) were separately heated in a sublimation apparatus under reduced pressure between 130-140° a portion of each material sublimed. The sublimates from each gave the same infrared spectra and had the same melting points. The residues from each sample were also the same.

The infrared spectra of the sublimates contained peaks at 2.96µ, 5.60µ, 5.66µ, 6.64, and 7.47µ. This material had a molecular weight of 247 (VPO). This molecular weight is very close to the molecular weight (236) of a 1:1 anhydride - hydrazine adduct with the following structure:



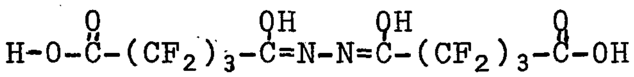
The infrared spectra is also consistent with this structure with the 2.96µ peak due to imino N-H stretch, the 5.60µ and 5.66µ peak due to carbonyl, and the 6.64µ peak due to imino N-H deformation.

The molecular weight of the residue was 495 (VPO) which is close to the molecular weight (476) of the diacylhydrazine derivative having the following structure:



$$\mathrm{HO-\overset{O}{\overset{\|}{C}}-(CF_2)_3-\overset{O}{\overset{\|}{C}}-\underset{H}{N}-\underset{H}{N}-\overset{O}{\overset{\|}{C}}-(CF_2)_3-\overset{O}{\overset{\|}{C}}-OH}$$

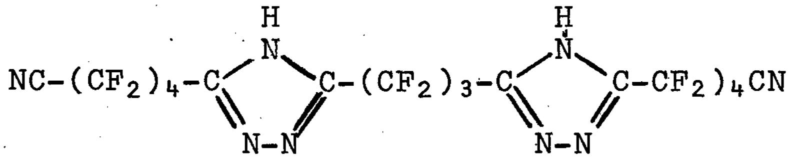
The infrared spectra of the residue contained peaks at 3.1μ, 3.28μ, 5.7μ, 6.0μ, 6.77μ, and 6.95μ. This spectra is not the same as the spectra of the diacylhydrazine derivatives which have perfluoroalkyl end groups. The major difference is that the spectra of the latter compounds contain no peak at 6.0μ. If this peak is due to C=N, the tautomeric form shown below could account for its presence:



$$\mathrm{H-O-\overset{O}{\overset{\|}{C}}-(CF_2)_3-\overset{OH}{C}=N-N=\overset{OH}{C}-(CF_2)_3-\overset{O}{\overset{\|}{C}}-OH}$$

The O-H groups of this structure would be expected to be highly associated through hydrogen bonding and could account for the peaks at 3.1 and 3.28μ. The peak at 5.7μ is probably due to the carbonyl of the acid end groups.

4.



Since the perfluoroadiponitrile needed for the preparation of this monomer was not available from stock, it was prepared from perfluorocyclohexene. This material was oxidized to perfluoroadipic acid by treating it with $KMnO_4$ in acetone. The oxidation was rapid (175 grams of perfluorocyclohexene reacted within two hours) and three oxidations yielded 414 grams of perfluoroadipic acid which represented a yield of 79%. The acid was esterified with absolute ethanol in benzene in the presence of a small amount of concentrated H_2SO_4. This esterification was carried out by refluxing the acid, ethanol, benzene, and H_2SO_4 and removing a water-ethanol-benzene azeotrope over a period of several days. When no more water could be removed the benzene and excess ethanol were removed under reduced pressure. The crude ester was washed with water, extracted with ether, and dried over Drierite. The viscous ester was distilled and a pale yellow liquid, 311 grams, was obtained between 210-221°C.

The ester was then treated with ammonia and 244 grams of light tan perfluoroadipamide was obtained The diamide was dehydrated with P_2O_5 and a total of 190 grams of perfluoroadiponitrile was obtained. The overall yield of perfluoroadiponitrile based on the quantity of perfluorocyclohexene was 45%.

The preparation of the dinitrile monomer consisted of two steps. The first step was the addition of perfluoroglutarhydrazide to a large excess of perfluoroadiponitrile to get a 2:1 molar perfluoroadiponitrile-perfluoroglutarhydrazide adduct. The second step was dehydration of this adduct to produce the dinitrile monomer which contained triazole rings.

The low solubility of perfluoroglutarhydrazide in non-polar and slightly polar organic solvents constituted a problem in the first reaction. Not only did the solubility of the hydrazide have to be considered in choosing a solvent but also the ease with which the excess perfluoroadiponitrile would react with the solvent, and the ease with which the excess perfluoroadiponitrile could be recovered had to be considered. Another problem that was expected was the formation of products other than the 2:1 molar perfluoroadiponitrile perfluoroglutarhydrazide adduct.

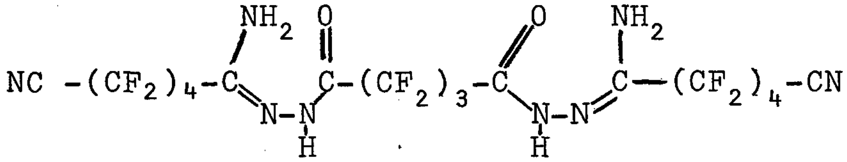
The first solvent used in this reaction was dioxane. A dioxane solution of 5.0 grams of perfluoroglutarhydrazide was added slowly to a large excess of refluxing perfluoroadiponitrile and a yellow solution was obtained. The dioxane and excess perfluoroadiponitrile were removed under reduced pressure and a tacky, yellow solid was obtained. This solid was taken up in boiling ether and 5.0 grams of white, ether-insoluble solid were obtained by filtering. The filtrate was evaporated to dryness to yield 7.5 grams of pale yellow solid. The 5.0 grams of white solid represented a yield of 60% of the desired product.

In an attempt to increase the yield of this white solid propionitrile was used next as the solvent for 7.3 grams of perfluoroglutarhydrazide. The same procedure was used in this reaction but in this case a white solid precipitated from the reaction mixture during the addition of the hydrazide solution. The excess perfluoroadiponitrile was distilled from the reaction flask and then the contents of the flask were filtered. The white solid was washed with ether and 12.5 grams of product represented a yield of 80% of the desired adduct.

The low solubility of perfluoroglutarhydrazide in propionitrile required that large quantities of hot solvent be used to keep the hydrazide in solution.

Preliminary tests showed that perfluoroglutarhydrazide was more soluble in acetonitrile than in propionitrile and that acetonitrile and perfluoroadiponitrile could be separated by distillation. Therefore acetonitrile was used next as a solvent in order to cut down the dilution of the perfluoroadiponitrile as the perfluoroglutarhydrazide was added. Although less solvent was needed to dissolve the perfluoroglutarhydrazide and a more compact reaction system could be used for the reaction, the yield of the desired product was essentially unchanged.

The white crystalline solid obtained from the above reactions had a melting point of 191-192°C and has been tentatively assigned the following structure based upon its infrared spectra:

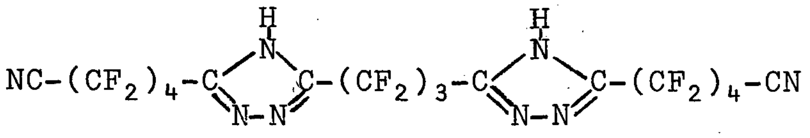


The infrared spectra of this compound contained peaks at 2.88, 3.05, and 3.15μ due to N-H, a weak peak at 4.4μ due to C≡N, a peak at 5.82μ due to C=O and a peak at 6.05μ due to C=N. Other absorption maxima were found at 6.15, 6.45, and 7.1μ. All the above peaks, with the exception of the peak at 4.4μ, are present in the infrared spectra of the product obtained from the similar reaction of 2:1 molar quantities of perfluorobutyronitrile and perfluoroglutarhydrazide.

The pale yellow solid obtained from the above reactions gave an infrared spectra very similar to the spectra of the white crystalline solid but the yellow solid melted over a very much larger temperature range.

The dehydration of the 2:1 molar perfluoroadiponitrileperfluoroglutarhydrazide adduct was carried out by heating this adduct with a large excess of P_2O_5 at atmospheric pressure, then removing the dehydrated product by subliming the mixture under reduced pressure. This process yielded a mixture of the dehydrated product and P_2O_5 which was separated by washing with dry ether. The yield of the dehydrated product was∼50% and the remainder of the adduct polymerized.

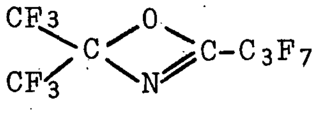
The dehydrated adduct had a melting point of 183-185°C and has been tentatively assigned the following structure based upon its infrared spectra:



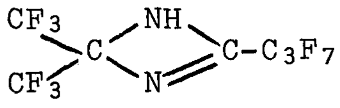
The infrared spectra of this compound contained a broad peak at 3.2-3.5μ due to cyclic N-H, a peak at 4.4μ due to C≡N, a peak at 6.88μ due to cyclic C=N, and other characteristic peaks at 7.1 and 7.5μ. All of these peaks with the exception of the peak at 4.4μ are characteristic of the previously prepared triazole model compounds.

C. Attempted Syntheses of New Ring Systems

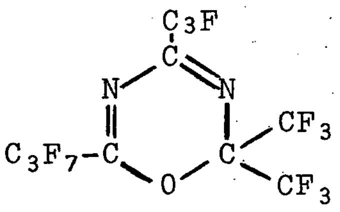
The objective of this portion of this project is the synthesis of the ring systems 1 to 4, study of the thermal and chemical stability of the model compounds, and incorporation of these structures into polymeric chains if their properties are desirable.



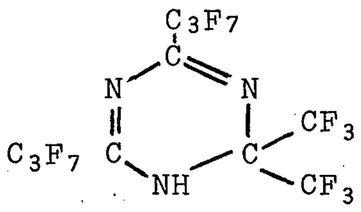
1



2



3

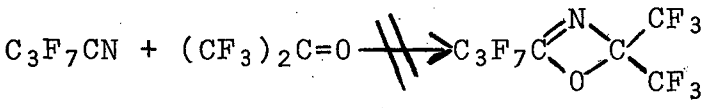


4

Ring systems 1 and 2 have not been achieved; for ring systems 3 and 4, intermediates have been made that show promise but final ring closure has not been obtained.

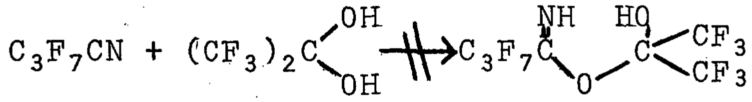
1. Attempted reactions of perfluorobutyronitrile with hexafluoroacetone, hexafluoroacetone hydrate and hexafluoropropane-2,2-diamine.

The following reactions were attempted as detailed in the Experimental Section (III):

a. 

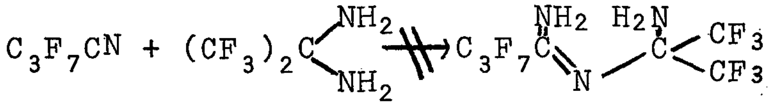
Experimental conditions for (a) included heating at 150°; heating at 170° with triethylamine catalyst; heating at 300° with ammonia catalyst; heating at 130° with ammonia catalyst.

b.



Experimental conditions for (b) included heating at 100° and at 240° and heating at 65° in the presence of sodium methoxide as a basic catalyst.

c.

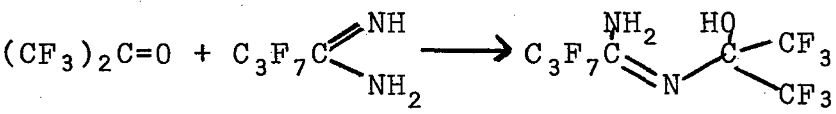


Experimental conditions for (c) included reaction in ether at 35°, heating at 62°, and heating at 82° in the presence of triethylamine as a basic catalyst.

None of these attempted reactions produced the desired product.

2. Reaction of hexafluoroacetone with perfluorobutyramidine.

Hexafluoroacetone (excess) and perfluorobutyramidine were placed in a flask at -78° and allowed to warm to room temperature under a reflux condenser. Reaction occurred to produce 5, whose structure was



5

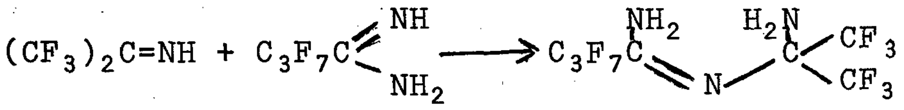
confirmed by elemental analysis and infrared spectra. The spectra suggests the presence of tautomeric forms.

Attempts were made to deammonate and cyclize 5 by pyrolysis and by heating with phosphorus pentoxide but ring closure (to a 4-membered heterocycle) could not be substantiated.

Perfluorobutyric acid formed a salt with 5; acylation of 5 with perfluorobutyryl chloride yielded a white low melting solid whose structure has not been established definitely.

3. Reaction of hexafluoropropane imine with perfluorobutyramidine.

Hexafluoropropane imine reacted with perfluorobutyramidine on warming the mixture from -78° to room temperature to give 6.



6

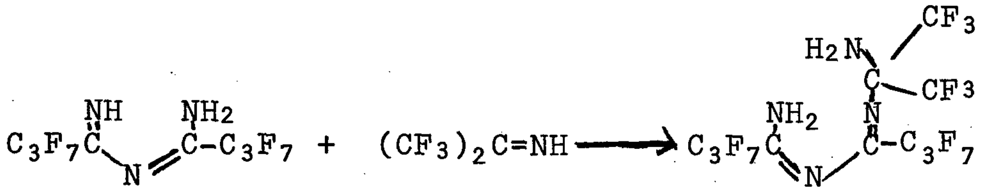
Product 6 was a colorless liquid boiling at 35-40° at 1-2 mm. Elemental analysis confirmed the composition and the infrared spectra was satisfactory for this structure.

4. Addition of hexafluoroacetone to N(perfluorobutyrimidoyl)perfluorobutyramidine

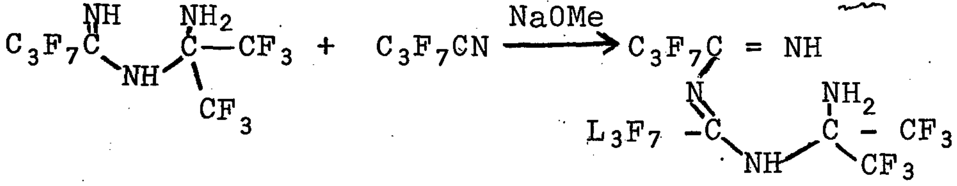
Hexafluoroacetone reacted with N(perfluorobutyramidoyl)perfluorobutyramidine at room temperature to give a white solid adduct; this product appeared to decompose on standing at room temperature in air or in vacuo and has not been investigated further.

5. Reaction of perfluorobutyronitrile with the adduct of hexafluoropropane imine and perfluorobutyramidine and reaction of hexafluoropropane imine with N(perfluorobutyrimidoyl)perfluorobutyramidine

The title reactions of this section should produce the same final product; however, they are shown below as 7a and 7b since their infrared spectra were not identical. This difference may be in the possible tautomeric forms.



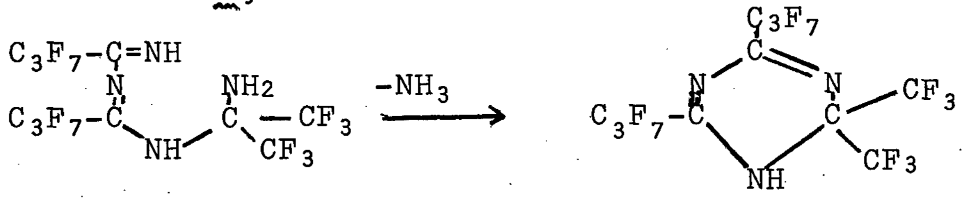
7a



7b

Both 7a and 7b decompose slowly on standing at room temperature. In the use of (a) the reaction conditions appear to be very critical and in several instances only partial conversion to the product has been achieved. Since separation of the product from N(perfluorobutyrimidoyl)-perfluorobutyramidine is very difficult the attempted cyclization reactions have mostly been carried out on the product from reaction (b).

Deammonation of 7 should produce the substituted dihydrotriazine 8, and a number of attempts have been made to find the proper conditions for this ring closure.



8

Hydrogen chloride has frequently been used to effect cyclizations, with the elimination of ammonium chloride. Reaction of (7b) with hydrogen chloride produces a hydrochloride. Only 1 unit of hydrogen chloride reacts giving a 1:1 salt. When heated in a melting point tube this salt first starts melting at 125° and bubbles start appearing at 145°, above which temperature decomposition proceeds rapidly, a white solid subliming up the tube leaving ammonium chloride in the bottom. Heating the salt in a sealed tube at 145°C resulted in decomposition giving ammonium chloride, perfluorobutyronitrile and solid gaseous products and also solid organic products which have not been identified. The latter appear to decompose rapidly on standing. Similarly no cyclized product has been obtained by heating the salt at 135°-145°C in a sublimation apparatus, only an unstable white solid and ammonium chloride being obtained.

Attempts to achieve cyclisation of (7b) by heating with acetic acid have been unsuccessful. Acetic acid does not form a salt with this compound, and heating these two compounds together at 95° gives perfluorobutyramidine and other products.

D. Poly(perfluoroalkylene-1,2,4-triazoles)

1. Reaction of the silver salt of 3,5-bis(perfluoropropyl)-1,2,4-triazole with divalent metal halides

Several reactions were carried out between the silver salt of 3,5-bis(perfluoropropyl)-1,2,4-triazole and the divalent metal salts, HgI_2, CdI_2, and ZnI_2. The solvents used were THF, butyronitrile, and absolute ethanol. Each reaction was carried out by dropping a solution of the metal salt into a refluxing solution of the silver salt.

Two products were obtained from the HgI_2 reaction. The major product (80%) was a white solid which melted between 65-86° and gave the same infrared spectra as the compound obtained from HgO. The minor product (20%) was a white solid which melted between 190-210° and decomposed between 300 and 340°. This product was recrystallized from toluene and dried at 130° under reduced pressure. From this recrystallization, 0.5g of 3,5-bis(perfluoropropyl)-1,2,4-triazole was also obtained. This triazole was not present in the sample before the recrystallization, therefore it was formed from the Hg-adduct either by hydrolysis or decomposition of this adduct during the recrystallization process.

Analysis of the minor product showed that its structure consisted of two triazole rings for each mercury ~~atom. The infrared spectra of this material was the same as~~ the spectra of the low melting, major product, having peaks at 7.4μ due to the C_3F_7 groups, 6.95μ due to the triazole rings and a broad peak at 2.9-3.0μ which disappeared when the compound was heated to 130° under reduced pressure.

The product obtained from the CdI_2 reaction was a white, hygroscopic solid which melted between 285-290° and decomposed when heated above 300°. This compound gave an infrared spectra similar to the spectra of the product obtained from ZnO and 3,5-bis(perfluoropropyl)-1,2,4-triazole. It contained peaks at 7.4μ, 6.8μ, 2.9-3.0μ, and 2.7μ. The broad peak at 2.9-3.0 disappeared when the compound was sublimed at 130° under reduced pressure.

The product obtained from the 2:1 molar quantities of 3,5-bis(perfluoropropyl)-1,2,4-triazole and ZnI_2 was identified by its melting point and infrared spectra as the same product that was obtained from the $Zn(OAc)_2$ and ZnO reactions.

In order to obtain more information about the triazole-zinc adduct obtained in the above reaction, a reaction of 1:1 molar quantities of the silver salt and ZnI_2 was carried out. In this reaction a THF solution of the silver salt was added to a THF solution of ZnI_2 at room temperature. The THF used was freshly distilled from "dri Na". After the addition was completed, a quantitative yield of silver iodide was removed from the THF solution by filtration and the filtrate was evaporated to dryness under reduced pressure. The residue was a pale white solid whose infrared spectra was the same as the spectra of the previously obtained zinc adduct with the exception that it did not have peaks at 2.7 and 2.9-3.0μ. This residue was dissolved in ether; a red solution was obtained when either petroleum ether, carbon tetrachloride, or chloroform was added to the ether solution. A white solid precipitated from each of these mixed solvents overnight. The infrared spectra of these white solids was identical to the spectra of the previously prepared zinc adduct which contained peaks at 2.7 and 2.9-3.9μ. These results indicate strongly that the initially formed product was one which had both a triazole ring and an iodide ion attached to the zinc atom. Dissociation of this compound or complex formation with the solvents could account for the red color and hydrolysis of the initially formed product could account for the formation of the final product which would have a triazole ring and a hydroxyl group attached to the zinc atom.

Since hydrolysis appeared to be involved in these reactions, the possibility of hydrolysis of the zinc-nitrogen bond of the triazole-zinc adduct was investigated. If this bond is easily hydrolyzed, this could account for the lack of formation or isolation of the bis-triazole-metal compounds. When a sample of the triazole-zinc adduct was heated in refluxing 95% ethanol for 18 hours, 25% of the compound was hydrolyzed. Another sample of the triazole-zinc adduct was heated in a refluxing 40% aqueous THF solution for 18 hours and 43% of the compound was hydrolyzed.

2. Attempted acylation of 3,5-bis(perfluoropropyl)-1,2,3-triazole

Another possible method of obtaining a polymer cross-linked through the triazole rings is the use of acyl compounds as the cross-linking agent. This type of polymer should be more flexible than a polymer cross-linked through a divalent metal and the flexibility should also depend upon the chain length of the cross-linking agent. With this objective in mind several attempts were made to acylate the 3,5-bis(perfluoropropyl)-1,2,4-triazole, using both the triazole and also the silver salt of the triazole.

When the silver salt and a large excess of perfluorobutyryl chloride were rocked in a sealed tube for 48 hours at room temperature, the unreacted starting materials were recovered in quantitative amounts. When 0.015 moles of the silver salt and a large excess of perfluorobutyryl chloride were heated at 65° for 12 hours in a sealed tube, 0.013 moles of 3,5-bis(perfluoropropyl)-1,2,4-triazole and a quantitative yield of silver chloride were obtained. Essentially the same results (quantitative yields of 3,5-bis(perfluoropropyl)-1,2,4-triazole and silver chloride) were obtained when the silver salt and an excess of perfluorobutyryl chloride were heated in chloroform at 65° for 12 hours. Another attempted acylation using 3,5-bis(perfluoropropyl)-1,2,4-triazole and perfluorobutyryl chloride in the presence of triethylamine resulted in the formation of an almost quantitative yield of triethylamine hydrochloride and 3,5-bis(perfluoropropyl)-1,2,4-triazole.

Since quantitative yields of silver chloride and triethylamine hydrochloride were obtained under the conditions described above, this indicates that either the acylated product was very unstable or that the acylonium ion reacted with water before it could react with the anion of the silver salt. The latter possibility appears less likely in the reaction between the silver salt and perfluorobutyryl chloride at 65°. In this reaction the acid chloride was freshly distilled from PCl_5 and the purple silver chloride precipitated from the reaction solution before the tube was opened. The anhydrous conditions of the reactions were indicated by the fact that the silver salt and acid chloride were recovered uneffected when the reaction was carried out at room temperature.

Since the attempts to obtain an acylated triazole using perfluorobutyryl chloride were unsuccessful, acetyl chloride was next used as the acylating agent. Although this compound is not as reactive as the perfluoro compound, the electron donating effect of the methyl group should have a much greater stabilizing effect than the electron-withdrawing perfluoroalkyl group on the C-N bond of the acylated product. However, the triazole was recovered uneffected from a refluxing solution of 3,5-bis(perfluoropropyl)-1,2,4-triazole in excess acetyl chloride. The instability or lack of formation of an acylated perfluorotriazole can probably be attributed to the electron-withdrawing effect of the two perfluoroalkyl-substituents on the triazole ring.

3. Preparation and reaction of the silver salt of poly(perfluoroalkylene-1,2,4-triazole)

The silver salt of poly(perfluoroalkylene-1,2,4-triazole) was prepared in nearly the same manner as the model compound. The only difference in the two preparations was in the solvents used. The polymer was dissolved in THF and an alcoholic solution was used in order to decrease the possibility of the polymer precipitating from solution before the silver salt was formed. The product formed was a white solid which was insoluble in the alcohol-THF solution. The infrared spectra of this compound was very similar to the spectra of the model compound. However, there was a great difference in the melting properties and solubility of this compound and that of the polytriazole. This compound slowly darkened between 290 and 360°C but did not melt, whereas the polytriazole melted with darkening between 265 and 290°C. This polymer salt was not soluble in DMSO, DMF, acetonitrile, acetone, alcohol, ether, benzene, or carbon tetrachloride.

Since the best result toward obtaining a bis-triazole-metal adduct with the model compound was accomplished by using HgI_2, a sample of the silver salt of polytriazole was reacted with HgI_2. A suitable solvent could not be found that would dissolve the silver salt, so xylene was used in order to have a relatively high reaction temperature. The reactants were heated in refluxing xylene for 48 hours. After the inorganic salts were removed from the reaction mixture and the xylene was evaporated to dryness under reduced pressure, the only organic material recovered was polytriazole.

III EXPERIMENTAL

A. Poly(perfluoroalkylene-1,3,4-oxadiazoles)

1. Preparation of starting materials

a. Esterification of perfluorosebacic acid

Perfluorosebacic acid, 245 grams (0.5 moles), 184 grams of absolute ethanol, 800 ml. of benzene, and 2 ml. of conc. H_2SO_4 were placed in a single-necked round-bottom flask. The flask was fitted with a distillation head and its contents were refluxed overnight. A benzene-ethanol-water azeotrope was distilled from the flask over a period of three days. When the temperature of the azeotrope reached 75°, 200 ml. of absolute ethanol and 700 ml of benzene were added to the flask and an azetrope was distilled from the flask over an additional three days. After the excess ethanol and benzene were removed under reduced pressure, the crude ester, 262 grams, 96% yield, was also removed from the flask under reduced pressure. This crude ester was distilled between 4-5 mm pressure; 35 grams were obtained between 65-124°C and 222 grams at 125°C. The 222 gram portion represented an 82% yield.

b. Preparation of acyl chlorides from the perfluoroether-diacyl fluorides

The liquid perfluoroether-diacyl fluorides, 5.76g (1×10^{-2} m) were added to a 50 ml. round-bottom flask which contained a magnetic stirring bar and was fitted with a 25 ml. barostatic dropping funnel. As 25 mls. of distilled water was slowly added at room temperature heat evolved. After refluxing for 10 hours, the water was stripped from the reaction mixture by distillation. The remaining organic product was taken up in anhydrous diethyl ether. The solvent was then removed under reduced pressure leaving 5.90 gms. of a clear liquid product. The product was identified as the diacid by its infrared spectrum. The expected C=0 absorption was present at 5.6 with accompanying -0-H absorptions at 3.0 - 3.5μ. The yield was quantitative.

A 4 ml. portion of the perfluoro-ether diacid was refluxed in a large excess of phosphorous pentachloride overnight. The reaction mixture was then fractionated. After approximately 2 mls. of phosphorous oxychloride ($POCl_3$) were removed, boiling at 102°C, solids (PCl_5) began to sublime into the distillation head. The distillation pot was cooled and a liquid-solid (PCl_5) mixture remained. The clear liquid product (1.5 mls.) was recovered after filtration under a dry nitrogen atmosphere. It was subsequently identified as the diacylchloride by its infrared spectrum. No absorptions due to -O-H were present, only the acyl chloride -C=O peak at 5.5μ.

2. Polymerization reactions

a. Reaction of 1,3-bis(5-tetrazolyl) perfluoropropane, bitetrazole and perfluorosebacoyl chloride in xylene.

A 50 ml., 3-neck, round-bottom flask which contained a magnetic stirring bar, was fitted with a nitrogen inlet tube and a water-cooled distillation head which was open to the atmosphere through the vacuum line and 2-dry-ice traps. Under a dry N_2 atmosphere the freshly distilled (87-88° @ 9.5 mm) perfluorosebacoyl chloride, 5.3999 gms. (1.0246×10^{-2}m) was added to a tarred dropping funnel. The required amounts of 1,3-bis(5-tetrazolyl) perfluoropropane, 2.3598 gms. (0.819×10^{-2}m), and bitetrazole, 0.2824 gms. (0.204×10^{-2}m) were then added to the flask. Finally, the dropping funnel containing the solution of acid chloride in 7 mls. of dry xylene was attached. Air was removed and the flask was flamed and purged with dry N_2 repeatedly to insure dryness.

The acid chloride-xylene solution was then added dropwise to the tetrazoles at room temperature, final traces being washed into the flask with an additional 3 mls. of dry xylene. The white slurry was stirred and heated in an oil bath at 80° for 40 hours, 90° for 25 hours, 98° for 23.5 hours, 116° for 29 hours and 140° for 19 hours. A 10% excess of acid chloride, 0.5333 gms. (1.01×10^{-3}m) was added to the mixture at this point, the pressure was reduced to 431 mm Hg and xylene was distilled from the flask. Heating was then continued at 186° for 23.5 hours and at 197° for 46 hours. The pressure was reduced (0.01-0.02 mm Hg) and all volatile products were removed. Recovered was 6.76 gms. of amber elastomer.

An infrared spectrum indicated the product was poly oxadiazole having -COOH end groups. Lower molecular weight products were removed with boiling xylene, tetrahydrofuran and ethyl acetate. The remaining product was pressed into a film at 180°.

b. Reaction of the perfluoroether-diacyl chloride with 1,3 bis(5-tetrazolyl) perfluoropropane.

A 100 ml., 3-neck round-bottom flask, which contained a magnetic stirring bar, was fitted with an immersion thermometer and a water-cooled reflux condenser. Added to the reaction pot along with 4 mls. of dry xylene were 1.0554 gms. (3.66×10^{-3}m) of 1,3-bis (5-tetrazolyl) perfluoropropane which had been dried under reduced pressure. The perfluoro-ether diacyl chloride, 2.5136 gms. (4.12×10^{-3}m) was added by means of a syringe to a 10 ml. dropping funnel which had been tarred and fitted with a septum. The dropping funnel was then attached to the reaction pot and a dry nitrogen sweep was maintained over the system. The slow, dropwise addition of the acid chloride to the stirring slurry at room temperature was completed after 15 minutes. The solids in the reaction mixture appeared to become more curdly but no visible change was noted otherwise. After one hour an additional 4 mls. of dry xylene was added through the addition funnel to wash any adhering diacyl chloride into the reaction mixture.

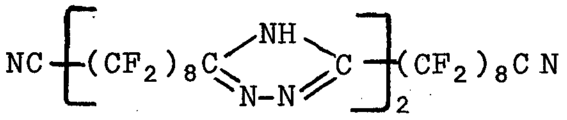
The reaction mixture was then heated gradually, over an 8 hour period, to reflux (140°C), no change being noted. However, at 140°C a yellow, insoluble gum had fallen to the bottom of the flask and gaseous HCl evolution was noted. After heating at 142-5°C for 80 hours the residue had become more viscous. When no further change occurred after 52 additional hours of heating, the reaction was terminated. The xylene was decanted and the light tan gummy product was dried under reduced pressure.

The product was insoluble in diethyl ether, chloroform, methanol, hot diglyme, hot acetonitrile and hot alcohol. Very slight solubility was noted in tetrahydrofuran and acetone. The product was soluble in ethyl acetate, methyl ester of trifluoroacetic acid and hot dimethylformamide.

Its infrared spectra showed the presence of the oxadiazole groups by its characteristic absorptions at 6.4 and 7.1µ. A weak absorption due to C=O was present at 5.5µ.

B. <u>Preparation of New Monomers</u>

1.



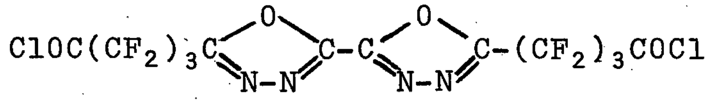
Perfluorosebaconitrile, 9.7 g (.02 m), and 20 ml of ether were placed in a two-necked, round-bottom flask.

The flask was fitted with a reflux condenser and a dropping funnel which contained 0.8 g (.0015 m) of perfluorosebachydrazide dissolved in 100 ml of a 1:1 mixture of THF and ether. The hydrazide solution was added dropwise to the stirring, refluxing nitrile solution. After the addition was completed, the contents of the flask were refluxed overnight. The solvents were removed under reduced pressure and 2.0 g of white solid was obtained. The infrared spectra of this solid had a peak at 4.4μ but otherwise was very similar to the spectra of the previously prepared perfluorobutyronitrile perfluorobutyrhydrazide adduct.

One gram of this material was heated at 280° under reduced pressure in a sublimation apparatus for one hour. During this period approximately one-half gram of white solid was collected on the cold finger, while the portion which did not sublime decomposed. The infrared spectra of the sublimate showed that ring closure had taken place and that the nitrile end-groups were still present.

Another gram of this intermediate material was heated in 25 ml of refluxing $POCl_3$ for two hours. The infrared spectra of the white solid recovered after this treatment showed that the nitrile end-groups were still present but only part of the material had been converted to the triazole structure.

2.



Solid bitetrazole, 3.01 gms. (2.18x10^{-2}m) was added to a 100 ml. round-bottom flask which contained a magnetic stirring bar. A solution of 26.9 gms. (9.7x10^{-2}m) of pure perfluoroglutaryl chloride in 25 mls. of dry ethyl acetate was prepared under a dry nitrogen atmosphere and added to a reaction flask. Immediately, a water-cooled, reflux condenser, open to the atmosphere through 2 dry-ice traps, was attached to the reaction flask. No reaction occurred at room temperature. The reaction mixture was then refluxed for 41.5 hours. At this time, a fine white suspension was present. The reaction mixture was cooled to room temperature and the volatile materials were removed under reduced pressure.

Remaining in the flask were 12.18 gms. of dry, white flakes, a quantitative yield. The product melted slowly between 188-193°C. A mull was prepared under a dry nitrogen atmosphere and an infrared spectrum was taken. Peaks attributable to the bioxadiazole function (6.4,6.8 and 7.3μ) and to the acyl chloride -C=0 function (5.55μ) were present. No absorption due to -OH was observed. As might be expected for such a product, the solubility behavior was unusual. In the common organic solvents a cloudy suspension was present. In larger amounts of the more polar, hot, solvents (acetonitrile, tetrahydrofuran, ethylacetate and acetone) solubility could be obtained. Cloudy suspensions occurred likewise in both hot water and methanol. The product was insoluble in petroleum ether.

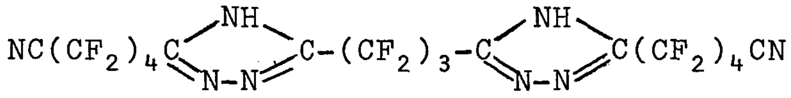
3. Reaction of perfluoroglutaryl chloride with hydrazine.

Perfluoroglutaryl chloride, 40 grams (0.145 moles), was placed in a two-necked, round-bottom flask which was fitted with a reflux condenser and a dropping funnel. Hydrazine, 0.48 grams (0.015 mls.), dissolved in 10 ml. of THF which contained 1 ml. of ethanol, was placed in the dropping funnel. The acid chloride was cooled to -40°C and the hydrazine was added. After the addition was completed the resulting white slurry was allowed to warm to room temperature. The white slurry was filtered and a quantitative yield of hydrazine hydrochloride was obtained.

4. Reaction of perfluoroglutaric anhydride with hydrazine.

Perfluoroglutaric anhydride, 222 grams (1.0 moles), was placed in a two-necked, round-bottom flask which was fitted with a reflux condenser and rubber septum. The flask was cooled to -40°C and 3.0 ml, 0.1 moles, of hydrazine were added slowly to the cooled, stirring liquid from a syringe through the rubber septum. A white tacky solid precipitated continuously as the hydrazine was added. After the addition was completed, the contents of the flask were allowed to warm to room temperature. The rubber septum was replaced with a glass stopper then the contents of the flask were heated to reflux. At this temperature the white solid almost completely dissolved giving a milky solution. This solution was refluxed overnight then cooled to room temperature. Upon cooling a white solid precipitated from the solution. This solid, 61 grams, was removed by filtering the contents of the flask and was identified as perfluoroglutaric acid from its melting point (92-95°C) and infrared spectra. The filtrate was evaporated to dryness under reduced pressure and a white residue was obtained. This residue was heated at 110°C under reduced pressure in a sublimation apparatus and 18 grams of additional perfluoroglutaric acid were collected on the cold finger. Approximately 5 grams of pale white residue did not sublime. This residue was treated with hot water and extracted with ether. The pale white solid was dried under reduced pressure after the ether was removed and 4.8 grams which softened at 145°C and became a very viscous liquid at 175°C was obtained.

The white solid obtained from the reaction of perfluoroglutaric anhydride and hydrazine, 78 grams, (the perfluoroglutaric acid was not removed) was mixed with approximately 80 grams of P_2O_5 in a single-necked, round-bottom flask which was fitted with a distillation head. The contents of the flask were heated at 120°C overnight, then 57 grams of perfluoroglutaric anhydride were distilled from the flask. The contents of the flask were then heated at 155°C under reduced pressure until no more liquid could be removed. During this heating period approximately 3 grams of white solid sublimed from the flask. The contents of the flask were cooled to room temperature and then treated with 200 ml of ether. No additional white solid was obtained upon evaporation of the ether. A small amount of water was added to the reaction mixture, then the aqueous solution was shaken with ether. The ether layer was separated and evaporated to dryness but no additional white solid was obtained. This white solid melted between 190-195°C and did not solidify upon cooling.

5. 

$\mathrm{NC(CF_2)_4C}\underset{\mathrm{N{-}N}}{\overset{\mathrm{NH}}{\qquad}}\mathrm{C{-}(CF_2)_3{-}C}\underset{\mathrm{N{-}N}}{\overset{\mathrm{NH}}{\qquad}}\mathrm{C(CF_2)_4CN}$

a. Preparation of perfluoroadiponitrile

1. Oxidation of perfluorocyclohexene

$KMnO_4$, 125 grams, 1.5 liters of acetone, and 150 ml of water were placed in a three-necked, round-bottom flask. The flask was fitted with a stirring rod, reflux condenser, and a dropping funnel which contained 175 gms of perfluorocyclohexene. The perfluorocyclohexene was added slowly to the stirring contents of the flask which were cooled in order to keep the temperature below 50°C. After the addition of the perfluorocyclohexene was completed, the resulting mixture was stirred for one hour then filtered. The acetone was removed under reduced pressure and 100 ml of conc H_2SO_4 was added to the slurry. The resulting acidic solution was extracted twice with 500 ml portions of ether. The ether was removed under reduced pressure and 153 grams, 79% yield, of perfluoroadipic acid were obtained.

2. Esterification of perfluoroadipic acid

Perfluoroadipic acid, 414 grams (1.4 moles), 313 grams of absolute ethanol, 1600 ml of benzene, and 5 ml of concentrated H_2SO_4 were placed in a single-necked, round-bottom blask. The flask was fitted with a distillation head and its contents were refluxed overnight. An azeotrope was distilled from the flask over a period of three days, then 200 grams of absolute ethanol and 1200 ml of benzene were added to the flask. The contents of the flask were again heated until the azeotrope taken off contained no water. The benzene and excess ethanol were removed under reduced pressure and a dark viscous liquid was obtained. This liquid was washed with water then extracted with ether. After the ether was removed under reduced pressure, the dark, viscous liquid was dried over Drierite and distilled. A pale yellow liquid, 311 grams, was obtained between 210-221°C at atmospheric pressure.

3. Perfluoroadipamide

Diethyl perfluoroadipate, 311 grams, and three liters of ether were placed in a five liter, three-necked, round-bottom flask. The flask was fitted with a stirring rod, dry-ice cooled reflux condenser and a gas inlet tube which extended below the surface of the contents of the flask. Dry ammonia was bubbled into the solution for ten hours then the contents of the flask were stirred for twelve hours. The contents of the flask were filtered and 234 grams of tan solid were obtained. The ether was removed under reduced pressure and 10 grams of tan solid were obtained.

4. Perfluoroadiponitrile

The crude perfluoroadipamide, 234 grams, and a large excess of P_2O_5 were intimately mixed in a single-necked, round-bottom flask. The flask was fitted with a packed column and a distillation head. The contents of the flask were heated at approximately 250°C for 48 hours. The perfluoroadiponitrile, 190 grams, 89% yield, was distilled from the flask between 62-64°C.

b. Reaction of perfluoroadiponitrile and perfluoroglutarhydrazide.

1. In dioxane

Perfluoroadiponitrile, 95 grams (0.38 moles), was placed in a two-necked, round-bottom flask which was fitted with a reflux condenser and a dropping funnel. Perfluoroglutarhydrazide, 5.0 grams (0.019 moles), was dissolved in 75 ml of dioxane and placed in the dropping funnel. The entire system was open to the atmosphere through two dry-ice traps. The hydrazide solution was added slowly to the stirring, refluxing perfluoroadiponitrile. After the addition was completed, the contents of the flask were stirred at room temperature for two hours. The excess nitrile and dioxane were removed under reduced pressure and a tacky, pale yellow residue was obtained. This residue was taken up in ether and 5.0 grams of ether insoluble white solid was separated by filtering the ether mixture. The ethereal filtrate was evaporated to dryness under reduced pressure and 7.5 grams of pale yellow solid was obtained.

2. In propionitrile

Perfluoroadiponitrile, 140 grams (0.55 moles), was placed in a two-necked round-bottom flask which was fitted with a distillation head and a dropping funnel. The entire system was open to the atmosphere through two dry-ice traps. The perfluoroglutarhydrazide, 7.3 grams (0.027 moles), was dissolved in 175 ml of hot propionitrile and placed in the dropping funnel. The hydrazide solution was added slowly to the stirring, refluxing perfluoroadiponitrile. After the addition was completed, the slightly cloudy solution was refluxed for one hour. During this period a pale white solid precipitated from the solution. The excess perfluoroadiponitrile, 121 grams, was distilled from the flask, then the contents of the flask were filtered. The pale white solid obtained from the filtration was washed with ether and filtered again. A white crystalline solid, 12.5 grams, which was ether insoluble was obtained. This solid melted at 191-192°C. The ether and propionitrile were evaporated to dryness under reduced pressure and 5.6 grams of yellow solid was obtained.

3. In acetonitrile

Perfluoroadiponitrile, 96.0 grams (0.38 moles), was placed in a two-necked, round-bottom flask which was fitted with a distillation head and a dropping funnel. The entire system was open to the atmosphere through two dry-ice traps. Perfluoroglutarhydrazide, 6.7 grams (0.025 moles), was dissolved in 200 ml of dry acetonitrile and placed in the dropping funnel. The hydrazide solution was added to the stirring, refluxing perfluoroadiponitrile over a period of eight hours. After the addition was completed, the contents of the flask were refluxed for 24 hours. During this period the white solid did not dissolve. The excess perfluoroadiponitrile, 81 grams, was distilled from the flask between 57-51°C. The contents of the flask were filtered and the precipitate, 15.0 grams, was washed with ether and dried. This 15.0 grams of white solid also melts at 191-192°C.

The perfluoroadiponitrile-perfluoroglutarhydrazide adduct, 12.0 grams, and a large excess of P_2O_5 were heated between 150-220°C at atmospheric pressure in a sublimation apparatus for 24 hours. During this period a mixture of the dehydrated adduct and P_2O_5 sublimed. This mixture was returned to the bottom of the sublimation apparatus and heated at 160-210°C under reduced pressure for 12 hours. During this period 9.0 grams of white sublimate was obtained. This sublimate was taken up in dry ether and the insoluble P_2O_5 was removed by filtration. The filtrate was evaporated to dryness under reduced pressure and 6.5 grams of white solid was obtained. This solid melted at 183-210°C under reduced pressure for 12 hours. During this period 9.0 grams of white sublimate was obtained. This sublimate was taken up in dry ether and the insoluble P_2O_5 was removed by filtration. The filtrate was evaporated to dryness under reduced pressure and 6.5 grams of white solid was obtained. This solid melted at 183-185°C and represented a yield of 57% of the dehydrated adduct.

C. Attempted Syntheses of New Ring Systems

1. Reactions of perfluorobutyronitrile with hexafluoroacetone

a. At 150°

In a previously evacuated heavy-walled glass ampoule of approximately 200 ml. capacity were condensed perfluorobutyronitrile, 2.35 g.(0.012 mole) and hexafluoroacetone, 4.0 g. (0.024 mole). After heating at 135° for 12 hours and 150° for 24 hours the ampoule was opened under reduced pressure and full recovery of the starting materials showed that no reaction had occurred.

b. With triethylamine at 170°

A trace amount of triethylamine was placed in the ampoule and the gases condensed as in (a). The ampoule was heated to 170° for 24 hours but again starting materials were fully recovered.

c. With 5 mole % ammonia at 300°

Into a dried, evacuated, heavy-walled glass ampoule of 100 ml. capacity were condensed perfluorobutyrnitrile, 2.93 g. (0.0151 mole), hexafluoroacetone, 5.0 g. (0.0301 mole) and ammonia, 0.041 g. The tube was heated for 18 hours at 300°. When taken off the inside of the tube was completely black and approximately 40% of starting materials were recovered. Most of the material in the tube was carbon decomposition. Ether extraction of the tube gave a small amount of unidentifiable brown solid.

d. With 5 mole % ammonia at 130°

Hexafluoroacetone (3.24 g, 0.018.5 mole), perfluorobutyronitrile (1.91 g, 0.00977 mole) and ammonia (0.0070 g, 0.000468 mole) were sealed in a heavy-wall glass tube which was heated at 130°C for 21 hours. A clear liquid was present in the tube after heating, and starting materials were recovered quantitatively on venting the reaction mixture to a vacuum system.

2. Reactions of perfluorobutyronitrile with hexafluoroacetone hydrate

a. At 240°

Hexafluoroacetone monohydrate was prepared by placing water, 0.92 g (0.051mole)in a 100 ml. capacity sealed glass tube and condensing in hexafluoroacetone, 8.5 g. (0.051 mole). The tube was allowed to warm to room temperature and hexafluoroacetone monohydrate was formed by an exothermic reaction giving a white solid. Perfluorobutyronitrile, 10.0 g. (0.051 mole) was now condensed into the tube which was sealed and heated at 100° for 24 hours. The tube was opened and the amount of gas recovered showed that no reaction had occurred. The tube was resealed and heated at 240° for 24 hours. Again, on opening the tube no reaction had occurred.

b. In the presence of a basic catalyst

Water (0.6 g approx.), in tetrahydrofuran (5ml) was first placed in a heavy-wall glass tube and excess hexafluoroacetone was then condensed in. The tube was then allowed to warm up and hexafluoroacetone hydrate (5.66 g, 0.0296 mole) was formed. The excess hexafluoroacetone was then pumped off, and approximately 1 mole % sodium methoxide (0.02 g) was added under an atmosphere of nitrogen. The tube was then pumped on a vacuum system and perfluorobutyronitrile (7.56 g, 0.0388 mole) was condensed in. The tube was sealed and heated at 65°C for 72 hours. Perfluorobutyronitrile was recovered, almost quantitatively on opening the tube, showing that little or no reaction had taken place.

3. Reaction of hexafluoropropane-2,2-diamine with perfluorobutyronitrile

a. At 35°

Hexafluoropropane -2,2-diamine 9.0 g. (0.050 mole) and 20 ml. dry ether were placed in a 100 ml. flask fitted with magnetic stirrer and dry ice reflux condenser. Perfluorobutyronitrile, 9.6 g (0.049 mole) was condensed in and allowed to reflux at room temperature for 30 minutes. The reaction mixture was then warmed to 35° for 20 minutes. No reaction occurred.

b. At 62°

The unreacted nitrile in the above experiment was taken off and the solution transferred to a heavy-walled glass ampoule of approximately 100 ml capacity into which the nitrile was then condensed; the ampoule was sealed and heated at 62° for 18 hours. On opening the ampoule the nitrile was recovered and no reaction had occurred.

c. With triethylamine at 82°

Triethylamine, 0.13 ml (2 mole %), as a basic catalyst, and 10 ml tetrahydrofuran were added to the ampoule by syringe and the nitrile was again condensed in. After heating at 82° for 18 hours on a rocker approximately half the nitrile was recovered. Distillation under pressure of the ether and tetrahydrofuran left a yellow semi-solid whose infrared spectrum showed it to be mainly 2,4,6-tris (perfluoropropyl)-1,3,5-triazine. Apparently the nitrile had reacted with itself.

4. Reaction of hexafluoroacetone with perfluorobutyramidine

Perfluorobutyramidine (30.0 g, 0.142 mole) was first placed in a flask and a reflux condenser was fitted. The apparatus was then evacuated and hexafluoroacetone (30.85 g., 0.186 mole) condensed in. The flask was maintained at -196° and fitted with a nitrogen sweep, the reflux condenser being cooled to -78°C, and allowed to warm to room temperature over a period of two hours. A colorless liquid was present in flask and this was stirred for one hour. The excess hexafluoroacetone was then allowed to boil off and the apparatus was then attached to a vacuum line and any excess hexafluoroacetone still present was pumped away. A colorless liquid was left in the flask and this was identified as N-(perfluoroisopropanol-perfluorobutyramidine, (53.5 g, 97%), b.p. 65°-70°C /1-2 mm. Anal. Cal'd. for $C_7H_3F_{13}N_2O$: C,22.24; H, 0.80; F,65.33; N,7.41. Found: C,22.51; H,1.10; F,65.05; N,9.18.

a. Reactions of the adduct from (4)

1. Pyrolysis

N-(perfluoroisopropisopropanol)-perfluorobutyramidine 5.1 g, (0.0135 mole) was sealed in a tube and heated at 210°C for five hours. A white crystalline solid was present in the tube after cooling. The tube was then cooled in liquid nitrogen and opened to a vacuum system but a negligible amount of gas was vented. A white solid (3.6 g) was left in the tube. This melted over a range (85-120°C) indicating that a mixture of compounds was present, which was not identified.

2. With phosphorus pentoxide

N-(perfluoroisopropanol)-perfluorobutyramidine (8.5 g, 0.0214 mole) and phosphorus pentoxide (13.0 g, 0.0915 mole) were placed in a flask, to which a reflux condenser and drying tube were then fitted. The flask was then heated on an oil bath at 110°-120°C for 10 hours. The organic material in the flask was then distilled out under vacuum to a trap cooled in liquid nitrogen (oil bath temperature 110°-130°C). A white solid and a colorless liquid were collected in the trap and a little solid material also sublimed into the delivery tube. The liquid in the trap was then poured out and distilled under vacuum to give a clear distillate (5.5 g.). This was identified as 2,4,6-tris(perfluoropropyl)-1,3,5-triazine by comparison of its infrared spectrum with that of an authentic sample. The solid remaining in the trap (1.3 g) consisted of an impure sample of perfluorobutyramidine (identification by ~~its~~ infrared spectrum).

3. With perfluorobutyric acid

N-Perfluoroisopropanol) perfluorobutyramidine (1.9 g, 0.00503 mole) and perfluorobutyric acid (1.2 g, 0.00561 mole) were each dissolved in 10 ml ether. The two solutions were then added to 75 ml ether and a white solid was immediately precipitated. The solution was filtered and the solid material collected (1.9 g.). Evaporation of the filtrate left a white residue (0.8 g). The ether insoluble material had a melting point of 235°C and was tentatively identified as the salt of N(-perfluoroisopropanol)-perfluorobutyramidine and perfluorobutyric acid. The residue obtained from evaporation of the ether was a less pure sample of the same compound.

4. With perfluorobutyryl chloride

N-(Perfluoroisopropanol)perfluobutyramidine (5.2 g, 0.0138 mole) and dry ether (25 ml) were first placed in a flask to which a reflux condenser was then fitted. Perfluorobutyryl chloride (10.5 g, 0.0458 mole) was then condensed in and the apparatus was fitted with a nitrogen sweep and allowed to warm up. The solution was then refluxed at 40°C for thirty minutes, and the excess perfluorobutyryl chloride distilled off. The ether solution was then filtered to remove a little insoluble white solid present (0.1 g). This was not identified. Evaporation of the ether gave a white crystalline solid (m.p. 38-45°C)(5.0 g). A little of the material was dissolved in ether and the solution shaken with water.

Separation of the ether layer followed by drying($CaSO_4$) and evaporation appeared to give a rather purer sample of the product. This compound has so far not been identified.

5. Reaction of hexafluoroacetone with N(perfluorobutyrimidoyl)perfluorobutyramidine

N(Perfluorobutyrimidoyl)perfluorobutyramidine (8.0g, 0.0197 mole) was first placed in a heavy-walled glass tube and hexafluoroacetone (3.52 g, 0.0212 mole) was condensed in. The tube was then sealed and allowed to warm up to room temperature for a further 17 hours. After this time a white solid together with a little liquid were present in the tube. The tube was then cooled in liquid nitrogen and opened to a vacuum system and hexafluoroacetone (0.65 g, 0.00392 mole) was recovered. A white solid (7.5 g) was obtained from the tube together with a little liquid. The solid appeared to decompose on in the air or in vacuo.

6. Reaction of hexafluoropropane imine with perfluorobutyramidine

Perfluorobutyramidine (8.5 g, 0.041 mole) was first placed in a flask to which a reflux condenser was then fitted. The flask was then evacuated and cooled to -196°C and hexafluoropropane imine (6.64 g, 0.043 mole) condensed in. The apparatus was then fitted with a nitrogen sweep and the reflux condenser was cooled to -78°C. The reaction mixture was then allowed to warm up from -78°C to room temperature over a period of approximately two hours with stirring. The colorless liquid in the flask was then stirred for a further hour after which time the reflux condenser was removed and any excess hexafluoropropane imine pumped off on a vacuum system. A colorless liquid was left in the flask and this was identified as N-(perfluoroisopropylamine)perfluorobutyramidine (14.7 g, 97%) b.p. 35°-40°C/1-2 mm. Anal. Cal'd. for $C_7H_4F_{13}N_3$: C,22.30; H,1:07; F,65.51; N,11.14. Found: C,22.50; H, 0.985; F,65.20; N,10.87.

a. Reaction of the adduct from (6) with perfluorobutyronitrile (N'(hexafluoropropane imine)-N-(perfluorobutyrimidoyl)perfluorobutyramidine).

A heavy-walled glass tube was first charged with N-(perfluoroisopropylamine)perfluorobutyramidine (4.0 g, 0.018 mole) and approximately 1 mole % sodium methoxide (0.008 g) was added under an atmosphere of nitrogen. The tube was then connected to a vacuum system and perfluorobutyronitrile (2.94 g, 0.0151 mole) was condensed in. The tube was then sealed and heated at 90°C for 24 hours. After heating the reaction mixture was slightly yellow in color. The tube was then cooled in liquid nitrogen and opened to a vacuum system. Perfluorobutyronitrile (1.07 g, 0.00549 mole) was recovered and the liquid remaining in the tube was filtered and distilled (b.p. 35°-37°/0.1 mm.). The molecular weight of the distillate was found to be 500. (Molecular weight required for a 1:1 adduct 572).

b. Reactions of (6a)

1. Salt formation with hydrogen chloride

N'-(Perfluoropropane imine)-N-(perfluorobutyrimidoyl)perfluorobutyramidine 5.8 g (0.0101 mole) and dry ether (20 ml) were first placed in a heavy-walled glass tube which was then connected to a vacuum system. Hydrogen chloride 0.43 g (0.0118 mole) was then condensed in and the tube sealed under vacuum. When the tube had warmed up to room temperature a white solid was seen in the ether solution, and the tube was allowed to remain at room temperature for sixteen hours. The tube was then opened and the ether decanted off leaving the white insoluble material, 1.5 g. Evaporation of the ether left a further sample of the white solid, 3.0 g, which was identified as a 1:1 salt of the two reactants (73%).

Using the procedure described above N'-(perfluoropropane imine)-N-(perfluorobutyrimidoyl)perfluorobutyrimidine 3.0 g (0.00526 mole), dry ether (15 ml) and hydrogen chloride 0.73 g (0.0199 mole (excess) were sealed in a heavy-walled tube which was allowed to stand at room temperature for 17 hours. The tube was then cooled to -196°C and vented to a vacuum system. Hydrogen chloride, 0.26 g., (0.0071 mole) was collected and the 1:1 salt of the two reactants was isolated as before (1.9 g) (60%).

2. Pyrolysis of the hydrochloride

a. Pyrolysis of the hydrochloride

The salt 0.55 g, (0.000904 mole) was sealed in an evacuated heavy-walled glass tube which was then heated to 110°C for 17 hours. The tube was then cooled and opened to a vacuum system. No gaseous products were recovered and only starting material was present.

b. In a sealed tube at 145°C

The salt 0.6 g (0.000986 mole) was first sealed in an evacuated heavy-walled glass tube and heated at 145°C for

14 hours. The tube was then cooled in liquid nitrogen and vented to a vacuum system. An impure sample of heptafluoronitrile ~ 0.085 g (0.00026 mole) was collected. The solid material left in the tube was then ether extracted. Part of the material was insoluble and this was identified as ammonium chloride ~ 0.05 g. Evaporation of the ether extract left a trace of what appeared to be a white paste. This decomposed to liquid and evaporated on standing in the air.

c. <u>In a sublimation apparatus at 155°-165°C</u>.

The salt 0.8 g (0.00132 mole) was first placed in a sublimation apparatus protected by a drying tube. The apparatus was then heated to 155-165°C for two hours. A white solid sublimed onto the cold finger and also onto the cooler parts of the sides of the apparatus. The apparatus was then allowed to cool and the sublimed material 0.7 g. was collected and identified as a mixture of the salt and other products by the infrared spectrum. The solid remaining in the bottom of the apparatus was identified as ammonium chloride.

d. <u>In a sublimation apparatus at 135°-145°C</u>.

The salt 0.95 g (0.00156 mole) was heated at 135°-145°C for 10 hours in the same apparatus as above. On cooling it was seen that some material had sublimed onto the cold finger and the upper walls of one apparatus. This was collected (0.4 g) and identified as starting material. The solid remaining in the bottom of the apparatus had a slightly pink coloration and this was extracted with 15 ml. ether. A little insoluble ammonium chloride was left and this was filtered off. Evaporization of the filtrate left a small amount of a white solid paste which changed to a liquid on standing in vacuo.

3. <u>In the presence of acetic acid</u>

N'-(Perfluoropropane imine)N-(perfluorobutyrimidoyl) perfluorobutyramidine 0.3 g (0.000524 mole) was dissolved in 5 ml ether and glacial acetic acid 1.05 g (0.0169 mole) was added. No precipitate appeared and after the solution had been allowed to stand for 30 minutes the ether was removed under vacuum leaving only starting materials.

In a further experiment in the presence of acetic acid, N'-(Perfluoropropane imine)N-(perfluorobutyrimidoyl) perfluorobutyramidine 1.3 g (0.00227 mole) and acetic acid acid 1.05 g (0.0169 mole) were heated at 95°C for 18 hours in a test tube fitted with a side arm and cold finger.

After the reaction mixture had cooled 10 ml ether and 10 ml water were added and the material was shaken. The organic layer was then separated and the ether was removed under vacuum leaving a white solid (0.3 g). The infrared spectrum showed that this was an impure sample of perfluorobutyramidine.

4. Pyrolysis

a. At 195°C

N'-(Perfluoropropane imine)N-(perfluorobutyrimidoyl)-perfluorobutyramidine 0.8 g (0.0014 mole) was sealed in air-evacuated heavy-walled glass tube which was then heated at 195°C for 19 hours. After reaction a white solid together with a little liquid was present in the tube which was then cooled in liquid nitrogen and vented to a vacuum system. The gas vented was not identified but the infrared spectrum indicated the presence of C-F bonds, and it probably consisted of hexafluorimine and other products. The solid obtained from the reaction, 0.4 g, was separated. Its infrared spectrum was unfavorable for the cyclised product, as it showed a complex absorption in the N-H str. region (Bands at 2.96, 3.14, 3.34 (broad) and 3.55μ (broad)), and it melted over the range 145-155°C.)

b. At 110°C

Heating the adduct in a sealed tube at 110° for 20 hours resulted in partial decomposition. The same gaseous and solid products were obtained as in the experiment above but approximately 50% of the starting material was recovered.

The above two reactions were carried out on the product resulting from the addition of hexafluoropropane imine and N-(perfluorobutyrimidoyl)perfluorobutyramidine.

7. Reaction of hexafluoropropane imine with N-(perfluorobutyrimidoyl)perfluorobutyramidine

N-(perfluorobutyrimidoyl)perfluorobutyramidine (4.6 g, 0.0113 mole) was first placed in a heavy-walled glass tube and hexafluoroimine (2.21 g, 0.0134 mole) was condensed in. The tube was then sealed and heated at 90°C for 19 hours. A colorless liquid was present after heating and the tube was then cooled and opened to a vacuum system. Unreacted hexafluoroimine (0.70 g, 0.00423 mole was recovered leaving a colorless liquid in the tube together with a trace of solid. Part of the liquid was distilled under reduced pressure (b.p.

35°/ 0.1 mm). The molecular weight of the distillate was found to be 473 (V.P.O.) (molecular weight required for a 1:1 adduct 572). The infrared spectrum was favourable for the expected addition product but no positive identification has yet been made.

D. Reactions of the Silver Salt of 3,5-bis(perfluoropropyl)-1,2,4-triazole with Divalent Metal Halides

1. Reaction of the silver salt with HgI_2

The silver salt of 3,5-bis(perfluoropropyl)-1,2,4-triazole, 27.6 g (.05 moles), and 50 ml of THF were placed in a two-necked, round-bottom flask which was fitted with a reflux condenser and dropping funnel. The HgI_2, 11.75 g (0.25 m), was dissolved in 50 ml of THF and added by means of the dropping funnel into the stirring, refluxing silver salt solution. After two hours the contents of the flask were filtered and 10.6 g of insoluble, yellow solid were removed. The filtrate was evaporated to dryness under reduced pressure and a pale yellow residue was obtained. This solid was mixed with acetone, then filtered to remove the insoluble yellow solids. The clear filtrate was evaporated to dryness and a pale white residue was obtained; this solid was taken up in 100 ml of chloroform which was heated to boiling and filtered hot to remove a white solid, 4.5 g, which melted between 190-210°C. The volume of the filtrate was reduced to 50 ml by evaporating under reduced pressure and 1.2 g of unreacted silver salt precipitated from the solution. After the silver salt was removed by filtration, the filtrate was cooled in an ice bath and 19.0 g of white solid precipitated from the solution. This solid melted between 65-86°C.

The 4.5 g portion was recrystallized from toluene and then dried at 130°C under reduced pressure.

2. Reaction of the silver salt with CdI_2

The silver salt of 3,5-bis(perfluoropropyl)-1,2,4-triazole, 8.7 g (.017 m), and 20 ml of n-butyronitrile were placed in a two-necked, round-bottom flask which was fitted with a reflux condenser and dropping funnel. The CdI_2, 2.9 g (.008 m), was dissolved in 40 ml of hot n-butyronitrile and placed in the dropping funnel. The stirring silver salt solution was heated to reflux and the CdI_2 solution was added dropwise. A yellow solid continuously precipitated during the addition of the CdI_2 solution. After the addition was completed, the contents of the flask were refluxed overnight. The contents of the flask were filtered and 3.6 g of yellow AgI was obtained. The filtrate was added to 150 ml of toluene and the resulting solution was cooled in an ice bath. A white crystalline solid, 3.8 g, recrystallized from this solution. This solid was hygroscopic and melted between 285-290°C; it sublimed under reduced pressure at 130°C. When a small portion of this white solid was dissolved in acetone and treated with aqueous $AgNO_3$, a very small amount of yellow solid precipitated and upon addition of more water, the white solid precipitated.

3. Reaction of the silver salt with ZnI_2

a. The silver salt of 3,5-bis(perfluoropropyl)-1,2,4-triazole, 4.1 g (.008 m) and 40 ml of absolute ethanol were placed in a two-necked, round-bottom flask which was fitted with a distillation head and dropping funnel. The ZnI_2, 1.27 g (.004 m), dissolved in 110 ml of absolute ethanol, was placed in the dropping funnel and added dropwise to the stirring, refluxing silver salt solution. After a small amount of the ZnI_2 solution had been added, the ethanol was distilled from the flask at approximately the same rate that the ZnI_2 solution was added. After the addition was completed, the contents of the flask were refluxed overnight. The contents of the flask were filtered and the filtrate was added to 100 ml of toluene. A pale white solid, 2.0 g, precipitated from this solution. This solid decomposed without melting when heated to 290-360°C and gave the same infrared spectra as the white solids obtained from the reaction of the triazole with $ZnCl_2$ and ZnO.

A sample, 7.15 g, of the Zn-triazole adduct and 60 ml of 95% ethanol were placed in a single-necked, round-bottom flask, which was fitted with a reflux condenser, and refluxed for 18 hours. The contents of the flask were filtered to remove the insoluble golden-brown solid and the filtrate was evaporated to dryness under reduced pressure. The white residue was placed in a sublimation apparatus and heated at 110°C under reduced pressure. 3,5-*bis*(Perfluoropropyl)-1,2,4-triazole, 1.8 g, was collected on the cold finger.

b. Zinc iodide, 3.4 g (.01 m) and 25 ml of THF were placed in a single-necked, round-bottom flask which was fitted with a dropping funnel. The silver salt, 5.12 g (.01 m), dissolved in 35 ml of THF, was placed in the dropping funnel and added dropwise to the stirring ZnI_2 solution at room temperature. After the addition was completed, the contents of the fask were filtered and 2.3 g of yellow solid were obtained. The filtrate was evaporated to dryness and the white residue was dissolved in ether. A red solution was obtained when either petroleum ether, carbon tetrachloride, or chloroform was added to the ether solution. A white solid precipitated from each of these red solutions overnight. This white solid was identified by its melting point and infrared spectra as the same triazole-zinc adduct that was obtained in the previous reactions.

E. Attempted Acylations of 3,5-bis(Perfluoropropyl)-1,2,4-triazole

1. Reactions of silver salt of 3,5-bis(perfluoropropyl)-1,2,4-triazole with perfluorobutyryl chloride.

a. At room temperature:

The silver salt, 10.24 g (.02m), was placed in a heavy-walled, glass tube. After the tube was cooled in liquid nitrogen and pumped free of air, perfluorobutyryl chloride, 33 g (.14 m), was condensed into the tube. The tube was sealed and rocked at room temperature for 48 hours. The white slurry did not dissolve during this period. The tube was cooled in liquid nitrogen and the acyl chloride was removed under reduced pressure; quantitative amounts of the starting materials were recovered.

b. At 65°C:

The silver salt, 7.57 g (.015 m), was placed in a heavy-walled, glass tube. After the tube was cooled in liquid nitrogen and pumped free of air, perfluorobutyryl chloride 40.4 g (.18 m), was condensed into the tube. The tube was sealed and heated at 65° for 12 hours. The tube was cooled in liquid nitrogen, opened under reduced pressure and the liquid removed. Fifty ml of ether were condensed into the tube, the contents of the tube were filtered to remove the ether insoluble solid, and the filtrate was evaporated to dryness under reduced pressure. 3,5-<u>bis</u>(perfluoropropyl)-1,2,4-triazole, 5.4 g, was recovered.

c. In chloroform:

The silver salt, 7.68 g (.015 m) and 40 ml of chloroform were placed in a heavy-walled, glass tube. After the tube was cooled in liquid nitrogen and pumped free of air, perfluorobutyryl chloride, 16.78 g (.072 m) was condensed into the tube. The tube was sealed and heated at 65-69° for 12 hours, cooled in liquid nitrogen and opened under reduced pressure to remove the liquid; 50 ml of ether were then condensed into the tube. The contents of the tube were filtered and 1.89 g of ether insoluble materials was obtained. After the ether was removed under reduced pressure, 6.0 g of

3,5-bis(perfluoropropyl)-1,2,4-triazole and a small amount of acetic acid were obtained.

2. Reaction of 3,5-bis(perfluoropropyl)-1,2,4-triazole with perfluorobutyryl chloride in the presence of triethyl amine

3,5-bis(perfluoropropyl)-1,2,4-triazole, 10.0 g (.025 m), 5.5 ml of triethylamine, and 35 ml of ether were placed in a heavy-walled, glass tube. After the tube was cooled in liquid nitrogen and pumped free of air, 8.48 g (.036 m) of perfluorobutyryl chloride were condensed into the tube. The tube was sealed and rocked at 25° for 24 hours. During this period a cream colored solid precipitated from the solution. The tube was cooled in liquid nitrogen and opened under reduced pressure. An additional 30 ml of ether were condensed into the tube and its contents were filtered. A white, water-soluble solid, 3.4 g, was obtained which decomposed at 254°C. The filtrate was evaporated to dryness under reduced pressure and a reddish-brown residue remained. This residue was dissolved in hot carbon tetrachloride and 9.4 g of 3,5-bis(perfluoropropyl)-1,2,4-triazole recrystallized from the cooled carbon tetrachloride solution.

3. Attempted reaction of 3,5-bis(perfluoropropyl)-1,2,4-triazole with acetyl chloride

3,5-bis(perfluoropropyl)-1,2,4-triazole, 7.65 g (.019 m), and 75 ml of acetyl chloride were placed in a single-necked, round-bottom flask. The flask was fitted with a reflux condenser which was open to the atmosphere through a dry ice trap. The resulting solution was refluxed for 24 hours, then the acetyl chloride was removed under reduced pressure. The 3,5-bis(perfluoropropyl)-1,2,4-triazole was recovered quantitatively.

F. Prepration and Reaction of the Silver Salt of Poly(perfluoroalkylene-1,2,4-triazole

1. Preparation of the silver salt

Poly(perfluoroalkylene-1,2,4-triazole), 6.84 g (0.01 moles of the monomeric unit), was dissolved in 30 ml of THF and placed in a single-necked, round-bottom flask which was fitted with a dropping funnel. Silver nitrate, 3.40 g (.02 m), was dissolved in 100 ml of 90% ethanol and placed in the dropping funnel. The silver nitrate solution was added dropwise to the stirring polytriazole solution at room temperature. During this period of addition a pale white solid continuously precipitated from the solution. After the addition was completed, the resulting slurry was stirred at room temperature overnight. The contents of the flask were filtered and 8.4 g of cream-colored solid were obtained. This solid slowly darkened and became black without melting when heated between 290 and 360°.

2. Reaction of the silver salt with HgI_2

The silver salt as prepared above in (1), 3.0 g (.0033 moles of the monomeric unit), 1.5 g (.0033 m) of HgI and 50 ml of xylene were placed in a single-necked, round-bottom flask. The flask was fitted with a reflux condenser and its contents were refluxed for 48 hours. During this heating period the red suspension in the flask turned yellow. The contents of the flask were filtered and the filtrate was evaporated to dryness under reduced pressure. A pale white solid, 2.24 g, was obtained which was identified as polytriazole from its infrared spectra.

Security Classification

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)*
University of Florida
Gainesville, Florida

2a. REPORT SECURITY CLASSIFICATION
Unclassified

2b. GROUP

3. REPORT TITLE
THERMALLY STABLE PERFLUORINATED POLYMERS

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*
Technical Report (1 March 1967 through 29 February 1968)

5. AUTHOR(S) *(Last name, first name, initial)*
Brown, Henry C.

6. REPORT DATE July, 1968

7a. TOTAL NO. OF PAGES

7b. NO. OF REFS

8a. CONTRACT OR GRANT NO. AF33(615)3782

b. PROJECT NO. 7340

c. Task No. 734004

d.

9a. ORIGINATOR'S REPORT NUMBER(S)
ML-TDR-64-142, Part V

9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*

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11. SUPPLEMENTARY NOTES

12. SPONSORING MILITARY ACTIVITY
Nonmetallic Materials Division, Air Force Materials Laboratory, Research & Technology Div.,Air Force Systems Command, W-PAFB, Ohio 45433

13. ABSTRACT

Studies of the poly(perfluoroalkylene-1,2,4-oxadiazole system have been continued; incorporation of bioxadiazole linkages in the polymer structure has led to significant changes in the polymer properties.

New monomers for the acyl chloride-tetrazole polymerization reaction have been developed; these monomers have, as a part of their structure triazole or bioxadiazole linkages which thus become incorporated in the final polymer.

Attempts have been made to synthesize new four and six membered heterocylic systems which have perfluoroalkyl substituents on the ring.

Limited further investigation of the metallic derivatives of perfluoroalkyl-substituted-1,2,4-triazoles has been carried out.

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Poly(perfluoroalkylene-1,3,4-oxadiazoles						
Fluorinated monomers						
Perfluoroalkyl-substituted heterocycles						
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