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SYNTHESIS OF POLY-HETEROCYCLICS

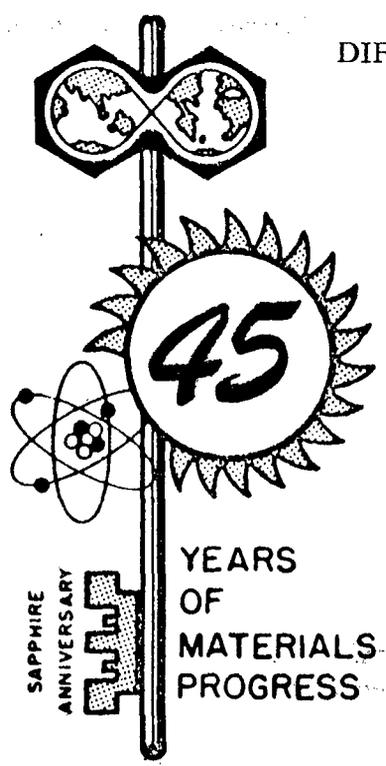
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KOPPERS COMPANY, INC.

MARCH 1962

DIRECTORATE OF MATERIALS AND PROCESSES
(MATERIALS CENTRAL)

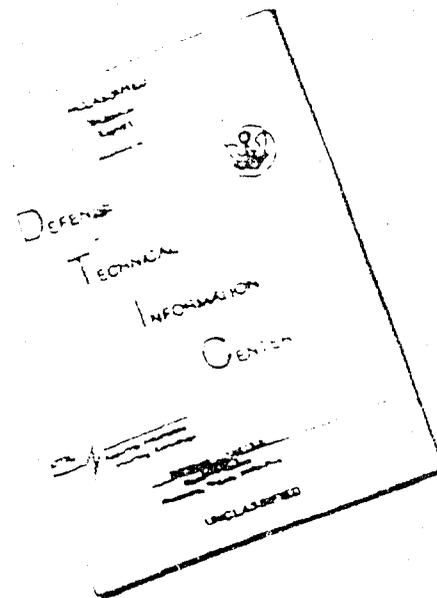
Project No. 7340



AERONAUTICAL SYSTEMS DIVISION
AIR FORCE SYSTEMS COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

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ASD-TDR-62-252

SYNTHESIS OF POLY-HETEROCYCLICS

TECHNICAL DOCUMENTARY REPORT NO. ASD-TDR-62-252
March 1962

Directorate of Materials and Processes
Aeronautical Systems Division
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio

Project No. 7340, Task No. 73404

(Prepared under Contract No. AF 33(616)-7021 S1(61-630)
by the Koppers Company, Inc., Monroeville, Pa.;
Philip E. Brumfield, Adolph V. DiGiulio, Paul Hergenrother,
Bernard Rudner and Samuel C. Temin, authors)

FOREWORD

This report was prepared by the Koppers Company, Inc., under USAF Contract No. AF 33(616)-7021 S1(61-630). This project was initiated under Project No. 7340, "Non-Metallic and Composite Materials", Task No. 73404, "New Chemicals and Methods". The work was administered under the direction of the Directorate of Materials and Processes, Aeronautical Systems Division, with Dr. G. F. L. Ehlers as project engineer.

This report covers work carried out from 1 February 1961 to 31 January 1962.

This work was under the general supervision of Dr. E. E. Donath, Manager Contract Research, Koppers Company, Inc. Technical assistance for portions of this project was provided by Richard A. Bafford and Dallas Schiegg. Assistance in characterization of products was provided by Robert Mainier, John E. Graham, Harold E. Sweeney, Robert F. Kratz, R. Sherman Detrick, John E. Thomas, Charles M. Hickey, Jr., and Gerald F. Cotton. Elemental analyses were by the Galbraith Laboratories or the Schwarzkopf Microanalytical Laboratory.

ABSTRACT

This project has as its goal the synthesis of organic polymers of high thermal stability. Two approaches are being followed; namely, the condensation of polymerization to form a chain of aromatic nuclei joined through heterocyclic groups and the polymerization of fluoroolefins containing heterocyclic groups to give fluorocarbon polymers with pendant heterocyclic substituents.

In a preliminary study started last year, eight model thiazole compounds with aryl substituents were prepared and compared as to thermal stability as a guide to designing polymer chains. In the model series the benzothiazole and 2,4-aryl-substituted thiazole structures were most stable. Two poly(benzothiazole) products, a poly(benzimidazole-benzothiazole) product, a poly(arylene-thiazolothiazole) product and a poly(azo-arylenethiazole) product have been obtained in almost quantitative yields in small scale reactions. All of these products were dark, infusible powders. One of the poly(benzothiazole) products was prepared in sufficient quantity to determine certain properties. It was insoluble in all solvents tested, formed a brittle disc by compression molding at 600°F, and showed thermal stability to over 600°C by thermogravimetric analysis (TGA).

The synthesis of perfluorocarbon polymers with pendant heterocyclic groups first requires the preparation of monomers with the structure $RCF=CF_2$, where R is a stable heterocyclic ring. Preparation of the polymers would permit a determination of the effect of non-volatile monomers on the depolymerization tendency of poly(perfluoroolefins). Several methods designed to produce the monomers have been examined without success. The first approach, involving the reaction of the metallo derivative of a heterocycle with tetra-fluoroethylene, or a halogenated derivative thereof, was abandoned. Currently attempts are underway to prepare 2-(trifluorovinyl)benzazoles via condensation of the properly substituted fluoroacids with ortho-substituted anilines. These precursors might then be converted to the monomers by dehydrofluorination, dehalogenation or decarboxylation.

PUBLICATION REVIEW

This technical documentary report has been reviewed and is approved.

FOR THE COMMANDER:

William E. Gibbs

William E. Gibbs
Acting Chief, Polymer Branch
Nonmetallic Material Laboratory
Directorate, Materials & Processes

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I. INTRODUCTION

In postulating structures for polymeric materials that would have a high degree of thermal stability, first consideration should be given to the relative stabilities of potential building units. Reference to various reports on decomposition temperatures for simple organic compounds will show that some structures, such as aromatic compounds, certain heterocyclic compounds, and fluorocarbons, have favorably high thermal resistance. A few examples of heat stable compounds are given in Table 1:

Table 1
Vapor Phase Decomposition of Simple Compounds¹

Compound	Decomposition Temperature, °F
Perfluorocyclohexane	1150-1200
Naphthalene	1150-1200
Thiophene	1100-1150
2-Phenylimidazole	1100
Benzothiazole	1025-1050
Biphenyl	950-1000
Benzimidazole	750-800
1,2,4-Triazole	800

In this program, the goal is the preparation of thermally stable polymers incorporating certain of these more stable structures.

One part of this program is the preparation of polymeric chains incorporating heterocyclic rings, particularly thiazoles, with connecting arylene units. The preferred approach is the condensation of polyfunctional arylene compounds with the formation of the heterocyclic ring as the polymer-forming reaction. The polymer chain is to contain no readily removable hydrogen, as represented by an aliphatic chain or a primary amide group.

In the other part of this program, perfluoroolefin derivatives of heterocyclic compounds are to be prepared. Addition polymerization of such monomers will lead to a fluorocarbon backbone with pendant heterocyclic groups. As in the preceding program, presence of labile hydrogens is to be avoided.

NOTE: Unless otherwise specified all temperatures given in this report are in °C.

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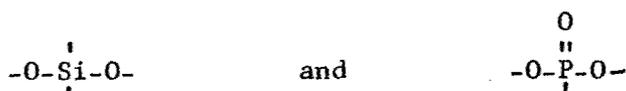
II. THIAZOLES

A. Introduction

This part of the report summarizes the work directed towards the preparation of thermally stable polyheterocyclics that contain heteroaromatic rings such as thiazoles in the polymer chains. Although not restricted to thiazoles, primary emphasis is directed to condensation reactions in which thiazole rings formed in the polymerization reaction are linked together by heat stable units, particularly arylene groups.

The nature of the connecting arylene groups is of paramount importance. There must be no labile hydrogen. For example, previous reports have indicated that polymers containing aliphatic chains decompose at relatively low temperatures. On the other hand, the arylene groups should preferably contain some bonds lending flexibility to the polymer chain. Fused arylthiazole groups would be expected to possess such a rigid structure as to be intractable.

Compound types known to be capable of imparting polymer flexibility without appreciable loss of stability include ethers, amines, sulfones, phosphine oxides and azos, provided that these bear only aromatic substituents. Of these, the ether linkage appears to be most desirable. Although certain ester linkages,



are probably at least as effective in imparting chain flexibility, compounds possessing them show decreased thermal stability.

The approach to the eventual preparation of a satisfactory polymer begins with the preparation of simple poly(arylthiazoles). The condensations to benzothiazoles and to 2,4-substituted thiazoles are expected to yield polymers of high thermal stability. From the simpler monomers, the study will proceed to the preparation of monomers containing structures which would be expected to improve polymer tractability, such as a diarylene ether derivative. Position isomerism in bonds to arylene groups could effect the properties of polymers. Incorporation of varying types of heterocyclic rings in the polymer chain might reduce the chain symmetry and thereby lower the melting point and increase the solubility of the polymers.

B. Summary

The initial phase of this project, comparison of the thermal stability of model thiazole derivatives, has been completed. 2-Phenylbenzothiazole and 2,4-diphenylthiazole were found to be most stable of the series. Several different types of polymers, containing these substituted thiazole groups, have been prepared in small-scale first experiments. These polymers are infusible and generally insoluble solids. These polymeric materials have been tentatively identified as a sulfur-bridged poly(benzothiazole), a poly(m-phenylene-benzothiazole), poly(p-phenylene-thiazolothiazole) and poly(p-phenylenazothiazole). Another polymer was obtained by amide formation, poly(p-phenylenamidobenzothiazole), but was abandoned because of the possible adverse effect of the amide linkage on stability. The cross-linked polymeric benzothiazole was obtained in sufficient quantity to permit preliminary testing.

Conversion of dehydrothio-*p*-toluidine (II, $n = 1$) to 2-(4'-aminophenyl)benzothiazole-6-carboxylic acid (III, $n = 1$) was accomplished by acetylation, permanganate oxidation, and hydrolysis. The preparation was accomplished in yields of approximately 90%. Since the yellow amino-acid did not melt below 300°C, it is believed to exist largely as the zwitterion.

Conversion of II to 2-phenylbenzothiazole-4',6-dicarboxylic acid (IV, $n = 1$) was effected by using different sequences of the following three reactions: (1) oxidation of the methyl group to a carboxy group, (2) diazotization of the amino group, followed by reaction with cuprous cyanide to yield the nitrile and (3) hydrolysis of the nitrile to a carboxylic acid. The preferred route proved to be first, conversion of II, by Sandmeyer reaction, to the nitrile, then an uninterrupted oxidation and hydrolysis of nitrile to 2-phenylbenzothiazole-4',6-dicarboxylic acid (about 57% yield).

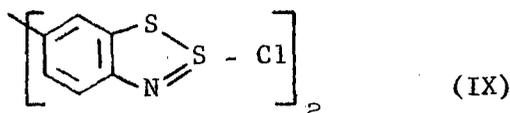
In view of Marvel's finding⁵ that phenyl esters gave improved condensations to poly(benzimidazoles), it was decided to convert the 2-phenylbenzothiazole-4',6-dicarboxylic acid to the diphenyl ester. By reaction with thionyl chloride, then phenol, diphenyl 2-phenylbenzothiazole-4',6-dicarboxylate has been successfully prepared in 61% yield. A preliminary attempt to prepare 2-(4'-amino-3'-mercapto-phenyl)benzothiazole-6-carboxylic acid (V, $n = 1$) by reaction of III with sulfur monochloride (the Herz reaction⁴) was unsuccessful.

A preliminary study of the feasibility of preparing intermediates from primuline base (II, $n = 2$) was begun. The acetyl derivative was prepared and oxidized by the permanganate method. The extreme insolubility of these primuline base derivatives made alkaline extraction of the oxidized product quite difficult. A total crude yield of acidic material amounting to 23% was collected, the product having the infrared absorption expected for 2'-(*p*-acetamidophenyl)-2,6'-bibenzothiazole-6-carboxylic acid (acetylated III, $n = 2$). Further study of this sequence of reactions has been postponed in favor of the more readily isolated intermediates from dehydrothio-*p*-toluidine.

b. Intermediates from Arylene Diamines

Both in this study of thiazoles and in the work of Marvel⁵ with imidazoles, the formation of fused ring systems is dependent upon the reaction of a carboxylic acid group with an aryl amine, having an ortho-mercapto group (to permit formation of a benzothiazole) or having an ortho amino group (to permit formation of a benzimidazole). Such intermediates as are being studied in this program are indicated in the following discussion.

Since benzidine is a readily available arylene diamine, initial studies were directed to its derivatives. The reaction of benzidine with sulfur monochloride⁴ produces a cyclic intermediate, postulated as having the structure:



Hydrolysis and alkaline digestion of this leads to the sodium salt of the mercapto compound. The 3,3'-dimercaptobenzidine (VII, X = S and Z = bond) formed by neutralization is difficult to purify. Solubility in dilute alkali or in dilute acid is very limited, and colloidal sulfur seems to accompany the dissolved product through the filter. Rapid crystallization from pyridine and ethanol gives a low recovery of yellow crystalline product, the bulk of the solute being transformed to a brown tar. Improved purification methods are being investigated.

A sample of 3,3',4,4'-tetraaminobiphenyl (VII, X = NH and Z = bond) was obtained from the Chemicals and Dyestuffs Division of Koppers Company, Inc.

The reaction of oxy-dianiline with sulfur monochloride⁴ in an attempt to form a dimercapto derivative (VII, X = S, Z = oxygen) that would yield more flexible polymers, resulted in purple tars whose infrared spectra were not consistent with the desired product.

c. Arylene Diacids as Intermediates

Reaction of ortho substituted arylenediamines to produce benzothiazole or benzimidazole units requires the employment of dicarboxylic acids in order to obtain polymers. Arylene diacids can be utilized in various forms; as the free acid, as the acid chloride or as an ester. Since Marvel⁵ found the phenyl esters particularly suited to the synthesis of poly(benzimidazoles), a similar utility for phenyl esters was anticipated in the preparation of poly(benzothiazoles).

Diphenyl isophthalate was prepared by the reaction of phenol with isophthaloyl chloride. In the hope of maintaining fluidity at even higher polymerization temperatures, the di(p-biphenyl) ester of isophthalic acid was also prepared.

As was previously noted, intermediates with flexibility in the arylene unit are desired for study. To this end, dimethyl oxy-bis-(4-benzoate) was prepared from methyl p-bromobenzoate and methyl p-hydroxybenzoate in the presence of caustic and activated copper. This ester is being hydrolyzed and converted to diphenyl oxy-bis-(4-benzoate).

3. Preparation of Polymers

Many of the monomer intermediates previously discussed have been employed in the preparation of polymers. Each of the polymers to be discussed represents a different structural type. Most of the experiments were carried out on a small scale. Polymers that show promise will be prepared on a larger scale, and previously noted structural changes will be incorporated in monomers in attempts to improve the properties of these more promising types.

a. Polymerization by Formation of Amide Groups

In a preliminary polymerization study, a polyamide was prepared by heating 2-(4'-acetamidophenyl)benzothiazole-6-carboxylic acid in a small tube equipped with an inlet for a nitrogen atmosphere. Polymerization appeared to take place between 300 and 435°. Titration of the acetic acid condensed in the dry-ice chilled trap indicated that the poly(2-phenylbenzothiazole-6-carbox-4'-amide) obtained had an

average degree of polymerization of about 3.3. When this polymer was heated to 535°, no more than a trace of sublimate appeared on the cooler part of the tube.

In another simplified polymerization, 2-(4'-aminophenyl)-benzothiazole-6-carboxylic acid was heated under nitrogen in the presence of a catalyst at 250° for 12 hours. The small amount of water collected in a cold trap appeared to have come from a hydrate. During heating at 300° for 11 hours, the sample changed from yellow to tan, suggesting polymerization. Further, the water collected in the cold trap at this temperature corresponded to one mole of water per mole of amino acid. A portion of this polymer, when heated to 505°, gave evidence of shrinking and darkening. During this last heating step, at above 460°, a trace of sublimate formed on the cooler portion of the tube. Infrared absorption curves of the polymer before and after heating to 505° were identical. The infrared spectrum of the sublimate showed a phenylbenzothiazole pattern, and absorption peaks believed to be due to -NH₂ and -C≡N, as well as a minor absorption for a -C=O group.

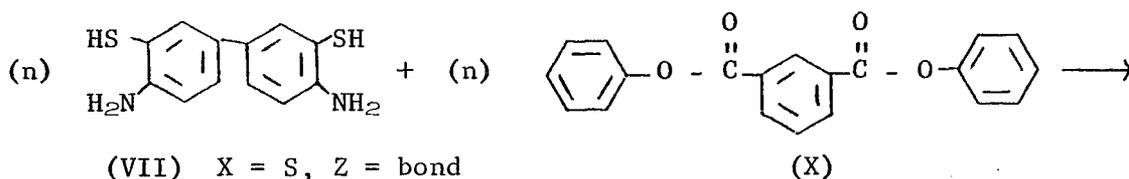
b. Polymerization by Condensation of Aryl Amines with Sulfur

The commercial reaction of *p*-toluidine with sulfur produces dehydrothio-*p*-toluidine (II, *n* = 1) and primuline base (II, *n* = 2) as the major products. The reaction could theoretically proceed to the polymer range with "n" becoming a large number, were the higher homologs more readily fusible. Use of high boiling organic solvents with *p*-toluidine and sulfur resulted in the same products as the melt reaction. When a mixture of anhydrous sodium tetrasulfide and potassium pentasulfide was used as a molten reaction medium, sulfur converted dehydrothio-*p*-toluidine (at 260° maximum reaction temperature) and primuline base (at 285° maximum reaction temperature) to apparently identical brown powders. Characterization of these products by infrared absorption analysis and by elemental analysis indicated that each was a poly(benzothiazole), probably cross-linked by sulfide bonds. A study of the physical properties of this product will be given in a later paragraph.

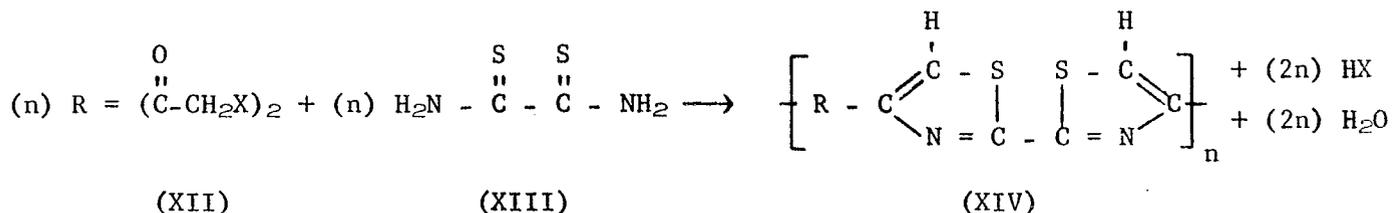
The melt reaction of *m*-toluidine with sulfur produced brown tars. Infrared absorption studies suggested the presence of carbonyl groups, indicating that undesired reactions were occurring.

c. Polymerization by Formation of Benzothiazole Groups

Polymeric benzothiazoles prepared from bis(*o*-mercapto-anilines) and arylenedicarboxylic acids (or their congeners) should, by analogy to the known benzimidazole polymers, be thermally stable. A first attempt to prepare representatives of this type, by heating terephthalic acid with 3,3'-dimercaptobenzidine, gave an infusible product that, on the basis of spectra was incompletely cyclized. However, heating with diphenyl isophthalate (X) to 400° gave a dark green, intractable polymer, the infrared absorption of which was consistent with the proposed structure



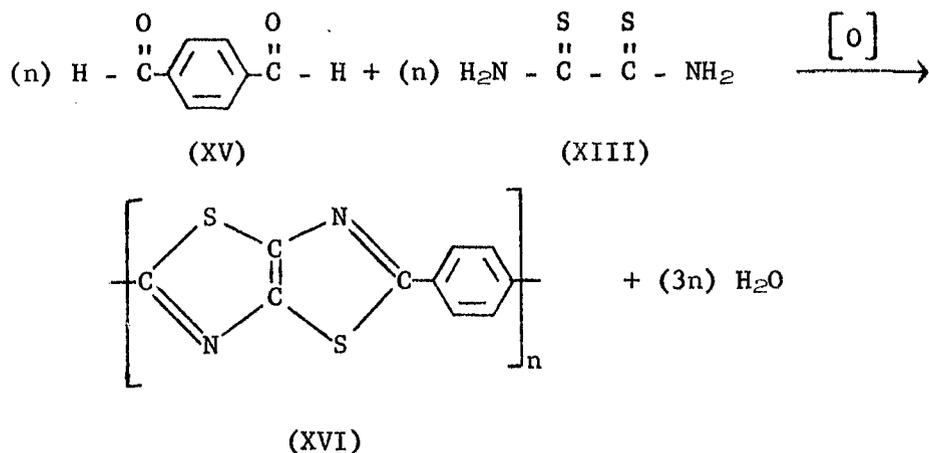
(a variation of the Hantzsch synthesis generally called "the King Reaction") pro-



duced only low-melting black tars, from which no identifiable product could be obtained. There was no solid isolated that might have been XIV (with R = bond), a chain of thiazole rings. This type of polymer has been prepared in other laboratories, with R as an alkylene or arylene linkage.

Since the reaction of aldehydes and rubeanic acid in the presence of air has recently been reported⁶ to yield (4,5-c) thiazolothiazoles, it appeared likely that use of di-aldehydes would lead to novel polymers. A mixture of glyoxal (XV, phenylene group replaced by a bond) and rubeanic acid (XIII) was heated in butanol in the presence of air. The product obtained was a black powder having no infrared absorption pattern. There was no evidence for the formation of a chain of thiazolothiazole groups.

On heating solutions of terephthalaldehyde (IX) and rubeanic acid (X) in triglyme, in one case with air as the oxidant, and in a second with sulfur, brown powders were obtained. The infrared absorption analysis of the two products showed

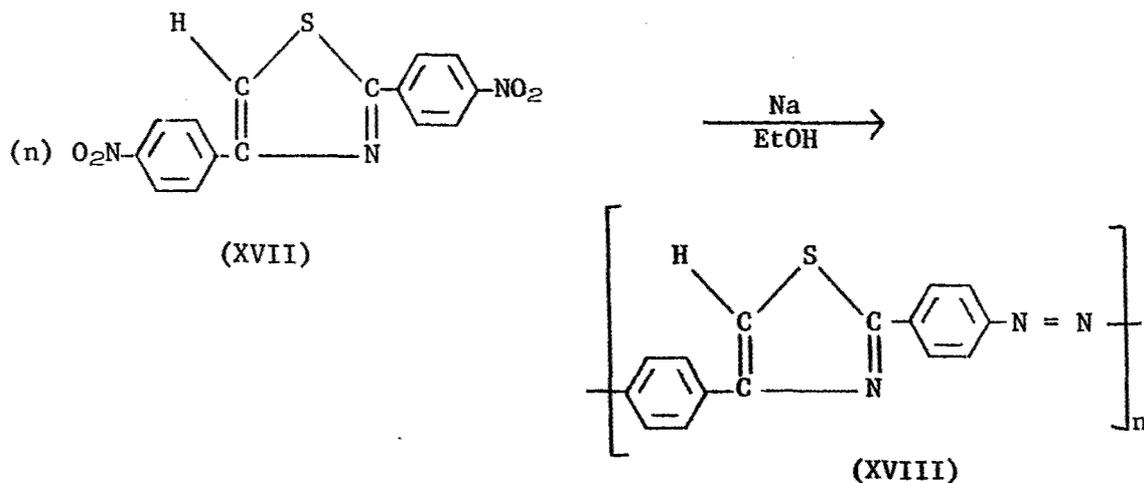


the same absorption peaks, but the presence of the thiazolothiazole group could not be confirmed. The elemental analyses for C, H, N and S were low, possibly due to incomplete combustion; relative values for nitrogen and sulfur were too low for the expected poly(phenylenethiazolothiazole) (XVI). A sample of this polymer, as Sample No. 910-W59DA1, has been submitted to ASD for TGA testing.

f. Polymerization by Formation of Azo Linkages

Thermally stable polymers containing thiazoles linked through their 2- and 4-carbons to arylene groups have been prepared in other laboratories⁵. The availability of 2,4-diphenylthiazole, and its established resistance to thermal

degradation, suggested it might be a useful intermediate. It was hoped that a polymeric phenyl-azo-phenylthiazole might have both flexibility and stability. The mixed acid nitration of 2,4-diphenylthiazole produced 2,4-bis(*p*-nitrophenyl)thiazole (XVII). The reduction of this compound over sodium amalgam gave a brown, infusible powder. Infrared absorption analysis showed absorption peaks characteristic of 1,4-phenyl substitution and of thiazoles but the presence of an -N=N- group could not be established. The elemental analysis was too low for all elements, except hydrogen, for the expected poly(azo-phenylthiazole) (XVIII).



A sample of this polymer, as Sample No. 910-W61A, has been submitted to ASD for TGA testing.

4. Characterization of Polymers

Polymers prepared under this program are to be studied for thermal stability, solubility, moldability and structural strength. Most of the reactions were first trials, being carried out on a small scale. Only the poly(benzothiazole) from the primuline fusion reaction has been obtained in sufficient quantity for testing.

a. Thermogravimetric Analysis

The ASD has requested that samples of polymers be submitted for thermogravimetric analysis and other characterizing tests. The TGA curve obtained for poly(benzothiazole), 910-W51A (the primuline fusion reaction), is shown on Figure 1. On the figure are also plotted values for polyphenyl and "Teflon", as reported by Doyle⁷. The TGA determination of ASD and of Doyle are carried out in the same manner. Calculation of decomposition temperatures was therefore adapted from the report by Doyle. The "differential procedural decomposition temperature", DPDT, was calculated from a plot of weight loss per hour, the temperature where the loss amounted to 10% per hour being taken as the DPDT, found to be 620° for Sample No. 910-W51A. The "integral procedural decomposition temperature", IPDT, was calculated from the ratios of areas under the TGA curve, using Doyle's equation:

$$T_{A*K*} = 875 A*K* + 25$$

For Sample No. 910-W51A, the IPDT was 690°C. Some representative values of decomposition temperatures are shown in Table 3, for comparison with the poly(benzothiazole). As was noted earlier in this report, relative stabilities of simple compounds do not necessarily predict the relative stabilities for the corresponding

Table 3

Thermogravimetric Analysis - Calculated Decomposition Temperatures

Polymer	IPDT, °C	DPDT, °C
Poly(benzothiazole) 910-W51A	690	620
Teflon	555	490
Polyphenyl	535	510
Silicone (SR 32)	505	450
Nylon 66	420	360
Polystyrene	395	330
Plexiglass	345	280

polymer. For example, the decomposition point for biphenyl (1010°F)^a is higher than that of 2-phenylbenzothiazole (943°F)^b, as shown in Table 2. The corresponding polymers, however, reverse the order of thermal stability, poly(benzothiazole) (620°C) showing a higher TGA value than does polyphenyl (510°C) as shown in Table 3 and Figure 1.

(a) 1010°F equals 543°C

(b) 943°F equals 505°C

b. Moldability of Polymers

Since the poly(benzothiazole), 910-W51A, was infusible and insoluble, a compression molding at high temperature was attempted. A small electrically-heated mold with a 7/8" diameter cylindrical cavity was adapted to a Vicat press capable of a maximum pressure of 20 tons. A 3/16" thick disc of the polymer was produced by a temperature of 600°F at a pressure of 20 tons after a holding time of 5 minutes. This disc was hard, but rather brittle.

In a statistically designed experiment, samples of the poly(benzothiazole) were compression molded at selected points, with temperatures of 400 to 600°F and pressures of 5 to 20 tons for holding times of 5 to 20 minutes. In the preliminary test, the thick disc obtained (under molding conditions as for Sample No. 7) had a Barcol hardness of 52-64. The thinner discs from this series were for the most part too fragile to permit a hardness test. This experiment is summarized in Table 4. Only Sample No. 3 survived removal from the mold and the hardness testing as a complete disc.

c. Structural Strength of Molded Polymers

The poly(benzothiazole) could not be tested for tensile modulus or flexural modulus, since molded shapes for these tests could not be obtained. When possible with polymeric products, such evaluations will be made.

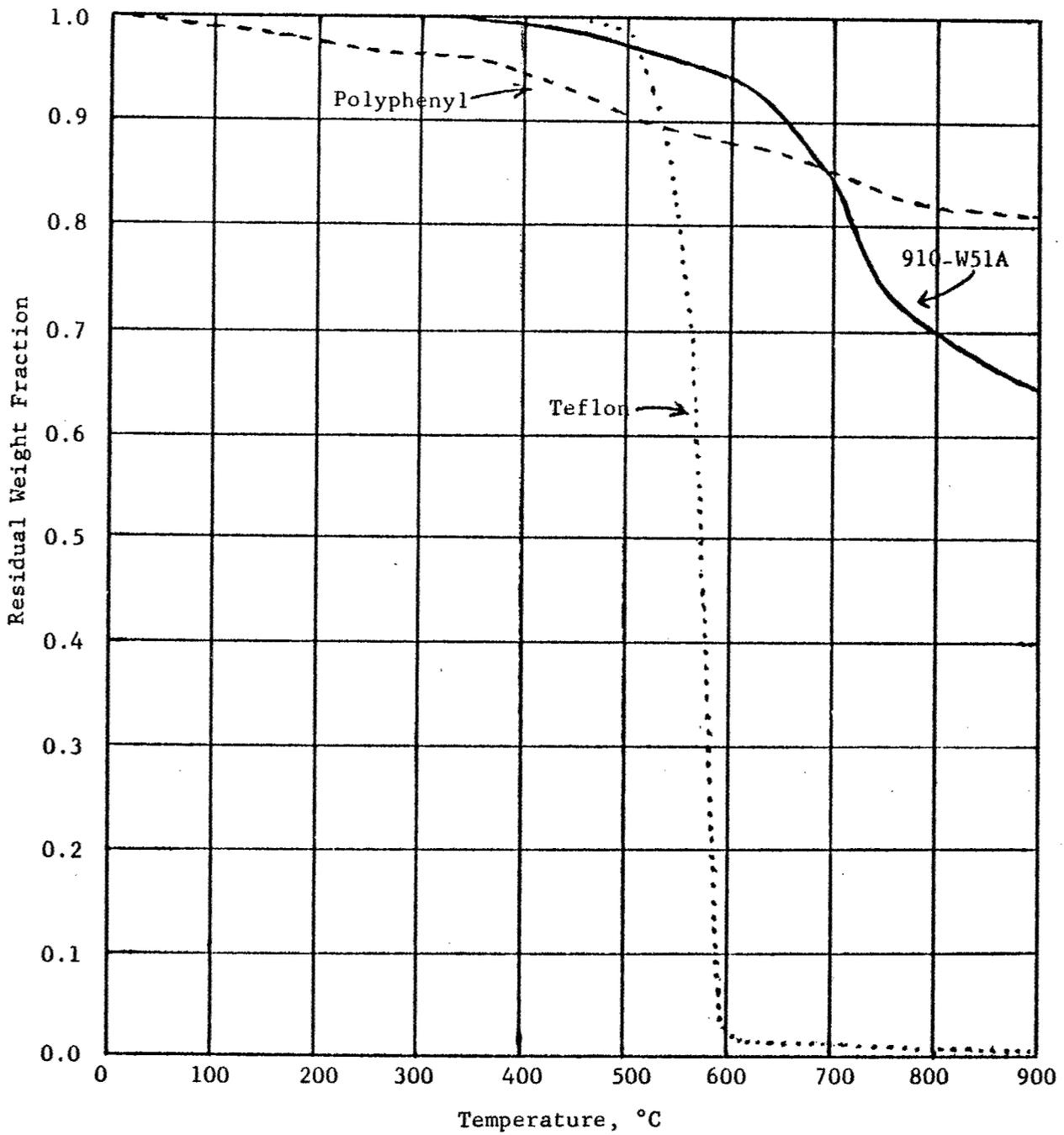


Figure 1 Thermogravimetric Analysis Data⁷ (150°C per hour)

Table 4

Compression Molding of Poly(benzothiazole) from
Sample 910-W51A - (Discs 7/8" diam. x 1/16" thick)

Sample Number	Temp., (°F)	Press., (tons)	Time (min.)	Appearance		Barcol Hardness
				Color	Rigidity	
1	600	20	20	dark brown	brittle	b
2	400	5	20	tan	very fragile ^a	b
3	400	20	5	medium brown	mod. sturdy	45-55
4	600	5	20	tan	mod. brittle ^a	b
5	500	12.5	12.5	medium brown	mod. sturdy	b
6	400	5	20	dark tan	fragile ^a	b
7	600	20	5	dark brown	brittle ^a	64-65
8	600	5	5	medium brown	brittle	b
9	400	20	20	medium brown	brittle	50-65
10	500	12.5	12.5	medium brown	mod. sturdy	60-65

(a) Disc broken during removal from mold.

(b) Needle of Barcol meter cracked disc before penetration far enough for obtaining value.

D. Experimental

1. Model Compounds

Characterization of the seventh model compound of the series, 2-(1-naphthyl)-4-phenylthiazole has been completed. The attempted preparation of 2-(2-biphenyl)-4-phenylthiazole has been abandoned. An eighth compound, 2-(4'-benzamidophenyl)-benzothiazole, has been prepared and characterized.

a. Preparation of 2-(1-naphthyl)-4-phenylthiazole

The previously reported 2-(1-naphthyl)-4-phenylthiazole had a melting point of 88-9° and a boiling point of 196° at 0.3 mm. of mercury. Its ultraviolet absorption spectrum had peaks at 275 and 322 millimicrons. A purified sample gave the following elemental analysis:

	% C	% H	% N	% S	% Total
Calc'd for $C_{19}H_{13}NS$:	<u>79.41</u>	<u>4.56</u>	<u>4.87</u>	<u>11.16</u>	<u>100.00</u>
Found:	79.39	4.36	5.06	11.49	100.30

A powdered sample, submitted to ASD for thermal testing, was found to decompose at 876°F.

b. Preparation of 2-(4'-Benzamidophenyl)benzothiazole

Of the various possible synthetic routes to the formation of 2-(4'-benzamidophenyl)benzothiazole, two reaction sequences were proposed. In the first approach, *p*-benzamidobenzoic acid was to be prepared from *p*-aminobenzoic acid and benzoyl chloride. This with *o*-aminothiophenol and zinc chloride should then yield the desired product. In the alternative approach, the reaction of *p*-nitrobenzoyl chloride with *o*-aminothiophenol would yield 2-(4'-nitrophenyl)benzothiazole, which could be reduced to the corresponding amino compound. Reaction of this 2-(4'-aminophenyl)benzothiazole with benzoyl chloride would yield the desired 2-(4'-benzamidophenyl)benzothiazole.

(1) Benzoylation of *p*-Aminobenzoic Acid

A solution of *p*-aminobenzoic acid (15.7 g., 0.11 mole) and sodium acetate (11.5 g., 0.14 mole) was prepared in 200 ml. of acetic acid. Benzoyl chloride (16.7 g., 0.12 mole) was added dropwise during 20 minutes to the stirred solution, a maximum reaction temperature of 40° being observed. A white solid began to separate and the mixture was heated to 70° for one hour. The mixture was diluted with water and the white solid was separated on a filter. Crystallization of the product from hot iso-amyl alcohol, to which increments of dimethylformamide were added until a clear solution was obtained, gave 20.5 g. (78% of theory) of *p*-benzamidobenzoic acid, melting at 300-1° (uncorr.), (lit. 290°).

(2) Attempted Reaction of *p*-Benzamidobenzoic Acid with *o*-Aminothiophenol in Solution

A mixture of *p*-benzamidobenzoic acid (17.9 g., 0.074 mole), *o*-aminothiophenol (9.3 g., 0.074 mole) and zinc chloride (10.1 g., 0.074 mole) was heated at vigorous reflux in 300 ml. of benzene for 4 hours. Since no water collected in

the Dean-Stark trap in the assembly and no other evidence of reaction could be detected, all but 30 ml. of the benzene was removed by distillation. Nitrobenzene (150 ml.) was added and the mixture was heated about 146° for 4 hours. The brown reaction mixture was cooled and stirred with 400 ml. of water. A brown solid was separated by filtration and dried to give 18.6 g. of a tan solid. Vacuum concentration of the nitrobenzene layer gave about 4 g. of a black gum. Attempts to obtain a crystalline product from this black gum failed. Crystallization of the tan solid from isoamyl alcohol gave a 9.0 g. of white crystals, melting at 291-3° (uncorr.), corresponding to the starting p-benzamidobenzoic acid.

(3) Attempted Reactions of p-Benzamidobenzoic Acid with o-Aminothiophenol in a Melt

A mixture of p-benzamidobenzoic acid (9.0 g., 0.037 mole) and o-aminothiophenol (4.6 g., 0.037 mole) was heated to 246° during 3 hours, without any appreciable change in appearance. After being heated at about 280° for an additional 3 hours, the melt became dark green. The only crystalline material isolated from the reaction mixture was p-benzamidobenzoic acid, melting at 290-4° (uncorr.).

(4) Preparation of 2-(4'-Nitrophenyl)benzothiazole

A solution of p-nitrobenzoyl chloride (25.0 g., 0.135 mole) was prepared in pyridine (100 ml.) at 40°. With stirring, o-aminothiophenol (16.9 g., 0.135 mole) was added dropwise during 0.5 hour, intermittent cooling being employed to hold the reaction temperature below 100°. Upon formation of solids in the reaction mixture, additional pyridine (100 ml.) was introduced and the mixture was stirred at 85° for 1.5 hours. The solid product separated by filtration from the cold reaction mixture was washed with water and dried. The 2-(4'-nitrophenyl)-benzothiazole (29.7 g., 86% of theory) melted at 237-8° (uncorr.), (lit.-231°).

(5) Reduction of 2-(4'-Nitrophenyl)benzothiazole

A mixture of 2-(4'-nitrophenyl)benzothiazole (29.7 g., 0.12 mole), tin (42.0 g., 0.35 g. - atom), hydrochloric acid (110 ml. of 37%), water (260 ml.) and ethanol (100 ml.) was stirred at reflux for 5 hours. An additional 40 ml. of 37% hydrochloric acid was added and the mixture was refluxed an additional hour. The resulting yellow slurry was cooled to 50° and made strongly alkaline. The yellow solid separated by filtration failed to melt (possibly a tin complex). This yellow solid was stirred with 500 ml. of 20% sodium hydroxide solution at 85-90° for 1.5 hours and filtered hot, then thoroughly washed with water. The dried yellow 2-(4'-aminophenyl)benzothiazole (25.0 g., 99% of theory) melted at 156-7° (uncorr.), (lit. - 155°).

(6) Preparation of 2-(4'-Benzamidophenyl)benzothiazole

A solution of 2-(4'-aminophenyl)benzothiazole (25.0 g., 0.11 mole) and sodium acetate (9.1 g., 0.11 mole) was prepared in 300 ml. of acetic acid at about 80°. Benzoyl chloride (16.4 g., 0.12 mole) was added dropwise during 10 minutes; slight exotherm carried the mixture to 85°. The reaction mixture was then stirred at reflux for 5 hours. Cooling, diluting with water, and filtering gave

as a tan solid 33.7 g. (93% yield) of the title compound. It was recrystallized several times from iso-amyl alcohol, to get white crystals, melting at 227.5-9.0°. The infrared absorption spectrum (Figure 2.a.) was consistent with the structure expected for 2-(4'-benzamidophenyl)benzothiazole. The ultraviolet absorption spectrum showed a very strong maximum at 330 millimicrons. A purified sample gave the following elemental analysis:

	% S	% H	% N	% S	% TOTAL
Calc'd for C ₂₀ H ₁₄ N ₂ OS:	72.72	4.27	8.48	9.69	95.16
Found:	72.71	4.34	8.41	9.72	95.18

A powdered sample submitted to ASD for thermal testing, decomposed at 667°F.

2. Intermediates from Dehydrothio-p-toluidine

The original goal for derivatives of dehydrothio-p-toluidine was the preparation of three intermediates. The first compound was 2-(4'-aminophenyl)benzothiazole-6-carboxylic acid (III), which could be polymerized to give a poly(amidobenzothiazole). The second compound was 2-phenylbenzothiazole-4',6-dicarboxylic acid (IV) that could be condensed with substituted arylene diamines (substituents being ortho amino or mercapto groups) to form poly(benzothiazolebenzazoles). Finally, 2-(4'-amino-3'-mercapto)benzothiazole-6-carboxylic acid (V), could be self-condensed to give a poly(benzothiazole).

a. Preparation of 2-(4'-Aminophenyl)benzothiazole-6-carboxylic Acid

A series of preliminary experiments were carried out in attempts to oxidize acetylated dehydrothio-p-toluidine to 2-(4'-acetamidophenyl)benzothiazole-6-carboxylic acid. Oxidation procedures tested without success were: sodium dichromate in acetic acid, selenium dioxide in acetic acid and potassium permanganate in water, alkaline buffer, acetone, and acetic acid.

(1) Acetylation of Dehydrothio-p-toluidine

Acetic anhydride (45.0 g., 0.44 mole) was added during 20 minutes to a refluxing solution of dehydrothio-p-toluidine (99.0 g., 0.41 mole) in acetic acid (500 ml.). The mixture was stirred at reflux for an additional 1.5 hours and then cooled and poured in an equal volume of ice water. The tan solid was separated from the red liquid by filtration. The washed and dried solid (115.3 g.) represented a quantitative yield of 2-(4'-acetamidophenyl)-6-methylbenzothiazole, melting at 233-34.5° (uncorr.), (lit. - 231-2°).

(2) Oxidation of 2-(4'-Acetamidophenyl)-6-methylbenzothiazole

A solution of 2-(4'-acetamidophenyl)-6-methylbenzothiazole (60.5 g., 0.22 mole) in pyridine (650 ml.) was added dropwise during one hour to a vigorously stirred solution of potassium permanganate (60.0 g., 0.38 mole) in water (200 ml.) and pyridine (100 ml.) at 60°. After the complete addition, the mixture was heated to and stirred at 95° for one hour with the disappearance of the purple color. Additional potassium permanganate (60.0 g., 0.38 mole) was added and the

reaction mixture was stirred at 95° for one hour with the disappearance of the purple color. Again potassium permanganate (40.0 g., 0.25 mole) was added and the mixture stirred and refluxed for three hours. The cooled brown mixture was filtered. Treating the brown filter cake with sodium bisulfite and concentrating the yellow pyridine filtrate gave yellow solids. The combined yellow solids were dissolved in 2500 ml. of 2% potassium hydroxide solution and filtered. Acidification of the yellow filtrate with hydrochloric acid gave 60.0 g. (90% yield) of yellow solid, 2-(4'-acetamidophenyl)-benzothiazole-6-carboxylic acid. No softening or melting could be detected below 330° on a standard melting point block. By dropping the powder onto a heated block at intervals of about 5°, a rapid transition was noted at 320°, the powder showing momentary softening then resolidifying. A purified sample (infrared absorption - Figure 4.b.) gave the following elemental analysis:

	<u>% C</u>	<u>% H</u>	<u>% N</u>	<u>% S</u>	<u>% TOTAL</u>
Calc'd for C ₁₆ H ₁₂ N ₂ O ₃ S:	61.62	3.87	8.97	10.26	84.72
Found:	61.35	3.95	8.92	10.29	84.51

(3) Preparation of 2-(4'-Aminophenyl)benzothiazole-6-carboxylic Acid

A portion of 2-(4'-acetamidophenyl)benzothiazole-6-carboxylic acid (20.0 g.) was refluxed in a mixture of acetic acid (200 ml.), 37% hydrochloric acid (300 ml.) and water (200 ml.) for 5 hours. The bright yellow suspension was cooled and filtered. The yellow solid was slurried with warm water, filtered and dried to yield 14.7 g. of yellow solid, infusible to over 360°. The infrared spectrum (Figure 3.d.) was consistent with the structure proposed for 2-(4'-aminophenyl)benzothiazole-6-carboxylic acid (III). The following elemental analysis was obtained:

	<u>% C</u>	<u>% H</u>	<u>% N</u>	<u>% S</u>	<u>% TOTAL</u>
Calc'd for C ₁₄ H ₁₀ N ₂ O ₂ S:	62.22	3.73	10.37	11.86	88.18
Found:	62.01	3.92	10.46	11.91	88.33

b. Preparation of 2-Phenylbenzothiazole-4',6-dicarboxylic Acid

Conversion of dehydrothio-*p*-toluidine to the diacid, 2-phenylbenzothiazole-4',6-dicarboxylic acid, could theoretically be achieved by any of three similar routes. One procedure would involve the diazotization of dehydrothio-*p*-toluidine followed by reaction with cuprous cyanide to give the nitrile. Permanganate oxidation and hydrolysis could then convert both the 4'-cyano and the 6-methyl group to carboxy groups. Alternatively, the same nitrile could first be hydrolyzed to a carboxylic acid, and the 6-methyl group could then be oxidized. The third procedure would involve diazotization of the amino acid, 2-(4'-aminophenyl)benzothiazole-6-carboxylic acid followed by reaction with cuprous cyanide. The resulting nitrile could then be hydrolyzed to convert the 4'-cyano group to the carboxylic group.

(1) Preparation of 2-(4'-Cyanophenyl)-6-methylbenzothiazole

A slurry of dehydrothio-p-toluidine (60.0 g., 0.25 mole) in 37% hydrochloric acid (250 ml.) and water (400 ml.) was heated to reflux with vigorous agitation for 15 minutes. The bright yellow slurry was cooled to 0° and sodium nitrite (18.0 g., 0.26 mole) in water (100 ml.) was added dropwise during one hour. The cooled mixture was stirred for an additional hour. After excess nitrous acid had been destroyed by the addition of urea, the pH of the orange suspension was adjusted to 7 with sodium carbonate. The resulting yellow slurry was added during 15 minutes to a solution (at 0°) of cuprous cyanide (23.3 g., 0.13 mole) and sodium cyanide (38.0 g., 0.78 mole) in water (400 ml.). Benzene (100 ml.) had been added to facilitate separation of the product. The resulting brown slurry was stirred at 5° for one hour, then permitted to warm to room temperature. The brown solid was filtered, washed with water and dried to give 69.3 g. of solid. Crystallization from iso-amyl alcohol gave a light orange solid (35.0 g., 56% of theory), melting at 187-191° (uncorr.), (lit. - 145°). Recrystallization from iso-amyl alcohol, in the presence of activated carbon, resulted in a white product, melting at 196-8° (uncorr.). The infrared absorption spectrum (Figure 3.a.) obtained was consistent with the proposed structure for 2-(4'-cyanophenyl)-6-methylbenzothiazole.

(2) Preparation of 2-Phenyl-6-methylbenzothiazole-4-carboxylic Acid

A suspension of 2-(4'-cyanophenyl)-6-methylbenzothiazole (9.0 g., 0.036 mole) in 37% hydrochloric acid (170 ml.) was stirred at reflux for 3 hours. The resulting orange suspension was cooled and poured into twice its volume of ice water. The bright orange solid separated by filtration was slurried with dilute sodium hydroxide, filtered and re-slurried with hot water, then again filtered. These alkaline filtrates were combined and acidified, precipitating a tan solid. Crystallization of this tan solid from iso-amyl alcohol gave the light yellow 2-phenyl-6-methylbenzothiazole-4'-carboxylic acid (5.1 g., 53% of theory), melting at 314-6° (uncorr.). The infrared absorption spectrum (Figure 3.c.) obtained was consistent with the proposed structure.

(3) Preparation of 2-Phenylbenzothiazole-4',6-dicarboxylic Acid
From 2-(4'-Cyanophenyl)-6-Methylbenzothiazole

A solution of 2-(4'-cyanophenyl)-6-methylbenzothiazole (9.0 g., 0.036 mole) in 200 ml. of pyridine was added dropwise during one hour to a stirred refluxing solution of potassium permanganate (21.6 g., 0.12 mole) in 100 ml. of water and 50 ml. of pyridine. After addition of about one-half of the nitrile solution the purple color disappeared. An additional 21.6 g. (0.12 mole) of potassium permanganate was added and the mixture was refluxed for 1.5 hours. The cooled brown mixture was filtered. The manganese dioxide filter cake contained only a trace amount of solid insoluble in aqueous bisulfite. The pyridine filtrate was concentrated and the resulting orange solid was extracted repeatedly with 2% potassium hydroxide solution. The combined alkaline filtrates were acidified with conc. hydrochloric acid to yield 7.2 g. (67% crude yield) of orange solid. The neutralization equivalent of the crude product was 218, compared with calculated values for 2-phenylbenzothiazole-4',6-dicarboxylic acid of 150 (anhydrous) or 168 (dihydrate). A reprecipitated sample gave a neutralization equivalent of 161, and had an infrared absorption curve (Figure 5.a.) identical to that of a rigorously purified sample of 2-phenylbenzothiazole-4',6-dicarboxylic acid (IV).

(4) Preparation of 2-(4'-Cyanophenyl)benzothiazole-6-carboxylic Acid

A suspension of 2-(4'-aminophenyl)benzothiazole-6-carboxylic acid (10.0 g. 0.037 mole) in 37% hydrochloric acid (50 ml.) and water (250 ml.) and water (250 ml.) was vigorously stirred and refluxed for 15 minutes. The yellow suspension was cooled to 0° and sodium nitrite (2.8 g., 0.041 mole) in water (50 ml.) was added dropwise during 20 minutes. The resulting bright yellow suspension was stirred at 5° for 45 min. After the excess nitrous acid was destroyed with sulfamic acid, the pH of the yellow suspension was adjusted to 7 with sodium carbonate. The neutralized diazonium salt suspension was added during 10 minutes to a clear solution of cuprous cyanide (3.4 g., 0.019 mole) and sodium cyanide (5.6 g., 0.11 mole) in water (250 ml.) cooled to 5°. The resulting orange-brown suspension was stirred at 5° for 2 hours and at 25° for 2 hours. Saturation with sodium chloride followed by filtration gave a brown solid that was dissolved in water. The red aqueous solution was filtered and the filtrate acidified with dilute hydrochloric acid to give 8.2 g. of a brown solid (78% crude yield). The infrared absorption spectrum verified the presence of a nitrile and was consistent with the proposed structure for 2-(4'-cyanophenyl)benzothiazole-6-carboxylic acid. A portion of brown solid recrystallized from 95% ethanol was recovered as a yellow solid, having the infrared absorption spectrum shown in Figure 3.b. The following elemental analysis was obtained:

	%C	%H	%N	%S	% TOTAL
Calc'd for $C_{15}H_8N_2O_2S$:	64.27	2.88	9.58	11.54	78.27
Found:	63.03	2.88	9.50	11.44	76.85

(5) Preparation of 2-Phenylbenzothiazole-4',6-dicarboxylic Acid by Hydrolysis of 2-(4'-Cyanophenyl)benzothiazole-6-carboxylic Acid

2-(4'-Cyanophenyl)benzothiazole-6-carboxylic acid (8.2 g., 0.029 mole) was added to 100% phosphoric acid (139 g.) at 30°. A slight exotherm developed during the next ten minutes, carrying the temperature to 33°. The mixture was slowly heated to 85° and stirred for two hours. The resulting dark red solution was poured onto ice and filtered. Drying the filter cake at 75°/15 mm. gave an orange-brown liquid that was then stirred and refluxed in 10% hydrochloric acid (150 ml.) for one hour. The brown suspension was cooled to 0° and sodium nitrite (2.1 g., 0.03 mole) in water (50 ml.) was added dropwise during fifteen minutes. The mixture was stirred at 5° for one hour and at 70° for two hours. Filtration of the cooled mixture gave 8.8 g. (101% crude yield) of brown di-acid. The neutralization equivalent of a sample of the brown solid was 242 (calculated value for the anhydrous acid is 150 and for a dihydrate, 168). Purification of the brown solid was attempted by solution in 1% potassium hydroxide (400 ml.) and successive treatments of the solution three times with charcoal. Acidification of the resulting yellow filtrate with dilute hydrochloric acid gave 4.0 g. of yellow solid whose neutralization equivalent was 149. This represents a 46% yield of the dicarboxylic acid. The infrared absorption spectrum was consistent with the structure proposed for 2-phenylbenzothiazole-4',6-dicarboxylic acid, Figure 5.a. The following elemental analysis was obtained.

	%C	%H	%N	%S	% TOTAL
Calc'd for $C_{15}H_9NO_4S$:	60.19	3.03	4.68	10.71	78.61
Found:	60.15	3.06	4.86	10.70	78.77

c. Preparation of Diphenyl 2-Phenylbenzothiazole-4',6-dicarboxylate

A mixture of 2-phenylbenzothiazole-4',6-dicarboxylic acid (4.73 g., 0.158 mole) and thionyl chloride (17.0 g., 0.143 mole) was refluxed for one hour. Another 17.0 g. of thionyl chloride was added and the mixture refluxed for an additional 1.5 hours. The excess thionyl chloride was removed under aspirator vacuum. Phenol (10.0 g., 0.14 mole) and the crude acid chloride residue were mixed and heated to 190° during one hour (a clear yellow solution formed at 80°.) The solution was stirred at 180-190° until gas evolution (HCl) ceased (0.5 hours). The solution was poured into 300 ml. of 95% ethanol and the resulting yellow solid separated on a filter. A slurry of the solid in 2% potassium hydroxide was filtered; acidification of the filtrate yielded 0.8 g. of starting material. The crude alkali washed product melted at 209-215°, and weighed 4.39 g. (61% crude yield). A portion of the diphenyl 2-phenylbenzothiazole-4',6-dicarboxylate, recrystallized from iso-amyl alcohol, was white and melted at 218-220°. The infrared absorption analysis curve (Figure 5.b.) was consistent with the proposed structure. The following elemental analysis was obtained:

	% C	% H	% N	% S	% TOTAL
Calc'd for $C_{27}H_{17}NO_4S$:	71.82	3.80	3.10	7.10	85.82
Found:	71.78	3.79	3.18	7.25	86.00

d. Attempted Preparation of 2-(4'-Amino-3'-mercapto)benzothiazole-6-carboxylic Acid

Conversion of 2-(4'-aminophenyl)benzothiazole-6-carboxylic acid (II, n = 1) to the 3'-mercapto derivative (IV, n = 1) was to be attempted (1) by chlorosulfonation to be followed by reduction and (2) by reaction with sulfur monochloride to be followed by hydrolysis.

(1) Chlorosulfonation of 2-(4'-Acetamidophenyl)benzothiazole-6-carboxylic Acid

2-(4'-Acetamidophenyl)benzothiazole-6-carboxylic acid (12.8g., 0.041 mole) was added portionwise from a powder addition funnel during 90 minutes to chlorosulfonic acid (62.0 g., 0.53 mole) at 25°. Slight gas evolution and a mild exotherm were observed. The reaction mixture was stirred at 25° for one hour and heated to 110° and stirred for one hour. During this period, rapid gas evolution was observed. When the gas evolution became slow, the temperature was raised and maintained at 140° for two hours. The partially cooled red solution was poured onto ice and filtered. The isolated dark brown solid was dissolved in water and filtered. The filtrate was saturated with sodium chloride to precipitate 16.5 g. of yellowish brown solid. The infrared absorption spectrum indicates the presence of the sulfonic group and suggests that the compound is the 3'-sulfonic acid.

(2) Attempted Preparation of 2-(4'-Amino-3'-mercapto)benzothiazole-6-carboxylic Acid

To a yellow solution of sulfur monochloride (20.4 g., 0.15 mole) in acetic acid (25 ml.) and acetic anhydride (2 ml.), 2-(4'-aminophenyl)benzothiazole-6-carboxylic acid (5.0 g., 0.019 mole) was added portionwise from a powder addition funnel during twenty minutes at 48°. The yellow suspension was stirred at reflux

temperature (111°) until the gas evolution ceased (seven hours). The cooled red suspension was filtered. The isolated red solid turned yellow after stirring with water (125 ml.) for one hour. Addition of 40% sodium hydroxide solution (25 ml.) and sodium bisulfite (3.0 g.) turned the yellow suspension a brighter yellow color and appeared to dissolve most of the solid present. The mixture was stirred at 63° for one hour, filtered, and the orange filtrate acidified with hydrochloric acid (odor of hydrogen sulfide observed). The resulting yellow solid (9.4 g.) was extracted at 25° with 2% potassium hydroxide solution (250 ml.) and filtered. Acidification of the brown filtrate gave 4.8 g. of yellow solid whose neutralization equivalent was 186 (calculated value for the anhydrous mercapto-carboxylic acid is 156 and for a dihydrate is 174). The infrared spectrum was essentially identical with that of the starting material. However, mercapto group absorption would be masked by carboxylic absorption. That the desired product was not obtained is shown by the elemental analysis:

	<u>% C</u>	<u>% H</u>	<u>% N</u>	<u>% S</u>	<u>% TOTAL</u>
Calc'd for C ₁₄ H ₁₀ N ₂ O ₂ S ₂ :	55.61	3.33	9.27	21.23	89.44
Found:	58.74	3.63	9.81	10.02	83.10

e. Preparation of Derivatives of Primuline Base

(1) Acetylation of 2'-(p-Aminophenyl)-6-methyl-2,6'-bibenzothiazole

A portion of primuline base (II, n = 2) was isolated from technical primuline fusion mass. A solution of 2'-(p-aminophenyl)-6-methyl-2,6'-bibenzothiazole (II, n = 2) (10.0 g., 0.027 mole) in 200 ml. of acetic acid was heated to reflux while acetic anhydride (4.0 g., 0.04 mole) was added during 10 minutes. After being stirred at reflux for 3 hours, the mixture was cooled and poured into ice water. The brown solid was collected on a filter, washed and dried. The 2'-(p-acetamidophenyl)-6-methyl-2,6'-bibenzothiazole (11.59 g., 100% yield) melted at 250-60°.

(2) Oxidation of 2'-(p-Acetamidophenyl)-6-methyl-2,6'-bibenzothiazole

The 2'-(p-acetamidophenyl)-6-methyl-2,6'-bibenzothiazole (11.59 g., 0.027 mole) was suspended in a mixture of pyridine (180 ml.) and water (20 ml.). With vigorous stirring and with the temperature held at 57-8°, potassium permanganate (12.6 g., 0.08 mole) in water (90 ml.) was added during one hour. After 2 hours at reflux, the purple color disappeared, additional permanganate (6.3 g.) was added and the mixture was refluxed for 3 hours more. After being cooled, the brown slurry was acidified with hydrochloric acid, treated with sodium bisulfite and filtered. The orange filter cake was slurried repeatedly with large volumes of 2% sodium hydroxide and 2% potassium hydroxide solutions. The filtered alkaline extracts, upon acidification, yielded 3.8 g. (23% crude yield) of dark orange solid, infrared absorption (Figure 4.d.) characteristics being consistent with the structure of 2'-(p-acetamidophenyl)-2,6'-bibenzothiazole-6-carboxylic acid (acetylated III, n = 2). It is presumed that an appreciable amount of the acid remained as such or as a salt in the orange filter cake. For comparison purposes, the infrared spectra of dehydrothio-p-toluidine (Figure 4.a.) and primuline base (Figure 4.c.) are included.

3. Intermediates from Arylene Diamines

Benzidine was chosen for initial study in the preparation of ortho derivatives of arylene diamines. Introduction of amino groups would permit formation of benzimidazole units and introduction of mercapto groups would permit formation of benzothiazole units. Amino groups can be introduced by nitration and reduction to the amine. Mercapto groups could be introduced by conversion to sulfonyl chlorides followed by reduction. Reaction of the arylene diamine with sulfur monochloride also could lead to the introduction of ortho mercapto groups.

a. Preparation of 3,3'-Dimercaptobenzidine

(1) Chlorosulfonation of N,N'-Diacetylbenzidine

Chlorosulfonic acid (36.0 g., 0.31 mole) was added dropwise during fifteen minutes to powdered N,N'-diacetylbenzidine (10.0 g., 0.037 mole) at 10°. The temperature was slowly raised to 90° when gas evolution essentially ceased. During the final hour of stirring the reaction mixture became very viscous. The dark viscous liquid was poured onto ice. No solid separated and various attempts to obtain a solid; such as freezing the dark aqueous solution, saturation with sodium chloride and neutralization proved unsuccessful. Concentration to a volume of 50 ml. and standing overnight gave a dark solid. The isolated dark solid was amorphous. It was thought that this black solid might be the 3,3'-disulfonic acid.

(2) Reaction of Benzidine Hydrochloride with Sulfur Monochloride

A suspension of benzidine hydrochloride (25.7 g., 0.1 mole) in sulfur monochloride (80.5 g., 0.60 mole) and acetic acid (150 ml.) was stirred at 95° for 18 hours. The suspension turned red-orange at 60°, purple at 70° and dark brown-red at 75° with a slight gas evolution. The dark red suspension was concentrated under a water aspirator to yield a residual dark red solid. The solid was ground fine and stirred in 100 ml. of water at 50-55° for 15 minutes. A solution of 10% sodium hydroxide (150 ml.) and 5.0 g. sodium bisulfite were added to the dark purple aqueous suspension. The temperature was gradually raised during 5 hours to 95°. The purple suspension turned to green then to yellow. Filtration gave a yellow-green solid. Repeated extractions of the yellow-green solid with 5% hydrochloric acid, followed by neutralization, gave 16.5 g. (66% crude yield) of yellow 3,3'-dimercaptobenzidine (melting at 255°C with darkening). A sample recrystallized from a pyridine-ethanol mixture melting at 283-285°, had the infrared absorption shown in Figure 2.3., and gave the following elemental analysis:

	% C	% H	% N	% S	% TOTAL
Calc'd for $C_{12}H_{12}N_2S_2$:	58.03	4.87	11.28	25.82	100.00
Found:	58.17	4.66	11.52	25.94	100.29

c. Attempted Preparation of Bis(4-Amino-3-mercaptophenyl) Ether

Oxydianiline (20.0 g., 0.1 mole) in acetic acid (100 ml.) was agitated while sulfur monochloride (85.0 g., 0.64 mole) was added in small increments. The addition of about 15 g. of sulfur monochloride in 15 minutes caused an exotherm from 30 to 47°, with gas evolution. Warming the deep purple mixture to 65° led to

another exotherm to 75°, with more gas evolution. With the mixture warmed to 80°, the remainder of the sulfur monochloride was added during 45 minutes. The mixture was then warmed to 90° with agitation, causing gas evolution for 3 hours, followed by an additional hour of heating. In attempting to strip off the excess sulfur monochloride with a water aspirator, the water backed up into the reaction flask. The resulting red tarry mixture was subjected to a series of extractive procedures, giving purple solids and purple solutions under alkaline conditions. A small sample of solid recovered from absorption on carbon gave an infrared absorption spectrum suggesting the presence of a mercapto group, but showing no evidence of 1,2,4-substitution on a benzene ring.

4. Arylene Diacids as Intermediates

The isomeric phthalic acids are the most readily available arylene diacids. The dibenzoic and oxydibenzoic acids are also possible intermediates. According to the work of Marvel⁵, the diphenyl esters of such diacids should react more smoothly than the free acids or the acid chlorides.

a. Preparation of Diphenyl Isophthalate

Following the general procedure of Marvel⁵, isophthaloyl chloride (101.0 g., 0.5 mole) and phenol (120 g., 1.28 moles) were heated to 170° and the resulting ester isolated. The white solid (149.8 g., 94% yield) melted at 139-140.5° (140-1° by Marvel), (Infrared spectrum - Figure 5.c.).

b. Preparation of Di(p-biphenyl) Isophthalate

A mixture of isophthaloyl chloride (40.4 g., 0.20 mole) and p-hydroxybiphenyl (76.0 g., 0.45 mole) was heated and stirred. The mixture was partially melted at 80° with evidence of slow evolution of gas. Continued heating resulted in rapid evolution of gas from the thin slurry at 110°. The mixture was heated at 140-5° for one hour at which time it solidified. The product was triturated with dilute potassium hydroxide solution and then with water. The white solid (91.9 g., 98% of theory) melted at 235-6.5°. Recrystallization of the di(p-biphenyl) isophthalate from toluene gave white plates melting at 235-6.0°.

c. Preparation of Dimethyl Oxy-bis(4-benzoate)

A mixture of methyl p-hydroxybenzoate (20.0 g., 0.13 mole) and potassium hydroxide (5.6 g., 0.10 mole) was stirred at 130°, forming a melt. A vacuum of 15 mm. of mercury was applied to remove water. To the resulting white solid mass, at 100°, was added methyl p-bromobenzoate (9.4 g., 0.044 mole) and freshly precipitated copper (0.1 g.). Upon heating to 165-170°, a purple melt formed. Additional methyl p-bromobenzoate (9.4 g., 0.044 mole) was then added and the mixture was stirred at 170° for 2 hours. The resulting brown melt was poured into 500 ml. of water containing 100 ml. of sodium hydroxide solution (10%). The light green solid obtained was collected on a filter, washed with water and recrystallized from methanol. The light green solid (10.0 g., 40% of theory) melted at 154-155.5°, (lit.-154° for dimethyl oxy-bis(4-benzoate)). The following elemental analysis was obtained:

	<u>%C</u>	<u>%H</u>	<u>% TOTAL</u>
Calc'd for C ₁₆ H ₄ O ₅ :	67.13	4.95	72.08
Found:	66.98	4.84	71.82

The infrared spectrum is shown in Figure 5.d.

5. Polymer by Formation of Amide Groups

a. Polymerization of 2-(4'-Aminophenyl)benzothiazole-6-carboxylic Acid

A small sample of 2-(4'-aminophenyl)benzothiazole-6-carboxylic acid (2.0 g.) was mixed with a catalyst (0.1 g. of MXI*) and heated under a nitrogen atmosphere at 250° for 12 hours. During this heating period, the water collected in a dry ice trap amounted to 0.45 mole per mole of aminocarboxylic acid. The appearance of the sample mixture was unchanged. The tube containing the sample was then heated at 300° for 11 hours. The water collected during this period amounted to 1.0 mole per mole of aminocarboxylic acid. The sample had darkened to a yellow brown. The polymerization product was slurried with hot dimethylformamide and filtered. The solid was vacuum dried. The dimethylformamide filtrate contained no unreacted aminocarboxylic acid. The infrared absorption spectrum (Figure 2.c.) of the polymer was consistent with the structure expected for the polybenzothiazole-polyamide polymer. Carboxylic acid group absorption could not be detected.

A sample of the polymer (0.5 g.) was heated in a tube under a nitrogen atmosphere to 505°, and held at that temperature for one hour. Darkening and moderate shrinking occurred at about 460°. At about 500°, a trace of sublimate began to accumulate on the cooled part of the tube. The dry ice trap connected to the system collected a trace of liquid (0.0036 g.). Infrared analysis of the dark brown polymer gave the same absorption pattern as the original polymer. The trace of sublimate gave infrared absorption peaks suggesting amino, nitrile and arylthiazole groups.

b. Polymerization of 2-(4'-Acetamidophenyl)benzothiazole-6-carboxylic Acid

A small sample of 2-(4'-acetamidophenyl)benzothiazole-6-carboxylic acid (0.3750 g., 0.0012 mole) was heated under a nitrogen atmosphere in a tube immersed in a molten salt bath. At 200°, vapors evolved that were condensed in a dry ice-cooled trap attached to the exit of the tube. The yellow acid gradually darkened as the temperature was increased from 300 to 535° during the next 10 minutes. The material turned dark brown and appeared to decompose slightly at 520°. After cooling, the dark brown granular solid was washed with dimethylformamide. The dimethylformamide wash contained no starting material. Infrared analysis of the

*Note: MXI = m-xylenediamine-isophthalic acid salt.

dark brown solid showed absorption characteristics of a secondary amide but no absorption characteristics of an aryl carboxylic acid could be detected. The liquid collected in the dry ice trap had the odor of acetic acid and was titrated with base. It was found that 0.7 ml. of acetic acid per mole of starting material had been trapped.

6. Polymer Formation by Reaction of Arylamines with Sulfur

In the previously reported reaction of p-toluidine and sulfur in refluxing (about 200°) 1,2,4-trichlorobenzene, approximately 30% of the theoretical yield of dehydrothio-p-toluidine was isolated. From the residual tarry material, a trace amount of an orange compound was obtained which was not identified, but was shown by infrared absorption to have no amino group.

a. Reaction of Sulfur with p-Toluidine in Bis(2-ethoxyethyl)ether

A small, stirred reactor was charged with p-toluidine (21.2 g., 0.2 mole), sulfur (19.5 g., 0.6 mole), sodium carbonate (5.0 g.) and bis(2-ethoxyethyl)ether (59.3 g.). The mixture was stirred and heated at reflux (about 190°) for 18 hours, a caustic scrubber being attached to the system to absorb any hydrogen sulfide generated. The resulting black syrup was poured into 400 ml. of water, depositing a black tar. A quantity of black solid in the reactor was dissolved in hot pyridine. A solvent extraction of the black tar yielded about one gram of a yellow solid, melting at 170-185°, appearing to be impure dehydrothio-p-toluidine. The black tars combined in pyridine solution were precipitated out in small increments by successive additions of heptane, followed by filtration. All such portions were gummy black solids. Infrared absorption studies indicated the presence of -OH groups, but the impurity of the fractions prevented any definite assignment of structure. It is believed that the semi-polymeric material contains benzothiazole units with some phenolic groups.

b. Reaction with p-Toluidine in Molten Polysulfides

Sodium sulfide ($\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$) and potassium sulfide (K_2S_x) were available in the form shown from chemical supply companies. A mixture of potassium sulfide (36.0 g.) and sodium sulfide (51.9 g.) was heated under a nitrogen atmosphere to about 280° to drive out water of hydration. After the addition of sulfur (20.0 g.), heating was continued, resulting in a melt which solidified to an orange mass at about 110-120°. Still under a nitrogen atmosphere, p-toluidine (15.0 g.) was added, and the mixture was heated and stirred at about 200° for 4 hours. No evidence of reaction was noted. Additional sulfur (10.0 g.) and continued heating caused a darkening of the reaction mixture. Continued stirring and heating from 200° to a final temperature of 260° during 13 hours resulted in a thick black paste. With the molten mass at about 120°, water was added and the mixture was rinsed from the apparatus to a final volume of 800 ml. of brown solution from which a black tar separated. The black tar was refluxed with iso-amyl alcohol in 100 ml. portions until a total of 400 ml. of clear orange solution was obtained. Successive cycles of cooling, filtering and concentrating of the iso-amyl solution gave small portions of yellow solids, totaling about 5 grams. Melting point and infrared absorption comparisons indicated these solids to be dehydrothio-p-toluidine and primuline base.

The black tar, insoluble in iso-amyl alcohol, was partially soluble in dimethyl formamide.

c. Reaction with m-Toluidine in a Melt

Following the standard procedure for the primuline reaction (with p-toluidine), a mixture of m-toluidine (43.9 g.) and roll sulfur (23.5 g.) was heated and stirred in the presence of 0.7 g. of sodium carbonate. After heating for 5 hours, a pot temperature of 228° was obtained and appreciable hydrogen sulfide was evolved, but a layer of m-toluidine remained. The resumption of heating for an additional 7 hours at 242-8° resulted in a dark brown viscous mass. Water was added dropwise to the melt and unreacted m-toluidine (8.8 g.) was steam distilled from the mixture. The brittle orange brown fusion mass obtained upon cooling was ground under a layer of water and filtered (65.2 g. of wet cake). The brown solid was refluxed with portions of iso-amyl alcohol, the total alcohol solution being about 600 ml. Dilution of the hot iso-amyl alcohol solution with 400 ml. of heptane, followed by cooling, resulted in the separation of a brown solid which was filtered and dried, weighing 4.1 g. and melting at 122-130°. Infrared absorption study (Figure 2.b.) indicated the probable presence of a benzothiazole structure similar to that of dehydrothio-p-toluidine but with absorptions characteristic of three adjacent hydrogen atoms on a benzene ring. The black tar insoluble in the hot iso-amyl alcohol was extracted with hot acetic acid (300 ml.), but only a trace of material dissolved. Most of the residual black tar was soluble in dimethylformamide (200 ml.) Addition of iso-amyl alcohol to the black dimethylformamide solution, followed by cooling, gave a brown solid, that melted over a wide range up to about 200°. Infrared absorption study suggested a benzothiazole structure, but a rather strong carbonyl absorption was also noted.

d. Reaction with Dehydrothio-p-toluidine in Molten Polysulfides

A mixture of anhydrous potassium pentasulfide (30.9 g.) and anhydrous sodium tetrasulfide (31.9 g.) was heated and stirred; the orange-brown melt was viscous at 130° and fluid at 200°. Dehydrothio-p-toluidine (10.0 g.) and sulfur (6.0 g.) were added to the melt at 160° and the mixture was then heated to 200-260° for 8 hours. After being cooled to 150°, the black tar was scraped into 600 ml. of water; the resulting brown suspension was heated to 90° and filtered. The brown filter cake was boiled with 200 ml. portions of benzene (5 times), followed by hot filtration. The brown solid was then successively boiled with portions of iso-amyl alcohol, dimethylformamide and pyridine, in each case followed by hot filtration. None of this last series of filtrates contained any appreciable amount of dissolved solids. The vacuum dried brown solid amounted to 10.4 g. A sample of this solid was heated on a spatula, darkening when the spatula approached red-heat and then glowing red without sintering or flaming. A sample of this brown solid was heated in an open tube to 485°; a faint orange deposit formed on the upper part of the tube at 300° but no other change being noted. In characterizing this product, the infrared absorption curve (Figure 6.a.) was as expected for a polybenzothiazole (comparison to moderate molecular weight primuline analog - Figure 6.b.), with no measurable absorption for the -NH₂ group. Approximately 1% suspensions of this brown solid in phenol and in 97% formic acid, after heating at 100° for several hours and filtering hot, gave quantitative recovery of

the brown solid. A sample of the brown solid suspended for several hours in 96% sulfuric acid at room temperature gave a yellow liquid phase and a brown gelatinous phase. Dilution with water gave a quantitative recovery of the brown solid with no evidence of sulfonation evident by infrared absorption study. Study of this brown solid by non-aqueous titration showed virtually no free amino groups (less than 0.1% titratable nitrogen). A sample submitted for elemental analysis gave the following results.

	<u>% C</u>	<u>% H</u>	<u>% N</u>	<u>% S</u>	<u>% TOTAL</u>
Calc'd for $(C_7H_3NS)_n$:	63.13	2.27	10.52	24.08	100.00
Found:	59.52	2.46	8.98	26.60	97.56*

* combustion residue - 5.6

e. Reaction with Primuline Base in Molten Polysulfides

A hemispheric reactor (500 ml.) fitted with an efficient agitator, thermometer and nitrogen inlet and vented to a dry ice-cooled trap, was charged with freshly prepared anhydrous sodium tetrasulfide (135.2 g.) freshly prepared anhydrous potassium pentasulfide (128.8 g.), sulfur (52.2 g.) and a commercial sample of primuline fusion mass (109.8 g.). The reaction mixture was carefully warmed, becoming fluid at 135°. The last traces of solid melted at 200°, forming a brown solution. At 233°, liquid began to collect in the dry ice trap. Heating was continued at 243° to 285°, for 9 hours. The mixture became black and difficult to stir. The dry ice trap was found to contain 12.1 g. of hydrogen sulfide. After cooling to about 120°, absolute alcohol was added. The dark orange hot alcohol solution was decanted through a sintered glass filter, fresh alcohol was added to the reactor, re-heated to reflux and again decanted. Continued treatment with hot alcohol had a final decantate with a light orange color. The solid residue was a dark brown mass. This solid was ground up in a mortar and pestle and slurried repeatedly with refluxing portions of fresh pyridine, until the filtrates became a light yellow. After the solid was rinsed with boiling water and vacuum dried, a dark yellow-brown powder (117.6 g.) was obtained. A sample of this product was held on a spatula next to a flame; as the spatula approached red heat, the powder darkened and began to glow red. After cooling, the black powder was examined by infrared absorption, along with a sample of the unheated product (Figure 6.a.). The spectra were similar to each other, showing the principal absorptions for the polymeric product previously formed from the dehydrothio-p-toluidine reaction with sulfur. A sample of this brown solid was heated in an open tube to 485°, showing a faint yellow deposit on the upper part of the tube at 370°, no other change being noted.

f. Characterization of the Poly(benzothiazole) from Primuline Base

The elemental analysis for the brown powder from the reaction of primuline base and sulfur was too high in sulfur. A sample had produced a trace of yellow sublimate on the wall of the tube at 370-485°. A portion (8.8 g.) of the brown powder in a vacuum sublimation apparatus held at 275° and 0.2 mm. of mercury for one hour, gave a trace of solid on the condenser surface and a residual brown solid weighing 8.6 g. (2.3% weight loss). The analyses for the original solid and for the evacuated sample (910-W51AS) were as follows:

	% C	% H	% N	% S	% TOTAL
Found: for original solid:	59.89	2.84	8.60	26.73	98.06
for 910-W51AS:	60.16	2.61	9.31	27.82	99.90
Calc'd: (a) Infinite poly- (benzothiazole), (C ₇ H ₃ NS) _n	63.13	2.27	10.52	24.08	100.00
(b) Polymeric (I), with n = 10 and 3 added sulfur groups, (C ₇₇ H ₃₉ N ₁₁ S ₁₃)	60.29	2.56	10.03	27.12	100.00

Samples of the brown powder were subjected to chemical reagents. One sample was suspended, along with zinc powder, in refluxing acetic acid for 6 hours. A second sample was suspended in 1:5 dilute nitric acid at 100° for 2 hours. A third sample was suspended overnight in an ethanol solution of sodium hydroxide. These samples, after thorough washing with hot water and with boiling dimethylformamide, were compared by infrared absorption analysis with the original brown powder and with the brown powder after heating under vacuum. All spectra were identical.

The brown solid poly(benzothiazole) was previously shown to be insoluble in iso-amyl alcohol, dimethylformamide, pyridine, formic acid and phenol. Samples of the brown powder were stirred in the following solvents, at the temperatures shown, under nitrogen:

Sample (g.)	Solvent (g.)	Temp. (°C)	Time (hrs.)	Residue* (g.)
0.13	Sulfolane (14.4)	235-9	2.0	0.13
0.08	Hexachlorobenzene (11.6)	235-9	2.0	0.07
0.10	N-methyl-2-pyrrolidone (14.7)	193-9	5.0	0.07
0.40	2-Phenylbenzothiazole (14.1)	255-71	2.0	0.39
0.40	Dimethylsulfoxide (32.8)	164-70	4.0	0.40

*Some residues were not recovered quantitatively, because of mechanical losses. No detectable solid separated out of any of the solvent filtrates.

7. Polymerization by Formation of Benzothiazole Groups

The condensation of an ortho-aminomercapto compound with a carboxylic function can proceed with the free acid, the acid chloride or an ester of the acid. The favored intermediate is the phenyl ester of the carboxylic function.

a. Condensation Polymerization of 3,3'-Dimercaptobenzidine and Terephthalic Acid

3,3'-Dimercaptobenzidine (1.1 g.) and terephthalic (1.1 g.) were thoroughly dried, mixed, and placed in a polymerization tube equipped with a nitrogen inlet and

and outlet, dry ice trap and thermometer. The mixture was heated from 225° to 302° over a period of three hours. Sintering and slight softening was noticed at 227°. A trace of condensate (H₂O?) was observed in the upper portion of the tube at 257°. The odor of hydrogen sulfide and darkening were detected at 265°. More condensate was observed at 287° and a white sublimate began to appear at 300°. The cooled dark greenish material was boiled in dimethylformamide and filtered. The yellow filtrate was concentrated to give 1.1 g. of orange-brown solid. The insoluble green solid weighed 1.0 g. and when heated in an open flame glowed red but did not melt. The infrared absorption spectrum of the insoluble material exhibited absorptions which indicates the presence of thiazole units and amide groups.

b. Condensation Polymerization of 3,3'-Dimercaptobenzidine with Diphenyl Isophthalate

A mixture of diphenyl isophthalate (5.6 g., 0.0176 mole) and 3,3'-dimercaptobenzidine (5.0 g., 0.0216 mole) was placed in a small flask equipped with nitrogen inlet and outlet. The flask was immersed in a silicone oil bath preheated to 180°. The temperature was raised to 300° during 1.5 hours. Slight melting and darkening occurred at 190° and a condensate began to appear at 223°. To facilitate the removal of phenol and water formed, the system was placed under a 0.1 mm. vacuum at 300°. After being cooled under nitrogen, the dark green brittle solid (7.0g.) was ground fine and returned to the flask. The flask was immersed in the silicone oil bath preheated to 270°C. During 2.0 hours, the flask was heated under vacuum at 0.1 mm. of mercury to 400°. The temperature was maintained at 400° for 0.5 hour. The dark solid was cooled under nitrogen, ground fine and boiled in pyridine, filtered and washed with hot ethanol. The insoluble dark green solid (6.0 g., 100% yield) had the infrared spectrum (Figure 6.c.) expected for a poly(benzothiazole). A sample submitted for elemental analysis gave the following results:

	<u>% C</u>	<u>% H</u>	<u>% N</u>	<u>% S</u>	<u>% TOTAL</u>
Calc'd for (C ₂₀ H ₁₀ N ₂ S ₂) _n :	70.14	2.94	8.18	18.73	99.99
Found:	66.61	2.90	7.65	16.48	93.64

In a second experiment, a mixture of diphenyl isophthalate (9.54 g., 0.03 mole) and 3,3'-dimercaptobenzidine (8.52 g., 0.03 mole) was again heated by an oil bath, under a nitrogen atmosphere. The bath temperature was slowly raised to 300° during 7 hours, condensate appearing at about 226°. The dark green solid was cooled and removed from the reaction flask, being found to contain glass fragments. Inspection of the reaction flask and thermometer well indicated that all surfaces in contact with the polymer had chips of glass pulled away, adhering now to the polymer. The polymer was ground fine, separating as many glass particles as possible, and returned to a reactor. The polymer was heated to a bath temperature of 400° during 6 hours, under a vacuum of 0.7 mm. of mercury. The resulting dark green solid was ground fine, extracted with boiling pyridine, dimethylformamide and ethanol, and vacuum dried. The product (10.7 g., 94% of theory) exhibited infrared absorption (Figure 6.c.) at 3.0 μ (N-H), very weak; at 5.8 μ (C=O), very weak; at 6.3 μ phenyl; at 6.4 μ (possibly C=N), shoulder; at 12.4 μ (1,2,4-aryl substitution), medium; and other absorptions attributable presumably to aromatic skeletal vibrations. A sample submitted for elemental analysis gave the following results:

	<u>% C</u>	<u>% H</u>	<u>% N</u>	<u>% S</u>	<u>% TOTAL</u>
Calc'd for (C ₂₀ H ₁₀ N ₂ S ₂) _n :	70.14	2.94	8.18	18.73	99.99
Found:	65.05	3.37	7.30	15.35	94.07

A correction for a reported residue of 4.5%, presumably due to glass, does not bring the analysis to the proper values, high hydrogen and carbon ratios and the 1.6% difference remaining, suggesting residual phenyl ester groups.

8. Polymerization by Formation of Benzimidazole Groups

As was noted in the preceding section, different forms of the carboxylic function can be used. Again the diphenyl ester is the preferred form.

a. Condensation Polymerization of 3,3',4,4'-Tetraaminobiphenyl and 2-Phenylbenzothiazole-4',6-dicarboxylic Acid

A mixture of 2-phenylbenzothiazole-4',6-dicarboxylic acid (1.96 g., 0.0066 mole) and 3,3',4,4'-tetraaminobiphenyl (1.4 g., 0.0066 mole) was placed in a polymerization tube equipped with nitrogen inlet and outlet. The tube was immersed in a silicone oil bath preheated to 220°. The reddish mixture immediately began to darken and melt (completely melted at 211°). At 226°, condensate began to appear and slight foaming was observed. The temperature was raised to 284° during 3 hours; condensation, darkening and foaming increased, then stopped during the last hour of heating. A sample of the product from a first heating step showed an infrared absorption curve indicating a high secondary amide content and some benzimidazole absorption. The black residue from the first heating step was ground and mixed with 0.5 g. of phosphorus pentoxide. This mixture was returned to the polymerization tube at 265° and heated slowly to 400° during 2 hours. The resulting black, brittle solid was slurried, then filtered, in turn with hot water, hot pyridine and ethanol. The dried black solid (3.08 g.) was insoluble and infusible. Infrared absorption study gave no absorption curve.

b. Condensation Polymerization of 3,3',4,4'-Tetraaminobiphenyl and Diphenyl 2-Phenylbenzothiazole-4',6-dicarboxylate

A mixture of 3,3',4,4'-tetraaminobiphenyl (4.94 g., 0.023 mole) and diphenyl 2-phenylbenzothiazole-4',6-dicarboxylate (10.4 g., 0.023 mole) was heated by a silicone oil bath, under a nitrogen atmosphere. At 160°, condensate appeared above the brown melt. At about 225°, the brown mixture solidified, heating continuing to 300° for a total reaction time of 7 hours. After cooling and grinding, the brown solid was examined by infrared absorption and found to have no absorption near 3.4 (N-H) and very weak absorption at 5.88 (C = O). The product was returned to the reaction flask and heated to a bath temperature of 400° during 6 hours under a vacuum of 0.7 mm. of mercury. The brown powder was cooled and extracted with boiling pyridine, then ethanol and vacuum dried. The product (10.7 g., 103% of theory) had an infrared absorption (Figure 6.d.) of a benzothiazole, with only a trace of absorption at 5.88 (C = O). A sample submitted for elemental analysis gave the following results:

	% C	% H	% N	% S	% TOTAL
Calc'd for $(C_{27}H_{13}N_5S)_n$:	73.78	2.98	15.94	7.30	100.00
Found:	71.15	3.21	14.09	7.27	95.72

A correction for a reported residue of 0.9% does not bring the analysis to the proper values for the expected poly(benzimidazole-benzothiazole).

9. Polymers from Rubenic Acid

Rubenic acid (dithiooxamide) can react with two equivalents of a haloacetyl compound to give a pair of connected thiazole units. Also, reaction with two aldehyde groups under oxidizing conditions produces fused thiazole rings, called a thiazolothiazole group. Use of a dialdehyde compound or a bis(haloacetyl) compound could therefore lead to polymers containing thiazole units. The simplest and most readily available compounds of these classes are glyoxal and halogenated diacetyl.

a. Reaction of Rubenic Acid with Glyoxal

Rubenic acid (13.0 g., 0.108 mole) was suspended in 200 ml. of propyl alcohol. Aqueous glyoxal (20.9 g., equiv. to 0.108 mole) was added at room temperature. After standing for 14 hours, the reaction mixture was unchanged. A small amount of iodine (0.1 g.) was added and the mixture was heated under a slow stream of air. At 80°, the suspension had changed to a deep red solution. A Dean-Stark trap was inserted in the apparatus and 70 ml. of benzene was added. After azeotropic distillation had removed all of the water (13.0 ml.) that would collect, the red solution was unchanged. The propyl alcohol and benzene were then distilled from the reaction mixture became black. When this black mixture was poured into 100.0 ml. of water, a black foam separated, over a black solution. A dried sample of this black solid was studied by infrared absorption, but showed no evidence of containing a distinct compound.

In a second reaction, butyl alcohol was employed as the solvent and vanadium pentoxide was used as the oxidation catalyst. An unidentifiable black powder again resulted.

b. Reaction of Rubenic Acid with Diacetyl and Bromine

Rubenic acid (8.3 g., 0.069 mole) was suspended in a solution of diacetyl (6.0 g., 0.069 mole) in 200 ml. of refluxing chloroform. Bromine (22.1 g., 0.138 mole) in 20 ml. of chloroform was added dropwise during one hour. The chloroform was distilled out during 2 hours, last traces being removed under a water aspirator. The black tarry residue was heated with water (150 ml.) and collected on a filter. The black tar was re-slurried twice with boiling water and filtered. The black tar was then dissolved in dimethylformamide and subjected to fractional precipitation. No definite product could be isolated.

c. Reaction of Rubenic Acid with Terephthalaldehyde

A mixture of rubenic acid (6.0 g., 0.05 mole) and terephthalaldehyde (6.7 g., 0.05 mole), in *n*-butyl alcohol (350 ml.), heated to reflux (117°); the yellow suspension changed to a red solution at slightly below reflux temperature. A slow stream of air was passed into the refluxing solution, a Dean-Stark trap being used to catch azeotroped water that might form. No change was evident after 2.5 hours. A crystal of iodine (ca. 0.1 g.) was added as a possible catalyst and heating at reflux was continued for 9 hours more. Only slight turbidity of the reaction mixture was noted. About 300 ml. of the *n*-butyl alcohol was distilled off, being replaced in the pot by 200 ml. of triglyme. Heating was continued at 195-205° for 10 hours, the mixture slowly changing to an orange slurry. The product was

collected on a filter as a quantitative yield of red powder. A test portion on a spatula showed no change when heated to red heat. Infrared absorption study of the product showed appreciable carbonyl content. Elemental analysis was as follows:

	<u>% C</u>	<u>% H</u>	<u>% N</u>	<u>% S</u>	<u>% TOTAL</u>
Calc'd for $(C_{10}H_4N_2S_2)_n$:	55.54	1.86	12.96	29.65	100.01
Found:	59.14	2.99	11.04	21.80	94.97

The low sulfur and high carbonyl suggest an undesirable hydrolysis of thioamide. A compression molding of a sample of this solid at 600°F and 20 tons of pressure gave a dark red disc which was hard but brittle.

In a second experiment, a suspension of rubeanic acid (12.0 g., 0.1 mole) and terephthalaldehyde (13.4 g., 0.1 mole) with sulfur (6.4 g.) in triglyme (500 ml.) was heated with agitation. At 110°, a deep red-orange solution had formed and at 135° a Dean-Stark trap was placed in the system, with 10 ml. of benzene added as azeotroping agent for water appearing in the reflux. During 3 hours, the reaction temperature was raised from 177 to 191°, 3 ml. of a yellow aqueous layer collecting in the trap. A sample of the red-brown solid separating was withdrawn and showed a strong infrared absorption at 5.9 μ (C = O). Heating was continued at 190-220° for 2.5 hours, a second sample of the red-brown solid showing less than half as much carbonyl absorption. After the addition of some crude phosphorus pentasulfide (10.0 g.), heating was continued at 180-219° for 12 hours. The reaction mixture was filtered and the solid was slurried with boiling dimethylformamide (100 ml.). After washing with two portions of boiling ethanol (100 ml. each), the infrared absorption of the solid showed a small absorption at 3.0 μ (N - H) and a small shoulder at 5.9 μ (C = O). The brown powder was slurried with sulfuric acid (300 ml.) at room temperature and filtered. The insoluble brown powder was thoroughly washed with hot water, with dilute sodium hydroxide (5%) and again with hot water. The sulfuric acid filtrate, upon dilution with ice water, yielded a red flocculent solid, which was similarly washed with water and caustic. The vacuum dried solids were a red-brown, infusible powder (19.4 g., 90% of theory) and red-black solid (from the sulfuric filtrate, 2.6 g.). Infrared absorption study (Figure 7.b.) (For comparison the spectrum of rubeanic acid is shown in Figure 7.a.), of the red-brown polymer showed a very small absorption at 3.0 μ (N = H) and a shoulder at 5.9 μ (C = O). The remaining absorption peaks showed 1,4-substitution (12.0 μ), phenyl group (6.3 μ) and C = N (shoulder at 6.4 μ). The red flocculent solid showed very strong carbonyl absorption (5.9 μ), the spectrum otherwise being similar to that of the principal product. The following elemental analysis was obtained:

	<u>% C</u>	<u>% H</u>	<u>% N</u>	<u>% S</u>	<u>% TOTAL</u>
Calc'd for $(C_{10}H_4N_2S_2)_n$:	55.54	1.86	12.96	29.65	100.00
Found:	55.49	3.19	9.48	21.15	89.41

10. Polymer with Azo-Arylene Linkages

The general thermal stability of aryl amines (such as triphenyl amine) and of thiazoles suggest that a bis(*p*-nitrophenyl)thiazole might undergo partial reduction to a poly-azo compound, that should exhibit thermal stability.

a. Nitration of 2,4-Diphenylthiazole

A solution of 2,4-diphenylthiazole in concentrated sulfuric acid (100 ml.) was cooled to -5° and treated with fuming nitric acid (40 ml.) in sulfuric acid (60 ml.). The resulting clear yellow solution was poured onto crushed ice mixed with sodium hydroxide (100 g. NaOH in 200 ml. of water). The green-yellow solid formed was collected on a filter and washed with water, then with dilute ammonia water, then with water. The dried yellow-green solid (34.2 g., 99% of theory) melted at $233-242^{\circ}$. A portion of the product was recrystallized from a mixture of benzene and heptane, giving greenish-yellow crystals melting at $247-9^{\circ}$, and an infrared absorption curve as shown in Figure 7.c. An elemental analysis was obtained as follows:

	<u>% C</u>	<u>% H</u>	<u>% N</u>	<u>% S</u>	<u>% TOTAL</u>
Calc'd for $C_{15}H_9N_3O_4S$:	55.04	2.77	12.84	9.80	80.45
Found:	55.27	2.74	12.56	10.00	80.57

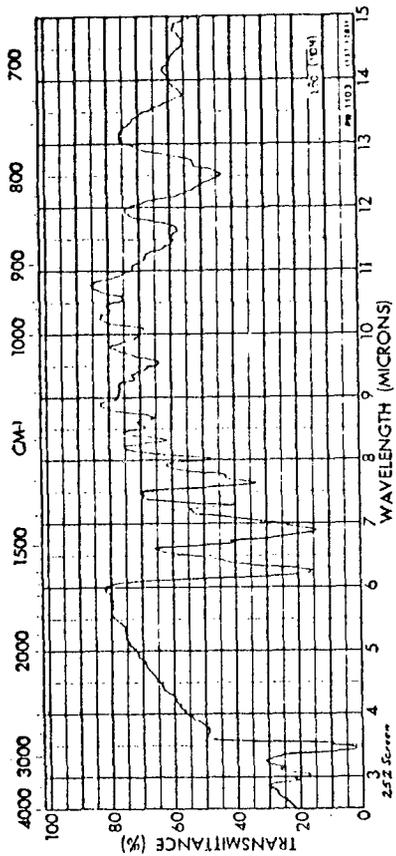
b. Sodium Reduction of 2,4-Bis(p-nitrophenyl)thiazole

A lump of sodium (7.36 g., 0.32 g.-atom) was placed in a flask under nitrogen with 5 ml. of dry mercury. Gentle warming induced the vigorously exothermic formation of an amalgam and additional mercury was added rapidly enough to maintain a molten alloy (total mercury = 1,945 g.). A suspension of 2,4-bis-(p-nitrophenyl)thiazole (13.1 g., 0.04 mole) in 700 ml. of dry toluene was added at 75° . A solution of ethanol (20 ml.) and toluene (30 ml.) was added slowly, with the reaction mixture stirred at 90° . A black suspension formed in the organic layer and the mixture was stirred at $90-99^{\circ}$ for 7 hours. With heat removed, excess ethanol (50 ml.) was added and the mixture was stirred for one hour. The organic layer was decanted from the mercury through a filter. The brown filter cake was washed with hot ethanol and with hot water, and dried. The brown powder was then carefully stirred into 400 ml. of concentrated sulfuric acid to give a dark red-brown solution. The filtered solution was poured onto 500 g. of ice. The red flocculent solid which separated was filtered, slurried with hot water, hot ammonia water (1:10) and repeatedly with hot water, being filtered at each washing. The red-brown solid (9.2 g., 88% of theory) was vacuum dried. The diluted sulfuric acid filtrate was neutralized to form a red floc. This red material was filtered, washed and dried to give a red-black solid (0.6 g.). Infrared absorption study (Figure 7.d.) of the main product showed a very weak absorption at 3.0μ (N - H), strong absorption at 6.25μ (phenyl), a shoulder at 6.4μ (C = N?), moderate absorption at 7.1μ (undetermined origin, possibly -N=N- between aryl groups) and strong absorptions at 11.75μ (1,4-substitution). Infrared absorption study of the acid soluble solid had moderate multiple absorptions at about 3μ (N-H) and no absorption at 7.1μ , otherwise exhibiting the same absorption pattern as did the major product. An elemental analysis of the polymeric product as follows:

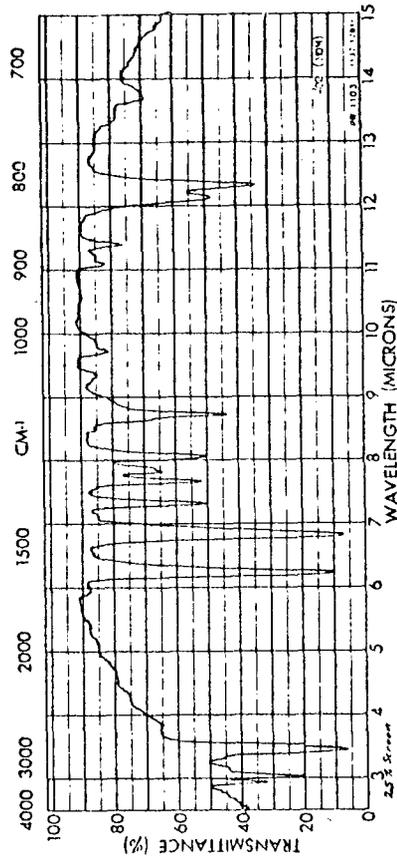
	<u>% C</u>	<u>% H</u>	<u>% N</u>	<u>% S</u>	<u>% TOTAL</u>
Calc'd for $(C_{15}H_9N_3S)_n$:	68.42	3.45	15.96	12.17	100.00
Found:	51.40	3.24	10.93	8.33	73.90

E. Conclusions

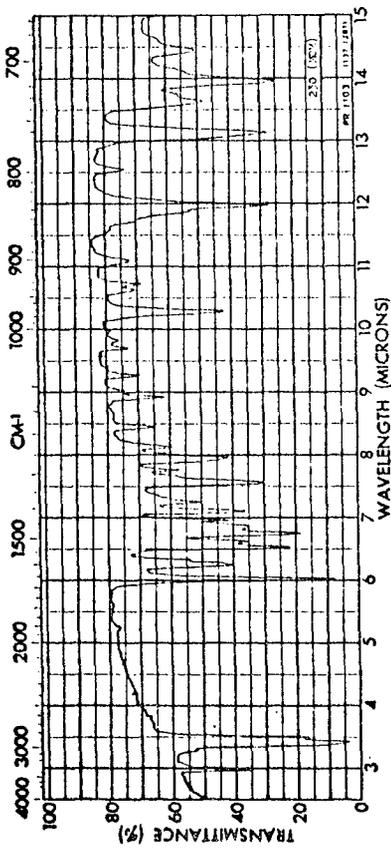
Polymers containing thiazole and benzothiazole units have been shown to have high thermal stability. The major problem is the formation of polymers with structural modifications in the connecting groups which will enhance solubility and moldability without greatly reducing thermal stability. Preparation of monomers of modified structure has been begun. For example, esters of oxy-bis(4-benzoic) acid are being prepared as intermediates for poly(benzothiazole) synthesis. Other linkages which might lend chain flexibility or improve solubility are to be incorporated into the monomers. Modifications of the polymerization procedures are to be studied, such as the use of organic solvents. Along with the incorporation of thiazole rings in the polymer chains, additional types of heterocyclics are to be included, such as imidazoles, oxazoles and possibly borazoles.



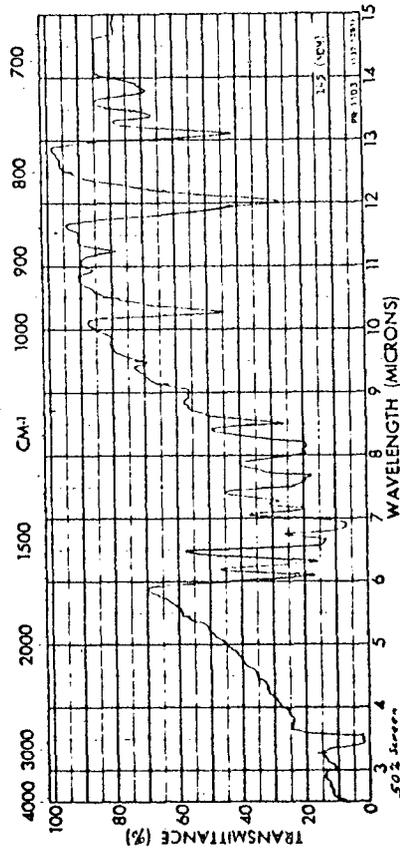
b. *m*-Toluidine plus Sulfur Product



d. 3,3'-Dimercaptobenzidine

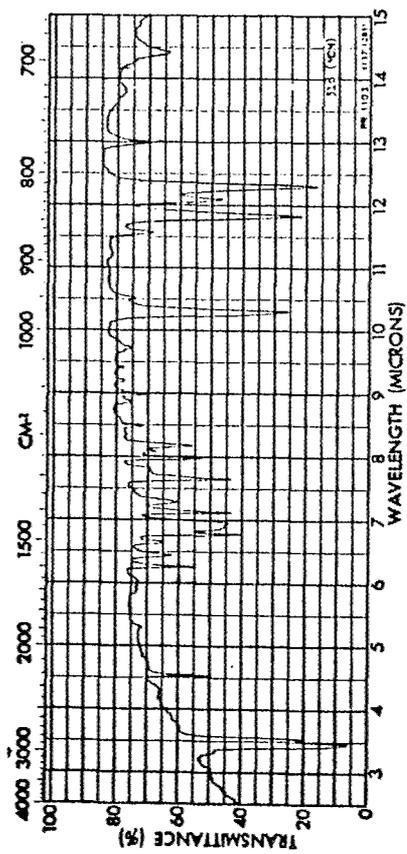


a. 2-(4'-Benzamidophenyl)benzothiazole

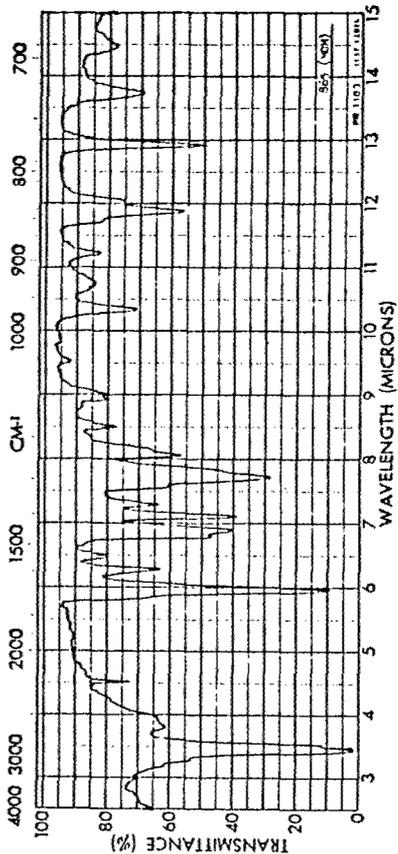


c. Poly-2-(*p*-phenylene)-6-carboxamido-benzothiazole

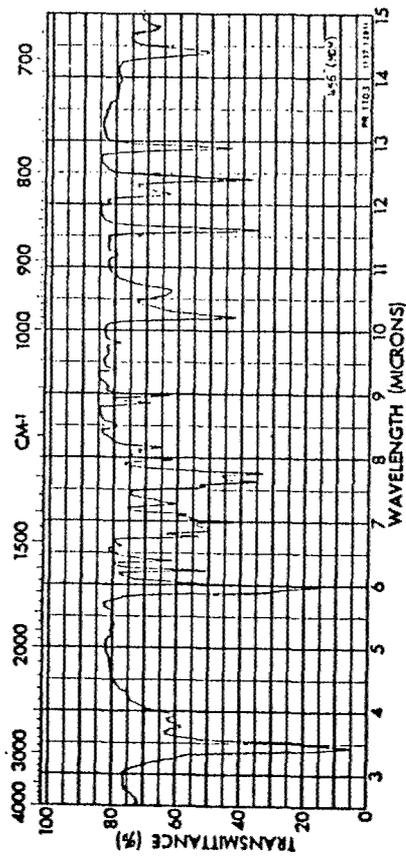
Figure 2. Infrared Absorption Spectra



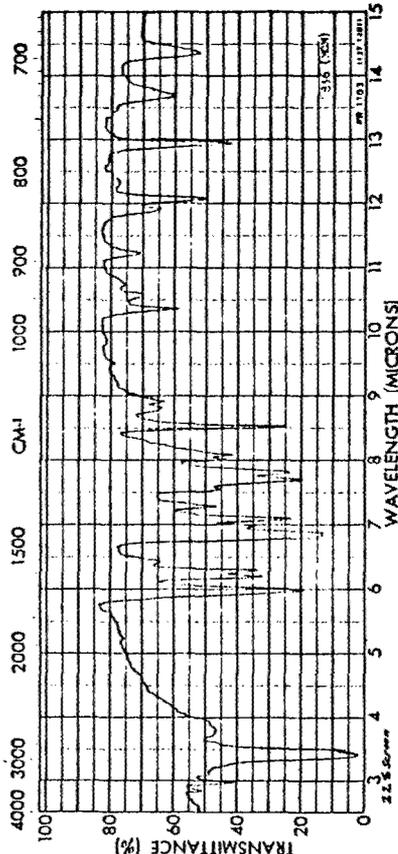
a. 2-(4'-Cyanophenyl)-6-methylbenzothiazole



b. 2-(4'-Cyanophenyl)benzothiazole-6-carboxylic Acid

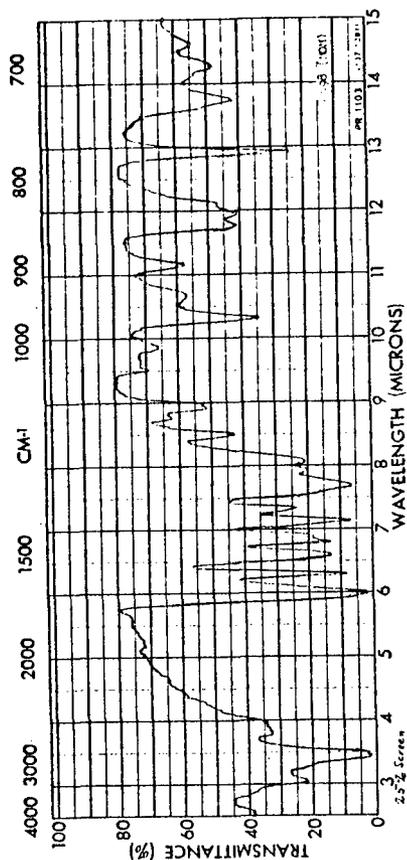


c. 2-Phenyl-6-methylbenzothiazole-4'-carboxylic Acid

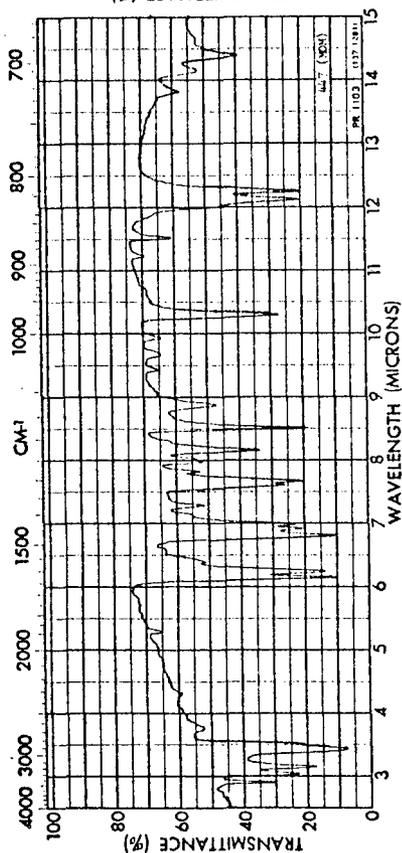


d. 2-(4'-Aminophenyl)benzothiazole-6-carboxylic Acid

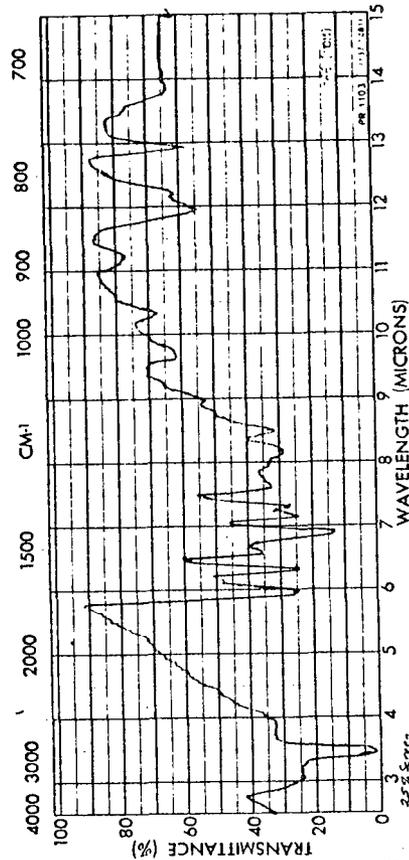
Figure 3. Infrared Absorption Curves



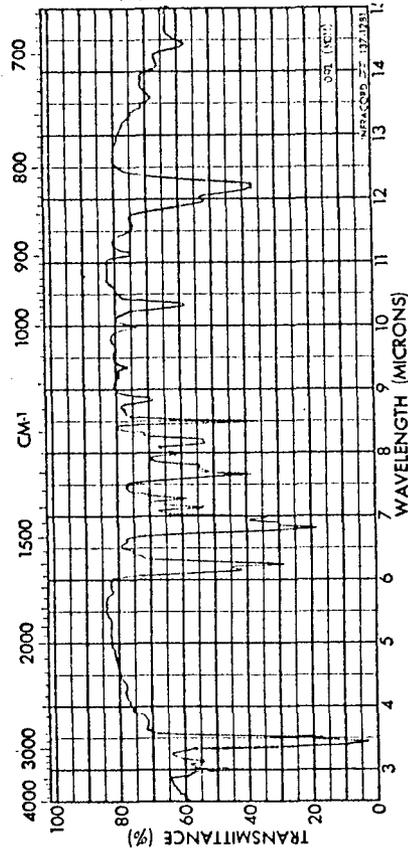
b. 2-(4'-Acetamidophenyl)benzothiazole-6-carboxylic Acid



a. 2-(4'-Aminophenyl)-6-methylbenzothiazole

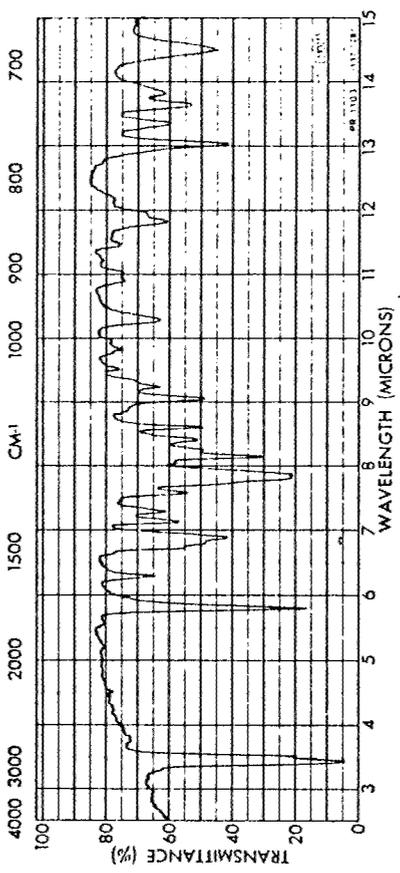


d. 2'-(p-Acetamidophenyl)-2,6'-bibenzothiazole-6-carboxylic Acid

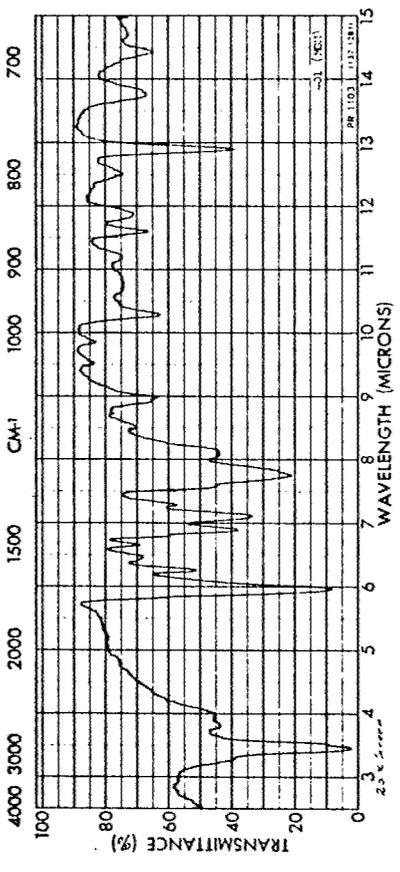


c. 2'-(p-Aminophenyl)-6-methyl-2,6'-bibenzothiazole

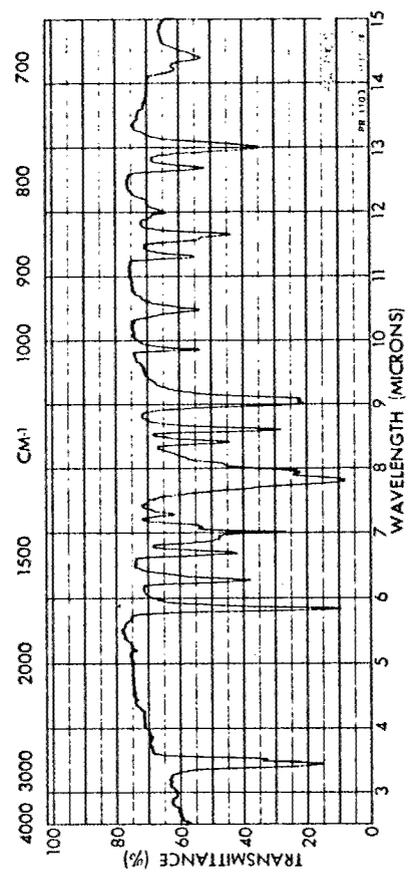
Figure 4. Infrared Absorption Spectra



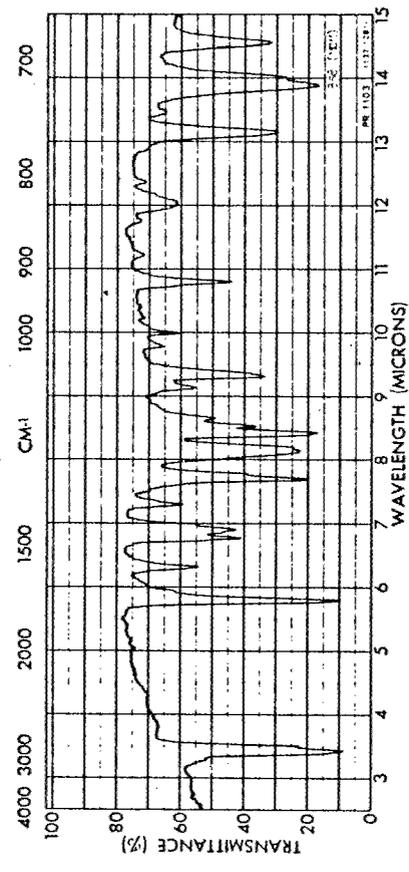
a. 2-(Phenylbenzothiazole)-4',6-dicarboxylic Acid



b. Diphenyl 2-(Phenylbenzothiazole)-4',6-dicarboxylate

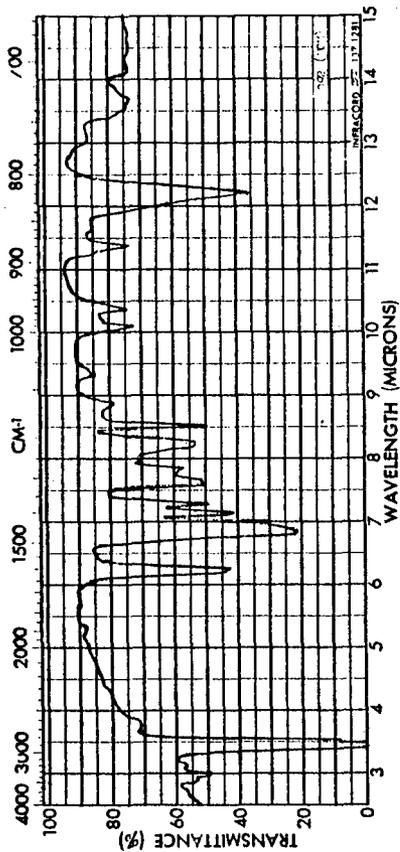


c. Diphenyl Isophthalate

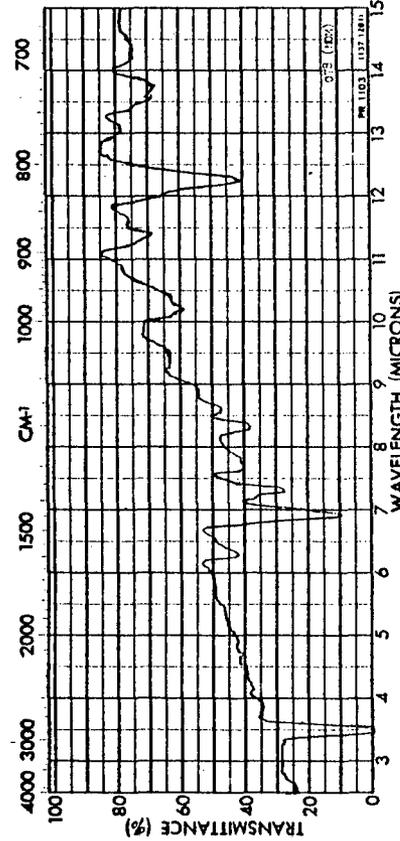


d. Dimethyl Oxy-bis(4-benzoate)

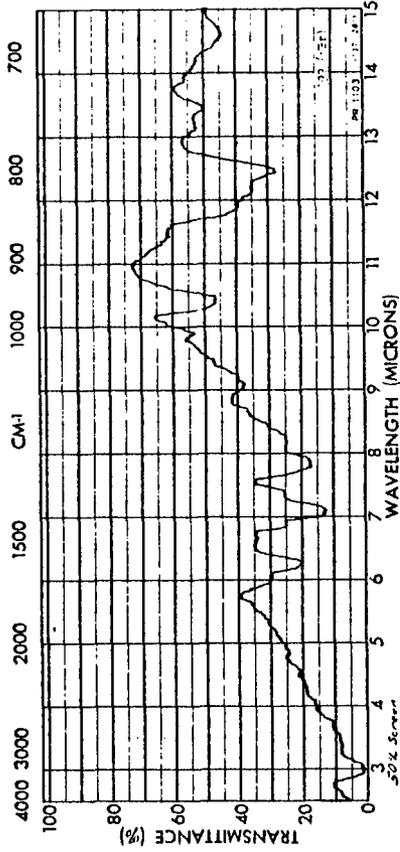
Figure 5. Infrared Absorption Spectra



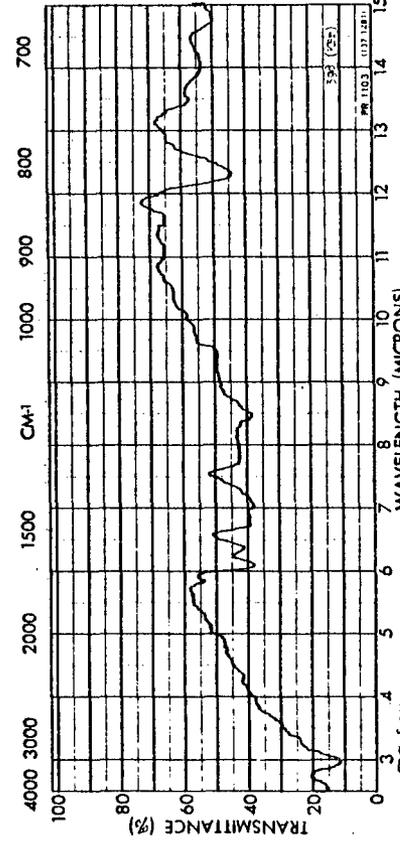
a. Poly-2,2-(p-phenylene)-6- $\sqrt{2}$,2'-(5,5'-bibenzimidazolylene)/benzothiazole



b. High Molecular Weight Primuline Component

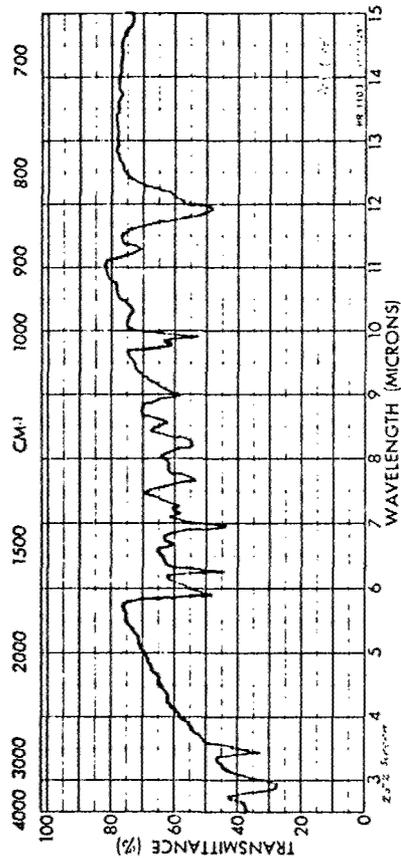


c. Poly-2-(m-phenylene)-2'-(6,6'-bibenzothiazole)



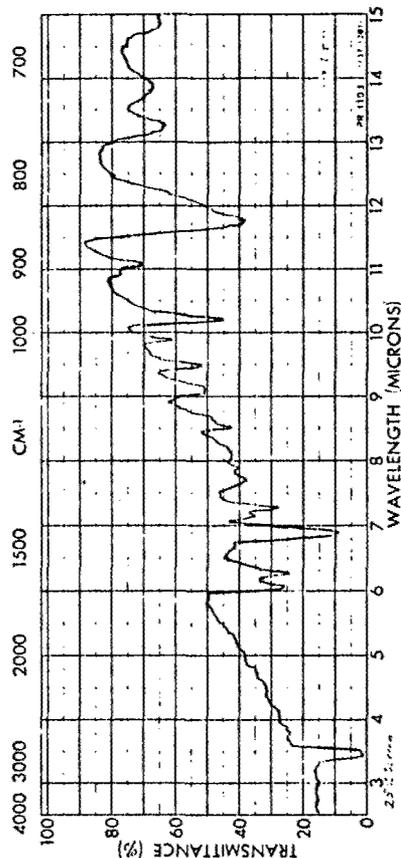
d. Poly-2-(p-phenylene)-6- $\sqrt{2}$,2'-(5,5'-bibenzimidazolylene)/benzothiazole

Figure 6. Infrared Absorption Spectra



a. Rubeanic Acid (Dithiooxamide)

b. Poly-2-(p-phenylene)-5-thiazolo-[5,4-d]-thiazole



c. 2,4-Bis(p-nitrophenyl)thiazole

d. Poly-2-(p-phenylene-azo-p-phenylene)-4-thiazole

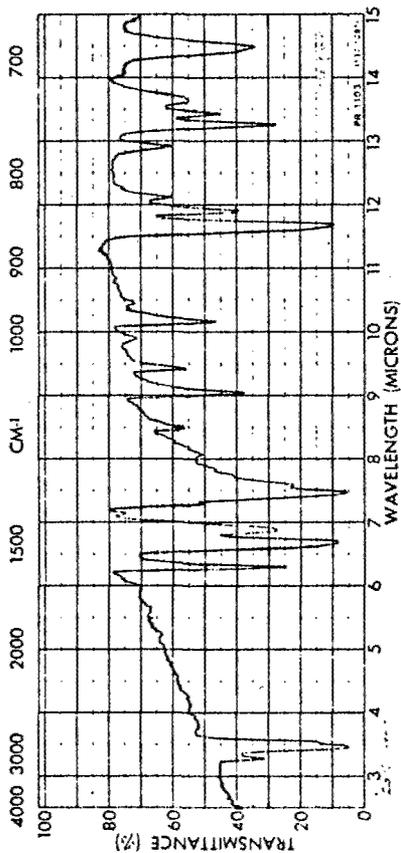


Figure 7. Infrared Absorption Spectra

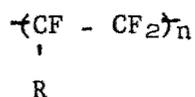
F. List of References

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2. Elderfield, R. C., "Heterocyclic Compounds", Vol. 5, J. Wiley and Sons, Inc. New York (1957).
3. Dale, J. W., et al, "Synthesis of 1000°F Stable Base Fluids", WADC TR 59-95, Part II, June 1960.
4. Warburton, W. K., "Arylthiazathiolium Salts and o-Aminoaryl Thiols", Chem. Rev. 57, 1011 (1957).
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(b) Vogel, H., and Marvel, C. S., "Polybenzimidazoles, New Thermally Stable Polymers", J. Poly. Science 50, 511 (1961).
6. Rotenberg, D. H., "Thiazolothiazoles, Carboxylic and Amino Derivatives", Thesis, Cornell University, June 1960.
7. Doyle, C. D., "Evaluation of Experimental Polymers", WADD TR 60-283, May 1960.

III. FLUOROOLEFINS

A. Introduction and Objective

The objective of this work is to explore the possibility of preparing heat stable polymers by polymerizing monomers containing a trifluorovinyl group attached to a stable heterocyclic ring. Preparation of such polymers of the type



where R is a stable heterocycle, would also permit a determination of the effect of non-volatile monomers on the depolymerization tendency of poly(perfluoroolefins). In addition, the bulky side group of these polymers should result in elevated glass temperatures and, thereby, improved performance over poly(tetrafluoroethylene) as a structural material at elevated temperatures.

Previously the reactions of various heterocyclic organometallics with tetrafluoroethylene and tetrafluorodibromoethane were investigated in an attempt to prepare the desirable trifluorovinyl heterocyclic monomers. These efforts were unsuccessful and, consequently, this approach was abandoned.

Currently, our efforts are being devoted to the preparation of 2-(trifluorovinyl)benzazoles. The initial work has been primarily directed to the synthesis of benzimidazole and benzothiazole derivatives, which, if successful, should be readily extended to include the benzoxazole analogs.

B. Summary

The synthetic route envisioned here involves the condensation of the properly substituted fluoroacid with an ortho-substituted aniline to produce benzazole intermediates which subsequently can be converted to the trifluorovinyl group by the general methods of dehydrohalogenation, pyrolysis, and dehalogenation. The syntheses of benzazole intermediates and precursor fluoro-acids which have been prepared are summarized below along with the several unsuccessful (to date) attempts to prepare a 2-(trifluorovinyl)benzimidazole.

1. 2,2,3,3-Tetrafluoropropionic acid and perfluorosuccinic acid have been prepared by the permanganate oxidation of the alcohol, 2,2,3,3-tetrafluoropropanol, and the olefin, 1,2-dichlorotetrafluorocyclobutene, respectively.

2. 2-(1,1,2,2-Tetrafluoroethyl)benzimidazole (TFB) has been prepared in 46% yield by the condensation of 2,2,3,3-tetrafluoropropionic acid with ortho-phenylenediamine in refluxing 4N hydrochloric acid.

3. The attempted dehydrofluorination of TFB with 17% sodium hydroxide proceeded in an undesirable direction, disodium oxalate and benzimidazole being the products formed. The use of refluxing triethylamine and potassium t-butoxide in dimethylsulfoxide solvent at various temperatures gave back, for the most part, unchanged TFB.

4. The reaction of 2,2,3,3-tetrafluoropropionic acid with ortho-aminothiophenol in refluxing 4N hydrochloric acid gave a product which is believed to be 2-(1,1,2,2-tetrafluoroethyl)benzothiazole.

5. The reaction of perfluoroscuccinic acid with ortho-phenylenediamine and ortho-aminothiophenol, respectively, gave the desired intermediates, 2-(1,1,2,2-tetrafluoro-2-carboxyethyl)benzimidazole (TFCEB) and 2-(1,1,2,2-tetrafluoro-2-carboxyethyl)benzothiazole (TFCEBT) in 65% and 75% yield, respectively.

6. The reaction of perfluoroglutaric acid with ortho-phenylenediamine gave the desired intermediate, 2-(1,1,2,2,3,3-hexafluoro-3-carboxypropyl)benzimidazole in 46% yield.

7. Pyrolyses studies of TFCEB and its sodium salt were undertaken. The pyrolysis of the sodium salt of TFCEB under reduced pressure yielded a sublimate mixture which is believed to contain the desired 2-(trifluorovinyl)benzimidazole as a component. Initial efforts at separation by fractional sublimation have been unsuccessful.

8. The silver salts of TFCEB and TFCEBT have been prepared. These will be utilized in attempts to prepare their respective iodo compounds (Hunsdiecker reaction) which may lend themselves to dehalogenation with zinc under mild conditions.

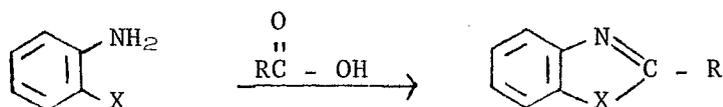
9. From the ozonization of the olefin, 3,4,4-trifluoro-4-bromo-3-chlorobutene-1, followed by hydrogen peroxide oxidation, was obtained a fluoro-acid, the neutralization equivalent value (244) of which compares favorably with the calculated value (241.5) for the desired acid, 2,3,3-trifluoro-3-bromo-2-chloropropionic acid. However, the elemental analysis was very poor for the desired acid. The condensation of this acid with ortho-phenylenediamine gave only a trace amount of what appears to be the desired intermediate (based on C, H, N analyses, and infrared spectrum), 2-(1,2,2-trifluoro-2-bromo-1-chloroethyl)benzimidazole.

An aqueous permanganate oxidation of the olefin yielded the same (impure) fluoro-acid in ca. 25-30% yield.

C. Discussion

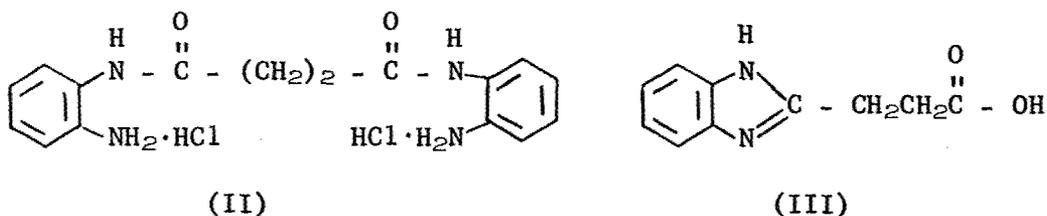
1. Introduction

The synthetic route envisioned here is the preparation of benzimidazole, benzothiazole, and benzoxazoles substituted in the 2-position with a fluoro-alkyl group which can subsequently be converted to the trifluorovinyl group. 2-Substituted benzimidazoles, benzoxazoles, and benzothiazoles are frequently prepared by the condensation of organic acids with an ortho-substituted aniline as shown below:

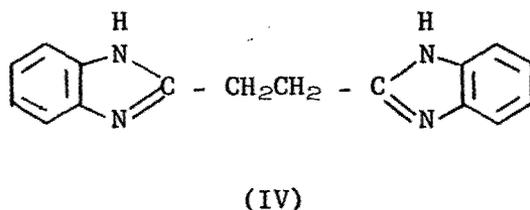


Recently a number of 2-perfluoroalkylbenzimidazoles, (I) X = NH, R = CF₃, CF₂CF₃, and CF₂CF₂CF₃, have been synthesized by this method^{2,3}. In these cases, the perfluoroalkyl substituents enhanced the acidity of the benzimidazole nucleus to such an extent that the azole could be titrated with base to give good equivalent weights.

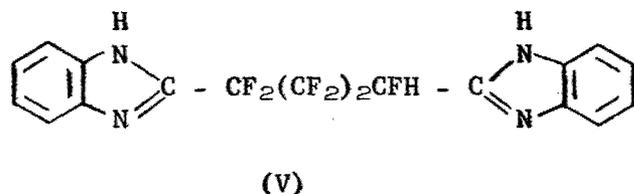
A number of dibasic acids also have been condensed with ortho-phenylenediamine. Succinic acid, when reacted in a 1:1 molar ratio with ortho-phenylenediamine in 4N hydrochloric acid⁴ has been reported to give a mixture of the compounds II and III.



Compound II could be converted by strong heating to the ethane bis-2-benzimidazole, IV.



Quite recently, Lane^{2a} reported the formation of the heptafluoro-adipobis-2-benzimidazole (V) by the condensation of the di-acid with ortho-phenylenediamine in refluxing 4N hydrochloric acid.



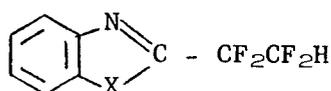
It appears to us, therefore, that this general route should prove fruitful in investigating the preparation of the desired trifluorovinyl benzazoles. By the judicious selection of the acid, a variety of monomer precursors would become available enabling us to investigate and evaluate three of the general methods, dehydrohalogenation, pyrolysis and dehalogenation, for introducing the double bond in fluorocarbons.

To date, a number of benzimidazoles and benzothiazoles have been prepared with substituents in the 2-position such that conversion to the desired 2-(trifluorovinyl)benzazoles may be possible by one of these three general methods.

2. Dehydrofluorination

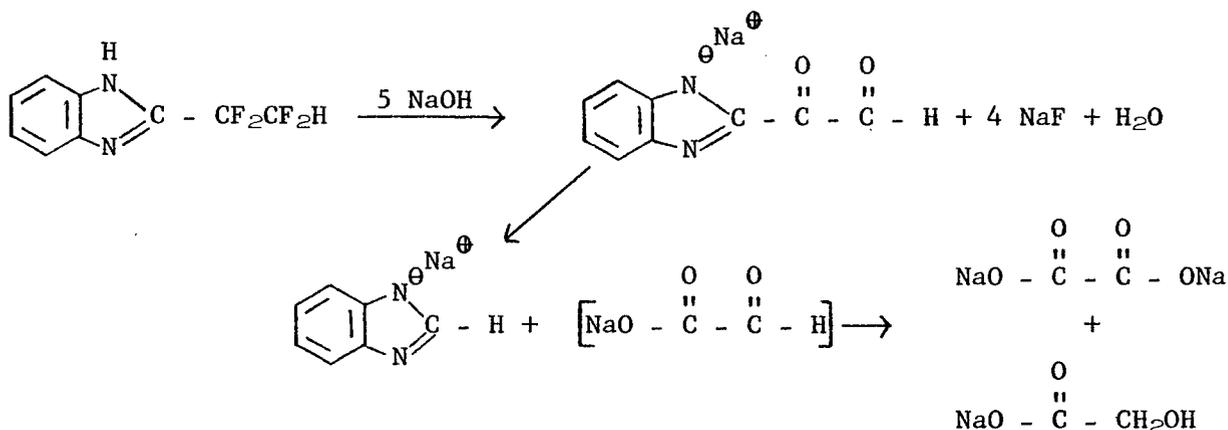
a. 2-(1,1,2,2-Tetrafluoroethyl)benzimidazole (TFB) and Its Attempted Dehydrofluorination

The condensation of 2,2,3,3-tetrafluoropropionic acid with ortho-phenylenediamine in refluxing aqueous hydrochloric acid gave the 2-(tetrafluoroethyl)benzimidazole (VI, X = NH) (TFB) in 46% yield.



(VI)

The attempted dehydrofluorination of TFB in refluxing 17% sodium hydroxide solution was unsuccessful. From the basic solution a small amount of insoluble material was obtained which proved to be the disodium salt of oxalic acid (by infrared determination). Also, the reaction mixture gave a strong test for the presence of inorganic fluoride ion. Neutralization of the reaction mixture to pH 5-6 caused the precipitation of a solid which proved to be silicon dioxide, obviously brought about by the attack of the reaction mixture on the glass vessel. Finally, from the neutralized reaction mixture a 60% yield of benzimidazole was isolated. Obviously, the reaction proceeded in an undesirable direction. A possible explanation for the formation of these products is indicated below:



The disodium salt of oxalic acid could arise from a Cannizzaro type reaction involving the aldehyde acid salt. No attempt was made to isolate the corresponding alcohol which would arise from such a reaction. Of course, other reaction schemes may be postulated to explain the products isolated.

Attempts to dehydrofluorinate TFB using refluxing triethylamine or potassium *t*-butoxide in dimethylsulfoxide at temperatures ranging from 35° to 130° were unsuccessful. TFB was recovered, for the most part, unchanged. Further attempts to dehydrofluorinate TFB have been temporarily suspended.

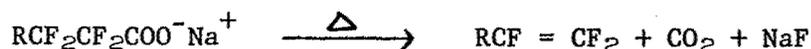
b. 2-(1,1,2,2-Tetrafluoroethyl)benzothiazole

Although difficulty was anticipated in the dehydrofluorination of TFB by basic reagents, the presence of the acidic hydrogen in the benzimidazole nucleus undoubtedly compounded the problem, since it is reasonable to expect that the salt (which would form initially) would be less susceptible to dehydrofluorination by basic reagents.

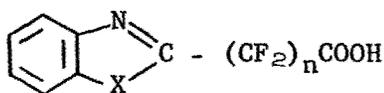
A more suitable compound for dehydrofluorination, of course, would be one in which the hydrogen atom was activated. In this case, the removal of HF occurs readily or even spontaneously. However, in the particular case on hand, the intermediates are unavailable or would involve extensive experimental difficulties in their preparation. Subsequently, an attempt to prepare 2-(1,1,2,2-tetrafluoroethyl)benzothiazole, (VI, X = S), which does not have an acidic hydrogen, was made by condensing 2,2,3,3-tetrafluoropropionic acid with ortho-aminothiophenol. A pure product was obtained which should prove to be the desired intermediate. An effort to dehydrofluorinate this intermediate will be made. However, it may also prove useful in the characterization of the products obtained when the pyrolysis studies of 2-(1,1,2,2-tetrafluoro-2-carboxyethyl)benzothiazole are initiated.

3. Pyrolysis

The pyrolysis of the sodium salts of perfluoro-acids is a useful method for the preparation of terminal fluoro-olefins^{5,6}. Consequently, several benzazolyl-



perfluoro-acids (VII) have been prepared in order to investigate this method for the preparation of the desired monomers.

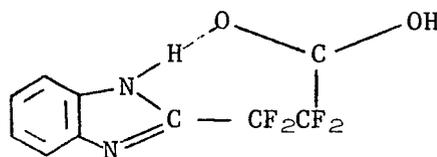


(VII) X = NH; S

a. 2-(1,1,2,2-Tetrafluoro-2-carboxyethyl)benzimidazole (TFCEB)

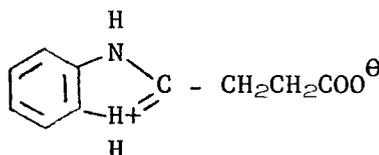
The reaction of perfluorosuccinic acid with ortho-phenylenediamine in refluxing 4N hydrochloric acid gave the acid 2-(1,1,2,2-tetrafluoro-2-carboxyethyl)benzimidazole (VII, X = NH, n = 2) in 65% yield. Very recently, K. J. Morgan⁷ has reported the infrared spectral studies of some benzimidazoles, among which are listed TFCEB. However, its mode of preparation and physical properties were not mentioned in this paper. Morgan reports absorptions for this compound at 3400 cm⁻¹ (mw), 2200-3000 cm⁻¹ (mw) (NH and OH) and 1676 cm⁻¹ (s) (C = O). Our product shows similar absorptions. On the basis of a study of the spectra of 2-benzimidazolylacetic acid and 2-benzimidazolyl-difluoroacetic acid, Morgan suggests that these acids and TFCEB probably exist as chelate-type structures, e.g., VIII. Very

interestingly, beta-2-benzimidazolylpropionic acid showed marked differences. The carbonyl band was replaced by a broad band at 1550 cm^{-1} and the C - O stretching



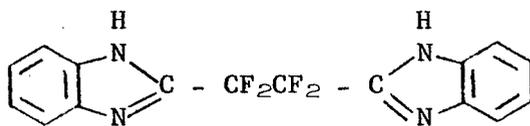
(VIII)

frequency was displaced to 1410 cm^{-1} . These shifts, and the absence of a discrete hydroxyl band, indicate that this acid is best regarded as the zwitterionic compound, IX.



(IX)

A second minor component, m.p. $> 330^\circ$, was also isolated from the perfluorosuccinic acid-ortho-phenylenediamine reaction. The analysis for this product, the infrared spectrum of which seems to be consistent for the bis structure, X, was poor. The total of the elements reported added up to only 93.48%. This material will be resubmitted for analyses.



(X)

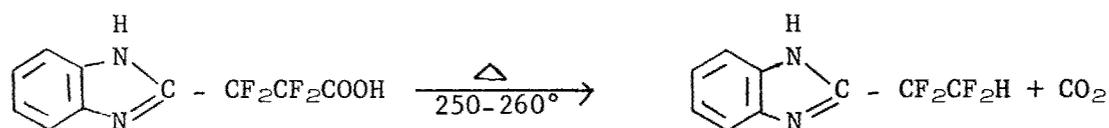
b. 2-(1,1,2,2,3,3-Hexafluoro-3-carboxypropyl)benzimidazole and 2-(1,1,2,2,-Tetrafluoro-2-carboxyethyl)benzothiazole

In a similar fashion, the reaction of perfluoroglutaric acid with ortho-phenylenediamine, and the reaction of perfluorosuccinic acid with ortho-aminothiophenol, respectively, have given the acid VII ($X = \text{NH}$, $n = 3$), 2-(1,1,2,2,3,3,-hexafluoro-3-carboxypropyl)benzimidazole in 46% yield and the acid VII, ($X = \text{S}$, $n = 2$), 2-(1,1,2,2-tetrafluoro-2-carboxyethyl)benzothiazole in 75% yield.

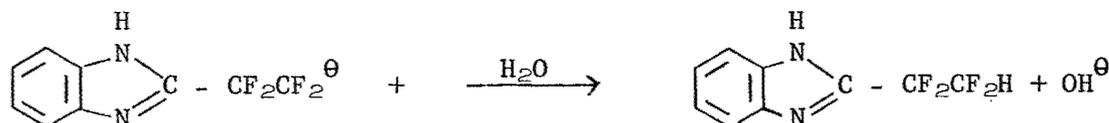
c. The Pyrolysis of 2-(1,1,2,2-Tetrafluoro-2-carboxyethyl)benzimidazole and Its Sodium Salt

Initial pyrolysis studies of the acid VII, ($X = \text{NH}$, $n = 2$) and its sodium salt have been carried out. This acid, when heated at $250\text{-}260^\circ$, decarboxylates with the formation of TFB. Likewise the decarboxylation of the moist sodium

salt at 260-290° at atmospheric pressure occurs with the formation of TFB. A



reasonable explanation for the formation of TFB is indicated by the equation below:

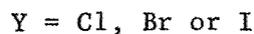
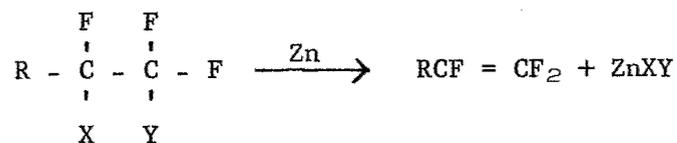


Pyrolysis of the anhydrous sodium salt at 240-285°/0.2 mm. yielded sublimates, which were obviously mixtures, carbon dioxide, and a residue which was predominantly inorganic fluoride. The infrared spectra of the sublimates showed new absorptions at 5.55 μ , 5.65 μ , 5.82 μ not present in the starting material. The trifluorovinyl group is known to absorb in this same general region. (However, it is possible that conjugation with an aromatic system may cause a shift to longer wavelengths). These results indicate that the reaction has proceeded to a certain extent in the desired direction.

Some effort was directed towards the separation of the components of the sublimate mixture by fractional resublimation at varying temperatures. Observation of the infrared absorptions bands of the fractions isolated indicated some separation had occurred. No pure products, however, were isolated. The details of this work are presented in the experimental. Further efforts to separate the mixture are in progress. The pyrolysis technique will also be extended to the salts of VII, (X = NH, n = 3) and VII, (X = S, n = 2).

4. Dehalogenation:

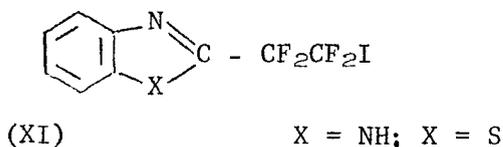
A third general method for preparing terminal fluoroolefins under rather mild conditions utilizes the dehalogenation of a properly substituted fluoro-compound with zinc as shown below:



a. Hunsdiecker reaction

A second approach utilizing the acids, VII, is being contemplated. Treatment of the sodium salts of the acids VII, (X = NH, n = 2) and VII, (X = S, n = 2) with silver nitrate solution gave an almost quantitative yield of the

silver salts. Attempts to prepare the iodo compounds XI, (Hunsdiecker Reaction)⁸ will be made. This type of compound may lend itself to dehalogenation with zinc under mild conditions.

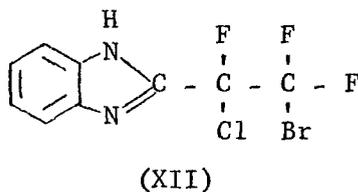


b. 2,3,3-Trifluoro-3-bromo-2-chloropropionic Acid and 2-(1,2,2-Trifluoro-2-bromo-1-chloroethyl)benzimidazole

In order to investigate this approach more fully, efforts were also made to prepare a suitably substituted fluoro-acid which could be condensed to form benzazoles.

The ozonization of the olefin, 3,4,4-trifluoro-4-bromo-3-chlorobutene-1 followed by aqueous hydrogen peroxide oxidation, gave a pure fluoro-acid, as determined by gas phase chromatography, having the correct neutralization equivalent for the desired acid, 2,3,3-trifluoro-3-bromo-2-chloropropionic acid. However, the elemental analyses, (C, H) for this compound was very poor. An aqueous potassium permanganate oxidation of the same olefin also gave the same acid in ca. 25-30% yield. Previous attempts to oxidize the olefin to the title acid with potassium permanganate in acetone, in the absence or presence of sodium bicarbonate, had been unsuccessful.

On the assumption that the above fluoro-acid was the desired acid, a small amount of this material (2.0 g.) was reacted with ortho-phenylenediamine to give a trace amount of a product believed to be the desired intermediate (based on infrared spectrum and C, H, N analyses), 2-(1,2,2-trifluoro-2-bromo-1-chloroethyl)benzimidazole (XII). However, if the zinc dehalogenation procedure is to prove feasible, the yield of the condensation reaction must be greatly improved. Efforts in this direction are currently underway.



D. Experimental

1. 2,2,3,3-Tetrafluoropropionic Acid

The permanganate oxidation of alcohols of the general type $\text{H}(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{OH}$ to the corresponding acids, $\text{H}(\text{CF}_2\text{CF}_2)_n\text{COOH}$, is described in the patent literature⁹ for alcohols where $n = 3, 4, 5,$ and 6 . 2,2,3,3-Tetrafluoropropionic acid was prepared from 2,2,3,3-tetrafluoropropanol-1 according to the patent procedure, except that water was used as solvent instead of acetic acid.

To a refluxing, stirred solution of 71 g. (0.538 mole) of tetrafluoropropanol in 400 ml. of water, was added, carefully in portions, 120 g. of solid potassium permanganate. After refluxing and stirring overnight, all the permanganate had been converted to manganese dioxide. The latter was reduced by the alternate addition, in portions, of mineral acid (total 46 g. conc. sulfuric acid, 150 g. conc. hydrochloric acid) and sodium sulfite (124 g.). The reaction mixture was heated to boil off most of the sulfur dioxide, cooled, saturated by the addition of 470 g. of sodium chloride, and extracted with four 200 ml. portions of ether. After drying over magnesium sulfate, the ether was removed by distillation through a 10 inch jacketed Vigreux column and the residue distilled to give the following fractions:

Fraction 1:	b.p. 125-129°, 18.16 g.,	n_D^{24}	1.3350
Fraction 2:	b.p. 129-131°, 16.31 g.,	n_D^{24}	1.3324
Fraction 3:	b.p. 131-132°, 30.96 g.,	n_D^{24}	1.3289

Total yield of fractions 1-3 was 65.43 g. Henne and Fox¹⁰ reported the chromic acid oxidation yields $\text{HCF}_2\text{CF}_2\text{COOH} \cdot 0.5 \text{H}_2\text{O}$, b.p. 131.5-2°; $\text{HCF}_2\text{CF}_2\text{COOH} \cdot 1 \text{H}_2\text{O}$, b.p. 136-137°; a patent¹¹ reports n_D^{25} 1.3290 for the acid.

2. 2-(1,1,2,2-Tetrafluoroethyl)benzimidazole (TFB)

ortho-Phenylenediamine dihydrochloride, 5.38 g. (0.0297 mole), and 4.0 g. (0.0244 mole) of 2,2,3,3-tetrafluoropropionic acid hydrate in 7.9 g. of conc. hydrochloric acid and 16 g. of distilled water were refluxed for 72 hours. The solution was neutralized with 10 g. of conc. ammonium hydroxide (28-30% NH_3) while cooling in ice-water, causing a precipitate to form. This solid was filtered and washed with 3 x 20 ml. distilled water and dried, yield 3.9 g. Continuous sublimation of the crude solid at 170-180° at atmospheric pressure gave 3.1 g. (47%) of pure TFB, m.p. 181-183°. A resublimed sample, m.p. 181-183° was submitted for elemental analysis.

	% C	% H	% N	% F
Calc'd for $\text{C}_9\text{H}_6\text{N}_2\text{F}_4$:	49.55	2.77	12.84	34.84
Found:	49.80	3.13	13.01	34.63

The 2-(tetrafluoroethyl)benzimidazole is definitely acidic in aqueous methanol solvent and takes up base. However, our titrations to date have been unsatisfactory due to the inability to obtain a good end point with thymolphthalein indicator.

3. Attempted Dehydrofluorination of TFB with:

a. Aqueous Base

TFB, 1.0 g., was refluxed for 19 hours with 3.0 g. of sodium hydroxide in 15 ml. of distilled water. A small amount of base-insoluble, flinty, white solid, 176 mg., was obtained after washing with distilled water and drying. The infrared spectrum of this solid showed no aromatic absorptions, and was practically identical to the spectrum of the disodium salt of oxalic acid.

One ml. of the clear yellow filtrate (total volume now 29.5 ml.) was acidified with acetic acid to pH 6 giving a small amount of solid which was separated by filtration. The clear filtrate was acidified with additional acetic acid, boiled, cooled and then 5 drops of a saturated CaCl_2 solution was added. Immediately a fine, heavy, gelatinous precipitate formed, indicating the presence of inorganic fluoride ion in the main filtrate.

The main filtrate was acidified to pH 5-6 with 6N sulfuric acid, precipitating 296 mg. of silicon dioxide (determined by infrared spectrum) which was removed by filtration. This filtrate was extracted initially with 2 x 50 ml. of ether and then with 2 x 50 ml. of chloroform. Removal of solvent from both extracts left muddy yellow solid residues in both cases. Purification of this material was eventually attained by sublimation at $165^\circ/0.25$ mm., to give initially a yellow-white solid which, on resublimation at $130-135^\circ/0.25$ mm., gave 0.326 g. (60%) of white solid, m.p. $168-171^\circ$. The infrared spectrum and melting point of this solid were identical to those of commercial benzimidazole. A small amount of unidentified residue was also obtained in this reaction.

b. Triethylamine

The 2-(tetrafluoroethyl)benzimidazole, 1.0 g. (0.0046 mole) was added to 10 ml. of triethylamine and refluxed for 16.5 hours, after which the solution was filtered to remove only traces of insoluble material. The triethylamine was removed by distillation leaving a tarry, resinous residue. This material was dried, transferred to a sublimation apparatus and sublimed at $180-185^\circ$, yielding 0.6 g. (60%) of unchanged TFB, m.p. $180-181^\circ$, mixed m.p. $180-181^\circ$. The unsublimed residue was a brownish black tar.

c. Potassium t-butoxide in Dimethylsulfoxide Solvent

(1) To 1.0 g., (0.0046 mole) of TFB in 10 ml. of anhydrous dimethylsulfoxide (DMSO) was added 0.52 g. (0.0046 mole) of potassium t-butoxide, the temperature rising initially from 28 to 40° . The mixture was maintained at $35-40^\circ$ for 19 hours. The solution was filtered and the solvent was removed under a vacuum of 2.0-2.5 mm., while heating the reaction flask with a hot-air blower. The 1.6 g. of viscous residue was taken up in water and filtered, giving 200 mg. of tan solid, m.p. about 175° with evidence of sublimation. The infrared spectrum of this solid showed it to be almost pure TFB. The filtrate upon acidification to pH 3-4 gave 0.65 g. of a pinkish solid, m.p. $170-174^\circ$. The infrared spectrum was identical to that of pure TFB. Sublimation of 100 mg. of this solid at $170-175^\circ$ yielded 98 mg. of pure TFB, m.p. $181-183^\circ$. Total TFB recovered, 0.85 g. (85%).

(2) The above reaction was repeated at a temperature of (a) $70-75^\circ$ for 48 hours and (b) 100° for 19 hours, giving back the TFB unchanged in 85% and 82% yield respectively.

(3) In another experiment, 3.25 equivalents of potassium t-butoxide (1.7 g., 0.0151 moles) to one equivalent of TFB was used, and the temperature of reaction was raised to $125-130^\circ$. The time of heating was 24 hours. After this period, substantial solid was suction filtered (with difficulty) and washed thoroughly with DMSO. This waxy solid readily dissolved in water to give a basic

solution. Acidification gave no solid. The brownish-green DMSO solution was evaporated in vacuo. The addition of water to the viscous residue and filtration gave 88 mg. of brownish solid. The attempt to sublime this material was unsuccessful. The infrared spectrum of the brownish-black residue showed very little or no C-F absorption in the 8-9 micron region. Acidification of the aqueous filtrate to pH 3-4 gave a voluminous tannish precipitate, 0.45 g., which was completely sublimed to give 0.44 g. (44%) of pure TFB. Ether extraction of the filtrate and evaporation yielded an additional 0.16 g. of TFB. Thus 60% of starting TFB was recovered unchanged.

4. 2-(1,1,2,2-Tetrafluoroethyl)benzothiazole

ortho-Aminothiophenol, 5.76 g. (0.046 mole) and 2,2,3,3-tetrafluoropropionic acid, 8.20 g. (0.05 mole) in 200 ml. of 4N HCl, were stirred and heated at reflux for 13 days. The solid formed was washed thoroughly with water. After drying, 5.7 g. reddish-black crude solid remained. This material was readily purified by sublimation at 50-60°/0.2 mm., giving rhombic crystals, 4.4 g. (42%), m.p. 62-64°. The crude material sublimes over practically quantitatively, and the yield of product should be greater than 50% but a substantial amount of the crude material was accidentally lost. This compound should prove to be the title compound. A resublimed sample will be submitted for elemental analyses.

5. Perfluorosuccinic Acid

This acid was prepared according to the procedure of Henne and Zimmer^{1,2} by the potassium permanganate oxidation of 1,2-dichlorotetrafluorocyclobutene in acetone, m.p. 102-115°, neut. equiv. 96.4; calc'd. 95, (Henne and Zimmerschied^{1,3} m.p. 86.4-87.4; Hazeldine⁶ reports m.p. 116° after distilling in vacuo over a small amount of phosphorus pentoxide. On exposure for several hours, the m.p. drops to that of the hydrate, 86°).

6. 2-(1,1,2,2-Tetrafluoro-2-carboxyethyl)benzimidazole (TFCEB)

Perfluorosuccinic acid, 10.9 g., (0.057 mole) and 10.4 g. (0.057 mole) of ortho-phenylenediamine dihydrochloride in 64 ml. of 4N HCl were stirred and refluxed for 4.5 days. The solid formed was washed with distilled water and dried to give 11.7 g. of pale-green solid (A), m.p. 248-250° (dec.). This solid was added to 100 ml. of 5% sodium hydroxide and the solution adjusted to a pH of about 6 with conc. HCl. The undissolved residue 0.82 g., (B), m.p. > 330°, was removed by filtration. This filtrate was then acidified to pH 1, with conc. HCl, giving 9.3 g. (65%) of a light tan solid, m.p. 250-251° (dec.), after washing with distilled water and drying.

An analytical sample was prepared by neutralizing a sample of crude product A in 25 ml. of distilled water to a pH ~ 6 with 0.1N NaOH solution, filtering and reacidifying. After standing overnight, fine white solid was obtained, m.p. 250-251° (dec.).

	<u>% C</u>	<u>% H</u>	<u>% N</u>
Calc'd for C ₁₀ H ₈ N ₂ F ₄ O ₂ :	45.81	2.31	10.69
Found:	45.50	2.50	10.56

The solid B, m.p. $> 330^\circ$ was purified by dissolving in 10% sodium hydroxide solution, filtering and reprecipitating by acidification. The infrared spectrum of this solid appears to be consistent for the bis structure X, since it is very similar to the infrared spectrum of TFB in the $2.4-8.8\mu$ region and contains no bands at 3.0μ , 6.1μ , 11.3μ and 12.3μ which are characteristic of the spectrum of TFCEB. Thus, TFCEB is not a contaminant. However, the elemental analysis received was not good, the total analysis adding up to only about 93%.

	<u>% C</u>	<u>% H</u>	<u>% N</u>	<u>% F</u>
Calc'd for structure X, $C_{16}H_{10}N_4F_4$:	57.40	3.01	16.71	22.70
Found:	56.48	3.50	14.27	19.23

7. Decarboxylation of TFCEB

a. A sample of the solid mixture A, m.p. $244-249^\circ$ (obtained in a different experiment) in a four inch test tube with an outlet leading to an 0.3 N barium hydroxide solution, was heated to $247-270^\circ$ at atmospheric pressure. Gas was evolved and substantial precipitate formed in the barium hydroxide solution indicating the evolution of carbon dioxide.

b. A sample of the solid, A, m.p. $244-249^\circ$, heated in a sublimator for ca. 5 hours at $250-260^\circ$, gave fluffy white sublimate, which were removed at intervals. The infrared spectrum of the unsublimed residue, 189 mg., was identical to the spectrum of the solid B, m.p. $> 330^\circ$.

The combined sublimate were resublimed, giving 315 mg. of pure TFB, (m.p. $180-182^\circ$, mixed m.p. $180-182^\circ$, and identical infrared spectra), and no residue. Total product recovered, 504 mg. (50.4%).

8. Pyrolysis of the Sodium Salt of TFCEB at Atmospheric Pressure

The sodium salt was prepared by neutralizing the solid TFCEB to pH 6-7 with slightly over one equivalent of sodium hydroxide solution, filtering and evaporating to dryness.

A sample of the sodium salt, 0.23 g. (not anhydrous), in a four inch test tube with hose connection and outlet immersed in a 0.3N barium hydroxide solution, was heated to $260-290^\circ$ at atmospheric pressure. Gas was evolved and substantial precipitate formed in the barium hydroxide solution indicating the evolution of carbon dioxide. Also substantial white solid had sublimed on the upper part of the test tube and black unsublimed residue remained in the bottom of the tube. Most of these solids, sublimate and residue, were scraped out, 0.13 g., and the mixture sublimed at $170-200^\circ$ to give 43 mg. of a white sublimate, m.p. $180-182^\circ$, and 70 mg. of a black unsublimed residue. The m.p. and infrared spectrum of the white sublimate were identical to that of TFB.

9. Pyrolyses of the Sodium Salt of TFCEB at Reduced Pressure

The pyrolysis was carried out in a sublimation unit. The system had a dry ice trap between the sublimation unit and the pump. The salt, 2.83 g., was gradually heated (to remove any excess water present before decarboxylation occurred) under

reduced pressures of 0.1 - 0.2 mm. No sublimation occurred up to a temperature of 230°. Some sublimation occurred at about 250° and increased progressively as the temperature was raised to 285°. The pyrolysis was interrupted at intervals to remove sublimates. Upon removal of the first sublimate, the trap was examined and found to contain 0.2-0.3 ml. of water and a small amount of white solid. Examination of the cold trap after removal of the second sublimate indicated only a trace of water and solid. From this point on, the cold trap was dispensed with. The pyrolysis was continued at 285°/0.15 mm. over several days with the intermittent removal of sublimate until apparently no more sublimate formed. The sublimates varied from fine brown powder to yellow-orange solids. The infrared spectrum in almost all cases showed absorptions at 5.5 μ , 5.6 μ , and 5.82 μ , although of varying intensities. The total yield of sublimates was 1.51 g. The unsublimed residue, a fine brown solid, was 0.60 g. A sample of this residue, 100 mg., was leached with distilled water and filtered. The undissolved brown solid, weighed 22 mg. (this value is low because of incomplete recovery). Part of the clear filtrate (about half) gave a positive fluoride test with saturated calcium chloride solution. Evaporation of the other half of the filtrate gave 27 mg. of white solid residue.

10. Attempted Separation of the Components of the Pyrolysis Sublimates by Fractional Sublimation

Several attempts to separate the mixtures obtained in the above pyrolysis by fractional sublimation under reduced pressure were unsuccessful. In one case nine sublimate fractions were taken off at intervals while heating the sample at temperatures ranging from 70° to \sim 210° at a pressure of 0.1-0.2 mm. The earlier fractions (five), which were removed up to a temperature of 120°, all showed infrared absorptions at 5.55 μ , 5.65 μ , and 5.82 μ of varying intensity. The first fraction showed the 5.55 μ band to be the strongest. However, the band progressively became weaker, with each succeeding fraction, until by the fourth fraction it was completely gone. At this point the 5.82 μ absorption was prominent although the 5.65 μ band was still present. However, these first five sublimate fractions only constituted a minor part of the original sample and also gave very wide melting point ranges. The fractions obtained at temperatures over 140° showed the complete absence of these three bands. An absorption at 6.0 μ was the prominent feature of the later sublimates and residues.

In another case, a pyrolysis sublimate which had a strong absorption at 5.55 μ and only minor absorptions at 6.0 μ showed considerable absorption changes after standing six weeks. The band at 5.55 μ became considerably reduced and the band at 6.0 μ became considerably stronger. Resublimation of 0.1 g. of this sample gave 33 mg. (two fractions) at 90-125°/0.15 mm., the infrared spectra of which showed absorptions in the 5.5-5.8 μ region and very little or no absorption in the 6.0 μ region. The infrared spectrum of the residue (\sim 65 mg.), however, showed only a very weak absorption at 5.82 μ and a strong absorption at 6.0 μ . The interpretation of these results at this time is uncertain. However, alpha, beta, beta-trifluorostyrene is known to undergo autoxidation (to benzoic acid and HF in moist air) and to dimerize to a cyclobutane derivative in a simple thermal reaction¹⁴ and these factors must be considered. The large melting point ranges obtained in all cases indicated that the resublimed sublimates were still mixtures.

11. 2-(1,1,2,2,3,3-Hexafluoro-3-carboxypropyl)benzimidazole

A reaction mixture composed of 7.6 g., (0.042 mole) of ortho-phenylenediamine dihydrochloride, 10 g. (0.042 mole) of perfluoroglutaric acid in 63 ml. of solution (solution of 4N in respect to HCl), was refluxed for 4 days, giving reddish-blue solid precipitate. This was filtered, washed thoroughly with distilled water, and dried to give a very fine grey-blue solid, 6.90 g., m.p. 250-253° (evidence of sublimation).

A sample of this solid, 1.0122 g., was neutralized to pH 7-8 (indicator paper) with 0.1 N sodium hydroxide. Most of the solid dissolved. The undissolved greenish-blue solid was filtered and washed thoroughly with distilled water and dried, 0.1183 g. The clear filtrate was acidified to pH 1 with concentrated HCl causing solid to gradually form. After standing overnight, the precipitate was filtered, washed with water, and dried to give 0.9063 g. of very small needles, m.p. 269-271° (with evidence) of sublimation). The crude product therefore contains 6.15 g. (47% yield) of free acid.

	<u>% C</u>	<u>% H</u>	<u>% N</u>	<u>% F</u>
Calc'd for C ₁₁ H ₈ N ₂ O ₂ F ₂ :	42.32	1.94	8.98	36.82
Found:	42.53	1.98	8.70	36.76

12. 2-(1,1,2,2-Tetrafluoro-2-carboxyethyl)benzothiazole (TFCEBT)

Perfluorosuccinic acid, 16.35 g. (0.087 mole) in 60 ml. of 4N HCl and 10.68 g. (0.087 mole) of ortho-aminothiophenol in 175 ml. of 4N HCl, refluxed for 12 days gave 19.7 g. of golden-brown crystalline solid. To this crude solid was added 88 ml. of 5% NaOH solution (slightly exothermic) with swirling. The mixture was allowed to digest for about 15 minutes, then filtered and the undissolved solid washed with 2 x 20 ml. of water. The undissolved solid after drying weighed 1.1 g. The muddy-green filtrate was made strongly acidic with concentrated HCl, causing the precipitation of tannish solid. After standing overnight, the mixture was filtered and the solid washed with water and dried. The yield of fine, tannish solid totalled 17.4 g., m.p. 198-201°. The addition of about 30 ml. of water to the clear filtrate caused the formation of additional white, flocculent solid, 0.5 g., m.p. 199-201°. Total yield of TFCEBT, 17.9 g., (75%).

An analytical sample, m.p. 201-202°, was prepared by dissolving a sample, m.p. 198-201°, in 0.1N sodium hydroxide, filtering and reprecipitating with conc. hydrochloric acid.

	<u>% C</u>	<u>% H</u>	<u>% F</u>	<u>% N</u>	<u>% S</u>
Calc'd for C ₁₀ H ₅ F ₄ NSO ₂ :	43.02	1.81	27.23	5.02	11.46
Found:	43.17	1.89	27.45	5.04	11.47

13. Preparation of the Silver Salts of TFCEB and TFCEBT

Treating the sodium salt solutions of TFCEB and TFCEBT with silver nitrate solution caused the initial precipitation of the silver salts in about 80-85% yield. Concentration of the solutions gave additional silver salt.

14. 2,3,3,-Trifluoro-3-bromo-2-chloropropionic Acid

a. Ozonization of 3,4,4,-Trifluoro-4-bromo-3-Chlorobutene-1

The olefin, 40 g. (0.179 mole) was dissolved in 360 ml. of methylene chloride, cooled to -78° and ozone (0.0021 mole/min.) passed through until a blue color was obtained (96 minutes). The calculated time for the theoretical uptake of ozone was 86 minutes. A stream of air was passed through the mixture for 5 minutes to remove the excess ozone. Then the cold reaction mixture was poured into a solution of 60 ml. of 30% hydrogen peroxide in 60 ml. of distilled water, and allow to slowly come to room temperature. After boiling off the methylene chloride, (Dean-Stark trap) an exotherm was noted. The reaction mixture was then refluxed for several hours until only a faint positive test for active oxygen was noted, and the solution indicated considerable acidity. The solution was cooled and subjected to liquid/liquid extraction for several days with ether. After drying, the ether was removed by distillation through a 12 inch Vigreux column. Anhydrous sodium bicarbonate, 18 g., was added over a period of time (evolution of CO_2) to the residue and allowed to stand overnight. The liquid phase of the solid-liquid mixture had a pH 8. Then 200 ml. of dry ether was added to the mixture and the undissolved solid was filtered and washed with three 25 ml. portion of dry ether. Eleven grams of undissolved solid was recovered. The clear ether solution was carefully distilled through a 12 inch Vigreux column, and, after removal of most of the ether, about 20 ml. of a fraction, b.p. about $50^{\circ}/60$ mm., was obtained. Then the residue was heated to $120^{\circ}/0.25$ mm. for 4 hours to remove all liquid volatiles. Dry ether, 200 ml. was added to the tan-brown solid, 16.67 g., which remained. Most of the solid dissolved. A residue, 1.85 g. was filtered off and washed thoroughly with dry ether. Under anhydrous conditions dry HCl gas was passed through the light brown ether filtrate (about 260 ml.) causing the precipitation of sodium chloride. After the removal of the sodium chloride, ~ 3.5 g., the ether solvent and excess HCl were carefully removed by distillation through a 12 inch Vigreux column. The residue was distilled at a pressure of 3-4 mm. to give the following fractions:

- | | |
|------------------------------------|---------------------------------------|
| (i) 0.88 g., b.p. $45-61^{\circ}$ | (iii-v) 7.68 g., b.p. $69-70^{\circ}$ |
| (ii) 3.06 g., b.p. $61-69^{\circ}$ | (vi-vii) 1.0 g., forced over. |

A gas phase chromatography study of fractions i, ii, and iii all showed essentially one absorption and a trace of impurity.

Redistillation of fractions i, ii, iii, 6.5 g., gave 4.62 g. (four cuts) b.p. $69^{\circ}/3.0-3.5$ mm. The neutralization equivalent found was 244; calc'd for the title acid, 241.5. The elemental analysis for this compound, however, was very poor. The data is listed below.

	<u>%C</u>	<u>%H</u>
Calc'd for $\text{C}_3\text{H}_1\text{F}_3\text{BrClO}_2$:	14.92	0.42
Found:	18.29	1.24

b. Aqueous Permanganate Oxidation of 3,4,4-trifluoro-4-bromo-3-chlorobutene-1

This reaction was carried out according to the procedure of La Zerte, et al,¹⁵ for the preparation of 2,3,3-trifluoro-2,3-dichloropropionic acid (CF₂ClCFC1COOH) from 3,4,4-trifluoro-3,4-dichlorobutene-1.

The olefin, 3,4,4-trifluoro-4-bromo-3-chlorobutene-1, 25 g. (0.112 mole) was added with stirring to a 15% aqueous solution of KMnO₄ containing 60 g. of the oxidant, the temperature being maintained at 60-65° during the addition. Then the reaction mixture was stirred for several hours and allowed to stand overnight. The mixture was cooled to -2° and 111 ml. of a 10% H₂SO₄ solution was added. With cooling bath removed, SO₂ gas was bubbled through to remove any excess of KMnO₄. The reaction mixture was extracted for several days with ether in a liquid/liquid extractor. After drying, the ether solvent was removed at atmospheric pressure by distillation through a 10 inch Vigreux column, and the residue was subjected to vacuum distillation. The infrared spectrum of the fraction, b.p. 78-82°/14 mm., 8.3 g., was almost identical to the spectrum of the product obtained in the ozonization of the starting olefin. Also the gas phase chromatogram of this fraction showed one major peak, and two minor ones. The retention time of this major constituent was identical with that of the product obtained from the ozonization reaction

15. 2-(1,2,2-Trifluoro-2-bromo-1-chloroethyl)benzimidazole

On the assumption that the product obtained from the ozonization (above) is the desired 2,3,3-trifluoro-3-bromo-2-chloropropionic acid, 2.0 g. of the acid and 1.5 g. of ortho-phenylenediamine dihydrochloride in 4N hydrochloric acid solution were refluxed for 66 hours with stirring. The red-black solution was poured into a beaker, and a small amount of heavy black, insoluble oil was noted. The main solution was decanted from this oil, which was then triturated and washed with water causing solidification to a grey-green solid. Filtration and washing of this solid with water gave 49 mg. of crude solid, m.p. 200-216°. Sublimation at 90-100° and 0.2 mm. gave a white solid, 32 mg., m.p. 243-245°. The infrared spectrum indicated a benzimidazole structure. Also a strong C-F absorption was noted at 8.75 μ . A resublimed sample was submitted for analyses.

	% C	% H	% N
Calc'd for C ₉ H ₅ N ₃ F ₃ ClBr:	34.47	1.61	8.93
Found:	34.29	1.74	8.68

E. Conclusion

The major problem in the preparation of fluorocarbon polymers with pendant heterocyclic groups has been the synthesis of the perfluorovinyl heterocycle monomers. Our work now indicates the benzazole derivatives of the perfluoro-acids to be promising intermediates. In addition to the study of the pyrolyses of the sodium salts of these acids, attempts to convert the silver salts to iodides by the Hunsdiecker reaction will be made. Such iodo compounds may lend themselves to dehalogenation with zinc under mild conditions. Finally, if benzazole intermediates utilizing the acid, 2,3,3-trifluoro-3-bromo-2-chloropropionic acid, can be prepared in reasonable yields, the compounds obtained should prove convenient for the con-

version to the 2-(trifluorovinyl)benzazoles.

Other thermally stable heterocycles are to be studied for incorporation in the polymers. These include the pyridyl, carbazolyl, thiazolyl and imidazolyl groups as possible attachments to the perfluorovinyl group.

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