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WADC TECHNICAL REPORT 55-221

PART VII

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FLUORINE-CONTAINING CONDENSATION POLYMERS AND RESINS

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Arthur M. Teller

Hooker Chemical Corporation

MARCH 1961

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WRIGHT AIR DEVELOPMENT DIVISION

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HOOKER CHEMICAL CORPORATION, New York, New York, FLUORINE CONTAINING CONDENSATION POLYMERS AND RESINS by D. Knutson, J. J. Kolano, R. N. Deleo, and A. M. Teller, March 1961. 37 p. incl. tables, 21 refs. (Project 7340; Task 73404) (WADC TR 55-221 Pt VII) (Contract AF 33(616)-5548) Unclassified Report Polyesters have been synthesized from fluorinated glycols and the corresponding hydrocarbon glycols. Some polyesters were prepared from fluorinated acids. Laminates prepared from these polyesters have been aged at elevated temperatures and their physical properties measured before and after aging. In general, the fluorinated glycol polyester laminates exhibit much better retention of (over)	UNCLASSIFIED	UNCLASSIFIED
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PART VII

FLUORINE-CONTAINING CONDENSATION POLYMERS AND RESINS

David Knutson
John J. Kolano
Rudolph N. Deleo
Arthur M. Teller

Hooker Chemical Corporation

MARCH 1961

Materials Central
Contract No. AF 33(616)-5548
Project No. 7340

WRIGHT AIR DEVELOPMENT DIVISION
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

FOREWORD

This report was prepared by the Hooker Chemical Corporation under USAF Contract No. AF 33(616)-5548. This contract 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 Materials Central, Directorate of Advanced Systems Technology, Wright Air Development Division, with Dr. G. F. L. Ehlers acting as project engineer.

This report covers work conducted from 1 February 1960 to January 1961.

The personnel of the Hooker Chemical Corporation assigned to the project were Dr. D. Knutson, Dr. J. J. Kolano, Research Investigators; Mr. R. N. Deleo, Mr. A. M. Teller, Technicians.

The appendix was prepared by the Department of Chemistry, Purdue University, on the continuation of work concerned with the investigation and development of new fluorine-containing monomers suitable for condensation-type polymers. This work was performed on a subcontract with the Hooker Chemical Corporation as part of Contract No. AF 33(616)-5548.

Personnel assigned to this project were Y. R. Dhingra and A. E. Martin, working under direct supervision of Professor E. T. McBee. Assistance was provided by Dr. H. P. Braendlin.

ABSTRACT

The two principal objectives of this research are to determine the effect of fluorine and fluorine content on the thermal and oxidative stability of polyester laminating resins; and to investigate the preparation of polymers from perfluoroglutaronitrile, perfluoroadiponitrile, perfluoroglutarimidine, and perfluoroadipamidine.

Polyesters have been synthesized from fluorinated glycols and the corresponding hydrocarbon glycols. Some polyesters were prepared from fluorinated acids. Laminates prepared from these polyesters have been aged at elevated temperatures and their physical properties measured before and after aging. In general, the fluorinated glycol polyester laminates exhibit much better retention of physical properties than their hydrocarbon analogs.

The report contains a description of synthetic work directed toward the synthesis of fluorine-containing compounds useful in polyester resin laminate preparation.

The preparation of laminates from perfluoroglutarimidine and perfluoroadipamidine is described. These laminates have low initial strength, but show good retention of strength and low weight losses on high temperature aging.

Research on the synthesis of certain novel or unusual fluorine-containing intermediates considered desirable for use on this project was performed at Purdue University under subcontract to Hooker Chemical Corporation. Details of this work are contained in the Appendix of this report.

PUBLICATION REVIEW

This report has been reviewed and is approved

FOR THE COMMANDER



A. M. LOVELACE

Chief, Polymer Branch
Nonmetallic Materials Laboratory
Materials Central

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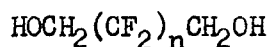
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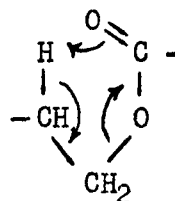
I. INTRODUCTION

The research being conducted by the Hooker Chemical Corporation under contract with the Materials Laboratory, Wright Air Development Division has two objectives. The first is to prepare fluorine-containing polyester resin laminates and to determine their thermal and oxidative stability; the second is to prepare polymers from perfluoronitriles or perfluoroamidines.

The resistance to thermal degradation of fluorine-containing addition polymers (polytetrafluoroethylene, polychlorotrifluoroethylene, etc.) has been amply demonstrated. It was felt that fluorinated polyesters might exhibit greater thermal stability than their hydrocarbon analogs. For one thing, polyesters prepared from $\alpha, \alpha, \omega, \omega$ -tetrahydroperfluoroalcohols (I) would contain no β -hydrogen atoms and therefore be unable to undergo normal ester



I



II

pyrolysis which takes place via the cyclic transition state (II). Further, the presence of fluorine in other portions of the polyester laminating resin (the acid segment and the cross-linking monomer) should also increase thermal stability.

The novel perfluoroamidine polymers prepared by Prof. Henry C. Brown possess excellent thermal stability. This has led to efforts to develop methods of polymerizing perfluoroglutaronitrile, perfluoroglutarimidine and perfluoroadipamidine, with particular emphasis being placed on determining suitable methods by which laminates may be prepared from these materials.

Research on the synthesis of fluorine-containing intermediates desirable for polymerization in this project has been performed by the Purdue Research Foundation under sub-contract to Hooker Chemical Corporation. Details of this work performed at Purdue during the contract year are contained in the Appendix of this report. The following is a list of work done at Purdue.

- - - - -
Manuscript released by authors February 1961 for publication as a WADD Technical Report.

1. The reaction between 3,3,4,4,5,5-hexafluoro-1,7-diiodoheptane and potassium cyanide, gave a number of unidentified products.
2. The reaction between 2,2,3,3,4,4-hexafluoropentane-1,5-ditosylate and potassium cyanide gave a very small quantity of a product which could not be characterized.
3. Several attempts to make the Grignard reagent of 3,3,4,4,5,5-hexafluoro-1,7-diiodoheptane under various conditions failed.
4. Samples of 4,4,5,5,6,6-hexafluoro-1,9-nonanediol and the corresponding hexafluoroazelaic acid were prepared.
5. A quantity of acetylene dicarboxylic acid was prepared in 70% yield.
6. Several attempts to obtain trifluorobutyne carboxylic acid by the treatment of acetylene dicarboxylic acid with sulfur tetrafluoride resulted in a large number of unidentified products.
7. Friedel-Crafts trifluoroacetylation of p-xylene gave a mixture (A) of p- and m-xylyl trifluoromethyl ketone in 64:36 ratio.
8. Treatment of mixture (A) with sulfur tetrafluoride gave the corresponding mixture (B) of isomeric pentafluoroethylxylenes in 98% yield.
9. Chromic acid oxidation of (B) gave an acid which analyzed for pentafluoroethylmethylbenzoic acid (C).
10. Neutral permanganate oxidation of (B) gave an acid (D), the amide derivative of which analyzed for a diacid amide.
11. The Friedel-Crafts trifluoroacetylation of m-xylene gave a product in 77% yield which was characterized as 2,4-dimethyltrifluoroacetophenone (E).
12. Treatment of (E) with sulfur tetrafluoride gave 2,4-dimethylpentafluoroethyl benzene (F), in 90% yield.
13. Neutral permanganate oxidation of (F) gave the corresponding diacid (G) in 68% yield.
14. Chromic acid oxidation of (F) gave a monoacid (H).
15. Friedel-Crafts trifluoroacetylation of o-xylene gave a mixture (I) of two isomeric ketones in 60% yield.

16. An attempted trifluoroacetylation of p-xylene with ferric chloride instead of aluminum chloride failed.
17. By varying the order of reagent addition in the Friedel-Crafts trifluoroacetylation of p- and o-xylenes isomerization could be suppressed and the pure ketones were obtained in 74% and 60% yield, respectively.
18. Pyromellitic anhydride was prepared in 91% yield.
19. The diimide of pyromellitic acid was prepared in 80.4% yield.
20. Pyromellitimide was reacted with sulfur tetrafluoride.
21. Dinitrodurene was prepared in 70% yield.
22. Dibromodurene was prepared in 84.4% yield.
23. n-Butyl lithium was reacted with 3,5-dibromobenzotrifluoride.
24. n-Butyl lithium was reacted with p-bis-(trifluoromethyl)benzene in n-butyl ether as solvent.
25. Perfluorobutyryl chloride was prepared in 72.2% yield.
26. Perfluorobutyryl chloride was reacted with p-xylene and aluminum chloride. The conditions used were too vigorous for a controlled reaction.

II. DISCUSSION

A. Fluorine-Containing Unsaturated Polyester Resins

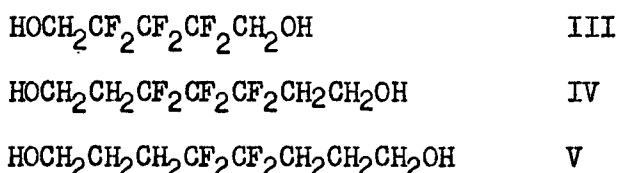
The purpose of this investigation is to determine how the substitution of fluorine for hydrogen effects the thermal and oxidative stability of polyester resin laminates. This has been accomplished by comparing laminates prepared from polyesters synthesized from fluorine-containing glycols or acids with laminates prepared from analogous hydrocarbon glycols or acids. The methods of polyester synthesis and the laminating and testing procedures has been previously described.¹

Most of the fluorinated polyesters prepared thus far^{1,2} have contained fluorine in the glycol portion of the molecule. With fumarate (and 33 mole percent isophthalate to reduce the crystallinity and the softening point) as the acid portion, polyesters have been prepared from difluoropropanediol, tetrafluorobutanediol, hexafluoropentenediol, and octafluorohexanediol. From these polyesters, and their hydrocarbon analogs, a considerable number of laminates were fabricated with various high temperature cross-linking monomers, including diallyl isophthalate, diallyl terephthalate, diallyl nadate, triallyl cyanurate and maleimide.² In general, the fluorine-containing resin laminates exhibited much better retention of their physical properties after high temperature aging than did their hydrocarbon counterparts. This was the case when the laminates were aged at 500°F or 600°F or when the specimens were tested at room temperature or at 500°F with all cross-linking systems save one.

When cross-linking agent consisted of mixtures of maleimide and triallyl cyanurate, the difference in performance (room temperature flexural strength after aging at 500°F) of the fluorinated and the hydrocarbon laminates became small. To determine whether or not there is a greater difference between the fluorine-containing and the hydrocarbon laminates at elevated temperatures, a series of laminates were prepared using mixtures of maleimide and triallyl cyanurate. These laminates were aged at 260°C (500°F) and tested at 260°C. The comparisons, are listed in Table I. The laminate prepared from an hexafluoropentenediol polyester cross-linked with maleimide (113A) showed excellent retention of high temperature strength, but unfortunately the corresponding hydrocarbon laminates (112A and 114A) both blistered on aging so that a comparison was impossible. The room temperature flexural strengths of pentenediol-maleimide-triallyl cyanurate laminates (99A and 100A) showed the normal decrease on aging, but the high temperature flexural strengths (laminates 120A and 121A) passed through a minimum at 8 to 25 hours. In order to confirm this anomolous behavior and also to determine the aging characteristics beyond 100 hours, Laminates 130 and 131 were prepared. The high temperature

flexural strengths of laminates 130 and 131 also exhibit a minimum at 8 to 25 hours, followed by a maximum at 100 to 150 hours, after which the strength again decreases. Thus the specimens appear to become weaker, then stronger, and finally weaker again. This type of behavior does not occur with room temperature testing nor with other cross-linking systems. At the present time, no adequate explanation for this phenomenon is apparent.

Samples of 3,3,4,4,5,5-hexafluoroheptanediol (IV) and 4,4,5,5,6,6-hexafluorononanediol (V) were obtained from Purdue University. These glycols were polyesterified and the resulting resins laminated. It was hoped that by comparing these laminates with those prepared from 2,2,3,3,4,4-hexafluoropentanediol (III) some information concerning the effect of the insertion of methylene segments between the hydroxyl group and the fluorinated portion of the molecule could be obtained. From inspection of Table II (60A, 65A, 128A



and 129A) it is obvious that the introduction of even one more methylene group has a pronounced deleterious effect on the thermal stability of the laminates.

The acid portion of most of the polyesters consists of 75% fumarate and 25% isophthalate. The isophthalate segments reduce the crystallinity and the melting points of the polyesters and improve their laminating properties. In Table II are listed results obtained from laminates prepared from polyesters in which the isophthalate groups were replaced with hexafluoroglutarate segments. By comparing the laminates (60A with 124A and 125A, and 65A with 126A and 127A), it can be seen that the increase in fluorine content afforded by the perfluoroglutarate does not improve the strength of the laminates.

TABLE I
HIGH TEMPERATURE TESTING OF MALEIMIDE-TRIALLYL CYANURATE LAMINATES

Laminate Code	Polyester	Monomer	R.T. Flex. Strength	Flexural Strengths x 10 ⁻³ at 260°C (500°F) (Weight Losses % Based on Laminates)						
				0 Hrs	8 Hrs	25 Hrs	50 Hrs	100 Hrs	150 Hrs	200 Hrs
113A	HFPD-FC-IPC	MI	73.4	39.9	42.3 (0.6)	38.3 (1.8)	37.9 (3.3)	37.9 (4.7)		
119A	HFPD-FC-IPC	MI-TAC 3:1	86.6	34.9	36.3 (0.7)	32.9 (2.0)	33.1 (3.5)	29.7 (6.3)		
112A	PD-FC-IPC	MI	85.2	Blistering on Aging						
114A	PD-FC-IPC	MI	85.2	Blistering on Aging						
120A	PD-FC-IPC	MI-TAC 3:1	92.7	25.5	11.7 (2.0)	10.2 (6.8)	18.6 (8.0)	25.4 (9.6)		
121A	PD-FC-IPC	MI-TAC 1:1	85.3	17.4	11.1 (2.6)	12.7 (6.4)	20.8 (7.8)	29.2 (9.5)		
130	PD-FC-IPC	MI-TAC 3:1	55.4	18.4	13.1 (2.8)	13.0 (6.3)	16.1 (7.7)	25.2 (8.8)	21.7 (11.0)	11.6 (13.1)
131	PD-FC-IPC	MI-TAC 3:1	67.3	12.3	12.9 (3.2)	9.5 (6.8)	15.5 (8.3)	20.8 (9.2)	23.6 (10.2)	12.2 (12.6)
99A	PD-FC-IPC	MI-TAC 1:1	b	53.9	48.7 (3.0)	47.5 (6.0)	37.0 (8.1)	24.9 (10.9)		
100A	PD-FC-IPC	MI-TAC 1:1	b	68.4	65.1 (2.5)	47.0 (7.7)	43.2 (9.5)	39.6 (10.8)		

a See page 7 for code.

b Room temperature flexural strengths.

TABLE II

ROOM TEMPERATURE TESTING OF VARIOUS LAMINATES

Laminate Code	Polyester	Monomer	Room Temp. Flex. Str. x 10 ⁻³ After Aging at 260°C (Wt. Losses % Based on Laminates)				
			0 Hrs	8 Hrs	25 Hrs	50 Hrs	100 Hrs
60A	HFDP-FC-IPC	TAC	46.6	44.4 (5.1)	37.0 (11.8)	34.8 (15.4)	33.5
128A	HFHepD-FC-IPC	TAC	32.1	28.6 (4.9)	23.6 (10.0)	20.9 (13.3)	10.7 (17.4)
129A	HFND-FC-IPC	TAC	27.3	24.8 (3.3)	19.5 (7.5)	13.7 (10.5)	6.6 (13.1)
65A	PD-FC-IPC	TAC	48.2	42.3 (5.5)	27.5 (10.6)	17.8 (13.0)	10.4
124A	HFDP-FC-HFGC	TAC	30.7	-	23.0 (15.4)	19.7 (17.7)	14.5 (20.3)
125A	HFDP-FC-HFGC	TAC	30.7	-	21.6 (15.9)	19.2 (18.2)	14.4 (21.2)
126A	PD-FC-HFGC	TAC	36.9	-	11.8 (12.5)	10.2 (13.6)	6.2 (15.8)
127A	PD-FC-HFGC	TAC	39.4	-	14.5 (12.8)	11.7 (14.2)	8.0 (16.5)

Panels were made with 6 plies 181 Volan A fabric.

Catalyst

0.75% tert-butyl perbenzoate

Cure Schedule

30' at 120°C (press)
60' at 175°C (oven)
60' at 200°C (oven)
60' at 260°C (oven)

Flexural tests were conducted on specimens 1/2" x 3 1/2" x thickness with 1 1/4" span.

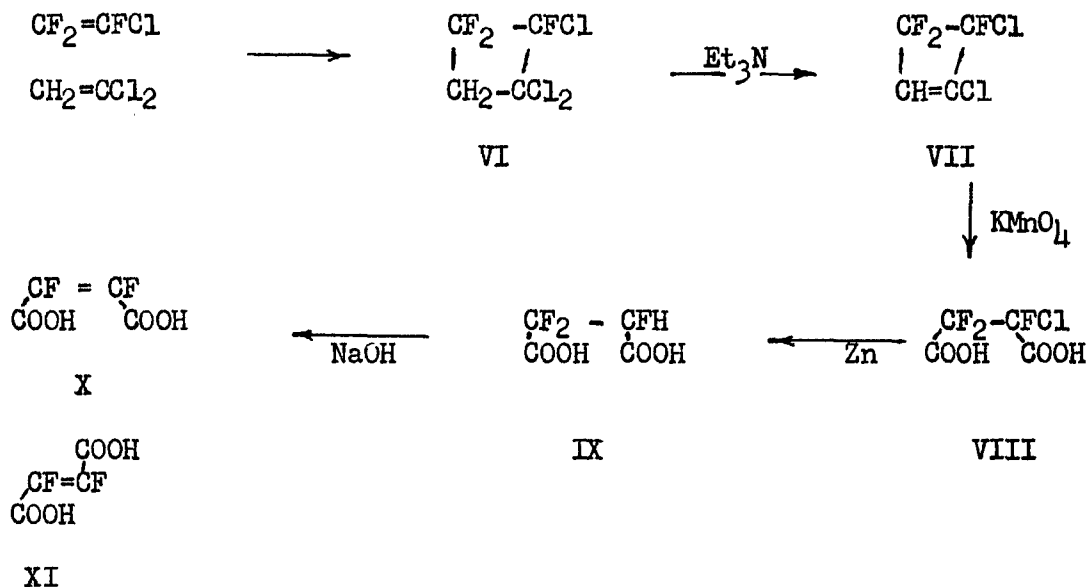
Code

HFDD 2,2,3,3,4,4-Hexafluoropentanediol
HFHepD 3,3,4,4,5,5-Hexafluoroheptanediol
HFND 4,4,5,5,6,6-Hexafluorononanediol
PD Pentanediol

FC Fumaryl Chloride
IPC Isophthaloyl Chloride
HFGC Hexafluoroglutaroyl Chloride
MI Maleimide
TAC Triallyl Cyamurate

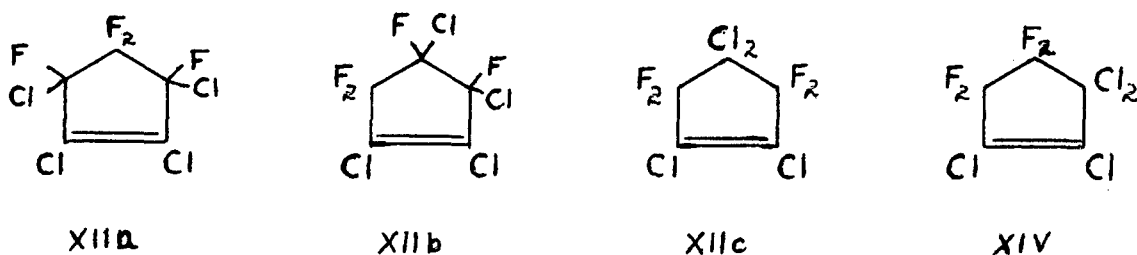
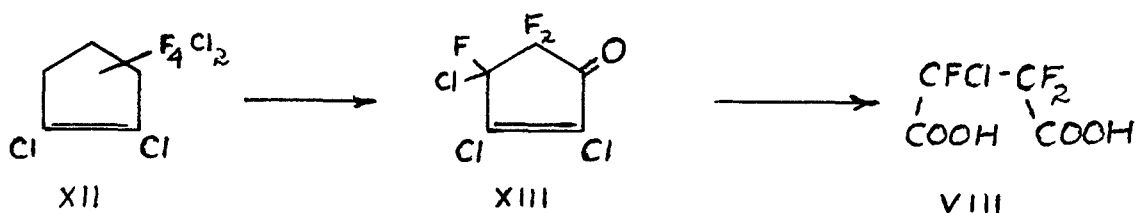
B. Intermediates

The synthesis of difluoromaleic and difluorofumaric acid was undertaken with two objectives in mind. Firstly, to examine the effect of substituting difluorofumarate for the fumarate segments in the polyesters; and secondly, since maleimide has proved to be the best cross-linking monomer for high temperature laminate preparation, it seemed desirable to investigate the properties of difluoromaleimide in this connection. In a recent article³ concerning the preparation of difluoromaleic derivatives, the copolymerization of difluoromaleic anhydride with styrene was described, which indicates that the difluoromaleic double bond can engage in polymerization reactions. The synthesis³ of difluoromaleic acid (X) and difluorofumaric acid (XI) is outlined below.



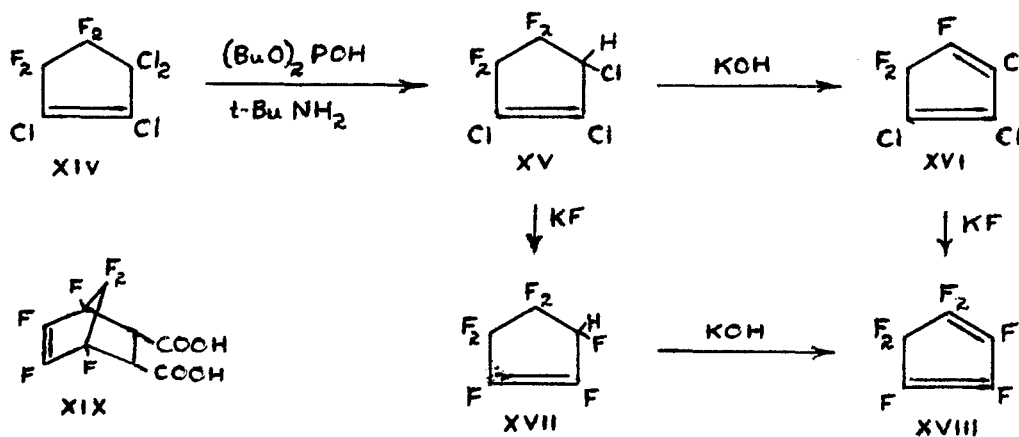
The action of base on trifluorosuccinic acid (IX) yields a mixture of X and XI which can be separated since the latter is less water soluble. Previous work^{1,4} has shown that the most satisfactory method to prepare fluorine-containing polyesters is through the acid chloride. Attempts to prepare difluorofumaryl chloride from the reaction of XI with benzotrichloride⁵ led to mixtures of the acid chloride and the anhydride. Treatment of this mixture with phthaloyl chloride and zinc chloride⁶ (a method used to convert maleic anhydride to fumaryl chloride) yielded a product that was 80% anhydride and 20% acid chloride.

Another route to chlorotrifluorosuccinic acid (VIII) was investigated.



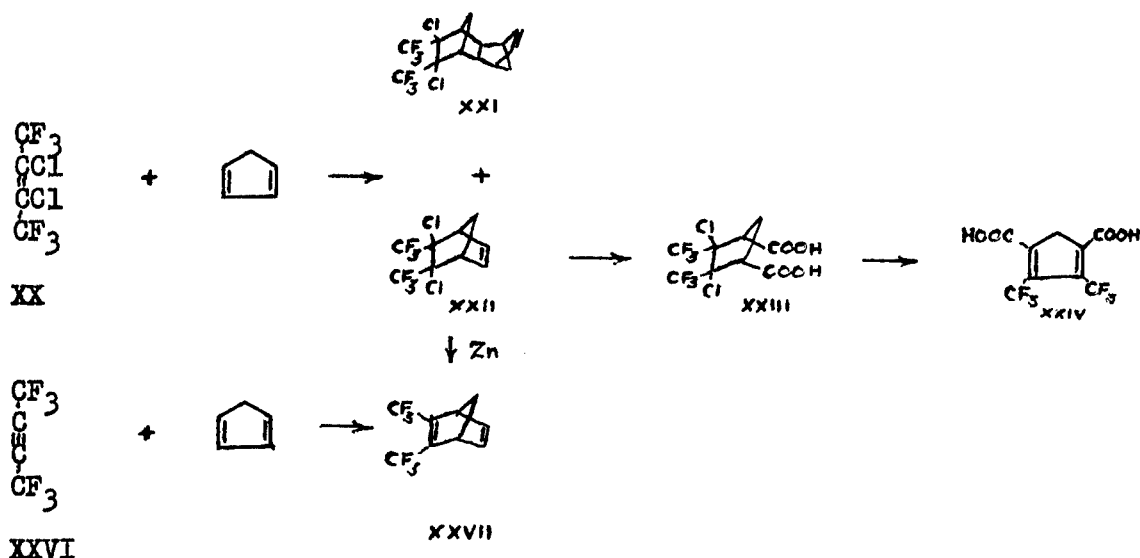
A mixture of tetrachlorotetrafluorocyclopentenes (XII and XIV) can be separated from the by-products from the fluorination of hexachlorocyclopentadiene or octachlorocyclopentene by distillation. Compound XII is freed from XIV by treatment of the mixture with concentrated sulfuric acid which converts the latter to the unsaturated ketone. The structure of XII is now known; but, since infrared spectroscopy reveals that two of the chlorine atoms are vinyl, there are only three possible structures, namely XIIa, XIIb, and XIIc. Either XIIa or XIIb could yield the desired product while isolation of the unconjugated ketone would at least establish the structure of the starting material. This approach was abandoned because the reaction of XII with chlorosulfonic acid yielded a complex mixture of products which contained little material boiling in the range expected for the ketone XIII.

Perfluorocyclopentadiene (XVIII) was desired for the preparation of the acid XIX, the fluorine analog of chlorendic acid. The following synthetic routes were investigated.



The trichlorotetrafluorocyclopentene XV was obtained in 78 per cent yield by the phosphite reduction of XIV. Since 1,2,3-trichloro-3,4,4,5,5-pentafluorocyclopentene is converted to perfluorocyclopentene on reaction with potassium fluoride in dimethyl formamide, it was expected that similar treatment of XV would yield XVII. However, the only volatile product isolated from the reaction was a trace amount of perfluorocyclopentene, probably formed from impurities of XV. Dehydrofluorination of XV with potassium hydroxide yielded a waxy solid, mp 210°, presumably a dimer of XVI. It was not possible to crack the dimer at 200°C at 5 mm pressure.

The addition of 2,3-dichlorohexafluorobutene-2 (XX) to butadiene, 2,3-dimethylbutadiene, and cyclopentadiene has been reported by Tarrant.⁷ The reaction was re-investigated with the hope that the adduct, XXII, could be oxidized, and



subsequently dehydrochlorinated to yield the cyclopentadienedioic acid, XXIV. It was felt that by comparing the cis-trans ratio of the starting butene, XX, with that of the unreacted material recovered from the reaction, some insight concerning the stereochemistry of the adduct, XXII, might be gained. From the following data it appears that the trans-butene adds more readily than the cis-butene.

TABLE III

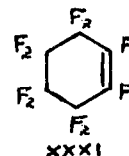
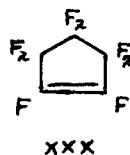
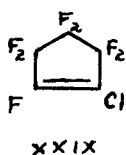
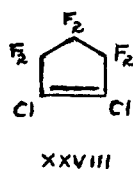
cis-trans CONTENT OF 2,3-DICHLOROHEXAFLUOROBUTENE-2

	Mole Percent	
	<u>cis</u>	<u>trans</u>
Starting Butene	43	56
Butene Recovered from Reaction at 155°C	69.5	30
Butene Recovered from Reaction at 205°C	83.5	15.6
Attempted Isomerization of the Butene at 200°C for 92 Hours	43	56.9

The addition of XX to cyclopentadiene at 200°C for 24 to 90 hours produces the adduct, XXII, in good yield. Other products are formed but only one, a compound analyzing for $C_{11}H_{12}Cl_2F_6$, was isolated. This compound probably has the structure, XXI.

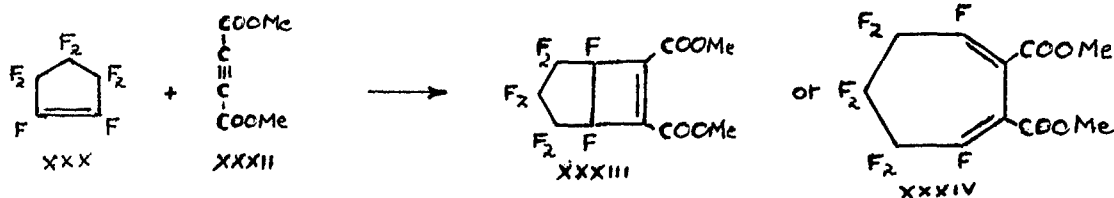
Attempts to oxidize the adduct, XXII, have met with little success. The use of sodium permanganate⁸, potassium permanganate, or 50% nitric acid⁹ causes considerable destruction of the molecule and leads to the isolation of small amounts of oily neutral and acidic material. It is possible that the first oxidation product, XXIII, suffers dehydrochlorination and further oxidation that results in complete fragmentation of the molecule. The adduct, XXII, was dechlorinated with zinc dust in refluxing glacial acetic acid to yield a compound tentatively assigned the bicycloheptadiene structure, XXVII. This same compound was also obtained by the addition of hexafluorobutyne (XXVI) to cyclopentadiene.

1,2-Dichlorohexafluorocyclopentene (XXVIII), a compound in which the chlorine atoms are of geometrical necessity cis, does not add to cyclopentadiene. It is of interest to recall that trans-2,3-dichlorohexafluorobutene-2 added more readily than the cis isomer. 1-Chloroheptafluorocyclopentene (XXIX), perfluorocyclopentene (XXX), and perfluorocyclohexene (XXXI)



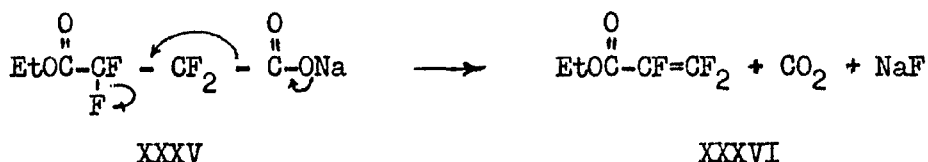
all add to cyclopentadiene. Solid compounds isolated from the addition of XXX and XXXI to cyclopentadiene analyzed for 1 to 2 adducts, presumably similar in structure to XXI.

Perfluorocyclopentene (XXX) also formed an adduct with dimethyl acetylenedicarboxylate (XXXII) in very low yield. The adduct exhibits strong infrared



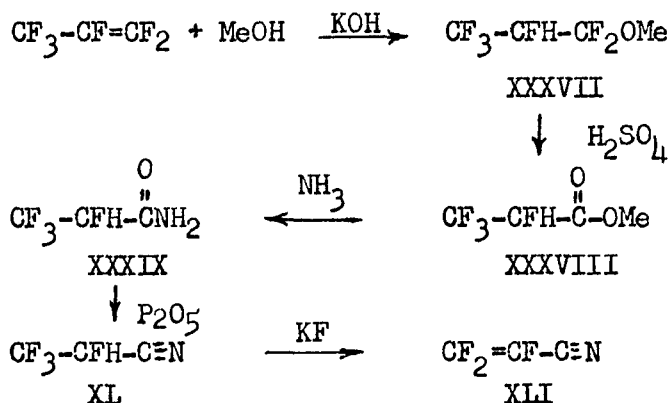
absorption bands at 5.75μ (ester carbonyl) and in the double bond region; it also shows a strong maximum at $277\text{ m}\mu$ in the ultraviolet with an extinction coefficient of $\sim 20,000$. The compound may have the structure XXXIII or its ring opening product XXXIV.

Several attempts were made to prepare perfluoroacrylic derivatives. The pyrolysis of the alkali metal salt of a perfluorocarboxylic acid yields a terminal olefin, carbon dioxide and the alkali metal fluoride.¹⁰ It was hoped that the pyrolysis of the sodium salt of the half ester of perfluorosuccinic acid (XXXV) would yield ethyl perfluoroacrylate (XXXVI). Perfluorosuccinic acid was dehydrated to the anhydride in 92% yield by dry distillation



from phosphorus pentoxide. Perfluorosuccinic anhydride was added to anhydrous ethanol containing one equivalent of sodium ethoxide. The excess ethanol was removed under vacuum and the resulting salt was pyrolyzed. Diethyl perfluorosuccinate and ethanol were the only organic products isolated. Preparation of the ester salt by neutralization of the half ester is not feasible since the half ester hydrolyzes extremely fast. Pyrolysis of the solid obtained from the reaction of the half ester with sodium hydroxide in ethyleneglycol dimethyl ether also yielded diethyl perfluorosuccinate.

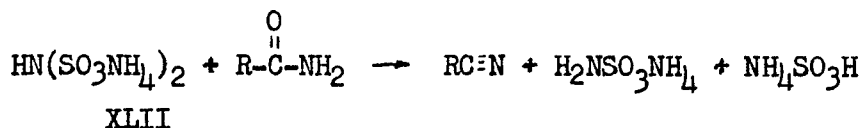
The synthesis^{11,12} of perfluoroacrylonitrile (XLI) outlined below:



Three attempts to dehydrofluorinate the trifluoropropionitrile, XL, over potassium fluoride at 500°C and 600°C did not yield perfluoroacrylonitrile (XLI).

C. Perfluorinated Nitriles and Amidines

In the synthesis of perfluoroglutarimidine the low yield step is the dehydration of the diamide to the dinitrile. Under the best conditions yet devised (dehydration of the amide with benzotrichloride), the optimum yield is about 60 percent. Therefore, the search for a better nitrile synthesis is a continuing one. A recent patent¹³ reports the dehydration of benzamide and butyramide with diammonium imidodisulfonate (XLII) in yields exceeding 90 percent. Diammonium imidodisulfonate (XLII) was prepared by heating ammonium sulfamide. Though XLII



did convert benzamide to benzonitrile, no perfluoroglutaronitrile was obtained when XLII was heated with perfluoroglutaramide. As might be expected, the heating of the imidodisulfonate produces considerable ammonia. This might explain the failure to isolate perfluoroglutaronitrile, since the compound readily reacts with ammonia.

Polymers prepared from perfluoroglutarimidine and perfluorobutyramidine appear to have excellent high temperature properties.^{14,15} One objective of this research is to investigate the polymerization of perfluoroglutarimidine and perfluoroglutaronitrile. Particular emphasis is being placed on determining suitable conditions under which these materials may be molded or laminated to give rigid materials which might have unusual thermal stability.

Glass cloth laminates were prepared from perfluoroglutarimidine by three methods. In the first method, the imidine was spread between layers of glass cloth and pressed at 200°C. The second method was similar to the first except a prepolymer was prepared by briefly heating the imidine at 200°C. The prepolymer was pulverized and laminated. The third method involved passing the glass cloth through a solution of the imidine in acetone, removing the solvent in a vacuum oven, and pressing at 200°C. The third method seems to be the best, but none of the methods gave satisfactory laminates, perhaps due to some of the difficulties listed below. At temperatures significantly below 200°C, the rate of polymerization is slow, but at temperatures much above its melting point (160°C) the imidine sublimes at a great rate. If a prepolymer is used, the fluid stage has such a brief

existence that the cloth is not impregnated. Even when the imidine is used, the fluid stage in the polymerization is of very short duration. This rapid solidification immobilizes the growing polymer resulting in low molecular weights which are reflected in the brittleness and relative weakness of the laminates. The polymer has little tendency to wet the glass, perhaps because of the large number of $-CF_2$ -groups. Another problem is moisture. It has been reported¹⁶ that the imidine is very sensitive to moisture in the air. Though previous studies performed in this laboratory on ammonia evolution during polymerization of the imidine did not reveal this extreme sensitivity, moisture is no doubt a factor to be considered. Tables IV, V and VI contain high temperature aging data on perfluoroglutarimidine and perfluoroadipamidine laminates. It can be seen that weight losses are relatively low and that the retention of strength is good, but the original strengths are low. It would appear that if laminates could be prepared with higher initial flexural strengths, they would have good high temperature properties.

TABLE IV

HEAT AGING OF PERFLUOROGLUTARIMIDINE LAMINATES (392°-600°F)

<u>Laminate</u>	<u>Room Temp. Flex. Strengths (% wt. loss based on laminates)</u>				
	<u>0 Hrs</u>	<u>2 Hrs 392°F</u>	<u>+ 10 Hrs 392°F</u>	<u>+ 24 Hrs 500°F</u>	<u>+ 24 Hrs 600°F</u>
4	17,500 8,700 12,500	(0.26)	(0.34)	(0.75)	15,800 (2.3)
5	15,700 14,300	(0.46)	(0.60)	(1.35)	18,100 (3.4)
6	14,200 16,500	(0.45)	(0.55)	(1.0)	16,600 (3.2)
7	16,400 11,000	(0.43)	(0.54)	(1.1)	15,100 (3.2)
8		(0.63)	17,100 (0.81)		
9		(0.94)	9,500 (1.1)		
10		(1.2)	(1.4)	15,500 (3.8)	
11		(0.58)	(0.79)	12,300	

TABLE V

HEAT AGING OF PERFLUOROGLUTARIMIDINE LAMINATES (600°-700°F)

Laminate	Room Temp. Flex. Strength (% wt. loss based on laminates)							
	0 Hrs	600°F			700°F			
		24 Hrs	48 Hrs	120 Hrs	1 Hr	2 Hrs	4 Hrs	6 Hrs
13 ^a *	18,500	(9.4)	6,500 (11.6)	6,600 (15.9)	(10.1)	(11.0)	(14.6)	5,900 (16.7)
14 ^b	13,700	(4.4)	13,300 (5.6)	8,600 (8.1)	(4.4)	(5.3)	(6.6)	4,700 (7.8)
15 ^b	10,700	(3.0)	13,000 (3.5)	9,300 (5.5)	(2.7)	(3.7)	(4.1)	6,400 (4.8)

- - - - -
^a Laminate 13 prepared by slowly increasing the temperature from 160-200°C in press.

^b Prepared with Teflon sheeting used to prevent laminate from sticking to chrome plated platens.

* Laminates have resin content of 28%.

TABLE VI

AGING AND TESTING OF PERFLUOROADIPAMIDINE LAMINATES

Laminate	Room Temp. Flex. Str. x 10 ³ (% wt. losses based on laminates)				
	0 Hrs	700°F		800°F	
		3 Hrs*	6 Hrs	1 Hr	
16	23.5	15.9 (11.2)	15.8 (13.4)	12.5 (17.1)	
17	22.9	13.0 (11.6)	12.6 (13.8)	9.6 (17.7)	

- - - - -
 * After post-curing 2 hours at 500°F and 1 hour at 600°F.

Polymerization of perfluoroglutaronitrile would eliminate the necessity of preparing the imidine. Perfluoroglutaronitrile has been thermally polymerized at 300-330°C. The resulting yellow, insoluble polymer softens and darkens at about 350°C but does not melt below 400°C. In an attempt to prepare a prepolymer, perfluoroglutaronitrile was added to an ether suspension of powdered potassium hydroxide. An ether soluble, low melting solid was obtained; however, this material could not be further polymerized by thermal means.

III. EXPERIMENTAL

A. Intermediates

Difluorofumaric Acid (XI). Difluorofumaric acid was prepared by the method of Raasch et. al.³ and had m.p. 268-270°C.

Difluorofumaryl Chloride. Difluorofumaric acid was prepared by the method of Raasch et. al.¹ A mixture of difluorofumaric acid (4.0 g., 0.026 moles) and benzotrichloride⁴ (8 cc.) was heated at reflux for 5 hrs. and then distilled at atmospheric pressure to yield 3.11 g. (62.5%) material b.p. 123-60°C. The product was redistilled yielding 2.64 g. liquid b.p. 118-126°C, n_D^{26} 1.4290. The infrared spectrum had peaks at 5.35, 5.5, and 5.65 suggesting the presence of anhydride. The above product (2.6 g.), phthaloyl chloride (7 cc.) and a few crystals of zinc chloride were heated at reflux overnight. The product was separated into three fractions by distillation. The center cut, 0.96 g. had b.p. 108-116, n_D^{25} 1.4253. The infrared spectrum again indicated anhydride contamination. The material analyzed 14.1% acid chloride and 83.2% anhydride.

Reaction of "Symmetrical" Tetrachlorotetrafluorocyclopentene (XII) with Chlorosulfonic Acid. A mixture of 27.8 g. (0.1 mole) XII and 75 ml. chlorosulfonic acid was allowed to stand 65 hours at room temperature, poured on crushed ice, and extracted with methylene chloride. Removal of the solvent and distillation yielded starting material. From a similar experiment that was run at reflux for 18 hrs. there was isolated 15.8 g. material that yielded two crystalline ketonic products, m.p. 121.5-122°C and 62.5-64°C. The 122° material showed $C=O$, 5.62 μ and λ_{max} 212 and 237 $m\mu$; the 64° compound two $C=O$, 5.6 and 5.71 μ and λ_{max} 207 and 306 $m\mu$. The melting points and spectral data are not compatible with the desired 2,3,4-trichloro-4,5,5-trifluorocyclopentenone, XIII.

1,2,3-Trichloro-4,4,5,5-tetrafluorocyclopentene (XV). To a solution of 1,2,3,3-tetrachloro-4,4,5,5-tetrafluorocyclopentene (278 g., 1.0 mole), t-butyl amine (146 g., 2.0 moles), and 1000 ml. methylene chloride was added dibutyl phosphite (194 g., 1.0 moles) according to the method previously described.² The crude product (190 g., 78%) was fractionated through a four foot, glass helices packed column to yield 105 g. material b.p. 143.5-144.2°C, n_D^{25} 1.4288-1.4291. Anal. calc. for $C_5HCl_3F_4$: Cl = 43.7%. Found: Cl = 44.1%. Vapor phase chromatography indicated 94% purity.

Fluorination of 1,2,3-Trichloro-4,4,5,5-tetrafluorocyclopentene (XV). A dry 500 ml. 3-necked flask was equipped with stirrer, thermometer, and a condenser connected to a dry ice trap. In the flask were placed 200 ml. dimethyl formamide, XV (24.3 g., 0.1 mole), and dry potassium fluoride (71 g., 1.2 moles).

The mixture was stirred at reflux 20 hours. Distillation yielded no material boiling below 140°C. The dry ice trap contained a small amount (1 g.) of material that was identified as perfluorocyclopentene by its infrared spectrum.

Adduct (XXII) of 2,3-Dichlorohexafluorobutene-2 (XX) and Cyclopentadiene. A Pyrex tube 19 x 25 x 700 mm was charged with XX (46.6 g., 0.2 mole, 43% cis, 56% trans), cyclopentadiene (13.2 g., 0.2 mole) and hydroquinone (0.3 g.). The tube was heated 15 hrs. at 135°C., then 8 hrs. at 155°C. The tube was cooled and opened. No acidic vapors were detectable with ammonia vapor. The unreacted starting materials were removed by distillation, 29.6 g. Vapor phase chromatography indicated that recovered XX was 69.5% cis and 30% trans. Filtration of the pot contents yielded 10.5 g. (17.5%) crystalline material.

A similar tube heated 15 hrs. at 170°C, then 15 hrs. at 205°C yielded 36 g. (60%) adduct. The recovered XX was 83.5% cis and 15.6% trans. Four tubes heated at 195° for 90 hrs. produced 202.5 g. (84%) adduct. After three recrystallization from methanol followed by sublimation, the adduct melts 172-174°C (sealed capillary). Lit⁵ m.p. 156-157°C.

A 1 to 2 adduct from the addition of 2,3-dichlorohexafluorobutene to cyclopentadiene was isolated from the mother-liquors from recrystallization of the 1 to 1 adduct. This compound melted 95-97°C. (sealed capillary). Analysis: Calc. for $C_{11}H_{12}Cl_2F_6$: C, 46.05%; H, 3.31%; Cl, 19.42%. Found: C, 45.92%; H, 3.25%; Cl, 19.51.

Attempted Addition of 1,2-dichlorohexafluorocyclopentene (XXVIII) to Cyclopentadiene. A tube was charged with XXVIII (49 g., 0.2 moles), cyclopentadiene (13.2 g., 0.2 mole) and hydroquinone (0.3 g.), sealed and heated at 135°C for 15 hrs. then at 155° for 8 hrs. Chromatography of the pot residue after distillation to recover the starting materials yielded 2 g. crystalline material. Recrystallization from ethanol, followed by sublimation gave white, waxy crystals m.p. 63.5-65.5°C (sealed capillary). The infrared spectrum shows no C-F bands. The product was probably tri-cyclopentadiene, m.p. 68°C. No adduct could be isolated from reactions run at 205° or at 300°C.

Adduct of Perfluorocyclopentene (XXX) and Cyclopentadiene. A Pyrex tube 19 x 25 x 700 mm was charged with perfluorocyclopentene (17.4 g., 0.1 mole), cyclopentadiene (6.6 g., 0.1 mole) and 0.3 g. hydroquinone. The tube was heated at 215°C for 128 hrs. The tube was cooled, opened, the contents filtered (to remove hydroquinone) and distilled to yield 10.12 g., b.p. 30-43 at 0.26 mm $n_D^{25} 1.3973$ (presumably 1 to 1 adduct) and 3.7 g. residue. Chromatography of the residue on alumina gave 3.55 g. solid, m.p. 67-74°C. Three crystallizations from methanol followed by sublimation raised the melting point to 79-81°C (sealed capillary). Analysis calc. for $C_{15}H_{12}F_8$ (1 to 2 adduct): C, 52.33%; H, 3.51%; Found: C, 52.77%; H, 3.82%.

Adduct of Perfluorocyclohexene (XXXI) and Cyclopentadiene. A Pyrex tube 19 x 25 x 700 mm was charged with perfluorocyclohexene (26.2 g., 0.1 mole), cyclopentadiene (7.3 g., 0.11 mole), and 0.3 g. hydroquinone. The tube was heated at 250°C for 6 days, cooled and opened. No acidic vapors were detectable with ammonia. The tube contents were filtered to remove hydroquinone and it appeared that some of the material evaporated during filtration. From distillation, 5.87 g. perfluorocyclohexene was recovered along with 7.62 g. liquid (containing some crystals) b.p. 50-88° at 0.33 mm, n_D^{25} 1.4150, and 2.88 g. material that solidified in the head. The solid material was recrystallized from methanol and sublimed m.p. 115-117.5°C (sealed capillary). Analysis: Calc. for $C_{16}H_{12}F_{10}$ (1 to 2 adduct) C, 48.74%; H, 3.07%. Found: C, 48.65%; H, 3.16%.

Perfluorosuccinic Acid. Diethyl perfluorosuccinate (200 g., 0.81 mole), 100 ml. ethanol, 400 ml. water and 10 ml. conc. sulfuric acid were refluxed 20 hours. The volume of the solution was reduced to about 200 ml., cooled, extracted 4 x 200 ml. with ether, and dried over magnesium sulfate. After removal of the solvent, distillation yielded diester (4.6%), half ester (12.2%) and diacid (60%).

Perfluorosuccinic Anhydride. The anhydride was prepared in 92% yield by the method of Henne and Richter.¹⁰

Pyrolysis of Sodium Ethyl Perfluorosuccinate (XXXV). In a 250 ml. 3-necked flask equipped with stirrer, dropping funnel, and condenser with drying tube (all glassware was dried in oven at 110°C) were placed 100 ml. anhydrous ethanol and 1.20 g. (0.052 mole) sodium. Perfluorosuccinic anhydride (8.6 g., 0.05 mole) was added dropwise with stirring. The reaction was stirred an additional 2 hrs. at room temperature and allowed to stand overnight. The excess ethanol was removed under vacuum and the resulting white salt was warmed 3 hrs. at 1 mm. pressure. The salt was pyrolyzed at 200-250°C at 1 mm. and the product collected in an ice trap (4.09 g.) and a dry ice trap (1.55 g.). By comparing their infrared spectra with the spectra of authentic samples, the material in the ice trap was shown to be diethyl perfluorosuccinate and that in the dry ice trap to be ethanol. Pyrolysis of the salt prepared from sodium hydroxide and ethyl perfluorosuccinate in ethylene glycol dimethyl ether also yielded diethyl perfluorosuccinate.

1-Methoxy-1,1,2,3,3,3-Hexafluoropropane (XXXVII). The compound was prepared by the method of Knunyants.¹¹ Six heavy walled, Pyrex tubes 19 x 25 x 700 mm. were charged with perfluoropropene (30 g., 0.2 mole), methanol (6.0 g., 0.2 mole), and potassium hydroxide (1.4 g., 0.025 mole). The tubes were heated 20 hours at 60°C. After unreacted perfluoropropene (31 g.) was recovered, the combined tube contents were poured into ice water. The organic layer was separated, washed with water, dried over phosphorus pentoxide and distilled to give 98.5 g. (60%) XXXVII b.p. 53-57°C.

Methyl α,β,β,β -Tetrafluoropropionate (XXXVIII). Two heavy walled, Pyrex tubes were charged with XXXVII (23.6 g., 0.114 mole), concentrated sulfuric acid (20 g.), and powdered glass (4.4 g.). The tubes were heated at 60°C for 3 hours. The reaction product was poured on crushed ice. The organic layer was separated, washed with water, dried over magnesium sulfate and distilled yielding 28.7 g. (83%) XXXVIII, b.p. 90-96°C, n_D^{20} 1.3192.

α,β,β,β -Tetrafluoropropionamide (XXXIX). Methyl α,β,β,β -tetrafluoropropionate (9.5 g., 0.059 mole) was added to 60 cc. conc. aqueous ammonia. The mixture was swirled until solution was effected (10 min.). The solution was extracted 3 x 75 ml. with ether, the ether extract washed with 10 ml. water, and dried over anhydrous magnesium sulfate. Removal of the ether left 7.02 gm. amide (81.5%).

α,β,β,β -Tetrafluoropropionitrile (XL). The amide obtained above was dehydrated without purification by distillation from 21 g. phosphorus pentoxide; 5.7 g. b.p. 40-43° was obtained (95%). Lit¹⁷ b.p. 42°C.

The following intermediates were prepared by methods previously described.^{1,2,10}

Diethyl perfluoroglutarate, 1141 g.
Perfluoroglutaramide, 1990 g.
Perfluoroglutaronitrile, 882 g.
Perfluoroglutarimidine, 431 g.
Ethyl perfluorobutyrate, 347 g.
Perfluorobutyramide, 162 g.
Perfluorobutyronitrile, 63.5 g.

IV. SUMMARY AND CONCLUSIONS

The following compounds have been prepared during the period of time covered by this report:

1. 1,1,2-Trichloro-2,3,3-trifluorocyclobutane
2. 1,4-Dichloro-3,3,4-trifluorocyclobutene
3. Chlorotrifluorosuccinic acid
4. Trifluorosuccinic acid
5. Difluorofumaric acid
6. Perfluorosuccinic acid
7. Perfluorosuccinic anhydride
8. Sodium ethyl perfluorosuccinate
9. 1,2,3-Trichloro-4,4,5,5-tetrafluorocyclopentene
10. 1-Methoxy-1,1,2,3,3,3-hexafluoropropane
11. Methyl α,β,β,β -tetrafluoropropionate
12. α,β,β,β -Tetrafluoropropionamide
13. α,β,β,β -Tetrafluoropropionitrile
14. Adduct of 2,3-dichlorohexafluorobutene-2 and cyclopentadiene
15. Adduct of perfluorocyclopentene and cyclopentadiene
16. Adduct of perfluorocyclohexene and cyclopentadiene
17. Diethyl perfluoroglutarate
18. Perfluoroglutaramide
19. Perfluoroglutaronitrile
20. Perfluoroglutarimidine
21. Ethyl perfluorobutyrate
22. Perfluorobutyramide
23. Perfluorobutyronitrile

Of the laminates prepared thus far, the fluorinated glycol polyester laminates have exhibited superior high temperature properties compared with the corresponding hydrocarbon glycol polyester laminates with one exception. When the cross-linking system consists of a mixture of maleimide and triallyl cyanurate, the difference in room temperature flexural strengths, after aging at 260°C, becomes small. It was, therefore, considered of interest to compare fluorinated and hydrocarbon laminates prepared with maleimide-triallyl cyanurate mixtures by examining their flexural strengths at 260°C. A hexafluoropentanediol polyester cross-linked with maleimide yielded a laminate that retained 95% of its initial 260°C flexural strength (39,900 psi) after aging 100 hours at 260°C. In this case a comparison was not possible because the analogous pentanediol polyester laminates blistered (delaminated in spots) on aging. Comparing the laminates prepared with mixtures of maleimide and triallyl cyanurate (3 to 1 and 1 to 1) is also somewhat awkward. The hydrocarbon laminates have low initial 260°C flexural strengths (12,000-25,000) become weaker after aging 8 to 25 hours (10,000-13,000), then stronger on aging 100 to 150 hours (24,000-29,000) and finally

weaker again (11,000-12,000) after aging 200 hours. The reason why these laminates become weaker, then stronger, and finally weaker again is obscure. The room temperature flexural strengths after aging at 260° do not show this behavior.

Laminates prepared from 3,3,4,4,5,5-hexafluoroheptanediol and 4,4,5,5,6,6-hexafluorononanediol polyesters indicate that as the hydrocarbon portion of the glycol is increased, the flexural strengths of heat aged specimens decreased. Substitution of perfluoroglutarate segments for the isophthalate portion of the polyester increases the fluorine content, but not the high temperature properties of the laminates.

Glass cloth laminates prepared from perfluoroglutarimidine and perfluoroadipamidine showed good retention of flexural strength after aging at 600 to 800°F, and in some cases very low weight losses. However, the initial flexural strengths of these laminates were low.

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VI. APPENDIX

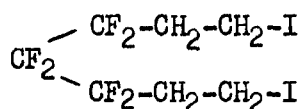
SUB-CONTRACT WORK PERFORMED AT PURDUE UNIVERSITY

This appendix comprises the summary report of the research performed at Purdue University under sub-contract to the Hooker Chemical Corporation during the 1960 contract year.

RESULTS AND DISCUSSION

I. a, -Bifunctional Fluorohydrocarbons

Although the synthesis of 3,3,4,4,5,5-hexafluoroheptane-1,7-diol and 3,3,4,4,5,5-hexafluoropimelic acid was achieved¹⁸, it was considered advisable to investigate possible shorter routes to the above mentioned diols and diacids. Thus attempts were made to prepare the Grignard reagent as well as the dicyano derivative of 3,3,4,4,5,5-hexafluoro-1,7-diiodoheptane. Treatment of one with molecular oxygen, followed by hydrolysis, and saponification of the other should yield the bifunctional compounds desired. However, neither the Grignard reagent, under various conditions, nor the dicyano derivative could be prepared. This is surprising since the mono-functional $C_2F_7CH_2CH_2I$ yields, for instance, the Grignard reagent quite readily¹⁹. The failure of the bifunctional analog to undergo the reaction must be ascribed to its tendency to adopt a cyclic conformation and thus to impart considerable steric hindrance on the reaction center.

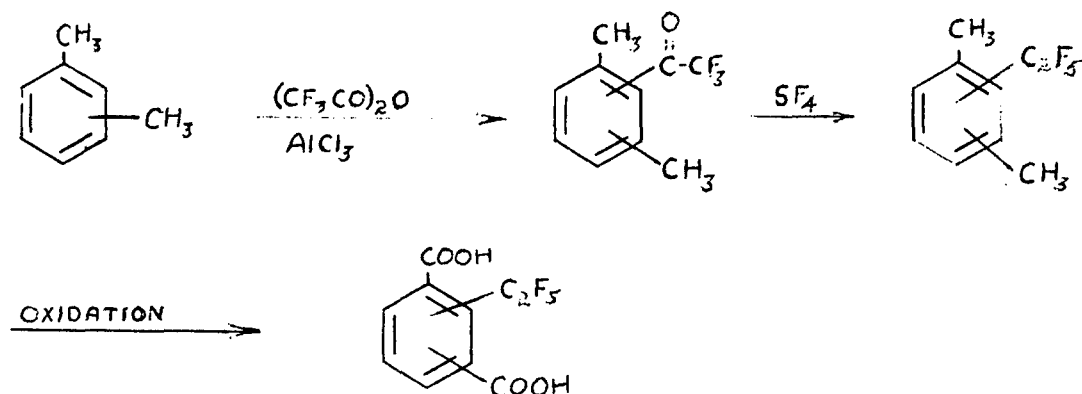


This has been suggested as explanation for the reluctance of this substance to undergo other, similar, reactions²⁰. Analogously, reaction between 2,3,3,3,4,4-hexafluoropentane-1,5-ditosylate and potassium cyanide in ethylene glycol as solvent, gave a very small amount of product which could not be characterized.

II. Perfluoroalkylbenzene di- and tri-carboxylic Acids

a. One route to perfluoroalkyl substituted poly-functional aromatic compounds was envisaged in the preparation of compounds such as trifluorobutyne carboxylic acid, with subsequent cyclo trimerization to the desired monomers. The analogous trimerization of hexafluorobutyne to the corresponding hexakis (trifluoromethyl)benzene has been known for some time. However, one manner of preparing a suitable acetylenic compound, the reaction of acetylene dicarboxylic acid with sulfur tetrafluoride failed to yield the desired $CF_3-C\equiv C-CO_2H$ but gave a number of products, instead, which either did not contain a triple bond and/or were non-acidic.

b. Another route, the preparation of pentafluoroethylphthalic acids by the following scheme was successful.



Friedel-Crafts trifluoroacetylation of *m*-xylene gave a ketone (E) in 77% yield, the structure of which was established, by its basic hydrolysis, to the known 2,4-dimethyl benzoic acid, as 2,4-dimethyl trifluoroacetophenone. However, similar reactions with *p* and *o*-xylene gave mixtures (A) and (I) of isomeric ketones respectively.

The gas phase analysis of mixture (A) showed the presence of 2,4-dimethyl trifluoroacetophenone (E) and 2,5-dimethyl trifluoroacetophenone in a 35:65 ratio and mixture (I) was shown, similarly, to contain (E) and 3,4-dimethyl acetophenone in a 27:73 ratio. No 2,3-dimethyl isomer could be detected. An attempt at using a milder catalyst, ferric chloride, in the trifluoroacetylation of *p*-xylene was unsuccessful. However, when the addition of xylene and the anhydride was reversed, isomerization could be suppressed completely with both *p*- and *o*-xylene. This indicates that the isomerization of the two xylenes took place before the introduction of the acetyl group, which would otherwise deactivate the ring. Indeed, the literature contains many examples of such isomerizations catalyzed by Lewis acids. Pure 2,5-dimethyl- and 3,4-dimethyltrifluoroacetophenone were obtained in yields of 74% and 60%, respectively, by this modified method.

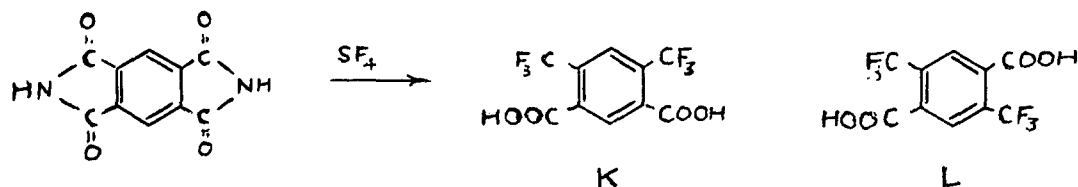
Fluorination of the keto group by reaction with sulfur tetrafluoride was achieved in yields of 90% and higher. Thus (E) gave 2,4-dimethyl pentafluoroethylbenzene (F) and the mixture (A) (fluorinated before suppression of isomerization was achieved) gave a mixture (B), containing (F) and the expected 2,4-dimethylpentafluorobenzene in a ratio of roughly 1:4. These fluorinations will, of course, be repeated with the pure *p*- and *o*-xylyl ketones.

Oxidation of the methyl groups, however, showed some interesting features. When an attempt was made to oxidize (F) with chromic acid, only a monocarboxylic acid could be obtained. Similarly, chromic acid oxidation of (B) gave, on repeated crystallization, an isomeric benzoic acid. However, neutral permanganate oxidation of (F) was successful in yielding the desired dicarboxylic acid (G). And again, permanganate oxidation of (B) gave an isomeric phthalic acid, whose pure diamide was prepared.

One reaction of p-xylene with perfluorobutyryl chloride was too vigorous and could not be controlled. It was not repeated since the reactions with perfluoroacetic anhydride proved easier and more economical.

c. A third approach to perfluoroalkyl substituted polyfunctional benzenes utilizes the chemistry of known benzene carboxylates.

Thus, phthalimide is known to react with sulfur tetrafluoride to give o-trifluoromethylbenzoic acid²¹. Analogously, the reaction with pyromellitic acid diimide should give one or both of the two isomers (K) and (L).



The diimide was prepared and reacted with SF_4 ; the product is under investigation.

Pyromellitic acid is known to react with SF_4 to give tetrakis (trifluoromethyl)benzene. Analogously, dibromopyromellitic acid should yield dibromotetrakis (trifluoromethyl)benzene, wherein the bromine should be replaceable by hydroxyl or other nucleophilic groups. In this synthesis, dibromodurene has been prepared. As next step, oxidation to dibromopyromellitic acid is envisaged.

d. The reaction of p-bis-(trifluoromethyl)benzene with n-butyllithium in ethyl ether, followed by carboxylation, gave a monoacid¹⁸. An attempt at introducing a second carboxyl group by reaction with the organometallic under more vigorous conditions failed. This approach has been abandoned.

EXPERIMENTAL

1. Reaction between 3,3,4,4,5,5-hexafluoro-1,7-diiodoheptane and Potassium Cyanide

20 g. (0.0435 mole) of 3,3,4,4,5,5-hexafluoro-1,7-diiodoheptane and 8.6 g. (0.130 mole) of potassium cyanide were mixed with 70 ml. of dimethyl formamide in a 200 ml., 3-necked flask, fitted with stirrer and condenser. The contents of the flask were heated to about 100°C and stirred for 48 hours. The flask was cooled to room temperature and 100 ml. of distilled water was added.

Since the aqueous layer did not separate from the organic layer, the mixture was extracted with ether and the ethereal solution dried over anhydrous magnesium sulfate. The ether was removed by evaporation and the remainder subjected to fractional distillation. The following fractions were collected:

Cut No.	B.P.	Weight
1	60-65°/760 mm.	0.5 g.
2	54°C/13 mm.	1 g.
3	75°C/13 mm.	1 g.
4	90-110°C/0.5 mm.	1 g.

Cuts Nos. 2 and 3 gave positive elemental test for F, I, and N. Cut No. 4 was too dark and impure for further characterization.

2. Reaction between 2,2,3,3,4,4-hexafluoropentane-1,5-ditosylate and Potassium Cyanide

In a flask (200 ml.) fitted with a Kornblum distillation head 100 ml. of ethylene glycol, 11 g. (0.02 mole) of hexafluoropentane ditosylate and 7 g. (0.10 mole) of potassium cyanide were placed. The flask was gradually heated to 180°C. The distillate, collected at this temperature, separated into two layers. The upper large layer consisted of the glycol, while the lower colorless layer, which was very small, gave a positive test for fluorine. However, the material was in too small a quantity for further characterization.

3. Attempted Preparation of the Grignard Reagent of 3,3,4,4,5,5-Hexafluoro-1,7-diiodoheptane

A dry 1-l. 3-necked flask was equipped with mercury seal stirrer, reflux condenser, dropping funnel and a gas inlet tube for passing dry nitrogen through the system. The condenser outlet was connected to a calcium chloride drying tube.

6.5 g. (0.26 mole) of pure magnesium metal was introduced into the flask and the apparatus was flamed under a nitrogen flush. 10 ml. of anhydrous ether containing a few drops of methyl iodide was added to start the reaction and then 30 g. (0.065 mole) of 3,3,4,4,5,5-hexafluoro-1,7-diiodoheptane dissolved in 500 ml. of anhydrous ether was added slowly. At intervals of ten minutes, the addition of ether was stopped and the flask heated on a water bath for a few minutes. After the addition was complete, the mixture was refluxed for one hour, cooled and poured, with constant stirring onto powdered dry ice in a large beaker. Stirring was continued until all the dry ice disappeared and CO₂ evolution stopped. The mixture was hydrolyzed with 40-50% sulfuric acid. The ether layer was removed and the aqueous layer extracted with ether. The combined ether layers were dried over anhydrous magnesium sulfate and ether removed by evaporation. Purification of the viscous residue yielded the starting material.

The reaction was repeated under actinic light, in the presence of magnesium amalgam, and at elevated temperature in n-butyl ether under actinic light. In no instance did reaction occur.

4. Preparation of Acetylene Dicarboxylic Acid

A slurry of 50 g. of the mono-potassium salt of acetylene dicarboxylic acid in 65 ml. of distilled water was placed in an ice-bath and stirred vigorously while conc. sulfuric acid was added until the solution remained acidic. The reaction mixture was extracted with three 50 ml. portions of ethyl ether and the combined layers concentrated at room temperature. The product was dried overnight in a vacuum desiccator containing phosphorus pentoxide. The product, a white powder, m.p. 176-177°C. was obtained in 70% yield.

5. Reaction between Acetylene Dicarboxylic Acid and Sulfur Tetrafluoride

A stainless steel tube was dried and charged with 23 g. (0.2 mole) of acetylene dicarboxylic acid and 3.5 g. of sodium fluoride as a catalyst. The tube was evacuated and then placed in a liquid nitrogen bath. It was subsequently charged with 100 g. (1.02 moles) of sulfur tetrafluoride. The tube was allowed to warm up to room temperature and left overnight. The tube was subsequently heated in an oil bath at the following rate:

Temperature °C	Hours
70	6
110	2
160	2
170	3

The tube was allowed to cool to room temperature. The unreacted sulfur tetrafluoride and other gases were passed through ether and finally collected

dry ice trap. The ethereal solution was mixed with 5% sodium hydroxide solution and stirred for three days. The bottom layer was separated, acidified with dilute sulfuric acid and extracted continuously with ether. The ether layer was separated, dried over anhydrous sodium sulfate and the ether evaporated. A small amount of liquid was obtained which was acidic and contained fluorine. However, the amount was too small for further purification.

A small amount of liquid (residue) was obtained from the reaction tube, by ether extraction. On distillation, two fractions were collected. Fraction 1 (65°/3 mm.) gave a positive elemental test for fluorine but its infrared spectrum did not show the presence of a triple bond. Fraction 2 was non-acidic. The residue, left over in the distillation flask, was too crude and various attempts to purify it failed.

6. Trifluoroacetylation of p-Xylene

A solution of 53 g. (0.5 mole) of p-xylene in 200 ml. of carbon disulfide was placed in a 1-l. 3-necked flask fitted with a mechanical stirrer, dropping funnel and reflux condenser bearing a tube to carry off the gas evolved. To this solution 149 g. (1.1 moles) of aluminum chloride was added and then, with rapid stirring, 105 g. (0.50 mole) of trifluoroacetic anhydride was added slowly over a period of 2 hours, during which time the temperature of the mixture rose and a rapid evolution of HCl gas took place. After all the anhydride had been added, stirring was continued for another two hours. The reaction mixture was decomposed by pouring it over ice water. The carbon disulfide was evaporated and the mixture extracted with three 150 ml. portions of ether. The ethereal solution was washed with water, 10% sodium hydroxide and water, respectively. The solution was dried over anhydrous calcium chloride and the ether removed by evaporation. The residue was subjected to vacuum distillation using a 1-foot fractionating column packed with glass helices. The ketone was collected at 70-71°C/7.5 mm. Yield: 85%. The vapor phase analysis showed the product to be a mixture (A), eventually identified as 2,4-dimethyltrifluoroacetophenone and 2,5-dimethyltrifluoroacetophenone, in a 35:65 ratio.

Anal. Calcd. for: $C_{10}H_9F_3O$, C, 59.45; H, 4.45; F, 28.21. Found: C, 59.12; H, 4.75; F, 28.32. B.p. 71°/7.5 mm.

7. Reaction between the Ketone Mixture (A) and Sulfur Tetrafluoride

A stainless steel tube was dried and charged with 37 g. (0.18 mole) of (A) and 0.1 ml. of water as a catalyst. The tube was placed in a liquid nitrogen bath and evacuated. It was subsequently charged with 54 g. (0.48 mole) of sulfur tetrafluoride. The tube was allowed to warm up to room temperature and placed in an oil bath and heated at 100°C for 8 hours. The tube was cooled to room temperature and the boiling material (SF_4) distilled into a dry ice trap. The residual liquid was transferred into an

Erlenmeyer flask and the tube rinsed 3 times with 20 ml. portion of dry ether containing 1 g. of sodium fluoride. The ethereal solution was filtered and the ether removed by evaporation. The residue was distilled, using a fractionating column, to give 40 g. (97%) of the product (B) (b.p. 160°C). The infrared spectrum showed no carbonyl absorption. The vapor phase analysis showed the presence of two isomers in a 25:75 ratio.

Anal. Calcd. for: $C_{10}H_9F_4$. C, 53.7; H, 4.02. Found: C, 53.51; H, 4.41.

8. Chromic Acid Oxidation of (B)

A 13 g. (0.058 mole) of the mixture (B), 106 g. of water and 48 g. (0.18 mole) of sodium dichromate were stirred mechanically in a flask fitted with a reflux condenser, while 142 g. of concentrated sulfuric acid was added gradually from a dropping funnel. The mixture was then heated for about two hours, cooled and diluted with 200 ml. of distilled water. The contents of the flask were extracted with ether and the ethereal solution treated with a 10% sodium hydroxide solution. The aqueous layer was separated and acidified with sulfuric acid. A precipitate was collected and washed with 50 ml. of water. Two crystallizations from hot benzene gave a solid (C), m.p. 156-158°C. Yield: 64%.

Anal. Calcd. for $C_{10}H_7F_5O_2$: C, 47.4; H, 2.75; F, 37.5. Found: C, 37.5; H, 3.00; F, 37.46.

9. Neutral Permanganate Oxidation of (B)

In a 1-l. 3-necked flask fitted with a mechanical stirrer, reflux condenser and a dropping funnel, 10 g. (0.045 mole) of the (B) and 500 ml. of distilled water were placed. The reaction mixture was allowed to stir and reflux gently. 29 g. of potassium permanganate was added in 3 portions. The refluxing was continued until all the permanganate color disappeared, which took 4 days. The mixture was decolorized, by treating with SO_2 gas, and filtered. The filtrate was concentrated by evaporation and acidified with sulfuric acid. The product was collected as a white solid which was recrystallized from benzene-ethanol. M.p. 214-218°C. Yield: 68%. The diamide derivative of the acid was prepared, m.p. 278°C.

Anal. Calcd. for $C_{10}H_7O_2N_2F_5$: C, 42.56; H, 2.48; N, 9.93; F, 33.7. Found: C, 42.36; H, 2.73; N, 10.01; F, 33.55.

10. Preparation of 2,4-Dimethyl Trifluoroacetophenone

m-xylene	- 53 g. (0.5 mole)
(CF_3CO_2)	- 110 g. (0.5 mole)
$AlCl_3$	- 149 g. (1.1 mole)
CS_2	- 250 ml.

The procedure followed was the same as in the case of p-xylene.
Yield: 77%.

Anal. Calcd. for $C_{10}H_9F_3O$: C, 59.4; H, 4.45; F, 28.2. Found: C, 59.60; H, 4.50; F, 28.00. B.p. 68°C . at 5 mm n_D^{21} 1.4770.

11. Preparation of 2,4-Dimethylpentafluoroethylbenzene (F)

A dry stainless steel reaction tube was charged with 28 g. (0.137 mole) of 2,4-dimethyltrifluoroacetophenone and 40 g. (0.37 mole) of sulfur tetrafluoride. The tube was heated at 110°C for 8 hours. For further experimental details see reaction 7, the preparation of (B). Yield: 85%.

Anal. Calcd. for $C_{10}H_9F_5$: C, 53.57; H, 4.02; F, 42.4. Found: C, 53.54; H, 4.26; F, 42.14. B.p. $164-165^\circ\text{C}$, n_D^{21} 1.4228.

12. Chromic Acid Oxidation of 2,4-Dimethylpentafluoroethylbenzene (F)

The procedure followed was the same as described in reaction 8, the preparation of (C).

Anal. Calcd. for $C_{10}H_7F_5O_2$: C, 47.4; H, 2.75; F, 37.5. Found: C, 47.26; H, 2.97; F, 37.46. M.p. $178-179^\circ\text{C}$.

13. Preparation of Pentafluoroethylbenzene 2,4-Dicarboxylic Acid (G)

10 g. (0.045 mole) of pentafluoroethyl-2,4-dimethylbenzene and 500 ml. of distilled water were placed in a 1-l. 3-necked flask fitted with a stirrer and a condenser. While the mixture was being stirred and refluxed, 30 g. of potassium permanganate was added in three portions. Refluxing was continued until the permanganate color changed. The reaction mixture was cooled to room temperature and filtered. The filtrate was concentrated by evaporation, and acidified. The product was collected as a white solid which was recrystallized from water-ethanol. Yield: 68%.

Anal. Calcd. for: $C_{10}H_5F_5O_4$: C, 42.2; H, 1.7; F, 33.5. Found: C, 42.06; H, 2.09; F, 33.65. M.p. $234-235^\circ\text{C}$.

14. Trifluoroacetylation of o-Xylene

The procedure followed was similar to the one described in reaction 6 for the preparation of (A). However, since the reaction had the tendency to become violent, an ice bath was used at intervals to cool the reaction mixture. Gas phase analyses showed the product to be a mixture of 2,4-dimethyl- and 3,4-dimethyltrifluoroacetophenone in a 25:75 ratio, approximately. Yield: 60%.

The two isomers were separated by fractional distillation using a spinning band column.

(1) Anal. Calcd. for $C_{10}H_9F_3O$: C, 59.45; H, 4.45; F, 28.2. Found: C, 59.70; H, 4.61; F, 28.05.

(2) Calcd. for $C_{10}H_9F_3O$: C, 59.4; H, 4.45; F, 28.19. B.p. 90°C. at 10 mm., n_D^{21} 1.4790.

15. Attempted Trifluoroacetylation of p-Xylene, Using Ferric Chloride as Catalyst

The procedure followed was the same as described in reaction 6, with ferric chloride instead of aluminum chloride. However, the starting material was recovered almost quantitatively.

16. Preparation of 2,5-Dimethyltrifluoroacetophenone

p-xylene	- 26 g. (0.025 mole)
$(CF_3CO)_2O$	- 55 g. (0.025 mole)
$AlCl_3$	- 75 g. (0.55 mole)
CS_2	-100 ml.

A 1-l. 4-necked flask, fitted with stirrer, dry ice condenser and two dropping funnels, was charged with carbon disulfide and catalyst. p-Xylene and trifluoroacetic anhydride were added dropwise, simultaneously, always allowing the presence of a little excess anhydride. The reaction was carried out at room temperature. Vigorous refluxing of trifluoroacetyl chloride was observed. On hydrolysis in the usual manner and purification, the product was collected by distillation, b.p. 68° at 5.5 mm. Yield: 74%, n_D^{21} 1.4691. The vapor phase chromatogram showed the presence of one compound only.

17. Preparation of 3,4-Dimethyl Trifluoroacetophenone

Procedure and quantities were the same as in reaction 16, using o-xylene. Yield: 60%, b.p. 70° at 5 mm.

18. Preparation of Perfluorobutyryl Chloride

A 200-ml. flask was charged with 32.1 g. (0.15 mole) of perfluorobutyric acid and 84.3 g. (0.6 mole) of benzoyl chloride. A dry-ice condenser was attached to the flask. A tube was attached to the condenser and connected to a trap in order to catch the gases given off. The reaction mixture was heated on a steam bath for a period of twelve hours. After cooling the reaction mixture, the dry ice condenser was removed and replaced by a fractionating column to which a total reflux head was attached. The product (25.2 g.) was distilled and collected in an ice trap, b.p. 38-41°C. (72.2% yield).

19. Reaction of p-Xylene with Perfluorobutyryl Chloride and Aluminum Chloride

Aluminum chloride (13.5 g.) and 21.2 g. (0.2 mole) of p-xylene were placed in a 250 ml. flask which was equipped with a magnetic stirrer, thermometer, a Friedrich condenser to which a drying tube was attached, and a side-arm addition funnel. The flask was warmed to 50°C. and the acid chloride was added very slowly, dropwise. After approximately half of the acid chloride had been added, the reaction became very exothermic and part of the material went half-way up the condenser. Only a black-rubbery material remained in the flask. The unreacted acid chloride was stored.

20. Preparation of Pyromellitic Anhydride

Pyromellitic acid (25.4 g., 0.1 mole) was placed in a 200 ml. flask with approximately 50 ml. (64.3 g.) of acetyl chloride. A tube was attached to the condenser and attached to two gas-wash bottles in order to collect exit gas (hydrogen chloride). The first bottle was empty and the second bottle contained an aqueous solution of sodium hydroxide. The reaction mixture was heated for a total of 13 hours on the steam bath. The contents of the flask were allowed to cool to room temperature and the crystalline solid was filtered off, leaving a red filtrate. The solid was washed three times with 50 ml. portions of anhydrous ether and placed in a vacuum desiccator. The desiccator was evacuated and the solid was allowed to dry overnight. Pyromellitic anhydride was obtained in 90.8% yield (20.8 g.). The anhydride can also be obtained by heating the acid above 260-270°C and collecting the sublimate.

21. Preparation of Pyromellitimide

A sublimation apparatus was loaded with a finely-ground mixture of 10.9 g. (0.05 mole) of pyromellitic anhydride and 35 g. of ammonium carbonate. The mixture was heated slowly to 180°C and then heated at 200-240°C for a period of 24 hours. Some of the ammonium carbonate which had thermally decomposed was found to recombine on the cold finger. The crude solid obtained was heated in an oven at 140°C. in order to rid the pyromellitimide of the ammonium carbonate mixed with it. In this manner, a pale-yellow solid was obtained (814 g., 80.4%), 440°C.

22. Reaction of Pyromellitimide with Sulfur Tetrafluoride

A stainless steel tube was dried in an oven at 120°C. overnight and charged with 8.7 g. of the diimide of pyromellitic acid and 3 g. of antimony trifluoride. The tube was flushed with nitrogen and closed. The tube was then evacuated in 0.5 mm., placed in a dry ice-trichloroethylene bath. After the tube had cooled to the temperature of the bath, 32 g. of sulfur tetrafluoride was transferred to the tube. The tube was then heated at 90°C for 2 hours, 110°C for 12 hours and 125°C. for a period of 24 hours. The tube

was allowed to cool to room temperature and then placed in a dry ice-trichloroethylene bath. The opening to the tube was connected to a glass tube which has been placed in a dry ice-trichloroethylene bath and the reactor tube was allowed to warm up to room temperature in order to collect the volatile materials from the reaction. The reactor tube was then opened and the solid materials shaken and/or scraped out into a beaker. The tube was then washed out with anhydrous ether several times. Some solid remained. The tube was then washed out with aqueous solutions of sodium hydroxide. The washings and solid obtained from this treatment were poured into another beaker. There was no evidence of charring or extensive decomposition. The solids and washings are currently being investigated.

23. Preparation of Dinitrodurene

A one-liter beaker was charged with 13.4 g. (0.1 mole) of durene (96.5% pure) dissolved in 100 ml. of chloroform and 50 ml. of concentrated sulfuric acid. An ice-water bath was used to cool the mixture. While the mixture was being stirred with a mechanical stirrer, 16 g. of fuming nitric acid were added dropwise from an addition funnel. The addition took 15-20 minutes. The mixture was allowed to stand for a few minutes and the sulfuric acid layer was separated. The chloroform solution was run into an aqueous solution of sodium carbonate. The chloroform layer was separated and washed several times with water, and then with an aqueous sodium bicarbonate solution to insure that it was completely acid-free, and again with water. The chloroform solution was dried over anhydrous magnesium sulfate, the magnesium sulfate filtered off and the chloroform distilled. A 70% yield was obtained by this method (15.4 g.). The dinitrodurene could be recrystallized from alcohol, m.p. 205-206°C.

24. Preparation of Dibromodurene

Durene (10 g., 0.075 mole) was placed in a beaker with 45 ml. of glacial acetic acid. A crystal of iodine was added. An addition funnel was charged with 25 g. (0.156 mole) of bromine dissolved in 20 ml. of glacial acetic acid and the bromine solution was added to the beaker, dropwise, with stirring, over a 10-15 minute period. The reaction mixture was allowed to stand for one hour. The resulting mass of liquid and solid was diluted with water. The solid was filtered off on a regular funnel and the residual solid was washed twice with alcohol and twice with 50 ml. portions of water. The solid was transferred with the filter paper to a Buechner filter and washed again with water. The solid obtained in this manner was white, and after it dried, weighed 18.4 g. The theoretical yield was 21.8 g. This represents an 84.4% yield of dibromodurene, m.p. 199-200°C.

25. Reaction of n-Butyllithium with 3,5-Dibromobenzotrifluoride in a n-Butyl Ether

n-Butyllithium was prepared as before (Org. Reaction VI, 352 (1951)). Lithium wire (4.3 g.) was reacted with 34.3 g. of butyl bromide in n-butyl ether.

A solution of 10.1 g. (.03 mole) of 3,5-dibromobenzotrifluoride in 100 ml. of n-butyl ether was added to a cold (0°C.) solution of the n-butyllithium in ether. The ice bath was removed and the reaction mixture was allowed to stir for one hour at room temperature. The reaction mixture was then re-fluxed for a period of four hours. After the reaction mixture had cooled to room temperature, it was poured into a beaker (with stirring) containing an excess of pulverized dry ice. After the dry ice had all sublimed, the basic mixture was acidified with cold, dilute sulfuric acid. The brown solid which separated was filtered off. Extraction of the solid with ethyl ether, treatment with charcoal and concentration yielded crystals of 2,5-bis(trifluoromethyl)benzoic acid, 5 g. (58%), recrystallized from pet. ether (35-7) m.p. 76-77°. The extraction residue, 6.5 g., melted in excess of 200°. Attempts at purification and identification failed.

HOOKER CHEMICAL CORPORATION, New York, New York, FLUORINE CONTAINING CONDENSATION POLYMERS AND RESINS by D. Kmtson, J. J. Kolano, R. N. Deleo, and A. M. Teller, March 1961. 37 p. incl. tables, 21 refs. (Project 7340; Task 73404) (WADC TR 55-221 Pt VII) (Contract AF 33(616)-5548) Unclassified Report Polyesters have been synthesized from fluorinated glycols and the corresponding hydrocarbon glycols. Some polyesters were prepared from fluorinated acids. Laminates prepared from these polyesters have been aged at elevated temperatures and their physical properties measured before and after aging. In general, the fluorinated glycol polyester laminates exhibit much better retention of (over)	UNCLASSIFIED	UNCLASSIFIED
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