

10-1901

First Annual Summary Report

THERMALLY RESISTANT POLYMERS FOR FUEL TANK SEALANTS

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1 July 1968 — 30 June 1969

CONTRACT NO. NAS8-21401
DCN-1-8-54-10236 (1F) and S1 (1F)

to

George C. Marshall Space Flight Center
National Aeronautics and Space Administration
Marshall Space Flight Center, Alabama 35812

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DAYTON, OHIO 45407



THERMALLY RESISTANT POLYMERS FOR USE AS FUEL TANK SEALANTS

by

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Prepared under Contract No. NAS8-21401
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National Aeronautics and Space Administration
George C. Marshall Space Flight Center
Huntsville, Alabama 35812

10 July 1969

ABSTRACT

Siloxane and perfluoroalkylene-containing polymers were investigated as elastomeric fuel tank sealant materials. Isocyanatophenyl- and isocyanatophenoxy-capped polysiloxane intermediates were prepared and polymerized by cyclotrimerization to form polyisocyanurate-linked polymers. Although the polymers having the phenoxy silicon bonding were hydrolytically unstable the phenylsilicon-bonded polymers were both hydrolytically and thermally stable.

Isocyanatophenyl-capped perfluoroalkylene intermediates were prepared and polymerized by cyclotrimerization. The resulting isocyanurate polymer was thermally stable. Perfluoroalkylene diisocyanate intermediates were prepared but these compounds could not be polymerized readily to form isocyanurates.

The feasibility of linking perfluoroalkylene chains through acetylene trimerization reactions was investigated with the model compound, perfluoropropyl ethynyl ketone. Cyclotrimerization of this compound to form tris(perfluorobutyl) benzene demonstrated this as a potential polymer linking reaction, but low yield and linear by-product formation obviate continued effort on this approach.

FOREWORD

This report is the First Annual Summary Report prepared by Monsanto Research Corporation, Dayton Laboratory, under Contract NAS8-21401, "Thermally Resistant Fuel Tank Sealants" for the George C. Marshall Space Flight Center of the National Aeronautics and Space Administration. The work was administered under the technical direction of the Propulsion and Vehicle Engineering Laboratory, George C. Marshall Space Flight Center, with Mr. James E. Curry as the contracting officer's representative.

The work was performed at the Dayton Laboratory of Monsanto Research Corporation under the direction of Dr. John Mann Butler, project leader. The investigators were Dr. Clayton Hathaway, Mr. Richard Quill and Mr. James Webster with technical assistance provided by Lewis Cash and Thomas Morrow.

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I. INTRODUCTION

This is the First Annual Summary Report on the new polymer development phase (Task A) of a multi-part program directed at the development of improved, thermally-resistant sealant materials for use in fuel tanks of advanced high speed aircraft. The objective of this task is the design and tailoring of new polymer systems which can be easily applied, cured in place, and have the modulus, adhesion, strength, elongation, resistance to permanent set and thermal hydrolysis and solvent resistance necessary to withstand temperatures to 500-600°F in contact with hydrocarbon fuels. In addition, these polymers must not contribute to stress corrosion of titanium.

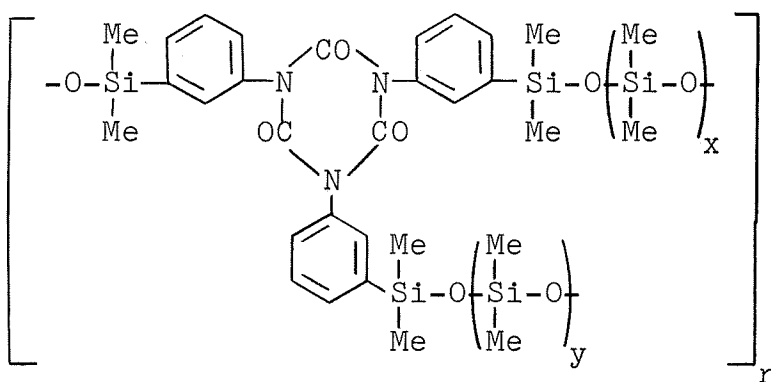
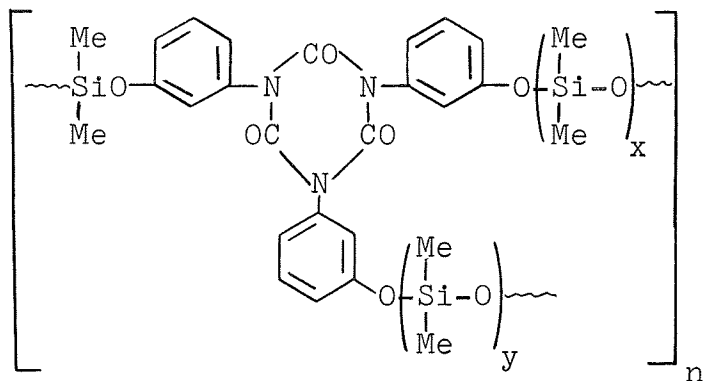
The new polymers proposed are based primarily on siloxane (silicone) and perfluorocarbon structures to incorporate the advantages in high temperature elastomeric properties offered by the siloxane polymers and the advantages in thermal stability and hydrocarbon fuel repellency offered by fluoropolymers.

Improved solvent resistance and greater thermal stability were to be imparted to the siloxanes and improved fabricability and stress corrosion resistance to the fluoropolymers. These improvements were to be achieved through the use of chain extending and cross-linking reactions that provide thermally and hydrolytically stable linkage that preferably also contribute to hydrocarbon insolubility.

Coupling of the siloxy and fluorocarbon segments was to be accomplished through isocyanurate and benzene ring formation. The thermally, oxidatively and hydrolytically stable isocyanurate ring is normally readily formed by a facile, low temperature addition type trimerization of an isocyanate. The polarity of the isocyanurate ring was also expected to raise the cohesive energy density and reduce swelling of the silicone polymer in a hydrocarbon fuel. The trimerization of acetylenic groups to aromatic rings also offered a potential low temperature, addition-type curing reaction resulting in the formation of thermally and oxidatively stable coupling groups.

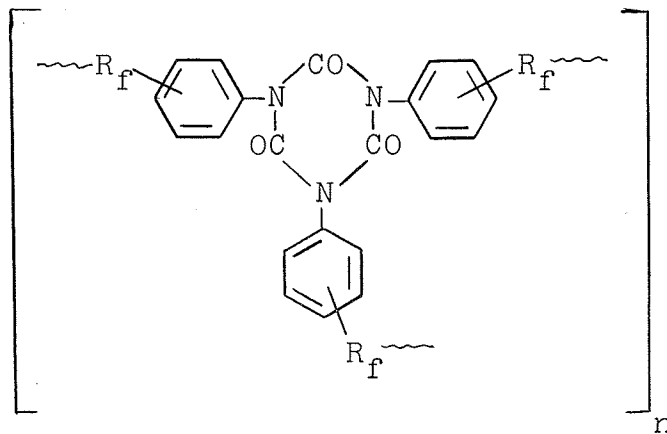
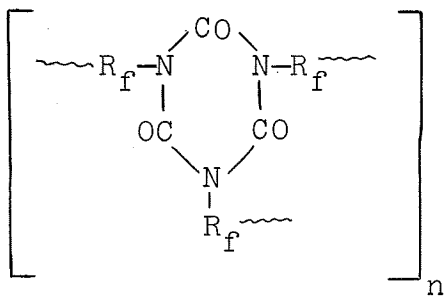
The introduction of an aromatic ring between the polymer backbone segment and the reactive coupling functional group was investigated as a technique for uniting both components in a stable prepolymer and for moderating the electronic effect of the backbone segment on the reactivity of the coupling functional group.

Three specific systems have been investigated in initial studies: System A - Isocyanurate-linked Siloxanes. The two types of structures (shown below) differ in their manner of linkage between the silicone atom and phenyl ring.

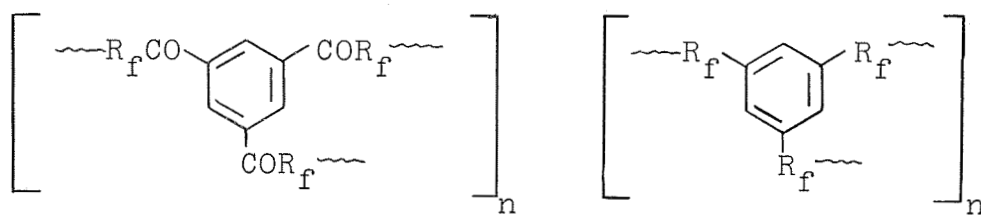


In these and subsequent structures the methyl group is represented by the symbol Me.

System B - Isocyanurate-linked Fluoropolymers.



System C - Aromatic Ring-linked Fluoropolymers.



The feasibility of linking perfluoroalkyl acetylenic intermediates by a cyclotrimerization reaction to form the aryl linking segments shown above was tested with model compounds.

II. SUMMARY AND CONCLUSIONS

Isocyanatophenyl capped siloxane prepolymers with silicon connected directly to an aromatic ring in the backbone have been prepared and polymerized through isocyanurate ring formation. These polymers have shown promising hydrolytic stability, thermal stability and JP-4 fuel resistance in preliminary evaluations. The polymer based on a tetrasiloxane segment showed a reasonable degree of extensibility, although less than generally desired for an elastomer. Similar isocyanatophenoxy-capped siloxane polymers containing an Si-O-C linkage joining the silicon and aromatic rings showed poor hydrolytic stability and were removed from further consideration. A further improvement in the elastomeric properties of the siloxane polymers is expected with slight additional lengthening of the siloxane segment, but at some sacrifice in hydrocarbon fuel resistance.

A perfluoroalkyl(aryl)diisocyanate containing an α,ω -perfluoropropylene segment has been prepared and converted to a rigid isocyanurate linked polymer that shows good thermal and hydrolytic stability. No polyisocyanurate could be obtained from completely aliphatic perfluorinated diisocyanates so these isocyanates were not further investigated. In future efforts polyisocyanurates from perfluoroalkyl(aryl)diisocyanates with longer perfluoroalkylene segments will be sought to provide elastomeric properties.

Model compound studies have demonstrated the technical feasibility of synthesizing and trimerizing perfluoroalkyl ethynyl ketones to perfluoroacyl benzene compounds. The synthesis of intermediates occurred only in poor yields, however. Preliminary attempts to trimerize a perfluoroalkyl acetylenic compound were unsuccessful. At the current stage of development this route does not appear attractive for extension to development of a sealant system.

III. RESULTS AND DISCUSSION

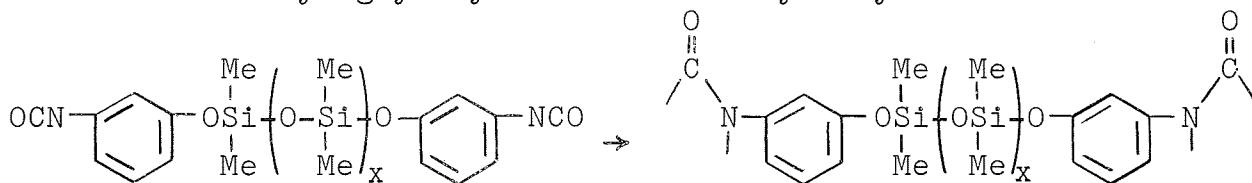
A. ISOCYANURATE-LINKED SILOXANES

The immediate objective of this first approach was to link siloxane prepolymers through cyclotrimerization of terminal isocyanate groups. Since the instability of the Si-N linkage precludes consideration of an isocyanatosilane structure, isocyanates linked to silicon through hydrocarbon moieties were employed. Aryl isocyanates were considered preferable to aliphatic isocyanate substituents because of greater reactivity of the aryl isocyanates and greater stability anticipated of the resulting products.

Both phenyl and phenoxy silicon linkages were considered to be applicable even though the possibility of greater hydrolytic instability of the latter was recognized. The hydrolytic stability of the aryloxysilanes is known to be greater than that of the simple alkoxysilanes. The stability of this linkage in a polymer, however, was considered to have a good chance of being adequate for the fuel tank sealant application. Furthermore, the ease of synthesis of isocyanatophenoxy siloxane intermediates in comparison with the isocyanatophenylsilyl intermediates made the former the preferred choice for initial evaluation.

1. Isocyanatophenoxy siloxanes.

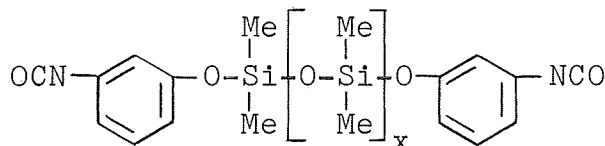
a. Polymer Preparation and Characterization. The polymerization of four isocyanatophenoxy capped siloxanes to isocyanurate polymers proceeded readily with an N,N,N',N'-tetramethyl-1,3-butane-diamine and allyl glycidyl ether cocatalyst system.



The absence of NCO absorption in the infrared spectra combined with model compound work discussed later indicated conversion to isocyanurate and possibly cyclic dimer had occurred.

The physical state and softening temperatures of the polymer products obtained are summarized in Table 1.

Table 1

CYCLOTRIMERIZATION OF ISOCYANATE-CAPPED SILOXANE INTERMEDIATES

Sample	x =	Cure Conditions		Product Properties	Vicat Softening Point, °C
		Time, hr	Temp. °C		
(1)	1	17	100	hard, brittle	95
(2)	2	24	100	hard	70
(3)	~3.5	84	100	flexible	20
(4)	11.8	86	100	soft-cheesy	--

By increasing the length of the siloxane segment, polymer flexibility and lower softening temperature were found to be attainable. The most interesting polymer had approximately 3.5 siloxy groups per siloxane segment and a tensile strength of 260 psi with 60% elongation. Thermogravimetric analysis showed relatively little weight loss below 350°C, (Figure 1).

The hydrolytic stability of the phenoxy siloxane polymers was unsatisfactory. The aryloxysilicon linkage, as discussed above, was recognized initially as a potential site of hydrolytic instability. When these polymers were boiled in distilled water, they were found to degrade at a surprisingly rapid rate. Furthermore, the unhydrolyzed polymer was found to be soluble in ethanol as well as acetone and dimethylformamide. Had infrared analysis not shown the absence of free -N=C=O groups, these observations would have suggested incomplete reaction. By comparison, hexamethylene polyisocyanurate when boiled in water for 24 hours appeared to be totally unaffected. These results suggested, therefore, that either the stable isocyanurate ring structure was not formed or that the aryloxy-silicon linkage was hydrolyzed more readily than expected.

An attempt was made to isolate and identify the products of hydrolytic degradation to gain further insight into the polymer structure and mode of hydrolysis. Although a polydimethylsiloxane oil was isolated, indicating Si-O-Ar bond cleavage, the anticipated isocyanurate triphenol (I) was not found. N,N'-di(*m*-hydroxyphenyl)urea (II)

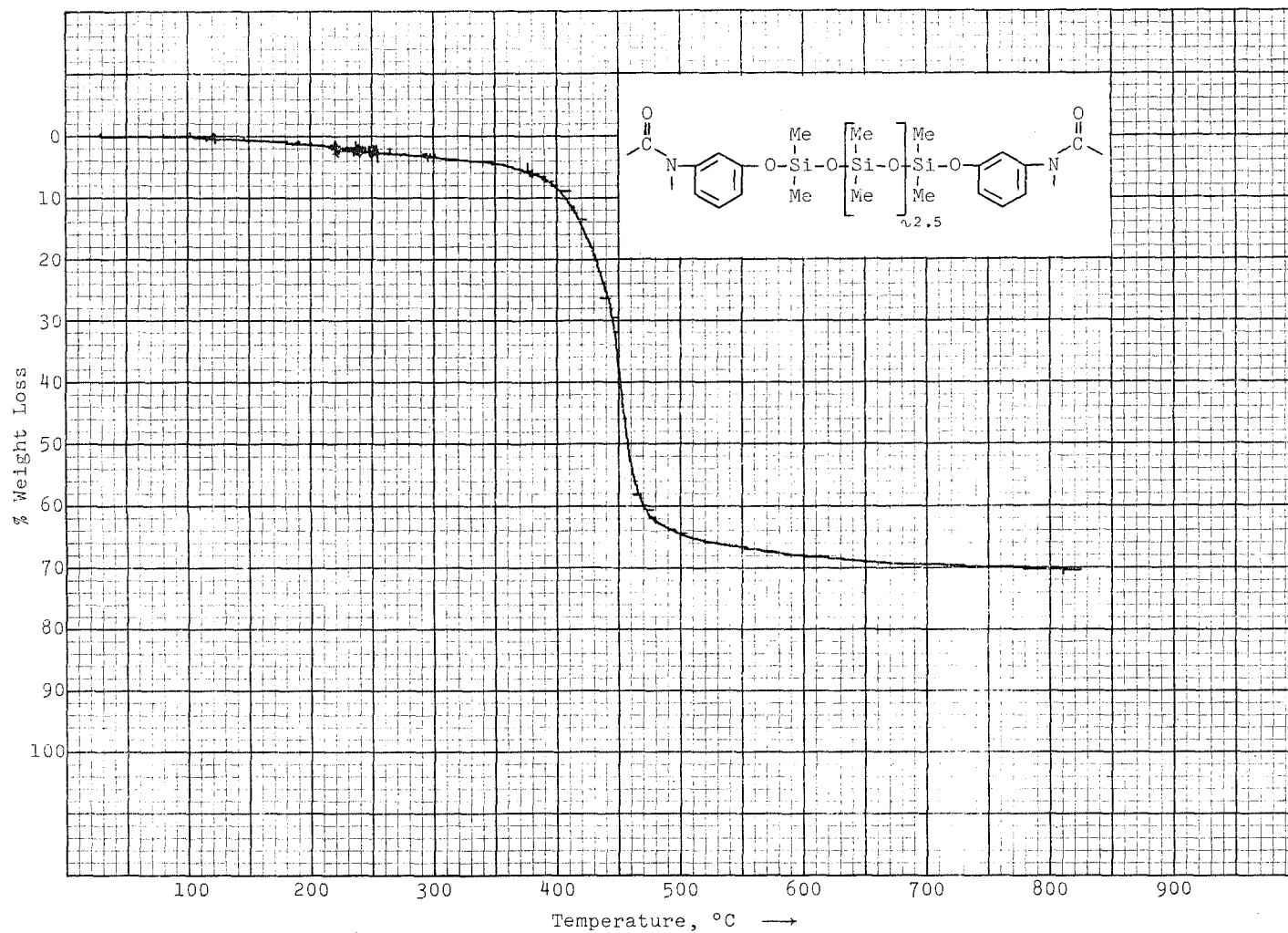
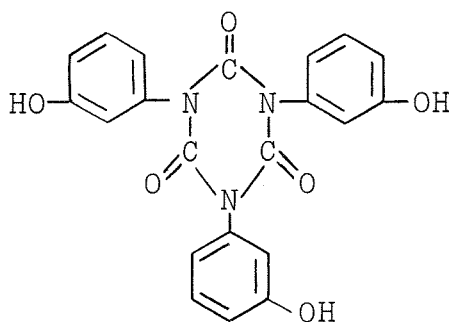
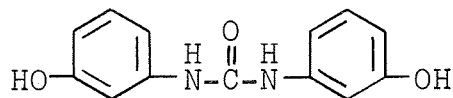


Figure 1. Thermogravimetric Analysis of Isocyanurate Polymer from Isocyanatophenoxysiloxane, Sample 100258, helium atmosphere, heating rate 3°C/min

was isolated from the hydrolysis mixture, along with *m*-aminophenol, however.

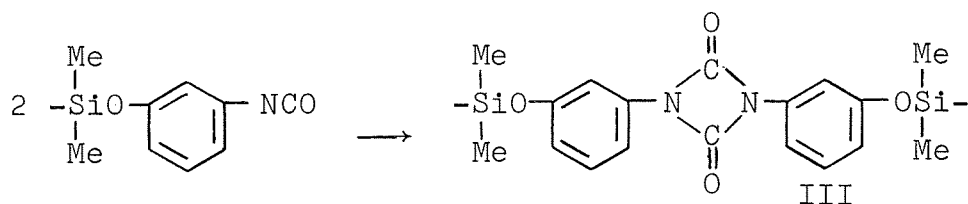


I



II

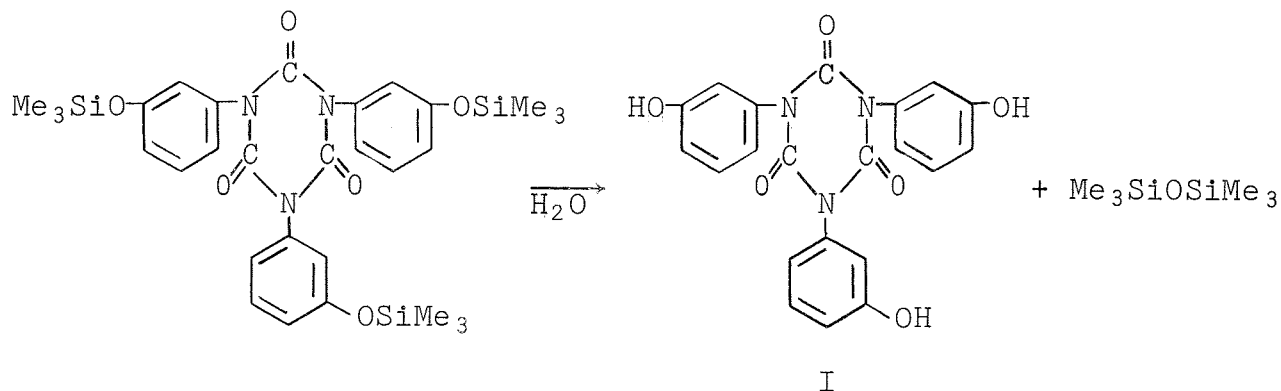
Isolation of II suggests that a structure other than an isocyanurate may have been formed in the polymerization. A dimer, III, which could be expected to hydrolyze to the urea, II, for example, could account for this product.



III

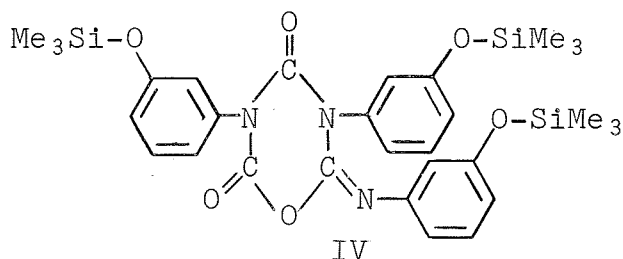
Since the structure of the products formed in these isocyanate polymerization reactions is important regardless of Si-O-phenyl hydrolysis, this polymer linking reaction was investigated further.

The preparation and hydrolysis of the polymer of the monofunctional *m*-trimethylsilyloxyphenyl isocyanate melted below 100°. This product was hydrolyzed by refluxing with water for 20 hours. A small portion of the total hydrolyzate was identified as II, bis(*m*-hydroxyphenyl)urea. When a portion of the above crude cyclic trimer was recrystallized from hexane, a white crystalline solid melting at 129-130° was obtained. This product was also formed directly in 90% yield upon polymerization of *m*-trimethylsilyloxyphenyl isocyanate in hexane solution. Hydrolysis of this purified trimer, by refluxing in water for 3 hours, formed a white crystalline solid melting at 358°. This product was identified as tris(*m*-hydroxyphenyl)isocyanurate (I).



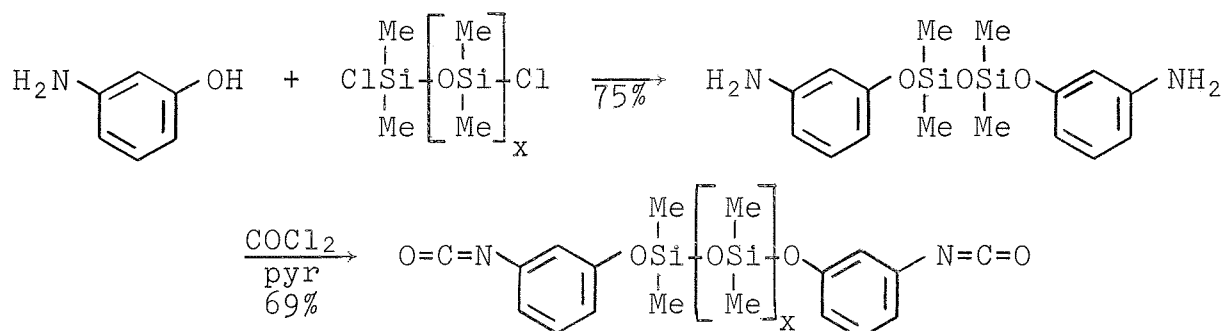
Although several interpretations as to the products formed in the polymerization and hydrolyses are possible, it is clear that the Si-O-phenyl linkage hydrolyzes quite rapidly in water under reflux conditions.

It is possible the isocyanurate is not the sole product formed in the bulk polymerization of these intermediates. Formation of some cyclic dimer III or even an "abnormal" trimer IV of the type described by Slotta and Tschesche could account for the formation of N,N'-bis(*m*-hydroxyphenyl)urea (Ref. 1).



The data does not preclude the possibility that the tris(*m*-hydroxyphenyl)isocyanurate upon extended hydrolysis is also converted to the bis(*m*-hydroxyphenyl)urea.

b. Isocyanurate Intermediate Synthesis. The isocyanato-phenoxydi- and trisiloxane intermediates were prepared by the following reaction sequence:



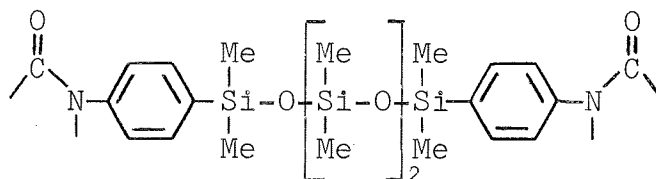
Initial attempts to convert the amine and amine hydrochloride to the isocyanate by reaction with phosgene were not successful. Small amounts of impure isocyanate were obtained but cleavage of the phenoxy group from the silicon by evolved HCl was suspected. Successful phosgenation was carried out by adding a solution of the amine to a cold mixture of phosgene in dry pyridine followed by warming to 25°C, filtering and distilling.

A higher molecular weight intermediate was prepared by alkali-catalyzed equilibration of a mixture of 1,3-bis(*m*-aminophenoxy)tetramethyldisiloxane and hexamethylcyclotrisiloxane and phosgenation of the diamine products. A small quantity of material averaging 4.5 silicons was also obtained by molecular distillation of the crude isocyanate intermediate.

2. Isocyanatophenylsiloxane.

a. Polymer Preparation and Characterization. Synthesis of alternative isocyanate-capped intermediates having the isocyanatophenyl group linked directly to the silicon was initiated after the isocyanatophenoxy siloxane intermediates were found to give polymers that hydrolyzed rapidly. Encouragement that improved polymer stability could be achieved was provided by model compound work that showed that the cyclic trimer of *p*-trimethylsilylphenylisocyanate possessed good hydrolytic stability.

These diisocyanate intermediates polymerized very readily with the N,N'-tetramethyl-1,3-butanediamine/allyl glycidyl ether co-catalyst system. The disiloxane formed a hard glassy brittle polymer, but the tetrasiloxane polymer shown below was a tough plastic. This change was sufficiently large to indicate that a further small extension of the siloxane chain segment might give the desired properties.



This polyisocyanurate had a tensile strength of 2000 psi with 13% elongation. When boiled for 24 hours in JP-4 fuel at 135°C the polymer swelled slightly and was found to have gained 30% by weight.

The torsional modulus versus temperature curve is shown in Figure 2. The thermal stability of the tetrasiloxane was not determined but the disiloxane showed slightly better thermal stability than the polymer containing the phenoxy-silicon linkage discussed earlier (Figure 3).

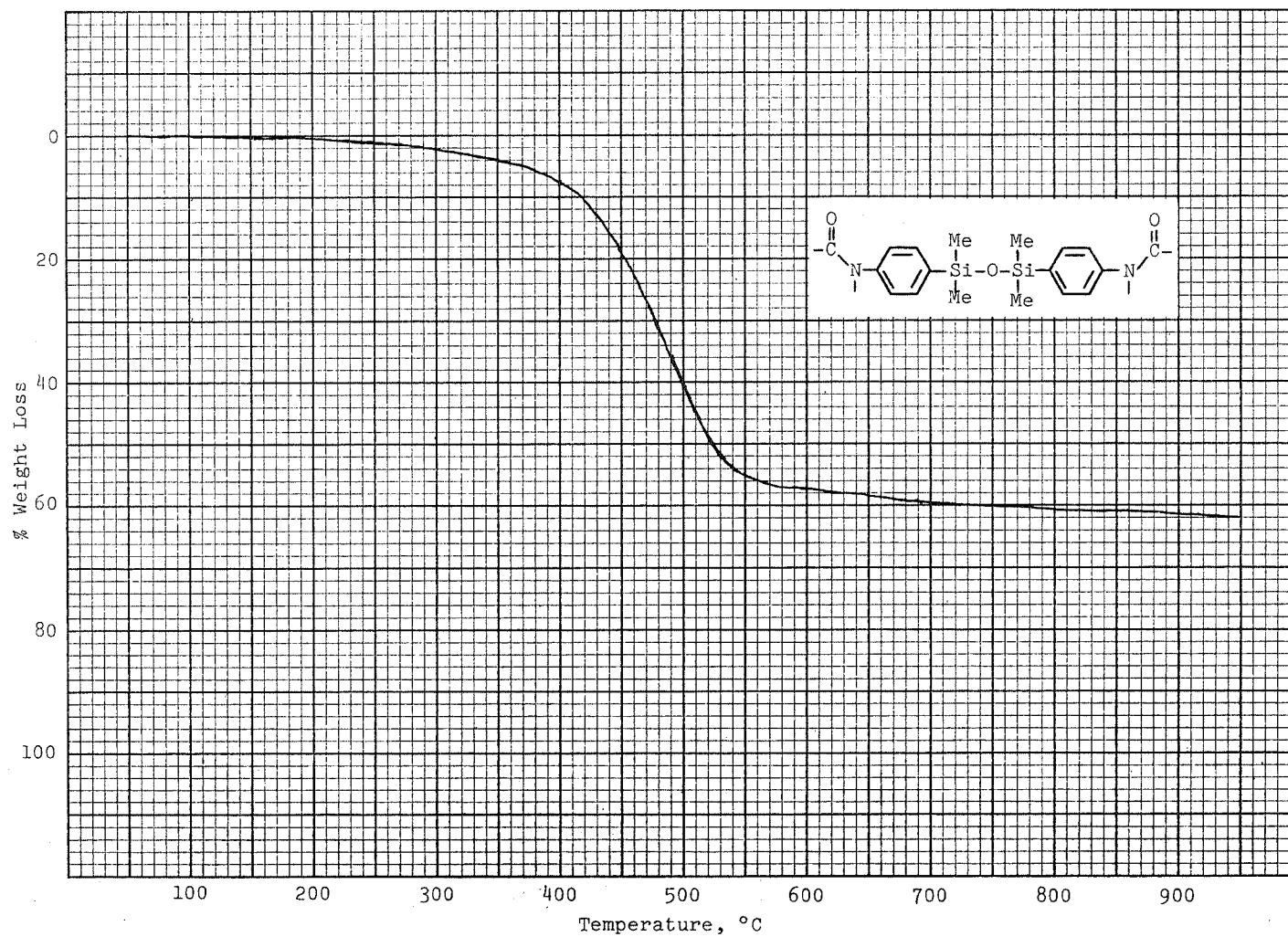
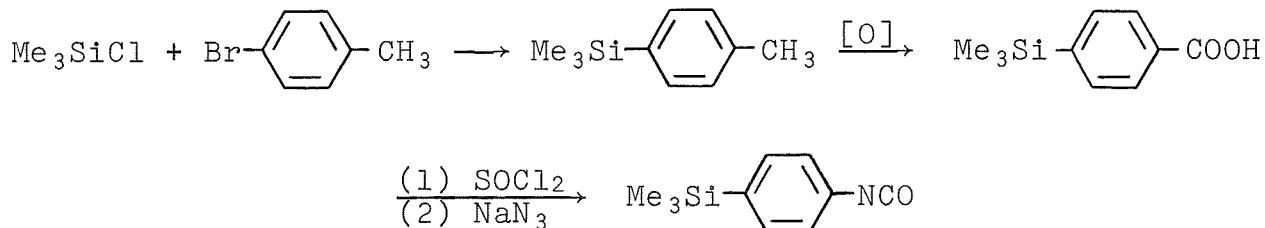
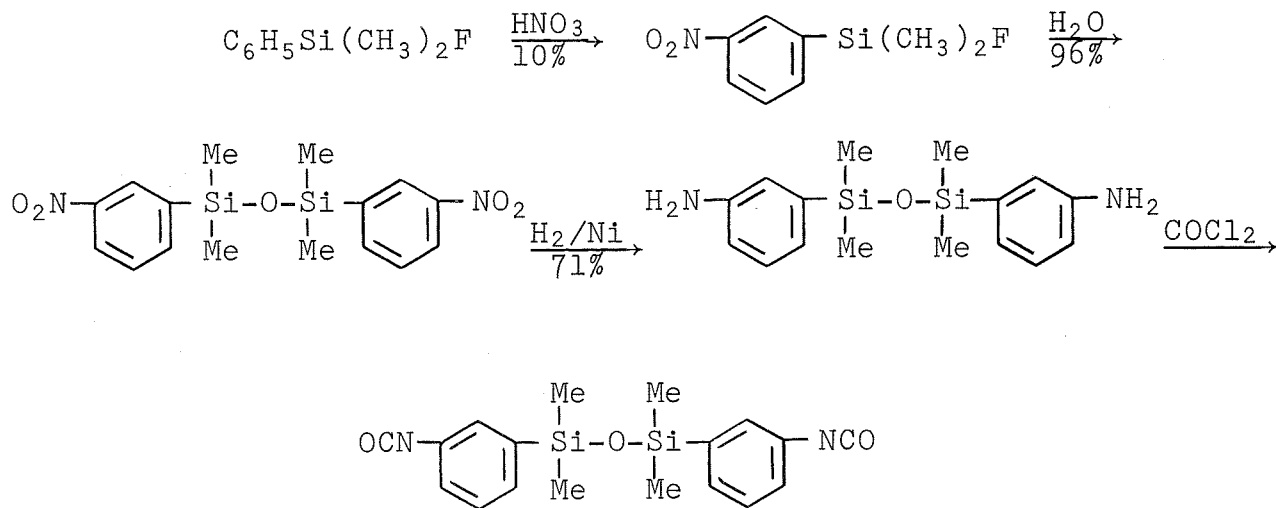


Figure 3. Thermogravimetric Analysis of Isocyanurate Polymers from Isocyanatophenylsiloxane, Sample 109338-A, temperature heating rate 3°C/min, helium atmosphere

b. Isocyanate Intermediate Synthesis. For model compound studies, the monofunctional *p*-trimethylsilylphenyl isocyanate was prepared from *p*-trimethylsilylbenzoic acid by the method of Sakata and Hashimoto (Ref. 2).



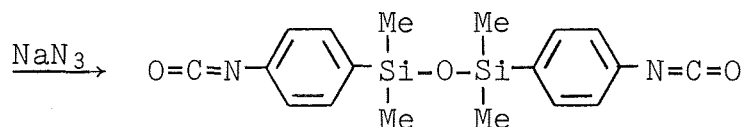
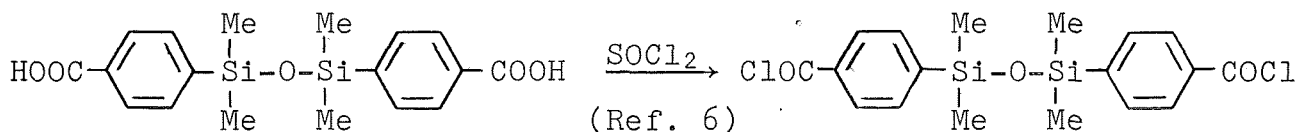
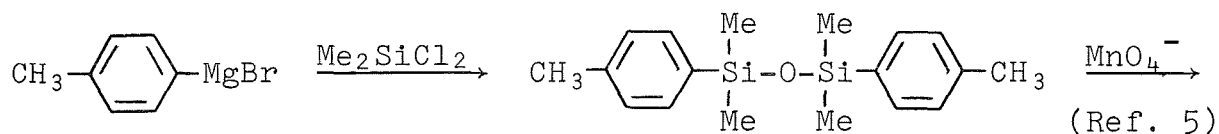
Three routes to difunctional isocyanatophenyl-terminated siloxanes were considered to be potentially applicable. The first route is outlined as follows:



Kuckertz (Ref. 3) has reported the synthesis of 3,3'-(tetramethyldisiloxanylene)dianiline by nitration of phenyldimethyl fluorosilane followed by hydrolysis and catalytic reduction.

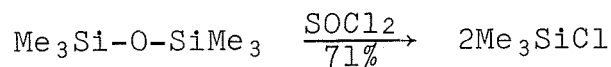
The major limitation appears to be the nitration, which gives a mixture of four products. Although the final step, phosgenation of 1,3-bis(*p*-aminophenyl)-1,1,3,3-tetramethyldisiloxane, to form the diisocyanate is reported to have been carried out in 70% yield (Ref. 4), cleavage of the phenyl group would appear to be a potential side reaction.

A second route involves the synthesis of 1,3-bis(*p*-tolyl)-1,1,3,3-tetramethyldisiloxane, oxidation to the dicarboxylic acid and conversion to the diisocyanate via the acid chloride and Curtius reactions as outlined below.



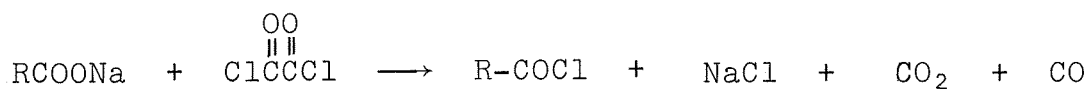
The 4,4'-(tetramethyldisiloxanylene)diphenyl isocyanate was prepared without difficulty by this second route using distilled acid chloride.

The satisfactory synthesis of the disiloxane acid chloride using thionyl chloride was somewhat surprising in view of the reported HCl-catalyzed reaction of thionyl chloride with hexamethyldisiloxane



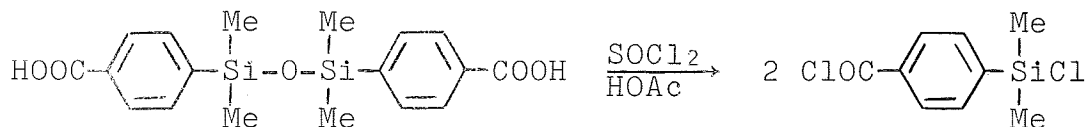
(Refs. 7 and 8) and possibility of phenyl-silicon bond cleavage under acidic conditions. The *para* carboxyl groups of tetramethyldisiloxanylenedibenzoic acid no doubt contribute to increased phenyl-silicon bond stability.

Until reference to work of Mal'nova and Mikheev was found, the use of thionyl chloride with the disiloxane was avoided because of the anticipated cleavage of the siloxane. The reaction of the sodium salt of the acid with oxalyl chloride as described by Adams and Ulich (Ref. 9) was employed to avoid formation of anhydrous hydrogen chloride.



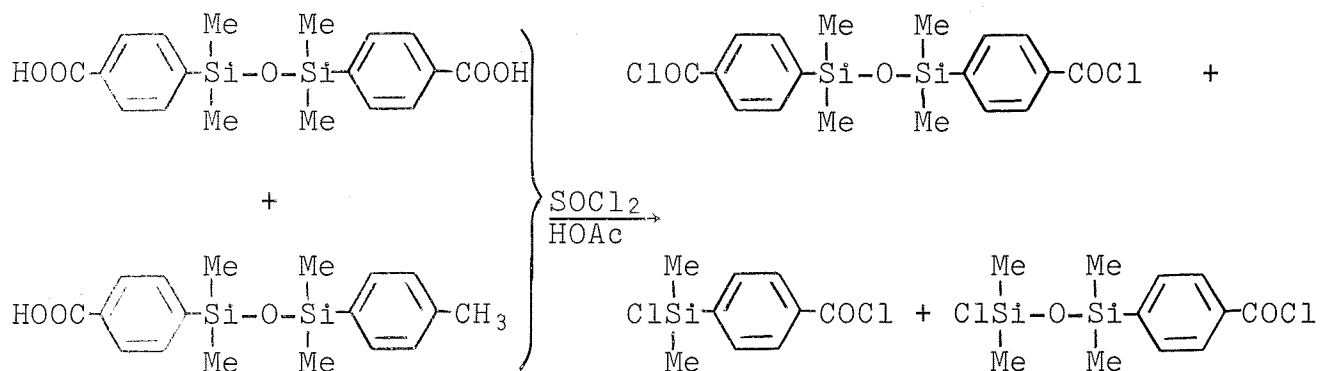
Attempts to convert the crude acid chloride to isocyanate, however, resulted in polymer formation upon attempted distillation.

Mal'nova and Mikheev reported that reaction of thionyl chloride with the diacid in the presence of a catalytic amount of acetic acid caused cleavage of the siloxane and formation of chlorodimethylsilylbenzoyl chloride (Ref. 6).



This conversion to chlorodimethylsilylbenzoyl chloride appeared to provide not only a convenient synthesis of this intermediate for subsequent conversion to higher siloxanes but also a method of eliminating unoxidized tolylsilane impurities by conversion to tolyldimethylchlorosilane which could be separated by distillation.

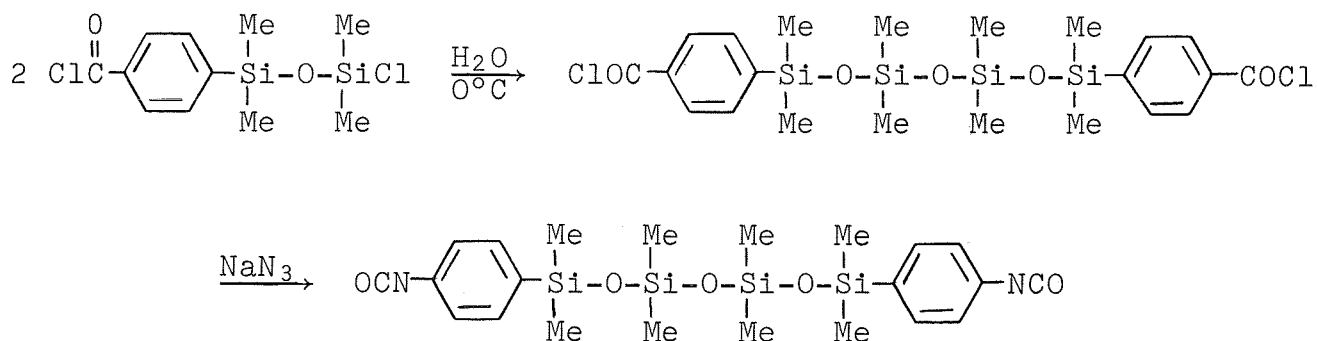
Treatment of crude 4,4-(tetramethyldisiloxanylene)dibenzoic acid with the thionyl chloride and acetic acid gave chlorodimethylsiloxydimethylsilylbenzoyl chloride in addition to chlorodimethylsilylbenzoyl chloride and diacid chloride.



Isolation of chlorodimethylsiloxydimethylsilylbenzoyl chloride suggests that the tolyl group was preferentially cleaved from the silicon, a conclusion not inconsistent with the stabilizing effect of the carbonyl substituted on the phenyl-silicon bond.

Possibly related to this effect was the observation that the specific refraction values found and calculated for the two liquid products did not agree within the normal limits of error. This disparity between observed and calculated molar refractions was attributed to an exaltation of the molar refraction by the *para* carbonyl chloride substituent, a physical manifestation analogous to the decreased chemical reactivity of the phenyl-silicon bond caused by a *para* carbonyl chloride substituent.

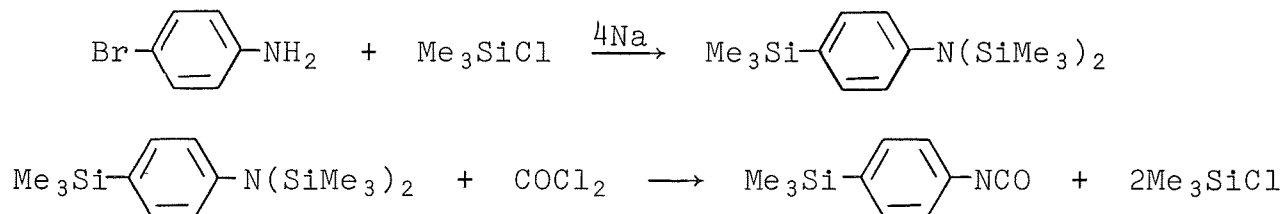
The isolation of *p*-(chlorodimethylsiloxydimethylsilyl)benzoyl chloride provided a convenient route to the tetrasiloxane intermediate through selective hydrolysis of the silicon chloride.



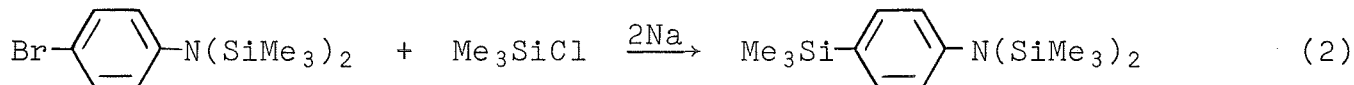
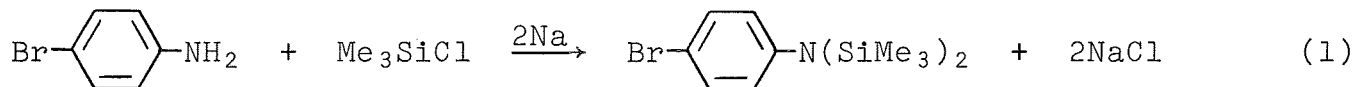
Subsequent reaction with sodium azide as in the previous experiments formed the diisocyanate.

Co-hydrolyses of chlorodimethylsilylbenzoyl chloride with dimethyl-dichlorosilane should form polysiloxanes also, but the success of this method will depend on reaction conditions and relative hydrolysis rates of the chlorosilanes. A trial hydrolysis of phenyldimethylchlorosilane with tetramethyldisiloxanediol, for example, gave a mixture of products that appeared to include cyclic dimethylsiloxanes as well as a mixture of phenyldimethylsilyl-terminated linear siloxanes.

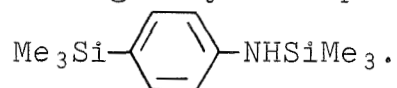
An effort was made to prepare the isocyanatophenylpolysiloxane intermediates by a third route considered to be potentially simpler than those described above. This route involved a sodium coupling of a chlorosilane with *p*-bromoaniline followed by direct conversion to the isocyanate with phosgene.



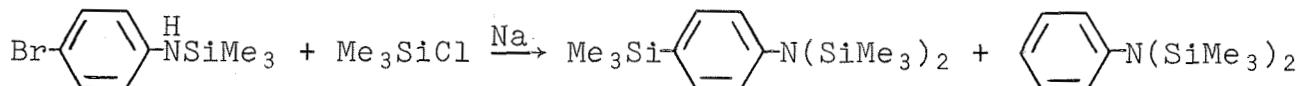
It was assumed that the disilylation of the amine hydrogens (Reaction 1) would precede the sodium coupling reaction (Reaction 2).



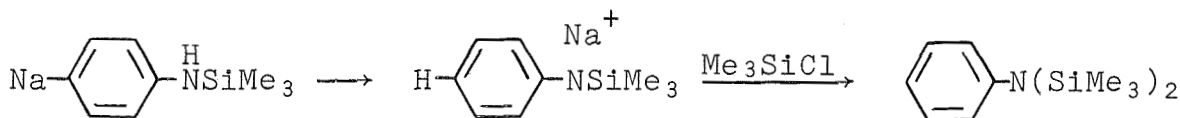
Attempts to carry out this reaction directly from bromaniline gave a mixture of close-boiling silylated products, $C_6H_5NHSiMe_3$, $C_6H_5N(SiMe_3)_2$ and



When *N*-trimethylsilylbromoaniline was employed as the starting material, the desired *p*-trimethylsilyl-*N,N*-bis(trimethylsilyl)aniline and by-product *N*-phenylhexamethyldisilazane were obtained.



Isolation of the latter suggests that the bromo substituent reacted with sodium to form the aryl sodium derivative, which immediately exchanged with the amine hydrogen, and was followed by silylation of the amine.

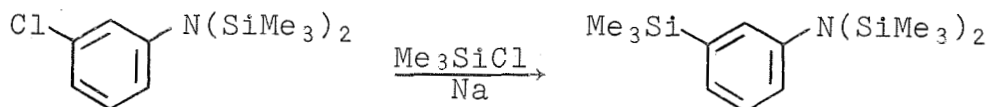


The feasibility of the conversion of the *N,N*-bis(trimethylsilyl)aniline intermediate to the isocyanate by reaction with phosgene as outlined above was demonstrated using the *N,N*-bis(trimethylsilyl)aniline that was isolated. Recovery of phenyl isocyanate and formation of trimethylchlorosilane upon treatment with phosgene proved the reaction shown below.



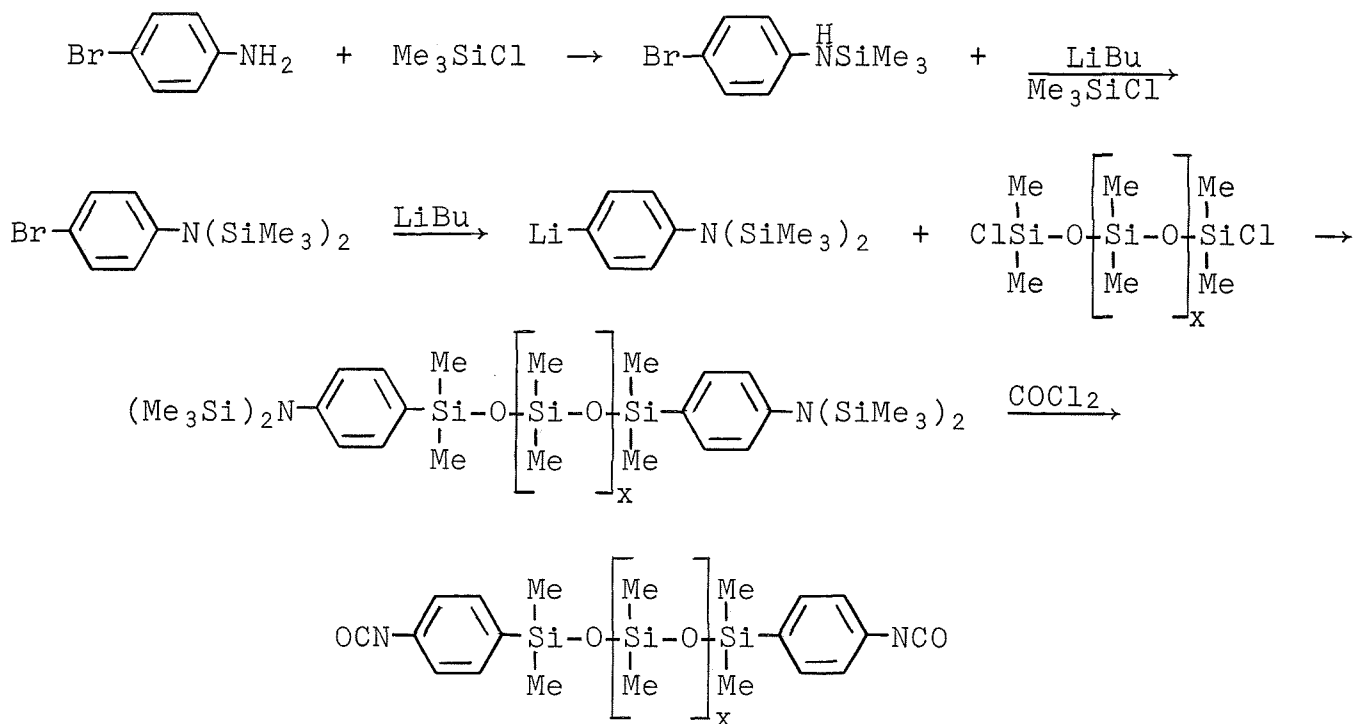
This reaction, phosgenation of a disilylamine, avoids the elimination of anhydrous HCl, and may prove useful in other isocyanate syntheses.

The sodium coupling of *m*-chlorophenylhexamethyldisilazane with trimethylchlorosilane was recently found to have been reported by Walton (Ref. 10) who obtained *N,N*-bis(trimethylsilyl)-*m*-trimethylsilylaniline in 73% yield.



The preparation of *N*-(*p*-lithiophenyl)hexamethyldisilazane from *p*-bromoaniline, as described by Walton, followed by coupling with α,ω -dichloropolysiloxane and then phosgenation should provide a

reasonably straightforward synthesis of the desired polysiloxane diisocyanates.

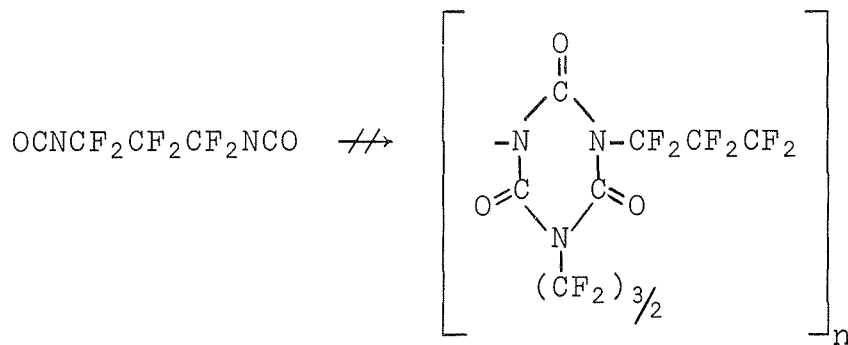


B. ISOCYANURATE-LINKED FLUOROPOLYMERS

The principal objective of the second approach was to determine the feasibility of linking fluoropolymer prepolymer segments through isocyanurate ring formation.

Isocyanate-capped short chain fluorocarbon prepolymers of two types have been prepared - with and without phenylene groups interposed between the isocyanate end groups and the fluoropolymer segments. The latter isocyanatophenyl capped prepolymers were found to trimerize satisfactorily whereas the fluoroalkyl isocyanates would not trimerize under the catalyst conditions examined. The greatest effort was therefore expended on the isocyanatophenyl capped polymers.

1. Perfluoroalkyldiisocyanates. Attempts to trimerize hexafluorotrimethylene diisocyanate with highly active catalyst/cocatalyst systems did not yield isocyanurate polymer.

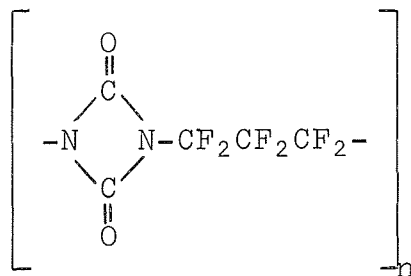


trimer

Triethylenediamine (DABCO), a solid catalyst, was insoluble in the monomer. The DABCO appeared to become encapsulated by insoluble polymer that may have prevented further polymerization. Tetramethylbutanediamine, a liquid catalyst, was also incompatible with the monomer and no polymer was obtained. The normally highly effective cocatalyst, allyl glycidyl ether, was used in both cases.

In further polymerization attempts using a solvent for the catalyst, greater compatibility of the amine with diisocyanate was achieved. Some solid formation was noted in solution polymerization attempts with the catalyst system shown in Table 2.

The small amount of product (<25%) obtained in this manner in the presence of a DABCO/allyl glycidyl ether cocatalyst system (Ref. 11) appeared by infrared spectral analysis and low melting temperature (81°C) to be a mixture of unreacted isocyanate and a thermally unstable dimer rather than the desired stable trimer.



dimer

Trimerization catalysts that showed no apparent polymer or other solid product formation are shown in Table 3. These systems, which have been reported in other work to be effective for the isocyanate-to-isocyanurate conversion, were ineffective with the perfluoroaliphatic isocyanates.

Table 2

SYSTEMS SHOWING POSSIBLE POLYMERIZATION
OF HEXAFLUOROTRIMETHYLENE DIISOCYANATE, 48 HRS AT 100°C

<u>Code</u>	<u>Catalyst^a</u>	<u>Appearance of Insoluble Product^c</u>	<u>Reference</u>
99870	DABCO/AGE ^b	1/4" light brown plug	11,12
99882	DABCO/AGE	1/2" brown plug, much clear gel on walls	11,12
99871	DABCO/AGE/SnBu ₂ (OAc) ₂	1/4" white opaque plug	13
99881	dimethylacetamide	1" brown plug	14
99874	calcium octoate	1/2" brown plug	--

^a3 Mole percent catalyst and cocatalyst concentration, based on isocyanate, unless otherwise indicated

^bDABCO = triethylene diamine

AGE = allyl glycidyl ether

^cIsocyanate monomer alone filled tube approximately 1.5 inches; 2x volume benzene was then added

Table 3

SYSTEMS SHOWING NO OR VERY SLIGHT POLYMERIZATION
OF HEXAFLUOROTRIMETHYLENE DIISOCYANATE, 48 HRS at 100°C

<u>Code</u>	<u>Catalyst^a</u>	<u>Comments</u>	<u>Reference</u>
99873	NaOCH ₃	no change in appearance, NaOCH ₃ insoluble	15
99875	LiC ₄ H ₉	very slight brown plug	16
99872	(C ₄ H ₉) ₃ SbO	clear, colorless solution	17
99876	C ₃ F ₇ CO ₂ H/DABCO	very slight precipitate, slight gel on walls, slight tar on walls	--
99880	DABCO/AGE ^b (DMAc solvent)	dark brown opaque solution	11,12
99886	pyridine acetate	very slight solid formation, no viscosity increase	--

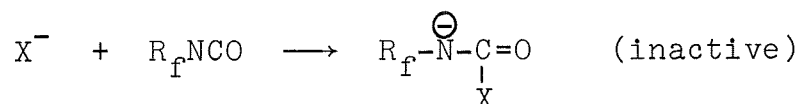
^a3 Mole percent catalyst concentration, based on isocyanate

^bDABCO = triethylene diamine

AGE = allyl glycidyl ether

The activity of the DABCO/allyl glycidyl ether catalyst/co-catalyst system was established by polymerizing phenyl isocyanate under the same polymerization conditions. A good yield (over 60%) of cyclic trimer, showing an infrared spectrum with no isocyanate absorption and strong, sharp absorption characteristic and high melting point (m.p. 282-288°C) of phenyl isocyanurate (m.p. 284-285°C) was obtained.

The deactivation of the perfluoroalkyl isocyanates toward trimerization under anionic catalysis likely results from lowered reactivity of an intermediate species such as the following:

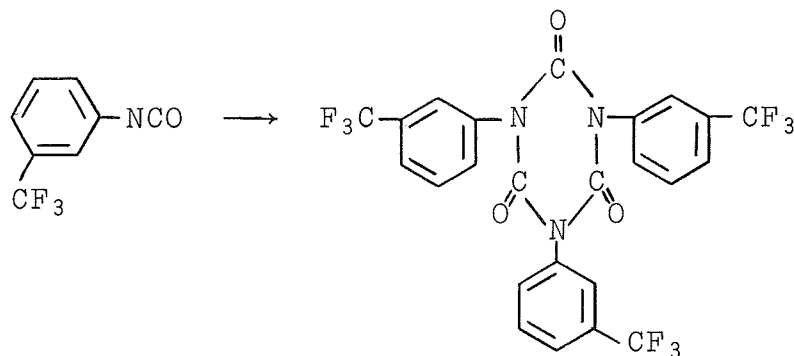


The strong electron-withdrawing character of the perfluoroalkyl group probably reduces the basicity of the anion sufficiently to inhibit further reaction with isocyanate. The failure of a large amount of isocyanurate formation to occur in a 1/1 mixture of the fluorodiisocyanate and phenyl isocyanate is consistent with this suggestion, particularly since phenyl isocyanate homotrimerized easily.

2. Perfluoroalkylaryldiisocyanates.

a. Model Compound Studies. Trimerization studies of a model perfluoroalkyl phenyl isocyanate showed that a phenylene group interposed between the fluoroaliphatic and isocyanate functions reduced the deactivating effect of the fluoroaliphatic group toward trimerization.

The melt trimerization of *m*-trifluoromethylphenyl isocyanate yielded tris(*m*-trifluoromethylphenyl) isocyanurate in the presence of 3 mole percent of tributylantimony oxide at room temperature. The melting range (200-203°C) and the infrared spectrum [bands at 1730 cm⁻¹(s), 758 cm⁻¹(s), and 700 cm⁻¹(s)] of the recrystallized product very closely resemble those of phenyl isocyanate trimer (Ref. 18). Also, the absence of bands at 3300 cm⁻¹ and 2275 cm⁻¹ indicate the absence of urethane, urea, or isocyanate functionality.



The same reaction was attempted using a DABCO (triethylene diamine) allyl glycidyl ether cocatalyst system. Some solid product was formed but an attempted recrystallization from ethanol yielded a syrup that showed IR adsorption characteristics of urethanes and/or ureas. On this basis, we believe that the initial solid formed was dimer.

A reasonably pure monomer was necessary before trimerization could occur. Residual acid chloride from which the isocyanate was synthesized was found to effectively inhibit the cyclization reaction.

b. Polymer Preparation and Characterization. In extending the model compound work to the preparation of polymers, isocyanatophenyl capped α,ω -hexafluoropropylene and α,ω -octafluorobutylene prepolymer intermediates were first prepared. The propylene intermediate was converted to polymer. The synthesis of the homologous tetrafluoroethylene diisocyanate could not be achieved. These fluoroalkyl segments were expected to be too short to impart elastomeric properties, but extension of this work to longer chain perfluoroalkyl and perfluoroalkyl-ether segments was planned after the synthesis procedure was established on more readily available systems.

The DABCO (triethylenediamine)/allyl glycidyl ether cocatalyst system was highly effective for polymerization of the propylene diisocyanate.

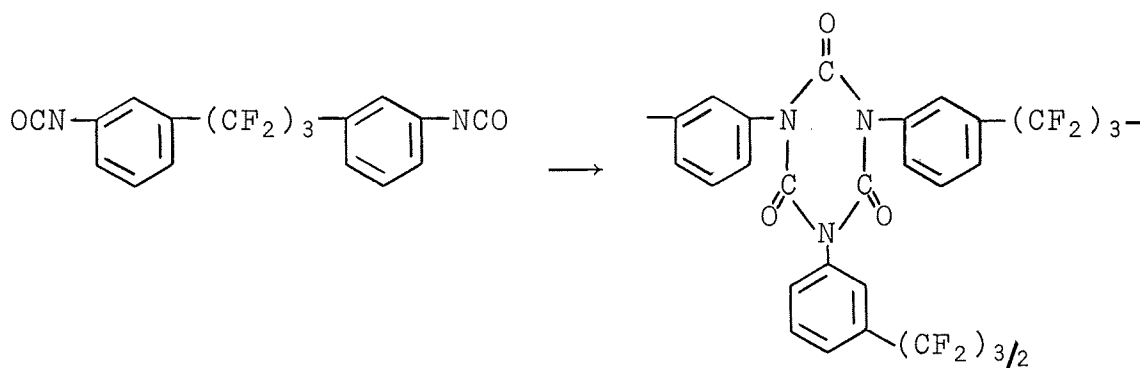
Isocyanurate formation occurred easily at room temperature by treating the isocyanate with 3 mole percent of DABCO (10% solution in benzene) followed by 3 mole percent of the allyl glycidyl ether. The solid polymers obtained were extremely hard and tough. The material softened around 260°C on a Fisher-Johns melting point apparatus but quickly regained its original shape after pressure-induced deformation. At 320°C, pressure applied with a laboratory spatula tore the specimen. During heating to 360°C and cooling to room temperature very little darkening of the sample occurred, although it seemed to be more brittle than before the heating cycle.

Infrared spectra confirmed that isocyanurate formation had indeed occurred but also indicated that trimerization was incomplete because a significant amount of free isocyanate was present. More complete reaction of the isocyanate group would be expected in longer chain diisocyanates that possess greater molecular flexibility.

Trimerization was also effected using solid DABCO with allyl glycidyl ether cocatalyst. The DABCO was dissolved in the liquid isocyanate before the ether was added. The mixture was allowed to stand 15 minutes at room temperature followed by 2 hours at 50°C,

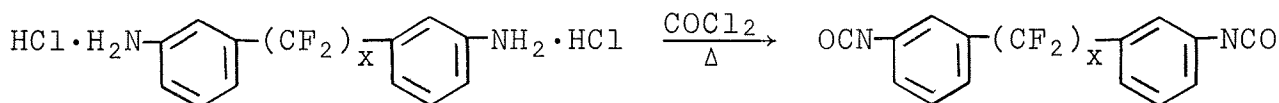
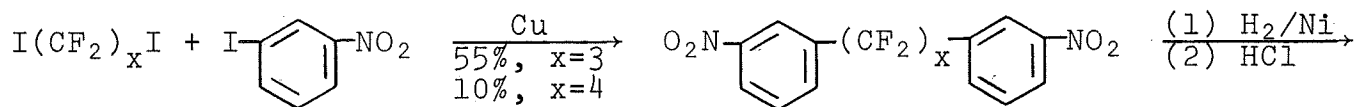
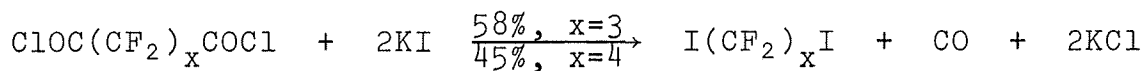
2 hours at 100°C, 2 hours at 195°C, and 2 hours at 250°C. A significant amount of isocyanate was still present after the 195°C cycle but had essentially disappeared after the 250°C cycle. The isocyanurate was again extremely hard and showed no change in weight or infrared absorption characteristics after being exposed to boiling water for 70 hours. Thermogravimetric analysis showed no weight loss up to 250°C (Figure 4).

Attempts to carry out the trimerization using tributylantimony oxide have been unsuccessful. The reaction is so rapid that encapsulation of the catalyst occurs, even at room temperature, and homogeneity of reaction is impossible. Solids obtained by this method were readily soluble in ethanol.



The small amount of the homologous perfluorobutylene diisocyanate prepared was not converted to polymer but would be expected to have properties very similar to those of the propylene derivative.

c. Isocyanate Intermediate Synthesis. The preparation of 1,3-di(*m*-isocyanatophenyl)hexafluoropropane and 1,4-di(*m*-isocyanatophenyl)octafluorobutane have been carried out by the following scheme. The yields obtained in the respective syntheses indicated following scheme.



>95%, x=3,4

90%, x=3,4

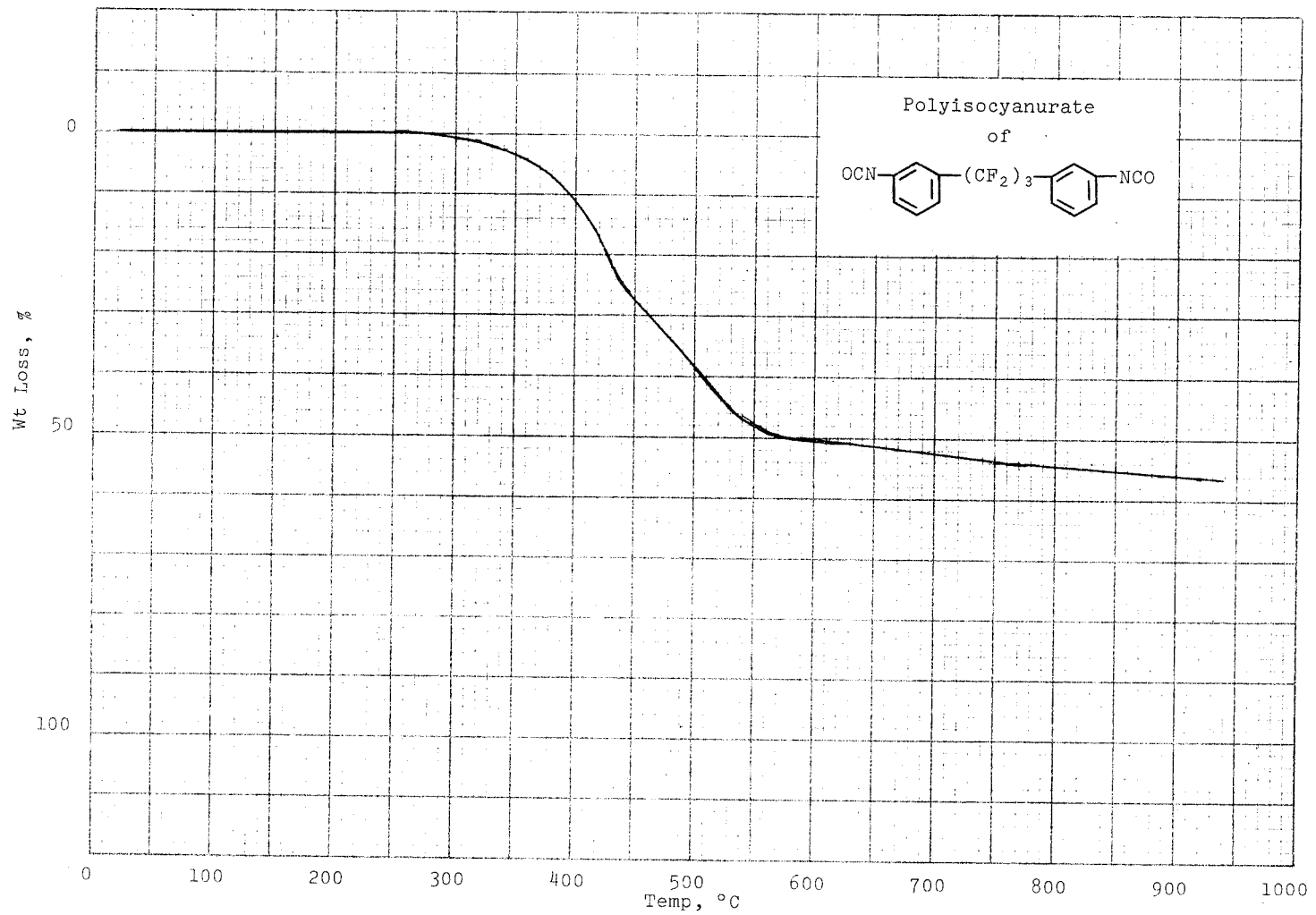
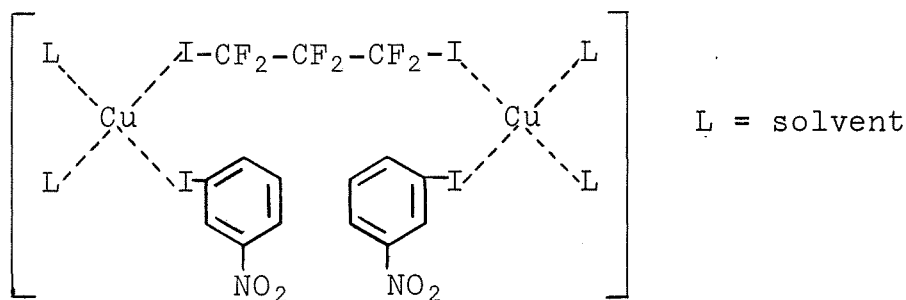


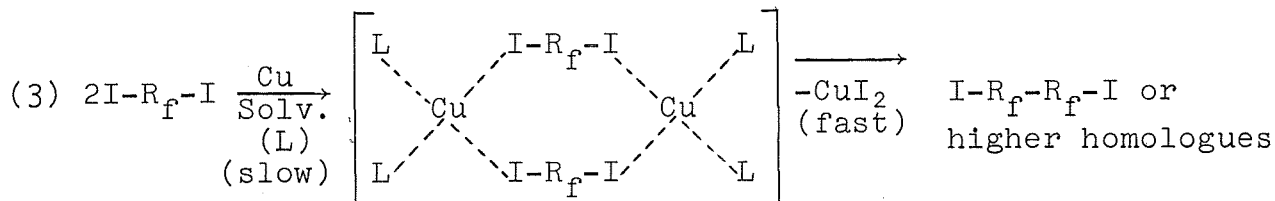
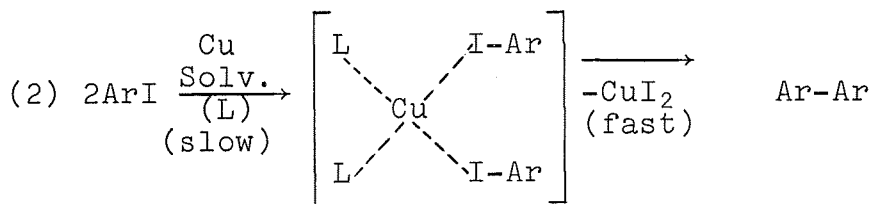
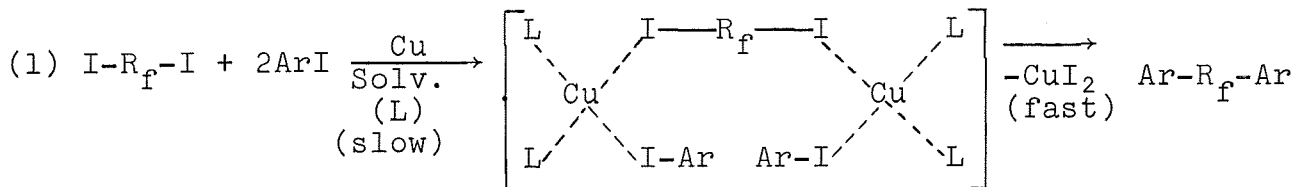
Figure 4. Thermogravimetric Analysis, Sample 113203-B, temperature heating rate 3°C/min, helium atmosphere

The critical step in this reaction sequence is the coupling between the perfluoroaliphatic diiodide and the aromatic iodide. Other work has indicated a higher yield for this coupling reaction using copper metal coupling rather than Grignard or other conventional coupling techniques.

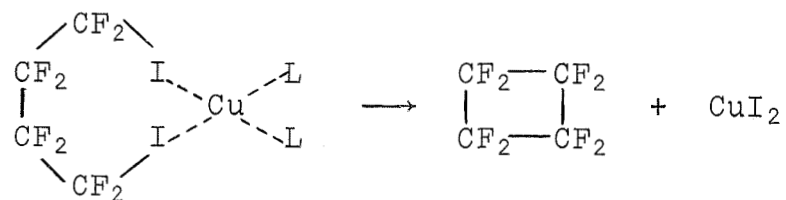
Experimental evidence indicates that the formation of a four-coordinated copper intermediate determines the rate and extent of conversion to the desired product.



The intermediate complexes believed to have the structures illustrated in equations 1, 2, and 3 are formed at temperatures below 100°C and are destroyed at temperatures above 115°C.

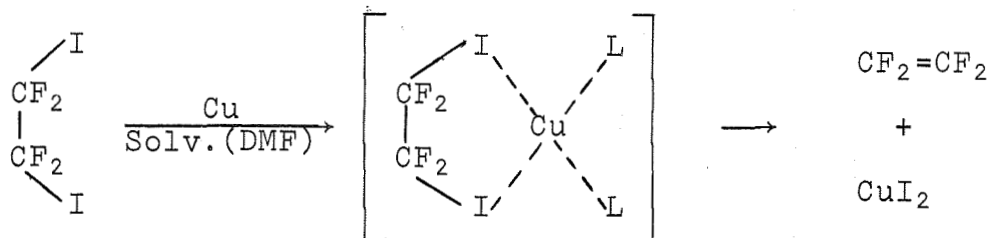


The poor coupling reaction yield utilizing the diiodobutane may possibly be explained by using the proposed copper intermediate model. Among possible side reactions that might compete to lower the yield of product, the most probable appears to be the formation of the relatively stable octafluorocyclobutane, as follows:



No attempt was made to recover the cyclobutane.

During the initial attempts at these coupling reactions, we had experienced no yield from 1,2-diodotetrafluoroethane where the formation of the stable tetrafluoroethylene ($\text{CF}_2=\text{CF}_2$) was possible by the intramolecular elimination of iodine.

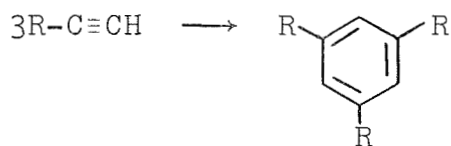


The coupling reaction with the larger chain (CF_2 units >4) diiodofluorocarbons is expected to proceed smoothly since no simple route to stable by-product formation exists (Ref. 19).

At all temperatures tested, the yield of coupled Ar-Ar product was highest, indicating reaction 2 was faster than reaction 1. Consequently, the formation of some biaryl is unavoidable. Reaction 3 is important only if the concentration of the aryl iodide is very low.

C. ACETYLENE TRIMERIZATION

1. Introduction. Cyclotrimerization of acetylene intermediates represents the third approach that was investigated in an attempt to develop thermally and chemically stable polymer linkages by means of addition reactions.



The literature contains many references to various acetylene polymerization reactions, and includes two comprehensive review papers (Refs. 20 and 21).

Under favorable conditions and with the proper catalysts, high yields of trisubstituted benzene compounds can be formed from terminal acetylenic compounds. The reaction is energetically very favorable but must be controlled by the catalyst to ensure formation of cyclic trimer rather than linear polymers. The variations in the products obtained as a function of catalysts and reaction conditions is shown by the results of phenylacetylene cyclotrimerization reported in the literature (Table 4).

Table 4

PHENYLACETYLENE CYCLOTRIMERIZATION

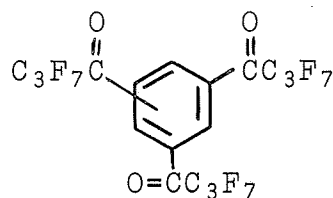
<u>Catalyst</u>	<u>Product</u>	<u>Reference</u>
$\text{Ni}(\text{CO})_2(\phi_3\text{P})_2$	35% linear trimer	22
$\text{Ni}(\text{CO})_2(\phi_3\text{P})_2$	20% 1,2,4-triphenylbenzene 1% 1,3,5-triphenylbenzene 50% linear trimer	22
$\text{NiCl}_2(\phi_3\text{P})_2 + \text{NaBH}_4$	50% triphenylbenzene	23
$\text{Hg}[\text{Co}(\text{CO})_4]_2$	70% 1,2,4-triphenylbenzene	24
$\text{R}_3\text{Al}/\text{TiCl}_4$	90% 1,3,5-triphenylbenzene 1,2,4-triphenylbenzene	25, 26

Probably the most effective and most specific catalyst for trimerization of many acetylene compounds is the Ziegler type aluminum alkyl/titanium tetrachloride complex. The fact that the acetylene trimerization reactions occur under mild conditions forming highly stable substituted benzene products makes them potentially useful for the cure-in-place sealant application. The efficacy of this potential coupling reaction depends largely upon developing a suitable catalyst system.

The first objective was to determine the feasibility of linking fluorocarbon chain segments through an acetylenic trimerization reaction. To do this, the synthesis of a simple fluorocarbon acetylenic compound was undertaken. Perfluoropropyl ethynyl ketone was chosen as a model compound because of the ease with which methyl ethynyl ketone (1-butyne-2-one) was reported to trimerize with seemingly innocuous materials such as piperidine acetate (Ref. 27).

Difficulties in the synthesis of the desired ketone led to a search for an alternate model monomer system. The synthesis of a perfluoroalkyl acetylene derivative was therefore initiated near the end of the current work. Success with the model compound was to be followed by preparation of difunctional acetylenic compounds.

2. Cyclotrimerization of Model Acetylenic Compounds. A model compound, perfluoropropyl ethynyl ketone, was prepared from sodium acetylide and perfluorobutyric anhydride in 30% yield after several unsuccessful attempts by other methods. The compound is relatively unstable. Trimerization appeared (by NMR analysis) to take place with several catalysts, yet was often incomplete. It was not until mercury bis(cobalt tetracarbonyl) catalyst was employed that complete conversion to what appeared to be a mixture of linear and cyclic products was obtained. Approximately 40% of the product was isolated by distillation and shown unequivocally to be the cyclic trimer,



Vapor phase chromatography showed a major and minor component, possibly representing the 1,2,4 and 1,3,5 isomers.

The effectiveness of various polymerization catalysts was determined by comparing the polymerization of phenylacetylene with results shown in published data. Both the mercury bis(cobalt octacarbonyl) and Ziegler type catalysts gave results comparable with published data. These results are summarized in Table 5.

The difficulty in synthesis, questionable stability, and difficulty in cyclotrimerizing the acetylenic ketone prompted investigation of a perfluoroalkyl acetylene. Although a small quantity of perfluoroheptyl acetylene (3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-pentadecafluoro-1-nonyne) was prepared, the results of a single attempt to polymerize this product were inconclusive.

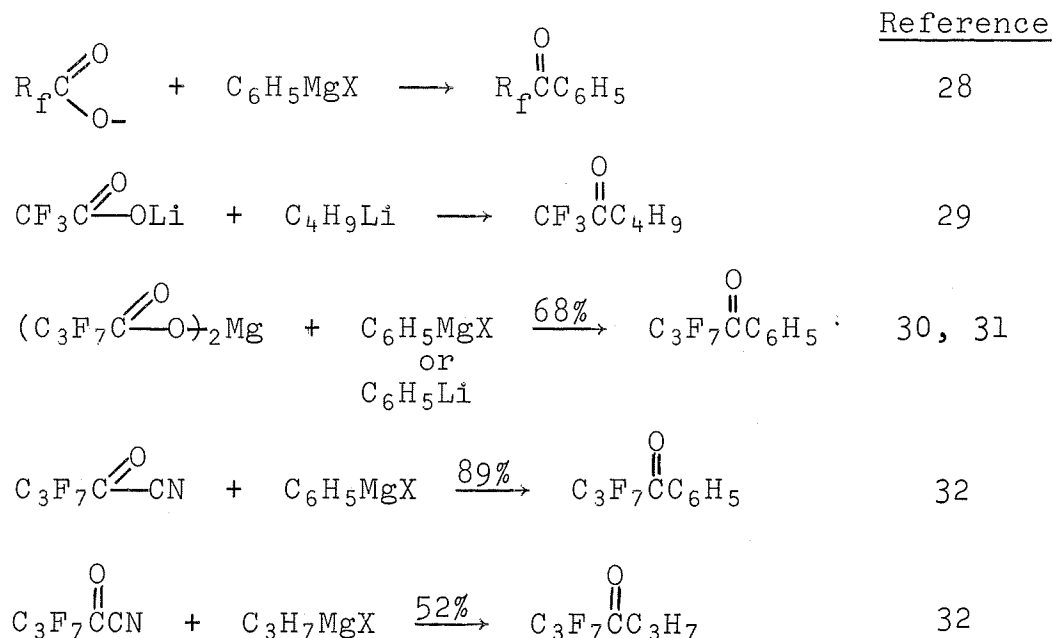
3. Synthesis.

a. Perfluoropropyl Ethynyl Ketone. Although no acetylenic perfluoroalkyl ketones have been reported in the literature, both perfluoro (alkyl and aryl) ketones and acetylenic ketones are known. Perfluoroalkyl substituted ketones have been prepared by reactions of organometallic intermediates (Refs. 28, 29, 30, 31, and 32) with perfluoroaliphatic acids, salts and esters and nitriles.

Table 5

ACETYLENIC POLYMERIZATIONS

<u>NBP</u>	<u>Acetylene Compound</u>	<u>Catalyst</u>	<u>Solvent</u>	<u>Time, hr</u>	<u>Temp., °C</u>	<u>Results</u>
100303	C ₃ F ₇ COC≡CH	pyr. acetate	benzene	18	25	dark, viscous residue
100324	C ₃ F ₇ COC≡CH	pyr. acetate	benzene	1	80	recovered ketone and brittle solid residue
91520	C ₃ F ₇ COC≡CH	pyr. acetate	benzene	16	70	exothermic evidence of aromatic compound
91517	C ₃ F ₇ COC≡CH	Ni(CO) ₂ (φ ₃ P) ₂	benzene	1 1	45 70	dark, viscous residue
91543	C ₃ F ₇ COC≡CH	Hg[Co(CO) ₄] ₂	dioxane	16	100	~40%(C ₃ F ₇ CO) ₃ C ₆ H ₃ + solid product
100306	C ₆ H ₅ C≡CH	pyr. acetate	benzene	16	70	no reaction
91538	C ₆ H ₅ C≡CH	Hg[Co(CO) ₄] ₂	dioxane	1	40-105	exothermic 60 yield (C ₆ H ₅) ₃ C ₆ H ₃
111705	C ₆ H ₅ C≡CH	Al(iBu) ₃ TiCl ₄	hexane	0.5 16	50-80 25	exothermic, 1,3,5 (C ₆ H ₃) ₃ C ₆ H ₃ and 1,2,4 (C ₆ H ₅) ₃ C ₆ H ₃
111704	C ₇ F ₁₅ C≡CH	Al(iBu) TiCl ₄	hexane	16	25	slight exotherm, in- conclusive



In all of these reactions, the perfluoroalkyl group stabilizes the ketonic intermediate thereby inhibiting formation of tertiary alcohol, the usual product of such reactions.

Acetylenic ketones have been prepared through ethynyl organometallics (magnesium, sodium, and lithium derivatives) that react with aliphatic and aromatic acid halides, anhydrides and esters to form acetylenic ketones (Refs. 33, 34 and 35).

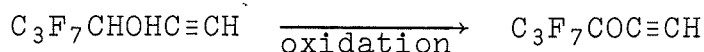
Ketone products rather than tertiary alcohols are formed because of the decreased reactivity of the acetylenic organometallic intermediates in comparison with the analogous aliphatic reagents.

Initial attempts to apply these reactions to the synthesis of perfluoropropyl ethynyl ketone were not successful. Several experiments did show evidence of acetylenic, fluorine-containing products boiling higher than expected for perfluoropropyl ethynyl ketones, although specific products were often not isolated and identified. Separation of pure products by distillation was hampered in several instances by formation of a complex between the perfluoro products and tetrahydrofuran. Recovered perfluorobutyric acid and tetrahydrofuran, for example, formed a complex boiling higher than either component. A fraction considered to be a complex or azeotrope of perfluoropropyl diethynylcarbinol and tetrahydrofuran was also isolated.

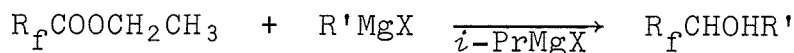
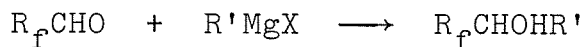
Heptafluoropropyl ethynyl ketone was finally synthesized by reaction of perfluorobutyric anhydride with sodium acetylide. Isolation of this product in the subsequent experiments was also hindered

by the chemical reactivity of the compound. The compound was obtained by rapid distillation of the more volatile portion of the reaction mixture under vacuum and without heating. Subsequent redistillation of this product mixture caused a portion of the product to polymerize and form higher boiling residues. These experiments are summarized in Table 6.

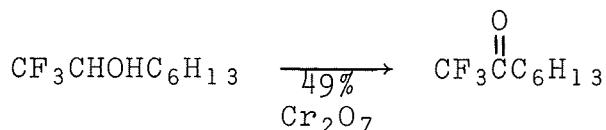
An alternate approach to the synthesis of $C_3F_7COC\equiv CH$, the oxidation of the corresponding secondary alcohol to the ketone, was also investigated briefly.



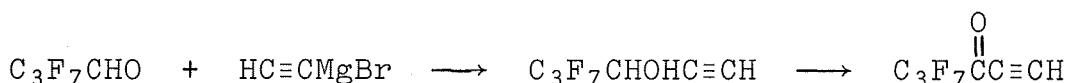
The formation of a secondary alcohol in good yield by reaction of a Grignard with a fluorinated aldehyde or even an ester is fairly well established (Refs. 36 and 37).



Conversions of secondary acetylenic alcohols and secondary fluoroalcohols to ketones have been reported (Refs. 35, 38 and 39).



The applicability of these reactions to an acetylenic fluoroalcohol was considered to have a high probability of success.



A reasonably good yield (63%) of carbinol was obtained in the first step shown above although the distilled product contained tetrahydrofuran in approximately 1 part to 2 of carbinol. Whether this resulted from an azeotrope or a molecular complex was not determined.

A single oxidation attempt showed evidence (by IR) of the perfluoropropyl ethynyl ketone formation but most of the alcohol was recovered unreacted.

b. Perfluoroheptylacetylene. Synthesis of a perfluoroalkyne model compound was investigated because of the difficulties associated with the ethynyl ketone synthesis. Synthesis of 3,3,3-trifluoropropyne by the following route has been reported (Ref. 40).

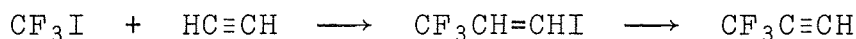


Table 6

REACTIONS OF ACETYLENIC ORGANOMETALLICS
WITH PERFLUOROBUTYRIC ACID DERIVATIVES

NBP	Reactants ¹		Time, hr	Temp., °C	Results
	A	B			
91487	HC≡CMgBr 0.15	(C ₃ F ₇ COO) ₂ Mg 0.075	0.5 18	-25 25	~30% recovered C ₃ F ₇ COOH
91494	HC≡CMgBr 0.2	C ₃ F ₇ COOMgBr 0.12	0.5	-10-0	~50% recovered C ₃ F ₇ COOH as THF·C ₃ F ₇ COOH complex
91490	HC≡CMgBr 0.2	C ₃ F ₇ COCl 0.14	0.5 0.5	10-15 25	30% C ₃ F ₇ COH(C≡CH) ₂ IR shows C≡CH, C-F in residue
100261-1	HC≡CMgBr 0.1	C ₃ F ₇ COOCH ₃ 0.1	1.5 1.5	-20 25	>60% recovered C ₃ F ₇ COOH IR shows C≡CH, C=O, C-F in residue
100261-2	HC≡CMgBr 0.1	C ₃ F ₇ COOCH ₃ 0.1	1.5 1.0	20 25	>65% recovered C ₃ F ₇ COOH IR shows C≡CH, C=O, C-F in residue
91498	NaC≡CH 0.15	C ₃ F ₇ COCl 0.12	0.5 1.0	-20 25	Solid, non-volatile residue IR shows C≡CH, C=O, C-F
91500	NaC≡CH ~0.14	C ₃ F ₇ COOLi 0.11	1.0 18	-20 25	90% recovered C ₃ F ₇ COOH
100266	LiC≡CH 0.166	C ₃ F ₇ COCl 0.175	1.5 1.5	-20 25	IR shows C≡CH, C=O, C-F in residue and in high boiling distillate
100278	NaC≡CH 0.2	(C ₃ F ₇ CO) ₂ O 0.2	2.0	25	IR suggests -C≡CH containing esters
100282	NaC≡CH 0.2	(C ₃ F ₇ CO) ₂ O 0.2	0.5	20	27% C ₃ F ₇ COOC(C≡CH) ₂ C ₃ F ₇
100287	NaC≡CH 0.19	(C ₃ F ₇ CO) ₂ O 0.19	0.5 1.0	15-20	C ₃ F ₇ ^O CC≡CH trace + C ₃ F ₇ COOC(C≡CH) ₂ C ₃ F ₇
100291	NaC≡CH 0.21	(C ₃ F ₇ CO) ₂ O 0.19	0.5 1.5	-15-20 20	22% C ₃ F ₇ COC≡CH + C ₃ F ₇ COOC(C≡CH) ₂ C ₃ F ₇
100315	NaC≡CH 1.13	(C ₃ F ₇ CO) ₂ O 1.13	4.0	-50-5	32% C ₃ F ₇ COC≡CH 14% C ₃ F ₇ COCC ₃ F ₇ (C≡CH) ₂

¹Reactant A added to B except 91490, 100261-2 and 100282 where B added to A

Two unsuccessful attempts were made to add pentadecafluoroheptyl iodide to acetylene with pressures at or slightly above atmospheric pressure with azodiisobutyronitrile as catalyst. Brace, for example, reported 88% yield of adduct at 50°C in the addition of $C_7F_{15}I$ to an acetylenic acid (Ref. 41). The lack of success of this addition to acetylene was considered to be largely a matter of low acetylene pressure. Low pressure was employed to avoid conditions that can lead to a spontaneous acetylene detonation reaction. By employing thermal activation at 165°C at a pressure of 75 psi, a 59% yield of the adduct 3,3,4,4,5,5,6,6,7,7-8,8,9,9,9-pentadecafluoro-1-iodononene was obtained. Dehydroiodination over anhydrous potassium hydroxide gave a low yield of the acetylene compound. Formation of non-volatile brown residue suggested that polymerization also occurred.

IV. EXPERIMENTAL

A. ISOCYANURATE-LINKED SILOXANES

1. Isocyanatophenoxy siloxane Intermediates and Polymers.

1,3-Bis(3-aminophenoxy)tetramethyldisiloxane (95246). A solution of 1,3-dichlorotetramethyldisiloxane (345 g, 1.7 moles) in ether was added over 2 hours to a slurry of 3-aminophenol (372 g, 3.4 moles) in 2500 ml of ether. The mixture was refluxed for 3 hours. Anhydrous ammonia was passed into the mixture to liberate the free amine. Filtration followed by distillation afforded a 75% yield (448 g) of 1,3-bis(3-aminophenoxy)tetramethyldisiloxane b.p. 182°/0.2 mm, n_D^{25} 1.5473.

1,5-Bis(3-aminophenoxy)hexamethyltrisiloxane (95239). Reaction of 3-aminophenol (79 g, 0.722 mole) with 1,5-dichlorohexamethyltrisiloxane (100 g, 0.361 mole) in the manner described above gave 84 g (55% yield) of the diamine, b.p. 185°/0.12 mm, n_D^{25} 1.5213.

1,3-Bis(3-isocyanatophenoxy)tetramethyldisiloxane (95236). 1,3-Bis(3-aminophenoxy)tetramethyldisiloxane (38 g, 0.109 mole) was added to a mixture of phosgene (69 g, 0.69 mole) and pyridine (38 g, 0.5 mole) in ether at -50°. After warming to 25° and stirring for an additional 3 hours, the mixture was filtered and the filtrate was distilled. A 69% yield of 1,3-bis(3-isocyanatophenoxy)tetramethyldisiloxane, b.p. 154-156°/0.1 mm, n_D^{25} 1.5212, was obtained. Isocyanate equivalent 205, calcd 200.2.

1,5-Bis(3-isocyanatophenoxy)hexamethyltrisiloxane (95242). 1,5-Bis(3-aminophenoxy)hexamethyltrisiloxane (84 g, 0.2 moles) was added to a mixture of pyridine (71.5 g) and phosgene (125 g, 1.27 moles) at -50°. The mixture was allowed to warm to 25° overnight. Distillation, after removal of pyridine hydrochloride by filtration, gave an 82% yield of 1,5-bis(3-isocyanatophenoxy)hexamethyltrisiloxane, b.p. 170°/0.1 mm, n_D^{25} 1.5013. Isocyanate equivalents 239 and 242, calcd 237.

Hexamethylcyclotrisiloxane (109336). Dow Corning 200 fluid (300 g) was decomposed by heating to 400-420°C. The liquid that distilled was redistilled to give 107.9 g (36% yield) of hexamethylcyclotrisiloxane, b.p. 136°C/740 mm.

Isocyanatophenoxy siloxane Mixture by Siloxane Equilibration (100251). A mixture of hexamethylcyclotrisiloxane (67 g, 0.3 moles) and 1,3-bis(3-aminophenoxy)tetramethyldisiloxane (35 g, 0.1 moles) and ~0.1 g cesium hydroxide was stirred and heated at 140° under nitrogen. After

refluxing a few hours, 0.1 g of potassium hydroxide was added. After 16 hours the temperature had risen to 185°. The mixture was cooled, diluted with ether, washed with water (4 x 100 ml) and dried over MgSO₄. Volatiles were removed at 150° and 0.1 mm pressure leaving 87.6 g of oil. The residue was treated with phosgene and pyridine as described in previous experiments. Volatiles were removed by heating to 185° at 0.15 mm pressure to give 85 g of a liquid having an isocyanate equivalent of 597. A 63 g portion of the crude siloxane diisocyanate intermediate was passed through a Roto Film molecular still at 150° and a pressure of 0.02 mm. Distillate weighing 13.3 (equiv. weight of 291) and 46 g of residue (equiv. weight 868) were recovered.

Polymers from Isocyanatophenoxy siloxane Mixture (100251). A 20 g portion of the above intermediate prepared by siloxane equilibration (NCO equivalent 597) was mixed with 0.2 g of allyloxy-2,3-epoxypropane and 0.2 g tetramethylbutanediamine, degassed and poured into a sheet mold. After heating 86 hrs at 100° a bubble free sheet of a soft, cheesy polymer was obtained. The material softened and became sticky upon prolonged atmospheric exposure. Polymerization of the distillate with equivalent weight of 868 gave a tough, flexible sheet having a tensile strength of 260 psi with 60% elongation.

Hydrolysis of 1,3-Bis(*m*-isocyanatophenoxy)tetramethyldisiloxane Polymer (91521). A 3.71 g sample of polymer prepared from 1,3-bis-(*m*-isocyanatophenoxy)tetramethyldisiloxane, disintegrated within two hours upon boiling in water. The aqueous mixture was extracted with ether. Upon evaporation of the ether, 2.6 g of yellow solid remained. The aqueous phase gave 0.25 g of solid upon evaporation to dryness. Sublimation of this solid gave white crystals melting 117-120°C (*m*-aminophenol m.p. 122°C). The ether-extracted solid was pulverized and washed with ether. The residue was dissolved in alkaline solution and reprecipitated with acid. Recrystallization from water raised the melting point from 224-226°C to 225.5 to 226.5°C (Lit. 222°C, Ref. 42). This solid was identified as *N,N'*-bis(*m*-hydroxyphenyl)urea by an undepressed mixed melting point with an authentic sample prepared from *m*-aminophenol and phosgene. A hexane-soluble oil isolated from the ether extract was identified by its infrared spectrum as a dimethyl silicone.

m-Trimethylsiloxyaniline (100289). An ether solution of trimethylchlorosilane (108.5 g, 1.0 mole) was added over a period of two hrs to a stirred ether slurry of *m*-aminophenol (109 g, 1.0 mole). Anhydrous ammonia was passed into the white slurry for two hours. Solids were removed by filtration. Distillation of the ether solution afforded 137 g (66% yield) of *m*-trimethylsiloxyaniline, b.p. 75°C/0.25 mm, n_D^{25} 1.5211.

m-Trimethylsiloxyphenyl Isocyanate (100293). Phosgene (198 g, 1.98 moles) was condensed in 1500 ml ether at -50°C . Pyridine (113 g, 1.43 moles) was then added to the phosgene solution. *m*-Trimethylsiloxyaniline in ether was added dropwise over 90 minutes to the pyridine-phosgene solution at -20°C . After stirring overnight the mixture was filtered and distilled to give 91.5 g (62% yield) of *m*-trimethylsiloxyphenyl isocyanate, b.p. $85^{\circ}\text{C}/5\text{ mm}$, n_{D}^{25} 1.5007, isocyanate equiv.: found 210, calcd 207.3

Tris(*m*-Trimethylsiloxyphenyl) Isocyanurate (100347).

Reaction A. Triethylenediamine (0.15 g) and allyloxy-2,3-epoxypropane (0.15 g) were dissolved in 15 g of *m*-trimethylsiloxyphenyl isocyanate. The solution became exothermic and began to gel after 5-10 min. at 25°C . The sample was heated at 100°C for 21 hrs giving a product that was glassy at 25°C but poured easily at 100°C . An attempt to crystallize 4 g of the product from hot hexane yielded 1.9 g of pure product, mp $126.5-128.5^{\circ}\text{C}$. Fractions melting at $115-130^{\circ}\text{C}$ (0.8 g) and $93-240^{\circ}\text{C}$ (0.6 g) were also recovered.

Reaction B (100350). *m*-Trimethylsiloxyphenyl isocyanate (10.5 g), styrene oxide (0.2 g), and triethylenediamine (0.2 g) were dissolved in 100 ml of dry hexane. The reaction mixture was allowed to stand for three hours, during which time the solution was heated to 50°C several times. After adding half a drop of allyloxy-2,3-epoxypropane to the reaction mixture and allowing to stand overnight at room temperature, white crystals precipitated giving a 9.3 g yield of product, mp $126-129^{\circ}\text{C}$. A 4.2-g sample of the product was recrystallized from 200 ml of hexane yielding 3.5 g of tris(*m*-trimethylsiloxyphenyl) isocyanurate, mp $129-130^{\circ}\text{C}$.

Hydrolytic Stability Test of Tris(*m*-trimethylsiloxyphenyl) Isocyanurate (109301). Tris(*m*-trimethylsiloxyphenyl) isocyanurate (m.p. $129-310^{\circ}\text{C}$, 2.02 g) was refluxed with 20 ml of water for three hours and then allowed to stand for three days at room temperature. Distillation of the aqueous solution afforded a fraction with a boiling point that corresponds to the water/hexamethyldisiloxane azeotrope at $63-65^{\circ}\text{C}$. The organic phase was separated and identified by infrared spectrum as hexamethyldisiloxane. Evaporation of the water left a solid residue (0.3 g) melting at $356-358^{\circ}\text{C}$ with decomposition. The analysis suggests that the product is 1,3,5-tris(3-hydroxyphenyl) S-triazine-2,4,6-trione.

Anal. Calcd for $\text{C}_{21}\text{H}_{15}\text{N}_3\text{O}_6$: C, 62.2; H, 3.43; N, 10.38
Found: C, 60.3; H, 4.15; N, 9.97

2. Isocyanatophenylsiloxane Intermediates and Polymers.

p-Trimethylsilyltoluene (100329). *p*-Tolylmagnesium chloride was formed in tetrahydrofuran from 252 g (2.0 moles) of *p*-chlorotoluene and 48 g (2.0 g-atom) of magnesium. Dropwise addition of trimethylchlorosilane (217 g, 2.0 moles) followed by heating to 50-60°C completed the reaction. Hydrolysis, separation of the organic products and distillation gave 241 g (73% yield) of *p*-trimethylsilyltoluene, b.p. 84°C/18 mm n_D^{25} 1.4902.

<u>NMR Peak</u>	<u>Analysis Chem Shift (ppm)</u>	<u>Relative Area</u>	<u>Assignment</u>
A	7.0	4	aromatic proton
B	2.02	3	Ar- $\{CH_3\}$
C	0.05	9	Si(CH ₃)

p-Trimethylsilylbenzoic Acid (100338). Potassium permanganate (594 g, 3.77 moles) was added portionwise over two hours to a refluxing solution of *p*-trimethylsilyltoluene (206 g, 1.255 moles) in 1260 ml of pyridine and 630 ml of water. After heating for an additional 1.75 hours, the reaction mixture was cooled and filtered. The filtrate was concentrated to about 700 ml under vacuum on a rotating evaporator and then acidified with dilute acid to precipitate the acid, which was recovered by filtration. The yield of solid product after re-slurrying in water followed by filtration and drying was 174 g (71%) m.p. 115-117°C (Lit. 117-118°C, Ref. 43).

p-Trimethylsilylbenzoyl Chloride (100340). Reaction of *p*-trimethylsilylbenzoic acid (87.0 g, 0.45 mole) with a large excess of thionyl chloride (290 ml) by refluxing for 2 hours with 3 ml of pyridine gave, upon distillation, 76 g (80% yield) of *p*-trimethylsilylbenzoyl chloride b.p. 95°C/2 mm, n_D^{25} 1.5286; Lit. b.p. 76°C/1 mm, n_D^{25} 1.5315 (Ref. 43).

p-Trimethylsilylphenyl Isocyanate (100342). *p*-Trimethylsilylbenzoyl chloride (75 g, 0.354 mole) dissolved in 125 ml of acetone was added over a period of one hour to a solution of sodium azide (32.3 g, 0.496 mole) in 125 ml of water at 10-15°C. The reaction mixture was then stirred for 90 min. at 10-15°C. The top organic layer was separated, dried, and poured slowly into 345 ml of benzene at 70°C. Nitrogen was evolved slowly as the solution was stirred. Distillation of the resulting solution gave 58.6 g (87% yield) of *p*-trimethylsilylphenyl isocyanate, b.p. 105°C/10 mm, n_D^{25} 1.5163.

Tris(*p*-Trimethylsilylphenyl) Isocyanurate (100348). Triethylenediamine (0.05 g) and allyloxy-2,3-epoxypropane (0.05 g) were dissolved in *p*-trimethylsilylphenyl isocyanate (5.0 g). An exothermic reaction

occurred after 5-10 min., forming a granular crystalline product. A 4-g sample of this material was recrystallized from 400 ml of hexane yielding 2.2 g of a white crystalline product melting at 357-358.5°C, and having a molecular weight by vapor pressure osmometry of 570; theory for trimer, 573.9. A portion of this tris-(*p*-trimethylsilylphenyl) isocyanurate (1.0 g) was refluxed in 25 ml of water for three hours. The solid product recovered by filtration weighed 1 g after drying under vacuum at 65°, and melted at 356-358°C.

1,3-Bis(*p*-tolyl)tetramethyldisiloxane (109332). *p*-Tolylmagnesium chloride was prepared by the addition of a tetrahydrofuran solution of *p*-chlorotoluene (379.7 g, 3.0 mole) to magnesium shavings (73.0 g, 3.0 mole) in tetrahydrofuran. The Grignard solution was then added dropwise to excess dichlorodimethylsilane (874.4 g, 6.0 mole) in ether. The reaction temperature was controlled at 0-5°C during the addition. After stirring two hours at 40°C, the reaction mixture was filtered and the volatiles were removed, leaving a residue weighing 471 g. Hydrolysis, separation of the organic products, and distillation gave 306.2 g (65% yield) of 1,3-bis(*p*-tolyl)tetramethyldisiloxane, b.p. 113-114°C/0.09 mm, n_D^{25} 1.5158-1.5149. Lit. b.p. 143-144°C/1 mm, n_D^{25} 1.5135 (Ref. 2).

4,4'-Tetramethyldisiloxanylenedibenzoic Acid (109334, 109357). Potassium permanganate (704 g, 4.36 mole) was added at a rate of 50 grams per 15 minutes to a mixture of 1,3-bis(*p*-tolyl)tetramethyldisiloxane (305 g, 0.971 mole), 1320 ml of pyridine and 633 ml of water while maintaining the reaction temperature at 80-83°C. After heating another 1.5 hours and then stirring for 18 hours at room temperature, the reaction mixture was filtered. The filtrate was concentrated to 600 ml under vacuum on a rotating evaporator to remove the pyridine. The solution was then diluted with one liter of water and acidified with concd hydrochloric acid to precipitate the acid, which was recovered by filtration. The yield of 4,4'-tetramethyldisiloxanylene-dibenzoic acid after reslurrying in water followed by filtration and drying was 313.7 g (86.3% yield), m.p. 190-237°C.

The crude acid was purified by dissolving 281 g of the acid (m.p. 185-220°C) in a solution of sodium bicarbonate (63 g) in 1500 ml of water at 75°C. An insoluble oil layer that did not dissolve was removed and the solution was filtered. The acid was reprecipitated by the addition of concd hydrochloric acid, collected by filtration, and washed well with water. The solids were dried in a vacuum oven at 50°C affording 133.5 g (42.6% yield) of material identified as 4,4'-tetramethyldisiloxanylenedibenzoic acid by NMR analysis, m.p. 230-243°C, neut. equiv. 185.5°C, calcd neut. equiv. 187.2.

NMR Analysis

<u>Chem. Shift</u>	<u>Rel. No. Protons</u>	<u>Assignment</u>
8.12, 7.97 } J=8 cps }	4.0	aromatic protons
7.73, 7.10 } J=8 cps }		
0.42	6.3	Si{CH ₃ }

4,4'-Tetramethyldisiloxanylenedibenzoyl Chloride (109329). 4,4'-Tetramethyldisiloxanylenedibenzoic acid (55.0 g, 0.147 mole) (m.p. 205-234°C) was refluxed with a large excess of thionyl chloride (175 g, 1.47 mole). Distillation gave 33.5 g (55.5% yield) of the corresponding acid chloride, b.p. 146-152°C/0.01-0.06 mm, m.p. 50-56°C; Lit m.p. 54-55°, b.p. 200°C/3 mm (Ref. 6).

4,4'-(Tetramethyldisiloxanylene)diphenyl Isocyanate (109337).

Route A. 4,4'-Tetramethyldisiloxanylenedibenzoyl chloride (23 g, 0.056 mole) dissolved in 33 ml of acetone was added dropwise to a rapidly stirred solution of sodium azide (10.4 g, 0.16 mole) in 33 ml of water at 10-14°C. After stirring the reaction mixture for 80 min., the organic phase was separated and then decomposed by slowly adding to 150 ml of 70°C benzene. Evaporation of the benzene gave 19.7 g of crude product (95% yield) that, upon distillation, gave 12.5 g (60% yield) of 4,4'-(tetramethyldisiloxanylene)diphenyl isocyanate, b.p. 120-122°C/0.005 mm, n_D^{25} 1.5387, isocyanate equiv. found 187.1, calcd 184.3

Route B (109319) Attempted. The dry sodium salt of 4,4'-(tetramethyldisiloxanylene)dibenzoic acid (30 g, 0.1435 equiv.) prepared by neutralization of the acid with two equivalents of sodium bicarbonate, was added over 50 min. to a solution of oxalyl chloride (22 g, 0.173 mole) in 80 ml of benzene. The temperature was controlled at 40 to 45°C with slight cooling. The reaction mixture was filtered and solvent was removed under vacuum leaving to 15.1 g of crude acid chloride. A solution of the crude acid chloride (13.1 g, 0.064 equiv.) in 25 ml of acetone was added dropwise to sodium azide (5.8 g, 0.089 equiv.) in 25 ml of water over a period of 15 min. at 10-15°C. Gas was evolved from the acetone solution while stirring was continued for another hour at 10-15°C. The top, organic layer was then separated and poured into 50 ml of benzene at 70°C. Distillation of this solution yielded 8.9 g of polymeric residue but none of the desired product.

In a second experiment (109328) using crude, undistilled 4,4'-(tetramethyldisiloxanylene)dibenzoyl chloride, the product decomposed upon distillation to give a polymeric residue.

p-(Chlorodimethylsilyl)benzoyl Chloride and p-(Chlorodimethylsiloxy-dimethylsilyl)benzoyl Chloride (109341). Crude 4,4'-tetramethyldi-siloxanylenedibenzoic acid (33.5 g, 0.894 mole) was refluxed with a large excess of thionyl chloride (810 g, 6.83 mole) in the presence of 3.0 g of acetic acid for 6 hr. Distillation gave the following three products: 45 g (11%) of p-(chlorodimethylsilyl)benzoyl chloride, b.p. 120°C/5 mm, n_D^{25} 1.5411, d_4^{25} 1.2003; sp. refr. found 0.262, calcd 0.254; neut. equiv. found 79, calcd 77.6; and, 30 g (11%) of 4-(chloro-dimethylsiloxydimethylsilyl)benzoyl chloride, b.p. 133°C/5 mm, n_D^{25} 1.5030, d_4^{25} 1.134; sp. refr. found 0.260, calcd 0.253; neut. equiv. 104 calcd 102; and, 132 g (36%) of 4,4'-tetramethyldisiloxanylene-dibenzoyl chloride, b.p. 140-150°C/0.01 mm, m.p. 52-57°C.

4,4'-(Octamethyltetrasiloxanylene)dibenzoyl Chloride (109364). 4-(Chlorodimethylsiloxydimethylsilyl)benzoyl chloride (26.0 g, 0.085 moles) was slowly poured onto sufficient crushed ice to maintain the temperature below 0°. The organic material was extracted with dichloro-methane, washed with ice water and dried over calcium chloride. The solvent was then removed under vacuum leaving 22.7 g of liquid n_D^{25} 1.5096 (theoretical weight 23.7). The neut. equiv. in KOH/ethylene glycol was 149.5, calcd 139.5.

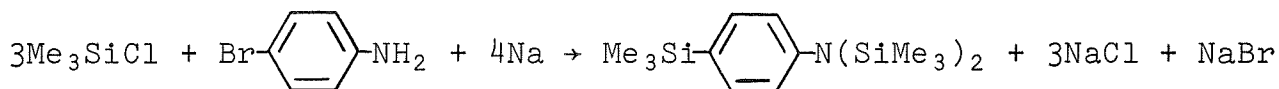
4,4'-(Octamethyltetrasiloxanylene)diphenyl Isocyanate (109366). Crude 4,4'-(octamethyltetrasiloxanylene)dibenzoyl chloride 21.0 g (0.075 equiv.) in 22 ml of acetone was added to a stirred solution of sodium azide (6.7 g, 0.105 mole) in 22 ml of water at 10-15°C. After a reaction time of 0.5 hours the organic phase was separated, dried and added to 100 ml benzene at 70°. The solution was heated at 75-80° with stirring for 40 minutes. The benzene was removed leaving 21.2 g residue. Infrared analysis showed the product was the azide rather than the isocyanate. Cautious heating at 70-75°/0.1 mm resulted in vigorous decomposition. Evidence of nitrogen evolution was observed until the temperature was 130°. (Decomposition of the azide in toluene at ~100° or higher rather than in benzene is recommended for future preparations). The attempt to distill the product was discontinued at a pot temperature of 160° because the pressure of 0.008 mm could not be maintained. The crude product was then passed through the Roto Film molecular still at 150°/13 micron pressure. Polymerization occurred in the still but 8.7 g of distillate was obtained also. This product had an isocyanate equivalent of 257, calcd 258.

Polyisocyanurate from 4,4'-(Octamethyltetrasiloxanylene)diphenyl Isocyanate (109366). Polymerization of this product occurred in 0.75 hrs at 25° when mixed with 1% by weight of allyl glycidyl ether and N,N,N',N'-tetramethyl-1,3-butanediamine. A 1/16" sheet of polyisocyanurate was formed by a similar polymerization of the diisocyanate at 100°/18 hrs. The tensile strength of micro test specimens was approximately 2000 psi at 13% elongation.

1,7-Diphenyloctamethyltetrasiloxane (109349). A mixture of chlorodimethylphenylsilane (34.0 g, 0.2 mole) and pyridine (15.8 g, 0.2 mole) in 200 ml of hexane was added over a 35-min. period to tetramethyldisiloxane-1,3-diol dissolved in 300 ml of benzene at 40°C. The pyridine hydrochloride that formed was separated by filtration and the filtrate was washed with water and dried over MgSO₄.

The distillation data indicate a mixture of siloxane products. A major fraction boiling at 71-80°C/0.02 mm, n_D^{25} 1.5102 appears to be largely 1,3-diphenyltetramethyldisiloxane. Lit: b.p. 106-108°C/3 mm, n_D^{25} 1.5149, Ref. 44.

p-Trimethylsilylaniline (91514). A mixture of trimethylchlorosilane (33 g, 0.304 mole) and *p*-bromoaniline (17.2 g, 0.10 mole) was added to 9.2 g (0.4 g-atom) of sodium dispersion in toluene at 103-105°C. The mixture was stirred for 45 minutes and then allowed to cool. Diglyme (150 ml) was added and the mixture was then stirred at 65-70°C for 16 hours followed by one hour at 85-90°C and 2 hours at 105°C. Filtration gave slightly more than the theoretical weight of sodium halide based on the equation



The residue contained little sodium and showed a positive qualitative test for bromine. Distillation gave, in addition to recovered toluene and diglyme, a small quantity (10 g) of methoxytrimethylsilane, and about 10 g of what appears to be impure *p*-trimethylsilyl *N*-trimethylsilylaniline. The product boiled over a narrow range with decreasing refractive index, b.p. 108°C/25 mm, n_D^{25} 1.5085-1.5075. Methanolysis followed by evaporation of excess methanol and methoxytrimethylsilane gave a residue that by IR appeared to be *p*-trimethylsilylaniline. Attempts to prepare the acetyl derivative, however, gave acetanilide m.p. 113-114°.

m-Trimethylsilylaniline (100336). In a second experiment trimethylchlorosilane was coupled with *m*-bromoaniline at a reaction temperature of 105-120°C in xylene. The product, as in the previous experiment showed decreasing refractive indices at nearly constant boiling point.

Fraction	Wt. (g)	b.p. (°C/mm)	n_D^{25}
6 - 7	2.9	92/14	1.5157-1.5150
8 - 9	4.0	93/14	1.5121-1.5131
10 - 11	4.1	94/14	1.5092-1.5109
12 - 13	4.7	95-6/14	1.4918-1.5049

The infrared spectra indicated a trimethylsilyl-substituted aniline derivative. NMR analysis indicated a mixture of products but tended to substantiate N and C trimethylsilyl substituents. Methanolysis resulted in isolation of aniline, b.p. 95°C/41 mm, n_D^{25} 1.5834, as determined by the infrared spectrum.

p-Bromo-N-trimethylsilylaniline (100326, 100327). An ether solution of trimethylchlorosilane (119 g, 1.1 mole) was added to a well-stirred mixture of p-bromoaniline (168 g, 0.95 mole) and triethylamine (111 g, 1.1 moles). After standing for 18 hours the solid was removed by filtration and the filtrate was distilled. An 82% yield was obtained of p-bromo-N-trimethylsilylaniline, b.p. 73°C/0.06 mm, n_D^{25} 1.5542, m.p. 39-41°C. Identification of the compound was confirmed by NMR.

Peak	Chem Shift (ppm)	Rel. Peak Area	Assignment
A	7.18	4	aromatic protons
B	6.46		
C	3.38	1	labile N{H}
D	0.21	9	NSi{CH ₃ }

p-Trimethylsilyl-N,N-bis(trimethylsilyl)aniline (100344). A solution of p-bromo-N-trimethylsilylaniline (73.2 g, 0.3 mole) and trimethylchlorosilane (65 g, 0.6 mole) in 350 ml of diglyme was added dropwise over a 2-hr period to a sodium (23 g, 1.0 mole) dispersion in 200 ml of toluene at 50-60°C. The slightly exothermic reaction mixture was heated intermittently to maintain a reaction temperature of 50 to 60°C. Heating was continued for an additional 2 hr. After standing for 68 hr the mixture was filtered and distilled to give three main product fractions, as follows:

Weight, g	Boiling Point, °C/mm Hg	n_D^{25}
1. 10.5	90-97/9	1.4898-1.4967
2. 31	98/9	1.4829
3. 10.9	133/9	1.4952-1.5119

Fraction 2 was identified as N-phenylhexamethyldisilazane by its NMR spectrum.

Chem. Shift (ppm)	Assignment	Relative Number
~6.9 multiplet	aromatic protons	5.0
~0 singlet	Si(CH ₃)	18.5

Fraction 3 was shown to be largely *p*-trimethylsilyl-*N,N*-bis(trimethylsilyl)aniline. A portion of this fraction was dissolved in a little methanol and then subjected to vacuum to recover the oily residue (n_D^{25} 1.5095). The oil, when added to cold acetic anhydride, formed a solid derivative that melted at 167-168°C after three recrystallizations from heptane. The melting point of this derivative (167-169°C) corresponds to the melting point reported by Benkeser and Brumfield (Ref. 45) for *p*-trimethylsilyl acetanilide (169-170°C). The infrared spectrum was consistent with this product also.

Phenylisocyanate from *N,N*-Bis(trimethylsilyl)aniline (109358). Phosgene (20 g, 0.2 mole) was condensed at -30° in 50 ml of ether containing 19.3 g (0.085 mole) of *N,N*-bis(trimethylsilyl)aniline. The mixture was warmed to room temperature. Infrared analysis showed isocyanate but also unreacted amine derivative. Toluene was then added and the mixture was heated to 70° as phosgene and ether was distilled. Phosgene was passed into the solution at 70° for 0.75 hr, whereupon the infrared spectrum indicated conversion to the phenylisocyanate product. Distillation gave trimethylchlorosilane, b.p. 57-58° and phenylisocyanate in 60% yield, b.p. 160-161°/25 mm, n_D^{25} 1.5340.

B. ISOCYANURATE-LINKED FLUOROPOLYMERS

1. Perfluoroalkyldiisocyanate Intermediates and Polymers.

Hexafluorotrimethylene Diisocyanate (99857-1). This diisocyanate was prepared by the Curtius rearrangement of perfluoroglutaryl diazide (Ref. 46). Sodium azide (39 g, 0.6 mole) was dissolved in 120 ml of water, 300 ml of xylene was added and the mixture was cooled to 5°C. A solution of 55.4 g (0.2 mole) of perfluoroglutaryl chloride in 200 ml of xylene was added during 45 minutes at a temperature of 4 to 8°C, maintained as necessary by cooling with an ice-water bath. The mixture was stirred for an additional 1.5 hr in the ice bath and then was allowed to warm to 15°C with stirring during an additional 0.5 hr. The xylene (upper) layer containing the intermediate acid diazide was separated, dried over anhydrous magnesium sulfate and filtered.

The azide was converted to diisocyanate by slow addition of the dried xylene solution to 75 ml of xylene at 112 to 116°C under nitrogen during 3 hr in a flask arranged with a condenser and receiver for simple stripping distillation. During the reaction, some diisocyanate was collected. A crude mixture of diisocyanate and xylene was then recovered by distillation to a head temperature of 137°C and a flask temperature of 141°C. The mixture was stored in the refrigerator until redistilled.

The crude distillation mixture was combined with the product from a preliminary preparation 0.5x the above scale and distilled through a 24-in. Vigreux column. A product with b.p. 81 to 83°C (Lit. b.p. 84-85°C, Ref. 46) was collected with no forerun (35.1 g, 0.15 mole, 50%). The product showed the characteristic isocyanate absorption peak at 4.35 μ in the infrared spectrum (Figure 5). The refractive index of n_D^{25} 1.3288 agreed reasonably well with the reported value of n_D^{25} 1.3302 (Ref. 46). ^1H and ^{19}F NMR and G.L.C. analysis indicated a purity of desired product of approximately 95-98% with a trace of entrained xylene and related aromatics as the major impurity. A repeat preparation of hexafluorotrimethylene diisocyanate (104644-104647) yielded a product with the same boiling range and infrared spectrum, n_D^{25} 1.3315; yield 42%.

Polymerization with DABCO/Allyl Glycidyl Ether Cocatalyst System (99859-1). The diisocyanate (1.0 g, 0.04 mole) was added to 0.01 g (0.00009 mole) of DABCO in a small vial, 1 small drop of allyl glycidyl ether was added and the vial was capped. The DABCO did not dissolve and no polymerization occurred during 96 hr at room temperature. Heating at 40°C for 3-7 hr periods caused some polymerization on the DABCO but not in the bulk of the liquid isocyanate. Following vacuum drying the solid product was soft and softened further upon heating to form a fluid melt at 81°C. The infrared spectrum of the solid product indicated almost complete disappearance of isocyanate and the probable formation of dimer or trimer as shown by a peak at 5.7 to 5.8 μ (Figure 6).

Polymerization with DABCO/Propylene Oxide Cocatalyst System (99863, 99864). DABCO was added as a 10% by weight solution in benzene (0.1 g, 0.12 ml) to 1.0 g of diisocyanate in a screw capped vial in a dry-box. Propylene oxide (0.02 g, 0.023 ml, 0.0004 mole) was then added. The DABCO appeared to precipitate as a white film on the vial walls (99863).

A duplicate mixture was prepared in a dry-box except that the diisocyanate was dissolved in 2.0 ml of benzene prior to addition of the DABCO solution (99864). The DABCO appeared to stay in solution. Both mixtures were heated for 10 hr at 60°C with some slight formation of a green color but no solid product. There was no viscosity increase in the diisocyanate.

Polymerization with Tetramethylbutanediamine/Allyl Glycidyl Ether Cocatalyst System (99859-2). The diisocyanate (1.0 g, 0.004 mole) was added to 0.01 g (0.00008 mole) of tetramethylbutanediamine and 1 drop of allyl glycidyl ether was added. The amine did not appear to be compatible with the diisocyanate. No polymerization occurred upon standing at room temperature for 96 hr or upon being heated for 3-7 hr periods at 40°C.

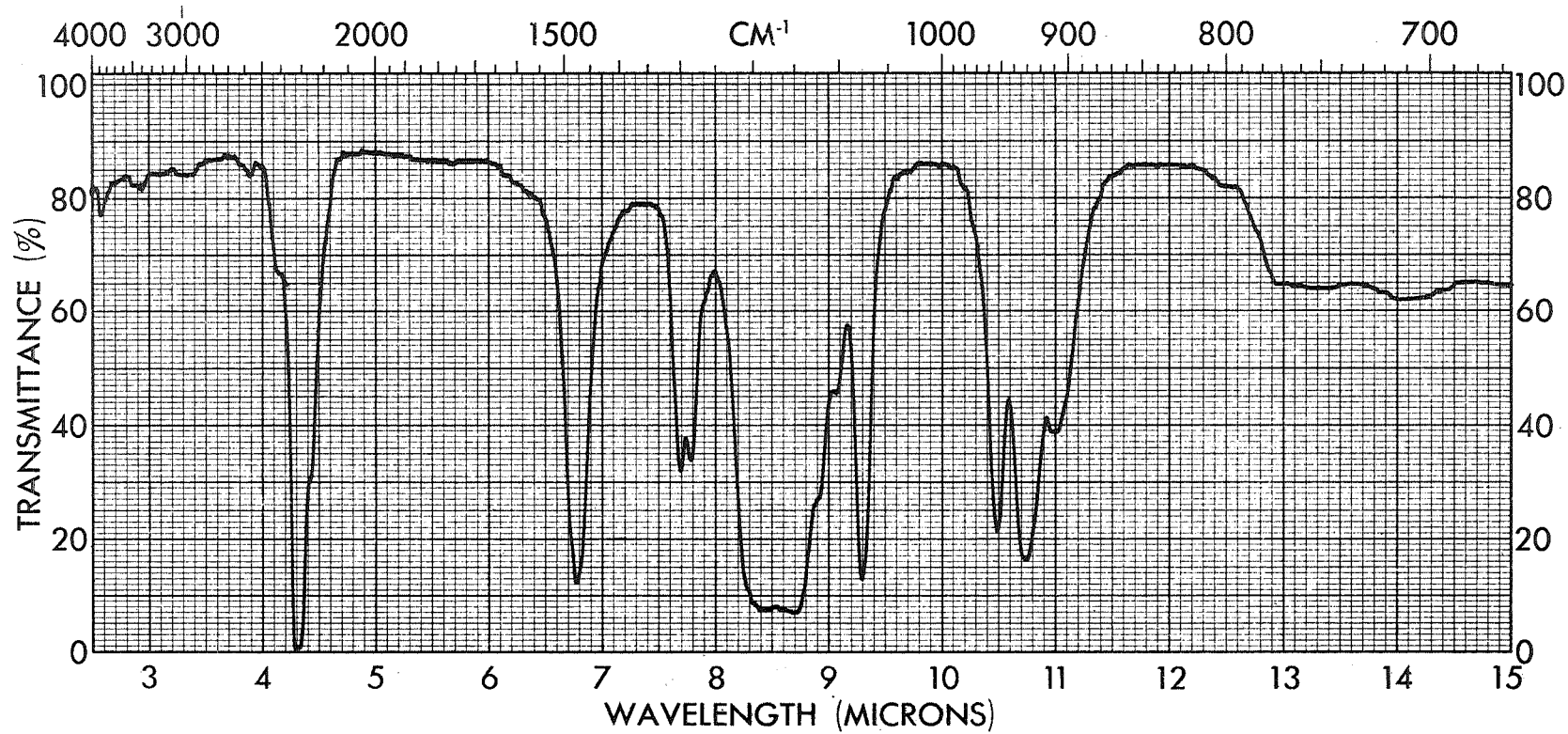


Figure 5. Infrared Spectrum of Hexafluorotrimethylene Diisocyanate

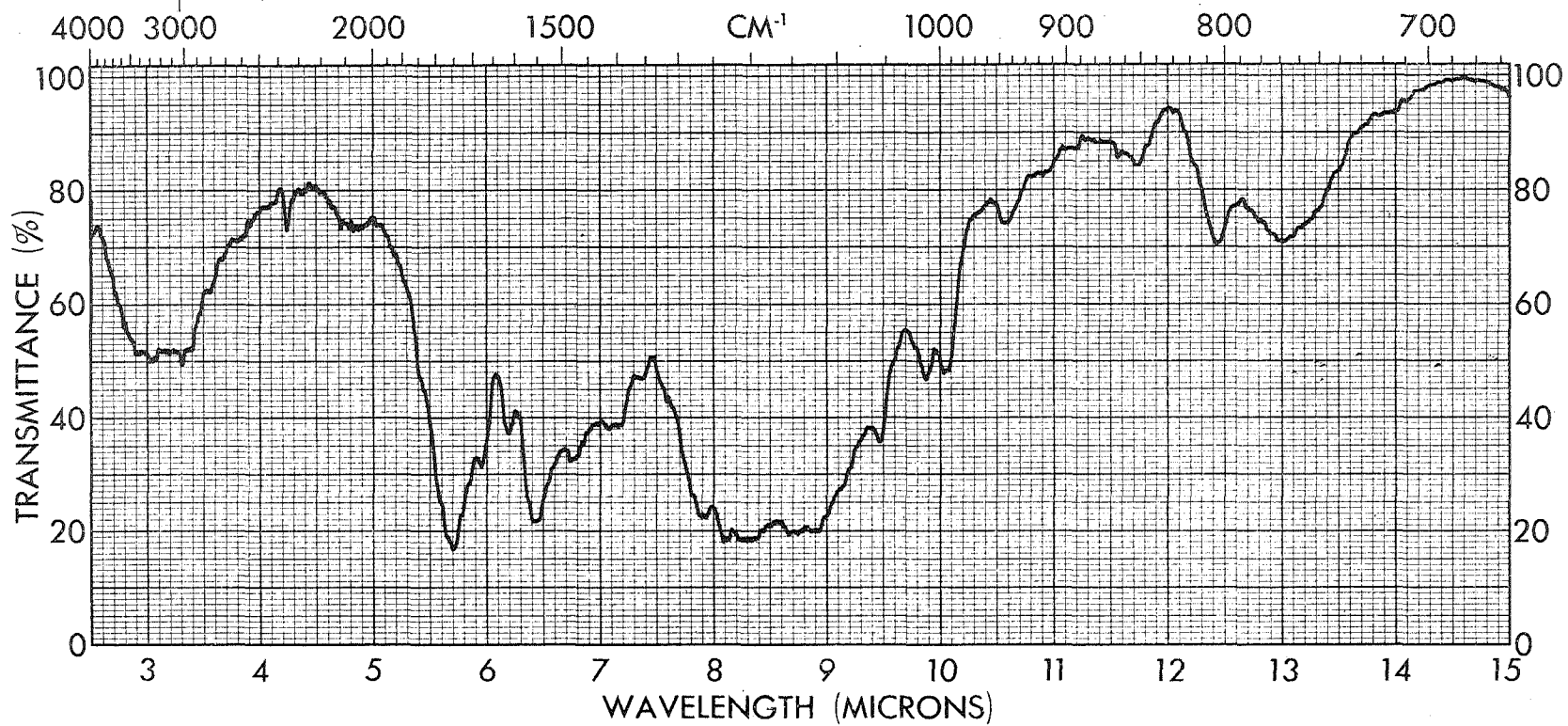


Figure 6. Infrared Spectrum of Low Melting Polymer from Hexafluorotrimethylene Diisocyanate

Polymerization with Miscellaneous Catalyst Systems, Sealed Tube Experiments. Hexafluorotrimethylene diisocyanate (1.0 g, 0.0043 mole) 2.0 ml of dry benzene, and (generally) 3 mole percent (0.00013 mole) of catalyst were added to a 10-mm OD, heavy-walled Pyrex tubing 9 in. long under a nitrogen atmosphere. The specific catalysts used are shown in Tables 2 and 3. The tube and contents were cooled under nitrogen in dry ice, the pressure was reduced to 200 mm Hg and the tube was sealed with a methane/oxygen flame. The tubes were then warmed to room temperature, allowed to stand overnight at room temperature and then heated at 100°C for 48 hr.

2. Perfluoroalkylaryldiisocyanate Intermediates and Polymers.

Trifluoromethylphenyl Isocyanate (104660). A solution of 42 g of *m*-trifluoromethyl benzoyl chloride in 100 ml of toluene was added dropwise over a 1.25-hr period to a mixture of 18.2 g of sodium azide, 50 ml of water, and 200 ml of toluene. During the addition the temperature was maintained between 25 and 30°C. The reaction was allowed to stir at room temperature for 3 hours, then was heated quickly to 40°C, and allowed to cool. The toluene layer was separated and dried over magnesium sulfate. The solution of the azide in toluene was then added dropwise to 50 ml of dry toluene at 100°C. This phase of the reaction was done under a nitrogen atmosphere, and any excess nitrogen coming from the decomposition of the azide was detected by means of a gas bubbler. The solution was refluxed an additional 1.5 hr and the toluene stripped off through a 15-in. Vigreux column attached directly to the reaction flask. The product was distilled through the same column at 15 mm and 65°C (yield 80%).

Tris(*m*-trifluoromethylphenyl) Isocyanurate.

Method A (104663). Tributylantimony oxide (0.0003 mole) was added to 2 g of *m*-trifluoromethylphenyl isocyanate (0.01 mole). Upon mixing the reagents a vigorous exotherm was noted and the reaction mixture became very viscous within several seconds. After 1 hour some solid had formed, and after standing 48 hours the reaction had become a solid mass. The solid was recrystallized from absolute ethanol to yield white crystals, m.p. 200-203°C.

Method B (104664). To 1.57 g of *m*-trifluoromethylphenyl isocyanate we added 0.35 ml of a 10% solution of DABCO (triethylene diamine) in benzene and 0.10 ml of allyl glycidyl ether. Upon mixing the reagents a slight exotherm was observed and a small quantity of finely divided white solid precipitated. After an hour this solid had gone into solution. After standing 48 hours at room temperature some yellow crystals had formed but attempts to recrystallize them from ethanol failed. Upon stripping the ethanol, a brown oil syrup was obtained. An IR spectrum was taken and this syrup contained bands characteristic of urethanes, ureas, or both.

Attempted Preparation of 1,2-Di-(*m*-Nitrophenyl)tetrafluoroethane (104665). A mixture of 100 g of *m*-iodonitrobenzene, 29 g of activated copper-bronze, and 100 ml of dimethylformamide was heated to 125°C. A solution of 25 g of 1,2-diiidotetrafluoroethane (Columbia Organic Chemical Co.) in 100 ml of dimethylformamide was added dropwise over a 2-hr period. The mixture was stirred at 120°C for 2 more hours. Upon working up the reaction mixture, no fluorine containing materials were found.

1,3-Diiiodohexafluoropropane (104671). 1,3-Diiiodohexafluoropropane was prepared by the method of Krespan (Ref. 47). Perfluoroglutaryl chloride (100 g, 0.361 mole) and potassium iodide (160 g, 0.966 mole) were placed in a 1-liter "Hastelloy-C" bomb under nitrogen. The bomb was heated to 270°C, cooled slowly to 205°C, and held there for 3 hr, making the total heating time 6 hr. After the bomb cooled to room temperature, the carbon monoxide was bled off and residual gases were removed by a nitrogen purge. The bomb was rinsed with 500 ml of chloroform and 500 ml of water. The large quantity of elemental iodine present in the organic layer was removed by shaking with several grams of mercury. The chloroform layer was dried (CaCl₂) and distilled yielding 1,3-diiiodohexafluoropropane (58%), b.p. 130-131°C at atmospheric pressure. The boiling point was consistent with that reported by Krespan, (infrared spectrum, Figure 7).

1,3-Di-(*m*-nitrophenyl)hexafluoropropane (104686). 1,3-Di-(*m*-nitrophenyl)hexafluoropropane was prepared by the method of McLaughlin (Ref. 48). A 250-ml, 3-necked flask equipped with a mechanical stirrer, thermometer, reflux condenser, and nitrogen inlet was charged with 18 g (0.045 mole) of 1,3-diiiodohexafluoropropane, 50 g (0.20 mole) of *m*-iodonitrobenzene, 25 g of activated copper-bronze (Ref. 49) and 60 ml of dimethylformamide (previously dried over P₂O₅ and distilled). The mixture was heated slowly to 125°C and held there for 90 min. After cooling to room temperature, the reaction mixture was filtered. The filtrate was shaken with 300 ml of water and 75 ml of dichloromethane. Upon separation of the organic layer, some crystals began to form. These were isolated and identified as 3,3'-dinitrobiphenyl (m.p. 200°C). The organic layer was dried (MgSO₄) and the dichloromethane plus some residual dimethylformamide stripped on a rotary evaporator under aspirator vacuum. The remaining liquid (*m*-iodonitrobenzene) was distilled off at 88°C/0.4 mm. The solids from the distillation pot were added to 100 ml of boiling ethanol. The undissolved solid (3,3'-dinitrobiphenyl) was filtered off and upon slight cooling (to ~60°C) the filtrate yielded more 3,3'-dinitrobiphenyl. Upon further cooling to room temperature, the ethanolic solution yielded crystals of 1,3-di-(*m*-nitrophenyl)hexafluoropropane (Figure 8), m.p. 92°C, yield 55%. See Table 7 for a more complete picture of the reaction conditions and subsequent results.

Anal. Calcd for C₁₅H₈F₆N₂O₄: C, 45.70; H, 2.04; N, 7.10
Found: C, 45.64; H, 2.04; N, 6.96

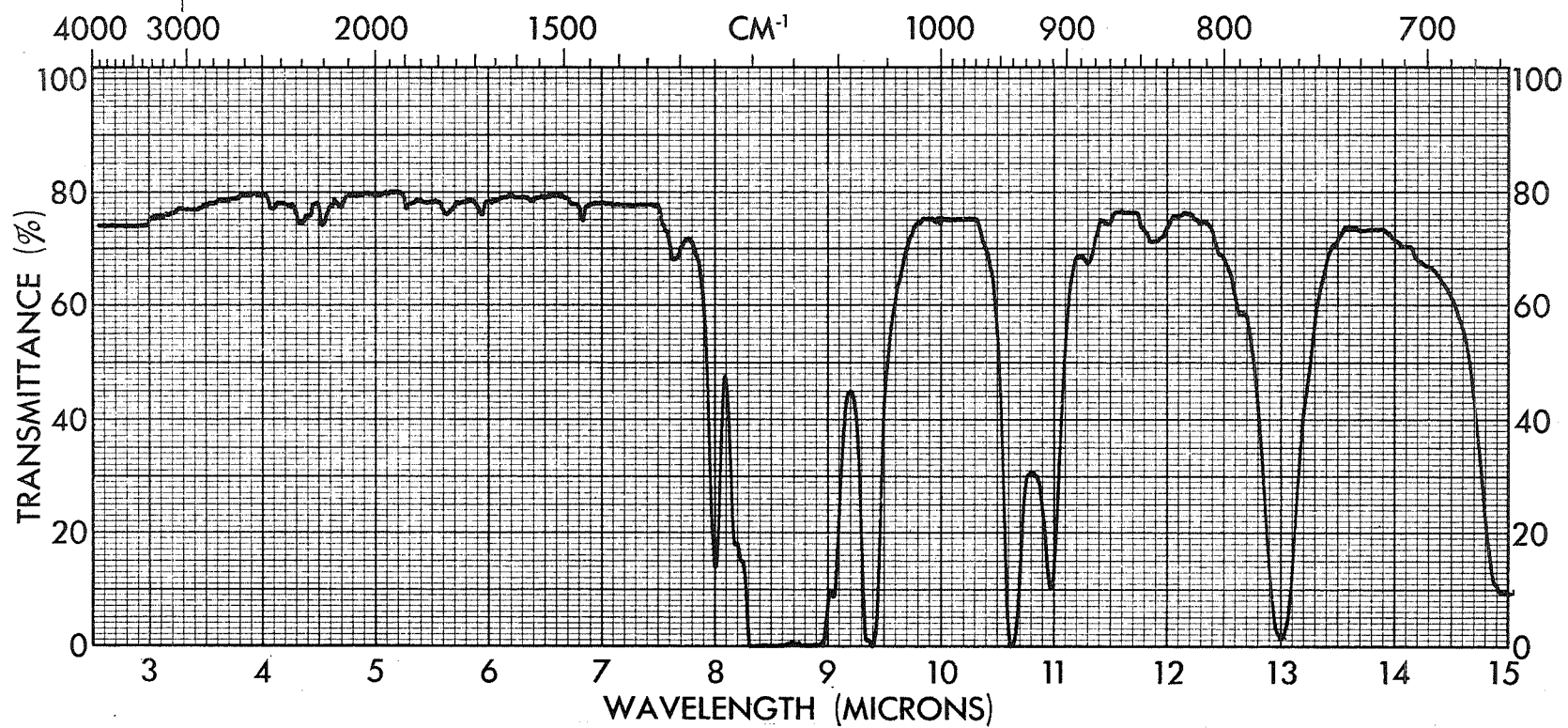


Figure 7. Infrared Spectrum of 1,3-Diiodohexafluoropropane

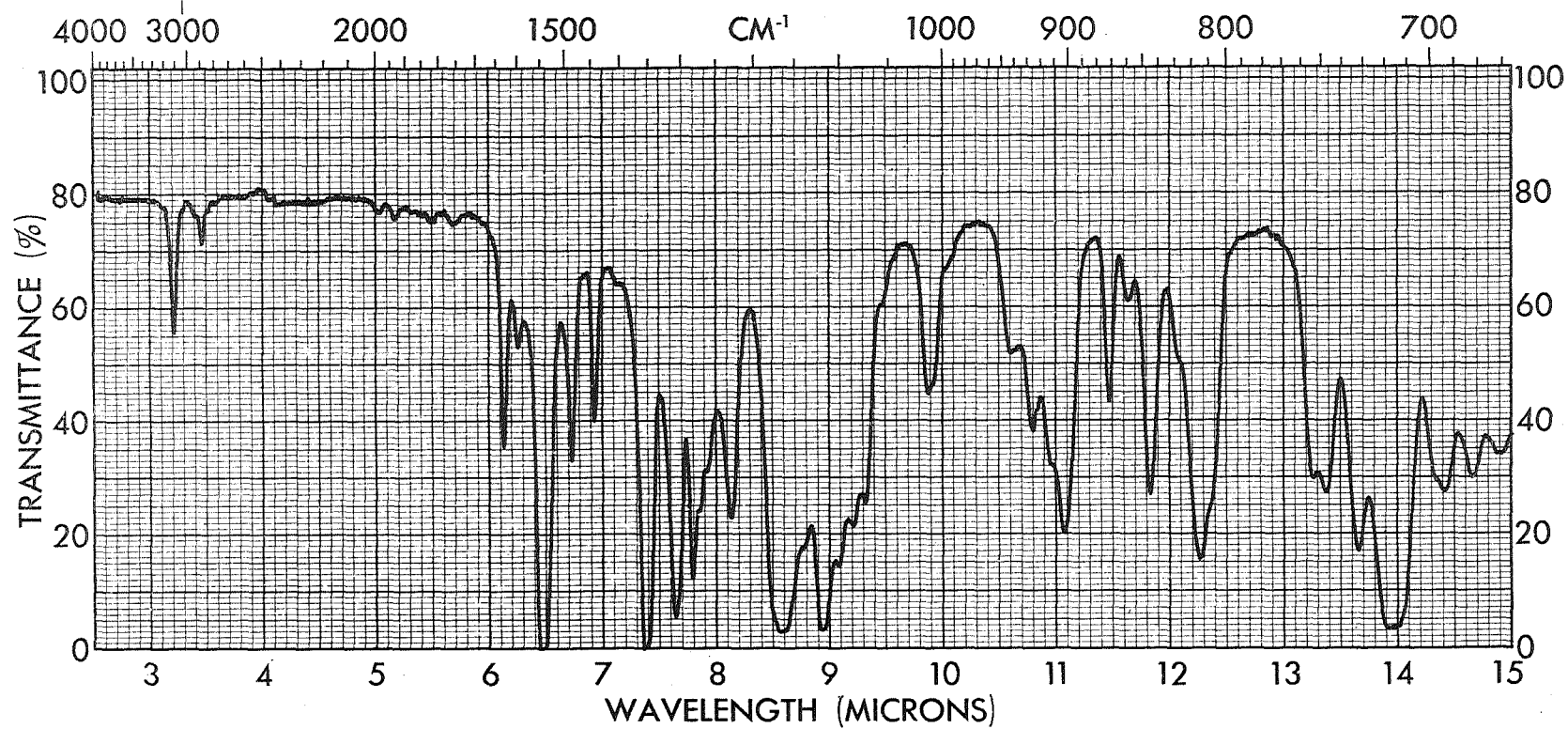


Figure 8. Infrared Spectrum of 1,3-Di-(*m*-nitrophenyl)hexafluoropropane

Table 7

REACTION OF 1,3-DIIODOHEXAFLUOROPROPANE WITH *m*-IODONITROBENZENE¹

<u>Code</u>	<u>Method</u>	<u>Heating Cycle</u>	<u>Results</u>
104673	all reagents mixed initially	heated to 132°C exothermed to 147°C	30% yield of 1,3-di-(<i>m</i> -nitrophenyl)hexafluoropropane
104675	<i>m</i> -IC ₆ H ₄ NO ₂ added over 20 minutes	110°-115°C for 1.5 hr	intermediate complex isolated
104678	intermediate from 104675 plus Cu <i>m</i> -IC ₆ H ₄ NO ₂ , DMF	125°C for 2 hr	1,3-di-(<i>m</i> -nitrophenyl)hexafluoropropane
104680	<i>m</i> -IC ₆ H ₄ NO ₂ added	heated to 110°; large exotherm to 150°C just after addition of <i>m</i> -IC ₆ H ₄ NO ₂ was started; stirred at 125°C for 1.6 hrs	polymers from aliphatic coupling
104684	added I(CF ₂) ₃ I in DMF over 15 min. period	125°C for 1.5 hr	5% 1,3-di-(<i>m</i> -nitrophenyl)hexafluoropropane
104686	all reagents mixed initially	stood overnight at room temperature then heated to 125°C for 1.5 hr	55%, 1,3-di-(<i>m</i> -nitrophenyl)hexafluoropropane

¹All reactions done in the presence of activated copper-bronze and dimethylformamide which was previously dried (P₂O₅) and distilled.

1,3-Di-(*m*-Aminophenyl)hexafluoropropane Dihydrochloride (104689).

1,3-Di-(*m*-nitrophenyl)hexafluoropropane (5 g) was dissolved in 175 ml of tetrahydrofuran and hydrogenated over Raney nickel at 25°C at 50 psi for 45 min. After the Raney nickel was removed and the THF stripped, the residual liquid was dissolved in 5 ml of ethanol. A solution of 4 g of hydrochloric acid in 25 ml of ethanol was added slowly to the amine solution while cooling with the aid of an ice bath. The white crystalline 1,3-di-(*m*-aminophenyl)hexafluoro propane dihydrochloride was filtered, washed with 25 ml of ethanol, and dried in a vacuum desiccator: melting range 180-185°C; yield 90%.

1,3-Di-(*m*-Isocyanatophenyl)hexafluoropropane (104691). A nitrogen-swept, 250-ml, 4-necked, flask equipped with a stirrer, condenser, dry nitrogen inlet, thermometer, heating mantle and gas dispersion tube adjusted to reach below liquid surface was charged with 4.6 g of 1,3-di-(*m*-aminophenyl)hexafluoropropane dihydrochloride and 175 ml of distilled-dried *o*-dichlorobenzene. Agitation was begun and phosgene added rapidly causing the temperature to rise to 45°C. As the exotherm subsided, the flow of phosgene was then increased to maintain a positive pressure and this condition was sustained until all of the solid had entered solution. The clear solution was then heated to 160°C, and dry nitrogen was bubbled through for 1.5 hr. The solution was then cooled to room temperature, the *o*-dichlorobenzene stripped off, and the residual liquid distilled at 145°C at 0.06 mm; yield, 88%. Infrared spectrum Figure 9.

Anal. Calcd for $C_{17}H_8F_6N_2O_2$: C, 43.25; H, 1.81; N, 6.30
Found: C, 43.49; H, 1.72; N, 6.38

Octafluorohexanedioyl Chloride (104698, 113201).

Method I. Into a 500 ml 4-necked flask equipped with a nitrogen inlet, magnetic stirrer, Vigreux column and thermometer were placed 50 g of perfluoroadipic acid (as obtained from 3M Company). While cooling with an ice-water bath, 78 g of solid phosphorus pentachloride were slowly added. The reaction mixture soon liquefied, effervesced vigorously, and exothermed to 32°C. The phosphorus oxychloride was distilled off at 65°C/150 mm. The product, octafluorohexanedioyl chloride, distilled at 110°C/150 mm and was collected in a dry-ice cooled receiver. Yield 45%.

Method II. Into a 200-ml nitrogen-flushed round-bottom flask was placed 25 g (0.086 mole) of perfluoroadipic acid. To this was added 60 g (0.5 mole) of thionyl chloride. Within several seconds, sulfur dioxide and hydrogen chloride began to issue forth, cooling the reaction flask in the process. After the initial bubbling subsided, 0.5 ml of pyridine and a trace (several milligrams) of solid potassium hydroxide were added. The reaction mixture was then heated to reflux for 4 hours. The unreacted thionyl chloride was distilled at 76°C at

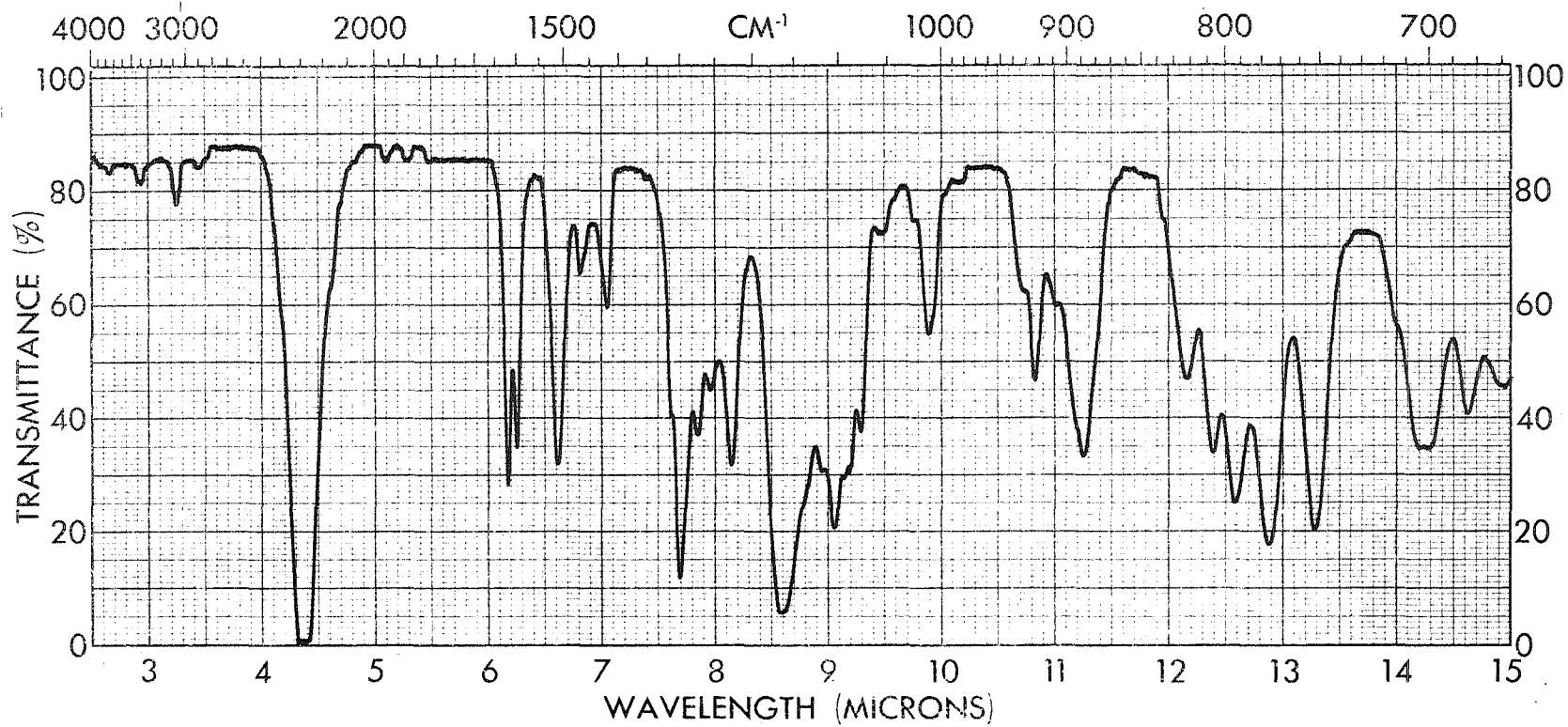


Figure 9. Infrared Spectrum of 1,3-Di-(*m*-isocyanatophenyl)hexafluoropropane

atmospheric pressure. The product distilled with a slight amount of decomposition at 132°C. The IR spectrum and boiling point of this product were very similar to those of perfluoroglutaryl chloride. Yield 72%.

1,4-Diiodooctafluorobutane (113207). Octafluorohexanedioyl chloride (60 g, 0.18 mole) and potassium iodide (91.5 g, 0.55 mole) were charged to a nitrogen-filled 180 ml stainless steel bomb. The bomb was heated to 250°C and allowed to cool gradually to 205°C and held there for 3 hr, making the total heating time 6 hr. After the bomb cooled to room temperature, the carbon monoxide was bled off and residual gases were removed by a nitrogen purge. The bomb was rinsed with 100 ml of chloroform and 200 ml of water. The organic layer was shaken with a solution of sodium bicarbonate until effervescence ceased. The chloroform layer was then dried (CaCl₂) and distilled, yielding 1,4-diiiodooctafluorobutane (42%), b.p. 122-124°C/346 mm Hg. The boiling point and infrared spectrum (Figure 10) were the same as those reported by Hauptschein (Ref. 50).

1,4-Di-(m-nitrophenyl)octafluorobutane (113209). The same procedure as for 1,3-di-(m-nitrophenyl)hexafluoropropane was used. The yield, however, was surprisingly low. The infrared spectrum (Figure 11) was very similar to that of its homolog, m.p. 95°C, yield 10%.

Anal. Calcd for C₁₆H₈F₈N₂O₄: C, 43.25; H, 1.81; N, 6.30
Found: C, 43.49; H, 1.72; N, 6.38

1,4-Di-(m-aminophenyl)octafluorobutane Dihydrochloride (113216). A 95% yield of 1,3-di-(m-aminophenyl)octafluorobutane dihydrochloride was obtained using the procedure employed in the preparation of the propane analog.

1,4-Di-(m-isocyanatophenyl)octafluorobutane (113217). The same procedure as for 1,3-di-(m-isocyanatophenyl)hexafluoropropane was used. The infrared spectrum (Figure 12) was very similar to that of its homolog, m.p. 83°C, yield 90%.

Anal. Calcd for C₁₈H₈F₈N₂O₂: C, 49.55; H, 1.85; N, 6.42
Found: C, 50.17; H, 1.92; N, 6.39

mol. wt: (calcd) 436.26; (found) 433.

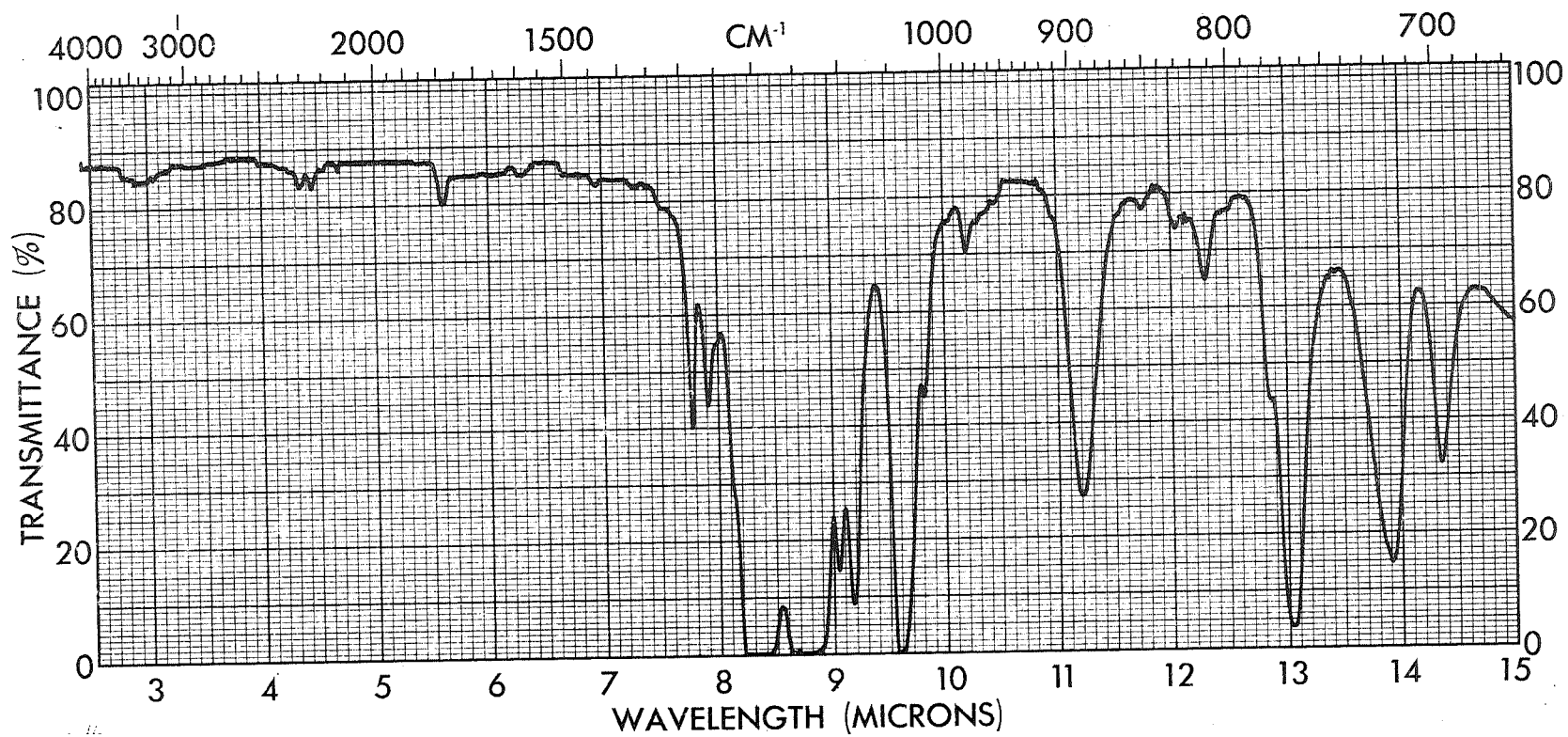


Figure 10. Infrared Spectrum of 1,4-Diiodooctafluorobutane

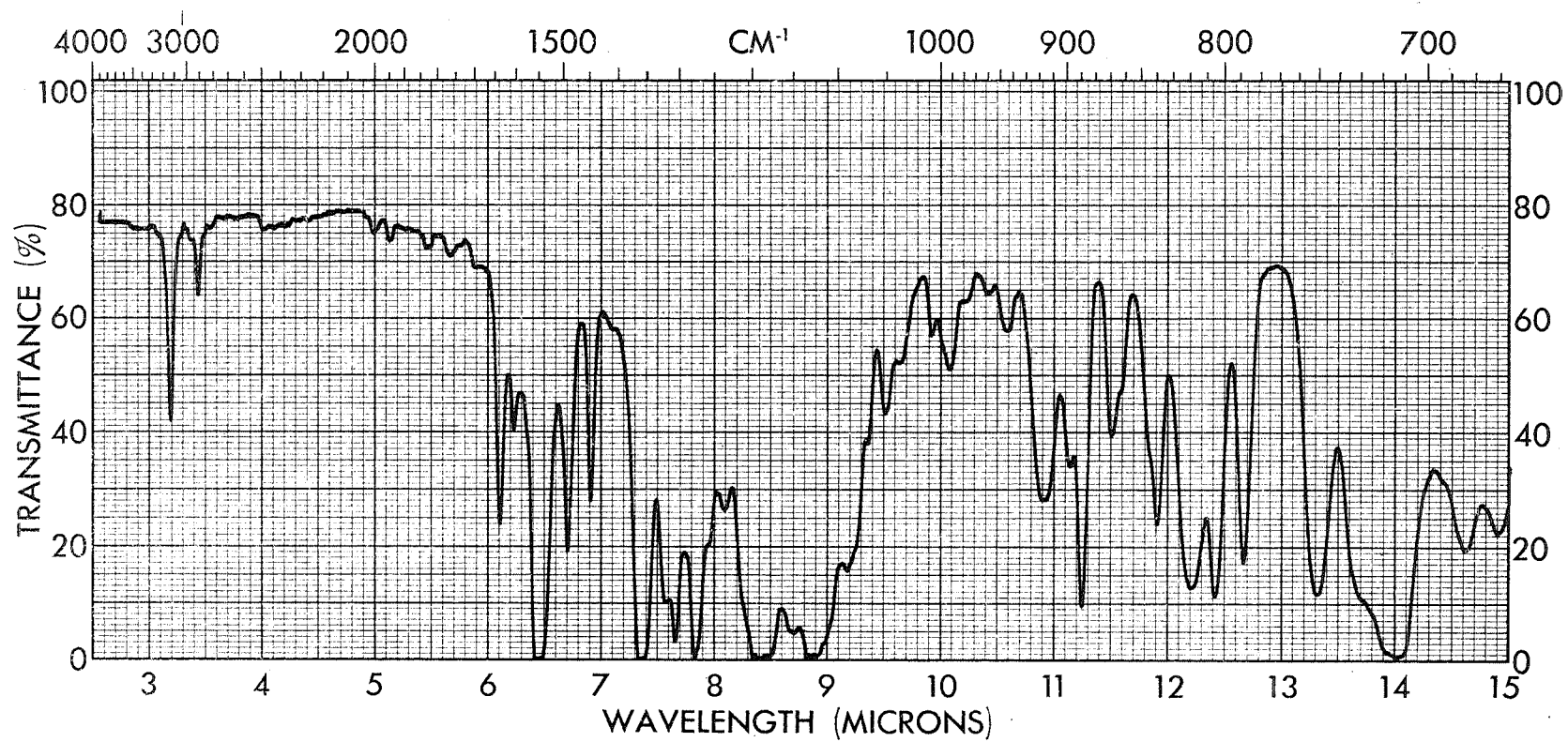


Figure 11. Infrared spectrum of 1,4-Di-(*m*-nitrophenyl)octafluorobutane

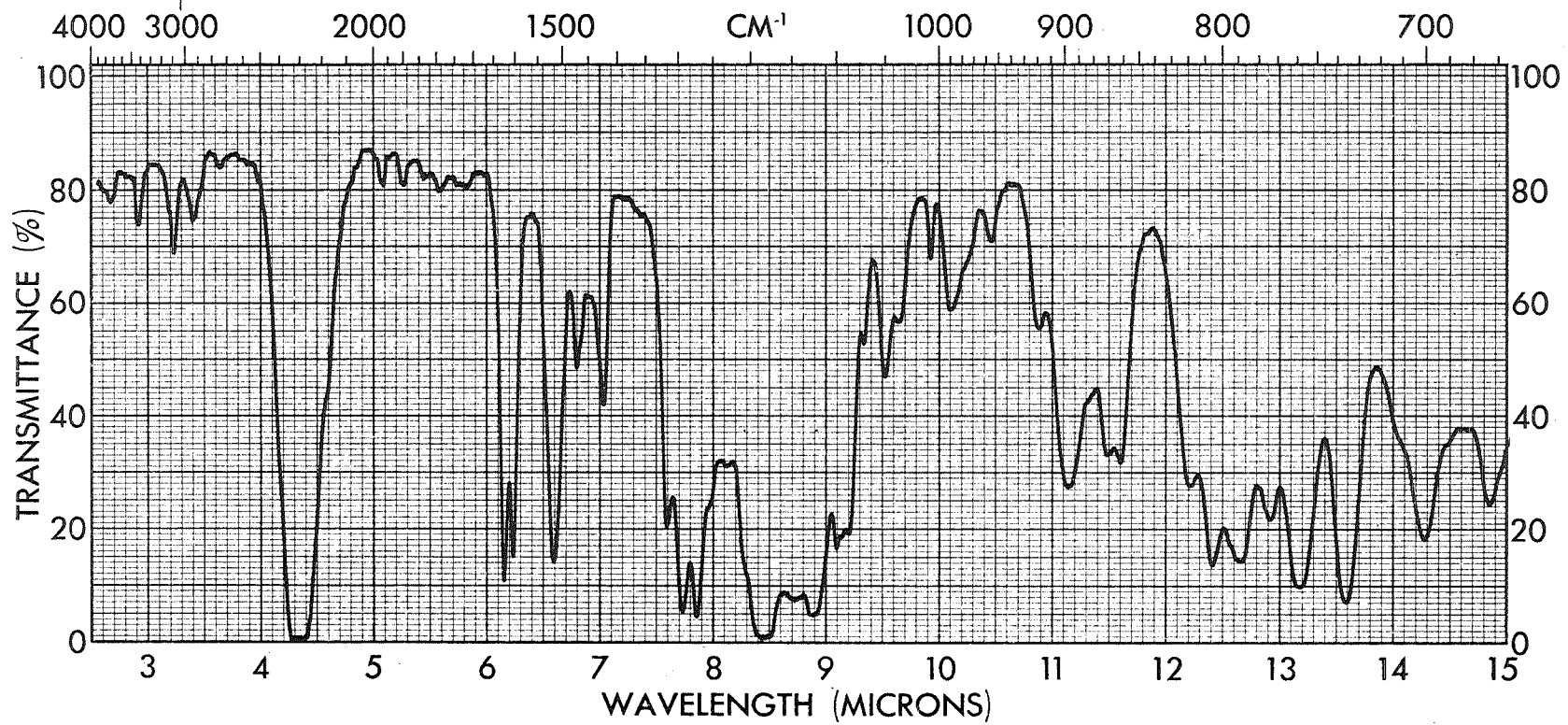


Figure 12. Infrared spectrum of 1,4-Di-(*m*-isocyanatophenyl)octafluorobutane

C. FLUOROALKYL ACETYLENIC COMPOUNDS

1. Heptafluoropropyl Ethynyl Ketone Synthesis.

a. Route A. Several experiments involving reactions of acetylenic organometallics and perfluorobutyric acid derivatives were carried out in a similar manner. The molar ratios, times temperature and results were summarized in Table 6.

Ethynylmagnesium bromide was prepared in tetrahydrofuran (THF) by the method of Jones, Skattebol and Whiting (Ref. 51) by adding ethyl Grignard to acetylene-saturated THF.

Sodium acetylide was prepared by passing purified acetylene into a sodium dispersion in xylene at 100-105° according to the method of Rutledge (Ref. 52). Acetylene was passed into sodium dispersion in xylene at 100-105°C until the intense purple color was discharged leaving a slurry of white solid. Solvent was removed under vacuum leaving the white, powdered sodium acetylide.

Lithium acetylide was prepared by gradual addition of a butyl lithium solution to ether being saturated by a rapid stream of acetylene.

Lithium, magnesium and bromomagnesium salts of perfluorobutyric acid were prepared as described by Blake (Ref. 30).

Heptafluorobutyric Anhydride (100273, 100275). A mixture of heptafluorobutyric acid 214 g (1 mole) and phosphorus pentoxide (100 g) was refluxed for 18 hours and then distilled. The infrared spectrum of distillate revealed incomplete conversion to anhydride. The volatile product was distilled rapidly and then heated 20 hrs over fresh P₂O₅. Distillation then gave 180 g (85%) of anhydride containing only a trace of free acid, b.p. 109°C/740 mm, $n_D^{25} < 1.3000$.

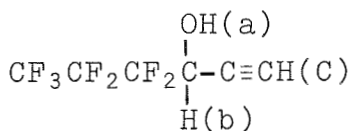
Heptafluoropropyl Ethynyl Ketone (100291, 100316). Sodium acetylide (10.1 g, 0.21 mole) in 100 ml of ether was added portionwise to heptafluorobutyric anhydride (76.8 g, 0.188 mole) in 125 ml of ether at -15 to -20°C. After stirring an additional hour, the reaction mixture was filtered to remove the sodium perfluorobutyrate. The filtrate was distilled rapidly to remove the more volatile components from higher boiling materials. Subsequent fractional distillation of this volatile material gave 10.4 g of perfluoropropyl ethynyl ketone, b.p. 39°C/225 mm, $n_D^{25} 1.3075-1.3083$, in 22% yield. Distillation of the higher boiling materials gave 11.3 g of 2,2,3,3,4,4,4-heptafluoro-1,1-diethynylbutyl heptafluorobutyrate, b.p. 63-64°C/16 mm, $n_D^{25} 1.3234-1.3246$.

In a second preparation 54.3 g sodium acetylide (1.13 moles) in 300 ml ether was added over 1.5 hours to 463 g of heptafluorobutyric anhydride (1.13 moles) in 300 ml ether at -50°C . Stirring was continued as the reaction mixture was permitted to warm. A foam began to form at -15°C . Foaming continued for two hours and increased as the mixture was cautiously permitted to warm to $+4^{\circ}\text{C}$. The reaction mixture was then filtered. Rapid separation of the volatile components from the filtrate and subsequent redistillation afforded a total of 78 g of perfluoropropyl ethynyl ketone, b.p. $41^{\circ}\text{C}/235\text{ mm}$, n_{D}^{25} 1.3066 (31% yield).

A 14% yield of 1,1-diethynyl-2,2,3,3,4,4,4-heptafluorobutyl heptafluorobutyrate, b.p. $55^{\circ}\text{C}/9\text{ mm}$ n_{D}^{25} 1.3247, d_4^{25} 1.550; sp. refr. 0.130, calcd 0.130, was isolated from higher boiling products. Identification of this product was based on the infrared spectrum that showed terminal acetylenic groups (3350 cm^{-1}), the carbonyl absorption at 1810 cm^{-1} instead of 1730 cm^{-1} that suggested an ester, and the boiling point that suggested a dimer of $\text{C}_3\text{F}_7\text{COC}\equiv\text{CH}$. The specific refraction values, though not conclusive, are consistent with the assignment of this structure.

b. Route B.

Heptafluoropropylethynylcarbinol (100270). Ethynylmagnesium bromide was prepared in tetrahydrofuran by the method of Skattebol, Jones and Whiting (Ref. 51). Heptafluorobutyraldehyde (35.2 g, 0.18 mole) was added dropwise to approximately 0.19 mole of ethynyl Grignard. After stirring for 1.5 hours the reaction mixture was poured onto ice containing 100 ml of 10% HCl. The organic product was separated, dried, and distilled to give 29.2 g of heptafluoropropylethynylcarbinol, boiling point $70^{\circ}\text{C}/99\text{ mm}$, n_{D}^{25} 1.3415. This product was subsequently shown by NMR to be a 2:1 complex of heptafluoropropylethynylcarbinol and tetrahydrofuran. The yield was 63% based on the carbinol content and the determination by NMR was consistent with the structure



Peak	Chem. Shift, ppm	Rel. Peak Area	Assignment
A	5.28	1.0	(a)
B	4.8	1.0	(b)
C	3.78	1.8	-{CH ₂ }-O- (THF)
D	2.6	1.0	(c)
E	1.89	1.8	-{CH ₂ }CH ₂ O- (THF)

Attempted Synthesis of Heptafluoropropyl Ethynyl Ketone by Oxidation of Heptafluoropropylethynylcarbinol (100279). Chromic acid oxidation of heptafluoropropylethynylcarbinol was carried out by the method employed by Bowden, *et al*, for the synthesis of phenyl ethynyl ketone from the corresponding alcohol (Ref. 39). After a reaction time of 18 hr at 25°C, volatile materials were removed under vacuum. A trace of the desired ketone appears to have been formed as determined by the infrared spectrum but the alcohol was largely recovered upon subsequent distillation.

2. 3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-Pentadecafluoro-1-nonyne Synthesis.

Attempted Preparation of 3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-Pentadecafluoro-1-iodo-1-nonene (91531, 91538). A 22 g (0.044 mole) quantity of freshly distilled pentadecafluoroheptyl iodide and 0.15 g of azodiisobutyronitrile were heated for two hours at 80-90°C with vigorous stirring in an atmosphere of purified acetylene. The violet color of iodine gradually formed but later disappeared upon heating to 120°C. No evidence of addition reaction was observed nor did heating for a second two-hour period with 0.15 g of fresh catalyst prove to be effective. Most of the perfluoroheptyl iodide was recovered by distillation, leaving a one gram residue. The infrared spectrum of this residue was essentially the same as that of the starting material.

A mixture of perfluoroheptyl iodide (16.6 g, 0.0335 mole), 0.15 g azodiisobutyronitrile, and 20 ml of redistilled butyrolactone as solvent was heated in an acetylene atmosphere at 900 mm (total pressure) with vigorous stirring. After two hours at 80-100°C, the organic two-phase mixture became almost colorless. The lower phase was washed with water and dried over MgSO₄. The infrared spectrum showed no change from that of perfluoroheptyl iodide except for a new absorption peak at 1800 cm⁻¹. This peak corresponds to the strong carbonyl absorption of butyrolactone and was therefore considered to be a trace of the butyrolactone.

1-Iodo-3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-Pentadecafluoro-1-nonene (111415). A one-liter autoclave was charged with 81.3 g of redistilled perfluoroheptyl iodide, flushed with acetylene and pressured to 30 psi at 25°C. The bomb was heated to 200°C for 6 hr. A pressure drop was observed at 160°C. Distillation afforded 50 g of adduct (59% conversion), b.p. 88°C/30 mm, n_D^{25} 1.3580-1.3585 and a recovery of 20 g of unreacted pentadecafluoroheptyl iodide.

3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-Pentadecafluoro-1-nonyne (91546). A portion of the above fluoro-iodononene (15.9 g) was added to 20 g of anhydrous potassium hydroxide and heated until vaporization was evident. Vacuum was applied to aid in removal of the fluoroacetylene product. The crude product was redistilled. Material boiling at 87-88°C/300 mm, est. n_D^{25} 1.291 was considered to be fairly pure. The infrared spectrum

showed strong absorptions at 3400 cm^{-1} and 2180 cm^{-1} , which frequencies are characteristic of a terminal acetylenic compound. Three fractions were obtained totaling 4 g and representing a 30% yield.

3. Acetylene Polymerizations.

Bis(triphenylphosphine)dicarbonyl Nickel (91517). This catalyst was prepared from nickel carbonyl and triphenylphosphine by the method of Rose and Statham (Ref. 53).

Bis(triphenylphosphine)nickel Dichloride (91523). Reaction of nickel chloride with triphenylphosphine following the method of Venanzi (Ref. 54) formed bis(triphenylphosphine)nickel dichloride catalyst.

Mercury Bis(cobalt tetracarbonyl) (100303). Mercury bis(cobalt tetracarbonyl) was prepared by the method of Hieber and Mitarb (Ref. 55). A solution of cobalt nitrate (17.5 g, 0.6 mole) in 40 ml of water was added to 400 ml of 12% ammonium hydroxide in a flask containing a carbon monoxide atmosphere. The reaction mixture was cooled to $10\text{-}15^{\circ}\text{C}$ and carbon monoxide gas was slowly passed into the solution while a solution of sodium dithionite (20 g, 0.015 mole) in 230 ml of 12% ammonium hydroxide was added over 4 hr, causing the reaction mixture to turn dark red. One ml of 33% formaldehyde was added and, after stirring for 10 min., mercuric cyanide (10.0 g, 0.0398 mole) in 50 ml of 12% ammonium hydroxide was added dropwise, causing a precipitate of yellow solid. After stirring for 30 min. the solid was collected on a fritted glass filter and was washed free of ammonium hydroxide with water. The crystals were dissolved in 110 ml of acetone. The solution was filtered to remove the free mercury. Addition of 400 ml of water reprecipitated the product, which was then collected by filtration and dried to give 14.4 g of mercury bis(cobalt tetracarbonyl).

Perfluoropropyl Ethynyl Ketone Trimerization (91548). A mixture of 9.0 g perfluoropropyl ethynyl ketone, 10 ml dioxane, and 0.5 g mercury bis(cobalt tetracarbonyl) was refluxed overnight. Evaporation of the solvent left 9.5 g of dark brown residue. Distillation under vacuum gave 3 g of liquid distillate and 4 g of a brown, friable solid. The liquid boiling at $80\text{-}87^{\circ}\text{C}/0.08\text{ mm}$ contained a major and a minor component as determined by vapor phase chromatography. The NMR spectrum shows multiple peaks in the aromatic region. The infrared spectrum indicated a carbonyl and fluorine containing aromatic compound. The mass spectrum showed major mass peaks at the following mass numbers:

<u>Mass Number</u>	<u>Assigned Fragment</u>
666	$C_6H_3(COC_3F_7)_3$
497	$C_6H_3(COC_3F_7)_2C=O$
469	$C_6H_3(COC_3F_7)_2$
328	$C_6H_3(COC_3F_7)(C=O-)_2$
300	$C_6H_3(COC_3F_7)C=O$
272	$C_6H_3(COC_3F_7)$
119	$-CF_2CF_3$
75	C_6H_3

Phenylacetylene Trimerization (91538). A mixture of phenylacetylene (10 g), mercury bis(cobalt tetracarbonyl) (1 g), and dioxane (25 g) was gradually warmed, with stirring, to 105°C, at which point an exothermic reaction became apparent. The heat was turned off but stirring was continued for 15 min. Volatiles totaling 31.5 g were removed leaving a residue of 6 g. From this was obtained 2 g of phenylacetylene and 4 g of a brown, taffy-like residue. Hexane dissolved all but 0.5 g of this residue. Several fractions in varying degrees of purity were isolated from the hexane solution. One fraction melting at 100.5-101°C was considered to be the 1,2,4-triphenylbenzene product, based on the reported melting point of 100.5°C (Ref. 26).

Phenylacetylene Trimerization with Ziegler Catalyst (111705). Phenylacetylene (5 g, 0.049 moles) dissolved in 10 ml of heptane was added dropwise with cooling to a stirred heptane slurry of Ziegler catalyst under an argon atmosphere. The catalyst was prepared by adding 0.061 g (0.32 mmoles) of titanium tetrachloride, and 0.19 g (0.96 mmoles) of triisobutylaluminum to 5 ml of heptane. Upon addition of phenylacetylene to this catalyst, a strongly exothermic reaction was observed and continued until after all of the phenylacetylene had been added. Following the reaction, methanol (20 ml) acidified with 4 ml hydrochloric acid was added with vigorous mixing. Tan crystalline solid 2.5 g, m.p. 173-177°C, was removed by filtration. This product was considered to be 1,3,5-triphenylbenzene based on the reported melting point of 172-173°C and the similarity between these results and published work (Ref. 25). The heptane phase from the filtrate was evaporated to dryness leaving an organic residue weighing 2.5 g, m.p. 89-95°C. This residue was considered to be impure 1,2,4-triphenylbenzene, m.p. 100.5°C (Ref. 25).

Attempted Trimerization of 3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-Penta-decafluoro-1-nonyne (91548). A 1.85 g quantity of 3,3,4,4,5,5,6,6-7,7,8,8,9,9,9-pentadecafluoro-1-nonyne (0.047 mole) was added to 0.15 g of mercury bis(cobalt tetracarbonyl) catalyst in 4 ml of dioxane. The mixture was heated for 2 hr at 100°C. Upon filtration and distillation, starting material was recovered and a brown oily residue was obtained. No evidence of aromatic ring formation was found.

Another attempt consisted of adding one gram of perfluoro-heptylacetylene dropwise to a cold heptane slurry Ziegler catalyst prepared as described for phenylacetylene polymerization. An initial exotherm was not sustained as the acetylene compound was added. After standing at room temperature overnight a few ml of acidified methanol was added. Workup of the material gave a trace of a fluorine containing oil but the results were considered inconclusive.

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