

ADDITION OF CARBONYL FLUORIDE TO ORGANIC
AND INORGANIC NITRILES

by

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Thesis submitted to the Graduate Faculty of the
Virginia Polytechnic Institute and State University
in partial fulfillment of the requirements for the degree of

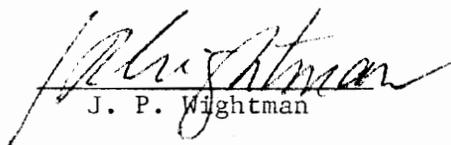
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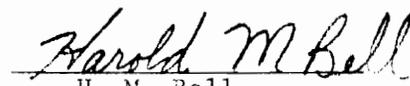
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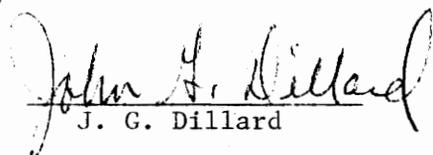
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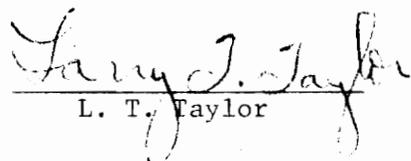
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ACKNOWLEDGMENTS

I wish to thank Dr. Alan F. Clifford for his suggestion of the original problem of this investigation and for the arrangements which allowed the work to proceed.

I wish to thank the analytical service personnel, Mr. Schaefer and Miss Tan, for the CHN analyses and mass spectra.

I also wish to thank Drs. Bell, Dillard, Taylor, and Wightman for their advice on the various problems which occurred in this investigation.

To Sara, my wife, I express my appreciation for "putting up" with me in the difficult times and for typing all of the research reports and rough drafts of the dissertation.

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CHAPTER I

ADDITION OF CARBONYL FLUORIDE TO ALIPHATIC NITRILES

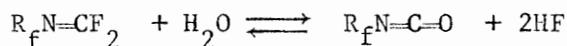
INTRODUCTION

Isocyanates are of interest and importance because of their high reactivity and use in the formation of polymers. Copolymers have been prepared from diisocyanates and bifunctional compounds such as glycols, diamines, and dicarboxylic acid amines. These polymers have been reported to be harder than Nylon, to absorb water less readily, to be unreactive, to have good electrical properties, and to have high resistance to outdoor exposure. Thus, the isocyanates polymers have found uses in fibers, elastomers, plastics, adhesives, and foams, and in modifying other polymers through cross linking.

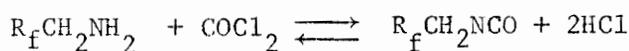
In the preparation of pentafluorosulfanylaminosulfur difluoride,¹ $\text{SF}_5\text{N}=\text{SF}_2$, from the reaction of thiazyl trifluoride and sulfur tetrafluoride in anhydrous hydrogen fluoride,² it was noticed³ that when thiazyl trifluoride was contaminated with carbonyl fluoride the pentafluorosulfanyl isocyanate⁴ was also obtained. The addition of the carbonyl fluoride across the sulfur-nitrogen triple bond suggested that it might also be added across the carbon-nitrogen triple bond of the appropriate aliphatic and aromatic nitriles to produce perfluoro isocyanates and α,α -difluoro isocyanates. Previous methods of preparing perfluoroalkyl isocyanates have been the Curtius rearrangement reaction:



or the controlled hydrolysis of perfluoroalkylimine compounds:



It has been reported that the Hofmann degradation will not work with perfluoroamides.⁵ Isocyanates with the α,α -dihydrogen perfluoroalkyl group⁶ have been reported to have been prepared by reacting the amine with phosgene:



Previous work with carbonyl fluorides by Fawcett et al.^{7,8} resulted in the formation of perfluoroalkyl isocyanates and α,α -difluoroalkyl isocyanates from the reactions of the appropriate nitriles with carbonyl fluoride in the presence of cesium fluoride and at mild temperatures. Their resulting reactions resulted in low to moderate yields of the α,α -difluoroalkyl isocyanates. They did not report any properties of the α,α -difluoroalkyl isocyanates.

Knowing that hydrogen fluoride adds across the sulfur-nitrogen triple bond, the purpose of this work was to investigate the addition of carbonyl fluoride to the carbon-nitrogen triple bond. Some of the questions to be answered were: How does the inductive effect of various aliphatics influence yield? How does changing the ratio of reactants to one another effect the yield? Were different products produced by varying the acidity or basicity of hydrogen fluoride? What different products, if any, would be produced if another anhydrous acid was used? Would heating the reaction mixtures improve the yield? Could urethanes and carbamates be made from the α,α -difluoroalkyl isocyanates and what are their properties?

EXPERIMENTAL

Vacuum System.

An all Pyrex glass high vacuum system free of mercury float valves was employed for handling the reactants and products. All stopcocks and ground glass joints were greased or waxed with Kel-F 90 grease (Minnesota Mining and Manufacturing Company) or with Halocarbon Wax (Halocarbon Products Corporation). Glass-to-metal connections were effected with stainless steel Swagelok (Crawford Fitting Company) unions using 1/4 inch Kovar to glass seals. A Teflon tape was applied to all fittings before connections were made. The stainless steel high pressure storage vessels were Whitey (Crawford Fitting Company) sample cylinders fitted with DK series valves. Hoke Monel sample cylinders were used for some of the reactions but the majority of the reactions were conducted in Kel-F test tubes (Argonne National Laboratory) fitted for vacuum work as described elsewhere.⁹

Reagents.

Carbonyl Fluoride. Carbonyl fluoride was purchased from the Matheson Company and was used without further purification as it contained only a small amount of impurities with carbon dioxide the major impurity.

Anhydrous Hydrogen Fluoride. Anhydrous hydrogen fluoride was used as received from Blockson Division of Olin Matheson. The water content determined by Karl Fisher determination was less than 0.03% by weight.

Sodium Fluoride. Sodium fluoride pellets were of technical grade from Harshaw Chemical Company. The pellets were dried in a muffle furnace at 400° to 450° for 24 hours, transferred to a drybox while still hot and stored in the drybox in a tightly sealed bottle until used.

The Synthesis of α,α -Difluoroethyl Isocyanate.

In a typical experiment 0.22 g (5.43 mmol) of acetonitrile (Fisher Spectrograde) which had been dried over Drierite and 0.39 g (5.89 mmol) of carbonyl fluoride were condensed into an evacuated, prefluorinated Monel cylinder. Anhydrous hydrogen fluoride was first distilled into a graduated Kel-F cylinder and 5 ml was then condensed under vacuum into the Monel cylinder. The reaction mixture was at room temperature for approximately 72 hours. The contents of the Monel cylinder were condensed onto NaF pellets contained in a dry Kel-F cylinder and were left in contact with the pellets for approximately two hours. The unabsorbed material was condensed back into the Monel cylinder and the cylinder was allowed to warm slowly while the emitted gases passed through traps of -78° (Dry Ice-trichloroethylene), -95° (toluene slush), and -131° (n-pentane slush), and finally into a -196° (liquid nitrogen) trap. The contents of the traps were identified by their infrared spectra. The -196° trap contained unreacted COF_2 ; -131° , the α,α -difluoroethyl isocyanate (3% yield); -95° , a trace of acetonitrile; and -78° , unreacted acetonitrile. The contents of the -78° trap could be further separated by passing them through a -45° (chlorobenzene slush) trap in which was found a semi-liquid of low vapor pressure which produced an infrared spectrum (Fig. 1, Table 1) resembling the previously reported infrared spectra¹⁰ of the acetonitrile and hydrogen fluoride complexes. When warmed to 40° or 50° C it readily reacted with glass to give large quantities of SiF_4 and acetonitrile. This material was probably $(\text{CH}_3\text{CF}=\text{NH}_2)^+(\text{HF})_x\text{F}^-$.¹¹ The Monel cylinder was then opened and found to

Table 1

Infrared Spectrum of $(\text{CH}_3\text{CF}=\text{NH}_2)^+(\text{HF})_x\text{F}$

Taken Between Salt Plates

cm^{-1}	Intensity*	Assignment
2941	m-v.b.	CH_3 asym and NH stretch
1809	m-v.b.	
1616	s-v.b.	C=N stretching and NH bending
1403	m-v.b.	CH_3 asym bend and HF_2^- stretch
1370	m-v.b.	CH_3 sym bend
1250	s.	CF stretch
1211	s.	CF stretch
1156	s.	CF stretch
1053	w.	CF stretch?
973	w.	CC stretch
932	m.	
847	m.	
823		
661	m.w.	

*m-v.b., medium and very broad; s-v.b., strong and very broad;

s., strong; w., weak; m., medium.

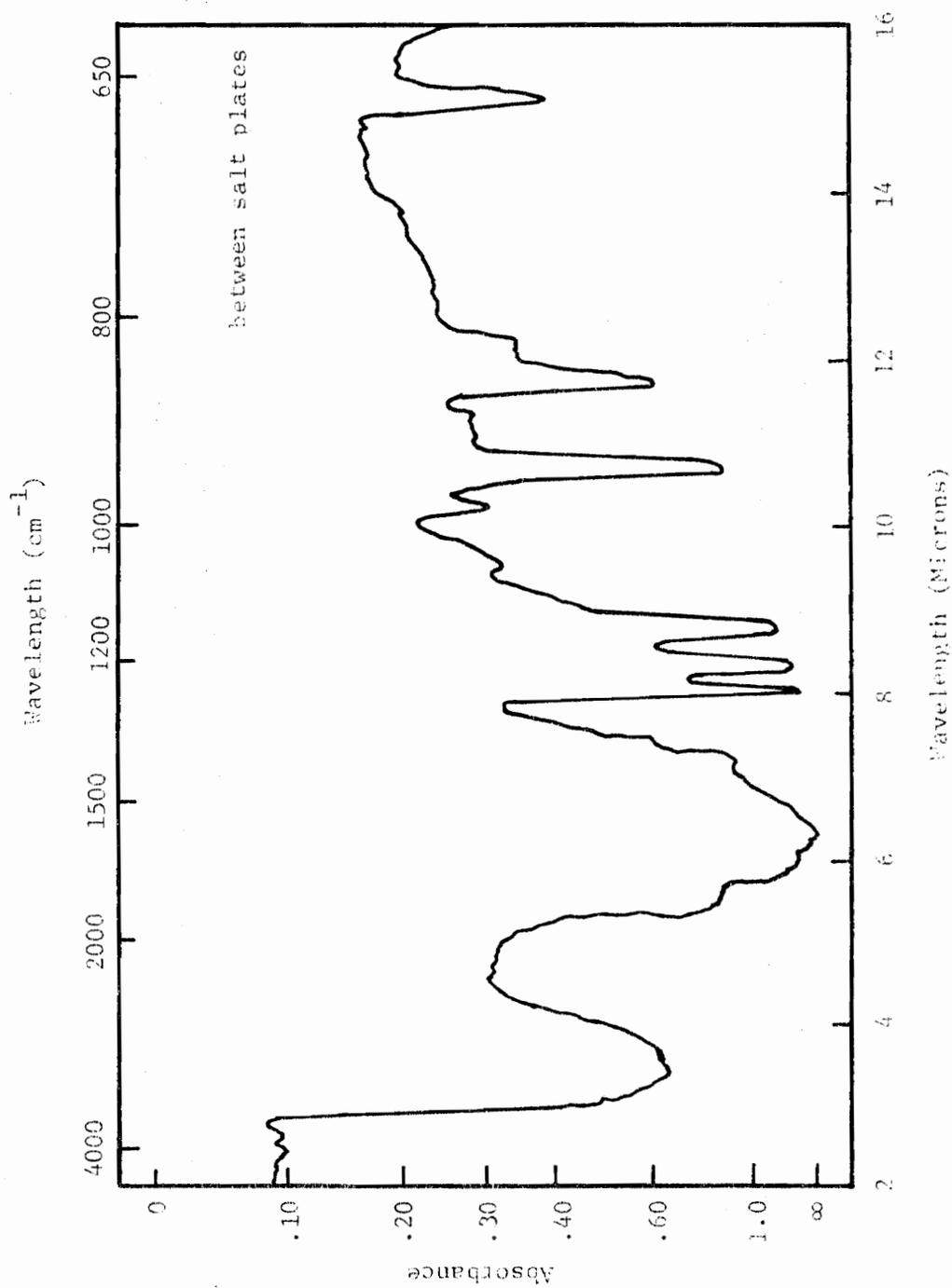


Figure 1. Infrared Spectrum of $(\text{CH}_3\text{CFNH}_2^+)(\text{F}^-)_x$

contain a dark brown solid material which gave an uninterpretable infrared spectrum. The material proved to be soluble in acids. Upon adding base to the solution, a white precipitate was obtained from the acid solution. Spot tests performed on the acid solution suggested that this material was a corrosion product from the Monel cylinder.

The Effect of Catalysts. In an attempt to increase the yield, the reaction mixture was made more basic by adding NaF (0.471 mmol). The result was a moderate increase in yield to about 6%. Addition of BF_3 (0.53 mmol) to a similar reaction mixture (making it more acidic) resulted in no observable reaction. A run using NiF_2 (0.31 mmol) as a catalyst for a short period of time (about 33 hrs.) resulted in formation of an amount of the isocyanate sufficient to identify by infrared spectrum, but not sufficient to purify.

The Effect of a Second Liquid Phase. In a modification of the reaction, benzene (Fisher Scientific, Spectrograde) was dried over molecular sieves and then measured out by condensing under vacuum into a graduated cylinder. The cylinder was allowed to warm to room temperature to obtain the volume of the liquid, usually 2.0 to 2.5 ml. The benzene was condensed into a Kel-F test tube. The acetonitrile was determined by $PV=nRT$ measurements and was condensed onto the benzene. Carbonyl fluoride was measured in the same manner and an approximate ratio of 1:1 to acetonitrile was established. Anhydrous hydrogen fluoride was condensed into a calibrated Kel-F tube, warmed to ice water temperature, and a measured volume was transferred to the reaction cylinder. The contents were allowed to warm to room temperature, where-

upon, two clear colorless phases formed at once. After about two hours the lower phase developed a clear yellow color whose intensity remained unchanged during the course of the reaction.

After various lengths of time the reactions (Table 2) were frozen and opened to see if any air or other non-condensable gas had been generated. In no case was any detected. A cooled Dewar flask was placed around the Kel-F test tube and the contents of the test tube were allowed to pass through thoroughly dried sodium fluoride pellets which were heated to 50° to 55°. This resulted in complete absorption of the HF while the integrity of the pellets was preserved. At higher temperatures the pellets would not retain the HF and at lower temperatures the pellets would not retain their integrity. The gas then passed through the usual traps. As identified by infrared spectroscopy, the -78° trap contained benzene and acetonitrile, the -95° trap had traces of benzene, acetonitrile, and, depending upon the speed of separation, $\text{CH}_3\text{CF}_2\text{NCO}$, the -131° trap contained the bulk of the isocyanate, and the -196° trap the unreacted COF_2 and a trace of carbon dioxide. Remaining in the reactor was a clear yellow liquid with a very low vapor pressure (nontransferable on the vacuum line). When it was heated to around 100° in a water bath, it decomposed to yield the isocyanate and acetonitrile, which could be separated as usual. The sum of the recovered COF_2 and the isocyanate formed both directly and from the yellow liquid was found to equal, within experimental error, the starting amount of COF_2 . Left in the Kel-F test tube was a very small amount of a cream colored solid material. Attempts made to purify and identify this material failed because of limited amount. By melting point and infrared spectrum

Table 2

Yields from the Addition of Carbonyl Fluoride to Acetonitrile[†] under Various Conditions

Run	CH ₃ CN mmol	COF ₂ mmol	Ratio CH ₃ CN: COF ₂	HF ml	Benzene ml	Time hrs.	Comments	% Yield*
1	5.4	5.89	0.92	5		75	0.03 g NaF	6
2	1.66	2.18	0.76	5		72	0.04 g NaF	trace
3	1.42	1.40	1.0	5		72	0.5 mmol BF ₃	
4	4.32	2.16	2.0	5		84	0.03 g NiF ₂	trace
5	3.72	2.47	1.5	?	3.	144		10.5
6	8.58	9.92	0.86	?	3.	432		21
7	3.24	3.3	1.0	trace	2.5	48		3
8	6.17	6.74	0.91	?	2.35	348		16.5
9	8.67	8.76	1.0	?	2.35	480		25.6
10	4.58	10.03	0.46	1.32	2.35	412		41.5
11	4.80	3.90	1.2	none	2.5	72		
12	5.32	5.14	1.0	trace	2.5	98.5	heated	trace
13	20.12	5.7	3.5	0.1	1.0	88	heated	6.8
14	20.12	6.26	3.2	0.15		68	heated	9
15	4.10	4.60	0.89	trace	2.5**	95		trace
16	19.5	3.04	6.4	5.5		120		10
17	100.0	7.79	12.8	0.94		108		19.5
18	23.0	2.44	9.4	1.68		336		44.7
19	9.58	10.2	0.94	0.59		240		20.8
20	11.1	12.7	0.87	1.88		380		15.9
21	9.1	10.1	0.90	0.48		62 days		82

*Based upon the reactant expected to be 100% consumed

**Chlorobenzene

[†]At ambient temperature unless noted

characteristics the possible 2,4,6-trimethyl-s-triazine, $(\text{CH}_3\text{CN})_3$, and 4-amino-2,6-dimethylpyrimidine, $(\text{CH}_3)_2\text{NH}_2(\text{HCCCNCN})$, were eliminated. The compound was not obtained when acetonitrile and anhydrous hydrogen fluoride were mixed and treated under identical conditions. Another possible identity for the solid was the disubstituted urea, N,N'-bis(α,α -difluoromethyl)urea, or its dehydrofluorination product, be(fluoroethylidene)urea, $\text{CH}_3\text{C}(\text{F})=\text{NC}(\text{O})\text{N}=\text{C}(\text{F})\text{CH}_3$.

Analysis of variation¹² was calculated on various categories of Table 2 with the following results: 1.) Solvents had no effect upon the reaction yield, 2.) When either carbonyl fluoride or acetonitrile was in excess the yield, based on the lesser, was increased, 3.) The amount of HF was critical, for if the mmol sum of the carbonyl fluoride and acetonitrile was less than one or greater than three times the mmol of hydrogen fluoride, the yield was reduced, 4.) The longer the time the larger the yield. Finally, by direct comparison the yield with sodium fluoride present was greater than when it was absent.

The Effect of Temperature. In another experiment, 2.5 ml of benzene, 0.340 g (5.14 mmol) carbonyl fluoride, 0.231 g (5.32 mmol) of acetonitrile, and a trace of HF were condensed into a prefluorinated Monel cylinder and contents were heated on a steam table for four days. After cooling with liquid nitrogen, the cylinder was opened and found to contain a large quantity of non-condensable gas which was identified, by the vapor density method, as being hydrogen. After removing the hydrogen, the material was passed through the traps described earlier. The -78° trap contained benzene and perhaps some CH_3CN , the -95° trap contained some of the isocyanate and a new compound with major peaks at 2083 and

676 cm^{-1} , the -131° trap contained more of the isocyanate and the new compound, and the -196° trap contained the unreacted carbonyl fluoride and a larger amount of CO_2 . This new compound was apparently acetylene isocyanate, HCCNCO , for the infrared spectrum was identical to those of monosubstituted acetylenes. The cylinder was opened in the drybox and found to contain a large quantity of a cream colored solid. This solid was different from the solid of the unheated reactions and was equally difficult to characterize. However, it may have been 6-fluoro-2-methyl-4(3H)-pyrimidone, $\text{C}(\text{CH}_3)\text{N}(\text{H})\text{C}(\text{O})\text{C}(\text{H})\text{C}(\text{F})\text{N}$. The corresponding chloride was made by Yanagida and co-workers¹³ from acetonitrile, phosgene, and anhydrous hydrogen chloride.

The concentration of anhydrous hydrogen fluoride was critical for, as the concentration of HF was increased (see Table 2), the yield of the acetylene isocyanate decreased as well as the yield of the solid. On the other hand, the α,α -difluoroethyl isocyanate yield increased with the increasing concentration of anhydrous HF.

Carbamyl Fluoride. On several occasions when the contents of the reactor were passed through the NaF pellets rapidly, the -131° would contain colorless crystals arranged in snow flake-like patterns. By allowing the α,α -difluoroethyl isocyanate to evaporate rapidly, a gas sample for analysis of these crystals could be obtained. (Table 3, Figure 2). This material rapidly etched the NaCl windows of the infrared cell and, when left in glass for 30 minutes, produced a large quantity of SiF_4 and α,α -difluoroethyl isocyanate. The material was probably α,α -difluoroethylcarbamyl fluoride, $\text{CH}_3\text{CF}_2\text{N}(\text{H})\text{C}(\text{F})\text{O}$.¹⁴

Table 3

Infrared Spectrum of α,α -Difluoroethylcarbonyl Fluoride

cm^{-1}	Intensity*	Assignment
3478	w.	NH stretch
1872	v.s.	CO stretch
1501	m.	NH bend
1403	w.	CH_3 asym bend
1289	m.	CF_2 stretch
1172	s doublet	CF_2 stretch
962	w.b.	CC stretch

* w., weak; v.s., very strong; m., medium; s., strong;

w.b., weak and broad.

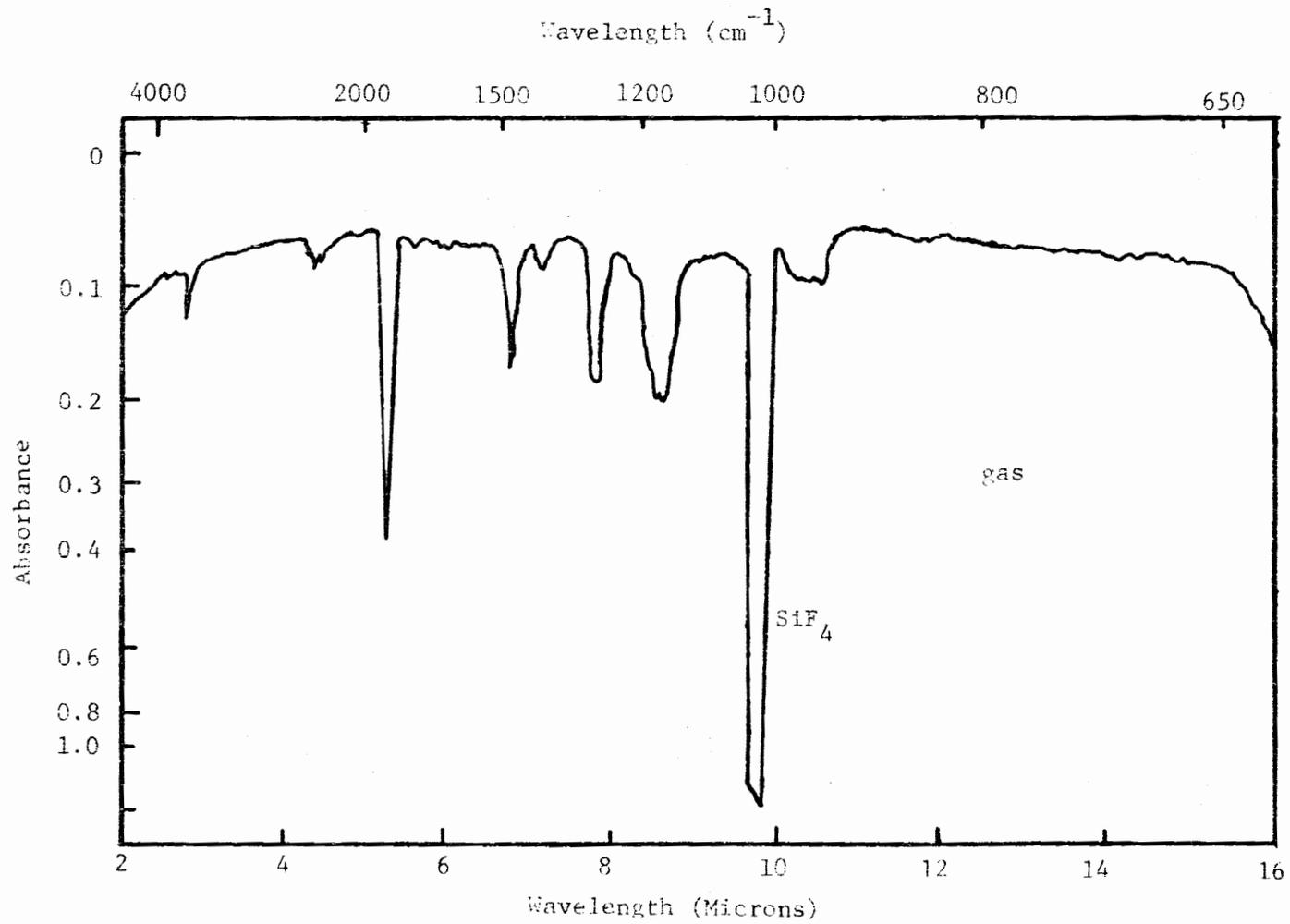


Figure 2. Infrared Spectrum of α,α -Difluoroethylcarbonyl Fluoride.

The Substitution of Anhydrous Hydrogen Chloride for Anhydrous

Hydrogen Fluoride. Anhydrous hydrogen chloride (Matheson Company) was used as the acid catalyst to test if the chloride or fluoride compound could be produced. When dried acetonitrile 0.161 g (3.93 mmol), dried benzene 1 ml, carbonyl fluoride 0.379 g (6.22 mmol), and HCl 0.923 g (25.3 mmol) were condensed into a Kel-F test tube and allowed to warm to room temperature, a single phase resulted. The following day the solution was clear yellow and several days later two phases appeared with the upper phase being clear and colorless while the lower phase was clear and yellow. A week later three phases were noted with the top two being described above and the third being solid needle-like crystals, which were possible $(\text{CH}_3\text{CCl}=\text{NH}_2^+)\text{Cl}^-$.¹⁵

After ten days at room temperature the reaction mixture was frozen and found to contain no non-condensable gases. The products were passed through the same temperature traps as described earlier. The -196° trap was found to contain unreacted COF_2 and COClF .¹⁶ The -131° trap contained COClF , COCl_2 , and α,α -difluoroethyl isocyanate, the -95° trap had a trace of benzene and acetonitrile, and the -78° trap contained the benzene and acetonitrile. The test tube contained a reddish-brown solid. When this was heated in a water bath, the decomposition material was passed through the traps described above. The -196° trap contained a gas which gave no infrared spectrum but had a vapor density molecular mass of 37.5, and was therefore thought to be HCl. The -131° trap contained $\text{CH}_3\text{CF}_2\text{NCO}$, and the -95° trap had a trace of SiF_4 , and the -78° trap contained some acetonitrile. Some of the solid was not decomposed

and the infrared spectrum, by salt plate smear, was not too different from the one recorded when anhydrous hydrogen fluoride was the acid. Spot tests of this material gave positive results for chloride but negative for fluoride.

Physical Properties of $\text{CH}_3\text{CF}_2\text{NCO}$.

Infrared Spectrum. The infrared spectrum of α,α -difluoroethyl isocyanate was recorded by a Beckman IR 5 Spectrometer with the results and assignments in Table 4 and illustrated in Figure 3. The spectrum and assignments were in agreement for related fluoride compounds.^{17,18}

NMR. The NMR spectra were run on the JOEL C-60-H at 60 MHz for the proton and at 56.446 MHz for the F-19. The proton was run using Freon-11 as the solvent which contained one drop of TMS. A triplet centered at -1.93 ppm with a coupling constant of 13.8 Hz was observed. The F-19 NMR showed a quartet at -19.8 ppm from external trifluoroacetic acid with $J=13.8$ Hz. This was in excellent agreement with $\text{CH}_3\text{CF}_2\text{NFC1}^{19}$ which, for the proton, has a triplet centered at -1.8 ppm and a coupling constant of 13 Hz and for the F-19 a quartet centered at -14.1 ppm.

Mass Spectrum. The mass spectrum, Table 5, was measured on a Hitachi-Perkin-Elmer RMU 6E mass spectrometer. Peaks of less than 3% relative intensity are not listed unless they have some special significance. The fragmentation pattern consistently reveals loss of CH_3 , F, HF, NCO, and H.

Vapor Pressure. The vapor pressure was measured with a constant volume manometer and was expressed by the equation:

$$\log P = - 1370.5/T + 7.4.$$

Table 4

Infrared Spectrum of α,α -Difluoroethyl Isocyanate

Taken at 14 Torr

cm^{-1}	Intensity*	Assignment
3035	v.w.	CH_3 asym
2415	v.w.	
2283	v.s.	NCO asym stretch
1439	m.b.	CH_3 asym bend
1173	s.b.	CF_2 stretch
940	m.b.	CC stretch

* v.w., very weak; v.s., very strong; s.b., strong and broad;
m.b., medium broad.

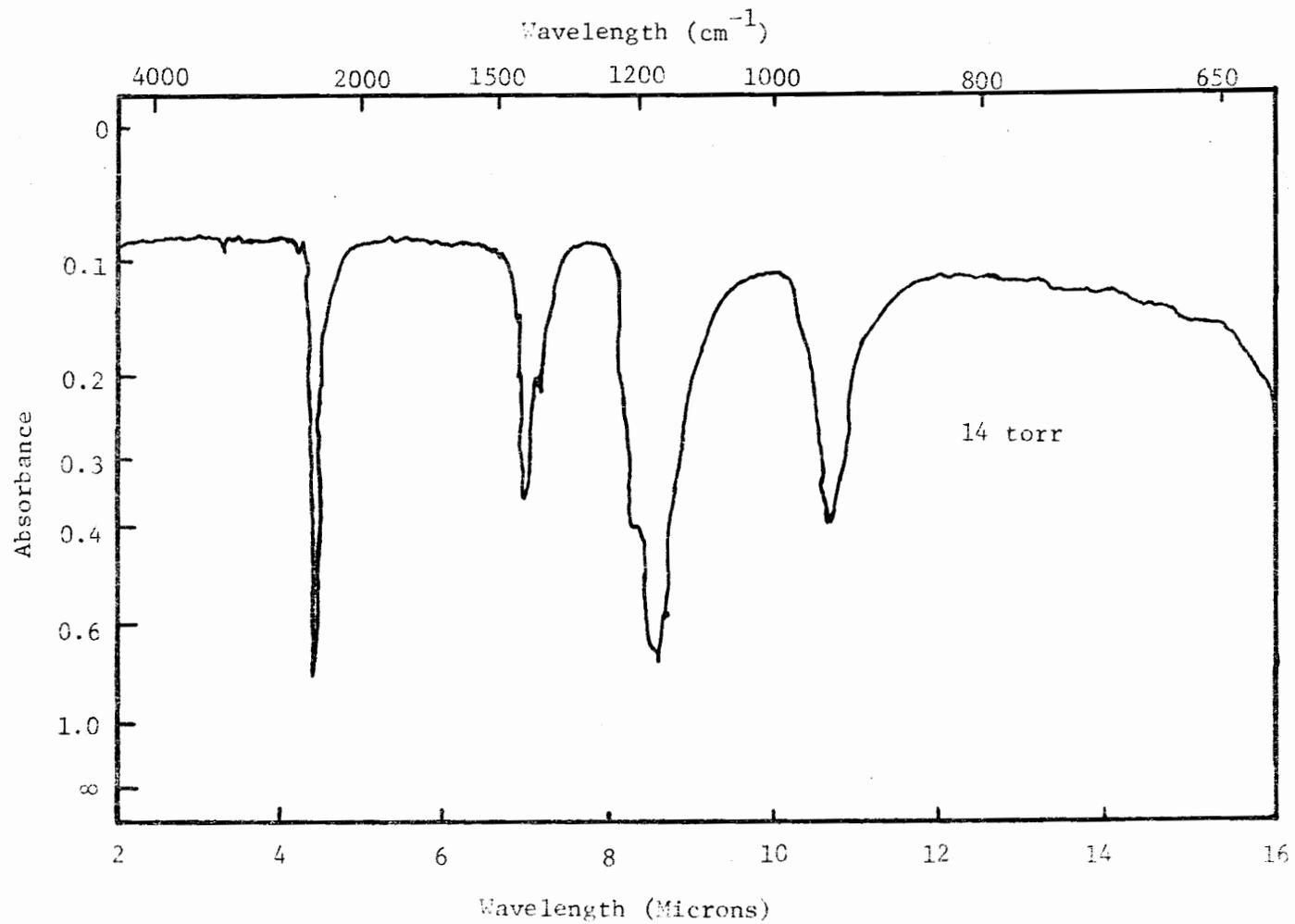


Figure 3. Infrared Spectrum of α,α -Difluoroethyl Isocyanate.

Table 5

Mass Spectrum of $\text{CH}_3\text{CF}_2\text{NCO}$ 50 ev Port Temperature 100°C Intensity Relative to CH_3CF_2^+

m/e	Relative Intensity	Ion
108	0.8	$\text{C}^{13}\text{H}_3\text{CF}_2\text{NCO}^+$ (Cal. 0.4)
107	11.0	$\text{CH}_3\text{CF}_2\text{NCO}^+$
93	2.2	
92	59.4	CF_2NCO^+
88	7.4	$\text{CH}_3\text{CFNCO}^+$
72	7.2	CH_3CFCN^+
66	3.8	COF_2^+
65	100.0	CH_3CF_2^+
64	19.8	CH_2CF_2^+
58	3.0	HCFCN^+
57	3.6	CFCN^+
54	5.0	CNCO^+
51	3.3	CHF_2^+
50	3.3	CF_2^+
47	23.4	CFO^+
45	18.1	CH_2CF^+
44	11.8	CHCF^+
43	54.4	C_2F^+
42	8.3	NCO^+
41	94.0	CH_3CN^+

Table 5 continued

m/e	Relative Intensity	Ion
40	52.5	CH_2CN^+
39	21.4	C_2HN^+ , HF_2^+
38	11.5	F_2^+ , C_2N^+
33	4.9	CH_2F^+
32	3.3	CHF^+ ,
31	5.8	CF^+
29	6.0	
28	45.8	CO^+ , N_2^+
26	5.5	CN^+ , C_2H_2^+
18	9.1	H_2O^+
15	10.7	CH_3^+
14	7.9	CH_2^+ , N^+
12	3.0	C^+

Temperature °K	Pressure mm of Hg
223.3	18.9
228.1	26.0
236.0	40.3
242.7	57.5
258.0	117.5
266.7	187.7
278.8	328.6

The extrapolated boiling point was 29° C., the heat of vaporization as calculated from the Clausius-Claperon equation was 6272 cal/mol deg., and the Trouton Constant was 20.7 cal/deg.

Melting Point. The melting point was determined in the high vacuum system using a conventional plunger type apparatus described by Sander-son.²⁰ The temperature was measured with a calibrated Chromel-Alumel thermocouple in conjunction with a Keithley 630 Potentiometric Electro-meter. The melting point was -98°.

Percentage of Fluoride Ion. The concentration of fluorine was measured by using an Orion 701 pH/mv meter in connection with an Orion fluoride specific electrode (model 90-01). The method used for the determination of the fluorine concentration was Gran's method^{21,22} (known addition method) with data reduction using a least squares program for the Digital Equipment Corporation's PDP-8/I computer. The known fluorine concentrations were prepared from Orion's 0.1 N sodium fluoride standard and 4 M sodium acetate-acetic acid buffer adjusted to a pH of approximately 5.8.

An infrared pure sample of α,α -difluoroethyl isocyanate was transferred to a weighing bulb and weighed. The bulb was returned to the vacuum line and the contents were condensed onto 5 ml of frozen 6 M NaOH solution, the bulb then being reweighed to determine the amount hydrolyzed. The NaOH solution was slowly warmed, refrozen and again allowed to warm slowly in order to allow all the isocyanate to hydrolyze. The NaOH solution was transferred to a volumetric flask and a volume of the above described buffer was added sufficient to make it 2 M in sodium acetate upon dilution to volume. The test solution would, therefore, very closely match the pH and ionic strength of the known fluorine solution. Calculated for $C_3H_3F_2NO$: 35.49% Found: 35.22%.

Some Reactions of CH_3CF_2NCO .

Formation of Carbamate. Ethanol was placed in a reaction flask with Mg metal and allowed to stand several days. Approximately 1 ml was measured out under vacuum and transferred to a glass reactor. α,α -Difluoroethyl isocyanate, 0.38 g (3.60 mmol), was condensed onto the ethanol and the mixture was allowed to warm toward room temperature with stirring. After 15 minutes the mixture was refrozen and allowed to warm slowly with the gaseous products passing through traps of -45° (chlorobenzene slush), -78° , and -131° , into a -196° trap. The material trapped in the -45° and -78° traps was identified by infrared spectrum to be excess ethanol. No material was discovered in the other two traps, nor was there any sign of etching of the reactor. When the Dewar flask was removed from around the reactor, a white crystalline solid was observed.

This sample was transferred to the drybox and opened under a dry, inert atmosphere. A Nujol mull of the sample gave an infrared spectrum (Table 6, Figure 4) that "fitted" the general pattern of urethanes and had major peaks which corresponded to the N-perfluoroalkyl carbamates discovered by Barr and Haszeldine.²³ The sample started to yellow immediately after removing the ethanol and when the sample was left in the ethanol for one day, only a yellow semi-solid material was recovered. After storage under an inert atmosphere for a day, white needle crystals sublimed onto the sides of the storage bottle and in the nonvolatile residue additional material had turned yellow. Some of the sublimed crystals were loaded into a microcapillary and submitted

for CHN analysis.	Calculated for $C_5H_9F_2O_2N$	Found
	C 39.4%	39.4%
	H 5.9%	5.42%
	N 9.15%	8.64%

After about two weeks all of the urethane had decomposed and the glass storage vessel appeared to have been etched.

Reaction with Water. About 0.25 g (2.35 mmol) of the isocyanate was frozen into a Pyrex flask and 20 ml of distilled water was drawn into the flask. This mixture was allowed to warm to room temperature. The isocyanate hydrolyzed readily and gave off an odor of acetic acid. The solution was divided into two parts, one being evaporated in a dish to give clear, colorless, star-like patterns which never completely dried. The other portion was used for spot tests²⁴ with positive

Table 6

Infrared Spectrum of α,α -Difluoroethyl Carbamate
Taken as a Nujol Mull

cm ⁻¹	Intensity*	Assignment
3296	m.	NH stretch
3077	v.w.	CH ₃ asym stretch
2908	s.	CH ₃ and Nujol
1724	b.s.	CO stretch
1532	b.s.	NH bend
1453	s.	CH ₃ asym bend
1404	w.	
1310	m.b.	CH ₂ twisting and wagging
1205	b.s.	CF ₂ stretch
1139	m.	
1107		
1081	m.	CF ₂ stretch
1000	m.	
963	w.	CC stretch
914	m.	
888	s.	
827	m.	
810		
785	m.	
727	m.	NH deformations

*m., medium; v.w., very weak; s., strong; b.s., broad and strong; w., weak;
m.b., medium broad.

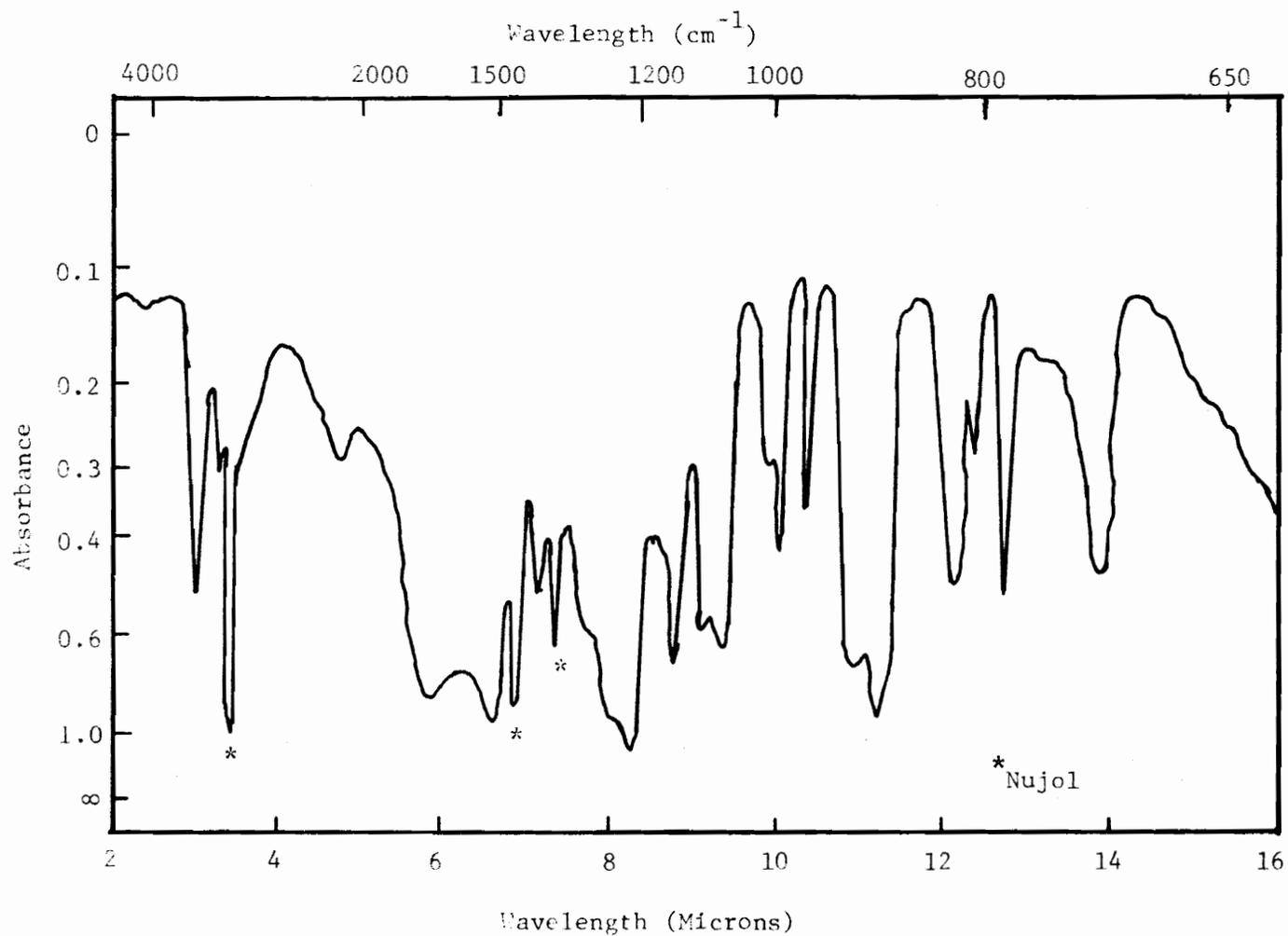
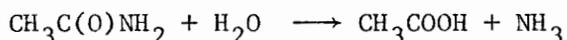


Figure 4. Infrared Spectrum of α, α -Difluoroethyl Carbamate.

results for ammonia, fluoride and acetate ion. No tests were run for acetamide, but it was presumably the intermediate in the postulated hydrolysis steps:



Reaction with NaF. In an attempt to produce acetylene isocyanate, α,α -difluoroethyl isocyanate, 0.561 g (5.246 mmol) was transferred to a stainless steel cylinder containing dried NaF pellets and was heated to 130° for five hours. Upon cooling, the infrared spectrum showed no changes or additional peaks. Thus, HF does not split out of the molecule under these conditions.

Reaction with Anhydrous Hydrogen Fluoride. A prefluorinated Monel cylinder containing 2.77 mmol of α,α -difluoroethyl isocyanate and 0.1 ml of anhydrous hydrogen fluoride was placed in a steam table for 69 hours. Upon cooling with liquid nitrogen, a non-condensable gas, found to be hydrogen, was observed. It is reported²⁵ that acetonitrile will complex nickel in anhydrous hydrogen fluoride. Thus, the fluorinated metal of the Monel cylinder would be complexed by the acetonitrile exposing a fresh surface for the hydrogen fluoride to attack and be reduced to hydrogen. The condensable material was passed through a trap of NaF at 55° and traps at -78° , -83.6° (ethyl acetate slush), and -131° , and into a liquid nitrogen trap. The -78° trap contained some SiF_4 but mostly acetonitrile; the -83.6° trap contained a small amount of α,α -difluoroethyl isocyanate; the -131° trap contained the rest of the isocyanate and the -196° trap contained carbonyl fluoride. The Monel cylinder was heated in a boiling water bath and additional COF_2 and $\text{CH}_3\text{CF}_2\text{NCO}$ were

recovered. The amount of α,α -difluoroethyl isocyanate recovered was 17.6% of the starting material. The Monel cylinder was opened and found to contain a brown solid unlike the previous solids of this reaction in Kel-F. Spot tests suggested that it was the oxidized metal of the cylinder.²⁵

Preparation of α,α -Difluoropropyl Isocyanate.

Propionitrile (Eastman Organic Chemical Practical), 0.8 ml (0.618 g, and 11.2 mmol), and carbonyl fluoride, 0.206 g (3.13 mmol), were introduced into a Kel-F test tube and mixed with anhydrous hydrogen fluoride which had been measured in a calibrated Kel-F tube 0.3 ml (0.3 g, and 15.0 mmol).

Thirty four days later the reaction mixture was refrozen (-196°) and opened. No non-condensable gases were found above the frozen reaction. The material was allowed to warm slowly and pass through a heated NaF trap to remove the HF, traps of -78° , -83.6° , -131° , and into a -196° trap. The -196° trap was found to contain mostly carbon dioxide, SiF_4 , and a trace of COF_2 . The only other trap containing material was the -78° trap which contained unreacted propionitrile and a material later identified as the α,α -difluoropropyl isocyanate. The two materials were separated by the fractional codistillation technique.²⁶ Some material was left in the Kel-F reactor and it was necessary to warm the reactor in a water bath to effect complete removal. The low vapor pressure of this material was probably due to the hydrogen bonding and the hydrogen fluoride added across the carbon-nitrogen double bond of the isocyanate group.¹⁴ An infrared spectrum of this material confirmed

that it was the fluorocarbamate of the α,α -difluoropropyl isocyanate probably mixed with the imine $(\text{CH}_3\text{CH}_2\text{C}(\text{F})=\text{NH}_2)^+(\text{HF})_x\text{F}^-$. Heating these materials caused their decomposition to the isocyanate and propionitrile. A very small amount of a cream colored solid remained in the Kel-F test tube. The yield of $\text{CH}_3\text{CH}_2\text{CF}_2\text{NCO}$ from this reaction was greater than 95% based on 100% consumption of carbonyl fluoride.

In another experiment, 0.8 ml of propionitrile (11.23 mmol), 1.107 g of carbonyl fluoride (16.77 mmol), and 0.15 ml of anhydrous hydrogen fluoride (7.51 mmol) in 336 hours yielded 96% of the isocyanate. Shorter reaction times were not attempted. When the above reaction was tried without the hydrogen fluoride, no reaction occurred.

Physical Properties of α,α -Difluoropropyl Isocyanate.

Infrared Spectrum. The infrared spectrum of this material (Table 7, Figure 5) gave strong supportive evidence^{17,18} that this was a higher homolog of α,α -difluoroethyl isocyanate.

Mass Spectrum. The mass spectrum (Table 8) exhibited the expected pattern for the α,α -difluoropropyl isocyanate including the isotopic ratio. The mass spectrum recorded a peak 20 units higher than the parent ion, which strongly implies that the isocyanate was contaminated with α,α -difluoropropylcarbonyl fluoride resulting from addition of HF to the isocyanate group.

NMR. In a Freon-11 solution the proton NMR gave a triplet at -1.15 ppm from TMS with a J_{HH} of 7 Hz which was assigned to the methyl group, and a multiplet at -2.10 ppm assigned to the methylene group (Fig. 6). The integration of triplet and multiplet gave a ratio of 3 to 2. The

Table 7

Infrared Spectrum of α,α -Difluoropropyl Isocyanate

Taken at 23 Torr

cm^{-1}	Intensity*	Assignment
3686	w.	
3070		
2992	m.	CH^{\bullet} stretching
2957		
2899		
2386		
2257	v.s.-b	NCO asym stretch
1494	s.	CH_2 scissoring
1439	v.s.	CH_3 asym bending
1363	m.	CH_3 sym bending
1291	s.	CF_2 stretching
1215	v.s.-b	CF_2 stretching
1160	v.s.-b	CF_2 stretching
1131	v.s.-b	CF_2 stretching
1052	s.	
996	v.s.-b	
968	v.s.	CC stretching
658	w.b.	

* w., weak; m., medium; v.s.-b, very strong and broad; s., strong;

v.s., very strong; w.b., weak and broad.

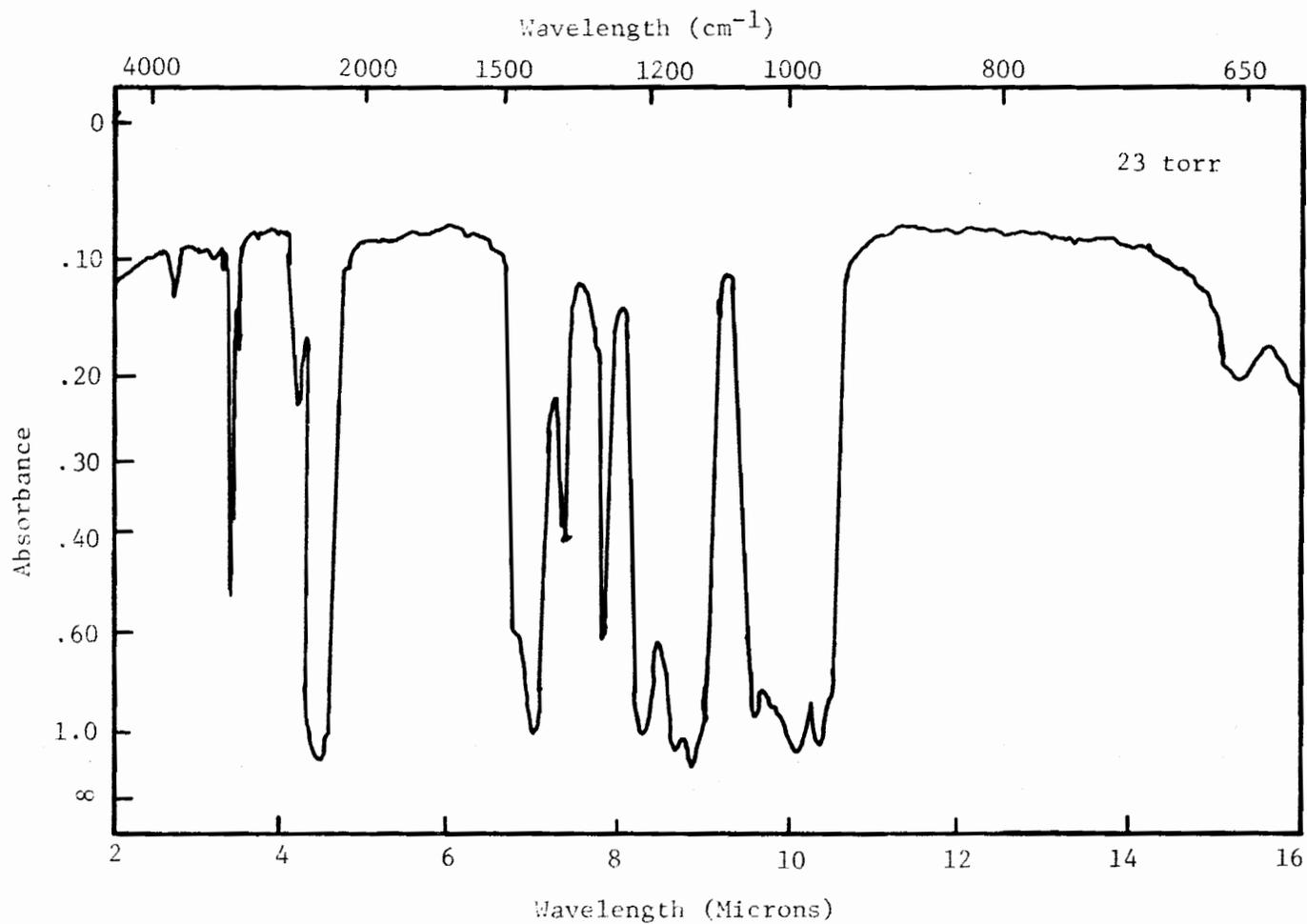


Figure 5. Infrared Spectrum of *o,o*-Difluoropropyl Isocyanate.

Table 8

Mass Spectrum of $\text{CH}_3\text{CH}_2\text{CF}_2\text{NCO}$

50 ev Port Temperature 160°C.

Intensity Relative to CF_2NCO^+

m/e	Relative Intensity	Ion
141	0.03	$\text{C}_2\text{H}_5\text{CF}_2\text{NHCFO}^+$
140	0.02	$\text{C}_2\text{H}_5\text{CF}_2\text{NCFO}^+$
121	0.14	$\text{CH}_3\text{CH}_2\text{CF}_2\text{NCO}^+$ (parent ion)
103	0.42	$\text{C}^{13}\text{CH}_5\text{CFNCO}^+$ (Cal. 0.37)
102	8.45	$\text{C}_2\text{H}_5\text{CFNCO}^+$
101	10.28	$\text{C}_2\text{H}_4\text{CFNCO}^+$
100	8.03	$\text{C}_2\text{H}_3\text{CFNCO}^+$
93	4.65	
92	100.00	CF_2NCO^+
80	4.79	$\text{C}_2\text{H}_2\text{CNCO}^+$
79	80.28	$\text{C}_2\text{H}_5\text{CF}_2^+$
78	32.96	$\text{C}_2\text{H}_4\text{CF}_2^+$
77	21.97	$\text{C}_2\text{H}_3\text{CF}_2^+$
75	4.79	C_2HCF_2^+
74	14.37	HCFNCO^+
73	8.03	CFNCO^+
72	4.23	CH_3FCN^+
64	7.32	CH_2CF_2^+
59	29.58	$\text{C}_2\text{H}_4\text{CF}^+$

Table 8 continued

m/e	Relative Intensity	Ion
58	3.66	$C_2H_3CF^+$
57	33.80	$C_2H_2CF^+$
56	10.99	C_2HCF^+
55	6.90	$C_2H_5CN^+$
54	14.65	$C_2H_4CN^+$
53	6.48	$C_2H_3CN^+$
52	11.41	$C_2H_2CN^+$
51	43.66	CHF_2^+
50	4.51	CF_2^+
47	14.79	COF^+
46	8.31	CH_3CF^+
45	9.86	CH_2CF^+
44	53.38	$CHCF^+$, CO_2^+
42	7.32	NCO^+
40	4.79	$C_2H_4C^+$, CH_2CN^+
39	7.18	$C_2H_3C^+$, HF_2^+
38	4.51	$C_2H_2C^+$, F_2^+
33	7.61	CH_2F^+ , O_2^+
32	6.20	CHF^+
31	8.87	CF^+
29	10.71	$C_2H_5^+$
28	45.35	$C_2H_4^+$, CO^+ , N_2^+
27	59.16	$C_2H_3^+$

Table 8 continued

m/e	Relative Intensity	Ion
26	23.94	$C_2H_2^+$, CN^+
25	4.51	C_2H^+
16	3.80	O^+
15	9.58	CH_3^+
12	3.38	C^+

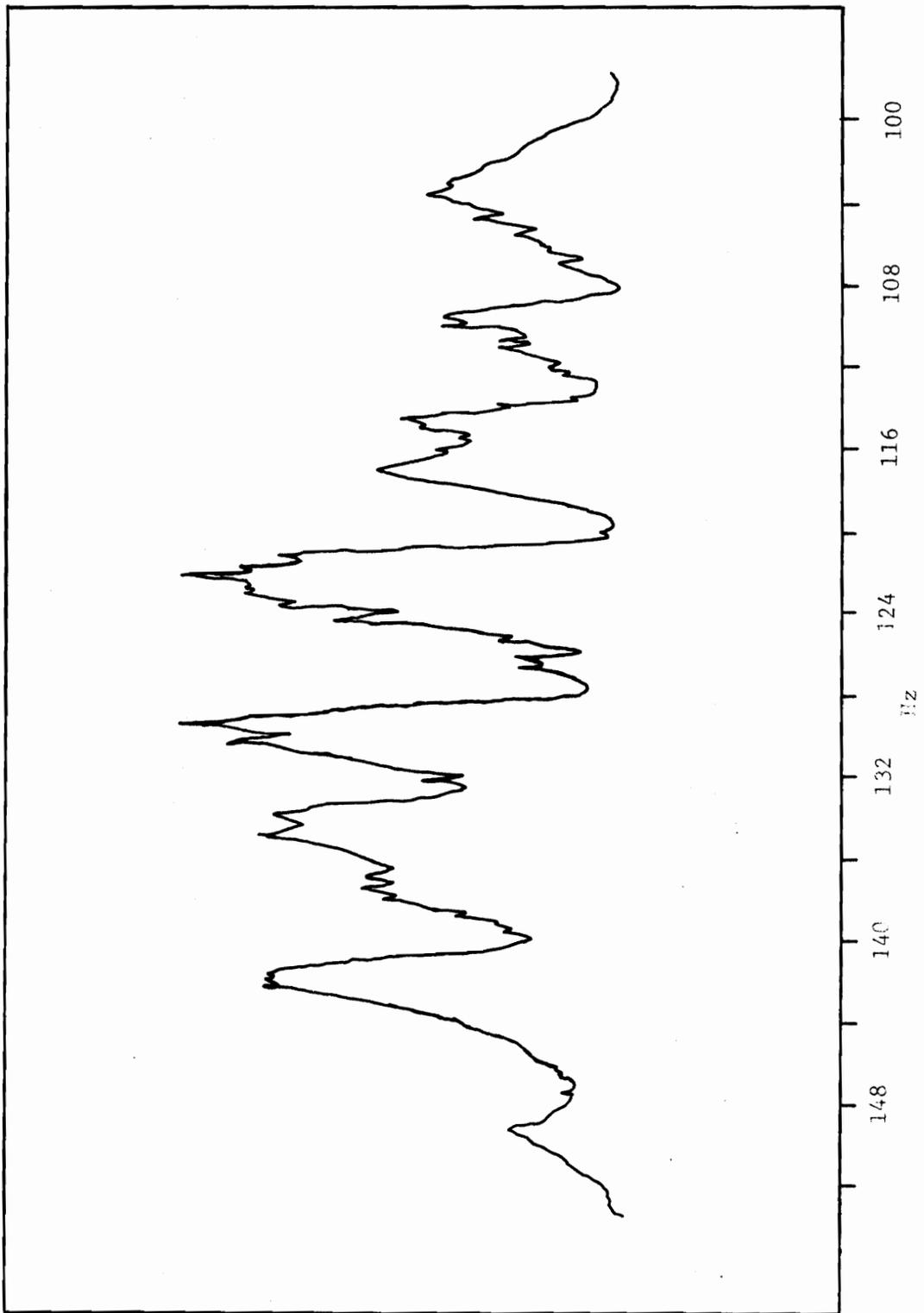


Figure 6. NMR of the Methylene Protons of α, α -Difluoropropyl Isocyanate.

F-19 NMR spectrum gave a triplet at -12.6 ppm from the external reference of trifluoroacetic acid with a J_{HF} of 13 Hz.

Vapor Pressure. The vapor pressure was recorded in the same manner as the earlier compound. The equation for the vapor pressure was $\log P = -1462.9/T + 7.3$. The heat of vaporization was found to be 6.7 kcal/mol deg and the Trouton constant 20.2 cal/deg. The extrapolated boiling point was 331° K.

Temperature °K	Pressure mm of Hg
236.0	14.0
242.7	18.7
258.0	36.7
266.7	61.2
278.8	109.0
297.3	265.9

Melting Point. The melting point was found to be lower than -130° C.

Fluorine Determination. The percentage of fluorine was determined in the manner described on page 20.

Calculated for $\text{C}_4\text{H}_5\text{F}_2\text{NO}$: 31.38% Found: 31.13%

Preparation of Pentafluoroethyl Isocyanate.

Continuing the study of the inductive effect on the addition reaction, trifluoroacetonitrile (PCR, Inc.) (0.47 mmol), used as received, since no impurities were determined from the infrared spectrum, carbonyl fluoride 1.44 mmol, and anhydrous hydrogen fluoride 0.1 ml (5.0 mmol) were condensed into a

Kel-F test tube. After 216 hours the reaction mixture was frozen (no non-condensable gases were found) and the volatile products passed through a warmed NaF trap and a series of cold traps. The liquid nitrogen and the -160.5° (iso-pentane slush) traps contained unreacted carbonyl fluoride and trifluoroacetonitrile. The -131° (n-pentane slush) trap contained material identified by infrared⁷ and mass spectra as perfluoroethyl isocyanate. There were no solids in the reaction flask. The yield of this isocyanate was approximately 5%. The yield was not increased by the addition of benzene and no reaction occurred by heating a solution of benzene, carbonyl fluoride, and trifluoroacetonitrile.

The Reaction of Cyanamide with Carbonyl Fluoride.

Hoping to synthesize the diisocyanate, OCNCF_2NCO , cyanamide (Eastman Organic Chemicals) (2.24 mmol) was transferred to a Kel-F test tube, the air removed and carbonyl fluoride (5.58 mmol) condensed onto the cyanamide followed by anhydrous hydrogen fluoride (15.0 mmol). The reactor was opened 7.5 days later after first freezing with liquid nitrogen. No non-condensable gases were found above the frozen mixture. The contents were allowed to warm and were treated in the same manner as the propionitrile reactions. The liquid nitrogen trap contained unreacted carbonyl fluoride and a compound which when separated on the co-distillation unit gave infrared^{23,28} and mass spectra identical to those of trifluoromethyl isocyanate. The traps at -83.6° (ethylacetate slush) and -131° did not contain any material while the trap at -78° contained a small amount of silicon tetrafluoride. In the bottom of the Kel-F test tube was a white solid which could be separated into two fractions

by treating with water. The water soluble material when recrystallized gave the infrared spectrum of cyanuric acid, $(\text{HOCN})_3$, as published in Sadtler²⁹ (#12,554) and was 1/3 the yield of trifluoromethyl isocyanate. The water insoluble material exhibited infrared spectrum identical to that of melamine, $(\text{H}_2\text{NCN})_3$, which may have formed as the result of the polymerization of cyanamide.³⁰

The Adiponitrile Reaction.

In another attempt to produce the diisocyanate, adiponitrile (Eastman Organic Chemicals) was dried over Drierite and a small quantity (4.4 mmol) was pipetted into a Kel-F reactor. The reactor was made vacuum tight, evacuated, and carbonyl fluoride (10.5 mmol) and anhydrous hydrogen (7.5 mmol) condensed into the reactor. Eight months and seven days later the reaction mixture was frozen with liquid nitrogen and opened to vacuum. A trace of non-condensable gas was present. After restoring vacuum the volatile contents were allowed to pass through sodium fluoride pellets at 50° C. and through several cold traps. The only cold trap with any contents was the liquid nitrogen trap which contained the unreacted carbonyl fluoride (7.8 mmol). Left in the reactor was a liquid which, when warmed to 80° C under vacuum, remained unchanged. The Kel-F cylinder was opened in the drybox and a smear of the liquid between salt plates was made for an infrared spectrum. The resulting spectrum (Table 9, Figure 7) suggested an isocyanate and HF had added across the isocyanate C-N double bond. The separation and purification proved impossible to accomplish in a convenient manner without decomposition due to

Table 9

Infrared Spectrum of the Adiponitrile Reaction Products

Taken Between Salt Plates

cm^{-1}	Intensity*	Assignment
3290	m.	NH stretch
2967	m.	CH_2 stretch
2269	v.s.	NCO and CN stretch
1832	s.	CO stretch
1758	m.	
1622	m.	CN stretch
1524	s-b.	NH stretch
1441	s.	CH_2 scissor
1386	m.	
1305	m.	
1237	s.	CF stretch
1210	v.s.	CF stretch
1059	s-b.	CF stretch
916	w.	
890	w.	
866	m.	
765	m.	CH_2 rocking
680	w.	CH_2

* m., medium; v.s., very strong; s., strong; s-b., strong and broad;
w., weak.

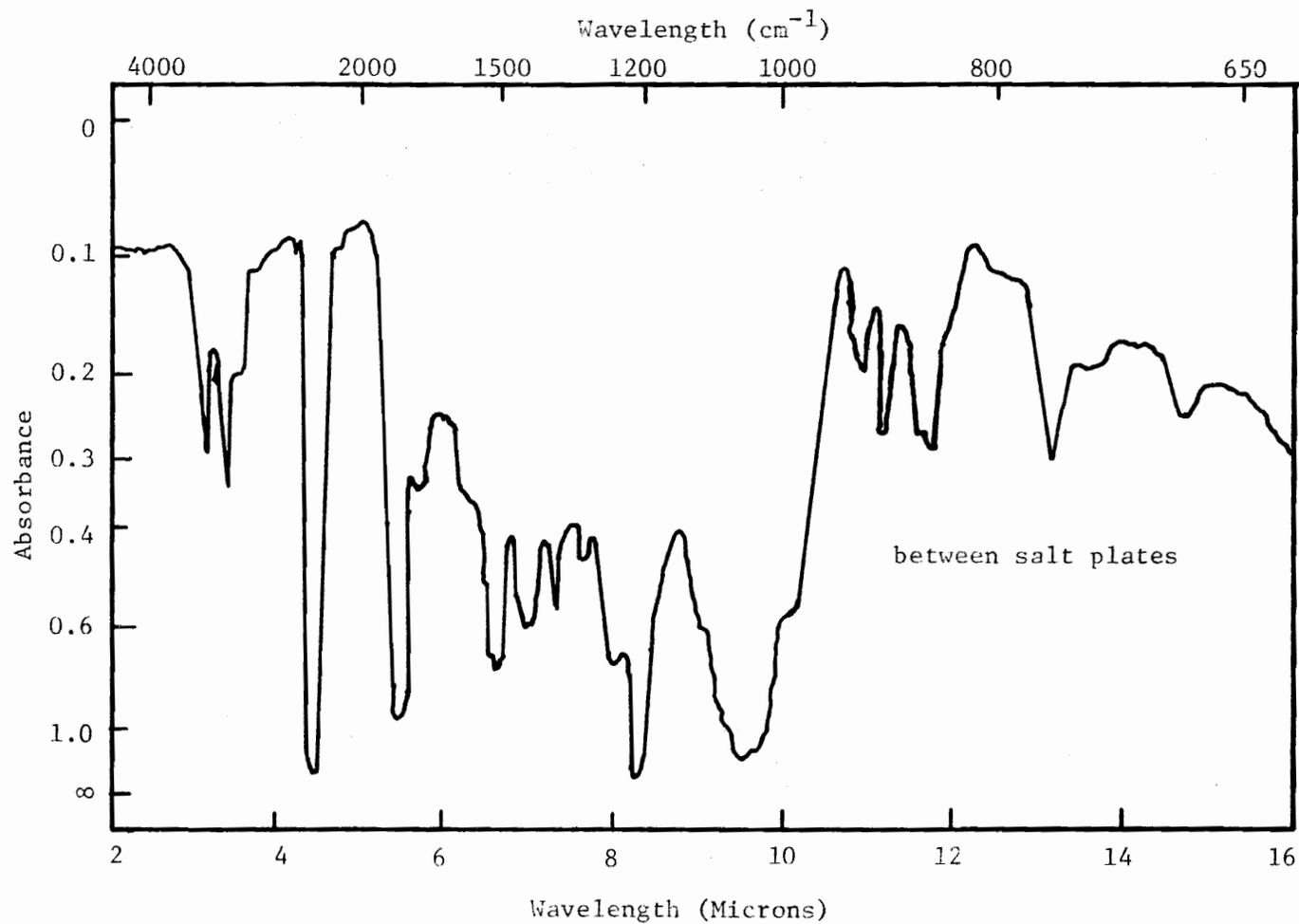


Figure 7. Infrared spectrum of the Adiponitrile Reaction Products.

heat or moisture. The mass spectrum of the raw product shows a $m/e = 221$ which could correspond to the loss of one fluorine from 1,6-diisocyanato-1,1,6,6-tetrafluorohexane, $\text{OCNCF}_2(\text{CH}_2)_4\text{CF}_2\text{NCO}$. This is in keeping with the long chain fluorine containing compounds which generally do not show the parent compound, but parent minus one fluorine. Additional fragmentation from the parent shows the loss of the second fluorine, $m/e = 202$, the loss of an isocyanate, $m/e = 198$, and the expected loss of isocyanate, fluorine, and hydrogen from these fragments. The mass spectrum also suggests that the monoisocyanate formed by showing a $m/e = 174$ with the losses of fluorine, isocyanate, and hydrogens. Thus, a mass spectrum of the raw product indicated that the diisocyanate, 1,6-diisocyanato-1,1,6,6-tetrafluorohexane, and the monoisocyanate, 1-isocyanato-5-cyano-1,1-difluoropentane had been produced (Table 10).

The Reaction with Cyanogen.

Preparation. Cyanogen was prepared by the decomposition of mercuric cyanide³¹ at 400°C under moderate vacuum, and was purified by passing it through traps of -78° , -131° , and -196° . The -131° trap contained infrared spectroscopy-pure cyanogen³² which was stored in a stainless steel cylinder and was used without further purification.

Reaction. In a typical reaction, 0.153 g (2.95 mmol) of cyanogen was measured and condensed with liquid nitrogen into a Monel cylinder along with carbonyl fluoride (0.434 g, 6.5 mmol) and 5 ml of anhydrous hydrogen fluoride.

Eight days later the hydrogen fluoride was removed by having the vapor above the reaction cylinder come in contact with sodium fluoride

Table 10

Mass Spectrum of Adiponitrile Reaction Products

70 ev 100°C

Intensity Relative to CF_2NCO^+ and $(\text{CH}_2)_3\text{CF}_2^+$

m/e	Relative Intensity	Ion
221	0.3	$(\text{CH}_2)_4\text{CF}_2\text{CF}(\text{NCO})_2^+$
220	3.0	$(\text{CH}_2)_3\text{CHCF}_2\text{CF}(\text{NCO})_2^+$
205	4.0	$\text{NCCH}_2(\text{CH})_3\text{CN} \cdot 5\text{HF}^+ ?$
202	0.7	$(\text{CH}_2)_4(\text{CF})_2(\text{NCO})_2^+$
198	18.5	$(\text{CH}_2)_4(\text{CF}_2)_2\text{NCO}^+$
179	0.7	$(\text{CH}_2)_4\text{CF}_2\text{CFNCO}^+$
177	3.0	$(\text{CH}_2)_2(\text{CH})_2\text{CF}_2\text{CFNCO}^+$
175	7.9	$(\text{CH})_4\text{CFCF}_2\text{NCO}^+$
174	1.3	$\text{NC}(\text{CH}_2)_4\text{CF}_2\text{NCO}^+$
173	3.3	$\text{NC}(\text{CH}_2)_3\text{CHCF}_2\text{NCO}^+$
172	15.5	$\text{NC}(\text{CH}_2)_2(\text{CH})_2\text{CF}_2\text{NCO}^+$
170	5.0	$\text{NC}(\text{CH})_4\text{CF}_2\text{NCO}^+$
169	3.3	$\text{NC}(\text{CH})_3\text{CCF}_2\text{NCO}^+$
168	3.3	$\text{NC}(\text{CH})_2\text{C}_2\text{CF}_2\text{NCO}^+$
163	3.3	$(\text{CH}_2)_3\text{CHC}_2(\text{NCO})_2^+$
162	3.0	$(\text{CH}_2)_2(\text{CH})_2\text{C}_2(\text{NCO})_2^+$
161	3.3	$\text{CH}_2(\text{CH})_3\text{C}_2(\text{NCO})_2^+$
159	4.0	$(\text{CH}_2)_3\text{CH}(\text{CF})_2\text{NCO}^+$
158	4.6	$(\text{CH}_2)_2(\text{CH})_2(\text{CF})_2\text{NCO}^+$
157	4.0	$\text{CH}_2(\text{CH})_3(\text{CF})_2\text{NCO}^+$

Table 10 continued

m/e	Relative Intensity	Ion
156	9.9	$(\text{CH})_4(\text{CF})_2\text{NCO}^+$; $(\text{CH}_2)_4(\text{CF}_2)_2^+$
155	9.9	$(\text{CH}_2)_3\text{CH}(\text{CF}_2)_2^+$; $\text{NC}(\text{CH}_2)_4\text{CFNCO}^+$
154	5.6	$(\text{CH}_2)_2(\text{CH})_2(\text{CF}_2)_2^+$; $\text{NC}(\text{CH}_2)_3\text{CHCFNCO}^+$
153	4.0	$\text{CH}_2(\text{CH})_3(\text{CF}_2)_2^+$; $\text{NC}(\text{CH}_2)_2(\text{CH})_2\text{CFNCO}$
152	7.9	$(\text{CH})_4(\text{CF}_2)_2^+$; $\text{NCCH}_2(\text{CH})_3\text{CFNCO}^+$
149	6.3	$\text{NCF}(\text{CH}_2)_2\text{CHCF}_2^+$
148	15.5	$(\text{CH}_2)_4\text{CF}_2\text{NCO}^+$
147	5.0	$(\text{CH}_2)_3\text{CHCF}_2\text{NCO}^+$
146	4.6	$(\text{CH}_2)_2(\text{CH})_2\text{CF}_2\text{NCO}^+$
145	8.9	$\text{CH}_2(\text{CH})_3\text{CF}_2\text{NCO}^+$
143	3.3	$(\text{CH})_3\text{CCF}_2\text{NCO}^+$
142	10.9	$(\text{CH})_2\text{C}_2\text{CF}_2\text{NCO}^+$; $\text{NCF}(\text{CH})_4\text{CCFN}^+$
141	13.2	$\text{CHC}_3\text{CF}_2\text{NCO}^+$; $\text{NCF}(\text{CH})_3\text{CCFN}^+$
139	3.6	$\text{NCFCHC}_3\text{CFN}^+$
137	4.6	$(\text{CH}_2)_4\text{CF}_2\text{CF}^+$
136	6.9	$(\text{CH}_2)_3\text{CHCF}_2\text{CF}^+$
135	25.1	$(\text{CH}_2)_2(\text{CH})_2\text{CF}_2\text{CF}^+$
134	12.2	$\text{CH}_2(\text{CH})_3\text{CF}_2\text{CF}^+$; $(\text{CH}_2)_3\text{CF}_2\text{NCO}^+$
133	21.4	$(\text{CH})_4\text{CF}_2\text{CF}^+$; $(\text{CH}_2)_2\text{CHCF}_2\text{NCO}^+$

Table 10 continued

m/e	Relative Intensity	Ion
132	12.5	$(\text{CH})_3\text{CF}_2\text{CF}^+$; $\text{CH}_2(\text{CH})_2\text{CF}_2\text{NCO}^+$; $\text{NC}(\text{CH}_2)_4\text{CF}_2^+$
131	10.6	$(\text{CH})_3\text{CF}_2\text{NCO}^+$; $\text{NC}(\text{CH}_2)_3\text{CHCF}_2^+$
130	3.3	$(\text{CH})_2\text{CCF}_2\text{NCO}^+$; $\text{NC}(\text{CH}_2)_2(\text{CH})_2\text{CF}_2^+$
129	6.0	$(\text{CH}_2)_4\text{CFNCO}^+$; $\text{NCCH}_2(\text{CH})_3\text{CF}_2^+$
128	13.5	$(\text{CH}_2)_3\text{CHCFNCO}^+$; $\text{NC}(\text{CH})_4\text{CF}_2^+$
127	6.0	$(\text{CH}_2)_2(\text{CH})_2\text{CFNCO}^+$; $\text{NC}(\text{CH})_3\text{CCF}_2^+$
126	4.9	$\text{CH}_2(\text{CH})_3\text{CFNCO}^+$
125	5.9	$(\text{CH})_4\text{CFNCO}^+$; $\text{NC}(\text{CH}_2)_2(\text{CH})_2\text{CFN}^+$
124	3.6	$(\text{CH})_3\text{CCF}_2\text{NCO}^+$; $\text{NCCH}_2(\text{CH})_3\text{CFN}^+$
123	6.9	$\text{NC}(\text{CH})_4\text{CFN}^+$
122	4.6	$\text{NC}(\text{CH})_3\text{CCFN}^+$
121	16.5	$\text{NC}(\text{CH})_2\text{C}_2\text{CFN}^+$
120	9.9	$(\text{CH}_2)_2\text{CF}_2\text{NCO}^+$
119	25.1	$\text{CH}_2\text{CHCF}_2\text{NCO}^+$
118	4.0	$(\text{CH})_2\text{CF}_2\text{NCO}^+$; $\text{CF}(\text{CH}_2)_4\text{CF}^+$
117	8.9	$\text{CHCCF}_2\text{NCO}^+$; $\text{CF}(\text{CH}_2)_3\text{CHCF}^+$
116	4.6	$\text{CF}(\text{CH}_2)_2(\text{CH})_2\text{CF}^+$
115	28.8	$(\text{CH}_2)_3\text{CFNCO}^+$; $\text{CFCH}_2(\text{CH})_3\text{CF}^+$
114	10.6	$(\text{CH}_2)_2\text{CHCFNCO}^+$; $\text{CF}(\text{CH})_3\text{CF}^+$
113	23.1	$\text{CH}_2(\text{CH})_2\text{CFNCO}^+$; $\text{NC}(\text{CH}_2)_4\text{CF}^+$
112	7.9	$(\text{CH})_3\text{CFNCO}^+$; $\text{NC}(\text{CH}_2)_3\text{CHCF}^+$
111	12.2	$(\text{CH})_2\text{CCFNCO}^+$; $\text{NC}(\text{CH}_2)_2(\text{CH})_2\text{CF}^+$

Table 10 continued

m/e	Relative Intensity	Ion
110	7.9	$\text{CHC}_2\text{CFNCO}^+$; $\text{NCCH}_2(\text{CH})_3\text{CF}^+$
109	15.8	$\text{NC}(\text{CH})_4\text{CF}^+$
108	10.9	$\text{NC}(\text{CH}_2)_4\text{CN}^+$ (starting compound)
107	20.8	$\text{NC}(\text{CH}_2)_3\text{CHCN}^+$
106	9.2	$\text{CH}_2\text{CF}_2\text{NCO}^+$; $(\text{CH}_2)_4\text{CF}_2^+$
105	30.4	$\text{CHCF}_2\text{NCO}^+$; $(\text{CH}_2)_3\text{CHCF}_2^+$
104	28.8	CCF_2NCO^+ ; $(\text{CH}_2)_2(\text{CH})_2\text{CF}_2^+$; $\text{NC}(\text{CH})_4\text{CN}^+$
103	17.8	$\text{CH}_2(\text{CH})_3\text{CF}_2^+$
102	3.3	$(\text{CH})_4\text{CF}_2^+$
101	5.6	$(\text{CH}_2)_2\text{CFNCO}^+$
100	72.6	$\text{CH}_2\text{CHCFNCO}^+$
99	5.9	$(\text{CH})_2\text{CFNCO}$
98	9.2	CHCCFNCO^+
97	20.8	
96	11.6	$(\text{CH}_2)_3\text{CNCO}^+$
95	21.4	$(\text{CH}_2)_2\text{CHCNCO}^+$
94	10.3	$\text{CH}_2(\text{CH})_2\text{CNCO}^+$
93	11.3	$(\text{CH})_3\text{CNCO}^+$
92	100.0	CF_2NCO^+ ; $(\text{CH}_2)_3\text{CF}_2^+$
91	49.5	$(\text{CH}_2)_2\text{CHCF}_2^+$
90	33.0	$\text{CH}_2(\text{CH})_2\text{CF}_2^+$
89	5.9	$(\text{CH})_3\text{CF}_2^+$

Table 10 continued

m/e	Relative Intensity	Ion
88	10.6	$(\text{CH})_2\text{CCF}_2^+$
87	72.2	CHC_2CF_2 ; $(\text{CH}_2)_4\text{CF}^+$; $\text{CH}_2\text{CFNCO}^+$
86	5.6	$(\text{CH}_3)_3\text{CHCF}^+$; CHCFNCO^+
85	33.0	$(\text{CH}_2)_2(\text{CH})_2\text{CF}^+$; CCFNCO^+
84	17.2	$\text{CH}_2(\text{CH})_3\text{CF}^+$
83	26.4	$(\text{CH})_4\text{CF}^+$
82	18.8	$\text{NC}(\text{CH}_2)_4^+$; $(\text{CH}_2)_2\text{CNCO}^+$
81	22.4	$\text{CH}(\text{CH}_2)_3\text{CN}^+$; $\text{CH}_2\text{CHCNCO}^+$
80	8.9	$(\text{CH})_2(\text{CH}_2)_2\text{CN}^+$; $(\text{CH})_2\text{CNCO}^+$
79	14.8	$\text{CH}_2(\text{CH})_3\text{CN}^+$; CHC_2NCO^+
78	17.5	$(\text{CH}_2)_2\text{CF}_2^+$
77	49.5	$\text{CH}_2\text{CHCF}_2^+$
76	26.4	$(\text{CH})_2\text{CF}_2^+$
75	8.2	CHCCF_2^+
74	25.1	CCCCF_2^+
73	5.0	$(\text{CH}_2)_3\text{CF}^+$; CFNCO^+
72	6.3	$(\text{CH}_2)_2\text{CHCF}^+$
71	44.6	$\text{CH}_2(\text{CH})_2\text{CF}^+$
70	25.7	$(\text{CH})_3\text{CF}$
69	33.0	$(\text{CH})_2\text{CCF}^+$
68	26.4	$(\text{CH}_2)_3\text{CN}^+$; $(\text{CH})_2\text{NCO}^+$
67	22.4	$(\text{CH})_2\text{CHCN}^+$; CHCNCO^+
66	14.8	$\text{CH}_2(\text{CH})_2\text{CN}^+$; COF_2^+

Table 10 continued

m/e	Relative Intensity	Ion
65	17.5	$(\text{CH})_3\text{CN}^+$
64	26.4	CH_2CF_2^+
63	7.6	CHCF_2^+
62	4.0	CCF_2^+
61	6.6	
60	3.0	
59	18.8	$(\text{CH}_2)_2\text{CF}^+$
58	8.3	CH_2CHCF^+
57	69.3	$(\text{CH})_2\text{CF}^+$
56	33.0	$(\text{CH}_2)_4^+$
55	49.5	$(\text{CH}_2)_3\text{CH}^+$
54	26.4	$(\text{CH}_2)_2\text{CN}^+$; $(\text{CH}_2)_2(\text{CH})_2^+$; CNCO^+
53	19.5	CH_2CHCN^+ ; $\text{CH}_2(\text{CH})_3^+$
52	14.2	$(\text{CH})_2\text{CN}^+$; $(\text{CH})_4^+$
51	27.7	CHCCN^+ ; $(\text{CH})_3\text{C}^+$
50	21.1	CF_2^+ ; CH_2C_2^+
49	3.3	C_4H^+
47	29.7	CFO^+
46	5.3	
45	7.3	CH_2CF^+
44	69.3	CHCF^+ ; CO_2^+
43	52.8	CCF^+
42	26.4	$(\text{CH}_2)_3^+$; NCO^+

Table 10 continued

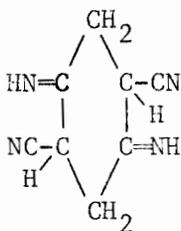
m/e	Relative Intensity	Ion
41	99.0	$(\text{CH}_2)_2\text{CH}^+$
40	13.2	$\text{CH}_2(\text{CH})_2^+$; CH_2CN^+
39	39.6	CHCN^+
38	10.6	CCN^+
37.5	1.0	CHCCF_2^{++}
33	7.6	
32	4.0	O_2^+
31	3.3	CF^+
29	23.1	C_2H_5^+
28	66.0	$(\text{CH}_2)_2^+$; N_2^+
27	33.0	CH_2CH^+
26	10.6	CN^+ ; $(\text{CH})_2^+$
18	26.4	H_2O^+
16	19.5	O^+
15	10.6	NH^+

pellets at 50° C for three hours. The volatile products were then passed through a series of cold traps. The liquid nitrogen trap contained silicon tetrafluoride. The -160° trap also contained some silicon tetrafluoride and a large amount of carbon dioxide. The -131° trap held some unreacted cyanogen. Left in the reaction vessel was a viscous liquid which when exposed to moist air fumed. An infrared spectrum of this liquid resembled anhydrous hydrogen fluoride. It appears that the carbonyl fluoride had been hydrolyzed to carbon dioxide and was recovered in that form. The source of the water was not ascertained. The recovered cyanogen was one tenth of the starting amount with the remaining probably complexed with the hydrogen fluoride forming an imine salt similar to the acetonitrile.^{10,11} There was no evidence to suggest the formation of $(CF_3)_2NH$ that Tullock³³ has reported from cyanogen and the cyanogen halides in anhydrous hydrogen fluoride. There was some evidence that the Monel cylinder had been etched by the HF-cyanogen mixture.

Reaction of Succinonitrile.

A chip of succinonitrile (American Cyanimide Company) was weighed out (3.2 mmol) and placed in a Kel-F reactor. It was made vacuum tight in the manner described elsewhere,⁹ evacuated, and carbonyl fluoride (6.4 mmol) and 4 ml of benzene were condensed into the vessel. At room temperature two clear colorless liquid phases were present with a smaller lower phase which was thought to be a succinonitrile-hydrogen fluoride complex. The upper phase was probably benzene. Three days later the reaction mixture was frozen with liquid nitrogen and, since no non-

condensable gases were detected, was allowed to warm with the contents passing through sodium fluoride pellets at 50° and various cold traps. The -45° trap contained nothing measurable. The -78° trap and -131° trap contained benzene and some silicon tetrafluoride. The -196° trap contained, within experimental error, all of the carbonyl fluoride. Left in the reactor was a rich red-brown semi-solid. A smear of this was made on salt plates for an infrared spectrum. This spectrum had only broad bands in the regions which suggest imine salts. It is postulated that one mole of hydrogen fluoride may have added to each nitrile group forming a salt similar to the acetonitrile salt,^{10,11} or as reported by Decombe and Verry,³⁴ succinonitrile, in the presence of hydrogen chloride, formed both a linear, $\text{NCCH}_2\text{CH}_2\text{C}(=\text{NH})\text{CH}(\text{CN})\text{CH}_2\text{CN}$, and/or a cyclic dimer,

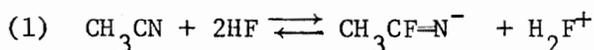


The hydrogen fluoride would be capable of catalyzing the formation of the same dimer.

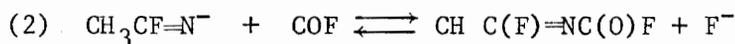
DISCUSSION

The addition of COF_2 to aliphatic nitriles to form the perfluoroalkyl and α,α -difluoroalkyl isocyanates was found to proceed only when an anhydrous acid was present. Presumably, the only requirement for the acid catalyst was that it should not be fluorinated by carbonyl fluoride and would not oxidize the organic reactant. It has been reported^{10,11} that acetonitrile will add one molecule of hydrogen fluoride across the

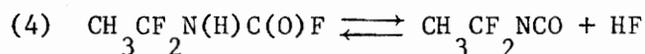
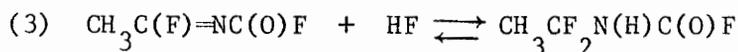
nitrile bond to form the imine $(\text{CH}_3\text{CF}=\text{NH}_2)^+(\text{HF})_x\text{F}^-$. However, Campbell³⁵ has done an NMR study of acetonitrile in anhydrous hydrogen fluoride and reported that the nitrogen-hydrogen resonance was not observed in "neutral" HF, nor did the chemical shift of hydrogen fluoride-acetonitrile support the presence of the N-H group. He concluded that the species $\text{CH}_3\text{CF}=\text{N}^-$ was in keeping with this data. However, the CH_3 proton resonance was gradually split into a triplet over the course of several days.³⁵ Thus the first step of the mechanism was probably



Once the anion was formed, it could attack the electropositive carbon of carbonyl fluoride eliminating a fluoride ion, or, alternately, it could be attacked by a carbonium ion (formed from carbonyl fluoride) eliminating hydrogen fluoride:



The intermediate could then rearrange directly to yield the isocyanate or by addition of one mole of hydrogen fluoride to form the carbamyl fluoride, followed by elimination of HF to give the α, α -difluoroalkyl isocyanate.



Another possibility is that the carbonyl fluoride formed a carbonium ion and attacked the nitrile directly. This seems unlikely, however, for increasing the acid strength with BF_3 which would increase the concentration of carbonium ions and thus the yield of the isocyanate, produced the opposite effect. With sodium fluoride present, the medium

would be less acidic and favor the formation of the anion in step (1) and produce the observed increase in yield of the isocyanate.

The lack of formation of a monochloro or gem-dichloro compound in the HCl-catalyzed reaction did not, in fact, support either mechanism. However, because of the greater leaving ability of the chlorine over that of the fluorine, any α -chloro compound would suffer hydrofluoroiodolysis under the conditions of the reaction. The carbonyl fluoride has been stored with anhydrous hydrogen chloride for an indefinite period of time without any detected formation of monofluorophosgene and the general preparation⁷ of carbonyl fluoride is from an acetonitrile-sodium fluoride mixture into which phosgene is bubbled. The formation of monofluorophosgene strongly supports the reversibility of step (2) and the formation of phosgene the reversibility of steps (2), (3), and (4). The addition of hydrogen fluoride to α,α -difluoroethyl isocyanate to yield acetonitrile and carbonyl fluoride was additional evidence of an equilibrium.

The analysis of variation of the acetonitrile reactions indicated that the benzene had no effect on the yield, but a more polar solvent may increase the yield. The chlorobenzene reaction (run 15) was not conclusive because only a trace of hydrogen fluoride was used. Both analysis of variation and direct comparison of experiments #10 and #18 to #20 (Table 2) show a shifting of the equilibrium in the presence of an excess of carbonyl fluoride or acetonitrile. With hydrogen fluoride present in 1 to 3 times the total quantity of acetonitrile and carbonyl fluoride, the yield of the α,α -difluoroalkyl isocyanate was increased.

The increase in the alkyl isocyanate yield under similar reaction conditions was in the order of increasing basicity; trifluoroacetonitrile (5%), acetonitrile (44.7%), and propionitrile (96%) and for the diisocyanate, cyanogen, succinonitrile, and adiponitrile with the latter being the only one observed to form the diisocyanate.

The mass spectra of the α,α -difluoroalkyl isocyanates showed the expected fragmentation pattern of loss of F, R, H, and NCO from the parent. The parent ion intensity decreased in going from the ethyl to the propyl compound as expected for fluoride containing compounds.

The α,α -difluoroalkyl isocyanates are clear colorless liquids at room temperature and will not decompose in dry glassware or at 130° over NaF pellets. However, in contact with water they hydrolyze rapidly to the corresponding acid as do the alkane isocyanates. The α,α -difluoroethyl isocyanate also reacts as expected with ethanol to produce the carbamate. However, the carbamate is unstable at room temperature and will slowly split out hydrogen fluoride.

SUMMARY

Carbonyl fluoride will add to alkyl and perfluoroalkyl nitriles and alkane dinitriles in anhydrous acids to form the corresponding α,α -difluoroalkyl isocyanate, perfluoroalkyl isocyanate, or $\alpha,\alpha,\omega,\omega$ -tetrafluoro- α,ω -diisocyanatoalkane. With acetonitrile the reaction proceeded slowly in anhydrous hydrogen fluoride or hydrogen chloride to yield a clear colorless liquid which was identified by infrared, mass, proton NMR, and fluorine-19 NMR spectroscopies to be α,α -difluoroethyl isocyanate. Increasing yields based on the lesser reactant were achiev-

ed by making the ratio of acetonitrile to carbonyl fluoride greater or less than one, having the optimum amount of anhydrous acid, the presence of an alkali metal fluoride and/or an increase in reaction time. The α,α -difluoroethyl isocyanate reacted with anhydrous ethanol to form the carbamate which slowly decomposed by splitting out hydrogen fluoride. The addition reaction proceeded more rapidly, in comparison to acetonitrile, with propionitrile and less rapidly with trifluoroacetonitrile. Cyanamide yielded trifluoromethyl isocyanate and cyanuric acid. Adiponitrile produced 1,6-diisocyanato-1,1,6,6-tetrafluorohexane and 1-isocyanato-5-cyano-1,1-difluoropentane.

CHAPTER II

ADDITION OF CARBONYL FLUORIDE TO ARYLFORMONITRILES

INTRODUCTION

Having investigated the addition of carbonyl fluoride to aliphatic nitriles to form the α,α -difluoroalkyl isocyanates, it seemed logical to extend the range of this reaction to the arylformonitriles. In so doing, it was found that not only was the aryl- α,α -difluoromethyl isocyanate formed, but aryltrifluoromethane and 2-hydroxy-4,6-diaryl-s-triazine as well. This reaction thus represents a possible new route to the ortho and para substituted trifluoromethyl compounds which have been difficult to synthesize directly because of the strong electron withdrawing effect of the trifluoromethyl group. Previous methods for the formation of the trifluoromethyl compounds have been 1) halogen exchange of benzylic halogens (Cl, Br) with antimony trifluoride,³⁶ anhydrous hydrogen fluoride,³⁷ sodium fluorosilicate,³⁸ or sodium hydrogen fluoride;³⁹ 2) substitution of an aromatic hydrogen by perfluoroalkyl radical formed from a perfluoroalkyl iodide;⁴⁰ 3) conversion from carboxylic acids with sulfur tetrafluoride;⁴¹ 4) trimerization of perfluoroacetylenes;^{42,43} and 5) exhaustive vapor-phase fluorination using cobalt trifluoride.⁴⁴ Various aryltrifluoromethanes have been found to have practical applications as pesticides, larvacides, microbiocides, herbicides, azo dyes, and a wide range of pharmaceuticals.⁴⁵

The coproduct to the aryltrifluoromethanes, 2-hydroxy-4,6-diaryl-s-triazine $\text{Ar}_2(\text{NC})_3\text{OH}$, may be used as intermediate to a wide range of useful s-triazines. Commercial applications of some of these s-triazines include dyestuffs, optical bleaches, coloration of halocarbons, pesticides, resins, explosives, medicines, herbicides, etc.⁴⁶

The chief method of making the 2-hydroxy-4,6-diaryl-s-triazines has been to take the appropriate aryl amidine, $\text{ArC}(=\text{NH})\text{NH}_2$, react it with phosgene, and heat the resulting urea to cause ring closure and loss of ammonia.

EXPERIMENTAL

Equipment.

The vacuum line and related equipment were described in Chapter I.

Reagents.

The carbonyl fluoride, anhydrous hydrogen fluoride and sodium fluoride pellets were treated as described in Chapter I.

Reaction of Benzonitrile.

In a typical reaction, 1 ml (9.8 mmol) of dry benzonitrile, $\text{C}_6\text{H}_5\text{CN}$, (Eastman Organic Chemical) was introduced into a Kel-F test tube containing a sodium fluoride pellet (0.95 mmol). The reactor, sealed with Halocarbon wax⁹, was connected to the vacuum system, the contents frozen with liquid nitrogen, and the air evacuated. Anhydrous hydrogen fluoride

(usually 14 to 15 mmol, see Table 11) and carbonyl fluoride (11.4 mmol) were condensed into the reactor and the assembly was allowed to warm to room temperature. If the reaction was to be heated to a higher temperature, the assembly remained at room temperature for six to twelve hours before being placed in the water bath. Unless this was done the Kel-F tube often ruptured. Two phases were noted in the case of reactions run above room temperature. The upper phase was the larger and was clear yellow-brown in color. This phase was probably benzonitrile and its reaction intermediates. The lower phase was non-existent at the start of the reaction and developed as a clear liquid over a 12 to 24 hour period to about drop size. The size of the drop did not appear to increase over a longer period of time. This lower phase was probably sodium fluoride-hydrogen fluoride solution.

After the appropriate amount of time the reactor was connected to the vacuum line, chilled with liquid nitrogen, and opened. No non-condensable gases were found. The contents of the reactor were allowed to warm with a pre-cooled Dewar flask around the test tube and pass through a trap of sodium fluoride pellets at 50° C, a -45° trap (chlorobenzene slush), and finally into a liquid nitrogen trap. A water bath of 85° to 90° was usually placed around the test tube reactor after it reached room temperature to aid in removing the volatile materials. The -45° trap was found to contain α,α -difluorobenzyl isocyanate. The contents of the liquid nitrogen trap were further separated by passing the gases through a -95° trap (toluene slush), a -131° trap (n-pentane slush), and finally a liquid nitrogen trap. The -95° trap contained the α,α,α -trifluorotoluene as identified by its infrared spectrum (Sadtlir²⁹ #232b)

Table 11

REACTIONS OF BENZONITRILE AND CARBONYL FLUORIDE^a

Run	C ₆ H ₅ CN mmol	COF ₂ mmol	HF mmol	Time Days	% Yield ^b CF ₃ ^c NCO ^d		Comments
0	0.8	1.0	5 ml	0.5			
1	1.8	1.1	12 ml	4.5			CO ₂ formed
2	2.9	5.0	5 ml	16.5			
3a	?	3.4	?	2.0			2.5 ml benzene, two phases
3b	4.9	9.9	20.0	27.0	3		
4	4.9	7.6	none	13.0			
5	4.9	3.6	0.24 ^e	14.0			CH ₃ C(O)F formed
6	4.9	6.4	12.5	12.5	15	?	NaF (.95 mmol)
7	4.9	6.9	12.5	121.0	20	trace	
8	9.8	9.9	20.0	2.0			Steam table
9	9.8	7.5	32.5	20.0			0° C,
10	9.8	9.7	14.5	23.0	1	14	NaF (1.91 mmol)
11	9.8	9.7	28.0	31.0	1	1.5	CsF (0.40 mmol)
12	9.8	9.7	20.0	21.0			BF ₃ (1.98 mmol) 100% trimer
13	9.8	9.3	none	1.5			Et ₃ N (31.9 mmol)
14	9.8	7.3	26.5	7.0			Et ₃ N (31.9 mmol)
15	9.8	13.5	52.5	20.0	trace		NaF (.95 mmol)
16	9.8	10.2	15.0	30.0	9	trace	NaF (.95 mmol)
17	9.8	11.4	14.5	4.5	18	17	NaF (.95 mmol), 50°
18	9.8	11.4	16.5	4.5			NaF (.95 mmol), 65°, leaked
19	9.8	7.9	14.0	4.5	5.5	8.6	NaF (.95 mmol), 65°
20	9.8	7.6	15.0	4.5	4.2	13.6	NaF (.95 mmol), 50°

^a Runs were at ambient temperature unless noted.

^b Based upon compound expected to be 100% consumed.

^c α,α,α -trifluorotoluene

^d α,α -difluorobenzyl isocyanate

^e acetic acid

and mass spectrum. The n-pentane trap contained some silicon tetrafluoride and a trace of α,α,α -trifluorotoluene. The final trap contained the unreacted carbonyl fluoride. The yield of isocyanate was determined by subtracting the amount of α,α,α -trifluorotoluene from the consumed carbonyl fluoride.

Left in the reaction vessel was a tan solid which was removed and stirred with 100% ethanol for ten to fifteen minutes. The solution was filtered off and the collected solid was found to be a mixture of sodium fluoride and 2,4,6-triphenyl-s-triazine.⁴⁷ The filtrate was evaporated and the solid identified as 2-hydroxy-4,6-diphenyl-s-triazine contaminated with 2,4,6-triphenyl-s-triazine. This solid was stirred with toluene and filtered, the undissolved solid being 2-hydroxy-4,6-diphenyl-s-triazine.

Physical Properties of $C_6H_5CF_2NCO$.

Infrared Spectrum. The infrared spectrum of α,α -difluorobenzyl isocyanate was recorded with a Beckman IR5 Spectrometer with the results and assignments listed in Table 12 and shown in Figure 8.

Mass Spectrum. The mass spectrum, Table 13, was measured on a Hitachi-Perkin-Elmer RMU-6E mass spectrometer. Peaks of less than 3% relative intensity were not listed unless they were of some special significance.

NMR. The NMR spectra were run on the JEOL C60H at 60 MHz for the proton and at 56.446 MHz for fluorine-19. Using Freon-11 as the solvent, the proton NMR spectrum showed a complicated pattern with the most prominent peak at -430 Hz (-7.17 ppm) from TMS (Figure 9). The fluorine

Table 12

Infrared Spectrum of α,α -Difluorobenzyl Isocyanate
Taken Between Salt Plates

cm^{-1}	Intensity*	Assignment
3057	w.	CH stretch (aryl)
2920	v.w.	CH stretch
2260	v.s.	NCO asym stretch
1824	w.	Overtone
1550	w.	
1434	m.	
1277	s.	CN stretch
1118	m.	CF stretch
1096		
1067	s.b.	CF stretch
1003	s.	CF asym stretch
769	s.b.	CH bend - monosubstituted
694	s.b.	CH bend - monosubstituted

*w., weak; v.w., very weak; v.s., very strong; m., medium; s., strong;
s.b., strong and broad.

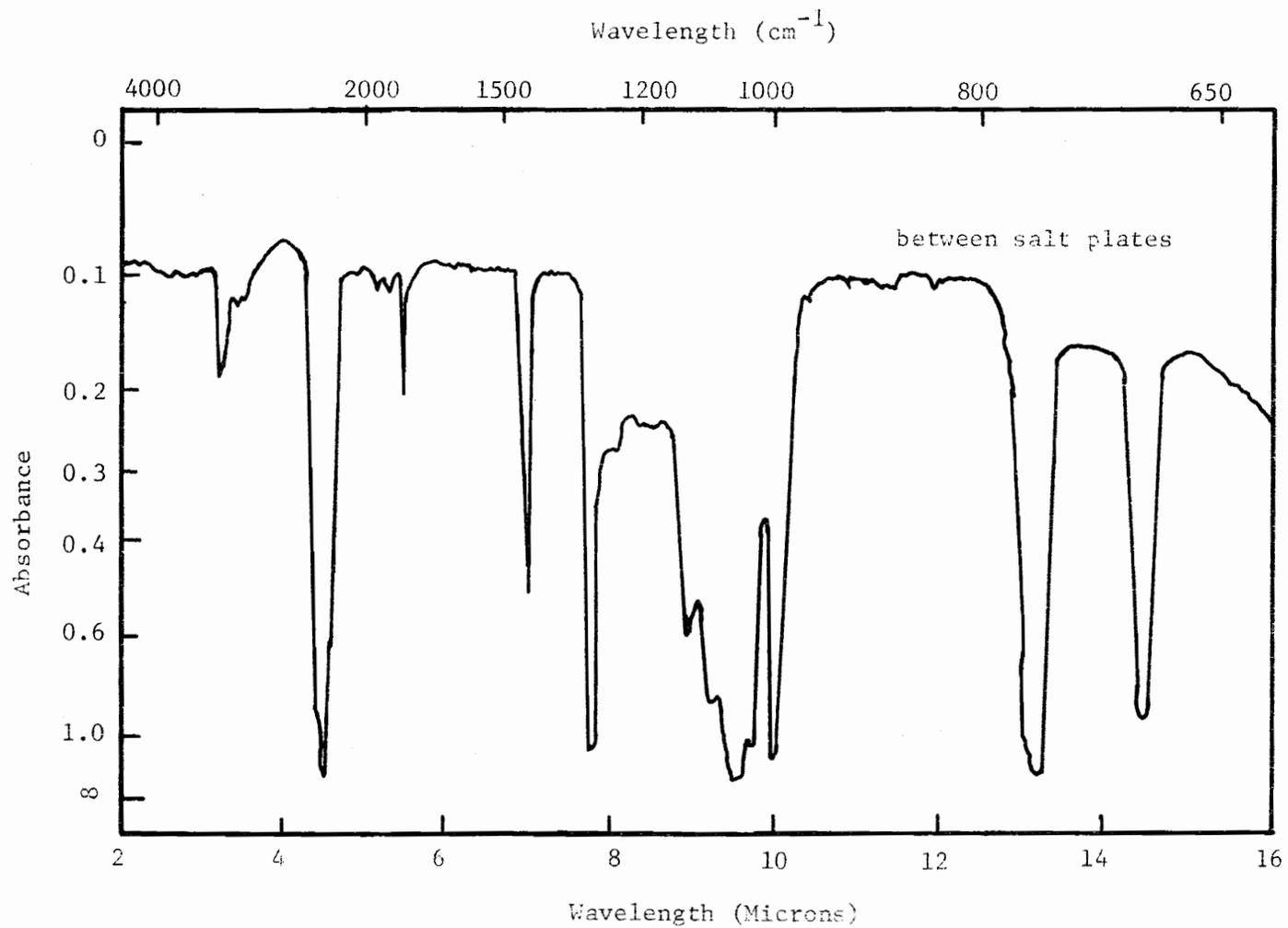


Figure 8. Infrared Spectrum of α,α -Difluorobenzyl Isocyanate.

Table 13

Mass Spectrum of α,α -Difluorobenzyl Isocyanate

70 ev Inlet at room temperature

Intensity Relative to CCF^+

m/e	Relative Intensity	Ion
170	0.8	$\text{C}^{13}\text{C}_7\text{H}_5\text{F}_2\text{NO}^+$ (Cal. 0.6)
169	6.2	$\text{C}_6\text{H}_5\text{CF}_2\text{NCO}^+$ (parent ion)
150	1.0	$\text{C}_6\text{H}_5\text{CFNCO}^+$
127	18.3	$\text{C}_6\text{H}_5\text{CF}_2^+$
96	3.2	$\text{C}_6\text{H}_5\text{F}^+$
85		SiF_3^+
77	4.2	C_6H_5^+
72	21.1	C_6^+
57	12.2	$\text{C}_2\text{H}_2\text{CF}^+$; CCFN^+
51	4.3	C_4H_3^+ ; C_2HCN^+
50	3.4	C_4H_2^+ ; CF_2^+
46	10.0	CFNH^+
45	16.8	CFN^+
44		CO_2^+ ; CHCF^+
43	100.0	CCF^+
42	6.8	NCO^+
41	3.6	C_3H_5^+
40	5.3	C_3H_4^+
39	4.3	C_3H_3^+

Table 13 continued

m/e	Relative Intensity	Ion
32	47.0	O_2^+
30	7.7	
29	17.7	COH^+
28	57.2	CO^+
27	14.2	$C_2H_3^+$
26	3.8	$(CH)_2^+$; CN^+
22	15.7	CO_2^{++}
18		H_2O^+
17	7.6	HO^+
16	41.8	O^+
15	6.8	NH^+
14	4.3	N^+
12	13.4	C^+

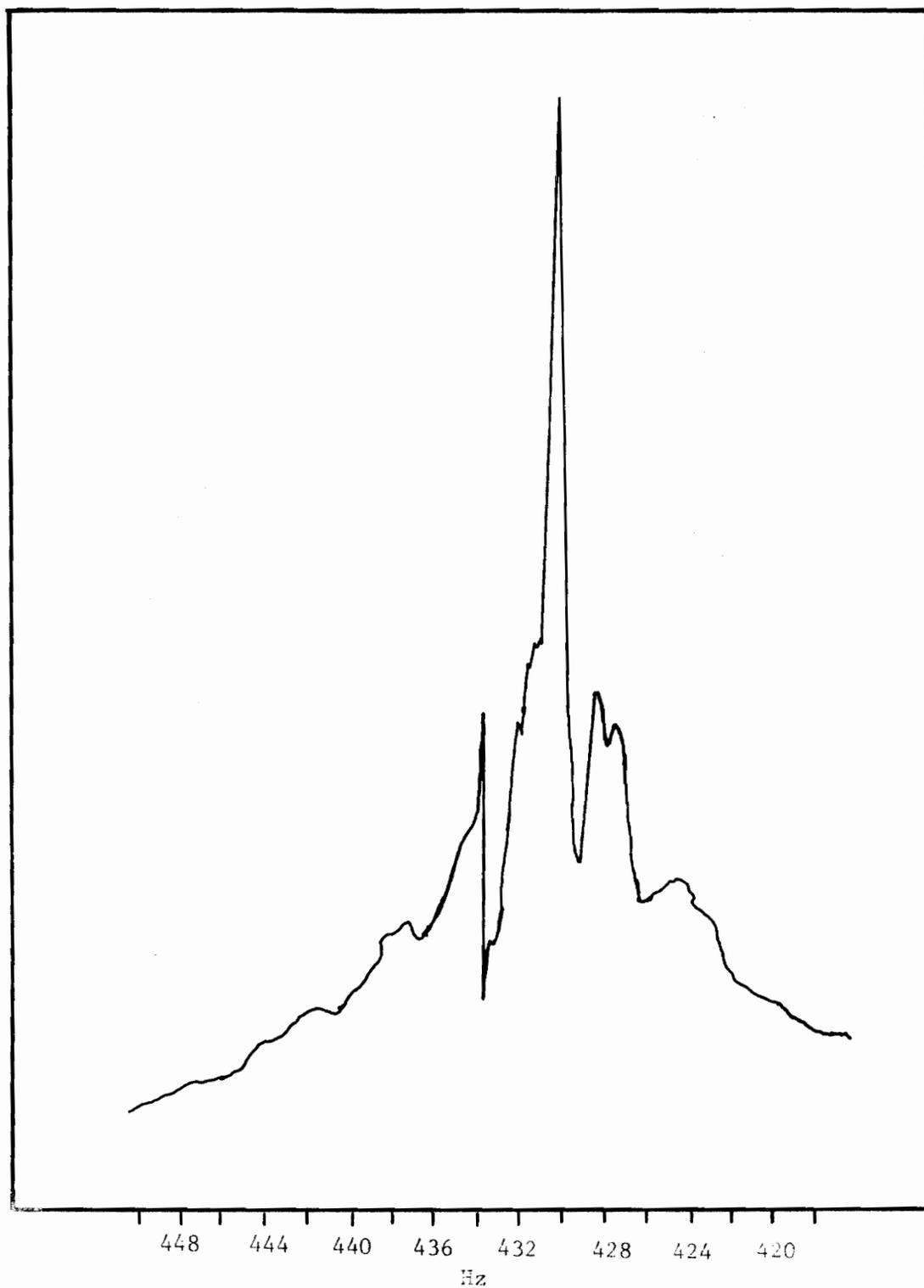


Figure 9. NMR of the Phenyl Protons of *o,o*-Difluorobenzyl Isocyanate.

resonance was a singlet at +57.8 ppm from Freon-11.

Vapor Pressure. The vapor pressure was not determined as the isocyanate proved difficult to free completely from silicon tetrafluoride and benzonitrile. However, it did transfer with difficulty on the vacuum line.

Physical Properties of 2-Hydroxy-4,6-diphenyl-s-triazine.

Infrared Spectrum. The infrared spectrum of 2-hydroxy-4,6-diphenyl-s-triazine was recorded as a Nujol mull. Its spectrum is recorded in Figure 10 and the assignments are listed in Table 14.

Mass Spectrum. Only those mass to charge ratios over 3% are listed in Table 15 except for those considered to be of some special significance.

CHN Analysis.

Element	Percent Calculated for $C_{15}H_{11}N_3O$	Percent Found
C	72.28	69.74
H	4.45	4.43
O	6.42	
N	16.86	15.09

Table 14

Infrared Spectrum of 2-Hydroxy-4,6-diphenyl-s-triazine

Taken in a Nujol Mull

cm ⁻¹	Intensity*	Assignment
3041	m.	CH aryl stretch
1660	s.	CO stretch
1590	m.	triazine ring
1547		
1533	s.	triazine ring
1489	m.	
1419	w.	
1314	w.	
1189	v.w.	
1171	v.w.	
1153	v.w.	
1065	v.w.	
1031	v.w.	
997	m.	
932	w.	
880	w.	
840	v.w.	
820	v.w.	triazine
773	m.	CH bend mono-substituted
715	s.	triazine

Table 14 continued

cm ⁻¹	Intensity*	Assignment
681	m.	CH bend mono-substituted

* m., medium; s., strong; w., weak; v.w., very weak.

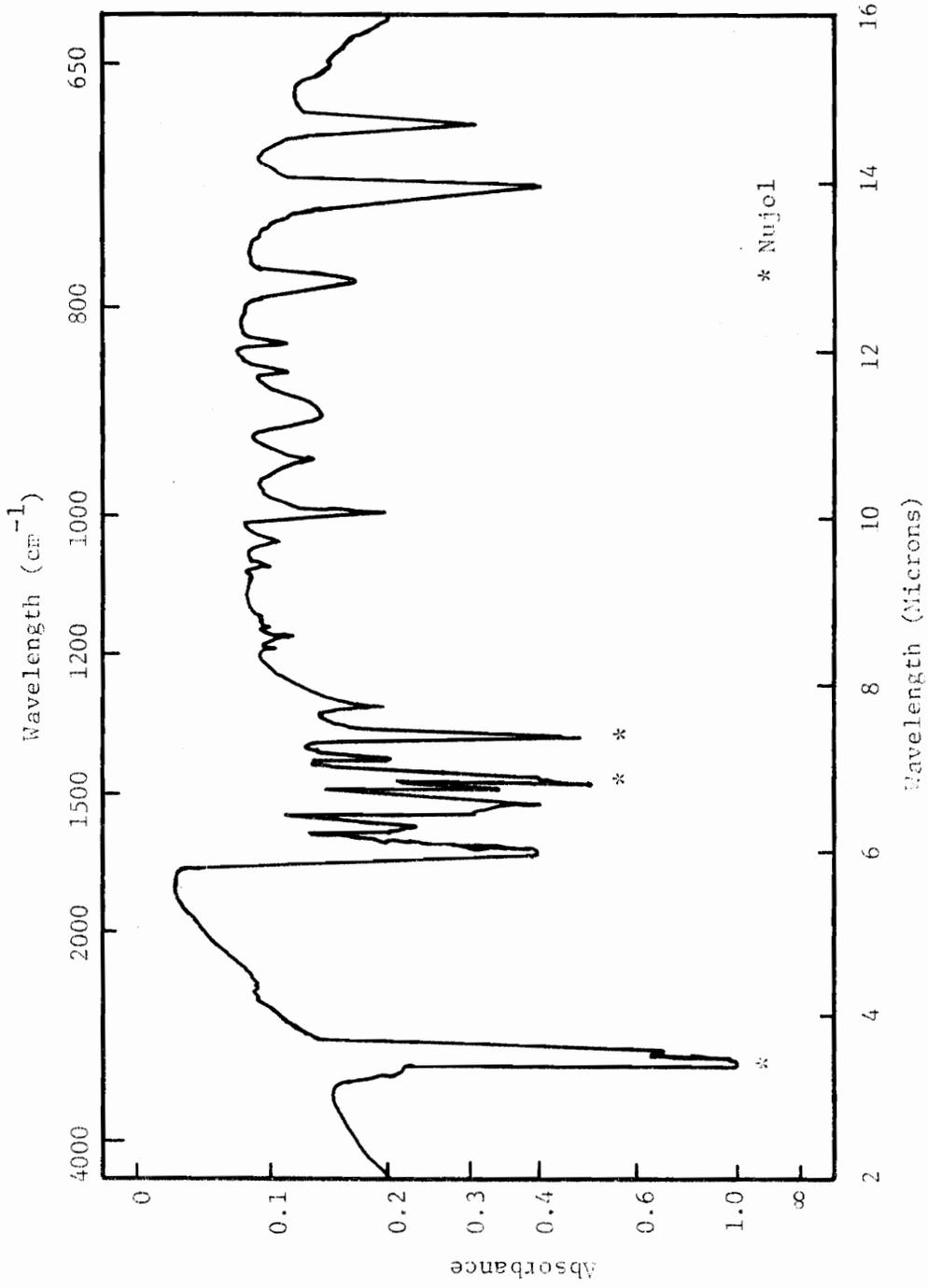


Figure 10. Infrared Spectrum of 2-Hydroxy-4,6-diphenyl-s-triazine.

Table 15

Mass Spectrum of 2-Hydroxy-4,6-diphenyl-s-triazine

50 ev 135° C at Sublimation Port

Intensity Relative to $C_6H_5^+$

m/e	Relative Intensity	Ion
250	10.0	
249	48.9	$(C_6H_5)_2(CN)_3OH^+$ (parent ion)
248	42.2	$(C_6H_5)_2(CN)_3O^+$
220	2.7	$C_6H_5C(N)NC(N)C_6H_5^+$
207	5.4	$C_6H_5CNC(NH)C_6H_5^+$
205	5.0	$C_6H_5CNC(N)C_6H_4^+$
180	4.4	$(C_6H_5)_2CN^+$
147	4.3	$C_6H_5C(NH)NCOH^+$
146	10.7	$C_6H_5C(NH)NCO^+$
145	7.0	$C_6H_5C(N)NCO^+$
139	4.7	
130	27.8	$C_6H_5C(NH)NC^+$; $C_6H_4CNCO^+$
129	13.9	$C_6H_5C(N)NC^+$
124.5	15.6	Double charge of parent
119	10.0	$HCC(CN)_3O^+$
118	10.0	$C_6H_5C(N)NH^+$
117	3.6	$C_6H_5C(N)N^+$
105	17.8	$HCCC(NC)NCO^+$; $H_2CC(H)(CN)_3^+$

Table 15 continued

m/e	Relative Intensity	Ion
104	96.7	$C_6H_5CNH^+$; $H_2CC(CN)_3^+$
103.5	2.1	Double charge, see m/e = 207
103	96.7	$C_6H_5CN^+$; $HCC(CN)_3^+$
102.5	3.1	Double charge, see m/e = 205
102	8.3	$C_6H_4CN^+$
92	5.6	$C_6H_5CH_3^+$ (solvent)
91	8.9	$C_6H_5CH_2^+$
90	6.3	$C_6H_5CH^+$
89	3.0	$C_6H_5C^+$
78	10.0	$(CN)_3^+$
77	100.0	$C_6H_5^+$
76	73.3	$C_6H_4^+$
75	10.0	$C_6H_3^+$
74	3.6	$C_6H_2^+$
65	6.1	$C_5H_5^+$
64	6.7	$C_5H_4^+$
63	7.3	$C_5H_3^+$
53	3.9	$HCNCN^+$
52	11.7	$(CN)_2^+$; $C_4H_4^+$
51	46.7	$C_4H_3^+$
50	6.2	$C_4H_2^+$
44	7.2	CO_2^+
41	4.4	$C_3H_5^+$

Table 15 continued

m/e	Relative Intensity	Ion
39	4.1	$(\text{CH})_3^+$
38	5.2	$(\text{CH})_2\text{C}^+$; CNC^+
36	8.3	C_3^+
18	6.7	H_2O^+

Melting Point. The melting point was determined to be 290° C. The value reported in the literature is 289° C.⁴⁸

The Tolunitrile Reactions.

In a characteristic reaction, the tolunitrile (Table 30) (Eastman Organic Chemical) was added to a Kel-F test tube along with thoroughly dry catalyst (if any). The Kel-F tube was made vacuum tight by the method described by Hyman *et al.*,⁹ the contents frozen with liquid nitrogen, and the air evacuated. Anhydrous hydrogen fluoride and carbonyl fluoride were condensed into the reactor and the mixture allowed to warm to room temperature. Before a reaction mixture was placed in the water bath, it was left at room temperature from six to twelve hours. After a period of time (Table 30), the mixture was frozen and checked on the vacuum line to see if any non-condensable gases had formed. None were found. The vessel was allowed to warm slowly with the product gases passing through a sodium fluoride pellet trap at 50° C, a -45° trap (chlorobenzene slush), and finally into a liquid nitrogen trap. The contents of these traps were further separated by passing through additional temperature traps depending upon the nitrile.

Left in the Kel-F reactor was a semi-liquid. When the vessel was opened in the drybox and an infrared spectrum taken of the material between salt plates, it showed broad bands which suggested an anhydrous hydrogen fluoride-nitrile complex. When the material was warmed in a water bath at 90° C under vacuum the volatile material collected was the nitrile. A solid was left in the Kel-F test tube which, when purified with various solvents, yielded the 2-hydroxy-4,6-diaryl-s-triazine and the

trimer, 2,4,6-triaryl-s-triazine.

para-Tolunitrile Reactions

The para-tolunitrile reactions (Table 30) when without a catalyst were of a single phase but when sodium fluoride was added two phases resulted. The lower phase was a solid in room temperature reactions but a clear, colorless liquid in the heated reactions. This phase was the lesser of the two.

After the reaction products were separated by trap to trap distillation, the contents of the liquid nitrogen trap were further separated by passage through a -78° trap, and a -131° trap into a -196° trap. The -78° trap contained material identified as α,α,α -trifluoro-p-xylene. The n-pentane trap contained a trace of the α,α,α -trifluoro-p-xylene and silicon tetrafluoride. The liquid nitrogen trap contained the unreacted carbonyl fluoride. The contents of the -45° trap were further separated by passing them through a 0° trap, a -45° trap, and a -131° trap. The 0° trap contained nothing. The -45° trap contained material identified as α -isocyanato- α,α -difluoro-p-xylene while the -131° trap contained a small amount of the α,α,α -trifluoro-p-xylene

The reaction vessel was opened and the yellow solid found was removed and stirred with ethanol. The mixture was filtered and the solid on the filter was treated several more times in the same manner. The solid was dissolved in toluene, recrystallized, and identified as 2,4,6-tri-p-tolyl-s-triazine. An authentic sample of the trimer was prepared from p-tolunitrile (8.28 mmol) and anhydrous hydrogen fluoride (41.0 mmol).

The filtrate was evaporated and the recovered crystals suggested that some trimer was still present. The crystals were treated with toluene, which removed the trimer, leaving 2-hydroxy-4,6-di-p-tolyl-s-triazine on the filter.

Physical Properties of α -Isocyanato- α,α -difluoro-p-xylene

Infrared Spectrum. The infrared spectrum is displayed in Figure 11 and the assignments are given in Table 6.

Mass Spectrum. Only those charge to mass ratios with intensities greater than 5 are listed in Table 17 unless they are of some special significance. The sample was found to slowly attack glass causing the large SiF_4 and CO_2 peaks in the fragmentation pattern.

NMR Spectrum. A sample of the α -isocyanato- α,α -difluoro-p-xylene was condensed into an NMR tube along with Freon-11 as solvent and F-19 reference and TMS for the proton reference. The methyl protons produced a singlet at -2.27 ppm from TMS with the aryl protons exhibiting an unsymmetrical quartet (Figure 12) centered at -7.13 ppm with a coupling constant of 8 Hz. The fluorine NMR spectrum consisted of a singlet at +54.5 ppm from Freon-11.

Table 16

Infrared Spectrum of α -Isocyanato- α,α -difluoro-*p*-xylene

Taken Between Salt Plates

cm^{-1}	Intensity*	Assignment
3049	w.	CH stretch (aryl)
2937	w.	CH_3 asym stretch
2336		
2258	v.s.	NCO asym stretch
1846	m.	
1812	m.s.	
1612	m.	
1488	w.	
1444	m.-b.	CH_3 asym bend
1328	m.	
1281	s.	CF stretch
1259	m.	
1214	m.w.	
1159	m.w.	
1073	v.s.-b.	CF stretch
1004	v.s.	CF stretch
821	s.	C-H bend 1-4 disubstituted benzene
761	s.	
743	m.	
687	m.w.	

* w., weak; v.s., very strong; m., medium; b., broad; s., strong.

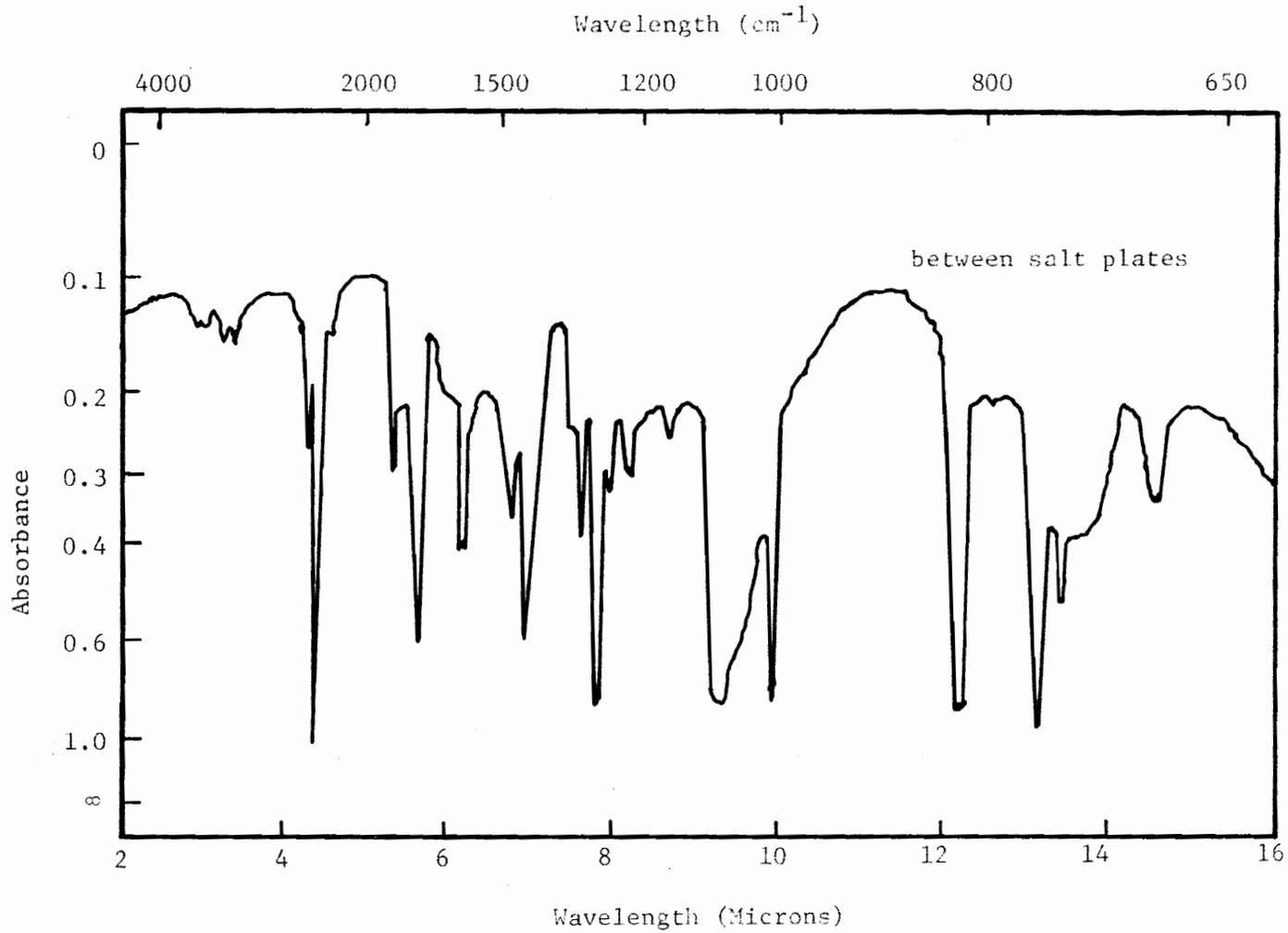


Figure 11. Infrared Spectrum of α -Isocyanato- α,α -difluoro-*p*-xylene.

Table 17

Mass Spectrum of α -Isocyanato- α,α -difluoro-*p*-xylene

70 ev 140° C temperature

m/e	Intensity	Ion
183	2	$\text{CH}_3\text{C}_6\text{H}_4\text{CF}_2\text{NCO}^+$ (parent ion)
168	2	$\text{C}_6\text{H}_4\text{CF}_2\text{NCO}^+$
167	21	$\text{C}_6\text{H}_3\text{CF}_2\text{NCO}^+$
141	8	$\text{CH}_3\text{C}_6\text{H}_4\text{CF}_2^+$
106	2	$\text{C}_6\text{H}_3\text{CF}^+$
104	94	SiF_4^+
103	7	$\text{CH}_3\text{C}_6\text{H}_4\text{C}^+$
91	16	$\text{CH}_3\text{C}_6\text{H}_4^+$
87	126	$\text{C}_6\text{H}_3\text{C}^+$
86	147	C_7H_2^+
85	230	SiF_3^+
82	16	$(\text{CH})_3\text{CCF}^+$
78	20	$(\text{CH})_4\text{CN}^+$
77	6	C_6H_5^+
76	4	C_6H_4^+
66	9	COF_2^+
51	7	C_4H_3^+
50	6	C_4H_2^+ ; CF_2^+
47	48	CFO^+
46	5	CFNH^+
45	14	$\text{C}_2\text{H}_2\text{F}^+$; CFN^+

Table 17 continued

m/e	Intensity	Ion
44	86	CO_2^+
43	7	CCF^+
42.5	35	SiF_3^{++}
39	6	C_3H_3^+
34	10	
33	74	$\text{H}_2\text{CF}^+ ?$
28	11	CO^+
22	7	CO_2^{++}
19	9	F^+
18	10	H_2O^+
16	12	O^+
12	2	C^+

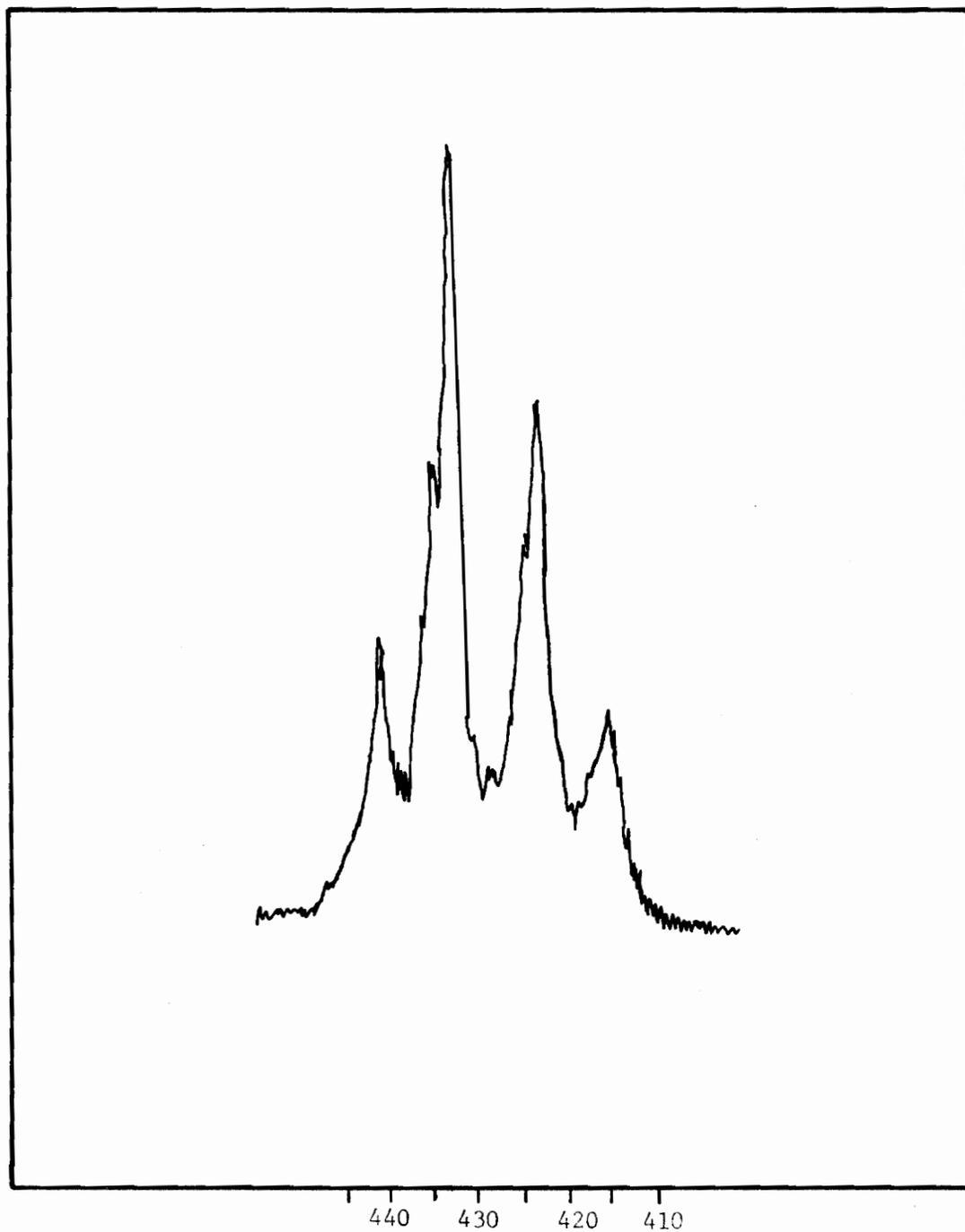


Figure 12. NMR of the Aromatic Protons of α -Isocyanato- α, α -difluoro-*p*-xylene.

Physical Properties of α,α,α -Trifluoro-*p*-xylene.

Infrared Spectrum. The infrared spectrum was recorded in the gas phase at 10 torr in a 100 mm cell. The spectrum is reproduced in Figure 13 and the assignments are given in Table 18. The trifluoromethyl assignments are in agreement with those of the large class of trifluoromethyl aryl compounds studied by Randle and Whiffen.⁴⁹

Mass Spectrum. Only those peaks whose mass to charge ratios were greater than 3% are listed in Table 19 unless they were of some special significance.

Physical Properties of 2-Hydroxy-4,6-di-*p*-tolyl-*s*-triazine.

Infrared Spectrum. The infrared spectrum of 2-hydroxy-4,6-di-*p*-tolyl-*s*-triazine was recorded as a Nujol mull (Figure 14) and the assignments are given in Table 20.

Mass Spectrum. Only those mass to charge ratios over 3% relative intensity are listed in Table 21 unless they were of some special significance. The spectrum also gave evidence that this triazine was still contaminated with impurities in that a mass/charge ratio at 351 would be for 2,4,6-tri-*p*-tolyl-*s*-triazine. Also peaks at 300, 299, and 281 m/e suggest that some $\text{CH}_3\text{C}_6\text{H}_4\text{C}(\text{F})=\text{NC}(\text{O})\text{N}=\text{CFC}_6\text{H}_4\text{CH}_3$ was still present which would be the precursor to the 2-hydroxy-4,6-di-*p*-tolyl-*s*-triazine and α,α,α -trifluoro-*p*-xylene.

Melting Point. The melting point was found to be 290° to 291° C. It has been reported as 290° C.⁴⁶

Table 18

Infrared Spectrum of α,α,α -Trifluoro-p-xylene

Taken at 10 Torr

cm^{-1}	Intensity*	Assignment
3043	v.w.	CH stretch ring
2947	v.w.	CH ₃ stretch
1631	v.w.b.	
1420	v.w.b.	CH ₃ asym bend
1332	v.s.	CF ₃ sym stretch
1239	v.w.	
1177	s.	CF ₃ asym stretch
1150	s.	CF ₃ asym stretch
1076	m.	
1028	w.	
833	m.	1-4 disubstituted benzene CH
744	w.	

* v.w., very weak; v.w.b., very weak and broad; s., strong; m., medium; w., weak.

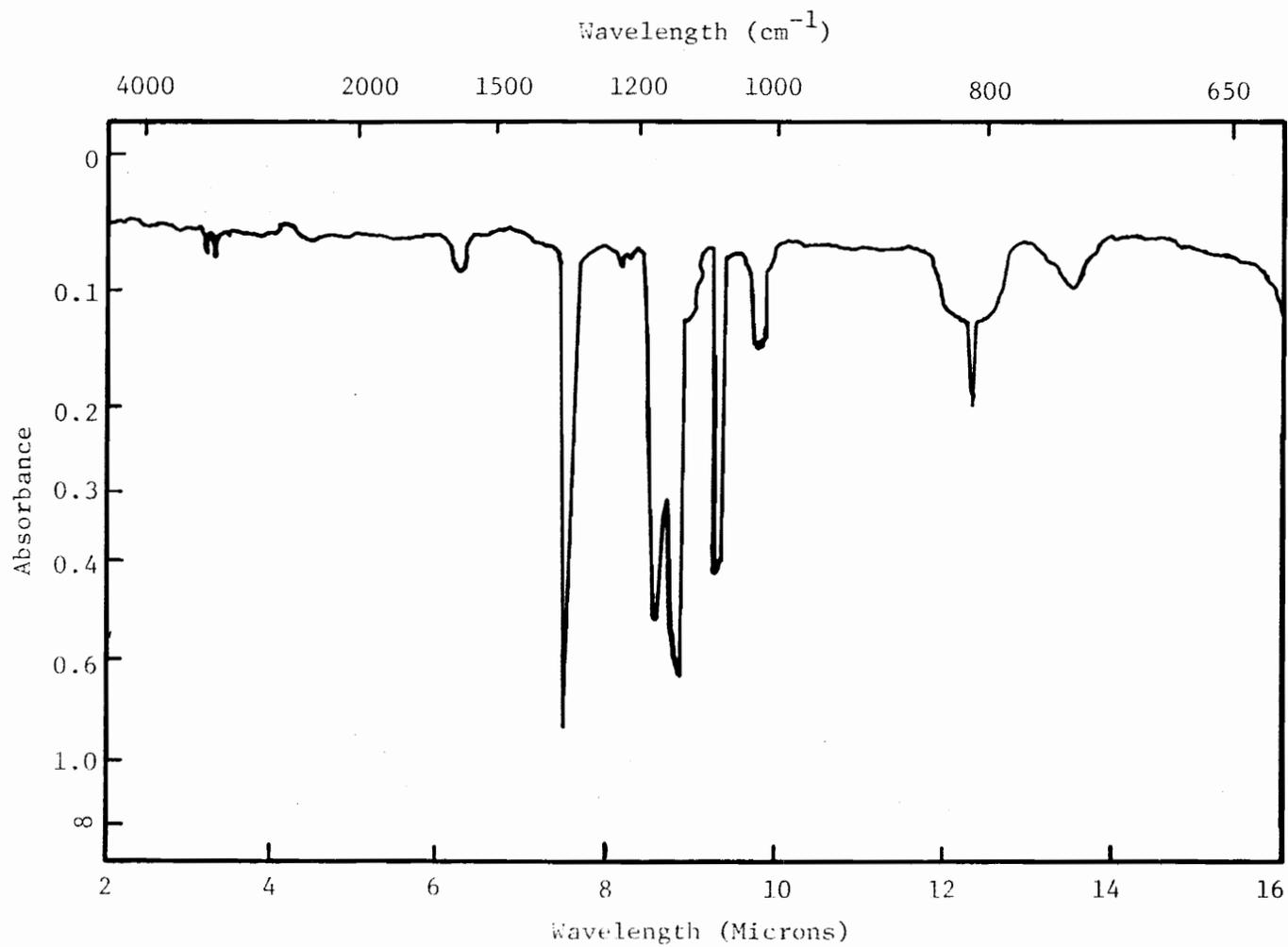


Figure 13. Infrared Spectrum of α, α, α -Trifluoro-*p*-xylene

Table 19 continued

m/e	Relative Intensity	Ion
92	17.9	$C^{13}C_6H_7^+$
91	100.0	$CH_3C_6H_4^+$
89	10.7	$CHC_6H_4^+$
85	4.2	SiF_3^+
83	7.1	$C_4H_4CF^+$
76	3.0	$C_6H_4^+$
75	7.7	$C_6H_3^+$
74	3.0	$C_6H_2^+$
70.5	1.8	$CH_3C_6H_4CF_2^{++}$
70	9.5	$C_3H_3CF^+$
69	20.8	CF_3^+
65	13.7	$C_5H_5^+$
64	6.0	$C_5H_4^+$
63	16.1	$C_5H_3^+$
62	6.6	$C_5H_2^+$
57	4.1	$C_3H_2F^+$
56	6.0	C_3HF^+
51	13.7	$C_4H_3^+$
50	6.6	$C_4H_2^+; CF_2^+$
48	3.6	C_4^+
46	3.0	$C_2H_3F^+$
44	7.7	$CHCF^+; CO_2^+$
43	17.9	CCF^+

Table 19 continued

m/e	Relative Intensity	Ion
41	7.7	$\text{CH}_3\text{CCH}_2^+$
39	14.3	C_3H_3^+
	3.0	C_3H_2^+
	7.7	CF^+
	7.7	CCH_3^+
	4.8	H_2O^+
	3.6	HO^+
	1.8	CH_3^+

Table 20

Infrared Spectrum of 2-Hydroxy-4,6-di-p-tolyl-s-triazine.

(Nujol mull)

cm ⁻¹	Intensity*	Assignment
3084	m.	CH stretch (aryl)
1686	v.s.	CO stretch
1618	w.	
1595	m.	triazine ring
1546	s.	triazine ring
1514	m.	
1467	v.s.	CH ₃ asym bend or triazine
1376	w.	CH ₃ sym bend
1316	w.	
1199	w.	
1089	w.	
1003	m.w.	
961	w.	triazine
939	w.	triazine
811	s.	1-4 di-substituted benzene CH bend
745	m.	
650	w.	

*m., medium; v.s., very strong; w., weak; s., strong.

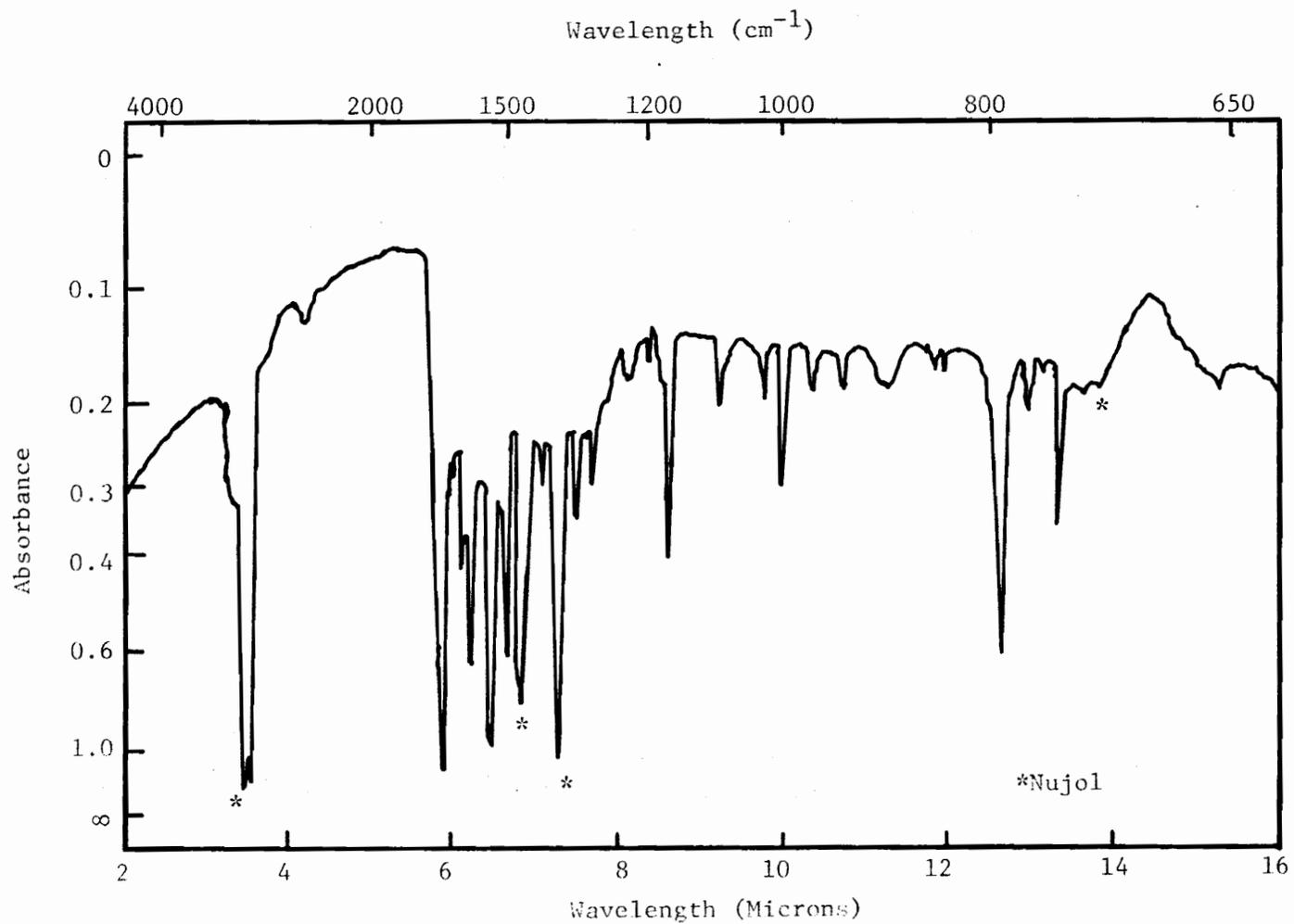


Figure 14. Infrared Spectrum of 2-Hydroxy-4,6-di-p-tolyl-s-triazine.

Table 21

Mass Spectrum of 2-Hydroxy-4,6-di-p-tolyl-s-triazine

50 ev

200° C

Intensity Relative to $\text{CH}_3\text{C}_6\text{H}_4\text{CNH}^+$

m/e	Relative Intensity	Ion
352	3.7	
351	8.4	$(\text{CH}_3\text{C}_6\text{H}_4\text{CN})_3^+$
300	1.6	$(\text{CH}_3\text{C}_6\text{H}_4\text{C}(\text{F})=\text{N})_2\text{CO}^+$
299	5.3	$\text{CH}_3\text{C}_6\text{H}_4\text{C}(\text{F})=\text{NC}(\text{O})\text{N}=\text{C}(\text{F})\text{C}_6\text{H}_4\text{CH}_2^+$
281	5.8	$\text{CH}_3\text{C}_6\text{H}_4\text{C}=\text{NC}(\text{O})\text{N}=\text{C}(\text{F})\text{C}_6\text{H}_4\text{CH}_3^+$
280	20.0	$\text{CH}_3\text{C}_6\text{H}_4\text{C}=\text{NC}(\text{O})\text{N}=\text{C}(\text{F})\text{C}_6\text{H}_4\text{CH}_2^+$
279	28.3	$\text{CH}_3\text{C}_6\text{H}_4\text{C}=\text{NC}(\text{O})\text{N}=\text{C}(\text{F})\text{C}_6\text{H}_4\text{CH}^+$
278	36.8	$\text{CH}_2\text{C}_6\text{H}_4\text{C}=\text{NC}(\text{O})\text{N}=\text{C}(\text{F})\text{C}_6\text{H}_4\text{CH}^+$
277	25.0	$(\text{CH}_3\text{C}_6\text{H}_4\text{CN})_2\text{NCOH}^+$ (parent)
263	5.2	$\text{C}^{13}_6\text{H}_{16}\text{N}_3\text{O}^+$
262	9.5	$\text{CH}_3(\text{C}_6\text{H}_4\text{CN})_2\text{CH}_2\text{NCOH}^+$
249	4.5	$(\text{CH}_3\text{C}_6\text{H}_4\text{CN})_2\text{NH}^+$
248	5.1	$(\text{CH}_3\text{C}_6\text{H}_4\text{CN})_2\text{N}^+$
235	10.5	$(\text{CH}_3\text{C}_6\text{H}_4\text{CN})_2\text{H}^+$
234	3.1	$(\text{CH}_3\text{C}_6\text{H}_4\text{CN})_2^+$
233	5.5	$\text{C}_{16}\text{H}_7\text{N}_2^+$
208	4.0	$\text{FC}=\text{NC}(\text{O})\text{N}=\text{C}(\text{F})\text{C}_6\text{H}_4\text{CH}_2^+$
196	0.3	metastable
161	5.8	$\text{CH}_3\text{C}_6\text{H}_4\text{C}(\text{NH})\text{NCOH}^+$

Table 21 continued

m/e	Relative Intensity	Ion
160	8.5	$\text{CH}_3\text{C}_6\text{H}_4\text{C}(\text{N})\text{NCOH}^+$
159	4.7	$\text{CH}_3\text{C}_6\text{H}_4\text{C}(\text{N})\text{NCO}^+$
144	15.5	$\text{CH}_3\text{C}_6\text{H}_4\text{CNCNH}^+$
143	5.2	$\text{CH}_3\text{C}_6\text{H}_4\text{CNCN}^+$
139.5	0.4	double charge m/e=279
138.5	3.7	double charge m/e=277
138.5	1.0	metastable
132	10.0	$\text{CH}_3\text{C}_6\text{H}_4\text{NH}_2^+$
131	6.3	$\text{C}_6\text{H}_4\text{CNCOH}^+$; $\text{CH}_3\text{C}_6\text{H}_4\text{CNN}^+$
130.5	1.2	double charge m/e=261
120	3.9	$\text{HCC}(\text{CN})_3\text{OH}^+$
119	43.2	$\text{HCC}(\text{CN})_3\text{O}^+$
118	100.0	$\text{CH}_3\text{C}_6\text{H}_4\text{CNH}^+$
117	99.0	$\text{CH}_3\text{C}_6\text{H}_4\text{CN}^+$
116	66.4	$\text{CH}_2\text{C}_6\text{H}_4\text{CN}^+$
104	3.0	$\text{C}_6\text{H}_4\text{CNH}_2^+$
92	6.8	$\text{C}^{13}\text{C}_6\text{H}_7^+$
91	63.2	$\text{CH}_3\text{C}_6\text{H}_4^+$
90	37.9	$\text{CH}_2\text{C}_6\text{H}_4^+$
89	31.6	CHC_6H_4^+
77	4.5	C_6H_5^+
69.3	2.4	metastable
69	3.6	HNCNCO^+

Table 21 continued

m/e	Relative Intensity	Ion
65	23.2	$C_5H_5^+$
64	4.2	$C_5H_4^+$
63	6.3	$C_5H_3^+$
51	4.5	$C_4H_3^+$
44		CO_2^+
43	3.9	$HNCO^+$
41	37.0	$C_3H_5^+$
40	77.9	$C_3H_4^+$
39	7.9	$C_3H_3^+$
36	6.3	C_3^+
34	3.9	
32		O_2^+
29	48.4	COH^+
28		$N_2^+; CO^+$
27	4.2	CHN^+
20	4.5	HF^+
18		H_2O^+
17		OH^+
16		O^+
14		N^+
12	1.4	C^+

Physical Properties of 2,4,6-Tri-p-tolyl-s-triazine.

Infrared Spectrum. The infrared spectrum of 2,4,6-tri-p-tolyl-s-triazine was recorded as a Nujol mull. Its spectrum is reproduced in Figure 15 and the assignments are given in Table 22.

Mass Spectrum. The mass spectrum showed an intense peak at $m/e=351$ (Table 21).

Melting Point. The melting point was 278° C, which agrees with literature value.⁵⁰

CHN Analysis.

Element	Percent Calculated for $C_{24}H_{21}N_3$	Percent Found
C	82.02	77.51
H	6.02	5.83
N	11.96	11.33

meta-Tolunitrile Reactions

The meta-tolunitrile reaction mixture showed two phases but the lower phase was a solid. At the end of the reaction time it exhibited a rhombohedral crystal pattern and was thought to be a sodium hydrogen fluoride. The upper phase was very dark burnt orange.

The contents of the liquid nitrogen trap from the original separation were further separated by allowing the gases to pass through a -95° trap, a -131° trap, and finally into the -196° trap. The -95° trap did

Table 22

Infrared Spectrum of 2,4,6-Tri-*p*-tolyl-*s*-triazine

Taken in a Nujol mull

cm ⁻¹	Intensity*	Assignment
1606	m.w.	
1581	m.	triazine
1507	s.	triazine
1403	m.	CH ₃ asym stretch
1295	m.w.	
1240	w.	
1211	w.	
1175	m.	
1146	m.w.	
1108	w.	
1018	m.w.	
853	m.w.	triazine
843	m.w.	triazine
795	s.	CH 1,4-disubstituted benzene
767	m.	

*m.w., medium weak; m., medium; s., strong; w., weak.

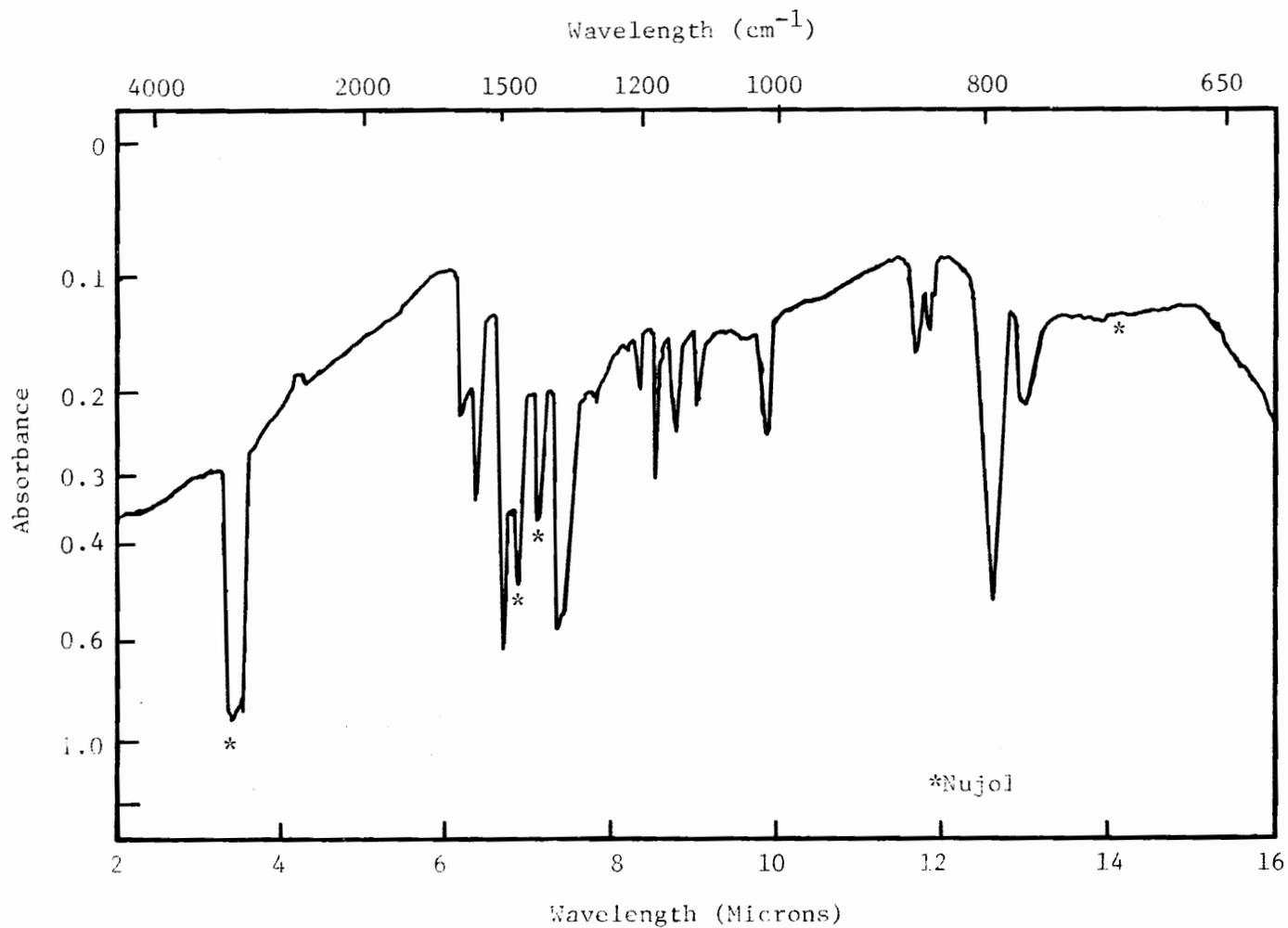


Figure 15. Infrared Spectrum of 2,4,6-Tri-p-tolyl-s-triazine.

not contain anything. The -131° trap contained material which was later identified as α,α,α -trifluoro-m-xylene. The -196° trap contained the unreacted carbonyl fluoride. The contents of the -45° trap were further separated by passing the gases through a water-ice slush trap, a -45° trap, and finally into a liquid nitrogen trap. The 0° trap contained unreacted m-tolunitrile. The -45° trap contained material which was identified as α -isocyanato- α,α -difluoro-m-xylene. Several passes were needed before the isocyanate was reasonably free of α,α,α -trifluoro-m-xylene. The -196° trap contained α,α,α -trifluoro-m-xylene along with some SiF_4 . The silicon tetrafluoride was removed and all of the α,α,α -trifluoro-m-xylene was weighed to determine the yield (see Table 30).

The Kel-F reaction vessel was opened and found to contain a cream colored solid. Dry toluene was added to the solid, the solid broken up, the contents dumped into a breaker and stirred for several minutes. When the solution was filtered a white solid collected on the filter. Following several more treatments with toluene and recrystallizing from ethanol, the solid was identified as 2-hydroxy-4,6-di-m-tolyl-s-triazine. The filtrate was evaporated to recover the soluble material and was identified as 2,4,6-tri-m-tolyl-s-triazine. An authentic sample of 2,4,6-tri-m-tolyl-s-triazine was prepared from m-tolunitrile (8.8 mmol) and anhydrous hydrogen fluoride (40.0 mmol).

Physical Properties of $\text{m-CH}_3\text{C}_6\text{H}_4\text{CF}_2\text{NCO}$.

Infrared Spectrum. The infrared spectrum (Table 23, Figure 16) exhibited the expected isocyanate peak and was in excellent agreement

Table 23

Infrared Spectrum of α -Isocyanate- α,α -difluoro-m-xylene

Taken Between Salt Plates

cm^{-1}	Intensity*	Assignment
3041	w.	CH ring (aryl)
2920	w.	CH_3 asym stretch
2319		
2257	s.	NCO asym
1841	m.	
1810	m.	
1487	m.w.	
1447	m.	CH_3 asym bend
1384	w.	CH_3 sym bend
1333	m.	CF_2 sym stretch
1288	m.s.	
1242	m.s.	
1195	m.s.	
1176	m.	CF_2 asym stretch
1170	m.	
1125	m.s.	CF_2 stretch
1074	s.-v.b.	CF_2 stretch
1004	w.	
993	w.	
919	w.	
885	w.	

Table 23 continued

cm^{-1}	Intensity*	Assignment
868	w.	
854	m.w.	
791	m.s.	CH bend; 1, 3 substituted benzenes
763	m.	
735	m.s.	
703	m.	CH bend; 1, 3 substituted benzens
691	w.	

* w., weak; s., strong; m., medium; v.b., very broad.

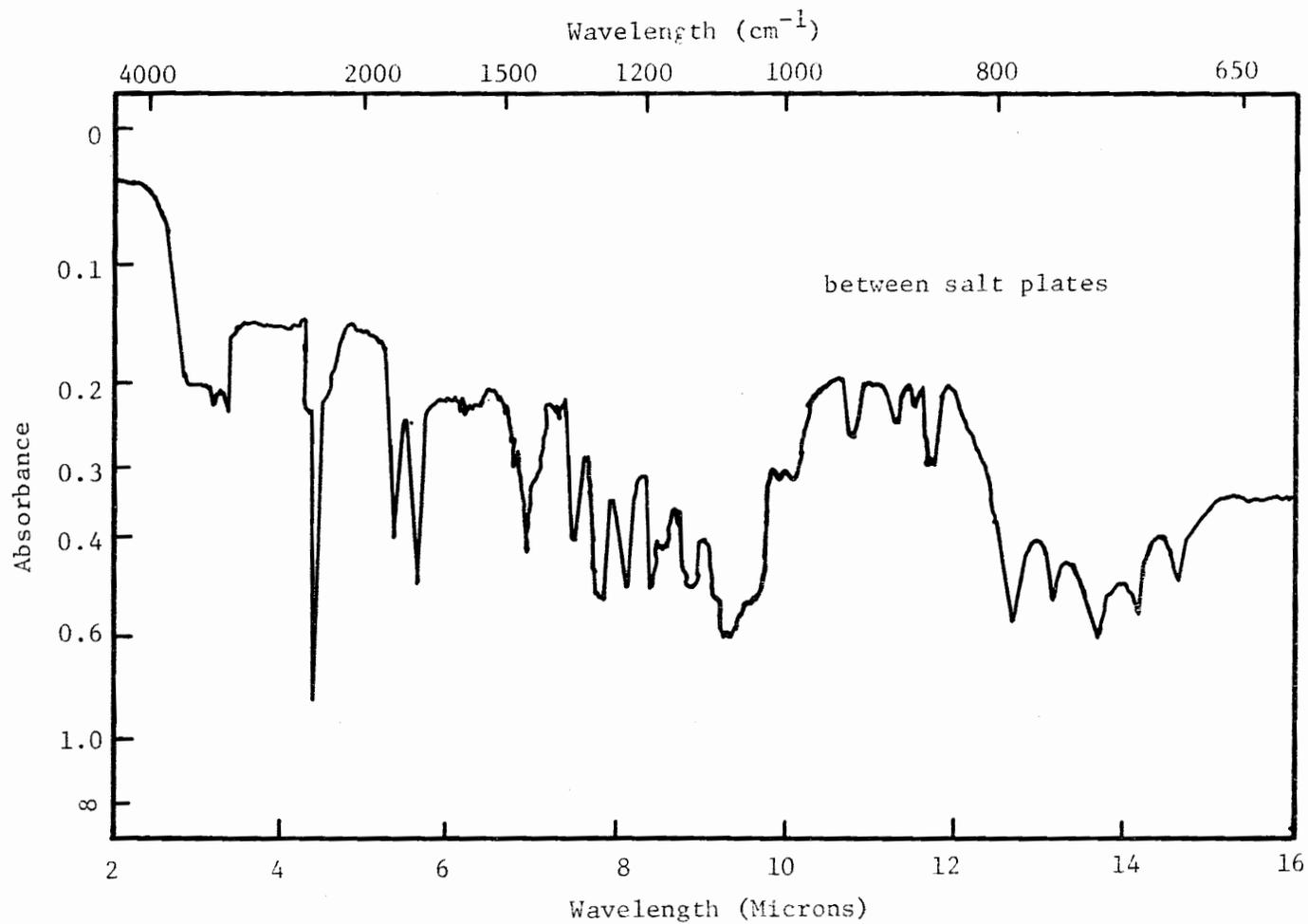


Figure 16. Infrared Spectrum of α -Isocyanato- α,α -difluoro-m-xylene.

with meta substituted benzenes.

Mass Spectrum. Unless the peaks were of special significance, those of less than 3% relative intensity were not listed in Table 24.

NMR Spectrum. A sample of α -isocyanato- α,α -difluoro-m-xylene was condensed into an NMR tube along with Freon-11 as solvent and F-19 reference and some TMS for the proton reference. The methyl protons produced a singlet at -2.28 ppm. The aromatic protons gave a complicated pattern (Figure 17) and was over the range of -7.15 to -7.50 ppm. The F^{19} spectrum showed a sharp singlet at +57.0 ppm from CCl_3F .

Vapor Pressure. The vapor pressure was not determined as the isocyanate proved difficult to separate from the α,α,α -trifluoro-m-xylene and the m-tolunitrile. It transferred very slowly on the vacuum system.

Physical Properties of α,α,α -Trifluoro-m-xylene.

Infrared Spectrum. The infrared spectrum was recorded in the gas phase in a 100 mm cell (Figure 18) and its assignments are given in Table 25: The trifluoromethyl assignments were in agreement with the

Table 24

Mass Spectrum of α -Isocyanato- α,α -difluoro-m-xylene

70 ev Source 70° C Inlet 60° C

Intensity Relative to $C_6H_4CH_3^+$

m/e	Relative Intensity	Ion
184	1.2	$C^{13}_8H_7F_2NO^+$ (Cal. 1.2)
183	13.1	$CH_3C_6H_4CF_2NCO^+$ (parent ion)
168	3.7	$C_6H_4CF_2NCO^+$
161	5.6	$C^{13}_7H_7F_3^+$
160	50.0	$CH_3C_6H_4CF_3^+$ (contamination)
159	22.2	$CH_2C_6H_4CF_3^+$
154	3.1	$C_5H_2CF_2NCO^+$
145	4.4	$C_6H_4CF_3^+$
142	8.7	$C^{13}_7H_7F_2^+$
141	80.0	$CH_3C_6H_4CF_2^+$
140	20.0	$CH_2C_6H_4CF_2^+$
139	6.3	$CHC_6H_4CF_2^+$
138	6.9	$CC_6H_4CF_2^+$
131	4.4	$C_6H_4CNCOH^+$
128	6.9	$C_6H_2CNCO^+$
127	8.1	$C_6H_5CF_2^+ ? ; C_6HCNCO^+$
126	21.2	$C_6H_4CF_2^+$
125	8.7	$C_6H_3CF_2^+$
120	4.4	$CHC_6H_4CF^+$
119	14.4	$CC_6H_4CF^+$

Table 24 continued

m/e	Relative Intensity	Ion
114	6.9	$\text{CH}_3\text{CCC}(\text{H})\text{CCF}_2^+$
113	4.4	$\text{CH}_2\text{CCC}(\text{H})\text{CCF}_2^+$
110	12.8	$\text{CH}_3(\text{CH})_4\text{CCF}^+$
109	38.2	$\text{CH}_3(\text{CH})_3\text{C}_2\text{CF}^+$
107	6.3	$\text{C}_6\text{H}_4\text{CF}^+$
105	3.7	$\text{C}_6\text{H}_2\text{CF}^+$
101	8.1	$\text{C}_4\text{H}_3\text{CF}_2^+$
99	10.0	C_4HCF_2^+
95	5.6	$\text{H}_2\text{CC}(\text{CH})_2\text{CCF}^+$
92	35.6	$\text{C}^{13}\text{C}_6\text{H}_7^+$; CF_2NCO^+
91	100.0	$\text{C}_6\text{H}_4\text{CH}_3^+$
90	20.0	$\text{C}_6\text{H}_4\text{CH}_2^+$
89	35.0	$\text{C}_6\text{H}_4\text{CH}^+$
88	7.5	$\text{C}_6\text{H}_4\text{C}^+$
87	7.5	C_7H_3^+
86	6.3	C_7H_2^+
85	4.4	SiF_3^+
83	13.7	$\text{C}_4\text{H}_4\text{CF}^+$
81	12.8	$\text{C}_4\text{H}_2\text{CF}^+$
78	3.7	$\text{C}_6\text{H}_6^+?$; $(\text{CH})_4\text{CN}^+$
77	11.2	C_6H_5^+
76	6.9	C_6H_4^+

Table 24 continued

m/e	Relative Intensity	Ion
75	76.2	$C_6H_3^+$
74	9.4	$C_6H_2^+$
73	6.3	C_6H^+
70.5	6.9	double charge see m/e=141
70	15.6	$C_3H_3CF^+$
69	30.0	CF_3^+
66	12.8	COF_2^+ ; SiF_2^+
65	55.0	$C_5H_5^+$
64	14.4	$C_5H_4^+$
63	60.0	$C_5H_3^+$
62	33.2	$C_5H_2^+$
61	11.6	C_5H^+
59	3.1	$C_3H_4F^+$
58	7.5	$C_3H_3F^+$
57	17.5	$C_3H_2F^+$
56	3.1	C_3HF^+
53	5.6	$C_4H_5^+$
52	11.6	$C_4H_4^+$
51	45.0	$C_4H_3^+$
50	36.9	$C_4H_2^+$; CF_2^+
49	4.4	C_4H^+
45.5	1.2	double charge see m/e=91
45	13.1	$C_2H_2F^+$; $C_6H_4CH_2^{++}$

Table 24 continued

m/e	Relative Intensity	Ion
44.5	4.4	double charge see m/e=89
44	67.5	CO_2^+
43	34.4	CCF^+
41	11.6	C_3H_5^+
40	55.0	C_3H_4^+
39	80.0	C_3H_3^+
38	25.6	C_3H_2^+
37	9.4	C_3H^+
36	42.5	C_3^+
35	4.4	
34	4.4	
32		O_2^+
31	15.6	CF^+
30	8.1	
29	45.0	C_2H_5^+
28		$\text{CO}^+; \text{N}_2^+$
27	20	CH_2CH^+
26	5.6	CHCH^+
22	3.1	CO_2^{++}
20	11.9	HF^+
18		H_2O^+
17		OH^+

Table 24 continued

m/e	Relative Intensity	Ion
16	35.0	O^+
15	5.6	CH_3^+
14	43.7	$N^+; CH_2^+$
12	0.6	C^+

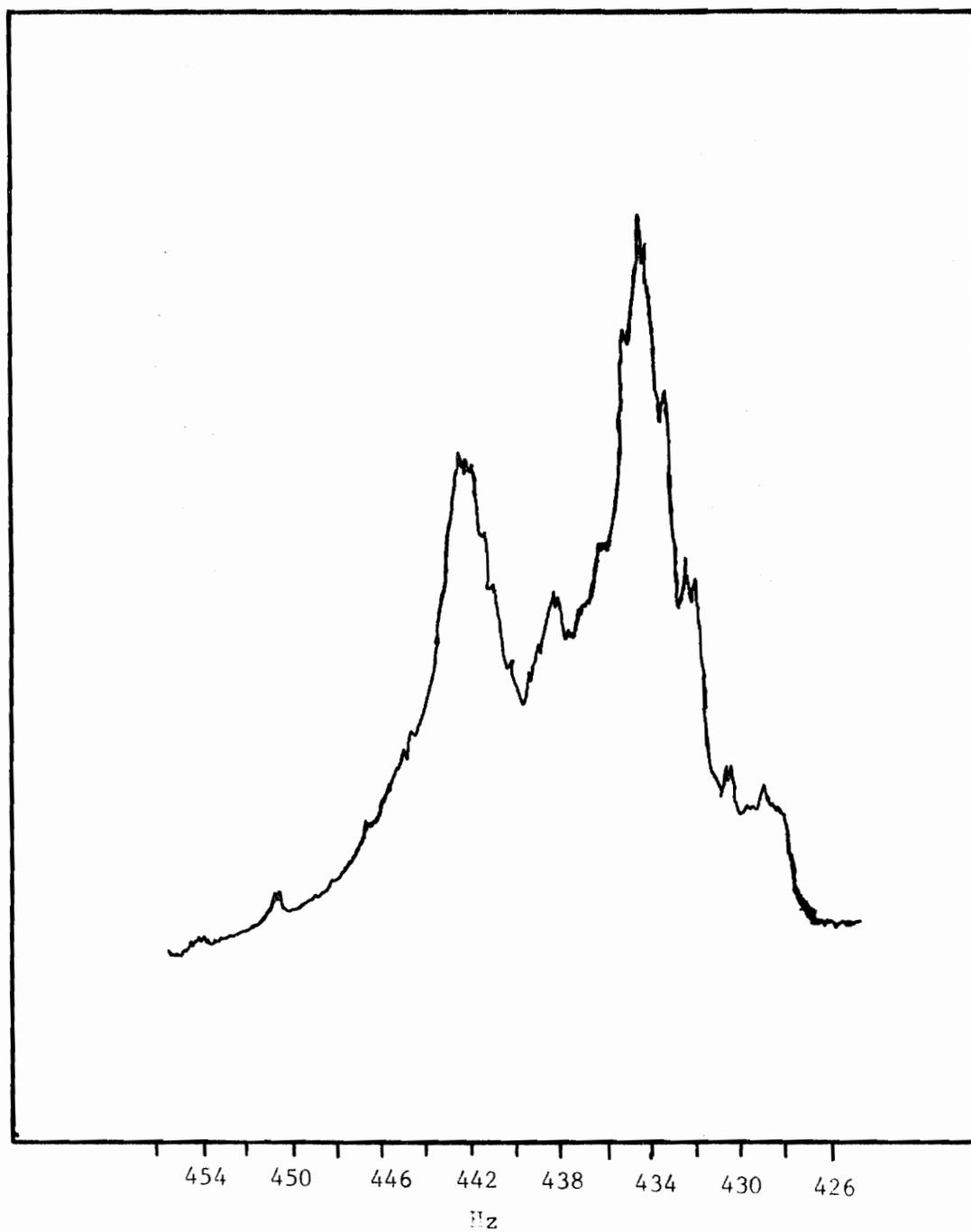


Figure 17. NMR of the Aromatic Protons of α -Isocyanato- α,α -difluoro-*m*-xylene.

Table 25

Infrared Spectrum of α,α,α -Trifluoro-m-xylene

taken at 7 torr

cm^{-1}	Intensity*	Assignment
3075	w.	CH stretch (aryl)
2941	w.	CH_3 asym stretch
1742	w doublet	
1605	w.b.	
1488	w.	
1455	m.	CH_3 asym bend
1334	v.s.	CF_3 sym
1206	s.	
1183	v.s.	CF_3 asym
1151	v.s.	CF_3
1106	m.b.	
1084	s.	
1034	v.s.	
918	w.	impurity
890		impurity
874	m.	
793	s.	CH bend; 1-3 disubstituted benzene
741	b.m.	
702	s.	CH bend; 1-3 disubstituted benzene
662	m.b.	

*w., weak; b., broad; m., medium; v.s., very strong; s., strong.

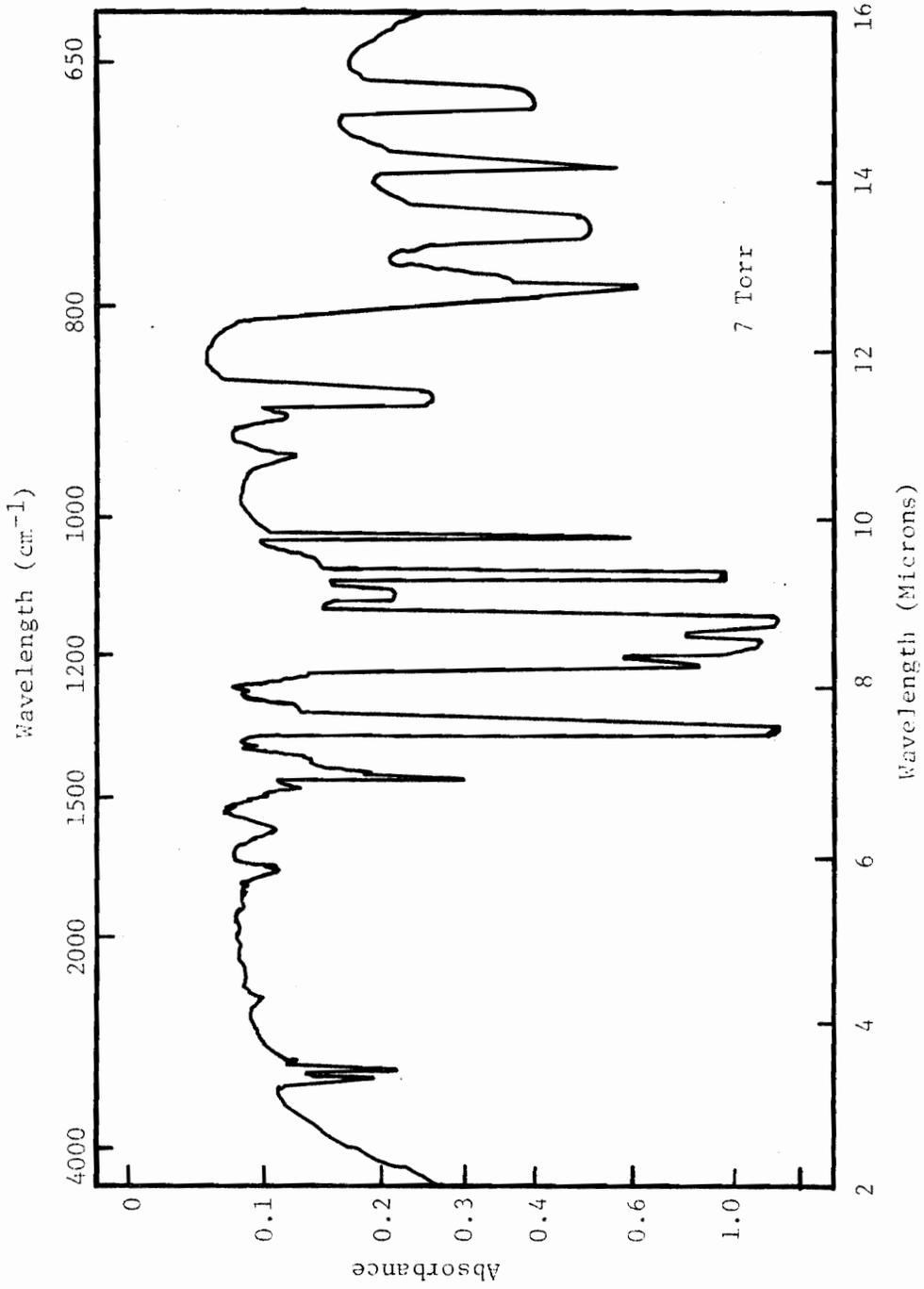


Figure 18. Infrared Spectrum of 2,6,6-Trifluoro-n-xylene.

trifluoromethylaryl compounds studied by Randle and Whiffen⁴⁹.

Mass Spectrum. Only those peaks whose mass to charge ratio were greater than 3% relative intensity were listed in Table 26 unless they were of some special significance.

Physical Properties of 2-Hydroxy-4,6-di-m-tolyl-s-triazine.

Infrared Spectrum. The infrared spectrum was recorded as a Nujol mull (Figure 19) and the assignments are given in Table 27.

Mass Spectrum. Only those mass to charge ratios over 3% relative intensity were listed in Table 28 unless they were of some special significance.

Melting Point. The melting point was determined to be greater than 360° C.

Physical Properties of 2,4,6-Tri-m-tolyl-s-triazine.

Infrared Spectrum. The infrared spectrum was recorded as a Nujol mull (Figure 20). The assignments are given in Table 29.

CHN Analysis.

Element	Percent Calculated for $C_{24}H_{21}N_3$	Percent Found
C	82.02	81.30
H	6.02	5.85
N	11.96	12.13

Table 26

Mass Spectrum of α, α, α -Trifluoro-m-xylene

70 ev Inlet 26° Source 60°

Intensity Relative to $\text{CH}_3\text{C}_6\text{H}_4^+$

m/e	Relative Intensity	Ion
161	4.5	$\text{C}^{13}\text{C}_7\text{H}_7\text{F}_3^+$ (Cal. 4.3)
160	47.2	$\text{CH}_3\text{C}_6\text{H}_4\text{CF}_3^+$ (parent)
159	18.3	$\text{CH}_2\text{C}_6\text{H}_4\text{CF}_3^+$
145	2.0	$\text{C}_6\text{H}_4\text{CF}_3^+$
141	15.9	$\text{CH}_3\text{C}_6\text{H}_4\text{CF}_2^+$
140	5.3	$\text{CH}_2\text{C}_6\text{H}_4\text{CF}_2^+$
119	4.9	$\text{CC}_6\text{H}_4\text{CF}^+$
109	11.0	$\text{CH}_3(\text{CH})_3\text{C}_2\text{CF}^+$
104	9.4	SiF_4^+
92	13.8	$\text{C}^{13}\text{C}_6\text{H}_7^+$
91	100.0	$\text{CH}_3\text{C}_6\text{H}_4^+$
89	4.9	CHC_6H_4^+
87	12.6	$\text{C}_6\text{H}_3\text{C}^+$
86	19.5	C_7H_2^+
75	3.7	C_6H_3^+
72	8.1	C_6^+
70	3.3	$\text{C}_3\text{H}_3\text{CF}^+$
69	2.4	CF_3^+
65	8.5	C_5H_5^+
63	8.5	C_5H_3^+

Table 26 continued

m/e	Relative Intensity	Ion
62	5.7	$C_5H_2^+$
57	4.1	$C_3H_2F^+$
51	5.7	$C_4H_3^+$
50	4.5	$C_4H_2^+; CF_2^+$
47	7.3	$C_2H_4F^+$
45	4.1	$C_2H_2F^+$
44		CO_2^+
43	28.5	CCF^+
39	11.0	$C_3H_3^+$
33	6.1	H_2CF^+
32	8.1	$O_2^+; HCF^+$
29	7.3	$C_2H_5^+$
28	30.5	$N_2^+; CO^+; CH_2CH_2^+$
27	6.1	CCH_3^+
18	12.6	H_2O^+
16	15.5	O^+
15	2.9	CH_3^+
12	3.3	C^+

Table 27

Infrared Spectrum of 2-Hydroxy-4,6-di-m-tolyl-s-triazine
Nujol mull

cm ⁻¹	Intensity*	Assignment
1662	v.s.	CO stretch
1596	v.w.	triazine ring
1556	m.	
1529	m.	triazine ring
1482	w.	
1416	v.w.	CH ₃ asym bend
1365	m.	CH ₃ sym bend
1303	v.w.	
1211	m.	
862	v.w.	triazine
806	v.w.	
789	m.	CH bend 1-3 substituted benzene
768	w.	
741	m.	
585	w.	

*v.s., very strong; v.w., very weak; m., medium; w., weak.

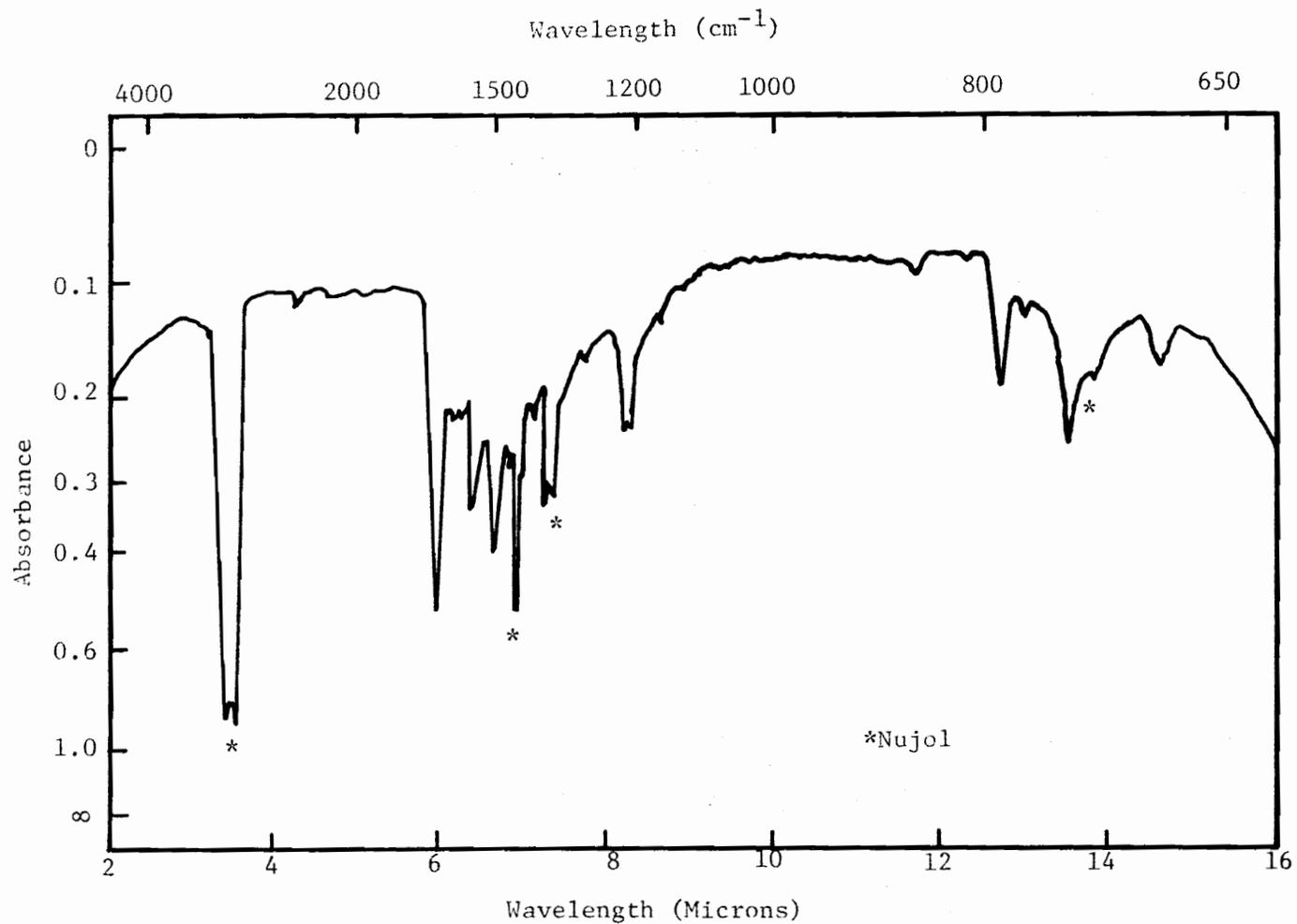


Figure 19. Infrared Spectrum of 2-Hydroxy-4,6-di-m-tolyl-s-triazine.

Table 28

Mass Spectrum of 2-Hydroxy-4,6-di-m-tolyl-s-triazine

70 ev

m/e	Intensity Relative to $(\text{CH}_3\text{C}_6\text{H}_4\text{CN})_2\text{NCO}^+$	
	Relative Intensity	Ion
278	2.2	$\text{C}^{13}\text{C}_{16}\text{H}_{15}\text{N}_3\text{O}^+$ (Cal. 2.2)
277	5.6	$(\text{CH}_3\text{C}_6\text{H}_4\text{CN})_2\text{NCOH}^+$ (parent)
276	100.0	$(\text{CH}_3\text{C}_6\text{H}_4\text{CN})_2\text{NCO}^+$
275	57.2	$\text{CH}_3(\text{C}_6\text{H}_4\text{CN})_2\text{CH}_2\text{NCO}^+$
262	2.2	$\text{CH}_3(\text{C}_6\text{H}_4\text{CN})_2\text{NCOH}^+$
261	12.4	$\text{CH}_3(\text{C}_6\text{H}_4\text{CN})_2\text{NCO}^+$
247	2.2	$(\text{C}_6\text{H}_4\text{CN})_2\text{NCOH}^+$
186	6.6	$\text{CH}_3\text{C}_6\text{H}_4(\text{CN})_3\text{OH}^+$
147	22.2	$\text{CH}_3\text{C}_5\text{H}_3(\text{CN})_2\text{OH}^+$
131	11.2	$\text{C}_6\text{H}_4\text{CNCOH}^+$
122	6.6	$\text{CH}_3\text{C}_3\text{H}_2(\text{CN})_2\text{OH}^+$
120	13.4	$\text{HC}_2(\text{CN})_3\text{OH}^+$
119	15.6	$\text{C}_2(\text{CN})_3\text{OH}^+$; $\text{CH}_3\text{C}_6\text{H}_4\text{CNH}_2^+$
118	22.2	$\text{CH}_3\text{C}_6\text{H}_4\text{CNH}^+$
117	23.4	$\text{CH}_3\text{C}_6\text{H}_4\text{CN}^+$
116	26.6	$\text{CH}_2\text{C}_6\text{H}_4\text{CN}^+$
106	8.8	$\text{C}_4\text{H}_3\text{CNCOH}^+$
105		$\text{C}_4\text{H}_2\text{CNCOH}^+$
92	55.6	$\text{CH}_3\text{CHCCNCN}^+$
91	57.8	$\text{CH}_3\text{C}_6\text{H}_4^+$

Table 28 continued

m/e	Relative Intensity	Ion
90	11.2	$\text{CH}_2\text{C}_6\text{H}_4^+$
89	13.4	CHC_6H_4^+
85	15.6	
83	20.0	
78	11.2	$(\text{CN})_3^+$; $\text{CH}_3\text{C}_4\text{NH}^+$
77	55.6	$\text{HC}_2(\text{CN})_2^+$; $\text{CH}_3\text{C}_4\text{N}^+$
76	8.8	C_6H_4^+
75	6.6	C_6H_3^+
74	6.6	C_6H_2^+
65	22.2	C_5H_5^+ ; HCCNCN^+
64	6.6	C_5H_4^+
63	13.4	C_5H_3^+ ; C_4NH^+
57	8.8	N_2COH^+
56	8.8	N_2CO^+
55	8.8	CNCOH^+
52	6.6	C_4H_4^+ ; $(\text{CN})_2^+$
51	33.4	C_4H_3^+ ; HCCCN^+
50	17.8	C_4H_2^+
47	11.2	
45	8.8	$\text{C}_6\text{H}_4\text{CH}_2^{++}$
44	51.2	CO_2^+
43	13.4	HNCO^+
41	22.4	C_3H_5^+

Table 28 continued

m/e	Relative Intensity	Ion
40	6.6	CH_3CCH^+
39	22.2	$(\text{CH})_3^+$; CCNH^+
38	26.6	$(\text{CH})_2\text{C}^+$; CCN^+
36	95.4	C_3^+
35	15.6	
32	123.4	O_2^+
29	11.2	COH^+
28		N_2^+ ; CO^+
27	10.0	CHN^+
18	55.6	H_2O^+
17	30.2	OH^+
16	13.4	O^+
14	6.6	N^+

Table 29

Infrared Spectrum of 2,4,6-Tri-m-tolyl-s-triazine

Taken as a Nujol Mull

cm ⁻¹	Intensity*	Assignment
3038	w.	CH aryl stretch
1521	v.s.	triazine ring
1435	w.	CH ₃ asym bend
1394	w.	
1362	m.	CH ₃ sym bend
1284	w.	
1225	v.w.	
1165	w.	
1128	w.	
1090	w.	
928	w doublet	
924	w doublet	
893	w.	
844	w.m.	triazine ring
773	s.	CH bend, 1-3 substituted benzene
689	s.	CH bend, 1-3 substituted benzene
648	w.	

* w., weak; v.s., very strong; m., medium; s., strong.

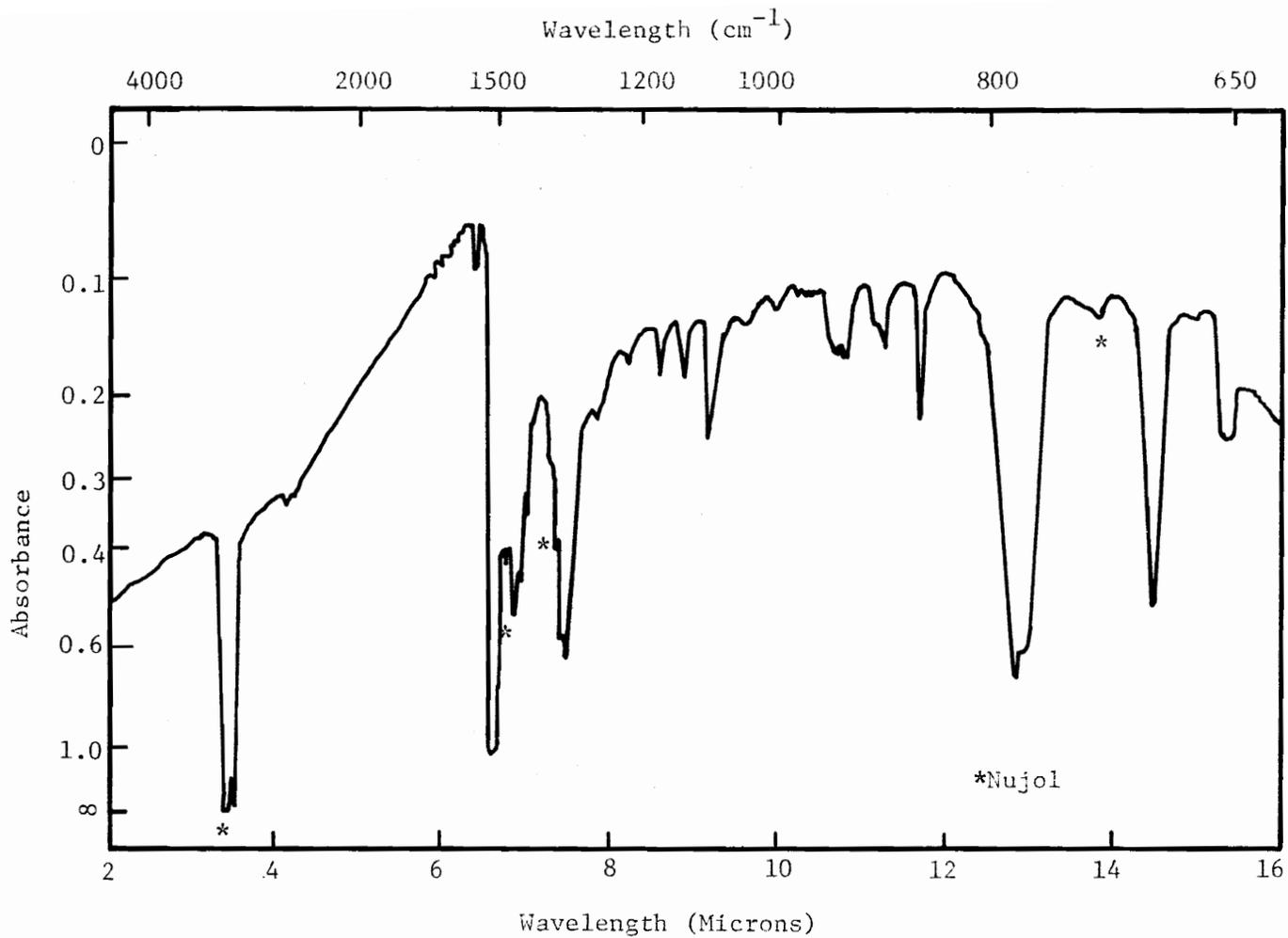


Figure 20. Infrared Spectrum of 2,4,6-Tri-m-tolyl-s-triazine.

Melting Point. The melting point was determined to be 152° to 153°

C. The literature value is 152° - 153° C.⁵⁰

ortho-Tolunitrile Reactions.

The ortho-tolunitrile reactions always resulted in two liquid phases with the upper phase being the larger. This was thought to be the nitrile, HF, and carbonyl fluoride complex. This phase was dark orange in color. The lower phase was clear colorless and believed to be the catalyst and anhydrous hydrogen fluoride solution.

Upon distillation of the products, the liquid nitrogen trap contained the unreacted carbonyl fluoride along with a trace of SiF₄. Within experimental error, no carbonyl fluoride was consumed. The -45° trap contained the unreacted nitrile except on the second run an additional infrared peak appeared at 2273 cm⁻¹, which is in the isocyanate region. A mass spectrum (gas phase) of the contents of this trap indicated only SiF₄ as present and a liquid phase infrared spectrum suggested the presence of o-CH₃C₆H₄C(F)=NH₂⁺HF₂⁻. Only a trace of the isocyanate may have been formed and no α,α,α -trifluoro-o-xylene.

An attempt to prepare a sample of 2,4,6-tri-o-tolyl-s-triazine was made by introducing 8.5 mmol of the nitrile and 40.0 mmol of anhydrous hydrogen fluoride into a Kel-F test tube. After standing 4.5 days at 50° C the reactor was opened, the HF removed with sodium fluoride pellets and the other volatile gases trapped in a liquid nitrogen trap. This trap, when investigated by infrared spectroscopy, was found to contain a large quantity of the unreacted nitrile and a small amount of

Table 30

The TOLUNITRILES Reactions--Yields and Conditions

	Nitrile mmol	COF ₂ mmol	HF mmol	Time days	NaF mmol	NCO %	Xylene %	Temp. ° C.
ORTHO	8.5	5.0	17.0	9	0.95	0	0	65
	9.4	10.0	16.0	4.5	0.95	trace	0	50
	9.4	8.9	13.5	4.5	0.99*	0	0	50
META	8.8	11.7	14.3	4.5	0.95	11.3	20	50
	9.7	9.7	12.5	4.5	0.95	11.3	11.2	50
PARA	8.3	9.8	30.0	28	none	0	0	R.T.
	8.3	13.1	52.0	41	0.95	trace	trace	R.T.
	8.3	10.6	12.5	37	0.95	10	1	R.T.
	10.4	10.2	17.0	4.5	0.95	11.2	11.5	50

* CsF

SiF_4 . Left in the Kel-F reactor was a very small amount of semi-liquid which gave an infrared suggesting $\text{o-CH}_3\text{C}_6\text{H}_4\text{C(F)=NH}_2^+\text{HF}_2^-$. Cook and Jones⁵⁰ succeeded in making this triazine in 10% yields by using chlorosulfonic acid at zero degrees. Therefore, this reaction was repeated except the temperature was 0° C. Again, there was no evidence for the triazine upon work-up of the mixture.

Reactions of p-Trifluoromethylbenzonitrile.

p-Trifluoromethylbenzonitrile (PCR, Inc., lot IC 3128) was weighed out (6.54 mmol), placed in a Kel-F test tube along with 0.95 mmol of sodium fluoride, and carbonyl fluoride (10.0 mmol) and anhydrous hydrogen fluoride (16.3 mmol) were condensed on top of it. The reactor was allowed to warm to room temperature and stand for about six hours. It was then placed in a water bath at 50° C for 4.5 days. The reaction mixture was frozen with liquid nitrogen and opened to the vacuum line. No non-condensable gases were found so the contents were allowed to pass through a NaF pellet trap at 50° C into a liquid nitrogen trap. The liquid nitrogen trap was allowed to warm slowly and its contents passed through several other traps. The -45° trap had some liquid and the gas phase infrared spectrum suggested p-bis(trifluoromethyl)benzene when compared to the spectrum published in Sadtler²⁹ (#864). The contents of this trap were further separated by allowing them to pass through a 0° trap, a -15.3° trap (benzyl alcohol slush), a -45° trap, and finally into a liquid nitrogen trap. The coldest trap had a small amount of material which was believed to be, from the infrared spectrum analysis,

p-bis(trifluoromethyl)benzene. The remaining three traps had material which was identified as p-trifluoromethyl- α,α -difluorobenzyl isocyanate and possibly some p-bis(trifluoromethyl)benzene. Thus, little or no separation occurred. The -95° trap and the -131° trap contained only traces of silicon tetrafluoride. The last trap, -196° , contained unreacted carbonyl fluoride (8.9 mmol). The reaction produced an approximately 16% yield of the isocyanate and only a trace of the p-bis(trifluoromethyl)benzene.

The yellow solid left in the Kel-F reaction vessel was stirred with ethanol for several minutes. The suspension was filtered and the white solid on the filter was identified as 2,4,6-tris-p-trifluoromethylphenyl-s-triazine. The solid recovered from the filtrate also proved to be the same with a very small amount of 2-hydroxy-4,6-bis-p-trifluoromethylphenyl-s-triazine.

Physical Properties of p-Trifluoromethyl- α,α -difluorobenzyl Isocyanate.

Infrared Spectrum. The infrared spectrum obtained on the vapor is reproduced in Figure 21 and assignments are listed in Table 31.

Mass Spectrum. Only those mass to charge ratios over 3% are listed in Table 32 unless they were of some special significance.

NMR Spectrum. A spectrum was taken on a sample of the p-trifluoromethyl- α,α -difluorobenzyl isocyanate with Freon-11 solvent and F-19 reference and TMS as the proton reference. The aryl protons gave a sharp singlet at -7.72 ppm. The fluorine spectrum consisted of two singlets, one at $+56.7$ ppm which was assigned to the fluorine atoms

Table 31

Infrared Spectrum of *p*-Trifluoromethyl- α,α -difluorobenzyl Isocyanate
(at autogenous pressure)

cm ⁻¹	Intensity*	Assignment
2273	v.s.	NCO asym
1441	m.	
1419	w.	
1331	v.s.	CF ₃ sym stretch
1286	m.	
1236	v.w.	
1185	s.	CF ₃ asym stretch
1160	s.	CF ₃
1097	s.	CF ₂
1077	s.	CF ₂
1031	s.	CF ₂
1008	s.	CF ₂
849	m.	CH bend, 1-4 substituted benzene

* v.s., very strong; m., medium; w., weak; s., strong.

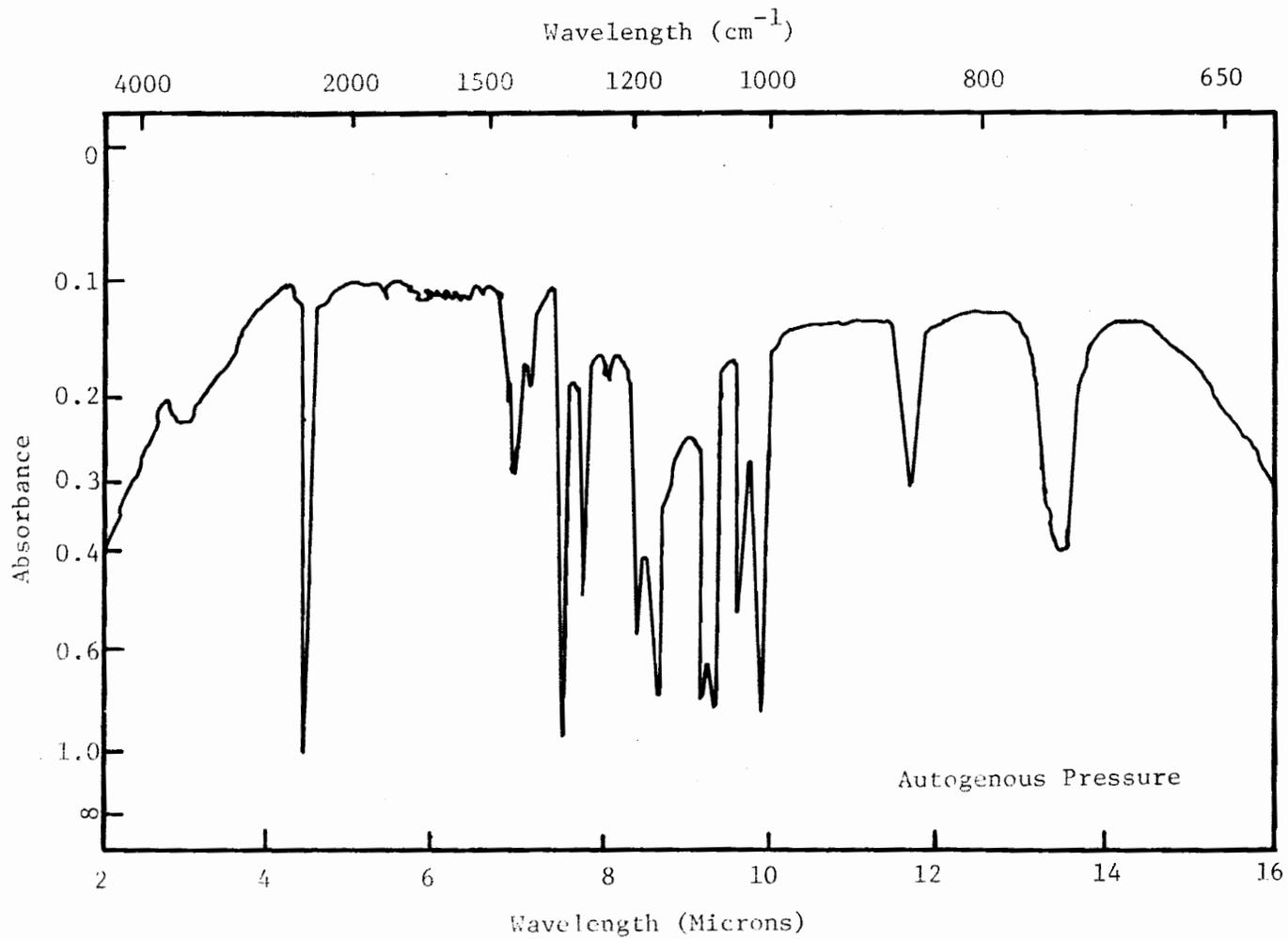


Figure 21. Infrared Spectrum of *p*-Trifluoromethyl- α,α -difluorobenzyl Isocyanate.

Table 32

Mass Spectrum of *p*-Trifluoromethyl- α,α -difluorobenzyl Isocyanate

	70 ev	Source 80° C	Inlet 40° C
m/e	Relative Intensity	Ion	
238	1.95	$C^{13}C_8H_4F_5NO^+$ (Cal. 1.9)	
237	20.0	$CF_3C_6H_4CF_2NCO^+$ (parent ⁺)	
218	9.2	$CF_3C_6H_4CFNCO^+$	
124	0.6	$CF_3C_6H_4CF_3^+$	
196	6.1		
195	8.2	$CF_3C_6H_4CF_2^+$	
176	1.4	$CF_3C_6H_4CF^+$	
172	8.9	$C^{13}C_7H_4F_3N^+$ (Cal. 8.4)	
171	100.0	$CF_3C_6H_4CN^+$	
170	23.3	$CF_3C_6H_3CN^+$	
168	3.3	$C_6H_4CF_2NCO^+$	
160.5	0.3	metastable	
153	3.1	$C^{13}C_7H_4F_2N^+$	
152	41.1	$CF_2C_6H_4CN^+$	
145	16.4	$CF_3C_6H_4^+$	
144	3.4	$CF_3C_6H_3^+$	
125	4.7	$CF_2C_6H_3^+$	
122	3.2		
121	87.8	$C_5H_4F_3^+$	
108.5	0.2	$CF_3C_6H_3CFNCO^{++}$	
107.5	0.2	metastable	

Table 32 continued

m/e	Relative Intensity	Ion
102	8.0	$C_6H_4CN^+$
100	3.5	$C_6H_2CN^+$; $C_4H_2CF_2^+$
99	4.2	$C_4HCF_2^+$
95	4.2	$(CH)_2CF_3^+$
94	4.2	$CHCCF_3^+$
85.5	1.7	$CF_3C_6H_4CN^{++}$
76	8.3	$C_6H_4^+$
75	16.4	$C_6H_3^+$
74	5.3	$C_6H_2^+$
69	6.4	CF_3^+
51	7.2	$C_4H_3^+$
50.5	0.2	$C_6H_3CN^{++}$
50	11.1	$C_4H_2^+$; CF_2^+
47	3.1	CFO^+
44	3.8	CO_2^+
31	1.8	CF^+

next to the isocyanate group and the other at +62.7 ppm which was assigned to the trifluoromethyl group. The fluorine resonance for *p*-bis(trifluoromethyl)benzene was determined by Muller and Carr⁵¹ to be +65 ppm from external Freon-11.

Vapor Pressure. The vapor pressure at room temperature was too low to be determined by standard vacuum line techniques.

Physical Properties of 2,4,6-Tris-*p*-trifluoromethylphenyl-*s*-triazine.

Infrared Spectrum. The infrared spectrum, recorded from a Nujol mull (Figure 22), is listed in Table 33.

Mass Spectrum. Only those peaks whose mass to charge ratios were greater than 3% are listed in Table 34. The spectrum also showed a small peak at $m/e = 385$, which could be the parent ion for 2-hydroxy-4,6-di-*p*-trifluoromethylphenyl-*s*-triazine. The intensity of this peak was confirmation, along with other evidence, that the amount of *p*-bis(trifluoromethyl)benzene formed was small.

Melting Point. The melting point was determined to be 259° to 260° C.

p-Nitrobenzonitrile Reactions.

p-Nitrobenzonitrile (Eastman Organic Chemicals) (0.174 g, 1.18 mmol) was placed in a Kel-F reactor and carbonyl fluoride (4.51 mmol) and hydrogen fluoride (25.0 mmol) were condensed into the reactor. After being at room temperature for twenty-four days, the mixture was frozen with liquid nitrogen and opened to the vacuum line. No non-condensable

Table 33

Infrared Spectrum of 2,4,6-Tris-p-trifluoromethylphenyl-s-triazine

Taken as a Nujol Mull

cm ⁻¹	Intensity*	Assignment
1951	v.w.	
1818	v.w.	
1597	m.	
1527	s.-b.	triazine ring
1418	m.	
1326	s.-b.	CF ₃ sym stretch
1242	m.	
1190	s.	CF ₃ asym stretch
1143	s.-v.b.	CF ₃
1109	s.	
1070	s.	
1021	s.	
983	m.	
974	m.	
873	s.	
848	s.	triazine
819	s.	CH bend, 1-4 substituted benzene
764	m.	
737	m.	

* v.w., very weak; m., medium; s.-b., strong and broad; s., strong; s.-v.b., strong and very broad.

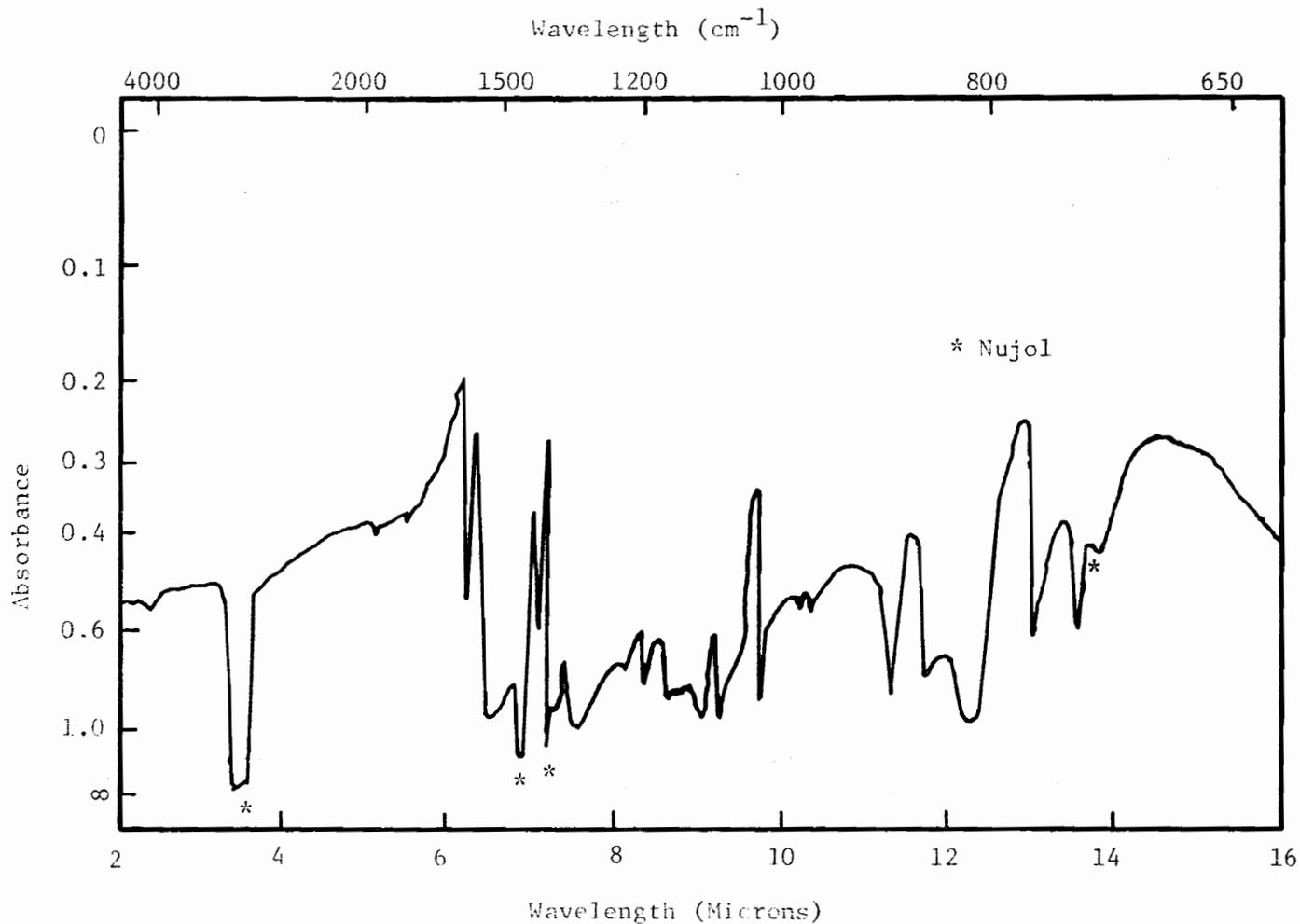


Figure 22. Infrared Spectrum of 2,4,6-Tris-p-trifluoromethylphenyl-s-triazine.

Table 34

Mass Spectrum of 2,4,6-Tris-p-trifluoromethylphenyl-s-triazine

70 ev	Intensity Relative to $\text{CF}_3\text{C}_6\text{H}_4\text{CN}^+$	
m/e	Relative Intensity	Ion
513	9.0	$(\text{CF}_3\text{C}_6\text{H}_4\text{CN})_3^+$ (parent)
512	42.3	$(\text{CF}_3\text{C}_6\text{H}_4\text{CN})_2\text{CF}_3\text{C}_6\text{H}_3\text{CN}^+$
494	1.7	$\text{CF}_2\text{C}_6\text{H}_4\text{CN}(\text{CF}_3\text{C}_6\text{H}_4\text{CN})_2^+$
493	5.8	$\text{CF}_2\text{C}_6\text{H}_3\text{CN}(\text{CF}_3\text{C}_6\text{H}_4\text{CN})_2^+$
412	5.4	$(\text{C}_6\text{H}_4\text{CN})_2\text{CF}_3\text{C}_5\text{H}_3\text{CNCF}_2^+$
387	4.4	$(\text{C}_6\text{H}_4\text{CN})_2\text{CF}_3\text{C}_3\text{H}_2\text{CNCF}_2^+$
342	2.2	$(\text{CF}_3\text{C}_6\text{H}_4\text{CN})_2^+$
341	4.2	$\text{CF}_3\text{C}_6\text{H}_4\text{CNCF}_3\text{C}_6\text{H}_3\text{CN}^+$
269	3.8	$\text{CF}_3\text{C}_6\text{H}_2\text{CNC}_6\text{H}_2\text{CN}^+$
267	3.9	doublet $\text{C}_3\text{H}(\text{C}_6\text{H}_4)_2(\text{CN})_3^+$; $\text{CF}_3\text{C}_6\text{CNC}_6\text{H}_2\text{CN}^+$
251	4.5	doublet $\text{CFC}_6\text{H}_4\text{CNCFC}_6\text{H}_3\text{C}^+$
219	4.6	doublet $\text{FCC}_6\text{H}_4\text{CNCC}_6\text{H}_2^+$; $\text{F}_2\text{CC}_4\text{H}_2\text{CNCC}_4\text{H}_2\text{CF}^+$
217	5.4	doublet $\text{F}_2\text{CC}_6\text{H}_4\text{CH}(\text{CN})_3^+$
215	4.6	$\text{F}_2\text{CC}_6\text{H}_2\text{CH}(\text{CN})_3^+$
213	5.8	$\text{FCC}_6\text{CH}(\text{CN})_3^+$
205	3.0	doublet $\text{F}_2\text{CC}_6\text{H}_4(\text{CN})_3\text{H}^+$
203	16.3	$\text{F}_2\text{CC}_6\text{H}_2(\text{CN})_3\text{H}^+$; $\text{C}_6\text{H}_3\text{CNC}_6\text{H}_4\text{CN}^+$
201	26.0	$\text{F}_2\text{CC}_6(\text{CN})_3\text{H}^+$; $\text{C}_6\text{H}_3\text{CNC}_6\text{H}_2\text{CN}^+$
198	3.5	$\text{CF}_3\text{C}_6\text{H}_4\text{CNCNH}^+$

Table 34 continued

m/e	Relative Intensity	Ion
197	7.1	$\text{CF}_3\text{C}_6\text{H}_4\text{CNCN}^+$
195	7.7	$\text{CF}_3\text{C}_6\text{H}_2\text{CNCN}^+$
187	3.6	$\text{C}_6\text{H}_3\text{CNCC}_6\text{H}_2^+$
185	10.6	$\text{FCC}_6\text{H}_4(\text{CN})_3^+$; $\text{CF}_3\text{C}_6\text{H}_4\text{CN}_2^+$
174	4.0	
173	53.8	$\text{FCC}_6\text{H}_4\text{C}(\text{NH})\text{NCCH}^+$
172	59.6	$\text{CF}_3\text{C}_6\text{H}_4\text{CNH}^+$; $\text{FCC}_6\text{H}_4\text{C}(\text{N})\text{NCCH}^+$
171	100.0	$\text{CF}_3\text{C}_6\text{H}_4\text{CN}^+$
170	87.2	$\text{CF}_3\text{C}_6\text{H}_3\text{CN}^+$
165	9.6	doublet $\text{C}_3\text{HC}_6\text{H}_4(\text{CN})_2^+$; $\text{CC}_6\text{H}_3(\text{CN})_3^+$
163	17.9	doublet $\text{F}_2\text{CC}_6\text{H}_3\text{CNC}^+$
155	3.8	doublet $\text{C}_6\text{H}_4(\text{CN})_3\text{H}^+$
153	19.8	$(\text{HCCCN})_3^+$; $\text{C}_3\text{HC}_6\text{H}_4\text{CNN}^+$
152	37.2	$\text{CF}_2\text{C}_6\text{H}_4\text{CN}^+$; $\text{CCCN}(\text{HCCCN})_2^+$
151	39.8	$\text{C}_6\text{H}_4\text{CNC}_4\text{H}^+$; $\text{CF}_2\text{C}_6\text{H}_3\text{CN}^+$
149	9.6	doublet $\text{CF}_2\text{C}_6\text{HCN}^+$
147	46.2	$\text{FCC}_6\text{H}_4\text{CNN}^+$
146	3.5	$\text{FCC}_6\text{H}_3\text{CNN}^+$
145	51.3	$\text{C}_6\text{H}_4\text{CF}_3^+$; $\text{FCC}_6\text{H}_2\text{CNN}^+$
144	5.4	$\text{C}_6\text{H}_3\text{CF}_3^+$
143	3.5	$\text{C}_6\text{H}_2\text{CF}_3^+$; $\text{CFC}_6\text{H}_2\text{CNC}^+$
139	3.1	$\text{C}_3\text{HC}_4\text{H}_2(\text{CN})_2^+$
137	17.0	doublet $\text{CF}_2\text{C}_6\text{H}_3\text{C}^+$

Table 34 continued

m/e	Relative Intensity	Ion
135	60.3	doublet $\text{CF}_2\text{C}_6\text{HC}^+$
132	4.5	$\text{CFC}_6\text{H}_3\text{CN}^+$
131	37.2	$\text{CFC}_6\text{H}_2\text{CN}^+$
126	4.5	$\text{C}_6\text{H}_4\text{CF}_2^+$; $\text{CF}_2\text{C}_4\text{H}_2\text{CN}^+$
125	8.0	$\text{C}_6\text{H}_3\text{CF}_2^+$; $\text{CF}_2\text{C}_4\text{HCN}^+$
124	3.7	doublet $\text{C}_6\text{H}_2\text{CF}_2^+$; $\text{CF}_2\text{C}_4\text{CN}^+$
123	8.0	C_6HCF_2^+
122	4.7	$\text{CFC}_4\text{H}_3\text{CNN}^+$
121	57.7	$\text{CFC}_4\text{H}_2\text{CNN}^+$; $\text{C}_6\text{H}_4\text{FCN}^+$
119	5.8	$\text{C}_4\text{H}_2\text{CF}_3^+$; $\text{CFC}_4\text{H}_2\text{CNC}^+$
118	5.8	C_4HCF_3^+ ; $\text{CFC}_4\text{HCNC}^+$
116	16.7	$(\text{CH})_2\text{C}(\text{CN})_3^+$; $\text{C}_6\text{H}_4\text{CN}_2^+$
113	3.0	$\text{C}_6\text{H}_3\text{CNC}$
112	3.2	$\text{C}_6\text{H}_2\text{CNC}^+$
111	14.1	C_6HCNC^+
110	6.0	C_6CNC^+
109	15.4	doublet $\text{CFC}_4\text{H}_3\text{CN}^+$
107	4.1	$\text{C}_6\text{H}_4\text{CF}^+$; $(\text{HC})_2\text{CCF}_3^+$; $\text{CFC}_4\text{H}_2\text{CN}^+$
105	5.8	doublet $\text{C}_6\text{H}_2\text{CF}^+$; CFC_4CN^+
103	19.2	$\text{HCC}(\text{CN})_3^+$
102	10.5	$\text{C}_6\text{H}_4\text{CN}^+$
101	38.2	$\text{C}_6\text{H}_3\text{CN}^+$; $\text{C}_4\text{H}_3\text{CF}_2^+$

Table 34 continued

m/e	Relative Intensity	Ion
100	3.8	$C_4H_2CF_2^+$; $C_6H_2CN^+$
99	4.3	doublet $C_4HCF_2^+$; CC_4HCNC^+
98	4.3	$C_4CF_2^+$
97	22.2	
96	8.3	
95	22.8	doublet $C_6H_4F^+$; $(CH)_2CF_3^+$
94	4.3	$HCCCF_3^+$
93	5.8	$C_6H_2F^+$
91	4.2	C_6F^+ ; $HCC(CN)_2N^+$
87	53.8	$HC_4F_2^+$
85	19.2	C_6HC^+
84	6.1	C_7^+
83	15.4	$C_5H_4F^+$
82	10.5	$C_4H_3CF^+$; $HCCF_3^+$
81	21.5	$C_4H_2CF^+$; CCF_3^+
79	5.8	
77	3.8	$C_6H_5^+$; $C_4H_3CN^+$; $HCCNCNC^+$
76	7.1	$C_6H_4^+$; $C_4H_2CN^+$
75	14.7	$C_6H_3^+$
74	3.1	$C_6H_2^+$
71	13.8	$C_4H_4F^+$
70	12.8	$C_4H_3F^+$
69	46.2	CF_3^+

Table 34 continued

m/e	Relative Intensity	Ion
68	6.0	HC_4F^+
67	17.6	C_4F^+
57	76.8	$\text{H}_2\text{C}_2\text{CF}^+$
56	14.4	HCCCF^+
55	24.4	CCCF^+
54	4.3	HCNCNH^+
53	4.2	HCNCN^+
51	8.0	C_4H_3^+ ; HCCCN^+
50	8.0	C_4H_2^+ ; CF_2^+
44	22.1	CO_2^+ ; HCCF^+
43	12.8	CCF^+
42	11.2	$\text{C}_2\text{H}_3\text{NH}^+$
41	9.6	$\text{C}_2\text{H}_2\text{NH}^+$
39	7.7	C_3H_3^+
38	3.4	C_3H_2^+ ; CCN^+
36	5.1	C_3^+
31	5.0	CF^+
29	10.9	H_3CCH_2^+
28	5.8	N_2^+ ; H_2CCH_2^+
27	10.3	H_2CCH^+ ; HCN^+
20	10.3	HF^+

gases were found, so the mixture was allowed to warm slowly and the volatile products to pass through a sodium fluoride pellet trap at 50° and several cold traps. The only trap containing any material was the liquid nitrogen trap which had the unreacted carbonyl fluoride. Fourteen percent (14%) had been consumed.

Left in the reaction vessel was a yellow solid. The vessel was opened, dry chloroform was added, and the reactor contents were emptied into a beaker and stirred for several minutes. The solution was filtered and a buff colored solid collected on the filter which proved to be 2,4,6-tri-p-nitrophenyl-s-triazine. (An authentic sample was made by treating p-nitrobenzotrile, 1.37 mmol, with anhydrous hydrogen fluoride (39.1 mmol) for five days). The filtrate was evaporated to recover the solids which proved to be unreacted p-nitrobenzotrile and p-nitrobenzamide (confirmed by mass spectrum and infrared spectrum which were identical to Sadtler's²⁹ #6252). p-Nitrobenzamide probably came from hydrolysis of p-nitro- α,α -difluorobenzylcarbonyl fluoride, $O_2NPhCF_2C(H)C(O)F$. The infrared spectrum of the latter compound corresponds to that of the solid before exposure to the solvent and moist air. p-Nitro- α,α -difluorobenzyl isocyanate was identified only in the mass spectrum.

In another experiment, 0.95 mmol of sodium fluoride was added. At the end of 7 days the reactor was opened and found to contain the same products as above. Consumption of carbonyl fluoride was 18.7%. The last reaction of this series was with sodium fluoride as a catalyst and with the reaction heated to 65° C for 4.5 days. The mixture formed

a liquid melt at this temperature while the previous mixtures were solid phase. The products were identified to be the above products except for the -45° trap which contained a very slightly volatile liquid. A smear of this liquid between salt plates gave an infrared spectrum suggesting an anhydrous hydrogen fluoride-nitrile salt. Carbonyl fluoride consumption was 16.7% but there was no evidence of any *p*-nitro- α,α,α -trifluorotoluene.

Physical Properties of *p*-Nitro- α,α -difluorobenzyl Isocyanate.

Infrared Spectrum. The infrared spectrum was recorded from a Nujol mull and was that of *p*-nitro- α,α -difluorobenzylcarbonyl fluoride contaminated by 2,4,6-tri-*p*-nitrophenyl-*s*-triazine. The spectrum is reproduced in Figure 23 and the intensity assignments are listed in Table 35.

Mass Spectrum. Only those mass to charge ratios over 3% relative intensity are listed in Table 36 unless they were of some special significance.

Physical Properties of 2,4,6-Tri-*p*-nitrophenyl-*s*-triazine.

Infrared Spectrum. The infrared spectrum, recorded from a Nujol mull, is reproduced in Figure 24 and the assignments are listed in Table 37.

Melting Point. The melting point was found to be greater than 360° C as reported in literature.⁵²

Table 35

Infrared Spectrum of *p*-Nitro- α,α -difluorobenzylcarbonyl Fluoride

Taken as a Nujol Mull

cm ⁻¹	Intensity*	Assignment
3322	w.	NH stretch
2222	w.	CN stretch
1806	v.s.	CO stretch
1598	m.	triazine
1518	v.s.-b	NO ₂ stretch; triazine
1457	m.s.	nujol
1409	w.	
1342	v.s.-b	NO ₂ sym stretch and CF ₂ sym
1291	s.	CF on C(F)O
1233	s.	
1227		
1177	s.	CF asym stretch
1105	m.	
1075	s.	CF stretch
1010	w.	
946	w.	
875		
857	s.	
842	s.	
826	s.	triazine

Table 35 continued

cm ⁻¹	Intensity*	Assignment
762		
755		
744	s.	CH bend 1-4 substituted benzene
694	w.	
680	m.	
633	m.	nitro-benzene

* w., weak; v.s., very strong; m., medium; v.s.-b, very strong and broad;
m.s., medium strong; s., strong.

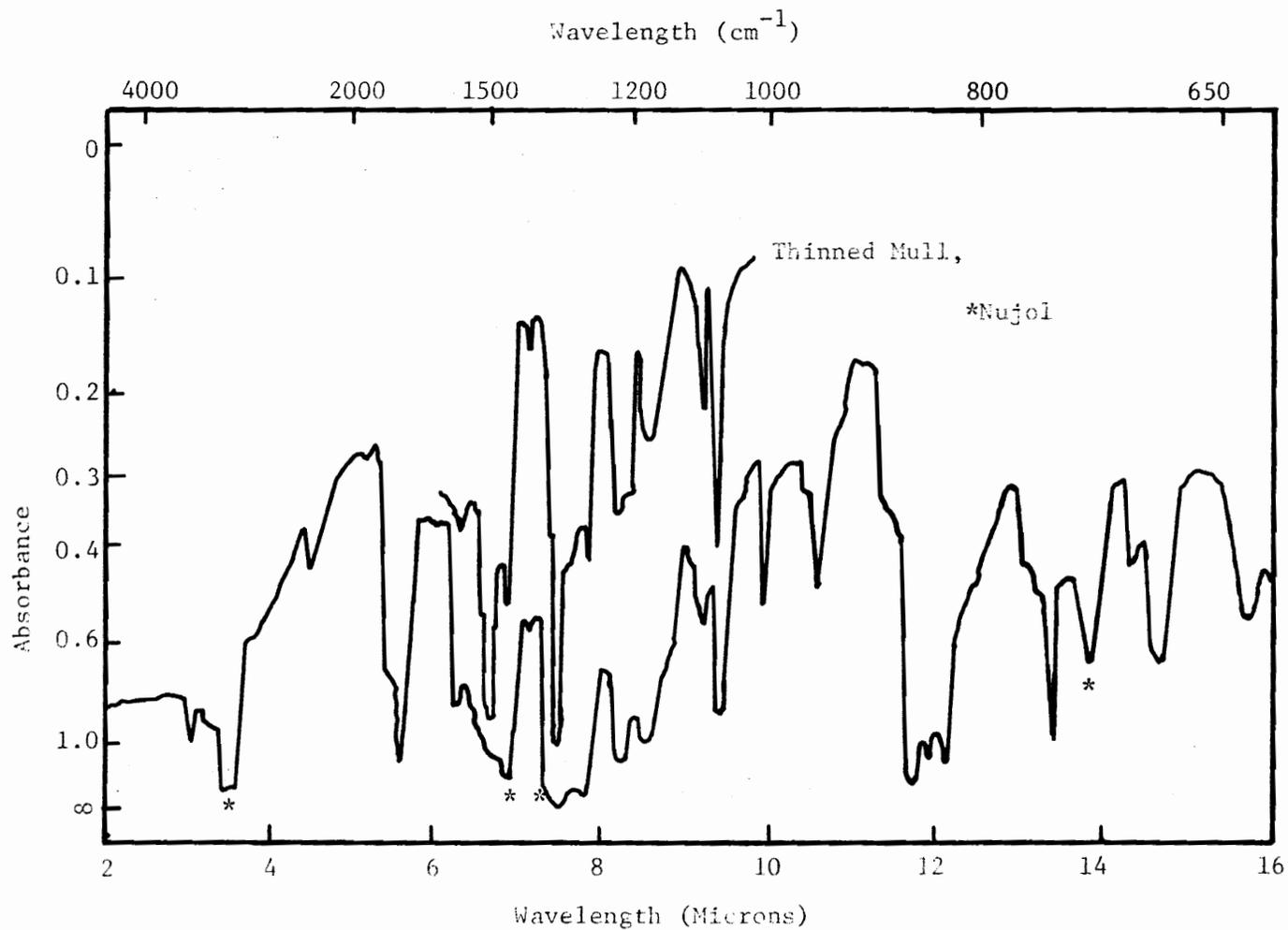


Figure 23. Infrared Spectrum of p-Nitro- α,α -difluorobenzylcarbonyl Fluoride.

Table 36

Mass Spectrum of *p*-Nitro- α,α -difluorobenzyl Isocyanate

70 ev

Intensity Relative to $C_6H_4^+$

m/e	Relative Intensity	Ion
215	4.0	$C^{13}H_4C_2N_2O_3^+$ (Cal. 4.0)
214	49.3	$O_2NC_6H_4CF_2NCO^+$ (parent)
198	2.0	$ONC_6H_4CF_2NCO^+$
195	4.4	$O_2NC_6H_4CFNCO^+$
184	8.9	$OC_6H_4CF_2NCO^+$
172	24.4	$O_2NC_6H_4CF_2^+$
169	7.8	$C_6H_4CF_2NHCO^+$
168	26.3	$C_6H_4CF_2NCO^+$
156	6.7	$C_5H_4CF_2NCO^+$
150	3.2	$C_6H_4CFNHCO^+$
149	20.9	$C_6H_4CFNCO^+$; $O_2NC_6H_4CNH^+$
148	98.7	$O_2NC_6H_4CN^+$
145	3.0	C_6CFNCO^+ ; $O_2NCCCHCCF_2^+$
142	3.1	$C_4H_2CF_2NCO^+$
141	3.3	$C_4HCF_2NCO^+$; $OC_6H_3CF_2^+$
140	8.9	$C_4CF_2NCO^+$; $OC_6H_2CF_2^+$
137	3.9	$C_5H_4CFNCO^+$
132	8.2	$ONC_6H_4CN^+$; $O_2NC_6H_2C^+$
128	7.6	$C_6H_2CNCO^+$
126	20.6	$C_6H_4CF_2^+$

Table 36 continued

m/e	Relative Intensity	Ion
125	88.6	$C_6H_3CF_2^+$; $C_4H_4CFNCO^+$
123	6.8	$C_4H_2CFNCO^+$
120	13.3	$C_6H_2NO_2^+$
119	4.4	
118	47.2	$OC_6H_4CN^+$; $C_5H_4CNCO^+$
114	70.8	$C_5H_4CF_2^+$
113	45.6	$C_5H_3CF_2^+$
107	3.8	$C_6H_4CF^+$
105	5.0	$C_6H_2CF^+$
104	4.4	$C_4H_2CNCO^+$
103	53.9	$C_6H_4CNH^+$
102	98.7	$C_6H_4CN^+$
101	12.7	$C_6H_3CN^+$
100	17.1	$C_4H_2CF_2^+$
99	20.2	$C_4HCF_2^+$
98	3.1	$C_4CF_2^+$
95	10.8	$C_5H_4CF^+$
94	5.1	$C_5H_3CF^+$
92	20.2	CF_2NCO^+ ; $OC_6H_4^+$
90	98.8	$C_5H_4CN^+$
89	7.0	$C_5H_3CN^+$
88	12.3	$C_6H_4C^+$; $C_3H_2CF_2^+$
87	5.8	$C_6H_3C^+$

Table 36 continued

m/e	Relative Intensity	Ion
86	5.4	$C_6H_2C^+$
85	51.6	SiF_3
83	6.1	$C_4H_4CF^+$
77	13.6	$C_4H_3CN^+$
76	100.0	$C_6H_4^+$
75	98.8	$C_6H_3^+$
74	19.3	$C_6H_2^+$
73	21.5	C_6H^+ ; $CFNCO^+$
72	4.9	C_6^+
69	10.1	$C_3H_2CF^+$
65	5.2	$C_4H_3N^+$
64	53.2	$C_5H_4^+$; $C_3H_2CN^+$
63	73.4	$C_5H_3^+$
62	43.1	$C_5H_2^+$
61	20.2	C_5H^+
60	4.4	C_5^+
57	3.4	$C_2H_2CF^+$
53	4.4	$HCCCO^+$
52	56.9	$C_4H_4^+$
51	98.8	$C_4H_3^+$
50	98.4	CF_2^+ ; $C_4H_2^+$
49	37.9	C_4H^+
48	5.3	C_4^+

Table 36 continued

m/e	Relative Intensity	Ion
47	43.1	CFO ⁺
46	17.1	NO ₂ ⁺
44	20.2	CO ₂ ⁺
41	3.3	CHCO ⁺
40	5.1	doublet; H ₂ F ₂ ⁺ ; CCO ⁺
39	70.3	C ₃ H ₃ ⁺ ; HF ₂ ⁺
38	70.0	C ₃ H ₂ ⁺
37	70.6	C ₃ H ⁺
36	7.6	C ₃ ⁺
32	44.3	O ₂ ⁺
31	10.1	CF ⁺
30	98.8	NO ⁺
29	5.1	COH ⁺
28	98.8	N ₂ ⁺ ; CO ⁺
27	69.0	C ₂ H ₃ ⁺
26	17.6	(CH) ₂ ⁺
25	3.4	C ₂ H ⁺
20	73.2	HF ⁺
19	3.0	F ⁺
18	98.0	H ₂ O ⁺
17	25.9	OH ⁺
16	6.3	O ⁺
14	4.4	N ⁺

Table 37

Infrared Spectrum of 2,4,6-Tri-p-nitrophenyl-s-triazine

Taken as a Nujol mull

cm ⁻¹	Intensity*	Assignment
1531	s.	triazine-NO ₂ stretch
1416	m.	triazine
1344	s.	NO ₂ sym stretch
1107	m.	
1011	m.	
881	m.	
866	w.	CN aromatic
831	s.	triazine
745	m.	CH bend, 1-4 substituted benzene
687	m.	

* s., strong; m., medium; w., weak.

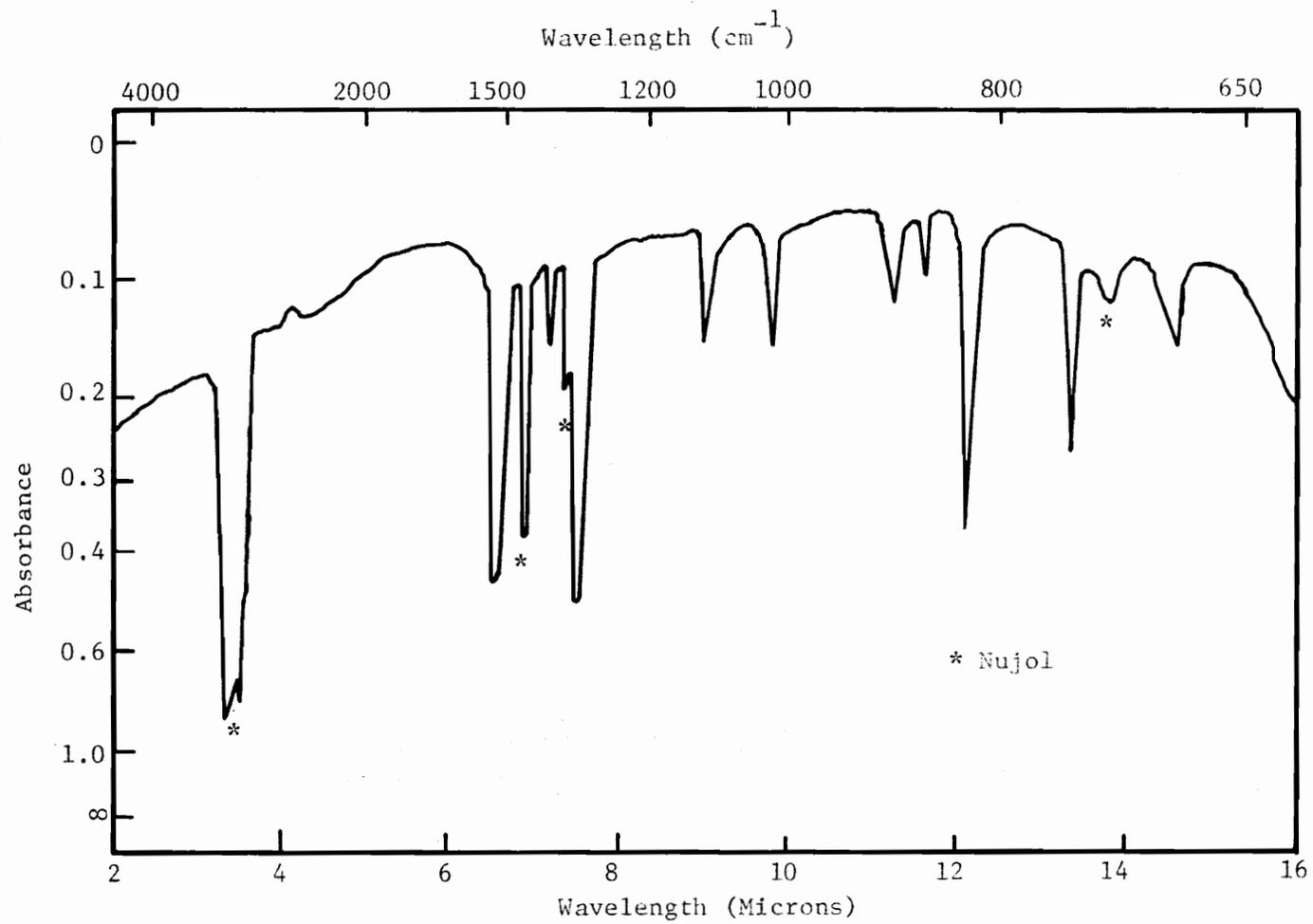


Figure 24. Infrared Spectrum of 2,4,6-Tri-p-nitrophenyl-s-triazine.

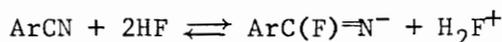
CHN Analysis

Element	Percent Calculated for C ₂₁ H ₁₂ N ₆ O ₆	Percent Found
C	56.76	51.26
H	2.72	287
N	18.90	18.01
O	21.60	

DISCUSSION

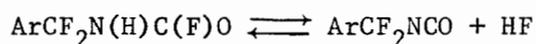
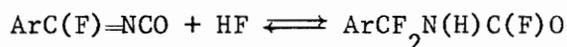
The formation of aryl- α,α -difluoromethyl isocyanates and the aryltrifluoromethanes did not proceed in the absence of anhydrous hydrogen fluoride. Presumably, the isocyanate formation would proceed with any anhydrous acid that was not fluorinated by carbonyl fluoride or did not oxidize the organic reactant.

The mechanism for the formation of the aryl- α,α -difluoromethyl isocyanate probably goes through an anion intermediate by the fluoride ion attacking the nitrile carbon:



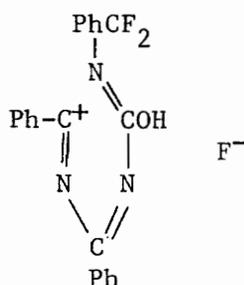
Suppression of the fluoride ion activity by addition of boron trifluoride did not produce any evidence of the isocyanate or trifluoromethyl compounds but instead lead to apparently 100% trimerization of the nitrile to 2,4,6-triaryl-s-triazine. On the other hand, increasing the fluoride ion activity did increase the yield of isocyanate. The anion then presumably reacted with carbonyl fluoride to produce the intermediate imine complex which may have rearranged directly to yield the isocyanate or could have added a mole of hydrogen fluoride to produce the carbamyl

fluoride followed by the elimination of a mole of hydrogen fluoride to give the isocyanate. $\text{ArC(F)=N}^- + \text{COF}_2 \rightleftharpoons \text{ArC(F)=NC(F)O} + \text{F}^-$



The *p*-nitrobenzotrile and carbonyl fluoride reaction did yield the carbamyl fluoride rather than the isocyanate, but there was no way of telling whether it was by the reaction mechanism outlined above or by addition of hydrogen fluoride to the isocyanate.

The mechanism proposed for the formation of aryltrifluoromethanes depends upon the formation of the isocyanates. Once the isocyanate is formed a molecule of nitrile would attack the carbon of the isocyanate. The carbon may be made more positive by protonation of the oxygen, $\text{PhCF}_2\text{N=C(OH)N=C(+)Ph}$. The positive carbon next to the aromatic ring may now be attacked by a second nitrile molecule:



Ring closure could follow by the electrons of the difluorocarbon-nitrogen bond shifting to the carbonium carbon with the positively charged molecule picking up a fluoride ion from its HF solvent sheaf to produce the α,α,α -trifluorotoluene. The aromatic compounds which have strong electron withdrawing groups, both inductive and resonance, do not produce the trifluoromethyl compounds in any significant yield.

This is probably due to the nitrile being too weak a base to attack the isocyanate and form the intermediates. On the other hand, the weak inductive donating group did not enhance formation of the trifluoromethyl compounds compared to benzonitrile.

The ortho-tolunitrile reaction does produce the isocyanate but in only the smallest trace quantities. It appears that the steric hindrance prevents the formation of the isocyanates and any additional polymerization.

The effect of hydrogen fluoride was found to be very critical for if none was present, (see Table 11 runs #4 and 13) no reaction occurred. However, if too much was present the yields of the trifluoromethyl compounds were reduced as well as the isocyanate (runs #15 vs #16; and on Table 30 the last three reactions of the para-tolunitrile). The molar ratio of carbonyl fluoride and nitrile was important for as the carbonyl fluoride decreased so did the yield (run #17 vs #20). The presence of alkali metal fluorides also improved the yield of both the isocyanate and the aryltrifluoromethanes. Possibly the aromatic resonance was enhancing the basicity of the nitrile group causing greater complexation and interaction with hydrogen fluoride. The alkali metal fluoride lowered the acidity of the acid and increased the chance of carbonyl fluoride attacking the nitrile group.

The higher temperatures (50°) increased the yield of the aryltrifluoromethanes by simply increasing their rates of reaction. The isocyanate formation was an equilibrium reaction while the aryltrifluoromethane was not. Thus, increasing the time increased the yield of aryltrifluoromethanes (#3b vs #7) while having no effect

on the aryl- α,α -difluoromethyl isocyanates.

The aryl- α,α -difluoromethyl isocyanates are clear colorless liquids at room temperature (this was not determined for the p-nitro- α,α -difluorobenzyl isocyanate) and are stable to hydrolysis in dry glassware. They are of low vapor pressure but do transfer slowly from trap to trap on the vacuum line. They are slightly more volatile than the parent nitrile.

No trend was observed in the F-19 spectra of the gem difluorides or in the asymmetric stretch of isocyanate in the infrared spectra as listed below:

RCF_2NCO R	F-19 NMR Ref. ext. CCO_3F	NCO Asym. Stretch cm^{-1}
methyl	+56.7 ppm	2283
ethyl	+63.9 ppm	2257
fluoro ²³		2283
trifluoromethyl ⁷		2273
phenyl	+57.8 ppm	2260
<u>p</u> -tolyl	+54.5 ppm	2258
<u>m</u> -tolyl	+57.0 ppm	2257
<u>p</u> -trifluoro- methylphenyl	+56.7 ppm	2273

The mass spectra fragmentation patterns of the aryl- α,α -difluoromethyl isocyanates were identical to the α,α -difluoroalkyl isocyanates except for the additional pattern of the aromatic ring and its substituent. The parent ion intensity of the aromatics was also greater, as expected, than the alkyl examples. The aryltrifluoromethanes also

gave a fragmentation of loss of fluorines from the parent plus the loss of the trifluoromethyl group. The 2-hydroxy-4,6-diaryl-s-triazines, $\text{Ar}_2(\text{CN})_3\text{OH}$, and 2,4,6-triaryl-s-triazines, $(\text{ArCN})_3$, showed intense parent ions. Their fragmentation pattern revealed the loss of the group (if any) on the aryl ring and one of the aryl groups from the parent triazine as well as the triazine ring opening and its loss of the arylformonitrile(s) and the expected fragmentation on the aryl part.

SUMMARY

Carbonyl fluoride will add to arylformonitriles in the presence of anhydrous hydrogen fluoride and alkali metal fluorides to produce the corresponding aryl- α,α -difluoromethyl isocyanate. The reaction proceeded more rapidly in the presence of alkali metal fluoride and at elevated temperatures. Increasing yields were achieved by having carbonyl fluoride in excess of the nitrile and the optimum amount of anhydrous hydrogen fluoride. The aryl- α,α -difluoromethyl isocyanates reacted with two additional moles of arylformonitrile to yield aryltrifluoromethanes and 2-hydroxy-4,6-diaryl-s-triazines. Alkali metal fluorides also enhanced this reaction and suppressed the formation 2,4,6-triaryl-s-triazine. With an electron withdrawing substituent on the aromatic ring, the reactions did not yield any significant quantity of the aryltrifluoromethanes but stopped at the aryl- α,α -difluoromethyl isocyanate stage. In the case of o-tolunitrile, steric hindrance apparently prevented the formation of the isocyanate as well as of the trimer.

CHAPTER III

PREPARATION AND REACTIONS OF PENTAFLUOROSULFANYL ISOCYANATE

INTRODUCTION

Pentafluorosulfanyl isocyanate, SF_5NCO , was first synthesized by Tullock *et al.*^{4,53} by the reaction of benzoic acid, sodium fluoride, and pentafluorosulfanyltrifluoromethylamine, $\text{SF}_5\text{N}(\text{H})\text{CF}_3$. Later, Rhyne and Clifford³ succeeded in preparing the pentafluorosulfanyl isocyanate by the simple addition of carbonyl fluoride to thiazyl trifluoride in anhydrous hydrogen fluoride. As described earlier in this dissertation, the addition of carbonyl fluoride to the cyanide bond was found also to be catalyzed by anhydrous hydrogen chloride. Hence, the purpose of this work was to investigate further the conditions of the addition, to investigate the possibility of some other anhydrous acids also catalyzing the formation of the pentafluorosulfanyl isocyanate, and to investigate some of its chemical properties. The properties of pentafluorosulfanyl isocyanate may be of industrial interest because of the possibilities of urethane polymers and the useful chemistry of substituted ureas.

During the preparation of pentafluorosulfanylamine, SF_5NH_2 , Clifford and Duncan⁵⁴ frequently noted a white insoluble solid in the bottom of the reaction vessels whose structure they could not determine but for which the empirical formula $\text{S}_2\text{F}_{12}\text{N}_2\text{H}_{2-4}\text{CO}$ was established by elemental analysis and mass spectrum and for which an infrared spectrum

was obtained.⁵⁵ Various attempts to produce this material have been unsuccessful, for both the reactants and the conditions necessary for the formation were elusive. The identity of this "Compound X" has been established.

EXPERIMENTAL

Equipment.

The vacuum line and related equipment were described in Chapter I.

Reagents.

Thiazyl Trifluoride. N-fluoroformyliminosulfur difluoride⁵⁶, FC(O)N=SF_2 , was prepared by the method described elsewhere⁵⁷ except that the reaction mixture was allowed to stand at room temperature for five hours. The yield was in excess of 75% and was much less impure than in the reported method. Thiazyl trifluoride was prepared by silver difluoride (Harshaw) fluorination of N-fluoroformyliminosulfur difluoride.¹ The by-product of the fluorination, carbonyl fluoride, was also used in this reaction.

Anhydrous Hydrogen Chloride. Anhydrous hydrogen chloride (Matheson Company) was used as received without further drying or purification.

The Synthesis of Pentafluorosulfanyl Isocyanate.

The Synthesis Catalyzed by Anhydrous Hydrogen Fluoride. Thiazyl trifluoride (5.02 mmol) was condensed into a Kel-F reactor followed by approximately 5 ml of anhydrous hydrogen fluoride. After reacting for

two days the hydrogen fluoride was removed by sodium fluoride pellets at 50° C leaving the pentafluorosulfanylamine.⁵⁴ The amine was condensed back into the reactor and 8.03 mmol of carbonyl fluoride and 4.46 mmol of NSF₃ added. Two days later the Kel-F reactor was opened after first chilling it with liquid nitrogen. When no non-condensable gases were found, the cylinder was allowed to warm slowly and its contents to pass through sodium fluoride pellets at 50° C and four other traps. The -45° trap was found to contain a small amount of the unreacted pentafluorosulfanylamine. The -78° trap contained the rest of the amine. The -131° trap contained some NSF₃ and most of the pentafluorosulfanyl isocyanate. The -196° trap contained some CO₂, a trace of SF₅NCO, and no carbonyl fluoride. With excess hydrogen fluoride present the yield was reduced and unreacted carbonyl fluoride was recovered.

The Synthesis Catalyzed by Anhydrous Hydrogen Chloride. Thiazyl trifluoride (5.11 mmol) was condensed into a Monel cylinder followed by 5.34 mmol of carbonyl fluoride and 10.03 mmol of anhydrous hydrogen chloride. The cylinder was allowed to warm to room temperature and remain for 96 hours. The Monel cylinder was then cooled with liquid nitrogen and found to contain no non-condensable gases. The Dewar flask around the cylinder was emptied of liquid nitrogen and replaced, and the contents of the slowly warming cylinder were passed through a trap of sodium fluoride pellets at 50° C and four other traps. The material in the -78° trap was silicon tetrafluoride and pentafluorosulfanylamine. The -112° trap (n-butyl bromide slush) contained SF₅NCO, SiF₄, NSF₃,

and COClF .¹⁶ The -131° trap contained additional SF_5NCO , NSF_3 , and COClF . The final trap contained unreacted carbonyl fluoride and some unabsorbed hydrogen chloride. The total amount of COClF formed was less than 3%.

The Monel cylinder was opened in the drybox and found to contain white needle-like crystals. These crystals dissolved in water to give a highly acid solution, a positive test for fluoride ion, chloride ion, and (upon evaporation of the solution) an infrared spectrum identical with that of sulfonamide. An infrared spectrum of the Nujol mull of this material (Figure 25, Table 38) strongly suggests that it was pentafluorosulfanylcarbonyl chloride, $\text{SF}_5\text{N(H)C(O)Cl}$.

The only data published on the infrared spectrum of the SF_5NCO was the isocyanate asymmetric stretch at 2276 cm^{-1} . Figure 26 shows the additional two peaks of the very simple spectrum (Table 39).

Reactions of Pentafluorosulfanyl Isocyanate with Anhydrous Hydrogen Fluoride.

Pentafluorosulfanyl isocyanate (1.52 mmol) was condensed into a Monel cylinder along with 0.8 ml of anhydrous hydrogen fluoride (40 mmol). Three days later the contents of the cylinder were frozen and found to have no non-condensable gases. From the slowly warming cylinder, the volatiles passed through a sodium fluoride trap at 50° and four other cold traps. The -196° trap contained a large quantity of COF_2 and minor quantities of SOF_2 , CO_2 , and SF_5NCO . The -131° trap contained small amounts of NSF_3 , SOF_2 , and SF_5NCO . The -78° trap contained a large amount of pentafluorosulfanylamine. The -45° trap did not contain

Table 38

Infrared Spectrum Pentafluorosulfanylcarbonyl Chloride

Taken as a Nujol Mull

cm ⁻¹	Intensity*	Assignment
3296	s.	NH stretch
1700	s.	CO stretch
1508	m.	NH bend
1208	m.	
1096	w.b.	CN stretch
917	v.s.	SF ₆ stretch
875	v.s.-b.	SF ₅ stretch
823	v.s.	SN stretch ⁵⁸
738	w.	NH wagging
700	m.	SF stretch

* w., weak; m., medium; v.s., very strong; s., strong; b., broad.

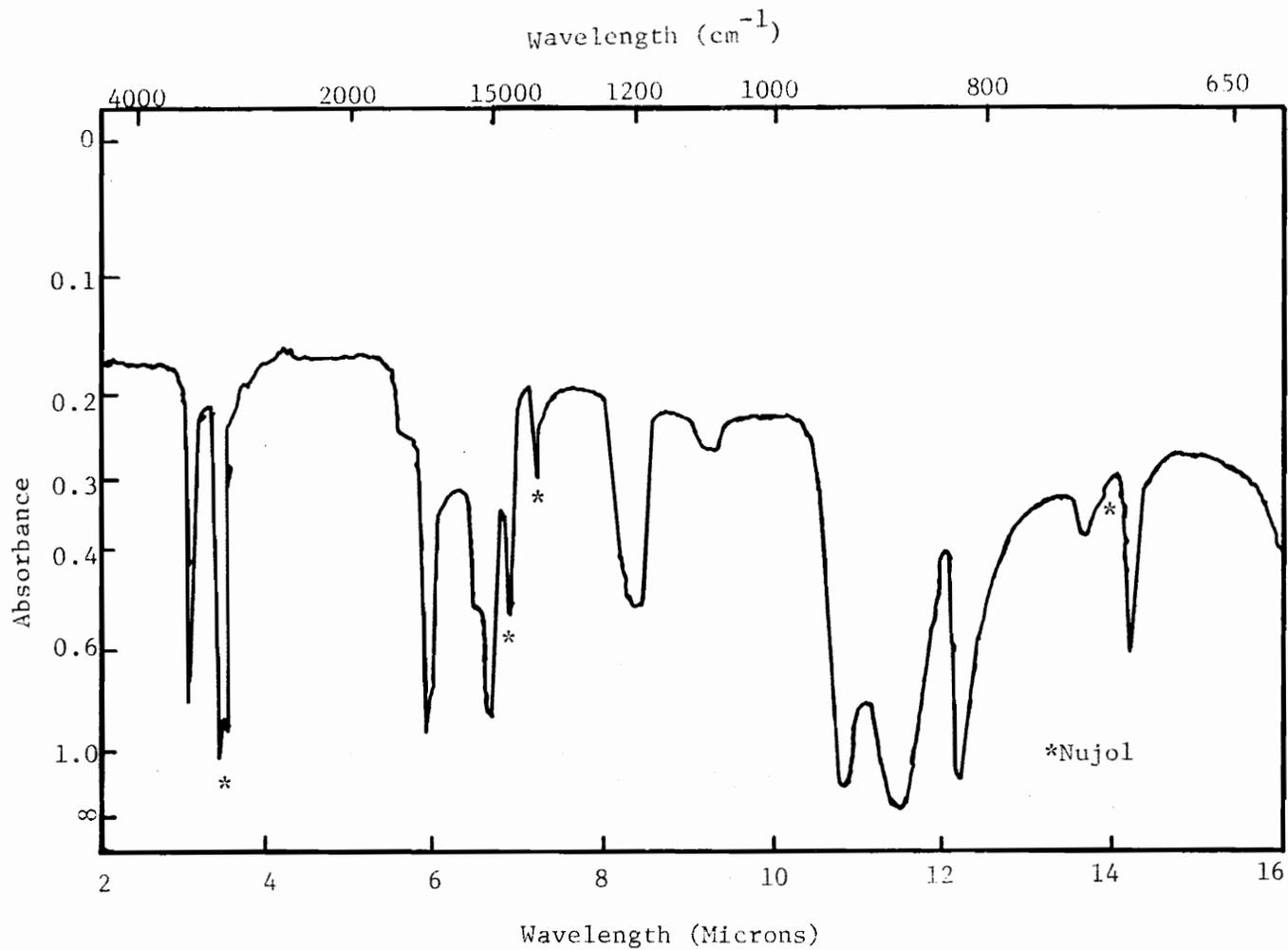


Figure 25. Infrared Spectrum of Pentafluorosulfanylcarbonyl Chloride

Table 39

Infrared Spectrum of Pentafluorosulfanyl Isocyanate

Taken at 4 Torr

10 cm cell

cm^{-1}	Intensity*	Assignment
2272	s.	NCO asym stretch
917	s.	SF ₅ stretch
875	s.-b.	SF ₅ stretch

*s., strong; b., broad.

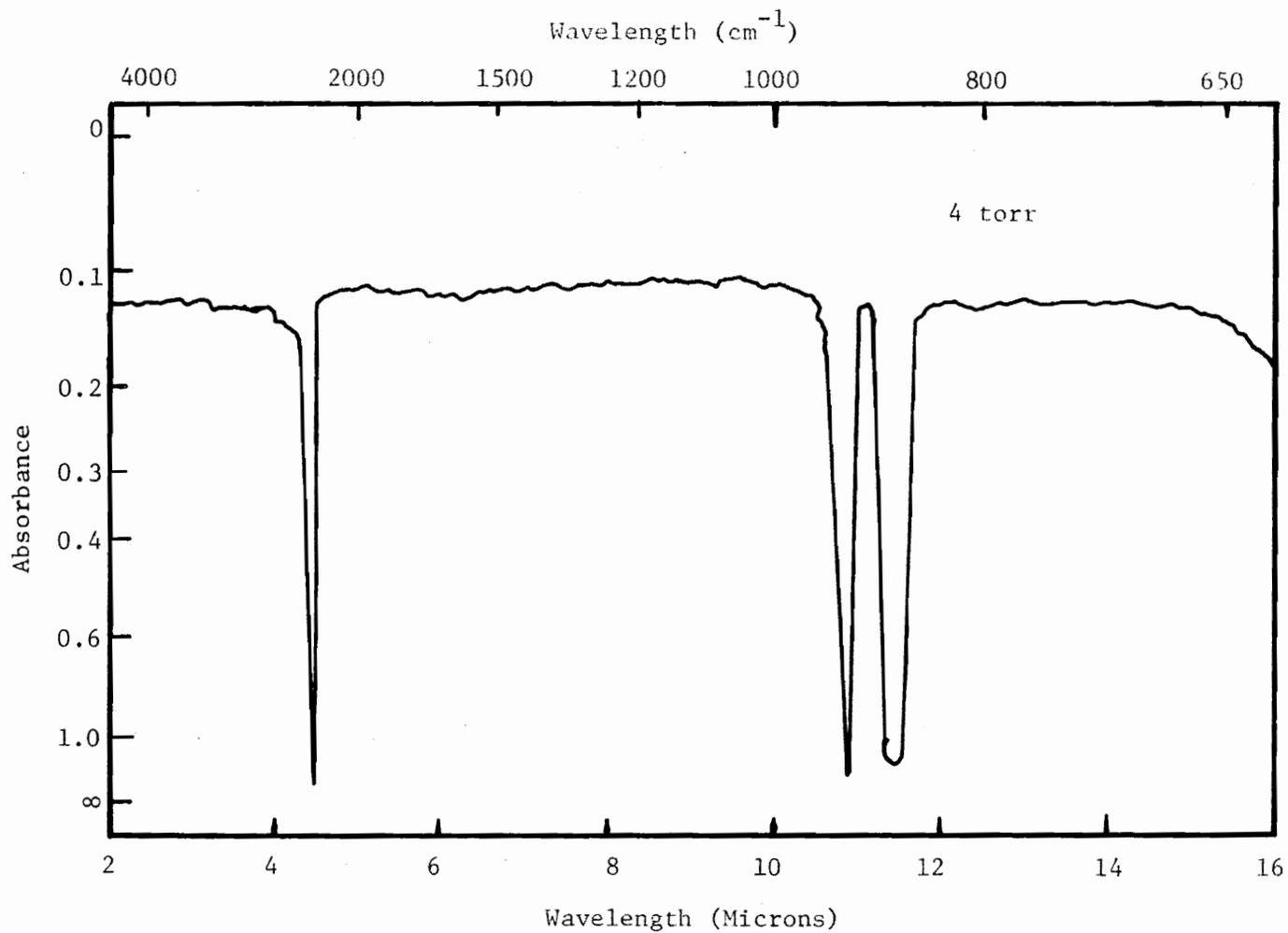


Figure 26. Infrared Spectrum of Pentafluorosulfanyl Isocyanate.

any material nor were there any solids in the cylinder. The formation of the pentafluorosulfanyl isocyanate appears, therefore, to be a reversible equilibrium.

The Synthesis of N,N'-Bis(pentafluorosulfanyl)urea.

Thiazyl trifluoride (6.89 mmol) was condensed into a Kel-F test tube reactor fitted for vacuum work⁹ followed by carbonyl fluoride (4.65 mmol). The reactor was transferred to the anhydrous hydrogen fluoride line and 2 ml (0.1 mol) of that acid were added. Sixty days later the reactor was opened to the vacuum line and found to contain SF_5NCO , SF_5NH_2 , NSF_3 , and carbonyl fluoride and its impurities. No solids or other reaction products were observed. The materials were condensed back into the reaction flask (no additional HF was added) and as the flask warmed, solids were observed to form. After several days no liquids were left in the flask, only solids. The vessel was opened to vacuum and the only volatile materials found were the impurities of carbonyl fluoride and unreacted thiazyl trifluoride or pentafluorosulfanylamine. The Kel-F test tube was opened in the drybox and a large quantity of white needle crystals recovered which were identified as N,N'-bis(pentafluorosulfanyl)-urea.

The more satisfactory method of synthesis was to prepare pentafluorosulfanyl isocyanate (9.48 mmol) and then add the pentafluorosulfanylamine (10.01 mmol). The major advantage of this method was the control of the hydrogen fluoride content. In the first method it was difficult to keep the amount of amine and thiazyl trifluoride in the correct ratio, resulting in less than optimum formation of the urea,

while in the second method the appropriate amount of amine was always present.

Physical Properties of SF₅N(H)C(O)N(H)SF₅.

Infrared Spectrum. The results are listed in Table 40 and shown in Figure 27. The spectral assignments are in agreement with those of related compounds.^{18,58,59}

NMR Spectrum. The NMR spectra were run on the JEOL C-60-H at 60 MHz for the proton and 56.446 MHz for the fluorine-19. The N,N'-bis(pentafluorosulfonyl)urea was dissolved in dry diethyl ether until a saturated solution was obtained. The proton resonance spectrum consisted of a broad band with no resolvable structure centered at -8.80 ppm from TMS. The fluorine-19 spectrum displayed two peaks at -151.3 and -150.3 ppm from trifluoroacetic acid. Integration of the fluorine spectrum gave a four to one ratio respectively. The fine structure of the expected AB₄ structure was not observed because of the low solubility of the urea in ether. The fluorine resonance of pentafluorosulfonylurea was in the center of the previously reported ranges.^{60,61,62}

Mass Spectrum. Peaks (Table 41) of less than 3% relative intensity were not listed unless they had some special significance. The parent ion did not appear because of the loss of two molecules of hydrogen fluoride, but otherwise the expected fragmentation pattern was shown. Lowering the temperature and/or the potential to 15 ev did not result in the appearance of the parent ion.

Table 40

Infrared Spectrum of N,N'-Bis(pentafluorosulfonyl)urea

Taken in Nujol Mull

cm ⁻¹	Intensity*	Assignment
4494	v.w.	NH free stretch
3306	m.	NH stretch
2721	v.w.	
2611	v.w.	
1701	m.b.	CO stretch
1538	m.	NH bend
1518	m.	NH bend
1210	w.	
1099	w.	CN stretch
915	s.b.	SF stretching
870	s.b.	SF stretching
818	s.	SN stretching
735	w.	NH wagging
699	m.	SF stretching

* v.w., very weak; m., medium; b., broad; s., strong.

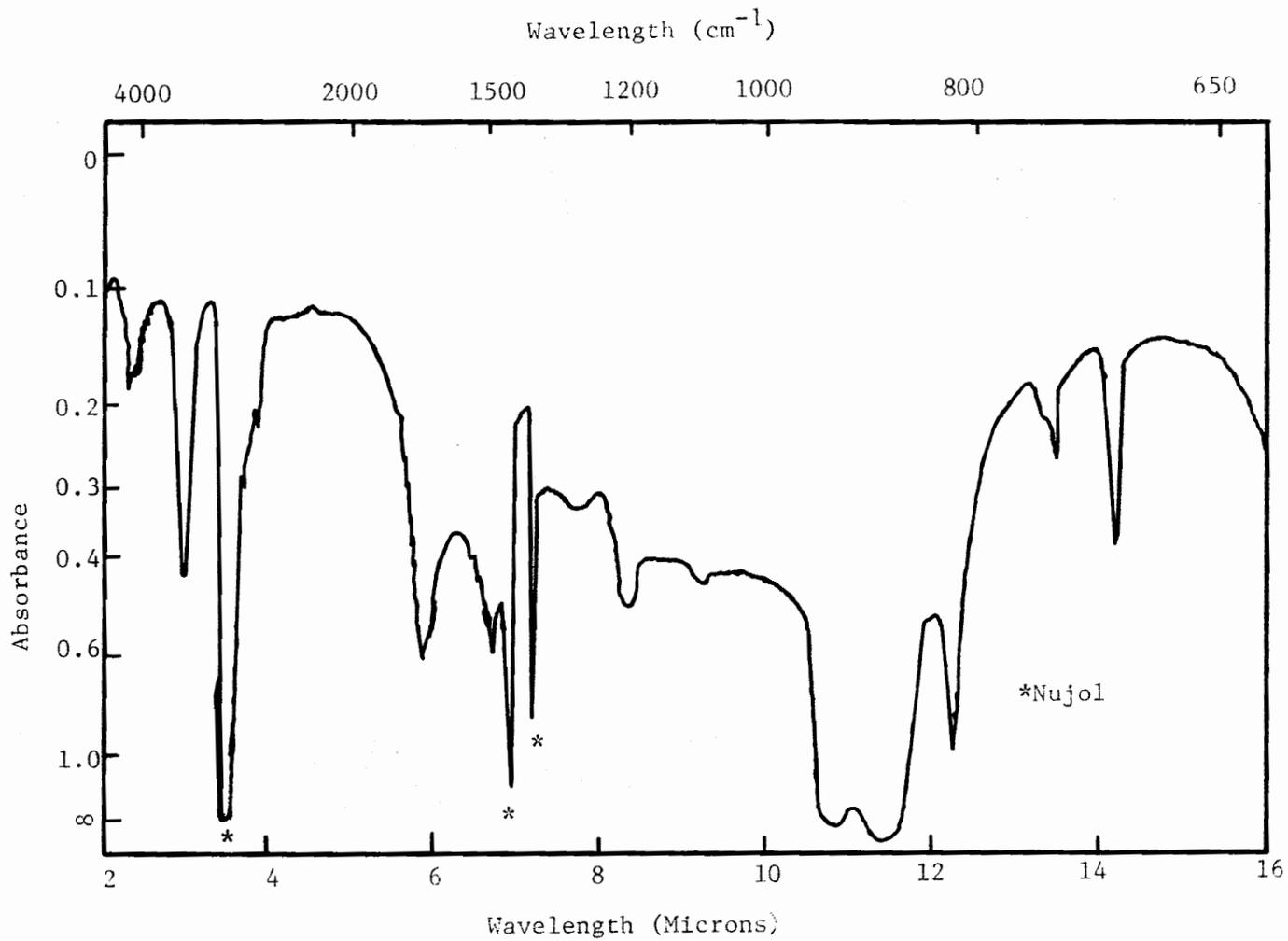


Figure 27. Infrared Spectrum of N,N'-Bis(pentafluorosulfanyl)urea.

Table 41

Mass Spectrum of N,N'-Bis(pentafluorosulfanyl)urea

70 ev

Inlet Temp. 120°

Intensity Relative to SF₅⁺

m/e	Relative Intensity	Ion
274	0.9	S ³⁴ SF ₈ N ₂ CO ⁺ (Cal. 0.9)
272	10.1	(SF ₄ N) ₂ CO ⁺
253	0.9	SF ₃ NC(O)NSF ₄ ⁺
171	1.2	
169	13.3	SF ₅ NCO ⁺
150	33.3	F ₄ SNCO ⁺
149	32.2	F ₄ SN(H)CN ⁺
144	6.4	SF ₅ OH ⁺
129	16.1	
128	6.1	
127	100.0	SF ₅ ⁺
126	21.6	SF ₂ NC(O)N ⁺
124	8.7	SF ₅ NH ₂ ⁺ ; F ₄ SO ₂ ⁺
112	7.0	F ₂ SNCO ⁺
108	10.1	SF ₄ ⁺
105	28.3	F ₃ SNH ₂ ⁺ ; F ₃ SO ⁺ ?
104	20.7	F ₃ SNH ⁺
103	39.1	NSF ₃ ⁺
102	3.2	
91	5.5	

Table 41 continued

m/e	Relative Intensity	Ion
89	64.4	SF_3^+
86	11.5	F_2SNH_2^+
84	16.6	NSF_2^+
83	4.2	
81	13.0	
76	7.7	
70	30.8	SF_2^+
69	3.0	
67	10.1	FSNH_2^+
66	5.5	COF_2^+ ; FSNH^+
65	14.7	NSF^+
64	4.0	
57	7.4	HNC(O)N^+
56	5.3	$\text{F}_2\text{SNCO}^{++}$
55	4.9	
51	9.2	SF^+
48	5.2	SNH_2^+ ; SO^+
47	89.7	CFO^+ ; SNH^+
46	20.7	NS^+
44	12.4	SF_3^{++} ; CO_2^+
43	8.3	HNCO^+
42	7.8	NSF_2^{++} ; NCO^+

Table 41 continued

m/e	Relative Intensity	Ion
41	8.7	
39	3.4	
38	3.3	F_2^+
36	3.4	
32	14.7	O_2^+ , S^+
29	7.8	HCO^+
28	51.7	N_2^+ ; CO^+
27	4.0	
20	37.9	HF^+
18	60.9	H_2O^+
17	16.1	OH^+

Decomposition Point. At 123° C the urea, in open air started to shrink from the sides of the melting point capillary. At 200° it apparently decomposed and disappeared completely from the melting point tube. Possibly hydrogen fluoride was split out producing a volatile product.

Elemental Analysis. The carbon, hydrogen, and nitrogen analysis was done by the Departmental analyst on a Perkin-Elmer 240 Elemental Analyzer. The sample was prepared for fluorine analysis by weighing out 0.1439 g of the substituted urea, hydrolyzing it in 6 N sodium hydroxide, treating the solution with 50 ml of 4 M potassium acetate-acetic acid buffer (pH approximately 5.8) and diluting to 100 ml with distilled water. Aliquots of this dilute solution were treated by the known addition method (Gran's Method).^{21,22} All portions of this solution were carefully collected and precipitated with barium chloride in a method described elsewhere⁶³ for the determination of the sulfate.

Element	Percent Calculated for $S_2F_{10}N_2H_2CO$	Percent Found
C	4.326	3.847
H	0.598	0.646
N	9.056	8.974
F	60.71	60.863
O		5.126
S	20.554	20.544

Solubility. The N,N'-bis(pentafluorosulfanyl)urea was found to be moderately soluble in dry diethyl ether and acetone but when exposed to wet ether or acetone seemed to decompose. It was apparently insoluble on chloroform and non-polar solvents. It was also insoluble in anhydrous hydrogen fluoride and thiazyl trifluoride.

Some Reactions of N,N'-Bis(pentafluorosulfanyl)urea.

With Anhydrous Hydrogen Fluoride. Approximately 0.1 g of N,N'-bis(pentafluorosulfanyl)urea was loaded into a Kel-F reactor and 0.95 ml of anhydrous hydrogen fluoride was condensed onto the solid. Upon warming to room temperature, it was noted that the solid did not dissolve and no visible reaction occurred. After 19 hours there was some solid remaining in the bottom of the test tube reactor and it had enlarged in crystal size. The reactor was cooled with liquid nitrogen but no non-condensable gases were found upon opening it. The contents of the slowly warming vessel passed through a trap of sodium fluoride pellets at 50°, a -45° trap, and a -196° trap. The -196° trap contained pentafluorosulfanyl isocyanate, carbonyl fluoride, and thiazyl trifluoride. Nearly half the urea was converted to the starting materials. Thus, in the presence of anhydrous hydrogen fluoride, the formation of the urea was reversible.

Upon Heating. Hoping to drive off two molecules of hydrogen fluoride, as apparently occurred in the mass spectrometer, 0.1 g of the urea was placed in a Kel-F test tube, evacuated, and heated to 90° in a water bath for four hours. The evolved gases were passed through NaF pellets and trapped at liquid nitrogen temperature. This trap contain-

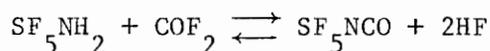
ed, upon investigating by infrared spectroscopy, thiazyl trifluoride, pentafluorosulfanyl isocyanate, carbonyl fluoride, and pentafluoro-sulfanylamine. Approximately one half of the urea was decomposed in this manner. When the reactor was opened, there was some visual evidence of urea sublimation but no other formation or compounds were detected.

With Triethylamine. Approximately 0.5 g of N,N'-bis(pentafluoro-sulfanyl)urea was loaded into a reactor, and 2.80 mmol of triethylamine frozen on top of it. As soon as the triethylamine was liquefied, the urea turned a deep red-brown color which intensified as it warmed. Occasionally bubbles could be seen rising from the crystals of urea. Forty hours later the small quantity of gas above the reaction mixture was identified as a mixture of thiazyl trifluoride and triethylamine. Remaining in the bottom of the vessel was a dark red viscous liquid which the infrared spectrum suggested was triethylammonium fluoride. When dry ether was added to the vessel and shaken vigorously, there was some discoloration of the ether. However, the isolated discolored material proved not to be particularly different from the parent substance. All of the material was soluble in chloroform.

DISCUSSION

Thiazyl trifluoride reacts with carbonyl fluoride in the presence of anhydrous hydrogen fluoride to yield pentafluorosulfanyl isocyanate. Although no kinetic studies have been made on this reaction, the thiazyl

trifluoride probably forms pentafluorosulfanylamine which in the classical organic synthesis with carbonyl fluoride forms the isocyanate. This mechanism is, however, difficult to envision for the anhydrous hydrogen chloride-catalyzed reaction, as it implies two chlorine atoms on a hexavalent sulfur atom. The mechanism may involve the addition of only one mole of hydrogen chloride across the thiazyl triple bond, giving $\text{ClF}_3\text{S}=\text{NH}$ which then reacts with carbonyl fluoride to produce the isocyanate. Another possible mechanism would be the protonation of the carbonyl fluoride to yield a carbonium ion which would attack the nitrogen of the thiazyl trifluoride, rearrange the fluorines to the sulfur, eliminate the proton to form the isocyanate. An acid was necessary for the formation of the isocyanate; however, excess hydrogen fluoride reversed the equilibrium:



The formation of N,N'-bis(pentafluorosulfanyl)urea proceeded with only a minimum of hydrogen fluoride. For optimum yield, great care was taken to have the hydrogen fluoride consumed when pentafluorosulfanylamine and carbonyl fluoride reacted to form the urea. Excess hydrogen fluoride resulted in incomplete reaction. However, once formed, the urea was insoluble in hydrogen fluoride but slowly reverted to the starting compounds.

In the mass spectrometer, the parent minus two hydrogen fluoride molecules was recorded rather than the parent ion. Any attempts to remove the hydrogen fluoride by chemical means met with failure.

SUMMARY

Pentafluorosulfanyl isocyanate was prepared by the addition of carbonyl fluoride to thiazyl trifluoride in the presence of anhydrous acids. Increasing the concentration of anhydrous hydrogen fluoride resulted in decreasing yield of the isocyanate while without an acid no isocyanate was formed. Pentafluorosulfanyl isocyanate in an excess of anhydrous hydrogen fluoride yielded the starting products. Isolated from anhydrous hydrogen chloride-catalyzed reaction was pentafluoro-sulfanylcarbonyl chloride.

N,N'-bis(pentafluorosulfanyl)urea was synthesized from pentafluorosulfanyl isocyanate and pentafluorosulfanyllamine; or from thiazyl trifluoride, anhydrous hydrogen fluoride, and carbonyl fluoride. The reaction was reversible in excess anhydrous hydrogen fluoride or when heated under vacuum to over 90° C. With triethylamine the urea decomposed.

CHAPTER IV

ATTEMPTS TO PREPARE AN INORGANIC DINITRILE

INTRODUCTION

The urethanes and carbamates made from organic diisocyanates with diamines and dialcohols have been found useful in many applications. However, they do not have all mechanical, chemical, or physical properties that are useful. Having shown in Chapter III that pentafluorosulfanyl isocyanate may react with pentafluorosulfanylamine to form N,N'-bis(pentafluorosulfanyl)urea, it seemed logical that if diamino-tetrafluorosulfane, $H_2NSF_4NH_2$, and diisocyanatotetrafluorosulfane, $OCNSF_4NCO$, could be made they would react to form a completely inorganic polyurethane. Such a polyurethane would have an entirely different set of mechanical and chemical properties from the organic analogs. No method has been reported for making the diamine or diisocyanate.

Pentafluorosulfanylamine has been made by reacting thiazyl trifluoride with anhydrous hydrogen fluoride⁵⁴ and pentafluorosulfanyl isocyanate has been made from thiazyl trifluoride and carbonyl fluoride in the presence of anhydrous hydrogen fluoride.³ If a compound such as $N\equiv SF_2N-R$ could be made in which the R-N bond could be hydrofluorinolized, then the diamine could be made with anhydrous hydrogen fluoride and the diisocyanate could be made in the same manner as the isocyanate. Glemser and co-workers^{64,65} have made the thiazyl compounds with a second nitrogen on the sulfur but not with the N-R bond hydrofluorinolizable. The same

technique was thought to be possible to make the desired compound.

Another possibility to make the diamine and diisocyanate would be to react thiazyl trifluoride with ammonia to produce $\text{N}=\text{SF}_2\text{NH}_2$ which would add HF to produce the diamine, $\text{SF}_4(\text{NH}_2)_2$. This could then react with carbonyl fluoride to produce the diisocyanate, $\text{SF}_4(\text{NCO})_2$. Glemser and Fild⁶⁶ reported that thiazyl trifluoride and ammonia were unreactive even at room temperature while Cohen and MacDiarmid⁶⁷ report that thiazyl trifluoride with ammonia underwent rapid reaction at low temperatures to yield an unidentified solid.

All of the above proposed reactions used thiazyl trifluoride as the starting compound and this material was expensive and time consuming to make.¹ Recently, Glemser and co-workers^{57,68} have reported synthesis of the compound mercuric iminosulfurdifluoride, $\text{Hg}(\text{N}=\text{SF}_2)_2$, which could be oxidized with silver difluoride to the thiazyl trifluoride. If the $\text{Hg}(\text{N}=\text{SF}_2)_2$ could be made from mercuric isocyanate and sulfur tetrafluoride, considerable time and savings could be achieved.



EXPERIMENTAL

Equipment.

The vacuum line and related equipment were described in Chapter I (page 3) of this dissertation.

Thiazyl Trifluoride.

Thiazyl trifluoride was made by silver difluoride oxidation of N-fluoroformyliminosulfur difluoride.

Reaction of Mercuric Isocyanate with Sulfur Tetrafluoride.

Mercuric isocyanate was precipitated⁶⁹ from a saturated methanolic solution of potassium cyanate to which mercuric chloride was rapidly added with stirring. After 15 minutes, the solution was filtered and the precipitate washed several times with methanol. The solid was dried under vacuum overnight before use. If the cyanate solution and subsequent precipitation were not carried out in a short time interval the resulting mercuric isocyanate was grossly contaminated with mercuric bicarbonate.

Two tenths gram (0.2 g) of the mercuric isocyanate (0.7 mmol) was weighed out and placed in a glass container. Approximately 25 ml of tetrahydrofuran was distilled from sodium aluminum hydride into the reaction vessel, the contents frozen with liquid nitrogen, and the air evacuated. Sulfur tetrafluoride (1.6 mmol) was condensed into the reaction vessel and the contents of the vessel allowed to warm slowly while monitoring the increasing pressure on the manometer. After four hours no increase in pressure was noted. The reaction mixture started as a colorless solution with the mercuric isocyanate suspended in the THF. As the reaction proceeded, it turned a clear yellow with the mercuric isocyanate suspended. When the volatiles were allowed to pass through a series of cold traps, a light tan solid was left behind in the reactor.

The -196° trap contained a trace of carbonyl fluoride. The -160° trap (iso-pentane slush) contained most of the carbonyl fluoride. The -131° trap had traces of THF, SO_2 , SiF_4 , and COF_2 . The -78° trap contained most of the THF. When the reaction vessel was opened in the drybox, a wax-like solid was found. The infrared spectrum showed none of the reported⁶⁸ characteristic peaks of mercuric iminosulfur difluoride. N-fluoroformyliminosulfur difluoride was not isolated from the products.

The Thiazyl Trifluoride and Ammonia Reaction.

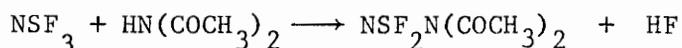
Ammonia (Matheson Company #HD6659) was dried with sodium metal and transferred to a stainless steel bomb. It was used without further purification. Thiazyl trifluoride (1.05 mmol) was condensed into a glass reactor followed by the dry ammonia (2.05 mmol). The container was allowed to warm in a cooled Dewar flask while the rising pressure on the manometer was monitored. The contents of the reactor did not liquefy at any time even after they were at room temperature. The gases which were evolved were condensed back into the reactor and allowed to warm in the same manner a total of four times. No decrease in total pressure of the system was observed after the third time. An infrared spectrum of the gas revealed only unreacted thiazyl trifluoride (0.71 mmol). The ratio of thiazyl trifluoride to ammonia consumed was exactly 1 to 6.

The reactor was opened in the drybox to recover the white solid. An infrared spectrum of the material in a Nujol mull was identical to that of ammonium fluoride. The material was readily soluble in water

and gave a positive test for ammonia ion. It was also hygroscopic.

The Thiazyl Trifluoride and Diacetamide Reaction.

This reaction was investigated in the hope that the diacetyl substituted ammonia would cleanly react with NSF_3 , substituting one fluorine only,



This compound should then hydrofluoroinolyze to NSF_2NH_2 or $\text{H}_2\text{NSF}_4\text{NH}_2$ and acetyl fluoride.

Diacetamide (1.14 mmol) (Aldrich Chemical Company, Inc.; lot 010607) and sodium fluoride (0.5 g) were introduced into a glass reaction vessel in the drybox. The glass reactor was made vacuum tight and evacuated. Five ml of dry ether was condensed on top of the solids followed by thiazyl trifluoride (1.22 mmol). The reaction mixture was allowed to warm in ice water and, following liquefaction of contents, was stirred. At the end of an hour the contents were frozen with liquid nitrogen and then allowed to warm with the volatile contents passing through several cold traps. The liquid nitrogen trap and the -131° trap contained nothing measurable. The -119° trap (bromoethane slush) contained a mixture of ether and thiazyl trifluoride. With separation all of the initial thiazyl trifluoride was recovered. The -78° trap contained ether. Left in the reaction flask was a white solid which gave an infrared spectrum identical with that of the starting compound diacetamide. Repeating the experiment for a five hour time period also resulted in no reaction.

Reasoning that the sodium fluoride was too weak a base to activate the diacetamide, triethylamine was substituted for sodium fluoride. This resulted in a dark orange wax-like solid forming on the sides of the glass reaction vessel. After removing the volatile components, a pool of non-volatile liquid was left in the bottom of the reaction vessel which was identified as triethylammonium fluoride. The wax-like solid did not appear to be the material of interest but rather a decomposition product. Running the reaction at 0° for 24 hours resulted in a decrease in the yellow material but no isolation of any new compounds. Changing the solvent from ether to light petroleum ether did not change the results of the ether runs at 0° or at room temperature.

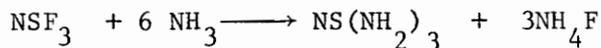
The final attempt at making this reaction successful was with triethylamine (5 ml) serving as base and solvent. At the end of two hours at room temperature the reaction solution was dark red. Some of the starting compounds were recovered. The non-volatile red liquid product did not separate or partition in various solvents. Running the reaction at 0° did not inhibit the formation of the red liquid. The red liquid was transferred in the drybox to a Kel-F reactor, made vacuum tight, and anhydrous hydrogen fluoride (78 mmol), benzene (5 ml), and carbonyl fluoride (4.6 mmol) were added to the reactor under vacuum. The reactor was allowed to warm to 0° and was held at that temperature for four hours before being allowed to warm to room temperature. Forty-eight hours later the reaction mixture was frozen and allowed to warm slowly with the volatile products passing through a NaF pellets trap at 50° C and several cold traps. The -45° trap had benzene in it.

The -78° trap had a small amount of benzene and SiF_4 . The -131° trap contained acetyl fluoride (the infrared spectrum was identical to the published spectrum⁷⁰) and a very small amount of pentafluorosulfanyl isocyanate, probably from a small amount of NSF_3 dissolved in the liquid. The -196° trap contained the unreacted carbonyl fluoride. The reactor was still found to contain the red liquid and an infrared spectrum of it was identical to that of triethylammonium fluoride.

DISCUSSION

The reactions with mercuric isocyanate and sulfur tetrafluoride to produce mercuric iminosulfurdifluoride were not successful. Although the expected by-product, carbonyl fluoride, was produced, there was no evidence of the mercuric iminosulfurdifluoride. Apparently the intermediate produced in the reaction decomposed, possibly to polymers of thiazyl fluoride and HgF_2 .

The ammonia-thiazyl trifluoride reaction did proceed but the products did not appear to be interesting enough to work up. Cohen and MacDiarmid⁶⁷ have also run the same reaction (except for a huge excess of ammonia) but have not reported the results in detail. In view of the ratio of thiazyl trifluoride consumed to the ammonia (1 to 6), it seemed likely that the reaction was:



It would be worthwhile to investigate the reaction further although it would not lead to the product of interest.

The thiazyl trifluoride and diacetamide reactions apparently lead to the formation of the desired compound. However, the thiazyl amine compounds made by Glemser and co-workers^{64,65} showed some decomposition at room temperature and explosive decomposition at elevated temperatures. Apparently the carbonyl group made the compound extremely unstable resulting in almost immediate decomposition at room temperature.

SUMMARY

Mercuric isocyanate does not produce mercuric iminosulfur difluoride by reaction with sulfur tetrafluoride.

Thiazyl trifluoride and ammonia react at low temperature to produce a white unidentified compound, possibly $\text{NS}(\text{NH}_2)_3$.

Thiazyl trifluoride and diacetamide react in triethylamine to produce a compound which apparently decomposes immediately to give unidentified products. The decomposition proceeds even at ice water temperatures.

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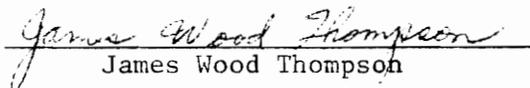
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VITA

James Wood Thompson was born in Wheeling, West Virginia on August 15, 1940. After graduation from Jewett Union Local High School, he enrolled in the College of Steubenville and graduated June, 1963 earning a Bachelor of Science Degree in Secondary Education with a major in chemistry and minors in physical science and mathematics. In September, 1963 he enrolled in graduate school at Purdue University and earned a Master of Science Degree in Chemistry while working as a teaching or research assistant. In September, 1965 he joined the chemistry staff of Kent Stat University as Instructor of Chemistry and taught chemistry and survey of physical science. Three years later he enrolled in the graduate school of Virginia Polytechnic Institute and State University and held a research appointment sponsored by the National Science Foundation.

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ADDITION OF CARBONYL FLUORIDE TO ORGANIC
AND INORGANIC NITRILES

by

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(ABSTRACT)

Carbonyl fluoride will add to alkyl and perfluoroalkyl nitriles and alkane dinitriles in anhydrous acids to form the corresponding α,α -difluoroalkyl isocyanate, perfluoroalkyl isocyanate, or $\alpha,\alpha,\omega,\omega$ -tetrafluoro- α,ω -diisocyanatoalkane. With acetonitrile the reaction proceeded slowly in anhydrous hydrogen fluoride or hydrogen chloride to yield a clear colorless liquid which was identified by infrared, mass, proton NMR, and fluorine-19 NMR spectroscopies to be α,α -difluoroethyl isocyanate. Increasing yields based on the lesser reactant were achieved by making the ratio of acetonitrile to carbonyl fluoride greater or less than one, having the optimum amount of anhydrous acid, the presence of an alkali metal fluoride and/or an increase in reaction time. The α,α -difluoroethyl isocyanate reacted with anhydrous ethyl alcohol to form the carbamate which slowly decomposed by splitting out hydrogen fluoride. The addition reaction proceeded more rapidly, in comparison to acetonitrile, with propionitrile and less rapidly with trifluoroacetonitrile. Cyanamide yielded trifluoromethyl isocyanate and cyanuric acid. Adiponitrile produced 1,6-diisocyanato-1,1,6,6-tetrafluorohexane and 1-isocyanato-5-cyano-1,1-difluoropentane.

Carbonyl fluoride will add to arylformonitriles in the presence of anhydrous hydrogen fluoride and alkali metal fluorides to produce the corresponding aryl- α,α -difluoromethyl isocyanate. The reaction proceeded more rapidly in the presence of alkali metal fluoride and at elevated temperatures. Increasing yields were achieved by having carbonyl fluoride in excess of the nitrile and the optimum amount of anhydrous hydrogen fluoride. The aryl- α,α -difluoromethyl isocyanates reacted with two additional moles of arylformonitrile to yield aryltrifluoromethanes and 2-hydroxy-4,6-diaryl-s-triazines. Alkali metal fluorides also enhanced this reaction and suppressed the formation of 2,4,6-triaryl-s-triazine. With an electron withdrawing substituent on the aromatic ring, the reactions did not yield any significant quantity of the aryltrifluoromethanes but stopped at the aryl- α,α -difluoromethyl isocyanate stage. In the case of o-tolunitrile, steric hindrance prevented the formation of the isocyanate as well as of the trimer.

Pentafluorosulfanyl isocyanate was prepared by the addition of carbonyl fluoride to thiazyl trifluoride in the presence of anhydrous acids. Increasing the concentration of anhydrous hydrogen fluoride resulted in decreasing yield of the isocyanate while without an acid no isocyanate was formed. Pentafluorosulfanyl isocyanate in an excess of anhydrous hydrogen fluoride yielded the starting products. Isolated from anhydrous hydrogen chloride-catalyzed reaction was pentafluorosulfanylcarbonyl chloride. N,N'-bis(pentafluorosulfanyl)urea was synthesized from pentafluorosulfanyl isocyanate and pentafluorosul-

fanylamine or from thiazyl trifluoride, anhydrous hydrogen fluoride, and carbonyl fluoride. The reaction was reversible in excess anhydrous hydrogen fluoride or when heated under vacuum to over 90° C. With triethylamine the urea decomposed.

Mercuric isocyanate does not produce mercuric iminosulfurdifluoride by reaction with sulfur tetrafluoride. Thiazyl trifluoride and ammonia react at low temperature to produce a white unidentified compound, possibly $\text{NS}(\text{NH}_2)_3$. Thiazyl trifluoride and diacetamide react in triethylamine to produce a compound which apparently decomposes immediately to give unidentified products. The decomposition proceeds even at ice water temperatures.