High temperature vapor phase reactions of nitrogen trifluoride with benzylic substrates

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ABSTRACT

At temperatures around 400 °C, nitrogen trifluoride (NF_3) readily reacts with benzylic substrates. Products vary with the substrate, but are all the result of difluoroamination at the benzylic position. Toluene and ethylbenzene produce benzonitrile. Cumene produces α-methylstyrene. Diphenylmethane produces benzanilide. Little or no direct fluorination or radical dimerization is observed.

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1. Introduction

1.1. Environmental issues of nitrogen trifluoride

Nitrogen trifluoride (NF_3) is the premier etching gas for the manufacture of silicon wafer computer chips as well as for plasma or thermal cleaning of Chemical Vapor Deposition chambers. World-wide production for 2008 was estimated at 4000 metric - tons. While supposedly 96–98% of NF_3 is destroyed in the process of being used, atmospheric measurements indicate that more than the remaining 2–4% is getting into the atmosphere. According to research from UC, Irvine [1] and the Scripps Institute of Oceanography [2], nitrogen trifluoride is much more prevalent in the atmosphere than was estimated by industry. This is of great concern as NF_3 has a GWP of 17,000 and amounts to 10.5 million - metric tons of CO_2 equivalent per year. For this reason, there have been calls to add NF_3 to the list of Kyoto Protocol reportable compounds. The studies indicated that the overall emissions are apparently being supplemented by leakages during production. However, such "leakages" would have to account for up to 16% of production, an unlikely scenario.

The venting of "off-specification" NF_3 by overseas manufacturing plants is a more plausible explanation for high atmospheric NF_3 levels. The specification for electronics grade NF_3 is "four nines",

that is 99.99% or better. Any upsets in manufacturing conditions that produce "off-spec" NF_3 produce material that cannot be reworked or purified. With a critical temperature of −39.2 °C and a critical pressure of 45.28 bar, manufacturing sites cannot store any appreciable quantity of "off-spec" NF_3 and so are forced to vent it. Scrubbing technologies are not up to the task and 25–100% of the NF_3 escapes trapping [3]. It is unlikely that manufacturers will adopt more expensive technologies that to destroy the offending NF_3 waste stream. Unless an economical alternative is offered, venting will continue as required and the atmospheric concentration of NF_3 will continue to rise. Even governmental regulation is unlikely to stop the introduction of NF_3 into the atmosphere (refer to the Kyoto HFC-23 Offset Program where manufacturers intentionally produced waste to receive credit for its disposal) [4].

It is the overall goal of this project to develop chemistries that will allow manufacturers to convert off-specification NF_3 to commercially valuable compounds, thus giving them economic incentive to do so. The availability of such a process could reduce intentional emissions and mitigate the Global Warming impact of NF_3 production.

1.2. Precedent for reactivity

The utility of nitrogen trifluoride is due to its known decomposition at elevated temperatures. When heated to temperatures above 250 °C, NF_3 exudes fluoride radicals which are reactive with metals and metal oxides and are thus useful in etching the silicon surfaces of computer chips. The early literature

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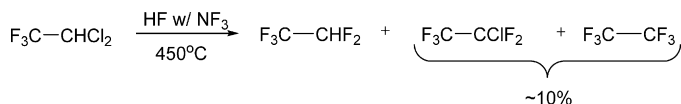
Scheme 1. Literature evidence of fluorination by NF3.

Scheme 2. Reaction of NF3 with toluene.

gives examples of NF3 reacting as a fluoride source with sulfur [5], non-metal and metal oxides [6,7] non-metal oxyhalides [8], cyanides [9], and phosphorus–sulfur compounds [10]. The nearest example to reaction with an organic compound is the reaction of NF3 with COCl2. NF3 has been shown to be able to add across select olefins to produce perfluoroamines [11].

Our own research has used NF3 to prevent or remove the carbonaceous deposits that foul high temperature vapor phase catalysts [12]. In particular, chromium fluoride catalysts used for fluorine-for-chlorine exchange reactions in the manufacture of hydrofluorocarbons were kept active with a co-feed of NF3. Example reactions were the preparation of difluoromethane (HFC-32), pentafluoroethane (HFC-125) and tetrafluoroethane (HFC-134a) from the appropriate hydrochlorocarbons. During the course of these reactions, it was observed that some of the product was halogenated to a greater extent than the original starting material. For example, appreciable quantities (10%) of pentahaloethanes were observed during the hydrofluorination of chlorotrifluoroethane (HFC-133a) to tetrafluoroethane (HFC-134a) (Scheme 1).

Similar by-product formation also results from the use of the oxidants Cl2 or O2 as a co-reagent. NF3 appears to also be acting as an oxidizing agent. Whether the NF3 is oxidizing the Cr^{III} catalyst to a reactive oxidation state, is oxidizing by-product HCl to Cl2, or is performing fluorine-for-hydrogen exchange directly is yet to be determined. It was none-the-less the intent of this project to harness the net fluorinating capability of NF3 to perform fluorination reactions and produce commercially saleable hydrofluorocarbons.

2. Results and discussion

2.1. Reaction of NF3 with toluene

It was assumed that at high reactor temperatures NF3 would be generating F radicals and N2, such as it does in etching processes. The reaction we chose to utilize this chemistry was benzylic fluorination. Benzylic fluorination of toluene would be expected to generate benzyl fluoride, benzyl difluoride and benzotrifluoride in various proportions. Benzotrifluoride, 1, is a valued compound that is considered to be an environmentally more acceptable substitute for dichloromethane (methylene chloride) in solvent applications.

In actuality, the results of the reaction of NF3 with toluene were quite different. In a reaction performed at 400 °C, the principle product was benzonitrile, 2. A short retroanalysis reveals that rather than benzylic fluorination, benzylic difluoroamination is occurring. An initial F radical abstracts a benzylic proton and the resulting benzylic radical is quenched by difluoroamino radical. The resulting difluoroamine is unstable and eliminates HF twice to
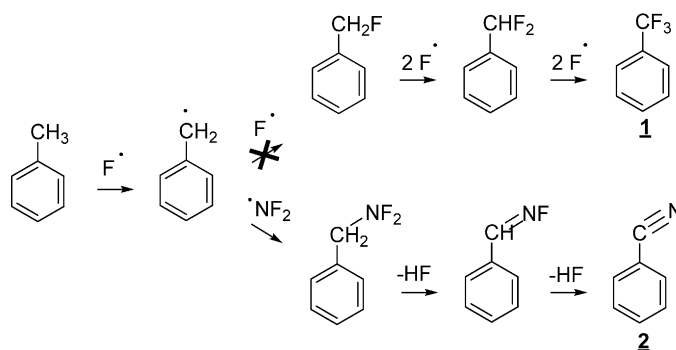
yield the isolated benzonitrile product (Scheme 2). This all occurs within the reactor (and not during aqueous work-up) as benzonitrile is also isolated when the product stream is alternatively vacuum stripped of HF. No fluorotoluenes or other light compounds were observed on GC. A complex mixture of heavy components made up the remaining mass balance.
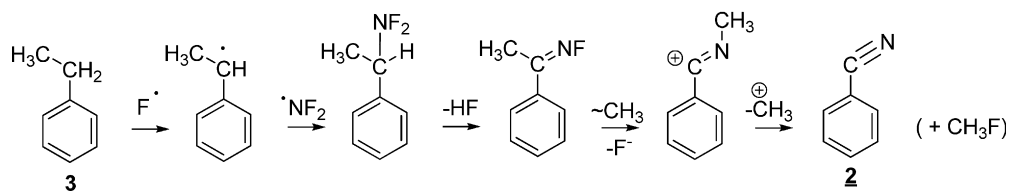
2.2. Reaction of NF3 with ethylbenzene

With NF3 clearly reacting via radical substitution at the benzylic position of toluene, we undertook the simple extension of the reaction to include 2° and 3° benzylic compounds. We were immediately surprised to see the results of reacting NF3 with the 2° substrate, ethylbenzene, 3. One might expect ethylbenzene to follow a similar mechanistic pathway as that of toluene. Indeed, difluoroamination at the benzylic position is apparently occurring, along with the elimination of one HF molecule. However at this point, the unstable fluoroimine intermediate apparently undergoes a Beckmann Rearrangement with subsequent fragmentation as the sole product of reaction is again benzonitrile, 2 (Scheme 3).
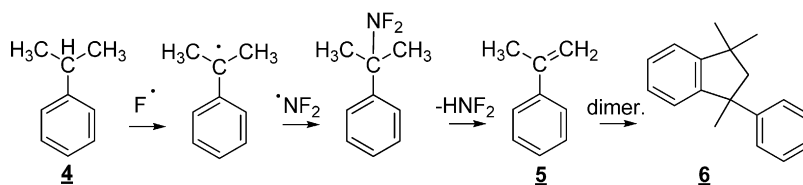
2.3. Reaction of NF3 with cumene

The simplest toluene analog with a 3° benzylic position is cumene, 4. Reaction of NF3 with cumene yielded a single heavy product which was difficult to characterize by NMR. This heavy product could be induced to crystallize and was identified by X-ray crystallography as 2,3-dihydro-1,1,3-trimethyl-3-phenyl-1H-indene, 6 [13]. This complicated molecule is, in fact, one of the three known dimers of α-methylstyrene, 5. So, it appears that cumene is reacting with NF3 in the normal manner to form a benzylic difluoroamine, followed by an elimination of HNF2 (Scheme 4).

One might expect cumene to follow the same course of reaction as ethylbenzene, that is, 3° substitution followed by CH3F elimination (via Beckmann rearrangement). However, we saw no evidence of the products of CH3F elimination such as acetophenone, 7, or acetophenone oxime, 8 (Scheme 5). One might then suspect that selectivity had been lost and that difluoroamination is occurring at the 1° position with elimination

Scheme 3. Reaction of NF3 with ethylbenzene.

Scheme 4. Reaction of NF₃ with cumene.
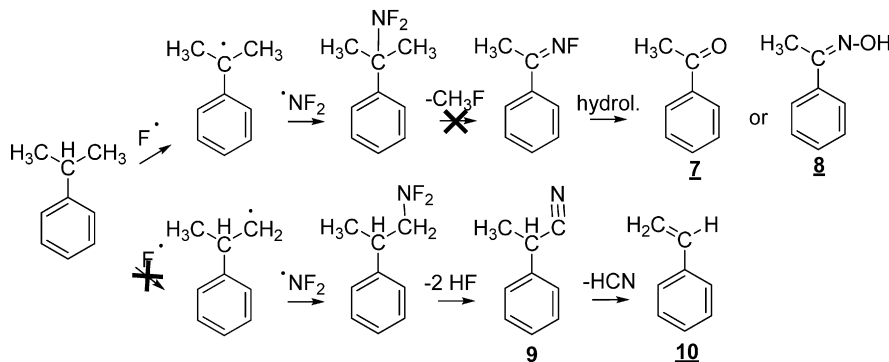
Scheme 5. Unobserved reactions of NF₃ and cumene.

of HNF₂ occurring in the other direction. However, in the case 1°
difluoroamination, HF elimination to the nitrile **9** would certainly
prevail and "plain-old" styrene, **10**, would result. So, cumene
appears to react as in Scheme 4 and a *3rd* mechanistic end-route
has been observed for our *3rd* substrate class.

2.4. Reaction of NF₃ with cymene: selectivity for 3° versus 1°

p-Cymene, **11**, is an aromatic molecule with a 1° substituent at
one end and a 3° substituent at the other end. The structure of *p*-
cymene offers the opportunity to perform a competitive selectivity
test of the NF₃ reaction on a single molecule. Reacting *p*-cymene
under NF₃-lean conditions afforded nitrile **12** and the α-methyl
styrene **13** (as dimer) in a 1:7 mole ratio (Scheme 6). This is a high
selectivity akin to that observed for Cl radical at 100 °C [14].

2.5. Other bifunctional substrates

We investigated the reactions of ortho-xylene, **14**, with NF₃ to
determine whether the rate of HF elimination from an intermedi-
ate difluoroaminobenzylic would be slow enough to allow for a
second, intramolecular, fluoroamination to occur as in Scheme 7.

In practice, *o*-toluonitrile and phthalonitrile (3:1) were the only
products isolated, indicative of mono- and disubstitution, respec-
tively. None of the isoindole that would result from intramolecular
substitution was observed.
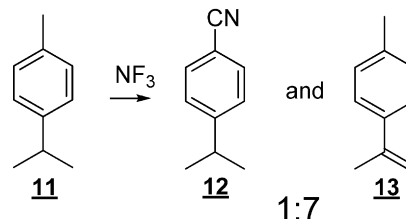
Scheme 6. Selectivity of NF₃ reaction.
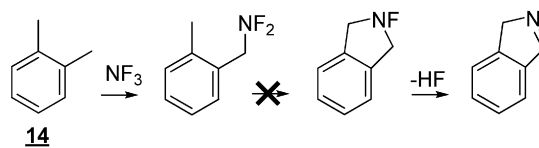
Scheme 7. Unobserved intramolecular fluoroamination.

As a cross-check, *p*-xylene was subjected to the same NF₃
reaction conditions. In this case monosubstitution was less
prevalent to disubstitution (2:3). In addition, some alkyl-alkyl
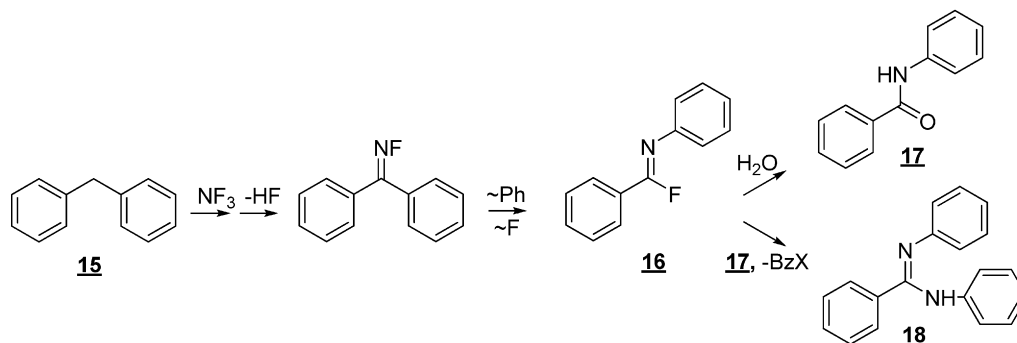radical coupling product was observed (2-xylyl-xylene).
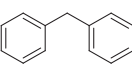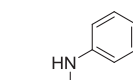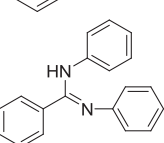


Scheme 8. Reaction of NF₃ with diphenylmethane.

Table 1
Products and yield of NF$_3$ reactions.

Substrate	Product(s)	Yield (%)
		46
		56
		59
		66
		39
		63
		53

2.6. Diphenylmethane

Diphenylmethane, **15**, reacted with NF$_3$ to produce two products. The major product was benzanilide, **17**, isolated in 45% yield, as the 4:3 co-precipitate with diphenylmethane. Again, this product is the result of difluoroamine formation, HF elimination and Beckmann Rearrangement, but without fragmentation (Scheme 8). This is the first example in which a hydrolysis product has been isolated in appreciable amounts. The second product was N^1,N^2-diphenylbenzamidine, **18**, isolated in 7.5% yield and identified by X-ray crystallography [13]. Condensation of benzanilide, **17**, with iminium fluoride, **16**, followed by loss of the benzoyl group is the likely source of this material. We isolated small amounts of benzoyl fluoride, anhydride and benzoic acid which support this route.

3. Conclusion

At 400 °C, NF$_3$ reacts with benzylic substrates to generate intermediate N,N-difluorobenzylamines. These unstable amines decompose by differing mechanisms based on their order of substitution. Primary difluoroamines decompose by exuding HF to generate nitriles (i.e. toluene, xylenes). Secondary difluoroamines decompose by rearranging and eliminating R–F (i.e. ethylbenzene, diphenylmethane), and tertiary difluoroamines decompose by the apparent elimination of HNF$_2$ (i.e. cumene, cymene). See Table 1.

It was the goal of this project to find a means by which waste NF$_3$ could be utilized in a manner in which valuable products might be generated. The expectation was to make fluorobenzylic compounds such as benzotrifluoride. In reality, we have discovered that the product profile is composed of nitriles, amides, and α-methylstyrene dimers, depending on substrate. Nitriles and amides have utility as synthetic building blocks and, surprisingly, the α-methylstyrene dimers are valued components of dielectric fluids. The results of this study are encouraging.

4. Experimental

4.1. General

Cumene, cymene, diphenylmethane, ethylbenzene and xylenes were purchased from Aldrich. Toluene was Sunnyside distilled from CaH$_2$. Nitrogen trifluoride was supplied by Fluoromar, LLC.

Reactions were performed in a single 1″ (2.5 cm) diameter tubular reactor, 24″ (61 cm) long, with two electrically heated temperature zones of equal length. An internal thermocouple array monitored the reactor temperature at five equally spaced points. The reactor was fed via a vaporizer/preheater of similar configuration in ″ (1.25 cm) diameter. The reactor was charged with CrF$_3$-on-carbon pellets that had been previously used to exhaustion in chlorofluorination reactions. This "spent" CrF$_3$-on-carbon was chosen for the reactor bed as it was expected to be resistant to degradation by NF$_3$ and devoid of any oxidizing power (a control experiment on toluene, absent NF$_3$, yielded unchanged toluene with no oxidation or disproportionation observed). The reactor bed was pre-heated to 385 °C under a flow of 50 ml/min N$_2$. This N$_2$ flow was maintained throughout the experiments as a precaution against pooling of reagents within the preheating system in the event of flow stoppages. A backpressure of 1 atm was maintained. The vaporizer/preheater temperature was controlled to maintain a vapor temperature 10 °C above the boiling point of the organic feedstock. The feedstock (i.e. toluene), NF$_3$ and N$_2$ were all fed together to the vaporizer/preheater and through the reactor. An exotherm was always observed and the NF$_3$ feed was controlled so as to keep the temperature of all internal thermocouples under 425 °C. Typically NF$_3$ feeds did not exceed 50 mole%. Generally there would be one or two thermocouples indicating the exotherm and hence the location of the reaction. Product was collected through a cold water condenser, washed with water to remove HF, neutralized with saturated NaHCO$_3$ and dried over Na$_2$SO$_4$. Unreacted starting material and product fractions were separated by fractional distillation and sometimes silica gel column chromatography.

Products were identified by ^{1}H and ^{13}C and ^{19}F NMR performed on a Bruker DPX-250. MS was performed on an Agilent 6210 Time-of-Flight spectrometer.

4.2. Cautionary notes

Nitrogen trifluoride is toxic by inhalation and should only be used in a well ventilated environment. In addition, trace by-products may be toxic and concentrated during distillation.

NF_3 is an oxidant and care must be taken to ensure operations outside the explosivity limits of the NF_3/hydrocarbon mixture. It is advisable that all metal surfaces be fluoride passivated. In instances where the NF_3 ratio exceeded 50 mole% and/or reactor inlet temperatures raised much beyond the boiling point of the substrate *detonations were observed* in the preheater system. In an instance where the NF_3 ratio was 100 mole%, an apparent NF_3 flame initiated at the NF_3/toluene mixing point (stainless steel tee) as evidenced by the tee becoming literally red-hot (700 °C) [15].

Anhydrous HF is a by-product of these reactions. Anhydrous HF causes *instantaneous* severe burns to the skin and mucous membranes. HF should be handled with full PPE protection. An ample supply of HF antidote gel should be kept on hand before handling HF. See reference for burn treatment procedures [16].

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