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SUBSTITUTION AND ADDITION REACTIONS OF NF_4BF_4 WITH AROMATIC COMPOUNDS

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SUMMARY

Benzene, toluene, and nitrobenzene interact rapidly with NF_4BF_4 in anhydrous HF to give, almost exclusively, fluorine substituted aromatic derivatives. Up to four hydrogens can be replaced in a rapid reaction, before a much slower addition reaction takes over. The direction of the substitution in C_6H_6, $C_6H_5CH_3$ and $C_6H_5NO_2$ and the lack of side chain fluorination in $C_6H_5CH_3$ support an electrophilic substitution mechanism. These rapid substitution reactions are followed by much slower fluorine addition reactions to give the corresponding cyclo-hexadienes and -hexenes. These addition reactions were also studied separately using tetra-, penta-, and hexa- fluorobenzene as the starting materials. In these addition reactions, almost no hydrogen substitution occurred. The addition of the first pair of fluorines always gave 1,4-cyclohexadienes in which the CF_2 group was adjacent to hydrogen on the ring. The addition of the second pair of fluorines resulted in the formation of cyclohexenes. These reactions occurred in high yield and offer a controlled, high yield path to dienes. All products were characterized spectroscopically and by comparison to literature data.

INTRODUCTION

The known methods for introducing fluorine into an aromatic ring are severely limited [1-3]. The classic Balz-Schiemann reaction [3] and methods, such as the decarboxylation of fluoroformates [4], are useful for the introduction of single fluorine atoms, but are generally less useful for multiple fluorine substitution. The use of elemental fluorine or electrochemical fluorinations result mainly in addition and not in substitution [3]. Halogen fluorides, such as ClF_3, BrF_3 or IF_5, produce in addition to fluorine substituted compounds large amounts of the corresponding halogen substituted compounds and also some addition products [3]. The yields of substitution products obtainable with halogen fluorides can be improved by the use of strong Lewis acids [2,3], however, the extreme reactivity of compounds, such as $ClF_2^+BF_4^-$ or $ClF_2^+SbF_6^-$, makes control of their reactions with organic compounds extremely difficult and unsafe. The use of transition metal fluorides, such as CoF_3 or CeF_4 [1], results in addition and saturation, requiring subsequent rearomatisation. Therefore, this method is limited to highly or perhalogenated aromatics. Pyrolysis of aliphatic fluorocarbons, such as $CFBr_3$ [5], can also produce fluoroaromatics. However, this method is limited again to the synthesis of perfluorinated aromatics [1]. Halogen exchange reactions, such as Cl versus F, using HF, alkali metal or metal fluorides are useful, but are restricted to systems strongly activated towards nucleophilic attack by fluoride ion [1]. Hypofluorites, such as CF_3OF, are useful for electrophilic and photolytic fluorinations [6,7]. The electrophilic fluorinations are limited again to activated aromatics, whereas the free radical photolytic fluorinations often lack selectivity resulting in $-OCF_3$ substituted by-products and side chain fluorination. The xenon fluorides and especially XeF_2 are promising reagents for electrophilic aromatic substitution [8], but the full extent of their usefulness is still unknown. The limited availability of xenon, its high price and the treacherous explosiveness of the hydrolysis product, XeO_3 [9], are drawbacks curtailing their extensive use.

Due to its brevity, the above listing of known methods of preparing aromatic fluorine compounds is obviously incomplete and the conclusions are generalized. However, it clearly emphasizes the need for a readily available and more generally usable reagent for electrophilic aromatic substitution.

The ideal reagent for electrophilic substitution would be a salt containing the F^+ cation. Unfortunately, such salts do not exist. As an alternative, salts containing complex fluoro cations of the type $XF_{(n+1)}^+$ could be used. To be a strong electrophile, such a cation should possess high electronegativity. Since highly electronegative fluorine compounds generally are very strong oxidizers, most of these cations react too violently with organic compounds to be of practical interest. The NF_4^+ cation, however, is an exception. It combines high electronegativity(oxidation state of nitrogen is +V) with high kinetic stability (it is isoelectronic with CF_4), and its reactions require significant activation energies [10]. Furthermore, salts, such as NF_4BF_4, offer the advantage of generating in an electrophilic aromatic substitution reaction only by-products, such as NF_3 and BF_3, which are unreactive towards the organic compounds. In view of these properties and its ready availability [11], NF_4BF_4 appeared to be an ideal candidate for electrophilic aromatic substitution reactions. In this paper, we report the results of screening reactions of NF_4BF_4 with various organic substrates which demonstrate the usefulness of NF_4BF_4 for these applications.

EXPERIMENTAL

Volatile materials were manipulated in a well-passivated (with ClF_3) stainless steel vacuum line equipped with Teflon FEP U traps, 316 stainless steel bellows seal valves and a Heise Bourdon tube-type pressure gauge. Hydrogen fluoride work was carried out in an all Monel and Teflon vacuum system. Transfers outside the vacuum line were carried out in a drybox. Infrared spectra were obtained using 5 cm path stainless steel cells with AgCl windows and a PE Model 283 spectrophotometer. Mass spectra were measured with an EAI Quad 300 quadrupole spectrometer and ^{19}F and ^{1}H nmr spectra were determined with a Varian EM390 spectrometer operating at 84.6 and 90 MHz, using $CFCl_3$ or TMS as internal standards, respectively. Positive chemical shifts are upfield from $CFCl_3$ and downfield from TMS. Raman spectra were recorded on a Cary Model 83 using the 4880 Å exciting line. Gas chromatographic data were obtained using a Varian Aerograph GC with a thermal conductivity detector under isothermal conditions (135°) with a stainless steel column (1/8" X 10') packed with Poropak PS. For the GC determination of the quantitative composition of mixtures, uncorrected peak areas were used since response factors were not available for all compounds. The solid NF_4BF_4 was prepared from NF_3-F_2-BF_3 at low temperature using UV activation, which gives analytically pure material [12].

NF_4BF_4 Reactions with Aromatics

C_6F_6. A sample of NF_4BF_4 (4.07 mmol) contained in a Teflon (FEP) ampoule was dissolved in anhydrous HF (4 ml) and cooled to -78°. Hexafluorobenzene (1.25 mmol) was condensed into the ampoule which was then warmed gradually while stirring magnetically. After being kept overnight at 0-10°, the clear, colorless solution was cooled to -78° and the volatile material quickly removed by condensation into a -196° trap. The -196° trap contained NF_3 (1.24 mmol) contaminated with traces of HF as shown by infrared spectroscopy. The reaction was allowed to continue for another day at room temperature. While maintaining the reaction ampoule at 0°, the volatile products and HF were separated by fractional condensation in a series of

U-traps cooled at -45, -78, and -196°. The -196° fraction, NF_3 and HF, was discarded and the -45° trap was empty. The -78° trap contained a white solid, which melted to a colorless liquid above 0°. Examination of this material by infrared [13] and gas chromatography showed it to be 1,4 perfluorocyclohexadiene (1.18 mmol, 94.3% yield, based on C_6F_6) with a slight amount (2-3%) of unreacted C_6F_6. Intense ions in the mass spectrum were observed at m/e (assign.):224(C_6F_8), 205(C_6F_7), 186(C_6F_6), 174(C_5F_6), 155 (C_5F_5,base), 136(C_5F_4), 124(C_4F_4), 117(C_5F_3), 105(C_4F_3), 93(C_3F_3), 86(C_4F_2), 74(C_3F_2), 69(CF_3), 55(C_3F), and 31(CF). The ^{19}FNMR spectrum showed two equal area multiplets at 113.1 and 158.3 ppm in agreement with the literature [14] for 1,4-C_6F_8. A white solid remained in the reaction ampoule and was shown by Raman spectroscopy [12] to be NF_4BF_4 (1.48 mmol).

$\underline{C_6F_5H}$. As before, a mixture of NF_4BF_4 (4.29 mmol) and C_6F_5H (1.35 mmol) in HF was stirred and warmed during several hours from -78° towards ambient temperature where it was kept for 12 hours. Evolved NF_3 (3.3 mmol) was monitored. After several more hours of stirring at room temperature, the products were separated by vacuum fractionation through U-traps cooled at -45, -78, and -196°. All material passed the -45° trap except for a small amount of NF_4BF_4 remaining in the reactor. The -196° fraction was discarded. The -78° trap contained 1.24 mmol of a colorless liquid whose infrared spectrum [1770(ms), 1740(s), and 1720 cm^{-1}(vs)] indicated that it was composed of more than one cyclohexene as well as unreacted C_6F_5H. Gas chromatography showed three components which were analyzed individually by mass spectroscopy. In order of elution they were;(1) 1,4-C_6F_8, 26.1%, (2) 1H-heptafluorocyclohexa-1, 4-diene, 66.3%, and (3) C_6F_5H, 7.6% with the composition based on GC peak areas. The mass spectra of the fractions agreed very well with published data [15] for the assigned compounds. In addition, the ^{19}F NMR spectra confirmed the formulated structures. For 1-H heptafluorocyclohexa-1, 4-diene a literature report of the NMR spectrum could not be found, but by comparison with related compounds [16,17] it was apparent that the observed resonances and area ratios were reasonable for that structure. Position of H or F, ppm or δ(rel. F area): 1-H, 5.93; 2-F, 127.7(1); 3-F, 115.2(2); 4-F, 160(1); 5-F, 155(1), 6-F, 101.7(2). The conversion of the C_6F_5H was 92%. The composition of the product was 28% 1,4-C_6F_8 and 72% 1,4-C_6F_7H, with a total of 91% of the organic material being recovered.

$\underline{p\text{-}C_6F_4H_2}$. A mixture of NF_4BF_4(4.18 mmol) and p-$C_6F_4H_2$(1.43 mmol) in 4 ml HF at -78° was stirred and warmed to 0° over 3 hours, followed by overnight stirring at 0-20°. Fractional condensation at -78 and -196° was used to separate HF and NF_3 from the products which were retained in the -78° trap. No unreacted NF_4BF_4 remained in the reactor. The original -78° fraction was furtherseparated by refractionating through -45 and -78° traps. The former contained 0.21 mmol of a colorless liquid whose infrared spectrum showed a strong band at 1710 cm^{-1} typical for the double bond of a -CF=CH- group. Analysis using GC/MS procedures showed this material to be 1H, 4H-hexafluorocyclohexa-1,, 4-diene [11]. Prominent mass spectral peaks were found at m/e (assign.): 188($C_6F_6H_2$), 169($C_6F_5H_2$), 150($C_6F_4H_2$), 138($C_5F_4H_2$), 137(C_5F_4H), 119($C_5F_3H_2$,base), 99(C_5F_2H), 94(C_3F_3H), 93(C_3F_3), 88($C_4F_2H_2$), 81(C_5FH_2), 80(C_5FH), 75(C_3F_2H), 69(CF_3), 68(C_4FH), 61(C_5H), 57(C_3FH_2), 56(C_3FH), 51 (CF_2H), 50(CF_2), 44(C_2FH), and 31(CF). The ^{19}F NMR spectrum for this compound agreed with published data [18]. Similar analysis of the -78° fraction showed it to be a mixture of unreacted p-$C_6F_4H_2$, the above described 1H,4H cyclohexa-1, 4-diene, and a compound of empiracal formula $C_6F_8H_2$. An infrared spectrum of the latter compound showed bands at cm^{-1}(intens.): 3070(w), 2960(w), 1710(ms), 1380(s), 1355(w), 1260(m), 1150(s), 1065(m), 1030(m), 743(mw), 637(w), 580(w), and 582(w). The bands near 3000 cm^{-1} are assignable to the carbon-hydrogen stretches of -C=C-H and $\geq$C-H groups while the 1710 cm^{-1} peak is typical of a -CF=CH- stretching vibration [19,20]. Strong ion peaks in the mass spectrum were at m/e (assign): 226($C_6F_8H_2$), 207($C_6F_7H_2$), 186(C_6F_6), 157($C_5F_5H_2$) 144 (C_4F_5H), 137(C_5F_4H), 119($C_5F_3H_2$), 117(C_5F_3), 113(C_3F_4H), 94(C_3F_3H), 93 (C_3F_3), 75(C_3F_2H), 69(CF_3), 57(C_3FH_2), 51(CF_2H), and 50(CF_2). The NMR spectra of the -78° fraction confirmed the presence of p-$C_6F_4H_2$, 1H,4H-hexafluorocyclohexa-1, 4-diene, and 1H,4H-octafluorocyclohexene; position of H or F, ppm or δ(rel. area) of 1H,4H-$C_6F_8H_2$:1-H,5.1(1); 2-F, 121.5(1), 3-F, 118.1(2), 4-H, 4.7(1), 4-F, 134.4(1), 5-F, 130.3(2), 6-F, 110.4(2). The conversion of starting material was 78%. The composition of the products was 53% $C_6F_6H_2$ and 47% $C_6F_8H_2$, with a total of 92% of the organic material being recovered.

$C_6H_5NO_2$. To a stirred solution of $C_6H_5NO_2$(10 mmol) in 5 ml HF at -78° was added dropwise over 30 min. a solution of NF_4BF_4(2.88 mmol) in 5 ml HF. Reaction of the NF_4BF_4 was shown by an increase in pressure due to NF_3 evolution. When all the NF_4BF_4 had been added the reaction was gradually warmed to 0° and left overnight. During the warming, the reaction solution changed from pale yellow to dark brown. Keeping the reaction ampoule at -45°, the NF_3, HF, and other volatile materials were pumped away through -78 and -196° traps. After the majority of the HF was removed, the reactor was maintained at 0°. The material passing the -78° trap was discarded. The -78° fraction consisted of a few droplets of a liquid with a low vapor pressure at ambient temperature. Mass spectroscopy of the vapor from the drops showed minor amounts of aromatic fluorocarbons which did not contain NO_2 substituents. These were of the empirical formula $C_6F_nH_{6-n}$(n=1-4). The principal ion peaks observed were m/e (assign.): 85($NO_2F{\cdot}HF$), 49(NOF), and 30(NO). Examination of the liquid, non-volatile at 0° which remained in the reactor, by NMR spectroscopy showed that five fluorinated compounds were present and all were found to be substituted nitrobenzenes by comparison of the observed chemical shifts with reported values [16]. By measurement of the area of the resonances the amount of each compound was calculated: o-$C_6FH_4NO_2$(15%), m-$C_6FH_4NO_2$(62%), p-$C_6FH_4NO_2$ (6%), 2,6-or 3,5-difluoronitrobenzene (15%), and 2,4-difluoronitrobenzene. The large excess of $C_6H_5NO_2$ employed, and still present, masked the ^1H spectra of these products and thus the ^{19}F spectra were relied on for identification.

$C_6H_5CH_3$. Toluene and NF_4BF_4(1:4 molar ratio) were reacted by condensing the hydrocarbon onto the stirred HF solution of the salt at -78°. Alternatively, toluene in HF at -78° was treated dropwise with a solution of NF_4BF_4 (1:2 molar ratio). In either case instantaneous reaction occurred and the solution became black. After warming to 0° for a few hours, these reactions were worked up in the usual manner. Much tar like residue remained in the reactor in each case. Infrared spectroscopic examination of the volatile species, trapped at -78°, showed strong bands near 1500 cm^{-1} confirming the presence of aromatic species. Mass spectra of these fractions showed in both experiments that only aromatic substitution products were present; these were of the empirical formula $C_7F_nH_{8-n}$(n=1-4). The low intensity of the m/e 69 and 51 peaks indicated the absence of CF_3 or CF_2H groups in these compounds with the observed intensities of these peaks being due to C_4FH_2 and C_4H_3 ions. From the reaction using a higher ratio of NF_4BF_4 to toluene a significant amount of $C_6F_4H_2$ was found, indicating some displacement of CH_3 from the ring. The n.m.r. spectra of these products confirmed that various fluorotoluenes were present [16], approximately in the amounts given (%): o-$C_6FH_4CH_3$(15), p-$C_6FH_4CH_3$(15), m-$C_6FH_4CH_3$(8),2,4-difluorotoluene (30), other di- and trifluorotoluenes (25), and 2,4,5,6-tetrafluorotoluene (7).

C_6H_6. To a stirred solution of benzene (3.18 mmol) in 4 ml HF at 0° was added dropwise over 25 min. a solution of NF_4BF_4 (3.33 mmol) in 5 ml HF. Reaction was instantaneous as indicated by NF_3 evolution and darkening of the solution. The alternative techniques whereby benzene vapor was condensed onto the stirred NF_4BF_4 solution at -78° or more concentrated solutions were mixed at -78° produced more charred and tarry products. Vacuum fractionation through cold traps separated the NF_3, BF_3, and HF from the less volatile products which were found to be mainly unreacted C_6H_6 (2 mmol) and fluorinated benzenes (0.9 mmol). The latter were identified by mass spectroscopy and were of the empirical formula, $C_6F_nH_{6-n}$ (n=1-4). More specific isomer identification and product ratios were determined by ^{19}F n.m.r. analysis of several fractions. No C_6F_6 was observed and only traces of C_6F_5H, $C_6F_6H_2$, and C_6F_7H were noted at higher NF_4BF_4: reactant ratios. A non-volatile black, oily residue was left in the reactor.

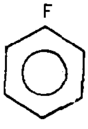
RESULTS AND DISCUSSION

It was found that NF_4BF_4 readily reacts with aromatic compounds. However, there is a pronounced difference between the reactions with aromatic hydrocarbons, on the one hand, and with highly fluorinated aromatics, on the other hand. With aromatic hydrocarbons, a vigorous ring hydrogen substitution occurred, even at -78° in HF solution. With highly fluorinated aromatics, a much slower fluorine addition was observed.

Substitution Reactions. The simplest aromatic hydrocarbon studied was benzene. Although some 'char' formation was observed in these reactions, its extent could be minimized by careful control of the reaction conditions. Substitution of hydrogen by fluorine occurred, as shown in the general equation:

$$nNF_4BF_4 + C_6H_6 \xrightarrow{HF} C_6F_nH_{6-n} + nNF_3 + nBF_3 + nHF$$

When the NF_4BF_4 to benzene ratio was about 1:1, the ^{19}F n.m.r. spectra of the fluorinated products showed all the intermediates expected for an electrophilic substitution up to $C_6H_2F_4$ with a typical product distribution (mol percent) being: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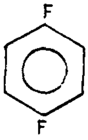
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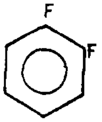
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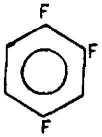
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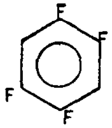
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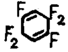
When the NF_4BF_4 to benzene ratio was increased to about 3:1, some hexafluorocyclohexadiene  was also observed, besides the above products, resulting from F_2 addition to para-tetrafluorobenzene. Mass spectra of the benzene fluorination products were also recorded and indicated the presence of some small amounts of pentafluorobenzene. However, as was also shown by the fluorination reaction of para-$C_6H_2F_4$ (see below), the main product from the fluorination of paratetrafluorobenzene is hexafluorocyclohexadiene and not pentafluorobenzene. These results show that substitution is the predominant mechanism for the introduction of the first four fluorines, whereas addition is the preferred mechanism for the introduction of any subsequent fluorines.

In order to further support the electrophilic aromatic substitution mechanism for NF_4BF_4, its reactions with two substituted benzenes, $C_6H_5CH_3$ and $C_6H_5NO_2$, were investigated. These were chosen for their well known ability to differentiate between an electrophilic and a free radical reaction path, based on the observed orth-meta-para product distribution.

In the toluene reaction, the ratio of NF_4^+ to toluene was in the range 2-4:1. Thus, an excess of fluorine was available (assuming one F/NF_4^+ is available for substitution) and multisubstitution was expected. The result of a very rapid reaction was :

$$C_6H_5CH_3 + NF_4BF_4 \xrightarrow[-78^o]{HF} C_6F_nH_{5-n}CH_3 \qquad \text{where } n=1-4$$

The mass spectra of the products strongly indicated that no side chain fluorination had occurred, in agreement with other spectroscopic evidence. Typical isomer distributions for the ring substitution were o-F (15), m-F (8), p-F (15), 2,4 di-F (30), and mixed di- and tri- F (25). Obviously, o and p- products predominate for this electron rich ring, a result which is compatible with an electrophilic subsitution process.

For the nitrobenzene reaction, a 3:10 mole ratio of NF_4BF_4: substrate was used. Even under these conditions, this reaction was less vigorous than those of benzene or toluene, as exemplified by a slightly slower NF_3 evolution and the lack of 'darkening' of the solution until the mixture was finally warmed to about 0^o. Fluorine substitution occurred to give $C_6F_nH_{5-n}NO_2$ (n=1-4) compounds. Minor amounts of $FNO_2 \cdot (HF)_n$ were formed and traces of $C_6F_nH_{6-n}$ species were observed, but overwhelmingly the NO_2 group was not displaced. The observed products were mainly monosubstituted with the following isomer distribution: o-F(16), m-F(62), and p-F(7).

The observation of predominantly ortho and para substitution and the lack of side chain fluorination in toluene, and the meta substitution in nitrobenzene establishes these NF_4BF_4 reactions as electrophilic substitutions.

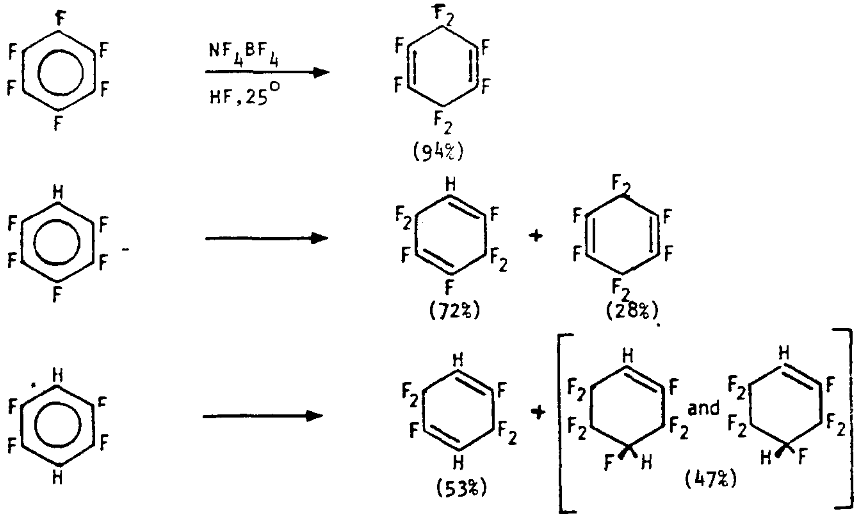
For nitrobenzene, the yield of fluorinated products was not determined due to separation problems caused by the low volatility of the products and the large excess of nitrobenzene used. However, in view of the high relative amount of mono-F species, and the limited amount of charring, it is estimated that the yield of substituted products was high. For the much more reactive C_6H_6 and $C_6H_5CH_3$, yields varied widely. Volatile, fluorinated species were observed equivalent to 30-60% of the aromatic starting compounds.

From these screening experiments it is readily apparent that NF_4^+ salts might be very useful reagents for the preparation of substituted fluoroaromatics, especially when multisubstitution is desired. No evidence for addition reactions was observed until at least 4 fluorines had been introduced into the ring. Also, it is apparent that milder, more controlled conditions are required to exploit fully this very active reagent. More dilute solutions, lower temperatures, and the possible use of other solvents, such as Freons, are obvious changes to be investigated. Nevertheless, a new method has been discovered for substituting H by F without affecting saturated or oxidized substitutents.

Addition Reactions

To obtain more data on the possible follow-on reactions of aromatics with NF_4^+ it was decided to examine systems which were already highly fluorinated. Furthermore, these starting materials are more inert toward the strongly fluorinating NF_4BF_4 thus allowing better control of the reaction. This study was also expected to show whether the apparent tendency of these systems to stop at the tetra- or penta- fluoro substitution stage was general.

Experiments were carried out using tetra-, penta-, and hexafluorobenzene as starting materials. All reacted gradually at, or near, ambient temperature. All solutions and products were colorless throughout the reactions. Liberated NF_3 and excess, unreacted NF_4BF_4 were recoverable. The products were identified spectroscopically and most of them have been reported in the literature, making their identification unequivocal. The overall results are shown by the equations.



For these three highly fluorinated benzenes, the addition of the first two fluorines occurs in para position to each other (1, 4 addition) and ortho to any hydrogen, if present. The addition of a second pair of fluorines cannot proceed by a 1, 4 mechanism without changing the ring into a bicyclo form, which is generally encountered only under photolytic conditions. Thus, the second pair of fluorines undergoes a 1, 2 addition to yield a cyclohexene.

For pentafluorobenzene, some substitution was also observed. At this point, we cannot say whether this is the result of a true substitution or of an addition-elimination reaction. In the case of p-$C_6F_4H_2$, the second F_2 addition produces the 1H,4H-octafluorocyclohexene which has two possible geometric isomers. Trace quantities of the saturated product, $C_6F_{10}H_2$, were also detected by mass spectroscopy.

CONCLUSIONS

The results of this study demonstrate the potential of NF_4^+ salts as powerful reagents for the introduction of fluorine into aromatic rings by electrophilic substitution. Up to four hydrogens can be substituted in aromatic systems in a rapid reactions, before a much slower addition reaction takes over. This slower fluorine addition reaction was also studied separately and produces the corresponding cyclo-hexadienes and -hexenes. The addition reactions are novel and offer a controlled, high yield path to dienes which have previously only been obtained as parts of complex mixtures [21]. More extensive studies are needed to define the full scope and usefulness of these NF_4BF_4 reactions.

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