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Reaction of XeF_2 and Substituted Benzenes. III. Mechanistic Studies[1]

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The substituent effects, HF catalysis, the products formed, the identification of several radical cations, molecular orbital calculations, a competition study, and the use of HCl and Cl_2 as trapping agents lead us to suggest that xenon difluoride reacts with aromatic compounds to form a complex containing XeF_2, HF, and C_6H_5R which may either collapse to give eventually a fluorobenzene or dissociate to form a radical cation which reacts with starting material to form biphenyls and polyphenyls.

Recently, we reported[2] that xenon difluoride is a useful reagent which effects substitution of fluorine for hydrogen in aromatic compounds to give fluoroaromatics in good yield.[3] It was of interest to examine the mechanism of this reaction. In a number of cases biphenyls, fluorinated biphenyls, and even polyphenyls were found to accompany the major product. Radical cations of benzene and substituted benzenes were proposed as intermediates for both the primary reaction and the formation of by-products.[3] An esr investigation of the reaction of xenon difluoride with substituted benzenes revealed that a variety of 4,4′-disubstituted biphenyl +1 ions were formed.[4] Monocyclic radical cations, however, were not observed.

The purpose of this paper is to present the evidence and to suggest mechanisms for the reactions of XeF_2 with aromatic compounds. In both the fluorination reaction and in the formation of biphenyls, the important intermediates have not been directly observed. The suggested mechanisms are based, therefore, on chemical reasoning, competitive reactions, and analogies and are thus subject to limitations implied by such evidence.

Results

Several important characteristics of the reactions of xenon difluoride with substituted benzenes are summarized.[2-4] (1) Substantial yields of monofluorinated substitution products are observed. (2) The reactions are catalyzed by anhydrous HF and do not proceed without it. (3) Substituent effects are similar to those observed in electrophilic aromatic substitution reactions. (4) Biphenyls and biphenyl radical cations are produced. (5) Fluorine addition products have not been observed.

Catalysis by HF.—The mechanism of fluorination must involve catalysis by HF, since no reaction takes place without it. Only small amounts of HF are necessary for initiation; since about 1.2 mol of HF is generated per mole of XeF_2 added, the reaction is autocatalytic in HF.[2] The oxidation of iodine or sulfur dioxide by XeF_2 is also catalyzed by a trace of HF. These findings were rationalized by assuming that HF facilitates ionization of XeF_2 to XeF^+.[5] However, conductivity measurements of XeF_2 in HF indicate that appreciable ionization does not take place,[6] although fluorine exchange between HF and XeF_2 does occur and is rapid enough to cause coalescence of the separated ^{19}F nmr peaks on warming from −20° to 0°.[7] Infrared measurements have indicated hydrogen bonding between XeF_2 and HF.[8] Thus, the observed acid

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[1] Work performed under the auspices of the U. S. Atomic Energy Commission.

[2] M. J. Shaw, H. H. Hyman, and R. Filler, *J. Amer. Chem. Soc.*, **92**, 6498 (1970).

[3] M. J. Shaw, R. Filler, and H. H. Hyman, *ibid.*, **91**, 1563 (1969).

[4] M. J. Shaw, J. Weil, H. H. Hyman, and R. Filler, *ibid.*, **92**, 5096 (1970).

[5] N. Bartlett and F. O. Sladky, *Chem. Commun.*, 1046 (1968).

[6] H. H. Hyman and L. A. Quarterman, "Noble Gas Compounds," H. H. Hyman, Ed., University of Chicago Press, Chicago, Ill., 1963, p 275.

[7] J. C. Hindman and A. Svirmickas, ref 6, p 251.

[8] N. J. Lawrence and G. D. Sturgeon, 157th National Meeting of the American Chemical Society, Division of Inorganic Chemistry, Minneapolis, Minn., April 1969, Abstract 137.

catalysis and the above data may be explained in terms of the equilibrium

$$XeF_2 + HF \rightleftharpoons \overset{\delta+}{F\text{-}Xe}\text{---}\overset{\delta-}{FHF}$$

It might be expected, therefore, that in the presence of HF, xenon difluoride would behave as an electrophile.

Mechanism of Formation of Biphenyls.—Although the formation of biphenyls and polyphenyls represents an unwanted process in the preparation of fluorobenzenes, the mechanism is of obvious interest. Thus, it is possible that the monocyclic precursors to the observed biphenyls and their +1 ions may also be intermediates in the fluorination reaction. Secondly, it has been suggested[9] that benzene radical cations do not react with neutral substituted benzenes (due to a loss in resonance energy), and it was deemed important to determine whether monocyclic radical cations are indeed intermediates in the formation of the biphenyls and their +1 ions.

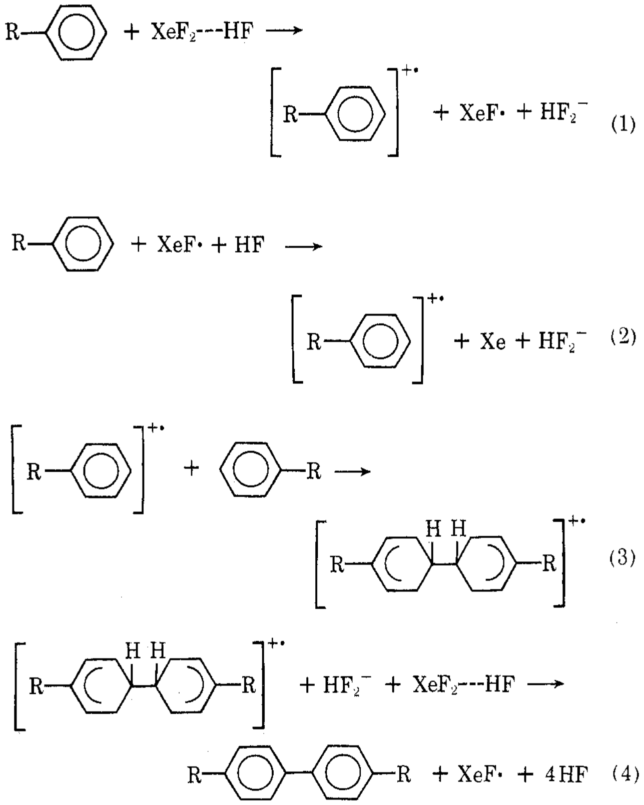
It seemed possible, *a priori,* that substituted phenyl radicals ($R\text{–}C_6H_4\cdot$), phenyl cations ($R\text{–}C_6H_4^+$), or protonated benzenes ($R\text{-}C_6H_6^+$) could be intermediates in the formation of substituted biphenyls. All of these species are thought to be capable of reacting with benzenes to give biphenyls[10–12] Since a variety of radical cations are observed when XeF_2 reacts with substituted benzenes, monocyclic radical cations were also considered as possible intermediates.

In chlorinated hydrocarbon solvents (*e.g.*, CH_2Cl_2 or CCl_4), chlorine abstraction by the phenyl radical has been observed,[13] but we did not observe any chlorobenzenes among the products of the XeF_2 reaction, which casts doubt on the intermediacy of the phenyl radical. Fortunately, the results of competitive reactions are available which provide a chemical test for the presence of the phenyl radical and phenyl cation. The phenyl radical generally exhibits a selectivity of about 4:1 toward nitrobenzene over benzene to produce predominantly 2- and 4-nitrobiphenyl, in preference to biphenyl.[10] The phenyl cation, on the other hand, exhibits a selectivity of about 3:1 toward benzene over nitrobenzene.[11] Of the nitrobiphenyls formed 84% is the meta isomer.[11] Early work in this laboratory has shown that nitrobenzene is soluble in anhydrous HF, is recovered unchanged from HF, and is negligibly protonated in anhydrous HF.[14] Thus, it is unlikely that the chemistry of nitrobenzene would be significantly affected by the presence of small amounts of HF.

Therefore, we conducted a competition experiment using XeF_2 and a 50:50 mixture of benzene and nitrobenzene and have observed that biphenyl and fluorobiphenyl are formed and that nitrobiphenyls are *absent* (see Experimental Section for details and other products). We conclude that it is very unlikely that either the phenyl cation or the phenyl radical is involved in the formation of biphenyls. The absence of nitrobiphenyls also strongly suggests that the monomeric precursor to the observed biphenyls and their +1 ions is an electrophilic species, since it reacts with benzene rather than with the more electron-deficient nitrobenzene ring.

A choice remains between a monomeric radical cation and a protonated benzene. Kovacic, *et al.*,[12] have proposed that protonated benzene is an intermediate in the reaction of benzene with metal chlorides in the presence of aluminum chloride and water. This mechanism seems unlikely when electron-donating substituents are present on the ring, since meta protonation would be required to explain the predominance of 4,4′-disubstituted biphenyls, which we find. In fact, the latter are not found as products in the reaction of metal chlorides and monosubstituted benzenes.[15] Our results are consistent with the formation of benzene radical cations which react as shown in Scheme I.

SCHEME I
SUGGESTED MECHANISM FOR DIMERIZATION



Wexler, *et al.*,[16] have demonstrated that the formation of $C_{12}H_{12}\cdot^+$ is the primary process in the high-pressure gas phase ion–molecule reaction of $C_6H_6\cdot^+$ with benzene. The gas phase reaction of toluene with its radical cation has been shown to yield $C_{14}H_{14}\cdot^+$.[16] Although mass spectrometry does not reveal the structure of these ions, it seems reasonable that these species are the dihydro intermediates proposed in Scheme I, eq 3. These data, combined with our experiments in solution, strongly suggests that benzene and substituted benzene +1 ions do, in fact, react to form biphenyls, which may be further oxidized. It remains to be shown

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(10) (a) D. H. Hey, A. Nechvatal, and T. S. Robinson, *J. Chem. Soc.*, 2892 (1951); (b) D. R. Augood, D. H. Hey, and G. H. Williams, *ibid.*, 2094 (1952).

(11) (a) R. A. Abramovitch and J. G. Saha, *Can. J. Chem.*, **43**, 3269 (1965); (b) J. B. Aylward, *J. Chem. Soc. B*, 1268 (1967).

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(13) D. H. Hey and W. A. Waters, *Chem. Rev.*, **21**, 193 (1937).

(14) H. H. Hyman and L. A. Quarterman, *J. Phys. Chem.*, **65**, 123 (1961).

(15) P. Kovacic and R. M. Lange, *J. Org. Chem.*, **30**, 4251 (1965), and references cited therein.

(16) (a) S. Wexler and R. P. Clow, *J. Amer. Chem. Soc.*, **90**, 3940 (1968); (b) S. Wexler and L. G. Pobo, *ibid.*, **91**, 7233 (1969); (c) S. Wexler and L. G. Pobo, *J. Phys. Chem.*, **74**, 257 (1970).

TABLE I

CALCULATED CHARGE DENSITIES FOR SUBSTITUTED BENZENE +1 IONS

	Charge					Convergence limit
R-C_6H_5	C_1	C_2	C_3	C_4	R	
NO_2	+0.192	+0.096	+0.080	+0.088	+0.028	0.031
CF_3	+0.106	+0.082	+0.085	+0.070	+0.214	0.015
H	+0.128	+0.070	+0.090	+0.128	+0.109	0.030
CH_3	+0.130	+0.073	+0.076	+0.064	+0.202	0.021
F	+0.276	+0.131	+0.103	+0.093	−0.176	0.014

whether benzene +1 ions are intermediates in the fluorination reaction.

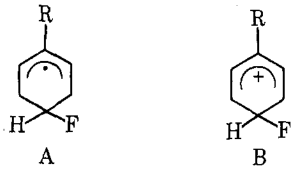
Mechanisms of Fluorination with XeF$_2$.—Fluorination of aromatic compounds with molecular fluorine in the gas phase yields only fluorine addition products and tars.[17] In view of the large amount of energy released in C–F bond formation, *ca.* 110 kcal/mol^{-1},[18] it is probable that fluorine addition products result from attack of fluorine atoms on the aromatic compound.

Recently, it has been shown that F_2 reacts with aromatic compounds at low temperatures in dilute solutions to give both addition and substitution products.[19] Substituent effects on the formation of substitution product were consistent with an ionic electrophilic substitution reaction. The reaction of benzene and substituted benzenes with XeF$_2$ bears some resemblance to the above fluorination. However, the absence of fluorine addition products suggests that neither fluorine nor fluorine atoms participate in or are produced during the reaction.

It was suggested that the mechanism of fluorination involves attack of fluoride ion on a benzene radical cation which is formed by oxidation with XeF$_2$–HF.[3] Perhaps the most important clue to the mechanism of the aromatic fluorination lies in the directional effect of the substituent. For monosubstituted benzene cation radicals, such effects have never been demonstrated.

Since the substituted benzene +1 ions were not observable by esr under the reaction conditions (nor have they ever been observed in solution), it was of interest to calculate the theoretical charge densities as a function of position and substituent in order to determine whether substituents were causing localization of positive charge, which would direct attack by F$^-$ to a particular position on the benzene ring. The Mulliken–Wofsberg–Helmhotz semiempirical method with charge interaction, as described by Carrol, *et al.*,[20] was used. The charge distributions for several positions on the aromatic +1 ions are listed in Table I. It is seen that, within the convergence limit, there does not appear to be any significant variation in charge on carbon atoms 2, 3, and 4 of the benzene ring for a given substituent. Therefore, if it is assumed that a fluoride ion or a polarized segment of a molecule equivalent to F$^-$ would attack the position of highest positive charge, it appears that substituents on these benzene +1 ions do not exert sufficiently strong orientational effects to determine the isomer distribution in the fluorinated products.

It might be postulated that the substituent effects are a function of the stability of the fluorocyclohexadienyl radical produced after attack of F$^-$ on a benzene radical cation. If the incorporation of fluorine into the benzene ring takes place *via* a fluorocyclohexadienyl radical A, substituent effects on this radical should be similar to those observed on homolytic aromatic substitution reactions. Since electron-donating substituents direct substitution predominantly to the ortho and para positions in both homolytic and electrophilic aromatic substitution reactions, the isomer distributions in these fluorinated products, cannot be used to distinguish between species A or B as potential intermediates.



A B

potential intermediate in fluorination

Fortunately, the effect of electron-withdrawing groups on the isomer distribution in the product provides a distinguishing test. The NO$_2$ substituent is particularly useful in this respect. When nitrobenzene is used, about 90% meta substitution is observed in electrophilic aromatic substitution reactions,[21] whereas less than 10% meta product is formed in homolytic aromatic substitution reactions.[22] When XeF$_2$ reacts with nitrobenzene, predominantly *m*-fluoronitrobenzene (m/(o + p) ratio = 2.4–3.9) is formed.[2] This is inconsistent with the directive effect of the NO$_2$ group in the formation of intermediate A. Therefore, it appears that a mechanism of fluorination in which fluorine enters the aromatic molecule by attack of F$^-$ on an aromatic +1 ion does *not* account for the bulk of the fluoro-aromatic compound produced.

Three mechanisms are consistent with the data thus far presented. In the first of these (Scheme II) fluorine atoms are abstracted from XeF$_2$ by a radical cation which is produced by oxidation of starting materials. The second mechanism (Scheme III) involves the rearrangement of a π complex to a σ complex in the step which determines the final isomer distribution. This mechanism is analogous to the nucleophilic-assisted two-electron transfer mechanism proposed for anodic substitution reactions.[23] On the whole this appears to be the most probable route for the incorporation of fluorine in the molecule.

In the mechanism shown in Scheme IV, a σ complex containing a xenon to carbon bond is implicated. Sta-

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(17) N. Fukuhara and L. A. Bigelow, *J. Amer. Chem. Soc.*, **63**, 2792 (1941).

(18) N. A. Sheppard and C. M. Sharts, "Organic Fluorine Chemistry," W. A. Benjamin, New York, N. Y., 1969, p 27.

(19) V. Grakauskas, *J. Org. Chem.*, **35**, 723 (1970).

(20) D. G. Carrol, A. T. Armstrong, and S. P. McGlynn, *J. Chem. Phys.*, **44**, 1865 (1966).

(21) L. M. Stock, "Aromatic Substitution Reactions," Prentice-Hall, Englewood Cliffs, N. J., 1968, p 43.

(22) G. H. Williams, *Int. Ser. Monogr. Org. Chem.*, **4**, 68 (1960).

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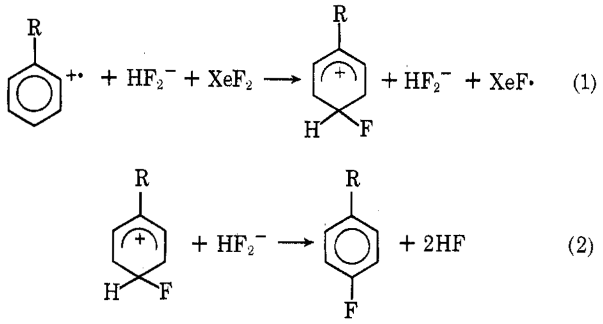
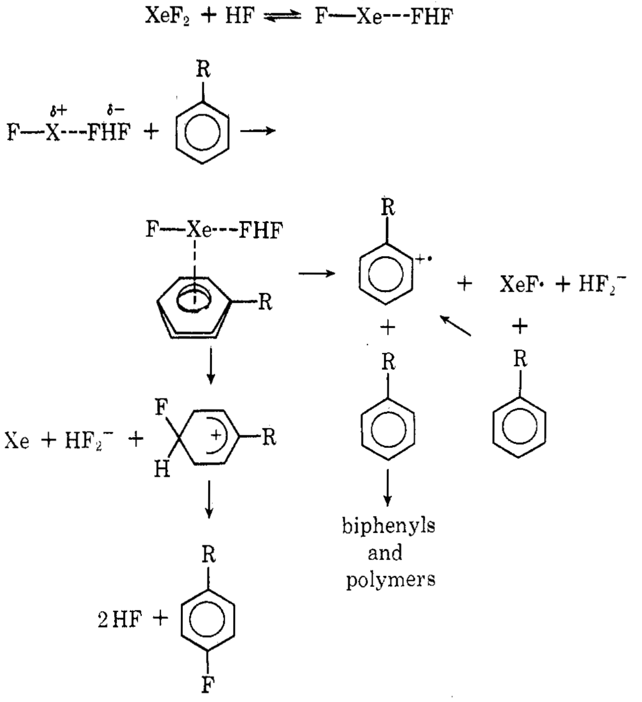
SCHEME II

A RADICAL CATION POTENTIAL MECHANISM FOR THE FLUORINATION OF AROMATIC MOLECULES WITH XeF_2



SCHEME III

A π COMPLEX POTENTIAL MECHANISM FOR THE FLUORINATION OF AROMATIC MOLECULES WITH XeF_2

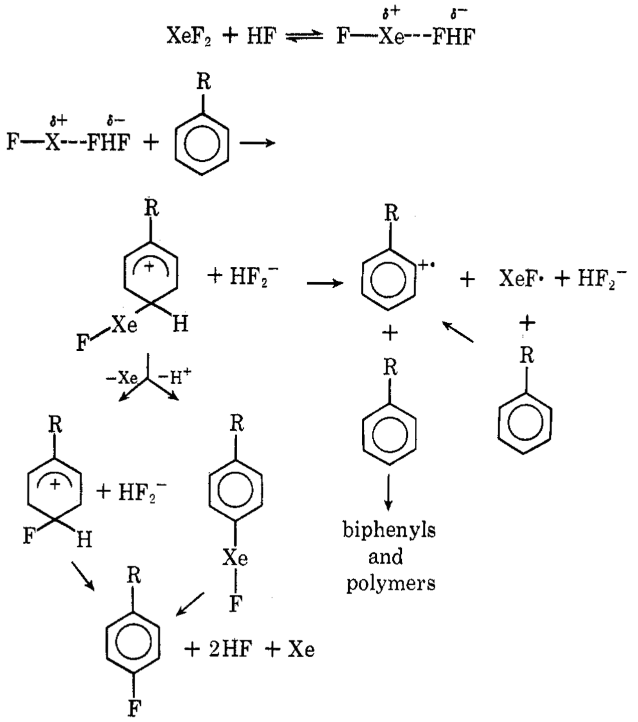


ble compounds containing xenon to carbon bonds have, as yet, not been prepared by a chemical reaction. However, bombardment of a mixture of xenon and methane with electrons in a mass spectrometer has yielded species containing Xe–C bonds.[24] Nefedov, *et al.*,[25] have observed nonvolatile xenon species to be formed on a tracer scale by the β decay of ^{131}I incorporated into iodobenzene and diphenyliodonium perchlorate, studied the xenon behavior, and concluded that the phenylxenonium ion, $C_6H_5Xe^+$, is formed. Thus, although no compounds of this nature have been reported on a macroscopic scale, compounds with xenon to carbon bonds cannot be entirely dismissed as possible intermediates in the fluorination reaction.

Effect of HCl and Cl_2 on the Fluorination Reaction.—We thought that the effect of hydrochloric acid or chlorine on the fluorination reaction might provide some insight into the mechanism. In a control experiment it was found that above *ca.* −50° HCl is slowly oxidized by XeF_2 to Cl_2. Therefore, when reactions were run in the presence of HCl at 25°, it was also necessary to consider the effect of Cl_2. Benzotrifluoride and nitrobenzene were selected for this study since the CF_3 and NO_2 groups are strongly meta directing in electrophilic aromatic substitution reactions and are ortho–para directing in homolytic aromatic substitution reactions.

SCHEME IV

A Xe BOND POTENTIAL MECHANISM FOR THE FLUORINATION OF AROMATIC MOLECULES WITH XeF_2



Before the results of these experiments are presented it is useful to note that neither benzotrifluoride nor nitrobenzene, themselves, reacted with Cl_2 under any of the experimental conditions employed. Toluene did react with Cl_2 to give substantial amounts of both benzyl chloride and ring chlorinated products and, hence, could not be used. As expected, none of the observed products are isomerized in the reaction medium. The hypothetical compound XeFCl is not formed by an exchange reaction between XeF_2 and HCl at any temperature between −75 and 25°.[26] It was necessary to consider how chlorine atoms, formed during oxidation of HCl, might react with these aromatic compounds. Chlorine atoms react with benzene to give chlorinated addition products as well as substitution products.[27] Since chlorinated addition products were not formed and predominantly meta chlorination is observed (ortho–para chlorine products would be expected for homolytic substitution on nitrobenzene), it is unlikely that reaction of chlorine atoms with nitrobenzene can account for the observed chlorinated products.

The results of these reactions are shown in Tables II and III. Several interesting features are apparent. In the presence of HCl, the formation of chloroben-

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(24) J. H. Holloway, "Noble Gas Chemistry," Methuen, London, 1968, p 59.

(25) V. D. Nefedov, M. A. Tropova, A. V. Levchenko, and U. P. Saikov, *Radiokhimiya*, **9**, 138 (1967); **10**, 611, 613, 616 (1968).

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Table II

Effect of Chlorine on the Reaction of Xenon Difluoride with Substituted Benzenes[a]

R–C_6H_5	RC_6H_5 added, mmol	XeF_2 added, mmol	HF added, mmol	Cl_2 added, mmol	%[b] RFC_6H_4 formed	Isomer distribution o	m	p	$m^c/(o+p)$ ratio	%[a] $RClC_6H_4$ formed	Isomer distribution o	m	p	$m^c/(o+p)$ ratio	% tar	Solvent
NO_2	18.8	6.1	18.0		67.9	14.5	41.8	11.6	2.4						32.1	CCl_4
NO_2	32.8	9.43	31.6	25.2	75.8	16.1	47.8	11.9	2.6	2.7	0.2	1.8	0.7	2.84	21.5	CCl_4
CF_3	23.6	7.8	5.4		79.6	25.0	43.5	11.1	1.8						20.4	CH_2Cl_2
CF_3	10.5	9.3	3.3	3.3	83.6	20.4	53.5	9.7	2.7	8.5	1.0	6.8	0.7	7.2	7.2	CH_2Cl_2
CF_3	36.6	10.6	50.0	50.0	70.5	13.4	46.3	10.8	2.9	18.9	2.5	13.9	2.5	4.2	10.6	CH_2Cl_2

[a] Reaction temperature was 25°. [b] Based on the amount of a starting material that reacted. [c] Corrected for two ortho and two meta positions.

Table III

Effect of HCl on the Reaction of Xenon Difluoride with Substituted Benzenes[a]

R–C_6H_5	RC_6H_6 added, mmol	XeF_2 added, mmol	HCl added, mmol	HF added, mmol	%[b] RFC_6H_4 formed	Isomer distribution o	m	p	$m^c/(o+p)$ ratio	%[a] $RClC_6H_4$ formed	Isomer distribution o	m	p	$m^c/(o+p)$ ratio	% tar	Solvent
NO_2	34.2	9.3		14.9	81.2	18.9	50.9	11.4	2.9						22.0	CH_2Cl_2
NO_2	33.7	9.7	16.7		40.1	13.5	23.9	2.7	2.2	31.1	6.9	21.3	3.0	3.2	28.8	CH_2Cl_2
NO_2	18.8	6.1		18.0	67.9	14.5	41.8	11.6	2.4						32.1	CCl_4
NO_2	27.6	8.8	23.7		29.7	9.3	16.3	4.1	1.8	41.5	5.0	34.3	2.2	7.1	29.8	CCl_4
CF_3	23.6	7.8		5.4	79.6	25.0	43.5	11.1	1.8						20.4	CH_2Cl_2
CF_3	60.0	17.3	8.2[d]		48.3	16.8	23.4	8.1	1.4	48.9	9.9	32.4	6.6	2.9	2.8	CH_2Cl_2

[a] Reaction temperature was 25°. [b] Based on the amount of starting material that reacted. [c] Corrected for two ortho and two meta positions. [d] After reaction it was found that 0.2 mmol of Cl_2 was present.

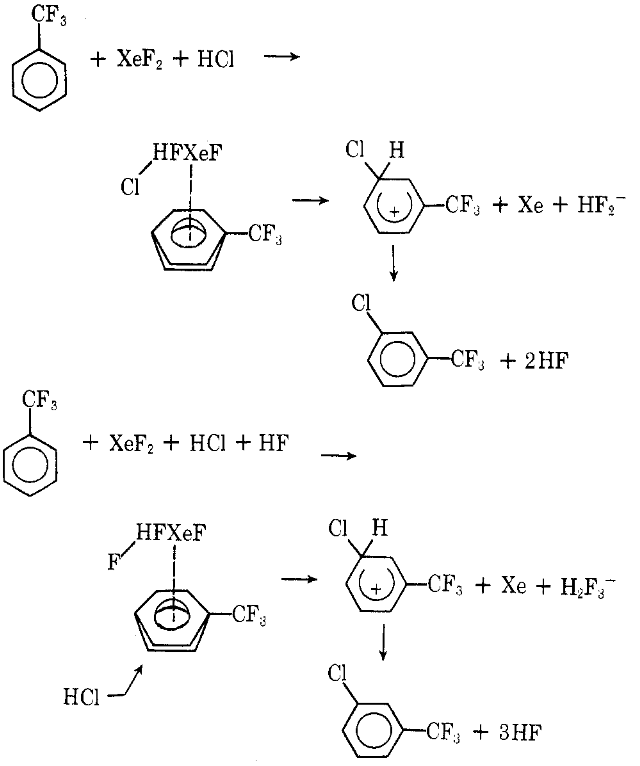
zenes is competitive with the formation of fluorobenzenes. Even when a large excess of Cl_2 is used only low yields of chlorobenzenes are obtained. Thus, it is clear that the significant yields of chlorobenzenes when HCl is used do not arise from a reaction involving Cl_2.

The question then arises, "How are chlorobenzenes produced when HCl instead of HF is added?" Since predominantly meta orientation by the CF_3 and NO_2 groups is observed in both the fluorination and chlorination reactions, the argument used above with reference to reaction of a fluoride ion would be applicable and, thus, it is unlikely that the bulk of the chlorinated product is formed by reaction of a monomeric radical cation with Cl^-. Addition of Cl_2 results in the formation of small amounts of chlorobenzotrifluoride (at the expense of tar formation), without, however, significantly affecting the yield of fluorobenzotrifluoride. This suggests that reaction of a radical cation with Cl_2 may be a side reaction. Reaction of a radical cation with Cl· would be less probable since the concentration of both species would be very low. However, these reactions cannot account for the high yield of chlorobenzotrifluoride when HCl is used. Thus, the formation of a complex between the aromatic and the xenon bearing molecule appears to be an essential part of the reaction mechanism.

In Scheme V we have illustrated two ways in which HCl may be incorporated in that complex. The essential difference between these two possibilities is the function of HCl. In one hypothesis, HCl is both a catalyst, polarizing the XeF bond, and a reagent, serving as a source of Cl^-. In the second HCl is only a source of Cl^-.

Scheme V

Role of HCl in Reaction of Aromatic Molecules and XeF_2



We find, however, that HCl is not an effective catalyst for reaction of XeF_2 with the aromatics. Xenon difluoride reacted immediately with benzotrifluoride at −75° when HF was used as a solvent to give a 50% yield of fluorobenzotrifluoride. However, when anhydrous HCl was used as the solvent, no reaction took place at −75° after 2 days. It is therefore clear that HCl does not polarize the Xe–F bond sufficiently to permit reaction with benzotrifluoride. Since HF is produced by oxidation of HCl with XeF_2 at the reaction temperature (25°), HF, not HCl, is the catalyst in these reactions, but HCl may still react with the complex as shown in Scheme V to incorporate chlorine in the aromatic molecule. This suggests that the fluorine, which is incorporated into aromatic compound, is derived from HF, not XeF_2. Summarizing our analysis at this point, the mechanism of fluorination of aromatic compounds with XeF_2 is best described by a process which is formally analogous to the nucleophile assisted two-electron transfer mechanism proposed for anodic oxidation substitution reaction, namely the formation of a complex between the aromatic molecule and an XeF_2–HF polarized molecule followed by reaction with HF and elimination of Xe.

Summary.—The products and characteristics of the reactions of xenon difluoride with aromatic compounds are best explained by a mechanism which involves the reaction between a complex of XeF_2 with HF a substituted benzene to yield an intermediate neutral complex molecule which may either react with HF and rearrange to give a fluorobenzene or fragment to give a monocyclic radical cation which then reacts to form a biphenyl. A competition study has provided presumptive evidence for monocyclic radical cations as intermediates in the formation of the observed biphenyls. The effects of HCl and Cl_2 on the reaction are consistent with this mechanism.

Experimental Section

The method of carrying out the reaction of XeF_2 with a number of aromatic molecules while varying solvent, temperature, and other reaction conditions and separating and analyzing the products both qualitatively and quantitatively has been described previously in detail.[2] In brief, purified reagents are handled in polychlorotrifluoroethylene equipment with air rigorously excluded, the rate of reactions controlled by adjusting the temperature or concentration of HF, products separated and quantitatively estimated using a variety of gas chromatographic columns, products characterized largely by ir, mass spectroscopic, and nmr techniques. The results of these experiments are basic to the development of the concepts stated in this paper.

Specific additional experiments carried out for this paper include the competitive reaction between nitrobenzene and benzene and the effect of Cl_2 and HCl on the reaction of XeF_2 with nitrobenzene and benzotrifluoride.

Cl_2 was reagent grade and used as available. Anhydrous HCl was purified in the following manner. A tank containing commercial "anhydrous HCl" was cooled to −75°, after which a measured amount was tranferred *in vacuo* to a 120-cc Kel-F tube at −196°. The tube, at −196°, was then evacuated to 5×10^{-6} Torr to remove O_2. The infrared spectrum of the resulting material revealed only the presence of HCl. These experiments were carried out exactly as described in ref 2, adding either Cl_2 or HCl at the start of the reaction in the amounts shown in Tables II and III, respectively. The competitive reaction experiment was carried out as follows.

Competitive Reaction between Nitrobenzene and Benzene with XeF_2.—A solution of 0.0288 mol of benzene and 0.0195 mol of nitrobenzene in 15.46 g of CH_2Cl_2 in a 29-cc Kel-F tube was degassed by the freeze–thaw technique until the change in pressure upon opening the tube to the pumping manifold was less than 10^{-5} Torr. The solution was then decanted *in vacuo* into another 29-cc Kel-F tube containing 0.019 mol of XeF_2 whose infrared spectrum indicated the absence of HF and XeF_4. The solution was frozen at −125° and *ca.* 0.03 mol of HF was added. Reaction began immediately after removal of the cooling bath as indicated by appearance of a dark green color and evolution of gas into a ballast volume. The reaction mixture was allowed to warm slowly to room temperature with occasional application of a Dry Ice bath to control the rate of gas evolution. The total reaction time was 2 hr. Xe (1 mol) was evolved per mol of XeF_2 used. Mass spectral analysis of the gas phase indicated the presence of *ca.* 5×10^{-5} mol of H_2. The gas phase was condensed into 1.000 *M* NaOH which was back-titrated with 1.000 *M* HCl. In this manner it was determined that *ca.* 0.011 mol of HF was generated in the reaction.

The liquid phase was distilled at 25° *in vacuo* into a 29-cc Kel-F tube by application of a liquid nitrogen bath. Comparison of the infrared spectrum of the distillate with known solutions indicated the presence of benzene and fluorobenzene. Gas chromatographic analysis of the distillate, using a flame ionization detector and a 15 ft × 0.25 in. column of 8.5% diethylene glycol succinate on Chrom G 70–80 mesh, revealed the presence of 0.74 g of benzene, 0.20 g of fluorobenzene, and a trace of *p*-difluorobenzene.

Fractional sublimation of the nonvolatile products at 225° and 0.4 Torr (conditions under which all nitro dimers would sublime) yielded 0.5 g of residue and 3.15 g of sublimate. Analysis of the sublimate on a 6 ft × $^1/_8$ in. 3% silicone oil (SF96) on Chrom G 80–100 column at 100° gave 2.11 g of nitrobenzene and 0.84 g of a mixture of biphenyl and fluorobiphenyl and indicated the absence of fluoronitrobenzenes. Mass spectral analysis indicated that the mixture of biphenyl and fluorobiphenyl was predominantly the former. At 175°, the column described above was capable of separating all three isomers and nitrobiphenyl. Chromatography of the sublimate at this temperature revealed the absence of all three nitrobiphenyls. It is estimated that if 1 mg of nitrobiphenyl had been present, it would have been detected. Using a mass spectrometer (Perkin-Elmer 270) as the detector, the presence and absence of the above products was further established, and also, trace amounts of polyfluorobiphenyls and terphenyls were found. Elemental analysis of the polymer gave N, 3.33; C, 77.5; H, 3.99; F, 5.5%. After correction for substituents, a C/H ratio of 1.45 is calculated and comparison of the limiting C/H for polyphenyl of 1.5 with the observed C/H ratio indicates a polyphenyl structure. The absence in the infrared region of the 3035-, 1603-, 1575-, 1190-, and 890-cm^{-1} bands for low-molecular-weight polyphenyls[28] indicates a high-molecular-weight polymer. The 695-cm^{-1} band in high-molecular-weight polyphenyls[28] was observed. The spectrum exhibited a strong C–F band and was further characterized by the complete absence of the characteristic NO_2 absorptions. Thus, it appears that the nitrogen in the polymer arises from a reaction other than ring to ring dimerization. No trace of chlorobenzene or chlorobiphenyl was found.

Mass balance was achieved within experimental error, *i.e.*, 2.39 g of nitrobenzene added and 2.11 g recovered; 2.25 g of benzene added and 0.74 g recovered, plus 0.20 g of fluorobenzene, 0.84 g of a mixture of biphenyl and fluorobiphenyl, and 0.54 g of polymer.

Registry No.—Xenon difluoride, 13709-36-9; nitrobenzene, 98-95-3; benzene, 71-43-2; $CF_3C_6H_5$, 98-08-8; $CH_3C_6H_5$, 108-88-3; FC_6H_5, 462-06-6.

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[28] C. S. Marvell and G. E. Hartzell, *J. Amer. Chem. Soc.*, **81**, 448 (1959).