Reactions of Xenon Fluorides with Organic Compounds[1,2]

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The fluorination of unsaturated and aromatic compounds with xenon fluorides was investigated. Unsaturated aliphatic compounds gave products which mainly arose from fluorine addition accompanied by rearranged products. The products which apparently were derived from HF addition were also obtained in the reaction of cyclohexene and of propyne. Aromatic compounds, except hexafluorobenzene, react with xenon fluorides to give ring substitution products. No side-chain fluorination of alkyl benzenes was detected. Competitive fluorinations of benzene–toluene and toluene–fluorobenzene mixtures with xenon tetrafluoride were also studied. Possible mechanisms for these reactions are discussed.

The direct addition of fluorine to unsaturated organic compounds has been difficult to control since the addition is usually complicated by accompanying substitution or cleavage of the carbon chain.[6] Recently, Merritt and coworkers have successfully modified the technique of direct fluorination with molecular fluorine by adding elemental fluorine to solutions of organic compounds in $CFCl_3$ at $-78°$ which circumvents the problems of charring, substitution, and fragmentation.[7] The reaction apparently proceeds *via* a polar mechanism. The discovery of xenon fluorides[8] made available a series of fluorinating agents which appeared to be capable of selective fluorination. An investigation of the reactions of xenon fluorides with unsaturated organic compounds might lead not only to improved techniques of fluorination but also to an increased understanding of the chemistry of xenon compounds. In this report we wish to describe the reaction of xenon fluorides with a number of aliphatic unsaturated compounds and aromatic compounds. Shaw, Hyman, and Filler reported recently that xenon difluoride reacts with benzene in a carbon tetrachloride solution and a catalytic amount of hydrogen fluoride to give fluorobenzene in 68% yield.[9] The solvent apparently has a moderating effect on this reaction.

Results

Fluorination of Unsaturated Aliphatic Compounds.— The three fluorides of xenon, XeF_2, XeF_4, and XeF_6, are known to be progressively more reactive.[10] Perfluoropropene was fluorinated smoothly by XeF_4 to give perfluoropropane, but apparently not by XeF_2.

This observation suggests that XeF_2 may not be an intermediate in the reaction of XeF_4 and perfluoropropene. The use of XeF_6 resulted in the fragmentation of perfluoropropene as indicated by the formation of CF_4 and C_2F_6.

Ethylene reacts with XeF_2 or XeF_4 to give 1,1- and 1,2-difluoroethane in 35 and 45% yields, respectively, together with 20% yield of 1,1,2-trifluoroethane, which was not identified previously.[2] Both 1,2-difluoroethane and 1,1,2-trifluoroethane were identified by their characteristic nmr spectra. Although a rather complex nmr spectrum was obtained for the trifluoroethane, the assignments of individual proton with specific coupling constants may be made unambiguously.

Fluroination of propene was more complex than that of ethylene. When propene was fluorinated with XeF_2, a volatile mixture containing six components besides xenon and propene was obtained. The following four compounds were either identified or tentatively identified: a difluoroethane, 2-fluoropropane, 1,1- and 1,2-difluoropropane in 9, 24, 46, and 12% glc area, respectively. Two minor components which totaled about 10% glc area were not characterized. The difluoroethane was tentatively identified as 1,1-difluoroethane by comparison of its mass spectrum with an authentic sample. Other compounds were characterized by their spectral properties. In the case of 1,2-difluoropropane, the 2 proton was not assigned probably due to the extensive coupling with geminal and neighboring protons and fluorines. When propene was fluorinated with XeF_4, the products obtained were more complex than those from XeF_2 reaction. Only 1,1-difluoropropane (65% glc area) and 1,2-difluoropropane (12% glc area) could be isolated and identified.[11]

Cyclohexene was fluorinated with XeF_4 with the hope that the isolation and characterization of 1,2-difluorocyclohexane might enable us to study the stereochemistry of fluorine addition. The main products, however, were found to be fluorocyclohexane (50%), 4-fluorocyclohexene (9%), and three or four difluorocyclohexanes (30%). The presence of difluorocyclohexane was indicated by nmr spectra which exhibited low-field protons and high-field protons in 1:4 ratio. None of the difluorides were the 1,1 isomer by reference to the ir spectrum of an authentic sample.

Propyne was found to be resistant to XeF_2 fluorination. After 100 days at room temperature, it gave a

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(2) A preliminary account of this work has been communicated: see T. C. Shieh, N. C. Yang, and C. L. Chernick, *J. Amer. Chem. Soc.*, **86**, 5021 (1964).

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(6) For example, see M. Hudlicky, "Chemistry of Organic Fluorine Compounds," Pergamon Press, New York, N. Y., 1961, p 68.

(7) (a) R. F. Merritt and T. E. Stevens, *J. Amer. Chem. Soc.*, **88**, 1822 (1966); (b) R. F. Merritt and F. A. Johnson, *J. Org. Chem.*, **31**, 1859 (1966); (c) R. F. Merritt, *ibid.*, **31**, 3871 (1966); (d) R. F. Merritt, *J. Amer. Chem. Soc.*, **89**, 609 (1967).

(8) (a) H. H. Claassen, H. Selig, and J. G. Malm, *ibid.*, **84**, 3593 (1962); (b) J. L. Weeks, C. L. Chernick, and M. S. Matheson, *ibid.*, **84**, 4612 (1962); (c) J. G. Malm, I. Sheft, and C. L. Chernick, *ibid.*, **85**, 110 (1963); (d) D. F. Smith, *J. Chem. Phys.*, **38**, 270 (1963); (e) E. E. Weaver, B. Weinstock, and C. P. Knop, *J. Amer. Chem. Soc.*, **85**, 111 (1963).

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

(10) N. Bartlett, *Endeavour*, **23**, 3 (1964).

(11) An equation showing the reaction of XeF_4 and propene to give 1,2-difluoropropane and XeF_2 as products was given without any other details in the literature: C. G. Krespan, *Science*, **150**, 13 (1965).

33% yield of 2,2-difluoropropane and at least nine other compounds, all of which are less than 10% of the principal product.

Fluorination of Aromatic Compounds.—Direct fluorination of benzene or toluene yields saturated compounds such as perfluorocyclohexane and fluorinated ring fragments.[12,13] Recently Shaw, Hyman, and Filler reported the fluorination of benzene with XeF_2 in CCl_4 to give fluorobenzene in 68% yield.[9] The fluorination of aromatic compounds with XeF_4 took place mainly as ring substitution rather than addition to the ring and gave apparently no products arising from side-chain substitution.

The reaction of XeF_4 with benzene at room temperature gave fluorobenzene in 13% yield together with very small amounts of biphenyl and fluorobiphenyls. Apparently only a small fraction of benzene is fluorinated, but it is fluorinated rather extensively.

Toluene is qualitatively more reactive with XeF_4 than is benzene, and the reaction appears to be more exothermic. The products consisted mainly of o-, m-, and p-fluorotoluene in 17.2, 3.2, and 12.4% yields, respectively. No benzyl fluoride was detected. Cumene was then reacted with XeF_4 with the hope that the tertiary hydrogen of the alkyl chain might be more reactive to fluorine substitution than the corresponding primary hydrogens of toluene. However, the reaction products contained a mixture of three isomeric fluorocumenes (13% total yield), fluorobenzene, and two other compounds which are apparently difluorocumenes, but no α-fluorocumene.

The main fluorinated products obtained from the reaction of fluorobenzene and XeF_4 were o-, m-, and p-difluorobenzene in 5, 2, and 21% yields, respectively. A small amount of a mixture consisting of polyfluoro aromatic compounds and other saturative fluorination products was also present, from which only 4,4'-difluorodiphenyl could be identified.

Hexafluorobenzene can react with a fluorinating agent only by addition to the aromatic system. After 25 days of contact with XeF_4 at room temperature, hexafluorobenzene gave perfluorocyclohexene (11%), perfluoro-1,4-cyclohexadiene (20%), and perfluoro-1,3-cyclohexadiene (4%).

Competitive Fluorination of Benzene–Toluene and Toluene–Fluorobenzene Mixtures with XeF₄.—In connection with the study of relative rates of fluorination of aromatic compound with XeF_4, competitive fluorination of benzene–toluene mixtures were studied. If the ratio of the two competitive rates is expressed as

$$\frac{d[T]}{d[B]} = \frac{k_T[T][X]}{k_B[B][X]}$$

where [T], [B], and [X] are the concentration of toluene, benzene, and XeF_4, respectively, then

$$\frac{k_T}{k_B} = \frac{\ln([T_i]/[T_f])}{\ln([B_i]/[B_f])}$$

where i and f denote initial and final concentrations of the reactants. Table I summarizes the results of competitive fluorination of benzene–toluene with XeF_4, and the value of k_T/k_B is estimated to be 1.9.

(12) N. Fukuhara and L. A. Bigelow, *J. Amer. Chem. Soc.*, **63**, 2793 (1941); G. H. Cady, *et al.*, *Ind. Eng. Chem.*, **39**, 290 (1947).

(13) R. N. Haszeldine and E. G. Walaschewski, *J. Chem. Soc.*, 2689 (1950).

TABLE I
CONTENTS OF LIQUID DISTILLATE AFTER THE COMPETITIVE
FLUORINATION OF A BENZENE–TOLUENE MIXTURE

Compd	Mg	Mmol	% of yield[b]
Benzene, initial			
	424	5.43	
final	271[a]	3.47	
Toluene, initial	485	5.17	
final	204[a]	2.22	
Fluorobenzene	30[a]	0.31	17.0
o-Fluorotoluene	56[a]	0.50	17.0
m- and p-fluorotoluene	51[a]	0.46	15.5

[a] Weights were determined by comparison with glc areas from mixtures of known compositions. [b] Based on aromatic compound consumed.

Similarly for competitive fluorination of a toluene–fluorobenzene mixture, a ratio of $k_T/k_{FB} = 1.1$ was obtained where FB is fluorobenzene.

The competitive ratios are, however, not consistent with the gross reactivity of these compounds with XeF_4; the reaction of toluene is essentially complete in less than 1 hr, benzene, a few hours, and fluorobenzene, 16 hr.

Futile Attempts in the Synthesis of an Organo-Xenon Compound.—Xenon is already known to form stable compounds with fluorine,[8,14] oxygen,[10,14] and chlorine.[15] A sufficiently electronegative organic moiety might also combine with xenon to form an organo-xenon compound with transient stability. Several attempts were made to synthesize compounds of the type R_fXeF_n where R_f is a perfluoroorganic group. It has already been shown that no organo-xenon compound was isolated in the addition of xenon fluorides to perfluoropropene as the intermediate. Neither the irradiation of a mixture of CF_4 and xenon with a Co^{60} source at $-196°$ nor the photolysis of hexafluorobenzene with XeF_4 at 254 nm gave any indication of the existence of an organo-xenon compound of transient stability.

Discussion

Xenon tetrafluoride react with most unsaturated compounds upon contact at room temperature or below, and react with moisture to give highly shock-sensitive xenon oxides. Due to the high reactivity and moisture sensitivity of XeF_4, a thorough investigation on the mechanism of its reaction with organic compounds will be rather difficult experimentally. Another difficulty in this mechanistic investigation is that F atom, F_2, or XeF_3 may be generated among the products which will react with the substrates more vigorously than the xenon fluorides and the reactions may be autocatalytic after the initial step.

Among three fluorides of xenon, XeF_2, XeF_4 and XeF_6, their reactivities with organic compounds correlate inversely with the strength of Xe–F bond in the respective fluorides. The reactivity increases as the number of F atoms attached to xenon increases or as the strength of Xe–F bond decreases;[10] for examples, XeF_4 reacts with perfluoro olefins while XeF_2 does not, XeF_4 reacts with aromatic compounds in the absence of

(14) H. H. Hyman, Ed., "Noble Gas Compounds," The University of Chicago Press, Chicago, Ill., 1963.

(15) H. Meinert, *Z. Chem.*, **6**, 71 (1966); S. F. A. Kettle, *Chem. Ind. (London)*, 1846 (1966).

catalysts while XeF_2 does so only in the presence of acids,[9] and XeF_6 reacts with organic compounds with extensive fragmentation. Since all our investigations were carried out in the absence of solvents, radical intermediates are usually favored under nonpolar conditions, but tightly bound ionic intermediates cannot be excluded from consideration.

In view of the fact that the relative reactivities of benzene, toluene, and fluorobenzene with xenon tetrafluoride are qualitatively similar to other radical substitution reactions (Table II), these reactions may

TABLE II
RELATIVE REACTIVITIES OF AROMATIC COMPOUNDS IN RADICAL SUBSTITUTION AREAS

Compd	Relative reactivities with			
	C_6H_5[a]	CH_3[b]	CF_3[c]	XeF_4
Benzene	1.0	1.0	1.0	1.0
Toluene	1.7	1.65	1.43	1.9
Fluorobenzene	1.3	2.2	0.35	1.8
Hexafluorobenzene		0.04		
Biphenyl	4.0	5.0		

[a] G. H. Williams, "Homolytic Aromatic Substitution," Pergamon Press, New York, N. Y., 1960, p 57. [b] *Ibid.*, p 101. [c] S. W. Charles, J. T. Pearson, and E. Whittle, *Trans. Faraday Soc.*, **59**, 1156 (1963).

proceed *via* radical intermediates. The formation of biphenyl and polyphenyl derivatives may also be justified with similar intermediates. Such interpretation is similar to the mechanism suggested by Hyman and Filler for the reaction of XeF_2 with benzene.[9] However, no side-chain fluorination was detected in the case of toluene or cumene, in contrast to most radical substitution reactions. The lack of reactivity of α hydrogen in radical aromatic substitution is not without analogy in the literature. Whittle and coworkers had shown that CF_3 radical reacts with toluene-α-d_3 to give predominantly CHF_3 indicating that hydrogen abstraction from side chain is not an important process in this reaction.[16] Similar observation had been made by Wilen and Eliel in the reaction of CH_3 radical with deuterated toluene.[17] In the series of radicals, CCl_3, CH_3, and CF_3, radical attack on aromatic systems becomes increasingly more important as the strength of the newly formed bond becomes higher.[18] The C–F bond is among the strongest covalent bonds known.[19] It is probable that xenon fluorides and fluorine atoms may prefer to attack the aromatic ring rather than the side chain. The formation of fluorobenzene from cumene may involve the direct attack of fluorine atom on C-1 followed by elimination of a 2-propyl radical, an analogous reaction has also been noted in the literature.[18] The formation of various products in the reaction of XeF_4 with aromatic compounds may be represented by the following sequence of reactions 1–4.
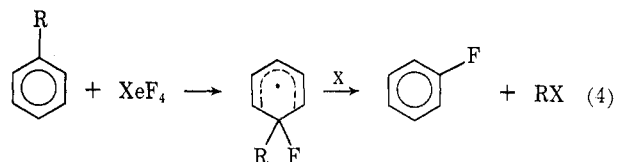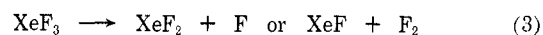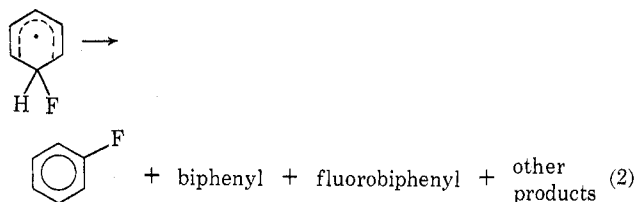

$$(1)$$
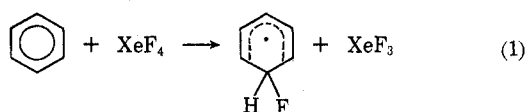
(16) S. W. Charles, J. T. Pearson, and E. Whittle, *Trans. Faraday Soc.*, **57**, 1356 (1961); S. W. Charles and E. Whittle, *ibid.*, **56**, 794 (1960).

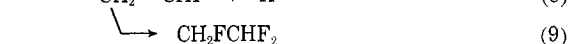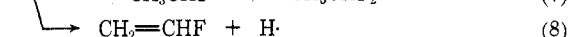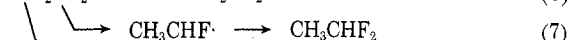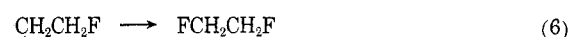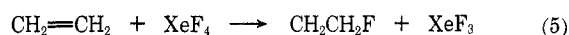(17) S. H. Wilen and E. L. Eliel, *J. Amer. Chem. Soc.*, **80**, 3309 (1958).

(18) S. W. Charles, J. T. Pearson, and E. Whittle, *Trans. Faraday Soc.*, **59**, 1156 (1963).

(19) S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965).

$$(2)$$

$$XeF_3 \longrightarrow XeF_2 + F \text{ or } XeF + F_2 \quad (3)$$

$$(4)$$

However, this explanation should be accepted with caution. Polar intermediates have been suggested in the reaction of xenon difluoride with inorganic compounds,[20] and the reaction between xenon difluoride and benzene is catalyzed by HF.[9] Therefore, ionic mechanisms can by no means be excluded from consideration.

We suggest that the reaction between xenon fluorides and aliphatic unsaturated compounds also proceed *via* radical intermediates. The reaction of ethylene with either XeF_4 or XeF_2 gives a mixture of 1,2-difluoroethane, 1,1,2-trifluoroethane, and 1,1-difluoroethane. Ethylene may react with xenon fluorides to give a 2-fluoroethyl radical (reaction 5). This radical may react further to give 1,2-difluoroethane (reaction 6), may rearrange to give 1-fluoroethyl radical which will react further to give 1,1-difluoroethane (reaction 7) or may lose a hydrogen atom to give fluoroethylene. The cleavage of a β-C–H bond in this radical is favored over that of the stronger β-C–F bond.[19] Fluoroethylene will then add an element of F_2 to give the trifluoroethane (reaction 9).[7c] 1,1-Difluoroethane is not formed *via* the rearrangement of 1,2-difluoroethane under the reaction condition.

$$CH_2{=}CH_2 + XeF_4 \longrightarrow CH_2CH_2F + XeF_3 \quad (5)$$

$$CH_2CH_2F \longrightarrow FCH_2CH_2F \quad (6)$$

$$\longrightarrow CH_3CHF{\cdot} \longrightarrow CH_3CHF_2 \quad (7)$$

$$\longrightarrow CH_2{=}CHF + H{\cdot} \quad (8)$$

$$\longrightarrow CH_2FCHF_2 \quad (9)$$

Formation of HF adducts, such as fluorocyclohexane from cyclohexene and 2,2-difluoropropane from propyne, may be attributed to the addition of HF formed in the substitution reactions to the unsaturated compounds.

Caution.—Xenon tetrafluoride is concerted into highly shock-sensitive xenon oxides with moisture. All necessary precautions given in the literature are to be taken.[21] Although XeF_2 is relatively safe to be handled, it may be contaminated with small amounts of XeF_4.[21d] It should also be handled with caution.

(20) N. Bartlett and F. O. Sladky, *Chem. Commun.*, 1045 (1968).

(21) (a) J. G. Malm and C. L. Chernick, *Inorg. Syn.*, **8**, 254 (1966); (b) C. L. Chernick, *J. Chem. Educ.*, **43**, 619 (1966); (c) J. H. Holloway, *Talanta*, **14**, 871 (1967); (d) W. E. Falconer and W. A. Sunder, *J. Inorg. Nucl. Chem.*, **29**, 1380 (1967).

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Infracord, a Beckman IR-7, or a Beckman IR-12 spectrophotometer; nmr spectra on a Varian Associates A-60 or A-56-60A spectrometer; mass spectra on an AEI MS-9 mass spectrometer. Gas chromatography separations were obtained with a Varian-Aerograph 90-P, 90-P-2, or 200 chromatograph with a column of silica gel, 28-200 mesh (0.95 cm × 3.1 m) for the separation of permanent gases, a column of 20% Carbowax 20M on 45-60 mesh Chromosorb P (0.95 cm × 6.1) for the aliphatic compounds, or a column of 20% Zonyl E-7 on 60-80 mesh Chromosorb P (HMDS treated, 0.95 cm × 4.6 m) for the aromatic compounds. The gc areas from the recorder chart were calculated by triangulation or with a Disc Integrator, Disc Instruments, Inc. Elemental analyses were performed by Mr. William Saschek of the University of Chicago or by the Micro-Tech, Inc., of Skokie, Ill.

Material.—Benzene (Mallinckrodt, reagent grade), toluene (Matheson Coleman and Bell), cumene (Eastman), and cyclohexene (J. T. Baker) were distilled over sodium through a tantalum spiral column rated at eight theoretical plates and stored over sodium wire until needed. Fluorobenzene (Pierce) was purified in the same way but without sodium. Hexafluorobenzene (Pierce) was purified by preparative gc. Tetrafluoromethane (99.7% min), ethylene (99.5% min), and propene (99.0% min) were purchased from the Matheson Company in the stated purities and were used without further purification. Propyne from the same source (96.0% min) was purified by removal of the impurities that were volatile at −112° (N_2-CS_2 slurry) *in vacuo.* Perfluoropropene (Peninsular) was purchased and used without further purification.

Xenon Fluorides.—The three xenon fluorides were prepared and purified by the published methods.[21a,d]

General Procedure.—The apparatus used was of the same type for the preparation of xenon fluorides.[21] Purified reactants were condensed at −196° in a 130-ml Ni vessel. The vessel was allowed to warm up to room temperature, and the course of reaction was followed by observing the change in pressure. It was assumed that the reaction had reached completion when no further change in pressure was noted. In cases where reactions were carried out in a quartz-made vessel, it was heated to 400° prior to use and evacuated overnight through the manifold to a pressure of 10^{-4} mm or less. The reaction products were first separated at the vacuum line by trapping at different temperatures and by gas chromatography. They were identified by their ir, nmr, and/or mass spectra.

Fluorination of Perfluoropropene.—A mixture of XeF_4 (0.156 g, 0.75 mmol) and perfluoropropene (0.192 g, 1.28 mmol) was allowed to react for 4 days. The mixture was distilled at −78°. The volatile materials (0.320 g) condensed at −196° and gave an ir spectrum identical with that of perfluoropropane (Matheson), and its gc analysis showed only xenon and perfluoropropane. The residue was shown to be the excess XeF_4 (0.023 g, 0.11 mmol, recovered) by examination of its ir spectrum. The reaction was 94% complete in 15 hr as determined by the vapor pressure of reaction mixture.

The reaction of XeF_2 (0.566 g, 3.35 mmol) with perfluoropropene (0.258 g, 1.71 mmol), after 6 days, gave 5% yield of perfluoropropane. The unreacted XeF_2 was recovered unchanged in 94% yield.

Fluorination of perfluoropropene (0.396 g, 2.64 mmol) with XeF_6 (0.201 g, 0.82 mmol) gave an organic mixture containing tetrafluoromethane (22%), perfluoroethane (19%), perfluoropropane (1%), and perfluoropropene (58%). Composition of the mixture was determined by the gc area. The residue (0.35 g) was not analyzed.

Fluorination of Ethylene.—Ethylene (0.220 g, 7.9 mmol) was brought into reaction with XeF_4 (0.958 g, 4.6 mmol) for 18 hr. The volatile materials showed three peaks besides xenon and ethylene in gc. The three compounds were separated and collected by preparative gc. Following a very small amount of unreacted ethylene, the first peak was identified to be 1,1-difluoroethane (35%) by comparison of its ir and nmr spectra to those of an authentic sample (Matheson). The second peak was 1,1,2-trifluoroethane (20%) as identified by its nmr spectrum: (CCl_4) δ 4.4 (d, t, d, 2 H, −CH_2F, $J_{HF(gem)}$ = 47 cps, $J_{HF(vic)}$ = 12.5 cps, J_{HH} = 4 cps), and 5.9 ppm (t, d, t, 1 H, −CHF_2, $J_{HF(gem)}$ = 55 cps, $J_{HF(vic)}$ = 5.5 cps, J_{HH} = 4 cps). The last peak was identified as 1,2-difluoroethane (45%) by its nmr

spectrum: (CCl_4) δ 4.5 ppm (d, d, J_{HF} = 77 cps, J_{HH} = 8.5 cps).

A mixture of XeF_2 (0.282 g, 1.67 mmol) and ethylene (0.034 g, 1.19 mmol) gave after 4 days identical products in similar yields as obtained from the reaction with XeF_4.

A solution of 1,2-difluoroethane of gc purity in CCl_4 was allowed to stand at room temperature for 2 weeks. The gc analysis showed only 1% area corresponding to 1,1-difluoroethane.

Fluorination of Propene.—Reaction of propene (0.330 g, 7.9 mmol) with XeF_2 (0.668 g, 3.9 mmol) resulted after 12 days in a mixture containing six components besides xenon and propene. The gc fractions were collected directly into nmr tubes containing a $CHCl_3$-CCl_4 mixture which would not freeze at −78°. The following compounds were identified: 2-fluoropropane (24% gc area) by comparison of its mass[22] and nmr[23] spectra with the published data; a difluoroethane (9% gc area) by comparison of its mass spectrum with 1,1-difluoroethane; 1,1-difluoropropane (46% gc area) by its nmr spectrum [δ 1.0 (t, 3 H, CH_3-, J = 7.2 cps), 1.8-2.0 (m, 2 H −CH_2-), and 5.8 ppm (t, t, 1 H, −CHF_2, J_{HF} = 58 cps, J_{HH} = 4.5 cps)], and by its mass spectrum [parent peak at m/e 80 ($C_3H_6F_2$)]; 1,2-difluoropropane (12% gc area) by its nmr spectrum [δ 1.4-1.5 (d, d, d, 3 H, −CH_3-, J_{HF} = 23 cps, J_{HH} = 6.5 cps, $J_{1,3-HF}$ = 1.5 cps), 4.5 ppm (d, d, d, 2 H, −CH_2F, $J_{HF(gem)}$ = 47 cps, $J_{HF(vic)}$ = 23-24 cps, J_{HH} = 5 cps)], the −CHF− was not detected apparently due to extensive coupling with neighboring H and F atoms, and mass spectral P − 1 peak, m/e 79 ($C_3H_5F_2$). About 10% of the gc area was not assigned. All products were volatile.

When propene (0.374 g, 8.91 mmol) was fluorinated with XeF_4 (0.803 g, 3.88 mmol) for 2 days, a complex mixture was obtained, in which only 1,1-difluoropropane (65% gc area) and 1,2-difluoropropane (12% gc area) could be collected and identified.

Fluorination of Cyclohexene.—Cyclohexene (1.139 g, 12.2 mmol) was fluorinated with XeF_4 (0.522 g, 2.67 mmol). After the reaction the liquid distillate (0.619 g) contained fluorocyclohexane (50% gc area), ir spectrum identical with an authentic sample;[24] 4-fluorocyclohexene (9% gc area), ir spectrum identical with an authentic sample,[25] nmr (CCl_4) δ 2.1 (m, 6 H), 4.7 (t, d, 1 H, −CHF−, J_{HF} = 48 cps, J_{HH} = 5 cps), and 5.7 ppm (s, 2 H); and three or four difluorocyclohexanes (30% gc area), nmr spectra exhibited low field protons to high field protons in a 1:4 ratio. None of the difluorocyclohexanes were the 1,1 isomer by reference to the ir spectrum of an authentic sample.[26] The residue (0.4 g) was not characterized.

Fluorination of Propyne.—The reaction of XeF_2 (0.818 g, 4.83 mmol) and propyne (0.401 g, 10.0 mmol) for 180 days gave 0.276 g of residue and 0.958 g of volatile products. The residue was chromatographed on alumina but the ir spectra of the fractions were featureless. The volatile fraction contained 54% propyne and 33% 2,2-difluoropropane by reference of an authentic sample.[27] At least nine other products, none of which is more than 10% of the principal products, appeared on the gc trace.

Fluorination of Benzene.—The reaction of XeF_4 (0.577 g, 2.78 mmol) with benzene (1.539 g, 19.8 mmol) took place with continuous evolution of gas (0.239 g) for a few hours. The reaction mixture was separated by distillation at −78° and at room temperature. The volatile fraction (1.361 g) was analyzed by gc and found to contain xenon, benzene (86% recovery), and fluorobenzene (0.36 mmol, 13% based on benzene consumed). The latter was identified by reference to Sadtler ir spectrum 3509.[28] The residue (0.148 g) was chromatographed on alumina. The first fraction (6 mg) eluted with pentane was shown to be a mixture apparently of 4 mg of biphenyl and 2 mg of fluorinated biphenyl by the uv, ir, and mass spectra, and combustion analysis [C, 87.6%; H, 8.6%; F (by difference), 3.8%]. The rest of the residue (0.142 g) could not be characterized.

Fluorination of Toluene.—The reaction of XeF_4 (0.723 g, 3.33 mmol) with toluene (1.47 g, 16.0 mmol) was more vigorous than

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(23) G. Olah, E. Baker, J. Evans, W. Tolgyesi, J. McIntyre, and I. Bastein, *J. Amer. Chem. Soc.*, **86**, 1363 (1964).

(24) P. Klaeboe, J. J. Lothe, and K. Lunde, *Acta Chem. Scand.*, **10**, 1469 (1965).

(25) The ir spectrum was kindly supplied by Dr. R. M. Joyce, Central Research Department, E. I. du Pont de Nemours Co., Wilmington, Del.

(26) The ir spectrum was kindly supplied by Dr. F. S. Fawcett, Central Research Department, E. I. du Pont de Nemours Co., Wilmington, Del.

(27) T. E. Stevens, *J. Org. Chem.*, **26**, 1629 (1961).

(28) Sadtler Research Laboratories, Philadelphia, Pa.

the reaction with benzene. At $-196°$ the interface of the two solids turned yellow. On warming to room temperature the contents of the reaction vessel went through several color changes, with the reaction eventually becoming vigorously exothermic. The vapor pressure of the system was constant after 15 min.

The liquid fraction (1.078 g) obtained from distillation at room temperature contained besides toluene and several low boiling components in small yields, o-fluorotoluene (0.132; 1.20 mmol, 17.2% yield) by reference to Sadtler ir spectrum 4658,[28] m-fluorotoluene (0.023 g, 0.23 mmol, 3.2% yield), and p-fluorotoluene (0.095 g, 0.86 mmol, 12.4 % yield). The yield was calculated by comparison with weighed, authentic samples. The m- and p-fluorotoluenes were not separable by gc but were identified by comparison with the Sadtler ir spectra 4657 and 4659.[28] Their yields were calculated by quantitative ir spectroscopy of the collected gc fraction. No benzyl fluoride was detected.

The residue (0.329 g) was subjected to combustion analysis: C, 74.60%; H, 6.64%; F (by difference), 18.76%. It was not further characterized.

Fluorination of Cumene.—Similarly, cumene (1.332 g, 11.1 mmol) was brought into reaction with XeF$_4$ (0.485 g, 2.35 mmol). The liquid distillate (0.754 g) contained, besides cumene, fluorobenzene (9 mg); o-fluorocumene [(10 mg, 1.5% yield); ir (CS$_2$) 800 cm^{-1}; nmr (CCl$_4$) δ 1.25 (d, 6 H, J = 7 cps), 3.2 (m, 1 H), 7.0 ppm (m, 4 H)]; m- and p-fluorocumene [(75 mg, 11.7% yield); ir (CS$_2$) 830 (two adjacent ArH), 780 and 720 (three adjacent ArH), and 870 cm^{-1} (one ArH); nmr (CCl$_4$) δ 1.25 (d, 6 H, J = 7 cps), 2.9 (m, 1 H), 7.0 ppm (m, 4 H)]; and two compounds, both apparently difluorocumenes [(4 and 6 mg); nmr (CCl$_4$) δ 1.25 (d, 6 H, J = 7 cps), 7.0 ppm (m, 3 H)]. No α-fluorocumene was detected.

Fluorination of Fluorobenzene.—A mixture of XeF$_4$ (0.525 g, 2.53 mmol) and fluorobenzene (1.505 g, 15.7 mmol) was allowed to react overnight. The reaction mixture was distilled at room temperature to leave solid residue. The liquid distillate (1.331 g) contained o-difluorobenzene (17 mg, 0.15 mmol, 5% yield), m-difluorobenzene (6 mg, 0.05 mmol, 2% yield), p-difluorobenzene (70 mg, 0.61 mmol, 21% yield), and an unidentified compound (1% yield). The yields were calculated by comparison with weighed, authentic samples, except in the case of m-difluorobenzene, which had the same retention time as fluorobenzene. Both mass spectral and ir analysis indicated the yield of this compound to be 2%. The identities of o- and p-difluorobenzene were established by reference to Sadtler ir spectra 18772 and 21861.[28]

The solid residue (0.187 g) gave a combustion analysis (C, 51.57%; H, 4.04%; noncombustibles, 1.39%; F (by difference), 43.00%], which indicated an empirical composition of C$_{17}$H$_{16}$F$_9$. It indicated a moderate amount of saturative fluorination. The residue was further chromatographed on alumina. The first fraction (13 mg) was composed of compounds that were largely aromatic in character, but it also contained some multiple bonds as indicated by the ir and the mass spectra: ir (CS$_2$) 2900, 833, 823, 810, 756 cm^{-1}; mass spectrum, m/e (identity) 302 (C$_{18}$H$_{10}$F$_4$), 284 (C$_{18}$H$_{11}$F$_3$), 209 (C$_{12}$H$_8$F$_3$), 208 (C$_{12}$H$_7$F$_3$), 190 (C$_{12}$H$_8$F$_2$). The ir spectrum of the second fraction (17 mg)

was identical with that of 4,4'-difluorobiphenyl (Sadtler ir spectrum 13483).[28] The mass spectrum indicated some contamination of this fraction with trifluorobiphenyl.

Competitive Fluorination of Benzene and Toluene.—A mixture of benzene (0.424 g, 5.43 mmol) and toluene (0.485 g, 5.17 mmol) was distilled into the reaction vessel and quickly frozen, and then XeF$_4$ (0.574 g, 2.78 mmol) was distilled into the reaction vessel. The mixture was warmed to room temperature and allowed to react for some time further with a rate that was intermediate between those of reaction of the individual compounds. The contents of the liquid distillate (0.610 g) are listed in Table I.

The residue (0.397 g) consisted of 62.17% carbon, 6.36% hydrogen, and 31.47% fluorine (by difference).

Competitive Fluorination of Fluorobenzene and Toluene.—Fluorobenzene (0.360 g, 3.76 mmol) and toluene (0.355 g, 3.86 mmol) were allowed to react competitively with XeF$_4$ (0.275 g, 1.33 mmol) in the same manner as had benzene and toluene. The liquid distillate (0.666 g) contained 0.337 g of fluorobenzene and 0.329 g of toluene. Hence $k_T/k_{FB} = 1.1$.

Fluorination of Hexafluorobenzene.—A mixture of hexafluorobenzene (3.639 g, 19.6 mmol) of XeF$_4$ (0.742 g, 3.58 mmol) was allowed to stand for 25 days. The unreacted XeF$_4$ was destroyed with ethylene. The liquid fraction (3.631 g) and the vapor fraction (0.539 g) contained together perfluorocyclohexene (11% yield), perfluoro-1,4-cyclohexadiene (20% yield), and perfluoro-1,3-cyclohexadiene (4% yield). The identities of these compounds were determined by reference to ir spectra of authentic samples.[29]

Another mixture of hexafluorobenzene (3.404 g, 18.3 mmol) and XeF$_4$ (0.664 g, 3.21 mmol) was irradiated with a low pressure mercury arc. The gas evolution was more brisk in the photoreaction than in the dark reaction and agitation greatly enhanced the rate. The yields were almost identical with those of the dark reaction, namely perfluorocyclohexene (4%), perfluoro-1,4-cyclohexadiene (27%), and perfluoro-1,2-cyclohexadiene (3%), without the appearance of any new products.

Fluorination of Xenon with Tetrafluoromethane.—Xenon (7.42 mmol) and tetrafluoromethane (0.904 mmol) were mixed by several freeze–thaw cycles on a vacuum manifold and irradiated for 9 hr at $-196°$ with a Co^{60} source (0.67 Mrad hr^{-1}, 1.25 MeV average). After irradiation, the volatile fractions were collected *in vacuo* at $-196°$ and at $-130°$ (N$_2$–pentane slurry) for 85 min. Mass spectral analysis showed only xenon isotope pattern, the CF$_3$ cation, but nothing at m/e greater than 136.

(29) J. Burdon and D. H. Whiffen, *Spectrochim. Acta*, **12**, 141 (1958).