Fluorination with XeF_2. 40.[1] The Important Role of π-Bond Disruption in Fluorine Addition to Phenyl-Substituted Alkenes

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Ionization potentials (IP) for 11 mono- and α,α-diphenyl-substituted acyclic and cyclic alkenes **1**–**11** were measured under the same conditions, using a mass spectrometric technique and applying electron impact ionization. The values, ranging from 8.68 eV for styrene (**1**) to as low as 7.67 eV for 1,2-dihydro-4-phenylnaphthalene (**10**), were correlated with the logarithms of the relative rates (k_{rel}, relative to 1,1-diphenylethene) of fluorine addition across the carbon–carbon double bond in HF-catalyzed reaction of the alkenes with XeF_2 in CH_2Cl_2 at room temperature. The linear relationship between log k_{rel} and IP with a regression slope of −2.08 and a correlation constant of 0.942, presented for the first time for any fluorination reaction of organic compounds, demonstrates that π-bond disruption is the rate-determining step in the fluorine addition process for the series of alkenes **1**–**11**. The course of reaction of the series of three 1-phenyl-benzocyclenes (**10**–**12**) with XeF_2 was investigated. The addition–elimination process, forming 3-phenyl-2-fluoro-1*H*-indene (**15a**), was found exclusively in the case of 3-phenyl-1*H*-indene (**12**), while the formation of diastereoisomeric pairs of vicinal difluorides (**13** and **14**), with the trans isomers slightly predominant, was established in the case of 1,2-dihydro-4-phenylnaphthalene (**10**) and 6,7-dihydro-9-phenyl-5*H*-benzocycloheptene (**11**). On heating the vicinal difluorides **13** and **14** HF was released, thus yielding 3-fluoro-4-phenyl-1,2-dihydronaphthalene (**15b**) and 6,7-dihydro-8-fluoro-9-phenyl-5*H*-benzocycloheptene (**15c**), respectively.

The special physicochemical characteristics[2] and the enhanced biological activity of fluorine-containing organic molecules[3] provides the impetus for the research in this field of organic chemistry in the last few decades. It has focused mainly on development of new reagents and methods for selective introduction of a fluorine atom into organic molecules.[4] XeF_2 is one of the mildest and the most selective[4a,5] members of the group of so-called "electrophilic" fluorinating reagents (F_2, fluoroxy and NF reagents, xenon halides...), which covers the fluorofunctionalization of a comprehensive spectrum of organic compounds.

The fluorination of alkenes with a variety of fluorinating agents was intensively studied,[4] and phenyl-substituted alkenes were often used as very convenient model molecules, but in contrast to other electrophilic reactions, only a few kinetic evaluations of the fluorination of alkenes as a function of their structure are known.[6] Generally, the introduction of a phenyl ring along the carbon–carbon double bond in the analogue series of alkenes considerably enhances the reactivity of the alkene toward electrophilic addition, while in the case of introduction of the second phenyl group, the relative reactivity strongly depends on the structure of the reagent and the geometry of the alkene,[7] as well as on ring size in the case of phenyl-substituted cycloalkenes.

Among several criteria used in assessing the mechanistic details of electrophilic addition to alkenes, the correlation of relative reactivity with vertical ionization potential (IP) was used in order to elucidate the nature and properties of reactive intermediates and activated complexes. Although some examples of correlations of the logarithm of relative rate factors with IP for different series of reactions were reported and discussed,[7,8] there appears to be a dearth of such data concerning the fluorination of unsaturated organic molecules. In order to make up this deficiency in the kinetic evaluation of the fluorination of the double bond, we now report some kinetic and stereochemical aspects of fluorine addition to phenyl-substituted alkenes with XeF_2.

Results and Discussion

Phenyl-substituted alkenes have many advantages as model substrates for the study of electrophilic addition reactions. The regioselectivity of the reactions and the

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(1) Part 39: Stavber, S.; Zupan, M. *Tetrahedron Lett.* **1993**, *34*, 4355.

(2) *Molecular Structure and Energetics: Fluorine Containing Molecules*; Liebman, J. F., Greenberg, A., Dolbier, W. R., Eds.; VCH Publishers: New York, 1988.

(3) (a) *Biomedicinal Aspects of Fluorine Chemistry*; Filler, R., Kobayashi, Y., Eds.; Elsevier: Amsterdam, 1982. (b) *Fluorine: The First Hundred Years*; Banks, R. E., Sharp, D. W. A., Tatlow, J. C., Eds.; Elsevier: Lausane, 1986. (c) Welch, J. T. *Tetrahedron* **1987**, *43*, 3123. (d) Mann, J. *Chem. Soc. Rev.* **1987**, *16*, 381. (e) Welch, J. T.; Eswarakrishnan, S. *Fluorine in Biorganic Chemistry*; John Wiley: New York, 1991.

(4) (a) *New Fluorinating Agents in Organic Syntheses*; German, L., Zemskov, S., Eds.; Springer-Verlag: Berlin, 1989. (b) Wilkinson, J. A. *Chem. Rev.* **1992**, *92*, 505.

(5) Zupan, M. Xenon Halide Halogenations. In *The Chemistry of Functional Groups Supplement D: The Chemistry of Halides, Pseudo-Halides and Azides*; Patai, S., Rappoport, Z., *Eds.*; Wiley: Chichester, 1983; Parts 1 and 2.

(6) Levy, J. B.; Sterling, D. M. *J. Org. Chem.* **1985**, *50*, 5615.

(7) Freeman, F. *Chem. Rev.* **1975**, *75*, 439.

(8) (a) Nelson, D. J.; Soundararajan, R. *Tetrahedron Lett.* **1988**, *29*, 6207. (b) Nelson, D. J.; Cooper, P. J.; Soundararajan, R. *J. Am. Chem. Soc.* **1989**, *111*, 1414.

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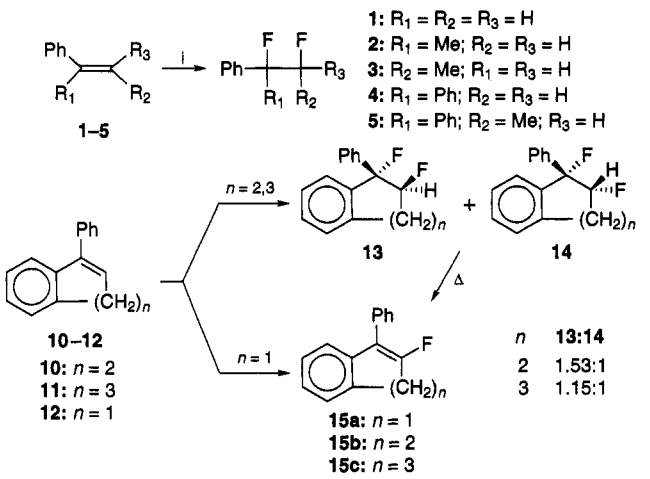
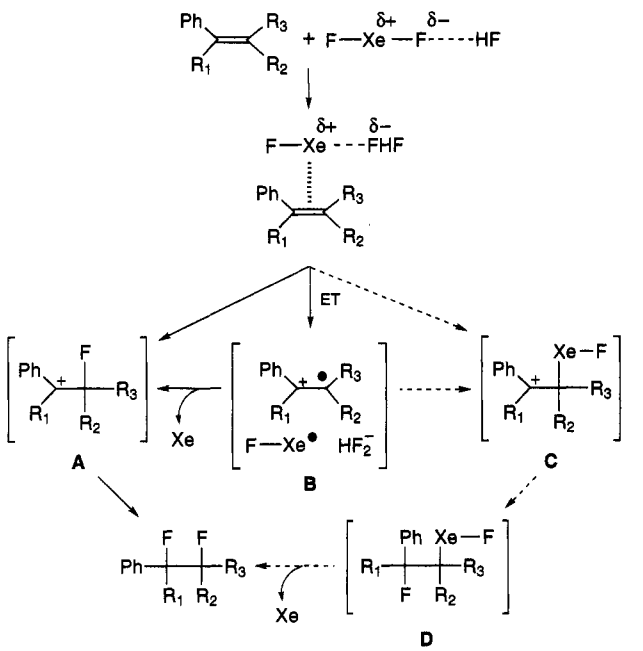
Scheme 1[a]



[a] Key: (i) XeF_2 (1 mmol); CH_2Cl_2 (2 mL); HF_g (cat. amount); T = rt; reaction time = α 0.5 h.

Scheme 2



stability of the reaction products, in addition to the distinctive possibility of modulation of electronic and steric effects by structural variations, are the decisive advantages in comparison with other alkenes when fluorination with modern fluorinating reagents is the subject of the study. For the present work we chose a set of 12 acyclic and cyclic mono- and α,α-diphenyl-substituted alkenes **1**–**12** (Scheme 1) whose reactions with XeF_2 were, except for the 1-phenylbenzocyclene triad **10**–**12**, already studied, but not kinetically evaluated. The interval of ionization potentials characteristic of acyclic mono or α,α-diphenyl-substituted alkenes is a narrow as 0.5 eV, but with the inclusion of 1-phenyl-1-cycloalkenes **8** and **9**, and particularly of the 1-phenylbenzocyclenes 1,2-dihydro-4-phenylnaphthalene (**10**), 6,7-dihydro-9-phenyl-5*H*-benzocycloheptene (**11**), and 3-phenyl-1*H*-indene (**12**), the interval was expanded to 1 eV. Nevertheless, the stereochemical course of the reaction of molecules **10**–**12** with XeF_2 had to be determined.

We have already demonstrated some stereochemical aspects of XeF_2-mediated fluorine addition across the carbon–carbon double bond in phenyl-substituted alkenes. Moderate to considerable excess of anti addition

Table 1. Relative Rate Factors (k_{rel}, Relative to 1,1-Diphenylethene) for the Fluorination of Phenyl-Substituted Alkenes with XeF_2

entry	alkene	k_{rel}	IP (eV)
1	styrene (**1**)	0.12	8.68
2	2-phenylpropene (**2**)	0.47	8.40
3	*trans*-1-phenylpropene (**3**)	0.76	8.36
4	1,1-diphenylethene (**4**)	1.00	8.24
5	1,1-diphenyl-1-propene (**5**)	2.8	8.14
6	indene (**6**)	1.2	8.40
7	1,2-dihydronaphthalene (**7**)	2.4	8.26
8	1-phenyl-1-cyclohexene (**8**)	6.6	8.08
9	1-phenyl-1-cycloheptene (**9**)	6.2	7.92
10	1,2-dihydro-4-phenylnaphthalene (**10**)	23.0	7.67
11	6,7-dihydro-9-phenyl-5*H*-benzocycloheptene (**11**)	3.2	7.91

was observed in a *trans* series of acyclic phenyl-substituted alkenes, while syn addition was preferential in *cis* analogues of the studied alkenes.[9] In the cyclic phenyl-substituted alkene series anti addition was preferential in the case of indene,[9] 1,2-dihydronaphthalene, acenaphthylene,[10] and 1-phenyl-1-cyclopentene,[11] an equal amount of both isomers was formed in the case of the 1-phenyl-1-cyclohexene, while syn addition was predominant in the case of 1-phenyl-1-cycloheptene.[11] We now report that in the case of XeF_2 fluorination of five-membered ring analogues in the 1-phenylbenzocyclene series, for 3-phenyl-1*H*-indene (**12**, Scheme 1), the addition–elimination process, thus forming 3-phenyl-2-fluoro-1*H*-indene (**15a**), was found exclusively even if the reaction time was reduced to a few minutes, the temperature lowered to 0 °C, and the reaction mixture was 5-fold diluted. On the other hand, the fluorination of 4-phenyl-1,2-dihydronaphthalene (**10**) or 9-phenyl-6,7-dihydro-5*H*-benzocycloheptene (**11**) with XeF_2 resulted in formation of diastereoisomeric pairs of vicinal difluorides **13** and **14**. The two components in each pair were separated by preparative TLC and their structures assigned on the basis of differences in their ^1H and ^{19}F NMR spectra and compared with the data for similar vicinal difluorides.[10,11] It was thus established that anti addition of fluorine, forming the isomer **13**, was slightly predominant in both cases. Vicinal difluorides **13** and **14** were unstable upon heating and readily transformed, after termal elimination of HF, to 2-fluoro-1-phenyl-substituted benzocyclene derivatives (**15b,c** Scheme 1).

Applying the known competitive technique, we compared the reactivities of alkenes **1**–**12** toward fluorine addition with XeF_2 and expressed them in terms of relative rates (k_{rel}, Table 1). We found that fluorine addition across the double bond in styrene is considerably slower (more than eight times) than in the case of 1,1-diphenylethene (**4**), which we used as the reference alkene. The introduction of a methyl group along the double bond enhanced the reactivity of the alkene so that in the case of 2-phenylpropene (**2**) fluorination with XeF_2 is twice as slow and the reactivity of *trans*-1-phenylpropene (**3**) is only 1.3 times as slow as the reference alkene, while 1,1-diphenyl propene (**5**) is already more reactive than 1,1-diphenylethene by a factor of 2.8. We also found that cyclic alkenes are much more reactive toward XeF_2 than their acyclic analogues and that the effect of ring size on reactivity is much more expressed in the benzocyclene series than in the phenylcycloalkene one. A small difference in relative reactivities was found between

(9) Zupan, M.; Pollak, A. *J. Org. Chem.* **1977**, *42*, 1559.
(10) Šket, B.; Zupan, M. *J. Chem. Soc., Perkin Trans. 1* **1977**, 2169.
(11) Zupan, M.; Šket, B. *J. Org. Chem.* **1977**, *43*, 696.

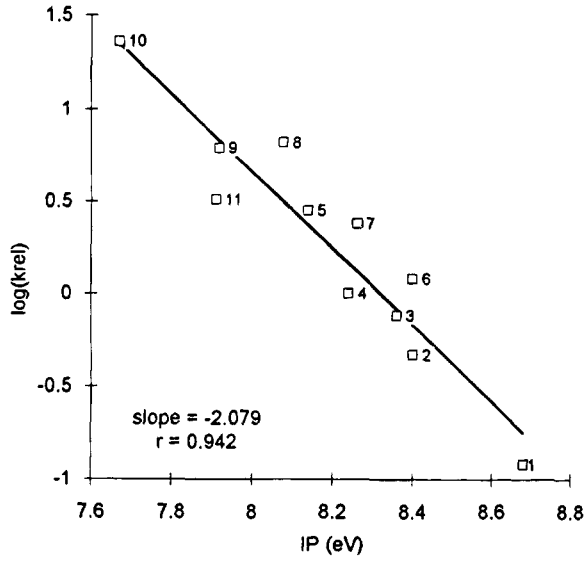


Figure 1. Plot of log k_{rel} for fluorination of mono- and α,α-diphenyl-substituted alkenes **1**–**11** using XeF_2 versus alkene ionization potential (IP).

phenylcyclohexene (**8**) and phenylcycloheptene (**9**), a considerable difference in relative rate factors for the pair indene (**6**) and 1,2-dihydronaphthalene (**7**) was established, while XeF_2-mediated fluorine addition to 1,2-dihydro-4-phenylnaphthalene (**10**) is faster by nearly 1 order of magnitude ($k_{rel} = 23$) in comparison to the seven-membered ring analogue 9-phenyl-6,7-dihydro-5*H*-benzocycloheptene (**11**, $k_{rel} = 3.2$), but the difference is still not so large as observed in the case of bromination[12] of this pair of alkenes.

It was generally accepted that an increase of electron availability at the carbon–carbon double bond (i.e., a decrease of IP) should increase the rate of electrophilic addition reaction. If there is the lack of steric effects in the transition-state structure and the disruption of the π system in alkenes, caused by the electrophilic reagent, is the rate-determining step of the reaction, then a linear correlation between the logarithm of k_{rel} and IP should be obtained.[7,8,13] The correlation plot log k_{rel}/IP for 11 phenyl-substituted alkenes treated in this study shown in Figure 1 indicates the trend of increasing reactivity on decreasing of IP and yields a linear relationship, demonstrating a very good correlation with the constant r[14] of 0.942 and a regression slope of −2.08.

The discussion of the possible mechanisms of fluorination of organic compounds with "electrophilic" fluorinating agent is far from closed. The main subject of the dispute is whether the reactions of named reagents with organic molecules carrying electron-rich reaction centers (C–C double bond, carboanion...) proceed through direct fluorine transfer, or through a two-step pathway where an electron trasfer (ET) precedes a fluorine radical transfer. Direct fluorine transfer, or in other words, the nucleophilic SN_2-type of attack of electron rich center on the fluorine atom, was declared unlikely in general[15] on the basis of various arguments, but mainly because of the extremely high enthalpy of formation of F^+ (420 kcal/mol), while the ET pathway was proposed as a reaction route in fluorination with some NF reagents[16] and fluoroxy reagents.[6,17] On the other hand, the use of the principle of the radical clock[18] was suggested as an important criterion for distinguishing among these two pathways, and citronellic enolate was proposed as a versatile precursor to a 5-hexenyl-type radical clock. On the basis of such a criterion the SN_2-type reaction route was postulated for reactions of a group of NF reagents with enolates, while ET was postulated as a competitive process[19] in the case of XeF_2-mediated reaction with enolates. A challenge for revision of interpretations of the mechanisms of fluorination with electrophilic fluorination reagents was also issued.[19] In our opinion it is rather difficult to generalize about the reaction mechanism of the reaction of electron-rich organic molecules with "electrophilic" fluorination reagents without risk of being more or less speculative. The reactions could run along a variety of reaction channels and select a channel, channels, or combination of them, which is favorable under particular reaction parameters. The structure of the reagent and the substrate, and their relative concentration, the reaction media, temperature, etc., are the main variables which exert crucial influence on the selection of the reaction pathway channel. In other words, it is not necessarily true that a particular reagent will chose the same reaction channel in the case of reaction with carboanions and alkenes or that the same channel is chosen when a particular set of organic compounds react with two different fluorination reagents. A lot of comparative studies concerning the reactions of different fluorination reagents with a selected series of organic molecules which are structural analogues, under comparable reaction conditions, have to be done in order to clarify the situation and contribute realistic details to the mosaic picture of what is really going on.

When discussing the mechanism of reactions of XeF_2 with unsaturated organic compounds the crucial role of acid catalysis must be taken into account, since the reactions proved to be very slow without it. A variety of acids can be used as catalysts depending on the reactivity of substrate.[5] Pentafluorothiophenol proved to be a useful catalyst for the reactions of very sensitive compounds with XeF_2, and boron trifluoride for those less reactive, while hydrogen fluoride is the most common catalyst used for this purpose. As a consequence of polarization with HF xenon difluoride behaves as a electron deficient species which readily interacts with the most electron rich part of an organic molecule, thus forming a π-complex-like intermediate, further decomposing by direct fluorine transfer to a β-fluorocarbonium ion (**A**) or following ET to a cation radical (**B**) transforming by $F^\bullet$ transfer to intermediate **A** which collapses with F^- to a vicinal difluoride product. On the basis of a recent report on the chemistry of ionic fluoroxenonium reagents in the presence of C–C double bonds,[20] a third possibility was introduced. In the proposed reaction pathway electrophilic attack of the fluoroxenonium cation at the double bond, thus forming organoxenonium intermediate

(12) Dubois, J. E.; Hegarty, A. F. *J. Chem. Soc. B* **1969**, 638.
(13) (a) Fukuzumi, S.; Kochi, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 2783. (b) Kochi, J. K. *Angew. Chem.* **1988**, *100*, 1331.
(14) Neter, J.; Wasserman, W.; Kutner, M. H. *Applied Linear Statistical Models*, 2nd ed.; Irwin: Homewood, IL, 1985.
(15) Christe, K. O. *J. Fluorine Chem.* **1984**, *25*, 269.
(16) (a) Umemoto, T.; Fukami, S.; Tomizawa, G.; Harasawa, K.; Kawada, K.; Tomita, K. *J. Am. Chem. Soc.* **1990**, *112*, 8563. (b) DesMarteau, D. D.; Xu, Z. Q.; Witz, M. *J. Org. Chem.* **1992**, *57*, 629.
(17) (a) Visser, G. M. B.; Boele, S.; von Halteren, B. W.; Knopes, G. H. J. N.; Hercheid, J. D.; Brinkman, G. A.; Hoekstra, A. *J. Org. Chem.* **1986**, *51*, 1466. (b) Stavber, S.; Planinšek, Z.; Zupan, M. *J. Org. Chem.* **1992**, *57*, 5334.
(18) Newcomb, M.; Curran, D. P. *Acc. Chem. Res.* **1988**, *21*, 206.
(19) (a) Differding, E.; Ruegg, G. M. *Tetrahedron Lett.* **1991**, *32*, 3815. (b) Differding, E.; Wehrli, M. *Tetrahedron Lett.* **1991**, *32*, 3819.
(20) Zefirov, N. S.; Gakh, A. A.; Zhdankin, V. V.; Stang, P. J. *J. Org. Chem.* **1991**, *56*, 1416.

(**C**), was suggested. On this basis anti attack by F^-, resulting in intermediate **D**, should follow, and nucleophilic substitution of Xe with the neighboring fluorine anion in an SN_2-type process should result in a cis vicinal difluoride product. As the authors stated that this mechanism can only apply to fluoroxenonium reagents, bearing good leaving groups (triflate, fluorosulfate perchlorate, but not alkoxy or halide), and since the stereochemistry of fluorine addition to phenyl-substituted alkenes by HF-catalyzed reaction with XeF_2 in the liquid phase is preferentially trans, this reaction pathway is less probable in this case.

On the basis of the results of this report, we are still unable to clearly discriminate between the two possible pathways of formation of the β-fluorocarbonium ion **A** (direct fluorine transfer or via cation radical **B**), but the linear correlation between the logarithms of relative rate factors and IP represents experimental evidence that the π-bond disruption is the rate-determining step in the fluorine addition to phenyl-substituted alkenes **1-11** by HF-catalyzed reactions with XeF_2 in CH_2Cl_2 at room temperature.

Experimental Section

^1H and ^{19}F NMR spectra were recorded at 60 and 56.45 MHz, respectively. Chemical shifts are expressed in ppm from Me_4Si or CCl_3F as internal standards. TLC was carried out on Merck PCS-Fertigplatten silica gel F-254. XeF_2 was prepared by a photosynthetic method,[21] and its purity was better than 99%. 1,1-Diphenylpropene, 1-phenylcycloheptene, 3-phenyl-1*H*-indene, and 6,7-dihydro-9-phenyl-5*H*-benzocycloheptene were prepared by known procedures,[12] while other alkenes were obtained from commercial sources and purified before use. HF (Fluka purum) was used as supplied, while solvents were purified before use. Since the values for IP obtained from various measuring techniques and literature sources[22] differ considerably, the IP for alkenes **1-11** were measured under the same conditions using a mass spectrometric technique, applying electron impact ionization and the values obtained from analysis of the ionization efficiency curves.[23]

Fluorination of Phenyl-Substituted Alkenes with XeF_2. General Procedure. To a solution of 1 mmol of alkene in dichloromethane (4 mL) was added 1 mmol of XeF_2 at room temperature, and anhydrous HF (0.1-0.2 mmol) was introduced over the reaction mixture. After a few seconds the colorless solution turned dark (blue or brown) and Xe gas was evolved. After half an hour, the reaction mixture was diluted with 20 mL of dichloromethane, washed with 20 mL of 10% aqueous $NaHCO_3$, water, dried over anhydrous Na_2SO_4 and the solvent evaporated in vacuo. The crude reaction mixture was analyzed by ^1H and ^{19}F NMR, and the amounts of fluoro-substituted products were determined by the addition of a known amount of octafluoronaphthalene as internal standard. Products were isolated by preparative TLC (SiO_2, petroleum ether (40-70 °C):CH_2Cl_2 = 3:1) or column chromatography (SiO_2, petroleum ether) and identified on the basis of their spectroscopic data. The yields listed below refer to isolated pure compounds.

3-Phenyl-2-fluoro-1*H*-indene (15a): 40%; mp 35.3-35.9 °C; NMR (CCl_4) δ_H 2.60-3.87 (m, 2H), δ_H 6.60-7.63 (m, 9H), δ_F -127.0 (broad s); MS *m/z* 210 (M^+, 100), 209 (35), 133 (13), 121 (26), 119 (80), 117 (85). Anal. Calcd for $C_{15}H_{11}F$: C, 85.65; H, 5.28. Found: C, 85.64; H, 5.06. ***trans*-1-Phenyl-1,2-difluoro-1,2,3,4-tetrahydronaphthalene (13b)**: 41%; semistable liquid; NMR (CCl_4) δ_H 1.92-3.55 (m, 4H), δ_H 4.90 ppm (dddd, *J* = 49.0, 10.5, 7.0, 3.5 Hz, 1H), δ_H 7.07-7.70 (m, 9H), δ_F -136.5 (dd, *J* = 10.5, 11.0 Hz, 1F), δ_F -194.5 (dddd, *J* = 49.0, 21.5, 11.0 Hz, 11.0 Hz, 1F); HRMS calcd for $C_{16}H_{14}F_2$ *m/z* 244.106, found *m/z* 244.106; MS *m/z* 244 (M^+, 2), 224 (74), 203 (14), 202 (15), 121 (31), 119 (98), 117 (100). ***cis*-1-Phenyl-1,2-difluoro-1,2,3,4-tetrahydronaphthalene (14b)**: 29%; semistable liquid; NMR (CCl_4) δ_H 1.80-3.20 (m, 4H), δ_H 4.90 (dddd, *J* = 48.0, 13.5, 7.2, 4.0 Hz, 1H), δ_H 7.07-7.60 (m, 9H), δ_F -151.7 (dd, *J* = 13.5, 13.5 Hz, 1F), δ_F -196.2 (m, 1F); HRMS calcd for $C_{16}H_{14}F_2$ *m/z* 244.1063, found *m/z* 244.1065; MS *m/z* 244 (M^+, 2), 224 (53), 121 (32), 119 (98), 117 (100). ***trans*-1-Phenyl-1,2-difluorobenzocycloheptane (13c)**: 38%; semistable liquid; NMR (CCl_4) δ_H 1.40-3.23 (m, 6H), δ_H 5.03 (dm, *J* = 48.0 Hz, 1H), δ_H 6.90-7.77 (m, 9H), δ_F -139.7 (dm, *J* = 11.0 Hz, 1F), δ_F -180.8 (dddd, *J* = 48.0, 23.0, 11.0, 11.0 Hz, 1F); HRMS calcd for $C_{17}H_{16}F_2$ *m/z* 258.1220, found *m/z* 258.1214; MS *m/z* 258 (M^+, 2), 238 (44), 192 (30), 121 (33), 119 (95), 117 (100). ***cis*-1-Phenyl-1,2-difluorobenzocycloheptane (14c)**: 31%; semistable liquid; NMR (CCl_4) δ_H 1.17-3.17 ppm (m, 6H), δ_H 5.43 (dddd, *J* = 48.0, 18.0, 6.0, 1 Hz, 1H), δ_H 6.93-7.67 (m, 9H), δ_F -135.8 (dd, *J* = 18.0, 18.0 Hz, 1F), δ_F -189.7 (m, 1F); HRMS calcd for $C_{17}H_{16}F_2$ *m/z* 258.122, found *m/z* 258.122; MS *m/z* 258 (M^+, 1), 238 (11), 121 (40), 119 (94), 117 (100).

Upon heating the isolated crude reaction mixtures at 200 °C, obtained from fluorination of **10** or **11**, released HF and after column chromatography purication **3-fluoro-4-phenyl-1,2-dihydronaphthalene (15b)** [61%; mp 47.3-47.7 °C; NMR (CCl_4) δ_H 2.4-3.33 (m, 4H), δ_H 7.03-7.63 (m, 9H), δ_F -103.3 (m); MS: *m/z* 224 (M^+, 100), 223 (16), 222 (23). Anal. Calcd for $C_{16}H_{13}F$: C, 85.67; H, 5.85. Found: C, 85.23; H, 6.13] and **6,7-dihydro-8-fluoro-9-phenyl-5H-benzocycloheptene (15c)** [65%; mp 89.6-90.1 °C; NMR (CCl_4): δ_H 2.2-3.0 (m, 2H), δ_H 7.0-7.6 (m, 3H), δ_F -98.3 (m); MS *m/z* 238 (M^+, 100), 192 (68), 147 (27), 129 (18). Anal. Calcd for $C_{17}H_{15}F$: C, 85.67; H, 6.36. Found: C, 85.58; H, 6.21] were obtained, respectively.

Determination of Relative Rate Factors (k_{rel}) for the Reaction of Phenyl-Substituted Alkenes 1-11 with XeF_2. The relative reactivities of the alkenes (entries 1-11, Table 1) were determined by competitive reactions, which was carried out as follows. A total of 1 equiv (1 mmol) of each alkene to be compared was dissolved in dry and freshly distilled dichloromethane (4 mL), 1 mmol of XeF_2 was added at room temperature, and HF (0.1-0.2 mmol) was introduced over the reaction mixture kept at 22 °C. After 30 min a known amount of octafluoronaphthalene and 20 mL of dichloromethane were added, the solution washed with 20 mL of aqueous $NaHCO_3$ and 20 mL of water and dried over anhydrous Na_2SO_4, and the solvent evaporated in vacuo. The amounts of fluoro-substituted products were determined from ^{19}F NMR spectra of the crude reaction mixtures using octafluoronaphthalene as additional standard. Applying this known competitive technique, relative reactivities expressed by relative rate factors (k_{rel}) were calculated from the equation[24] $k_{rel} = k_A/k_B = \log((A - X)/A)/\log((B - X)/B)$, derived from the Ingold-Shaw relation[25] where *A* and *B* are the amounts (in mmols) of starting material and *X* and *Y* the amounts of product derived from them. For optimal precision the competing alkenes were selected so that the relative reactivity of alkenes in each pair did not differ by more than 7. The relative rate factors thus obtained, collected in Table 1, are the averages of three measurements.

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(21) Williamson, S. M. *Inorg. Synth.* **1968**, *11*, 147.
(22) Levin, R. D.; Lias, S. G. *Ionization Potencial and Appearance Potencial Measurements, 1971-1981*; NSRDS-NBS 71: Washington, 1982.
(23) Bencze, L.; Marsel, J.; Popovič, A.; Lesar, A. *Org. Mass Spectrom.* **1993**, *28*, 1570.
(24) Pearson, R. E.; Martin, J. C. *J. Am. Chem. Soc.* **1963**, *85*, 3142.
(25) Ingold, C. K.; Shaw, F. R. *J. Chem. Soc.* **1927**, *130*, 2918.