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Effect of Reaction Conditions on the Kinetic and Activation Parameters for the Mild Introduction of Fluorine into Phenyl-Substituted Alkenes with Accufluor™ NFTh

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Abstract—Evidence for a bimolecular process in mild fluorine transfer from the F–L type of reagent (electrophilic fluorinating reagent) is presented. The corresponding second-order rate constants for the fluorination of phenyl-substituted alkenes with 1-fluoro-4-hydroxy-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (NFTh) in acetonitrile at 24°C with methanol as nucleophile, giving vicinal fluoro-methoxy adducts with a Markovnikov type of regioselectivity, are: k_2=9.1×10^{-3} M^{-1} s^{-1} for 1,1-diphenylethene (**1**), 2.7×10^{-2} M^{-1} s^{-1} for triphenylethene (**2**), 2.0×10^{-2} M^{-1} s^{-1} for tetraphenylethene (**3**), 5.5×10^{-3} M^{-1} s^{-1} for acenaphthylene (**7**) and 4.7×10^{-3} M^{-1} s^{-1} for 9-benzylidenefluorene (**10a**). The substitution of methanol as nucleophile for water had a negligible effect on the rate of the process, as well as the change of solvent polarity, indicating little change in the polarity of the rate-determining transition state in comparison with the reactants. Activation enthalpies (between 62 and 74 kJ mol^{-1}) and activation enthropies (between −75 and −37 J mol^{-1} K^{-1}) were determined for fluorination of **1** and **7** with NFTh in acetonitrile in the presence of methanol and water as nucleophiles. Hammett correlation analysis of the reaction of substituted 9-benzylidenefluorenes with NFTh in CH_3CN/CH_3OH gave a reaction constant ρ^+ of −0.95 which supports our belief in the mainly non-polar character of the rate-determining transition state.

Valuable information about the mechanism of a particular reaction may be obtained from kinetic data, but in the field of mild fluorination of alkenes the lack of kinetic evaluation is obvious since only few are known.[1–3] This situation, which in some cases could be ascribed to the high reactivity of the fluorinating reagents[4–8] (CF_3OF, CF_3COOF, $CsSO_4F$, XeF_2, etc.) and the very high sensitivity of these reagents to the reaction conditions (a small amount of HF, water, solvent polarity, reaction of the solvent with the reagent, etc.) has potential for improvement with the introduction of the N–F class of reagents[9,10] as optimally reactive, stable, non-explosive and non-expensive reagents for selective introduction of a fluorine atom into organic molecules. The properties of various fluorinating agents have also been studied on alkenes.[8] Phenyl-substituted alkenes have many advantages over other alkenes (stable products of fluorination, great possibility of modulation of electronic and steric effects by structural variations) and have often been used as model substrates in electrophilic fluorination,[5,8] as well as in other electrophilic addition reactions. The kinetics of bromination of these compounds have been the most extensively studied,[11–15] while kinetic information on chlorination of phenyl-substituted alkenes is rather scarce.[14,16–18]

1-Fluoro-4-hydroxy-1,4-diazoniabicyclo[2.2.2]octane bis-(tetrafluoroborate) (Accufluor™ NFTh) is a representative of the N–F group of reagents and was proven to be an effective and stable reagent for mild fluorination of phenyl-substituted alkenes.[19] Its oxidising power enables us to follow these reactions by iodometric titration[20] and thus determine some kinetic data. On the basis of these evaluations we can study the effect of the structure of phenyl-substituted alkenes and the effect of solvent polarity on the reaction kinetics, which could give us a better understanding of the mechanism of the mild fluorination of phenyl-substituted alkenes with NFTh.

Results and Discussion

Among the group of phenyl-substituted alkenes, 1,1-diphenylethene is the most often used model molecule for a wide range of reactions, since one phenyl group can stabilise an anionic, cationic or radical centre on one hand, while on the other the non-coplanar second phenyl group also regulates the reactivity of the molecule.[21] In the series of alkenes, substitution of the alkyl group by a phenyl ring usually increases the reactivity of the alkene toward

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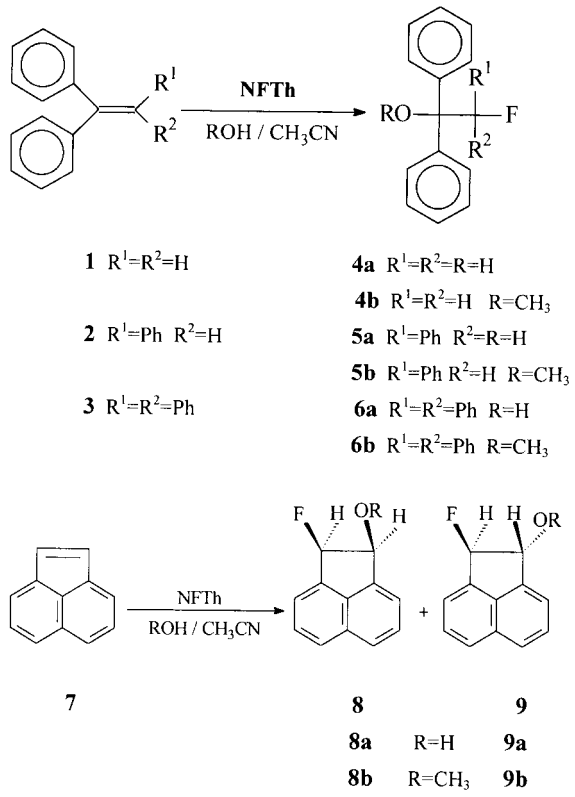


Scheme 1.

electrophilic addition.[22] We were curious how the introduction of a second, third or even fourth phenyl group around the double bond would effect the kinetics of the mild fluorination of substrates with NFTh. Besides, we were also eager to quantify the kinetic parameters of fluorine introduction into strained cyclic alkenes, where the determination of the product distribution and stereochemistry could give us additional information about the reaction mechanism.

We had already demonstrated that phenyl-substituted alkenes react with NFTh in acetonitrile in the presence of a nucleophile (methanol or water) giving fluoro-methoxy and fluoro-hydroxy adducts, respectively, in almost quantitative yield, with the nucleophile entering the molecule according to the Markovnikov rule[19] (Scheme 1). The stereochemical course of the NFTh fluorination of acenaphthylene was found to be only slightly *syn* prevalent in the presence of both nucleophiles.[19] We now investigated the kinetics of these reactions. First, we followed the progress of fluorination of triphenylethene (**2**) with NFTh in acetonitrile in the presence of methanol by iodometric titration and found that the rate of reaction obeys a simple second-order rate equation:

$$d[\text{F–L}]/dt = k_2[\text{F–L}][\text{alkene}] \quad (1)$$

Similar second-order rate behaviour was also observed for the fluorination of 1,1-diphenylethene (**1**), tetraphenylethene (**3**), acenaphthylene (**7**) and 9-benzylidenefluorene (**10a**) under the same reaction conditions. The effect of the structure of the alkene on the rate of fluorination is shown in Fig. 1. The first factor that affects the rate of the reaction is the number of phenyl groups around the double bond. It is evident that the introduction of second and third groups into the molecule increases the reactivity of the substrate in this reaction, while the rate of fluorination of tetraphenylethene (**3**) is somewhat diminished in comparison with the rate of fluorination of triphenylethene (**2**), which could be ascribed to steric factors.

A better insight into the mechanism of fluorination of alkenes **1**, **2** and **3** with NFTh could be obtained by comparison of the relative reactivities of these substrates in fluorination with the relative reactivities of the same alkenes in other reactions. In this manner, besides the effect of the alkene structure on the rate of reaction, the role of the reagent structure could also be evaluated. Some of these interesting data are gathered in Table 1 and it is obvious that the effect of the introduction of a third and fourth phenyl

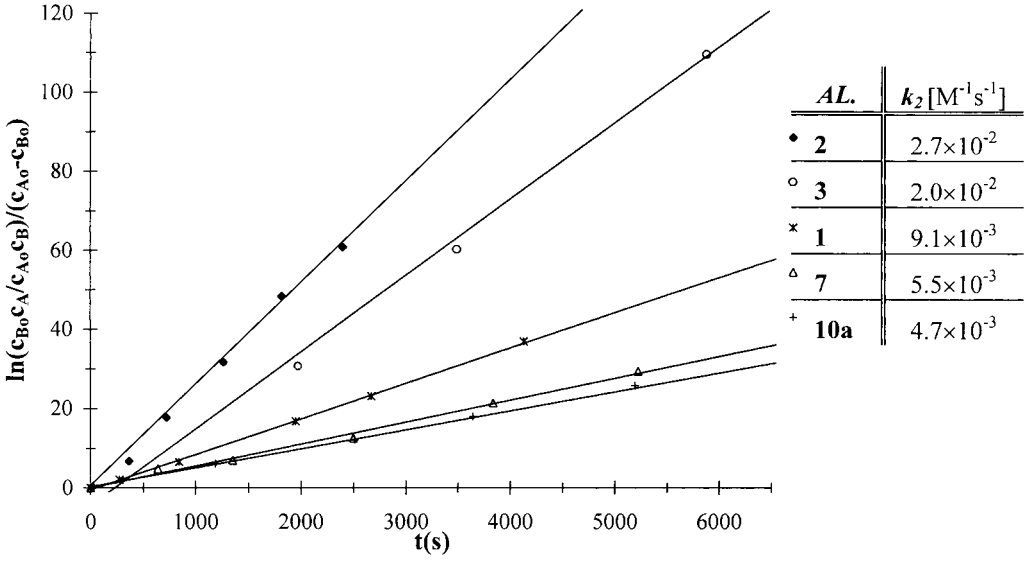


Figure 1. Effect of alkene structure on fluorination with NFTh in CH_3CN/CH_3OH at 24°C for 1,1-diphenylethene (**1**), triphenylethene (**2**), tetraphenylethene (**3**), acenaphthylene (**7**) and 9-benzylidenefluorene (**10a**).

Table 1. Effect of alkene and reagent structure on second-order rate constants for functionalisation of 1,1-diphenylethene (**1**), triphenylethene (**2**) and tetraphenylethene (**3**)

Reagent	Reaction conditions			k_2 [M^{-1} s^{-1}]	Relative rates	
	T [°C]	solvent	Ref.	(1)	2/1	3/1
NFTh	24	CH_3CN+CH_3OH[a]		9.1×10^{-3}	3.0	2.2
XeF_2/HF	20	CH_2Cl_2	3	–	2.5	2.8
$CsSO_4F$	30	$CH_2Cl_2+CH_3OH$[b]	3	–	7.7×10^{-1}	1.5×10^{-1}
CH_3COOOH	25.8	CH_3COOH	22	80	1.2×10^{-1}	–
$Cr_2O_2Cl_2$	10	CCl_4	22	3.77×10^{4}	3.1×10^{-2}	8.5×10^{-4}

[a] Ratio CH_3CN:CH_3OH=11:1.
[b] Ratio CH_2Cl_2:CH_3OH=1:5.

group into the molecule of the substrate strongly depends on the reagent used. There are similarities between relative rates of fluorination of 1,1-diphenylethene (**1**), triphenylethene (**2**) and tetraphenylethene (**3**) with NFTh and XeF_2 where the rate of reaction in almost all cases increases with the number of phenyl groups present in the molecule, while in all other cases, including fluorination of these alkenes with $CsSO_4F$, further introduction of a phenyl ring into 1,1-diphenylethene decreases the reactivity. The largest effect is noticed in oxidation with chromyl chloride where **1** is 32 times more reactive than **2** and even 1170 times more reactive than **3**. Freeman and co-workers established that the reaction is second-order in this case: first-order in alkene and first-order in the reagent. They suggested a rate-determining step with a slightly unsymmetrical three-membered cyclic activated complex, with partial positive charge development at the more highly substituted carbon atom.[22,23] A smaller, but similar effect was observed in the epoxidation reaction with peroxyacetic acid. A second-order reaction was established and a symmetrical three-membered cyclic activated complex postulated.[22]

Cyclic alkenes are often used as test compounds for study of the stereochemistry and kinetics of addition across a double bond. In these systems potential complications in the stereochemical course of the reaction due to possible rotation about the newly formed C–C single bond in the intermediate are avoided and the structure of the intermediate could be predicted with more certainty. In our case fluorination of acenaphthylene (**7**) with NFTh in acetonitrile in the presence of methanol gave almost equal amounts of two diastereoisomers, and on the basis of these results we could suggest an opened structure of the intermediate. The rate of the fluorination of **7** was almost halved in comparison with the rate of fluorination of **1** (Fig. 1).

Table 2. Effect of solvent polarity on the second-order rate constants for fluorination of 1,1-diphenylethene (**1**) and acenaphthylene (**7**) in acetonitrile–water solution (reaction at 24°C for **1** and at 30°C for **7**)

Solvent[a]	Y_{benzyl}[b]	k_2 [10^{-3} M^{-1} s^{-1}]	
		1	**7**
90% CH_3CN	−1.45	4.62	5.0
80% CH_3CN	−0.35	2.05	2.21
60% CH_3CN	0.81	1.05	0.81
40% CH_3CN	1.74	0.62	–

[a] % of CH_3CN in H_2O solution.
[b] Values from Ref. 25.

Further, we investigated the influence of the nature of the nucleophile on the rate of fluorination. We compared the second-order rate constants for the fluorination of 1,1-diphenylethene (**1**) and acenaphthylene (**7**) in acetonitrile in the presence of methanol and in the presence of water, and found that replacement of one nucleophile by another had no significant effect on the rate of the reactions, while the process was slowed down in the presence of water by a factor of 1.3 for **1** (in the presence of methanol $k_2=9.1\times10^{-3}$ M^{-1} s^{-1}, in the presence of water $k_2=6.7\times10^{-3}$ M^{-1} s^{-1}) and by a factor of 2 for **7** (in the presence of methanol $k_2=5.5\times10^{-3}$ M^{-1} s^{-1}, in the presence of water $k_2=2.8\times10^{-3}$ M^{-1} s^{-1}).

We extended our research to determine the effect of change in solvent polarity on the rate of fluorination. From the effect of variations in solvent polarity on the rate of the process we could get very useful information about the nature of the rate-determining transition state and the structure of the intermediates which are involved in this step. For this kind of study we could use solvents with different dielectric constants or mixtures of solvents for which Grunwald–Winstein values (Y) have already been determined,[24] as in the case of acetonitrile–water solutions, where very large variations were observed.[25] Unfortunately, fluorine introduction is quite solvent dependent, and even small changes in this reaction parameter could completely stop the process or alter its course. Fluorination of phenyl-substituted alkenes with NFTh proceeds really well only in acetonitrile and in the presence of a nucleophile; however, solubility problems also appear in mixtures where a lower amount of acetonitrile is present (less than 40%), but as mentioned earlier acetonitrile–water mixtures fortunately have a very large range of Y values.[25] But considering the data in the Table 2 it is obvious that even as large variations in Y as 3.19 units have a negligible effect on the rate of fluorinations of **1** and **7**, indicating a small change in the polarity of the rate-determining transition state in comparison with the reactants. It is well known that in the case of predominantly ionic reactions (e.g. bromination of methylideneadamantane[26] and solvolysis of *p*-methoxybenzyl chloride[27]) the effect of a change in solvent polarity on the rate of reaction is considerable (Fig. 2).

The already mentioned nature of NFTh also enabled its use to establish the activation parameters for its reactions, which gives us a good deal of information about the nature of the rate-determining transition state. We measured second-order rate constants for the fluorination of **1** and **7** in

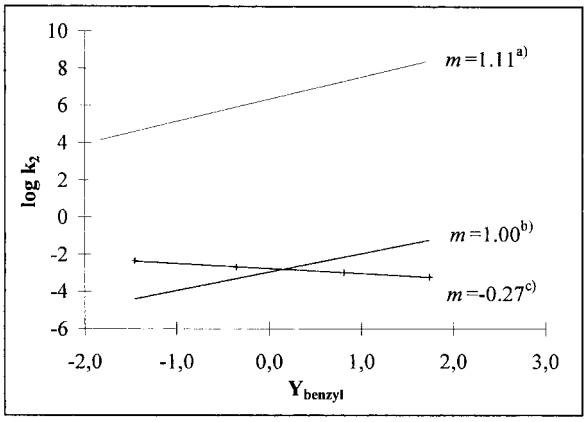


Figure 2. Comparison of the effect of solvent polarity (Y_{benzyl}[25]) on the rate of fluorination of 1,1-diphenylethene (**1**) and the rate of some ionic reactions.[26,27] [a]Bromine addition to methylideneadamantane, Ref. 26; [b]Solvolysis of *p*-methoxybenzyl chloride, Ref. 27; [c]Fluorination of **1** with NFTh in CH_3CN/H_2O at 24°C.

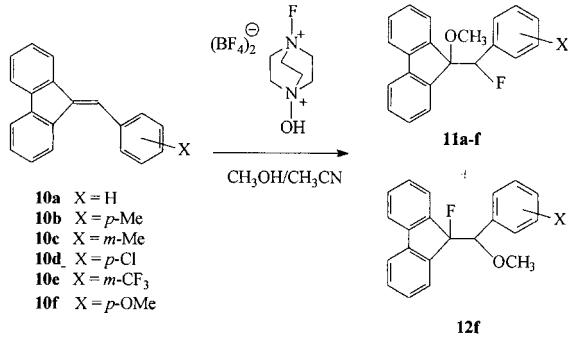
acetonitrile in the presence of a nucleophile at various temperatures and then activation enthalpies ($\Delta H^{\neq}$) and activation entropies ($\Delta S^{\neq}$) were determined. As is evident from Table 3, values of activation free energies ($\Delta G^{\neq}$) for fluorination of **1** and **7** differ only slightly in the presence of different nucleophiles, which is in accordance with the results obtained for the second-order rate constants. However, we found it interesting that this is the result of the action of two parameters ($\Delta H^{\neq}$ and $\Delta S^{\neq}$) operating in opposite directions: activation enthalpies ($\Delta H^{\neq}$) are lower in the presence of methanol for both substrates, but activation entropies ($\Delta S^{\neq}$) are higher in the presence of water, thus compensating for more unfavourable values of activation enthalpies ($\Delta H^{\neq}$) in this media and thus causing negligible change in the rate of fluorination by the substitution of one nucleophile for another.

In our investigation we also checked 9-benzylidenefluorene **10a** as an interesting model substrate in reaction with NFTh. This substrate is attractive from various points of view. Due

Table 3. Effect of substrate structure on activation parameters for fluorination with NFTh in CH_3CN

Alkene	Nu[a]	$\Delta G^{\neq}$ [kJ mol^{-1}][b]	$\Delta H^{\neq}$ [kJ mol^{-1}]	$\Delta S^{\neq}$ [J mol^{-1} K^{-1}]
1,1-Diphenylethene	CH_3OH	85±3	62±2	−74±4
1	H_2O	85±4	74±4	−37±3
Acenaphthylene	CH_3OH	86±4	63±3	−75±6
7	H_2O	88±3	74±3	−44±3

[a] Ratio of CH_3CN:Nu=11:1.
[b] $\Delta G^{\neq}$ is calculated from the equation $\Delta G^{\neq}=\Delta H^{\neq}-T\,\Delta S^{\neq}$ for T=30.0°C.



X	k_2 [$M^{-1}s^{-1}$]	k_{rel}
p-OCH_3	2.6×10^{-2}	5.5
p-CH_3	7.8×10^{-3}	1.6
m-CH_3	5.2×10^{-3}	1.1
H	4.7×10^{-3}	1.0
p-Cl	3.1×10^{-3}	0.66
m-CF_3	1.3×10^{-3}	0.28

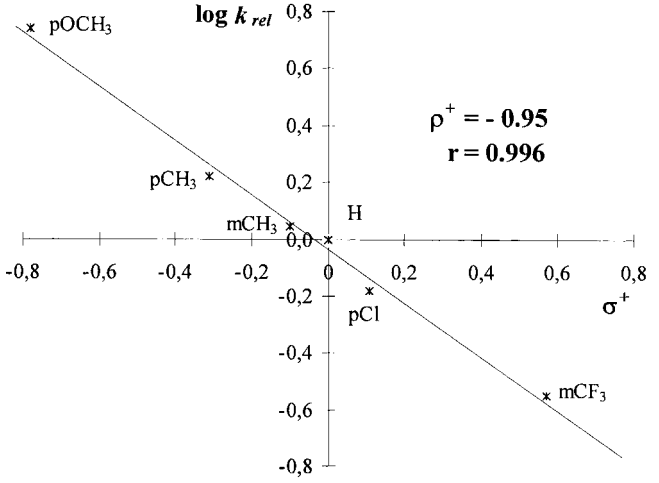
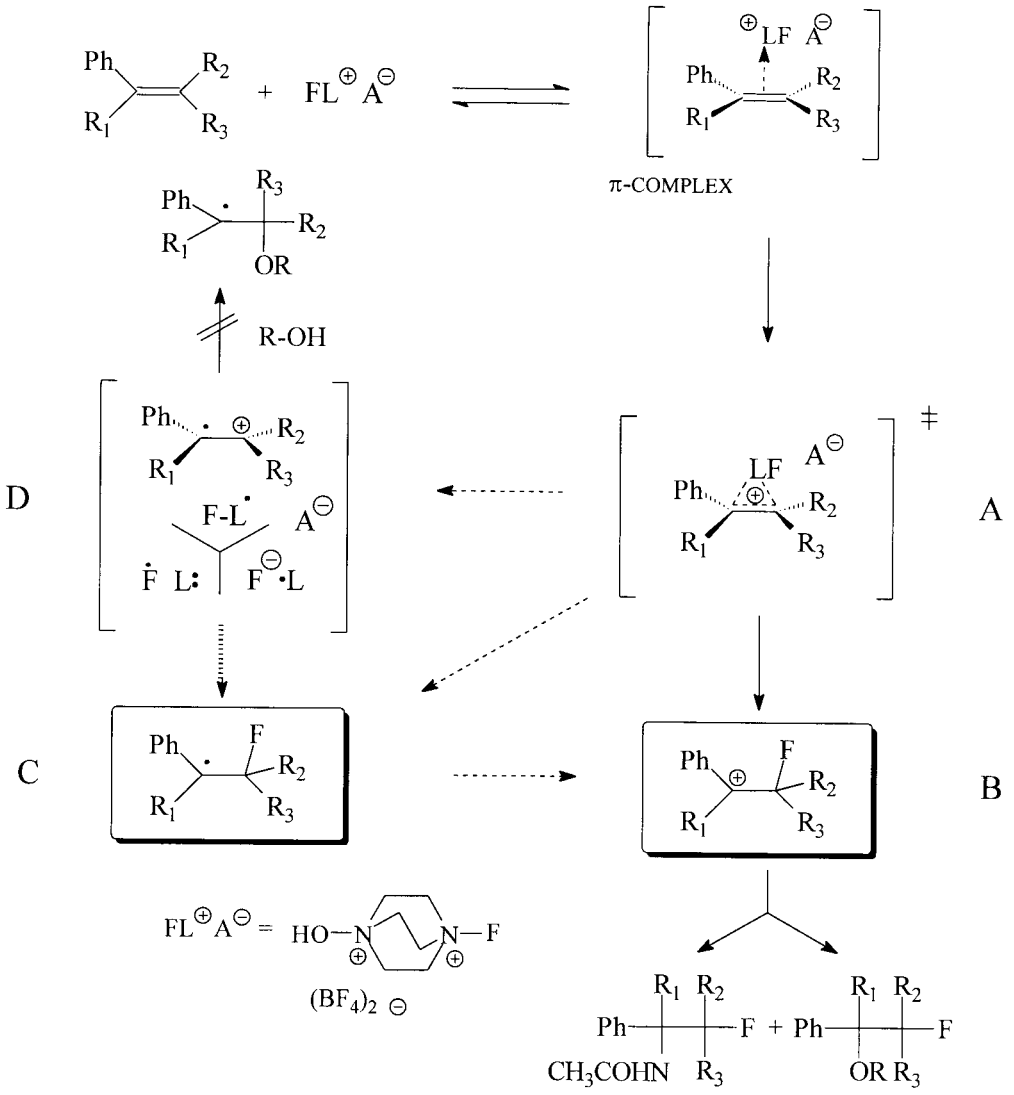


Figure 3. Hammett correlation plot (log k_{rel}/σ^+) for fluorination of substituted benzylidenefluorenes with NFTh in CH_3OH/CH_3CN.



Scheme 2.

to the double benzylic position in **10a** we could expect a higher fluorination rate of **10a** than in the case of fluorination of triphenylethene **2**, which is its structural analogue. But, on the other hand, this molecule was also recognised as a possible precursor for intermediates with anti-aromatic character,[28,29] which could slow down the reaction. By the introduction of substituents on the phenyl rings, especially on the benzylidene side of the molecule **10a**, we could also investigate the effect of another electronic manipulation of the alkene structure on the course of the reaction (Fig. 3). And such functionalisation could effect regioselectivity as well as the rate of reaction.

We established that the second-order rate constant for the fluorination of **10a** with NFTh in acetonitrile in the presence of methanol is diminished approximately six times in comparison with the second-order rate constant for fluorination of **2** under the same conditions (Fig. 1). This led us to the conclusion that the intermediate has at least a partial antiaromatic character. Furthermore, we found that the fluorination of functionalised substrates **10a**–**10e** regiospecifically resulted in the formation of products **11a**–**11e** according to the Markovnikov rule, while in the case of the *p*-methoxy substituted substrate, besides expected isolated product **11f**, we also isolated product **12f** (in a 20% relative yield) with an opposite regioisomery. It was very easy to distinguish between these two products, as for the Markovnikov type of product **11f** we saw a geminal coupling, which is twice as great as the vicinal coupling we saw for the **12f** type of product. It is obvious that the *p*-methoxy group on the phenyl ring of the benzylidene side of the molecule **10f** considerably stabilises the benzylic carbocation, thus forming the product **12f**, while in the case of other substituents the formation of a fluorenyl carbocation is solely formed. It is very instructive that the correlation value for the fluorination of *p*-methoxy derivative **10f** lies on a linear Hammett line (Fig. 3), suggesting that both intermediates leading to products **11f** and **12f** arise from the same transition state, which according to the low value of the reaction constant ($\rho^{+}=-0.95$) is believed to be of mainly non-polar character.

On the basis of the reported data we could now propose a mechanism for the fluorination of phenyl-substituted alkenes with NFTh (Scheme 2), and thus contribute to the discussion on the possible mechanisms of fluorination of organic compounds with 'electrophilic' fluorinating agents. The main subject of dispute is whether the reactions of this type of reagent with organic molecules carrying electron-rich centres (C–C double bond, carboanion …) proceeds through direct fluorine transfer, or through a two-step pathway where an electron transfer (ET) precedes a fluorine radical transfer. It has been suggested that in the case of the mild introduction of fluorine into phenyl-substituted alkenes with the N–F type of reagents the electron transfer process is the main reaction path.[9,10,30,31]

Laser flash photolysis generation of ion-radicals from styrene and its substituted derivatives clearly indicated that the primary process is the attack of a nucleophile at position C-2, which is both very dependent on the structure of the nucleophile and also the steric arrangement at C-2. The formation of a radical intermediate has also been proven.[32,33] In our fluorination reactions we observed opposite regioselectivity; the nucleophile or acetonitrile enters according to Markovnikov type of regioselectivity in all cases, even in the fluorination of substituted 9-benzylidenefluorenes, with the exception of the fluorination of the *p*-methoxy substituted substrate (**10f**), which speaks in favour of the β-fluorocarbonium ion structure **B** of the reactive intermediate. The stereochemical course of the fluorination of acenaphthylene (**7**), where two diastereoisomeric products (**8** and **9**) are formed almost in the ratio 1:1, supports the proposed mechanistic scheme with the intermediate with an opened structure. An additional argument for the opened structure of the β-fluorocarbonium intermediate has also been presented in one of our previous studies,[34] where the formation of fluoroacetamides from alkenes and phenyl-substituted alkenes which give less stable intermediates with NFTh in acetonitrile was reported. We also recently observed that in the reaction of F-TEDA with norbornene rearranged products were formed, suggesting the carbonium ion nature of the intermediate,[35] while a photochemically generated norbornene ion-radical reacted with a nucleophile forming a radical intermediate and no rearranged products were observed.[36]

The β-fluorocarbonium ion is most likely formed through a π-complex between the reagent and substrate and transition state **A** which has a mainly non-polar character. The low value of the reaction constant ρ^+ (−0.95), as well as the established small effect of change of solvent polarity on the rate of reaction supports this proposed mechanistic scheme. The values of activation enthalpies for the reported fluorinations are in the same range as values of activation enthalpies in the epoxidation reaction, which are proposed to follow the reaction course through transition states with the non-polar character. Finally, the fact that the fluorination is a second-order reaction speaks in favour of a bimolecular rate-determining step of the reaction.

However, the formation of cation-radicals could not be completely excluded in these reactions, although we mentioned that photochemically generated cation-radicals reacted with nucleophiles with opposite regioselectivity[32,33] to what we observed. However, direct comparison between these two processes is obviously not entirely correct, especially as we do not have enough information about the structure of the electron accepting species ($F–L^{\cdot}$ or $F^{-}L^{\cdot}$ or $:L\ F^{\cdot}$). For this reason we also included the possibility of the formation of a cation-radical and anionic part of the fluorinating agent pair **D** in the proposed mechanistic scheme, which could be further transformed into the radical intermediate **C**, and in the next very fast step the β-fluorocarbonium intermediate **B**. The alternative reaction of the proposed pair **D** with alcohol or water is not optional.

Experimental

1-Fluoro-4-hydroxy-1,4-diazoniabicyclo[2.2.2]octane bis-(tetrafluoroborate) (NFTh) was obtained from commercial sources and used without further purification. 1,1-Diphenylethene (**1**) (Merck), triphenylethene (**2**) (Merck), tetraphenylethene (**3**) (Merck) and acenaphthylene (**7**) (BDH Reagent) were also obtained from commercial sources and purified before use: **1** was distilled, **2**, **3** and **7** were crystallised, 9-benzylidenefluorene (**10a**) and *p*-methyl (**10b**), *m*-methyl (**10c**) and *m*-trifluoromethyl (**10e**) substituted 9-benzylidenefluorenes were prepared by Grignard reaction from 9-fluorenone (Fluka) and substituted benzylhalide (all from Aldrich) and elimination of water from the alcohol, while 9-(*m*-chlorobenzylidene)fluorene (**10d**) and 9-(*p*-methoxybenzylidene)fluorene (**10f**) were prepared from fluorene (Janssen Chimica) and *m*-chlorobenzaldehyde (BDH Reagent) or *p*-methoxybenzaldehyde (Fluka) in ethanol in the presence of a strong base[37] and crystallised before use. Acetonitrile (Merck), methanol (Merck) and methylene chloride (Merck) were purified by distillation and stored over molecular sieves. KI (Merck) and a standard solution of $Na_2S_2O_3$ (Riedel-de-Haen) were used as received. ^1H and ^{19}F NMR spectra were recorded at 60 and 56.45 MHz, respectively, in $CDCl_3$ solutions. Chemical shifts are expressed in ppm from Me_4Si or CCl_3F as internal standards. TLC was carried out on Merck PCS-Fertigplatten Silicagel F-254.

Fluorination of substituted 9-benzylidenefluorenes with NFTh

Isolation and separation of products. To a solution of 1 mmol of the substrate (**10a**–**10f**) in a mixture of 10 mL of acetonitrile and 1 mL of methanol (in the case of the less soluble *p*-chloro substituted substrate **10d**, 45 mL of acetonitrile and 4.5 mL of methanol was used), 1 mmol of NFTh was added and the reaction mixture was stirred for 24 h at room temperature. The solvent was partially removed under reduced pressure, the residue diluted with 30 mL of methylene chloride, washed with a saturated solution of sodium hydrogencarbonate and water and dried over sodium sulphate. After evaporating the solvent, the crude reaction mixture was analysed by ^1H and ^{19}F NMR spectroscopy, where yields and the relative ratio of fluorinated products formed were determined from the ^{19}F NMR spectra using octafluoronaphthalene as internal standard. In all cases, between 85 and 98% of substituted vicinal methoxy fluoride were formed. Products were separated and purified by

preparative TLC (SiO_2, *n*-C_6H_{14}:CH_2Cl_2=2:5) and crystallisation from *n*-C_6H_{14}, while their structure and purity was verified by NMR, mass spectrometry and combustion analysis. The yields listed below refer to pure compounds.

9-Methoxy-9-[1-fluoro-1-methylphenyl]fluorene (11a). 135 mg (44%); mp 95.0–95.6°C (mp lit.[3]=95.9–96.9°C); NMR ($CDCl_3$): δ_H 2.9 (s, 3H), 5.6 (d, $^2J_{HF}$=46 Hz, 1H), 5.7–8.8 (m, 13H); δ_F −185.0 (d, $^2J_{FH}$=46 Hz, 1F).

9-Methoxy-9-[1-fluoro-1-(p-methylphenyl)methyl]fluorene (11b). 106 mg (33%); mp 142.3–142.4°C; NMR ($CDCl_3$): δ_H 2.2 (s, 3H), 2.9 (s, 3H), 5.8 (d, $^2J_{HF}$=46 Hz, 1H), 6.7–7.8 (m, 12H); δ_F −185.0 (d, $^2J_{FH}$=46 Hz, 1F); MS: *m/z* 318 (M^+, 0.1%), 196 (25), 195 (100), 180 (37), 152 (19), 123 (6); HRMS calcd for $C_{22}H_{19}OF$ *m/z* 318.1420, found *m/z* 318.1419; elem. anal. calcd for $C_{22}H_{19}OF$: C 82.98%, H 6.03%, found C 83.50%, H 5.88%.

9-Methoxy-9-[1-fluoro-1-(m-methylphenyl)methyl]-fluorene (11c). 156 mg (48%); mp 116.5–117.7°C; NMR ($CDCl_3$): δ_H 2.1 (s, 3H), 2.9 (s, 3H), 5.7 (d, $^2J_{HF}$=46 Hz, 1H), 6.4–7.8 (m, 12H); δ_F −184.7 (d, $^2J_{FH}$=46 Hz, 1F); MS: *m/z* 318 (M^+, <0.1%), 196 (29), 195 (100), 180 (33), 152 (18), 123 (9); HRMS calcd for $C_{22}H_{19}OF$ *m/z* 318.1420, found *m/z* 318.1429; elem. anal. calcd for $C_{22}H_{19}OF$: C 82.98%, H 6.03%, found C 83.43%, H 5.99%.

9-Methoxy-9-[1-fluoro-1-(p-chlorophenyl)methyl]-fluorene (11d). 154 mg (45%); mp 131.4–132.0°C; NMR ($CDCl_3$): δ_H 2.9 (s, 3H), 5.8 (d, $^2J_{HF}$=46 Hz, 1H), 6.6–7.7 (m, 12H); δ_F −184.0 (d, $^2J_{FH}$=46 Hz, 1F); MS: *m/z*: 338 (M^+, 0.3%), 196 (24), 195 (100), 180 (36), 152 (19), 143 (9); elem. anal. calcd for $C_{21}H_{16}OFCl$: C 74.44%, H 4.77%, found: C 74.81%, H 5.05%.

9-Methoxy-9-[1-fluoro-1-(m-trifluoromethylphenyl)methyl]-fluorene (11e). 215 mg (58%); mp 76.9–78.2°C; NMR ($CDCl_3$): δ_H 2.9 (s, 3H), 5.9 (d, $^2J_{HF}$=46 Hz, 1H), 6.9–7.8 (m, 12H); δ_F −64.2 (s, 3F), −184.0 (d, $^2J_{FH}$=46 Hz, 1F); MS: *m/z*: 372 (M^+, 1%), 196 (24), 195 (100), 180 (36), 177 (8), 152 (17); elem. anal. calcd for $C_{22}H_{16}OF_4$: C 70.95%, H 4.34%, found: 71.47%C, 4.53%H.

The crude reaction mixture obtained after fluorination of *p*-methoxy substituted derivative of 9-benzylidenefluorene **10a** showed two signals in the ^{19}F NMR spectra: at δ_F −180.5 (d, $^2J_{FH}$=45 Hz) for *9-methoxy-9-[1-fluoro-1-(p-methoxyphenyl)methyl]fluorene* (**11f**) and at δ_F −165.7 (d, $^3J_{FH}$=14 Hz) for *9-fluoro-9-[1-methoxy-1-(p-methoxyphenyl)methyl]fluorene* (**12f**) in the ratio 4:1. The crude reaction mixture was crystallised from *n*-C_6H_{14} and analysed by mass spectroscopy, where fragmentation of both regioisomers were present: MS *m/z*: 334(M^+, 6%), 314 (10), 239 (20), 196 (100), 195 (88), 180 (88), 165 (27), 152 (82), 151 (66), 139 (98), 96 (46); HRMS calcd for $C_{22}H_{19}O_2F$ *m/z* 334.1369, found *m/z* 334.1375. After several crystallisations of the crude reaction mixture from *n*-C_6H_{14} *9-methoxy-9-[1-fluoro-1-(p-methoxyphenyl)methyl]fluorene* (**11f**) was isolated as a white crystalline product (mp 135.5–137.3°C, elem. anal. calcd for $C_{22}H_{19}O_2F$ C 79.01%, H 5.74%, found C 79.36%, H 5.59%).

Determination of second-order rate constants for fluorination of alkenes with NFTh

Various amounts (0.3, 0.45, 0.6, 0.9, 1.2 mmol) of substrate (1,1-diphenylethene (**1**), triphenylethene (**2**), acenaphthylene (**7**), 9-benzylidenefluorene (**10a**) and substituted 9-benzylidenefluorene (**10b**–**10f**)) were dissolved in a thermostatted mixture of 35 mL of acetonitrile and 5 mL of methanol (or 5 mL of water for **1** and **7**), while 0.3 mmol of tetraphenylethene (**3**), due to its low solubility, was dissolved in a mixture of 45 mL of acetonitrile and 5 mL of methanol, then 20 mL of a thermostatted acetonitrile solution of NFTh (0.6 mmol) was added and the reaction mixture further stirred at 24°C. The progress of NFTh consumption was monitored by iodometric titration and at various times, 10 mL aliquots of reaction mixture were mixed with 20 mL of ice cold 0.02 M KI and the liberated iodine was titrated with 0.05 M $Na_2S_2O_3$. Second-order rate constants were calculated from the equation:

$$1/(c_{A0} - c_{B0}) \times \ln (c_{B0} \times c_A)/\ln (c_{A0} \times c_B) = k_2 \times t \qquad (2)$$

and are presented in Fig. 1 for fluorinations in the presence of methanol as nucleophile, but for fluorination in the presence of water their values are k_2=6.7×10^{-3} M^{-1} s^{-1} for the fluorination of **1** and k_2=2.8×10^{-3} M^{-1} s^{-1} for fluorination of **7**.

For the Hammett correlation plot relative rate factors for substituted benzylidenefluorenes (**10a**–**10f**) were calculated from k_2 values and are presented in Fig. 3.

Influence of solvent polarity on second-order rate constant in fluorination of 1,1-diphenylethene (1) and acenaphthylene (7) with NFTh

1.2 mmol of 1,1-diphenylethene (**1**) or acenapthylene (**7**) was dissolved in 40 mL of acetonitrile–water mixture (acetonitrile–water 34+6; 28+12; 16+24 and 4+36 only for **1**, **7** precipitated from a 40% acetonitrile–60% water mixture) and thermostatted at 24°C for **1** and at 30°C for **7,** 20 mL of a thermostatted acetonitrile solution containing 0.6 mmol NFTh was added and stirred. The progress of NFTh consumption was monitored by iodometric titration. The results are presented in Table 2 and Fig. 2.

Determination of thermodynamic parameters for fluorination of 1,1-diphenylethene (1) and acenaphthylene (7) with NFTh in the presence of methanol or water

1.2 mmol of 1,1-diphenylethene (**1**) or acenapthylene (**7**) was dissolved in a mixture of 35 mL of acetonitrile and 5 mL of methanol or water, solutions were thermostatted at three different temperatures (24, 30 and 38°C) and 20 mL of a thermostatted acetonitrile solution of NFTh (0.6 mmol) was added. The reaction mixture was stirred and the progress of NFTh consumption was monitored by iodometric titration. A linear correlation between the k_2 and temperature was observed and activation parameters were

calculated by linear regression from the equation:

$$\ln (k_2/T) = \ln (k_b/h) + \Delta S^{\neq}/R - \Delta H^{\neq}/RT \quad (3)$$

Results are presented in Table 3.

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