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Scientific Paper

The Effect of Reaction Conditions on Activation Parameters for the Mild Introduction of Fluorine into Phenyl Substituted Alkenes with *Selectfluor*™ F-TEDA-BF_4[†]

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[†] Dedicated to the memory of Prof. Dr. Tatjana Malavašič

Abstract

1-Chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis-(tetrafluoroborate) (*Selectfluor*™ F-TEDA-BF_4) reacted with phenyl-substituted alkenes in acetonitrile and Ritter-type fluoroamidation was observed, while in the presence of a nucleophile (H_2O, MeOH), the formation of vicinal fluorohydroxy or fluoromethoxy alkanes was the predominant process. Mild fluorine introduction obeys a simple rate equation:

$$v = d[F\text{–}TEDA\text{-}BF_4]/dt = k_2\,[F\text{–}TEDA\text{-}BF_4]\,[alkene]$$

and the following second order rate constants were determined in acetonitrile at 22 °C: $k_2 = 9.0\times10^{-3}M^{-1}s^{-1}$ for trans-stilbene (**1a**), $2.0\times10^{-3}M^{-1}s^{-1}$ for cis-stilbene (**1b**), $8.4\times10^{-3}M^{-1}s^{-1}$ for 1,1-diphenylethene (**1c**) and $0.29\times10^{-3}M^{-1}s^{-1}$ for styrene (**1d**) (calculated from $k_2 = 3.9\times10^{-3}M^{-1}s^{-1}$ at 50 °C), while the presence of a nucleophile had no a significant effect on the second order rate constants. Activation enthalpies were between 72.7 $kJmol^{-1}$ and 65.5 $kJmol^{-1}$ in acetonitrile, while the presence of a nucleophile lowered the activation enthalpies for **1a**, **1b**, **1c**, whereas higher values were observed for styrene. Activation entropies were between –37.9 e.u. and –68.7 e.u. in acetonitrile, the presence of nucleophile lowering the activation entropy for **1a**, **1b**, **1c**, while the opposite effect was observed for styrene. Solvent polarity variation (Grunwald-Winstein Y_{benzyl}) had a very small effect on the rate of fluorination of styrene and 1,1-diphenylethene, indicating a small change in the polarity of the rate determining transition state in comparison with the reactants.

Key words: Selectfluor™ F-TEDA-BF_4, alkenes, fluorination, kinetics, activation parameters

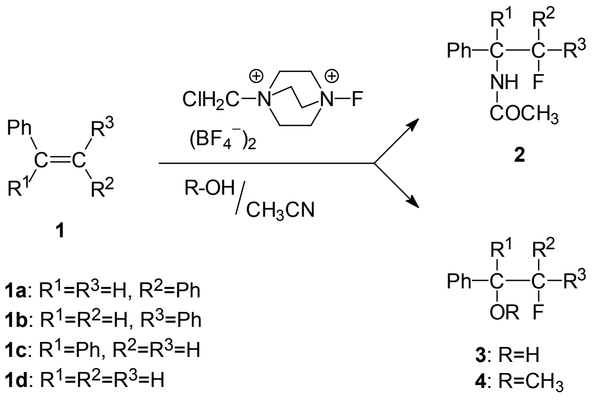
Introduction

Phenyl substituted alkenes are very convenient substrates for investigation of the role of the reagent on the functionalization of alkenes. Rate constants, activation parameters and in some cases also the Hammett ρ values were often determined and used as convenient tools for mechanistic evaluation.[1–4] Halogenation of phenyl substituted alkenes has been extensively studied. The kinetics of their bromination were most widely investigated,[5–8] analogueous informations about chlorination reactions are less extensive,[8] while recently some investigations dealing with the kinetics of fluorine introduction in organic compounds were reported.[9] The lack of kinetic data on the mild introduction of fluorine into organic molecules using "electrophilic" fluorinating reagents like CF_3OF, CF_3COOF, $CsSO_4F$, XeF_2, etc. could be ascribed in some cases to their high reactivity and high sensitivity to the reaction conditions.[10–15] On the other hand, one of the most important breakthroughs in modern organofluorine chemistry has been accomplished in the nineties of the last century by the introduction and broad synthetic application of organic molecules incorporating a reactive N-F bond as mild fluorinating reagents.[16] Being easy handling bench top materials, usually with optimal stability/reactivity characteristics and attractive costs, N-F reagents have revolutionarily changed the perception of synthesis of fluorinated organic compounds. Three main type of N-F reagents are used for this purpose: neutral N-fluoro amines (R^1R^2NF), N-fluoropyridinium and related salts, and quaternary N-F salts ($F\text{-}N^+R^1R^2R^3Y^-$). The most widely used member of the last group is 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) known under the trade name of Selectfluor™ F-TEDA-BF_4.[16e, f] In order to obtain some further information about the mechanism of selective mild introduction of a fluorine atom into organic compounds with the electrophilic-type of fluorinating reagents, we decided, encouraged by the fact that various reactions of F-TEDA-BF_4 could be easily followed by iodometric titration,[17] to study their reactions with phenyl substituted olefins with special attention to the effect of the structure of the target compounds and solvent polarity on the rate of fluorination.

Results and discussion

It has already been demonstrated that phenyl substituted olefins[18] reacted with F-TEDA-BF_4 at room temperature or at slightly evaluated temperatures, while the structure of the product depended on the reaction conditions and the structure of the alkene (**1**). Vicinal fluorohydroxy (**3**) or fluoromethoxy derivatives (**4**) were formed in the presence of water or methanol,[19,20] while Ritter-type[21] of functionalization giving vicinal fluoroacetamides(**2**) was observed in acetonitrile (Scheme 1). First we investigated the kinetics of the reaction of *trans*-stilbene (**1a**) with F-TEDA in an acetonitrile-water mixture, following the progress of reaction by iodometric titration. We found that the rates of fluorination obey a simple second order rate equation: $v = d[F\text{–}TEDA]/dt = k_2\,[F\text{–}TEDA]\,[alkene]$.

The effect of variation of *trans*-stilbene concentration on the pseudo first order rate constants is presented in Figure 1, while the effect of alkene structure on its fluorination with F-TEDA-BF_4 in acetonitrile is shown in Figure 2. Similar second order rate behaviour was also observed for the reactions of F-TEDA-BF_4 with *cis*-stilbene, 1,1-diphenylethene and styrene in acetonitrile, acetonitrile-water and acetonitrile-methanol mixtures (molar ratio **1**: F-TEDA-BF_4: ROH= 2: 1: 7.5). As evident from Table 1, the presence of a nucleophile did not have an important effect on the second order rate constants, in spite of the fact that different products were actually formed (**2**, **3**, **4**).



Scheme 1

Further, we investigated activation parameters for the introduction of fluorine into phenyl substituted alkenes (**1**) in acetonitrile, acetonitrile-water and acetonitrile-methanol mixtures, and from their dependence on temperature $\Delta H^{\neq}$ and $\Delta S^{\neq}$ were determined. As evident from Table 1, the values of the activation enthalpies in acetonitrile are almost the same for styrene, *trans*- and *cis*-stilbene, but lower for 1,1-diphenylethene. On the other hand, larger differences were observed for the entropy factors, being the largest for styrene and the lowest for *trans*-stilbene for the reactions in acetonitrile. The presence of ROH lowered $\Delta H^{\neq}$ of fluorination for 1,1-diphenylethene, *cis* and *trans*-stilbene, while an increase in activation entalpy was observed in reactions with styrene, where the enthalpy was found to be higher in methanol than in water. A similar effect of the variation of solvent was also evident from the entropy factor, where values were lower in the presence of a nucleophile in the case of 1,1-diphenylethene, *cis*- and *trans*-stilbene, while in the case of styrene a shift from –68.7 e.u. in acetonitrile to –26.3 e.u. in the presence of methanol was observed.

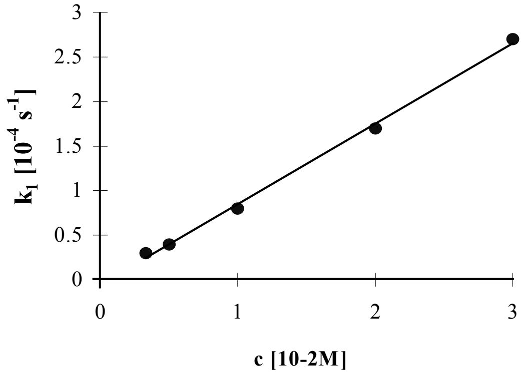


Figure 1. The effect of trans-stilbene (**1a**) concentration on the pseudo first order rate constant of fluorination with F-TEDA ($c_0 = 1\times10^{-2}$M) at 22 °C in an acetonitrile-water mixture ($c_{water} = 7.5\times10^{-2}$M).

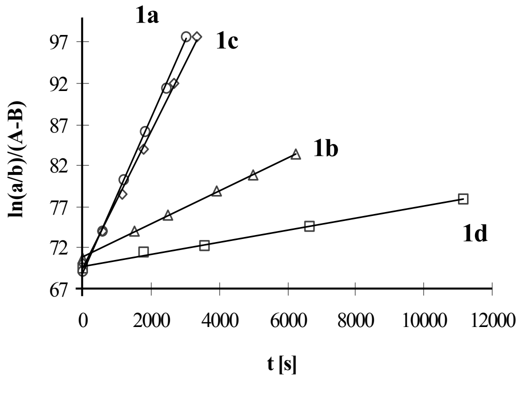


Figure 2. The effect of alkene structure on fluorination with F-TEDA in acetonitrile at 22 °C for ○ trans-stilbene (**1a**), Δ cis-stilbene (**1b**), ◊ 1,1-diphenylethene (**1c**) and at 30 °C for □ styrene (**1d**).

Important information about the nature of the intermediates involved in transformation of alkenes could be obtained by using solvents with various dielectric constants, or by using a mixtures of solvents where Grunvald-Winstein Y values were already determined[22] as in the case of acetonitrile-water mixtures.[23] As evident from Table 2, variation of Y in the range of 3.19 units had a very small effect on second order rate constants for 1,1-diphenylethene and styrene.

The effect of solvent polarity on various functionalizations of the sp^2 carbon atom is presented in Figure 3; in bromination of methylideneadamantane[24] and solvolysis of p-methoxybenzoyl chloride[25] very large effects were observed (ionic reactions) in comparison with the values determined for styrene fluorination with F-TEDA-BF_4, indicating small changes in the polarity of the rate determining transition state in comparision with the reactants.

Table 2. The effect of solvent polarity on the second order rate constants for fluorination of 1,1-diphenylethene and styrene in acetonitrile-water solution.[a]

Solvent [b]	Y_{benzyl} [c]	k_2 [$10^{-3}M^{-1}s^{-1}$]	
		1,1-Diphenyletene	Styrene
90An	–1.45	4.9	2.6
80An	–0.35	3.2	2.1
70An		2.8	
60An	0.81	2.8	2.3
50An		3.4	
40An	1.74		3.6

[a] Reactions at 22 °C for 1,1-diphenylethene and at 50 °C for styrene. [b] % v/v of acetonitrile in water solution. [c] Values from ref. 23.

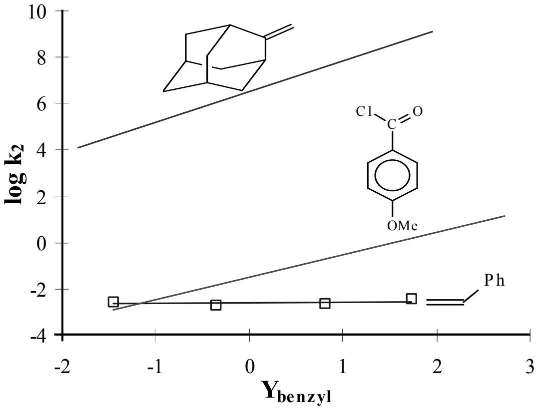
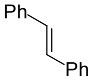
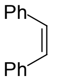
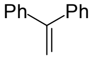
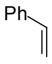


Figure 3. The effect of solvent polarity (Y_{benzyl}) on fluorination of styrene with F-TEDA-BF_4 in an acetonitrile-water mixture at 50 °C (□) in comparison with bromine addition to methylidene-adamantane[24] and solvolysis of *p*-methoxybezoyl chloride.[25]

Table 1. The effect of alkene structure (1), nucleophile (Nu)[a] and reaction temperature on the second order rate constants for fluorination with F-TEDA.

Alkene	Nu	T [°C]	K_2 [$10^{-3}M^{-1}s^{-1}$]	ΔH≠ [$kJmol^{-1}$]	ΔS≠ [$Jmol^{-1}K^{-1}$]
 **1a**	–	17.0	5.3 ±0.4	72.7	–37.9
		22.0	9.0 ± 0.3		
		27.0	14.8 ± 0.4		
	H_2O	17.1	5.5 ±0.1	71.1	–43.0
		22.0	9.5 ±0.1		
		26.9	14.9 ±0.5		
	MeOH	17.0	5.7 ±0.1	68.9	–50.6
		22.0	9.1 ±0.4		
		27.0	15.1 ±0.5		
 **1b**	–	16.9	1.2 ±0.1	72.2	–51.7
		22.0	2.0 ±0.1		
		27.0	3.5 ±0.1		
	H_2O	16.9	1.4 ±0.0	68.4	–63.7
		21.9	2.3 ±0.06		
		27.0	3.8 ±0.15		
	MeOH	17.1	1.5 ±0.1	64.0	–78.7
		22.0	2.3 ±0.2		
		27.1	3.7 ±0.1		
 **1c**	–	17.0	5.3 ±0.1	65.5	–62.6
		21.9	8.4 ±0.2		
		27.0	13.5 ±0.5		
	H_2O	17.2	5.3 ±0.1	64.7	–65.6
		22.0	8.2 ±0.2		
		27.1	13.3 ±0.2		
	MeOH	17.1	5.5 ±0.3	60.9	–78.0
		22.0	8.8 ±0.5		
		27.1	13.0 ±0.5		
 **1d**	–	50.0	3.9 ±0.0	72.0	–68.7
		54.9	6.4 ±0.3		
		50.0	9.0 ±0.2		
	H_2O	30.0	0.57 ±0.1	76.1	–56.0
		34.9	0.94 ±0.1		
		40.0	1.57 ±0.01		
	MeOH	30.1	0.51 ±0.04	85.5	–26.3
		35.0	0.88 ±0.01		
		39.9	1.52 ±0.02		

[a] Concentration of alkene ($2\times10^{-2}M$), F-TEDA-BF_4 ($1\times10^{-2}M$) and R-OH ($7.5\times10^{-2}M$); molar ratio of alkene: F-TEDA-BF_4 : R-OH= 2: 1: 7.5.

In order to compare the reaction parameters for fluorination reactions of phenyl-substituted alkenes by F-TEDA-BF_4 with parameters for functionalization by other reagents, second order rate constants for various transformations of styrene and relative rates for the same transformations for 1,1-diphenylethene and *trans*-stilbene are presented and compared in Table 3.

Table 3. The effect of reagent on second order rate constants for functionalization of styrene (**1d**) and the relative reactivities for 1,1-dipheylethene (**1c**) and *trans*-stilbene (**1a**).

Reagent	React. cond.	Ref.	k_2 [$M^{-1}s^{-1}$]	Relative rates	
			1d	**1c/1d**	**1a/1d**
Br_2	MeOH; 25 °C	26	1.53×10^3	28	0.0071
CrO_2Cl_2	10 °C, CCl_4	27	2.9×10^1	12.3	0.16
CrO_3	0.002M H_2SO_4 in 95% $MeCO_2H$; 25 °C	28	2.78×10^{-2}	2.2	1.32
$MeCO_3H$	MeCOOH; 26 °C	29	1.12×10^{-2}	4.29	0.6
F-TEDA	7.5×10^{-2}M H_2O in MeCN; 22 °C		2.5×10^{-4}*	32.8	38

* calculated from k_2 of 0.57×10^{-3} $M^{-1}s^{-1}$ at 30 °C.

It is evident that the introduction of a second phenyl group on the same carbon atom increased the rate of the transformation and the effect strongly depended on the reagent used. In all demonstrated examples 1,1-diphenylethene was more reactive than styrene, and increased reactivity was especially evident for the reaction with F-TEDA-BF_4, while only in the case of the reaction with ArSCl was a decrease in reactivity observed, where a relative rate factor of 0.4 was found.[30] Introduction of a second phenyl group on the second carbon atom was reflected in lower reactivity compared to styrene in the case of bromination with Br_2, chlorination with CrO_2Cl_2 and epoxidation with MeCOOOH, a small increase of reactivity was observed in the case of reaction with CrO_3, while interestingly, fluorination of *trans*-stilbene with F-TEDA was found to be significantly faster than reaction with styrene.

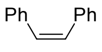
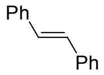
The effect of the reagent on the activation parameters for various transformations of styrene, *p*-nitrostyrene and 1,1-diphenylethene are presented in Table 4. It is evident that fluorine introduction with F-TEDA-BF_4 into these alkenes required a higher energy of activation than chlorine and bromine addition reactions; however the similarity in energy profile with peroxyacids is evident.

Table 4. The effect of reagent on activation parameters for styrene (**1d**), *p*-nitrostyrene and 1,1-diphenylethene (**1c**).

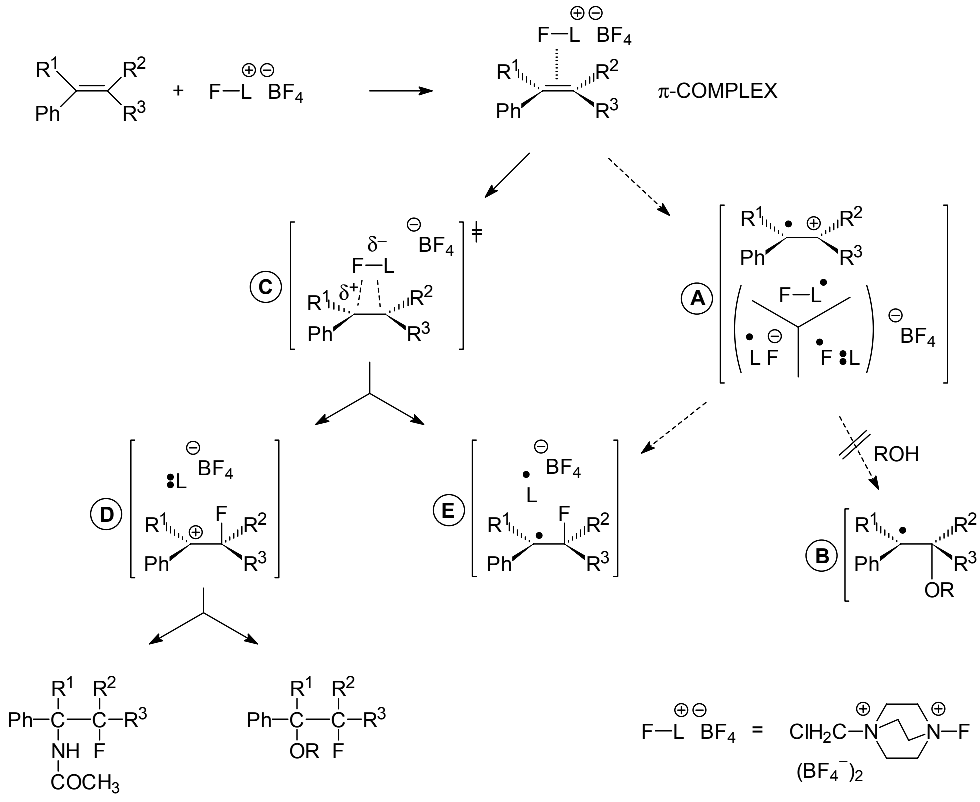
Alkene	Reagent	Ref.	$\Delta H^{\neq}$ [$kJmol^{-1}$]	$\Delta S^{\neq}$ [$Jmol^{-1}K^{-1}$]
Styrene (**1d**)	Br_2	31	19.7	–157.4
	ISCN	30	32.2	–184.2
	CrO_2Cl_2	27	33.9	–99.6
	NOCl	30	38.1	–154.9
	ArSCl	30	54.0	–129.8
	$MeCO_3H$	32	54.4	–131.8
	$PhCO_3H$	30	59.4	–104.6
	F-TEDA		76.1	–56.0
p-NO_2-Styrene	Br_2	34	37.7	–159.0
	Cl_2	34	22.2	–123.5
1,1-Diphenyl-ethene (**1c**)	CrO_2Cl_2	27	13.8	–147.8
	F-TEDA		64.7	–65.6

The effect of alkene geometry and reagent on relative reactivities and activation parameters for transformations of *cis*- and *trans*-stilbene are presented in Table 5. It is known that the rate of bromine addition was strongly influenced by solvent polarity and activation parameters for bromine addition in acetic acid[33] were closer to F-TEDA-BF_4 fluorination of stilbene than those observed for styrene derivatives[31] (Table 4). However, relative reactivities were quite different and bromination of the *cis*-isomer is faster than for *trans*-analogue, while for fluorination with F-TEDA-BF_4 the opposite situation was established.

Table 5. The effect of reagent structure and geometry of 1,2-diphenylethene on relative rates and activation parameters.

Alkene	 **1b**			 **1a**		
Reagent	Br_2[33]	CrO_2Cl_2[27]	F-TEDA	Br_2[33]	CrO_2Cl_2[27]	F-TEDA
$\Delta H^{\neq}$ [$kJmol^{-1}$]	53.5	37.5	68.4	52.3	34.2	71.1
$\Delta S^{\neq}$ [$Jmol^{-1}K^{-1}$]	–90.0	–158.7	–63.7	–100.9	–110.9	–43.0
k(**1b**)/k(**1a**)	2.96	1.79	0.24			

It has been suggested that the electron transfer process is the main reaction path for mild introduction of fluorine into phenyl substituted olefins with the N-F type of reagents.[16,35,36] Laser flash photolysis generation of ion-radicals from styrene and its substituted derivatives clearly indicated that the primary process is attack of a nucleophile at position C-2, and formation of a radical intermediate has also been proven.[37,38] On the other hand, it has been demonstrated that attack of the nucleophile on ion radicals at position C-2 is also very dependent on the nucleophile structure and steric arrangement at C-2; the second order rate constants for methanol incorporation are as follows:[37] 1.8×10^8 $M^{-1}s^{-1}$ for styrene, 1.9×10^8 $M^{-1}s^{-1}$ for 2-phenyl-propene, 9.7×10^6 $M^{-1}s^{-1}$ for E-1-phenyl-propene and 2×10^5 $M^{-1}s^{-1}$ for 1-phenyl-2-methyl-propene. Scheme 2 presents possible reaction pathways for mild introduction of fluorine into alkenes with F-TEDA-BF_4. In the first step the formation of a π complex is suggested, followed by an electron transfer from the alkene to F-TEDA-BF_4 thus inducing a formation of cation radical with a positive charge on C-2 (similar to laser flash photolysis studies[37]) and of F-L$^\bullet$ which could decompose to a pair consisting of the fluoride anion and L$^\bullet$, or a fluorine radical and **L:** (intermediate A). However, attack of acetonitrile, water or methanol on C-2 was not observed, but in spite of this fact the situation in the proposed intimated pair **A** is not clear since attack by fluoride anion on the ion radical



Scheme 2

could not be excluded. Solvent polarity studies and structural variation of the alkene indicated only a small difference in the polarity of the reactants and the rate determining transition state, supporting the formation of a fluoro-substituted radical **E**. The nonpolar nature of the rate determining step is also supported by the low Hammet value ρ^+ of –1.42 for fluorination of substituted 1,1-diphenylethenes[20] (the following ρ^+ values for styrene derivatives were determined: –1.3 for $C_6H_5CO_3H$,[40,41] –2.03 for ArSCl,[30] –2.08 for NOCl,[30] –2.48 for CF_3OF,[42] –2.59 for JSCN,[30] –3.18 for methoxymercuration,[43] –3.22 for chlorination,[34] –4.5 for bromination[44]).

On the other hand, the recent observation that with F-TEDA-BF_4 norbornene gave rearranged 2-exo-acetamido-7-syn-fluoronorbornane and 2-exo-acetamido-7-anti-fluoronorbornane suggested the carbonium ion nature of the intermediate,[39] and for this reason we believe that the rate determining transition state in fluorination of alkenes has a nonpolar nature **C**, while further processes are much faster. The fluoro carbonium ion **D** reacted either with acetonitrile giving Ritter-type[45] of products or with methanol or water, where the nucleophile entered according to Markovnikov type of regioselectivity. In addition, in the present study we observed some similarity in the kinetic behaviour of fluorination of phenyl substituted olefins with F-TEDA-BF_4 and their epoxydation with peracids what indicates possible analogy in geometry of the structure of rate determining transition state.[32]

Experimental

1-Chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) was crystallised from an acetonitrile-methanol mixture and dried in a vacuum at 20 °C for 5 hours. Styrene (Merck), 1,1-diphenylethene (Merck, Aldrich), *cis*-stilbene (Aldrich) were distilled and *trans*-stilbene was crystallised before use. Acetonitrile (Merck) and methanol (Merck) were purified by distillation and stored over molecular sieves. KI (Merck) and standard solution of $Na_2S_2O_3$ (Riedel-deHaën)) were used as received. Characterisation data for the products **2**, **3**, and **4** were already reported.[19–21]

Determination of pseudo first order rate constants for the reaction of trans-stilbene with F-TEDA-BF_4: To 35 mL of a thermostatted acetonitrile-water solution (4.125 mmol of water) of various amount of *trans*-stilbene (0.275, 0.55, 1.1, 1.65 mmol), 20 mL of a thermostatted acetonitrile solution of F-TEDA-BF_4 (0.55 mmol) was added and stirred at 22 °C. After various times 10 mL aliquots were mixed with 20 mL of ice cold 0.02M KI and the liberated iodine titrated with 0.05M $Na_2S_2O_3$. A linear correlation was found for $lnc = f(t)$. Pseudo first order rate constants were calculated and the effect of trans-stilbene concentration on k_1 is presented in Figure 1.

Determination of rate order and activation parameters for fluorination with F-TEDA-BF_4: To 35 mL of a thermostatted acetonitrile (or mixtures containing 4.125 mmol of water or methanol) solution of 1.1 mmol of substrate (**1a**, **1b**, **1c**, **1d**), 20 mL of a thermostatted solution of F-TEDA-BF_4 (0.55 mmol) was added and stirred at various temperatures. The progress of F-TEDA-BF_4 consumption was monitored by iodometric titration. Second order rate constants were calculated from the equation: $1/(A–B) \ln(Ba/Ab) = k_2t$ and a linear relationship was found. The effect of alkene structure on second order rate constants is presented in Figure 2 and Table 1. Further, we investigated the effect of the temperature on k_2. A linear correlation was found and activation parameters were calculated by linear regression from the equation: $\ln(k_2/T) = \ln(k_B/h) + \Delta S^{\neq}/R - \Delta H^{\neq}/RT$. Results are presented in Table 1.

The effect of solvent polarity on second order rate constants for fluorination of 1,1-diphenylethene (1c) and styrene (1d): 1.2 mmol of 1,1-diphenylethene (**1c**) or styrene (**1d**) was diluted in 40 ml of acetonitrile-water mixtures (acetonitrile-water= 34+6; 28+12; 22+18; 16+24; 10+30; 4+36), thermostatted at 22 °C for **1c** and at 50 °C for **1d**, 20 mL of a thermostatted acetonitrile solution containing 0.6 mmol F-TEDA-BF_4 was added and stirred. The progress of F-TEDA-BF_4 consumption was monitored by iodometric titration. The results are presented in Table 2 and Figure 3.

Acknowledgements

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Povzetek

Reakcije 1-klorometil-4-fluoro-1,4-diazoniabiciklo[2.2.2]oktan bis(tetrafluoroborata) (*Selectfluor^{TM}* F-TEDA-BF_4) s fenil substituiranimi alkeni vodijo v acetonitrilu ob prisotnosti nukleofilov (voda, metanol) do nastanka vicinalnih fluorohidroksi oz fluorometoksi alkanov, medtem ko v samem acetonitrilu prevladuje Ritterjev tip transformacije in nastanek vicinalnih fluoro acetamidov. Hitrost reakcije sledi enačbi:

$$\nu = d[\text{F-TEDA-BF}_4] / dt = k_2\,[\text{F-TEDA-BF}_4]\,[\text{alken}]$$

in za reakcije v acetonitrilu pri 22 °C so bile določene sledeče konstante reakcijskih hitrosti: $k_2 = 9.0\times10^{-3}M^{-1}s^{-1}$ za *trans*-stilben (**1a**), $2.0\times10^{-3}M^{-1}s^{-1}$ za *cis*-stilben (**1b**), $8.4\times10^{-3}M^{-1}s^{-1}$ za 1,1-dipfenileten (**1c**) and $0.29\times10^{-3}M^{-1}s^{-1}$ za stiren (**1d**) (izračunano iz $k_2 = 3.9\times10^{-3}M^{-1}s^{-1}$ pri 50 °C). Ugotovljeno je bilo, da prisotnost nukleofila ne vpliva bistveno na vrednosti konstant reakcijske hitrosti. Za reakcije v acetonitrilu so bile določene aktivacijske entalpije vrednosti med 72.7 kJ/mol in 65.5 kJ/mol, s tem da je prisotnost nukleofila povzročila znižanje aktivacijskih entalpij v primeru **1a-c** in zvišanje v primeru stirena. Aktivacijskim entropijam reakcij v acetonitrilu so bile določene vrednosti med –37.9 in 68.7, prisotnost nukleofila je vrednosti znižala v primeru **1a-c** in zvišala v primeru stirena. Spremembe polarnosti topila ovrednotene z Grunwald-Winstein faktorji niso vplivale na reakcijske hitrosti fluoriranja stirena in 1,1-difeniletena kar kaže na to, da se polarnost reakcijskega kompleksa v prehodnem stanju, ki določa hitrost reakcije ne razlikuje bistveno od polarnosti reaktantov.