Stereochemistry and Some Kinetic Aspects of Fluorination of Phenyl-Substituted Alkenes with Selectfluor™ Reagent F-TEDA-BF_4

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Reactions of phenyl-substituted alkenes with Selectfluor™ fluorinating reagent F-TEDA-BF_4 in the presence of various alcohols resulted in the formation of vicinal fluoroalkoxy adducts with Markovnikov type of regioselectivity. The stereochemistry of the fluoro-methoxylation addition reaction was found to be slightly *syn* predominant in the case of (*Z*)-stilbene, indene, and dibenzosuberenone, while equal amounts of both diastereoisomers were formed in the case of (*E*)-1-phenyl-1-propene and acenaphthylene. In the phenyl-substituted benzocyclene series the stereochemistry of fluoro-alkoxylation was found to be dependent on ring size and on the structure of the alcohol. The resulting vicinal fluoroalkoxy adducts were transformed by heating in aqueous HBr to 2-fluoro-1-phenylbenzocyclenes. Correlation of the logarithms of relative rates of fluoro-methoxylation reactions in a series of ten α-phenyl and α,α-diphenyl acyclic and cyclic alkenes with the ionization potentials of these alkenes resulted in a linear relationship with a slope of -2.75. Correlation of $\log k_{rel}$ for the present reaction with those for the reaction of the same alkenes with $CsSO_4F$ or XeF_2 yielded excellent linearity for the pair F-TEDA/$CsSO_4F$ and scarcely good one for the pair F-TEDA/XeF_2. The Hammett correlation analysis of the reaction of substituted 1,1-diphenylethenes with F-TEDA in MeCN/MeOH solvent gave the reaction constant ρ^+ of -1.42, so indicating a moderate electron deficiency on the reactive center in the rate-determining step of the reaction.

The use of a variety of organic compounds incorporating a reactive N–F bond as reagents for fluorination of organic molecules[1] represents significant progress in research dealing with site-selective introduction of a fluorine atom into organic molecules. The impetus for very intense research in this field of organic chemistry[2] is the well-established role of the fluorine atom in bioactive organic molecules.[3] Efforts to find optimally reactive, less toxic, non-explosive, more stable, and cost-effective chemical reagents capable of transfer of a fluorine atom site-selectively into a comprehensive range of organic molecule, promises to be rewarded with the promotion of 1-alkyl-4-fluoro-1,4-diazoniabicyclo[2.2.2.]octane salts[4] as versatile fluorinating reagents,[5a] already commercially available under the trade mark Selectfluor™ reagents. The 1-chloromethyl-4-fluorobis(tetrafluoroborate) analogue F-TEDA-BF_4 has been studied intensively in last two years, resulting in effective selective fluorofunctionalization of activated,[5] and methyl-substituted benzene derivatives,[6] carboanions,[6] phenyl-substituted alkenes,[6,7] and alkynes,[8] steroid enol acetates and silyl enol ethers,[6] organometallic[9] and β-dicarbonyl compounds,[10] organic sulfides[6] and benzenethiols,[5b] arylalkyl *t*-alcohols,[11] and indole derivatives,[12] as well as oxidation of benzylic alcohols and benzaldehydes.[13]

The most valuable information about the reactivity of a new fluorinating reagent can be obtained by studying its reactions with target model substrates which have already been investigated with other reagents. The distinctive possibility of modulation of electronic and steric effects by structural variations, the stability of the fluorinated products and the regioselectivity of the reactions make phenyl-substituted alkenes the most suitable model organic molecules for the study of so-called "electrophilic" fluorination of alkenes and, widely used targets in the comparative study of various reagents,[2] though so far only few kinetic evaluations of fluorination as a function of the structure of the alkene were reported.[14] We now report the stereochemical course and some kinetic aspects of fluorination of pheny-substituted alkenes with F-TEDA-BF_4.

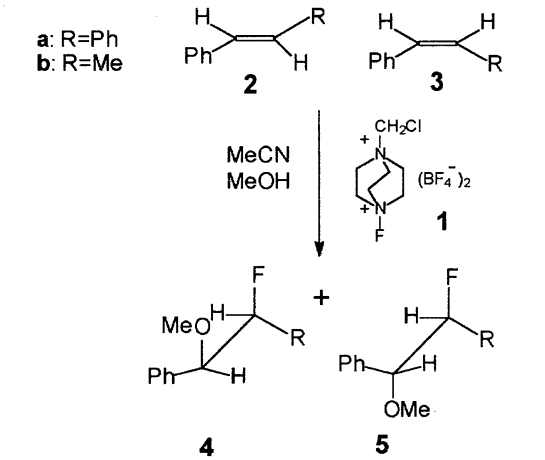
Results and Discussion

In earlier brief reports[6,7] concerning some reactions of phenyl-substituted alkenes with F-TEDA-BF_4 in acetonitrile solution, the addition process across a double bond with collaboration of an external nucleophile and introduction of a fluorine atom following Markovnikov type regioselectivity was observed. As nothing was mentioned about the result of these reactions in the absence of a nucleophilic species in the reaction mixtures, we first of all checked this issue and found that only with two of the examined alkenes (1,1-diphenylethene and triphenylethene), did reaction with F-TEDA in anhydrous acetonitrile result in addition-elimination products (1,1-diphenyl-2-fluoroethene or triphenylfluoroethene) in reasonable yield (75%), while in the case of the other alkenes studied in this report only very low conversion of starting material or in some cases very complex reaction mixtures could be obtained. Even the use of 2,6-dimethyl- or 2,6-di-*t*-buthylpyridine, often used as bases in order to

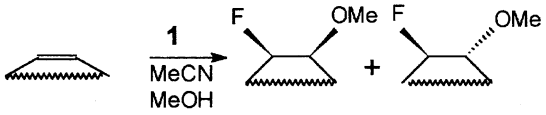
favor the addition-elimination reaction,[1a] did not improve the course of reaction in favor of fluoro-substituted alkenes.

(*E*)- and (*Z*)-1,2-diphenylethenes (**2a**, **3a**) are the most often used test compounds for the elucidation of the stereochemical course of addition reactions on acyclic alkenes, and results vary depending on the fluorinating reagent used.[15] In Scheme 1 some results concerning the stereochemistry of addition reactions across the double bond in acyclic and cyclic phenyl-substituted alkenes mediated with an acetonitrile solution of F-TEDA in the presence of methanol are collected. In the case of **2a** the addition was found to be *anti* predominant resulting in twice as much of the *erytro* 1,2-fluoro-methoxy adduct **5a** as the *threo* diastereoisomer **4a**.[6] The *Z*-isomer of alkene (**3a**), however, gave only a slight excess of the *syn* adduct, while in the case of (*E*)-1-phenyl-1-propene (**2b**) equal amounts of both diastereoisomers were formed. The results in the case of **2a** are similar to those obtained after fluorine addition using $XeF_2/CH_2Cl_2/HF$,[16] while methoxy-fluorination using $CsSO_4F$/MeOH[15] or CF_3OF/MeOH[17] gave an opposite stereo predominance. On reacting F-TEDA in MeCN/MeOH with **3a** the same ratio of diastereoisomers were obtained as in the case of $XeF_2/CH_2Cl_2/HF$[16] or $CsSO_4F$/MeOH.[15]

In order to avoid potential complications in the stereochemical course of the reactions that exist in acyclic systems due to the possibility of rotation about a newly formed



Alkene	R	*Syn*	:	*Anti*	Yield (%)
2a	Ph	28		72	75
3a	Ph	55		45	78
2b	Me	50		50	75

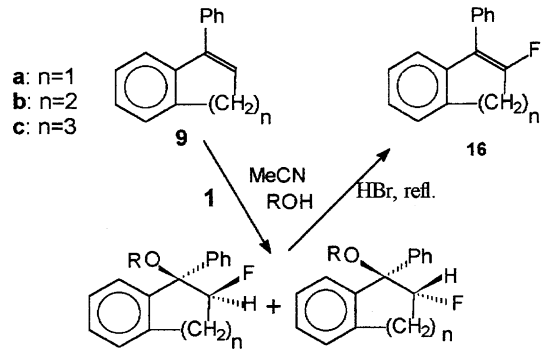


Alkene	*Syn* (**a**)	:	*Anti* (**b**)	Yield (%)
Indene (**6**)	58		42	85
Acenaphthylene (**7**)	50		50	75
Dibenzosuberenone (**8**)	57		43	76

Scheme 1.

C–C single bond in the carbonium ion or radical intermediate, depending on their life time and the energy barrier resisting free rotation, we extended our studies to phenyl-substituted cycloalkenes. Fluorination of indene (**6**) with the F-TEDA/MeCN/MeOH system resulted in the formation in high yield of 2-fluoro-1-methoxyindane, *syn* adduct **6a** being moderately predominant over *trans* diastereoisomer **6b**, while an equal amount of the two vicinal fluoromethoxy isomers was found after the reaction of acenaphthylene (**7**), and again moderate predominance of *syn* addition was observed in the case of dibenzosuberenone **8**.

1-Phenyl-substituted benzocyclenes have many advantages as tools for elucidation of the course of addition reactions, not only from the stereochemical but also from the kinetic point of view. An additional phenyl group lowers the ionization potential of the molecule by more than 0.5 eV in comparison with unsubstituted benzocyclenes and by around 0.2 eV in comparison with their acyclic analogues[14c] (Table 1), considerably influencing their reactivity.[14c,14d] Because of the profusion possibility of conformers of reactive intermediates or products, the ring magnitude in 1-phenyl-benzocyclenes also plays an important role in the stereochemistry of addition reactions, as well as in their kinetics[14c,14d,18]. Reaction of 3-phenyl-1*H*-indene (**9a**, Scheme 2) with F-TEDA in a 10 : 1 solution mixture of MeCN and the corresponding alcohol resulted in formation of diastereoisomeric pairs of 2-fluoro-1-alkoxy adducts in high yield. In the case of methanol or ethanol as the source of the nucleophile the formation of *syn* adducts was found to be predominant, while in the case of isopropyl alcohol an equal amount of both diastereoisomers were formed. The six-member ring analogue in the studied triad 4-phenyl-1,2-dihydronaphthalene (**9b**) transformed differently, however, and *anti* addition of fluoro-alkoxy moieties was found to



n	R	*Syn*		*Anti*		Yield(%)
1	Me	(**10a**)	73	(**11a**)	27	80
	Et	(**12a**)	75	(**13a**)	25	80
	i-Pr	(**14a**)	50	(**15a**)	50	77
2	Me	(**10b**)	37	(**11b**)	63	79
	Et	(**12b**)	40	(**13b**)	60	74
	i-Pr	(**14b**)	31	(**15b**)	69	75
3	Me	(**10c**)	1	(**11c**)	99	82
	Et	(**12c**)	57	(**13c**)	43	80
	i-Pr	(**14c**)	86	(**15c**)	14	75

Scheme 2.

Table 1. Relative Rate Factors (k_{rel}, Relative to 1,1-Diphenylethene) for the Methoxy-Fluorination of Phenyl-Substituted Alkenes with F-TEDA in MeCN 10 : 1

Entry	Alkene	k_{rel}	IP/eV[14c]
1	2-Phenyl-1-propene	0.64	8.40
2	*trans*-1-Phenyl-1-propene	0.54	8.36
3	1,1-Diphenylethene	1.00	8.24
4	1,1-Diphenylpropene[7]	8.60	8.14
5	Indene	0.47	8.40
6	1,2-Dihydronaphthalene	0.63	8.26
7	1-Phenylcycloheptene	29.0	7.92
8	3-Phenyl-1*H*-indene[7]	27.8	7.73
9	1,2-Dihydro-4-phenylnaphthalene[7]	32.2	7.67
10	6,7-Dihydro-9-phenyl-5*H*-benzocycloheptene[7]	11.3	7.91

be preferential in the case of all three alcohols, their relative ratio being almost independed of the alcohol used. The most well expressed role of the structure of the alcohol on the stereochemistry of fluoroalkoxylation was found in the case of 9-phenyl-6,7-dihydro-5*H*-benzocycloheptene (**9c**). The methanol mediated reaction gave almost diastereospecifically *anti* adduct, while in the presence of ethanol or 2-propanol a moderate to prevalent excess of *syn* addition was found. Treatment of diastereoisomeric pairs of fluoro-alkoxy ethers (**10a**—**15c**) with aqueous HBr resulted, after immediate elimination of the corresponding alcohol, in formation of the 2-fluoro-1-phenyl-substituted benzocyclene derivative (**16**, Scheme 2).

When comparing the stereochemical results obtained in this study with those reported for the reactions of caesium fluoroxysulfate in methanol[14d] or XeF_2 in CH_2Cl_2 with the 1-phenylbenzocyclene triad **9a**—**c** we can see that the stereochemical course of the addition reactions is not very different in the case of reactions of **9a** with F-TEDA and $CsSO_4F$, and is almost the same for all three reagents in the case of **9b**, but very different in the case of the seven-member ring analogue **9c**, strongly depending on the reagent and kind of nucleophile used. In the latter case the flexibility of the benzocycloheptane ring make the reaction system very sensitive to any modulation of reaction parameters.

A phenyl group, bonded along a C–C double bond, usually significantly enhances the reactivity of the alkene toward electrophilic addition, while the reactivity after introduction of supplementary phenyl groups depends on the structure of the reagent and the geometry of the alkene.[19] In our preliminary communication[7] and recent papers[14b,14d] we already reported some data on the relative reactivity of phenyl-substituted alkenes as a function of their structure in reactions with modern fluorinating reagents, and confirmed that these facts are valid also for these reactions. Relative reactivities, expressed as relative rate factors (relative to 1,1-diphenylethene), for a set of ten phenyl-substituted alkenes whose reactions with F-TEDA in MeCN/MeOH solution were studied, are collected in Table 1. Comparison of these data with those obtained for the reactions with XeF_2[14b,14c] or $CsSO_4F$[14b,14d] shows that the introduction of a second phenyl group at the geminal position considerably enhances, and at the vicinal position suppresses the reactivity of the alkene in the case of all three reagents, while the reactivity after the introduction of the third or fourth phenyl group strongly depends on the structure of the reagent. In the mono-phenyl-substituted series the reactivity of cyclic alkenes was not found to be appreciably different from their acyclic analogues, while in the case of α,α-diphenyl-substituted alkenes the cyclic analogues are much more reactive than the acyclic ones. Correlating relative rate factors (K_{rel}) for the F-TEDA/MeCN/MeOH mediated reaction of the set of α-phenyl-, and α,α-diphenyl-substituted alkenes (Entries 1—10, Table 1) with their vertical ionization potentials (IP) indicates the trend of increasing reactivity with decreasing IP, resulting in a linear relationship with a very high correlation constant (Fig. 1). The result follows the generally accepted postulate 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, while the linearity of the relationship demonstrates that there is the lack of steric effects in the transition-state structure, and the disruption of the π-bond in the alkenes caused by the reagent is the important, if not the rate-determining step of the reaction,[19—21] at least for the set of alkenes studied. The correlation plot is similar to those recently reported for fluorine addition with XeF_2[14c] or methoxy-fluorination of a similar set of phenyl-substituted alkenes with $CsSO_4F$,[14d] but, however, shows the highest level of negative trend. Therefore we also examined the cross correlation of the k_{rel}/IP plots, and the results shown on Fig. 2 reveal an excellent linear corre-

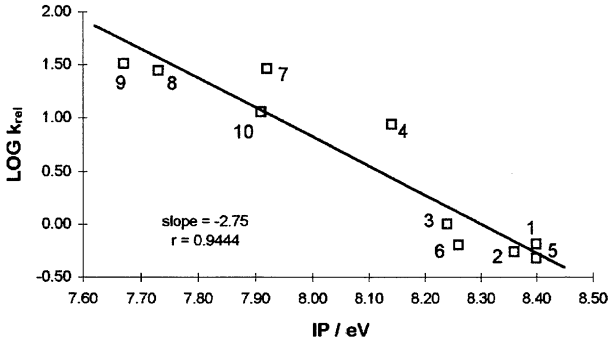


Fig. 1. Plot of log k_{rel} for methoxy-fluorination of mono- and α,α-diphenyl-substituted alkenes (Entries 1—10, Table 1) using F-TEDA-BF_4 versus alkene ionization potential (IP).

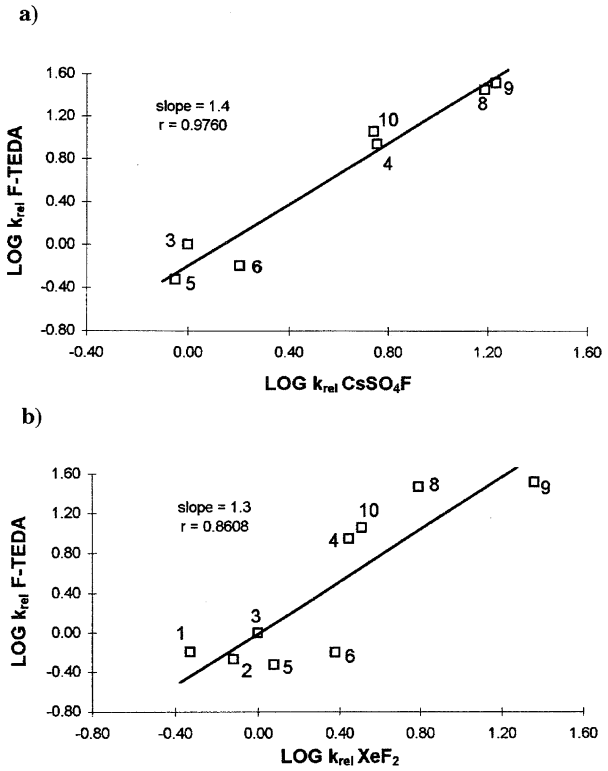


Fig. 2. a) Correlation plot of relative rates of methoxy-fluorination of phenyl-substituted alkenes (Entries 1—10 Table 1) with $CsSO_4F$[14d] and F-TEDA. b) Correlation plot of relative rates of fluorination with XeF_2[14c] and methoxy-fluorination with F-TEDA of phenyl-substituted alkenes (Entries 1—10, Table 1).

lation for the methoxy-fluorination reactions with F-TEDA and $CsSO_4F$, and a scarcely good one for fluorine addition with XeF_2 and methoxy-fluorination with F-TEDA, thus indicating that the former pair of reactions must have a very similar course, while for the latter pair significant differences in mechanistic details are probable.

Hammett correlation analysis, often used as a very instructive procedure for the elucidation of the nature of reactive intermediates involved in organic reactions, was, however, not so frequently applied in assessment of the mechanistic details concerning the fluorination of organic compounds. Actually, when discussing the fluorination of alkenes, only in the study of the fluorination of substituted styrene derivatives with CF_3OF was the effect of substituents on the course of the reaction evaluated with the Hammett procedure.[14a] We correlated the relative rate factors for the fluorination of substituted 1,1-diphenylethenes with F-TEDA in MeCN/MeOH and the Brown–Okamoto's substituent constants[22] (σ^+) using the Hammett equation, and the correlation plot $\log k_{rel}/\sigma^+$, shown in Fig. 3, was found to be a straight line with a regression slope $\rho^+ = -1.42$ and an excellent correlation coefficient. The sign and the magnitude of the reaction constant (ρ^+) indicates a moderate electron deficiency on the reactive centre in the rate determining step of the reaction. The value of the reaction constant obtained for the methoxy-fluorination

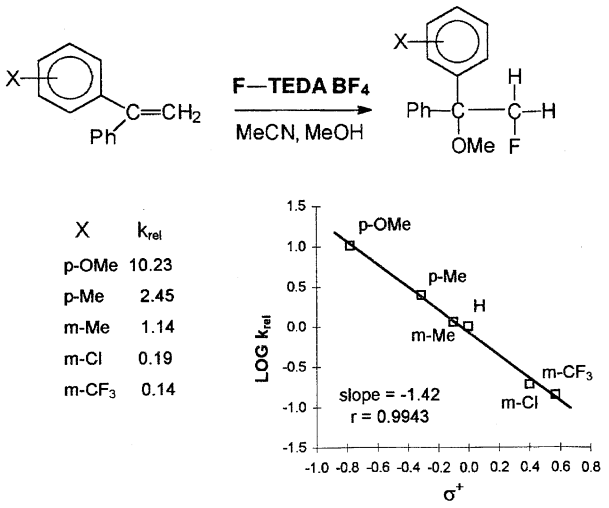


Fig. 3. Hammett correlation plot ($\log k_{rel}/\sigma^+$) for methoxy-fluorination of substituted 1,1-diphenylethenes with F-TEDA in MeCN/MeOH 10 : 1.

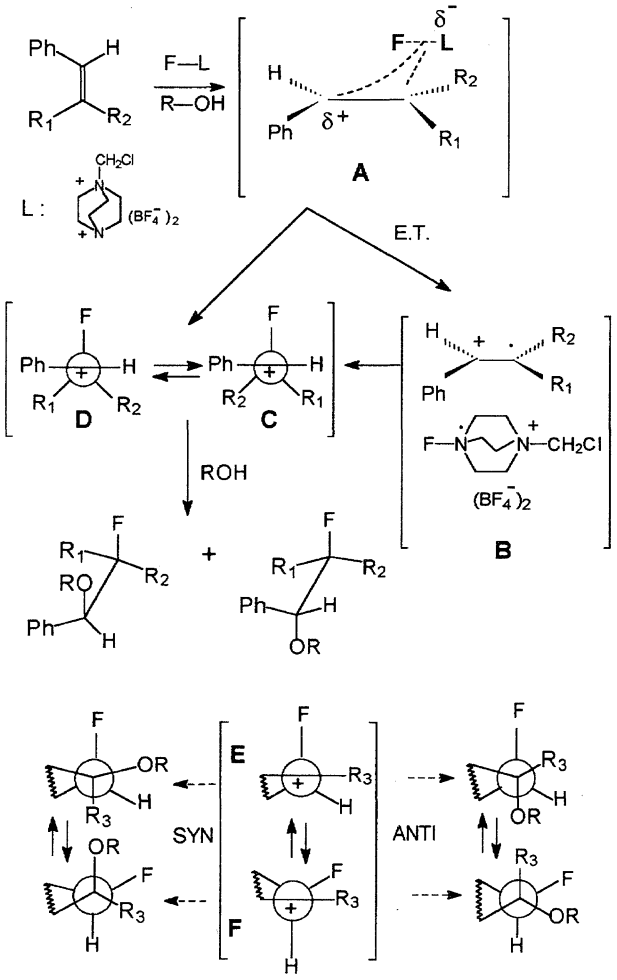
of 1,1-diphenylethenes with F-TEDA is lower than the constant obtained for the fluorination of substituted styrenes with CF_3OF,[14a] or those characteristic of various electrophilic addition reactions on phenyl-substituted alkenes,[18,19] and not considerably higher than those obtained for reactions where free-radical intermediates were involved as reactive intermediates. Therefore, we checked the effect of free-radical scavengers on the course of the reaction but did not find any suppression of the conversion of the starting alkene or change in stereochemistry of the addition if the reactions were carried out in the presence of oxygen or nitrobenzene.

The mechanism describing the fluorination of organic molecules with usually called "electrophilic" fluorinating reagents is still a subject of considerable debate and controversy among fluorine chemists. The main dilemma is dealing with the "electrophilicity" of a fluorine atom or its positively polarized character in these reagents, since the reaction process appears to require the removal of an electron pair from fluorine, the most electronegative element, thus forming F^+ species, which is energetically very unfavorable. On the basis of various arguments the existence of "electrophilic" or even positively polarized fluorine was declared in general to be unlikely,[23] while an interesting compromise, describing the direct transfer of a fluorine atom into an organic molecule over electron-rich moieties, introduced the concept of an S_N2-like reaction of an electron-rich centre (C–C double bond, carboanions..) with a fluorine atom attached to a good leaving group in the reagent.[24] In this case it is unnecessary that electrons be removed from the fluorine prior to reaction with the nucleophile, since concerted displacement of a good leaving group need never a development of deficiency of electrons around the fluorine atom. But the dilemma remains and is formulated in the question whether the primary process proceeds through a direct fluorine transfer (FT), or a single electron transfer (ET) from an electron-rich centre on the substrate to an electron deficient reagent. In the case of alkenes the subject of the debate is

whether a fluoro carbonium intermediate is directly formed by FT of through a two-step process where a ET, thus forming a cation radical intermediate, precedes the formation of a β-fluoro carbocation. The formation of a cation radical is very likely since the reagents in question are known as very strong oxidants and an ET pathway was proposed as a reaction route in fluorination with some fluoroxy[14a,25] as well as N–F reagents,[1a,1b] but criticized in the case of the reactions of carboanions with various N–F reagents where the principle of a radical clock was used as a criterion for distinguishing between the two reaction pathways.[26]

First of all we feel the need for some terminological unification on the matter and propose the term **F–L** fluorinating reagents for the group of reagents usually called, but controversially, "electrophilic fluorinating reagents". Descriptor **L** represents the ligand part of the fluorinating reagent to which a reactive fluorine atom is attached and could be an atom, but is usually larger, in some cases even a very sophisticated structural block. An active fluorine atom is usually bonded to the ligand part **L** through a fluorine-oxygen (fluoroxy reagents: CF_3OF, CH_3COOF, CF_3COOF, $CsSO_4F$ etc.), a fluorine-xenon (XeF_2 and related reagents) or a fluorine-nitrogen bond (NF reagents: *N*-fluoropyridinium salts, *N*-fluorosulfonimides, F-TEDA etc.). All these reagents have at least one common characteristic, i.e. the electron density flow in the first stage of electron exchange in reactions mediated by them is directed from an electron rich centre on the substrate towards an electron deficient one on the reagent. Secondly, in our opinion on the basis of presently known facts it is not possible to generalize about the reaction mechanism of organic molecules with F–L reagents without the risk of being speculative. Under various reaction conditions the reactions could run along a variety of reaction channels and the selection of a favorable channel or a combination of them is governed by the structure and the nature of the substrate (kind and position of the active electron-rich center, ionization potential, nature of a possible leaving group etc.), the structure and the nature of the reagent (nature of the reactive bond, basicity of the leaving group L^-, oxidation potential etc.), the reaction media, temperature, the relative concentration of substrate and reagent, and other reaction variables. It is not necessary that a particular F–L reagent chooses the same reaction channel in reactions with different kinds of substrate organic molecules, or that a similar channel is chosen when a particular kind of substrate reacts with different F–L reagents. Extensive comparative studies of the reactions of selected series of model compounds with various F–L reagents under similar reaction conditions should help in clarifying the situation and enable more general conclusions to be drawn.

On the basis of experimental results from this and some recent work,[6,7] we propose the reaction mechanism schematically shown in Scheme 3, as so far the most realistic description of the reaction pathway of the fluorination of phenyl-substituted alkenes with F-TEDA. The interaction between an electron-available phenyl-substituted C–C double bond and an electron demanding reagent provokes an electron density flow directed towards the F–L reagent, and results in a π-like complex (**A**), carrying electron deficiency at the α-phenyl-substituted carbon atom. The important role of the alcohol molecule(s) as the moiety supporting the interaction complex and the source of the external nucleophile must also be taken into account, since, with few exceptions, without its presence the reaction is suppressed or becomes very complex. Very little could be said about the geometry of the coordination of the π-like complex **A**, and theoretical calculations similar to those reported recently for fluorine addition to alkenes[27] would also be very helpful. Electron(s) exchange[28] between the electron-rich double bond and the electron deficient reagent can proceed through at least two channels: — by direct fluorine transfer (FT) following S_N2-like displacement of the L part of the reagent, thus forming a β-fluoro carbocation (**C** and **D**), — or by single electron transfer (ET) resulting in formation of a cation radical **B**.



Scheme 3.

In the latter case the cation radical **B** can be further transformed to the β-fluorocarbonium ion by collapsing with $F–N^{\bullet}(CH_2CH_2)_3N^+–CH_2Cl(BF_4^-)_2$, or by reaction with another molecule of F–L. The β-fluorocarbocation derived from acyclic phenyl-substituted alkenes can rotate around the newly formed C–C single bond and isomerisation **C/D** could take place. In the case of cyclic analogues, how-

ever, the isomerisation **E/F** governed by the flexibility of the ring must be taken into account. In the final phase of the addition reaction collapse of the β-fluorocarbocation with an alkoxy nucleophile can occur from the *syn* or *anti* side, resulting in a vicinal fluoro-alkoxy adduct. According to the observed Markovnikov type of regioselectivity and the lack of radical inhibition effects on the course of addition reactions it appears that β-fluorocarbocations are important intermediates in these reactions. The almost complete lack of stereoselectivity and the absence of rearranged products[1b] led us to the conclusion that their open structure is much more favored in comparison with bridged or phenonium ion one. The slight to moderate *syn* prevalent stereochemistry of fluoro-alkoxy addition observed in several cases could be explained by ion pairing phenomena as the consequence of the participation of an external nucleophile in the coordination of intermediates, while *anti* stereochemical prevalence in the case of fluoro-alkoxylation of **9b** and fluoro-methoxylation of **9c** is caused by steric effects as a consequence of flexibility of the ring, rather than by any bridging in the fluorocarbonium intermediate.

On the basis of the results of this report, we are still unable to discriminate unequivocally among the processes (FT or ET) which dominate the formation of a β-fluorocarbonium ion. In spite of the fact that IP is defined as the removal of one electron from the molecule, thus forming a cation radical, the linear correlation between reactivities and IP does not necessarily indicate an ET mechanism since many such correlations were reported for reactions declared to be purely ionic.[19,20] Some theoretical clarification of this controversy is in any case necessary, but the value of the reaction constant (ρ^+), obtained from the Hammett correlation (Fig. 3), which lies in between values characteristic for ionic reactions and those involving free radical intermediates, speaks in favor of the existence of the ET reaction pathway as one of the probable reaction channels in the formation of β-fluorocarbocation intermediate in the fluorination of phenyl-substituted alkenes with F-TEDA.

Experimental

^{1}H 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. F-TEDA-BF_4 from Air Products and Chemicals, Inc., Allentown, USA was used without additional purification. 1,1-Diphenylpropene, 1-phenylcycloheptene, 3-phenyl-1*H*-indene, 6,7-dihydro-9-phenyl-5*H*-benzocycloheptene, and substituted 1,1-diphenylethenes were prepared by known procedures,[18] while other alkenes were obtained from commercial sources and purified before use. The values for ionization potentials of phenyl-substituted alkenes (Table 1), measured under the same conditions using a mass spectrometric technique, applying electron impact ionization, were taken from the literature.[14c] Relative reactivities expressed by relative rate factors (k_{rel}) were calculated from equation[29] $k_{rel} = k_A/k_B = \log((A-X)/A)/\log((B-Y)/B)$, derived from the Ingold–Shaw relation,[30] where A and B are the amounts (in mmols) of starting material and X and Y the amounts of products derived from them. The relative rate factors, obtained by this often used and frequently described competitive technique,[14,20] and collected in Table 1 and Fig. 3, are the averages of three measurements.

Fluorination of Phenyl-Substituted Alkenes with F-TEDA-BF_4. General Procedure. To a solution of 2 mmols of phenyl-substituted alkene in 20 mL of dry MeCN, 2 mL of corresponding alcohol and 708 mg (2 mmols) of F-TEDA-BF_4 were added and the reaction mixture was stirred at room temperature for one hour (in the case of the reactions carried out in the absence of alcohol and in the case of fluoro-methoxylation of **8**, the reaction mixture was heated under reflux for two to six hours), then diluted with 40 mL of CH_2Cl_2, washed with a 10% aqueous solution of $NaHCO_3$ and water, dried over anhydrous Na_2SO_4, the solvent removed under reduced pressure and the crude reaction mixture thus obtained was analyzed by ^{1}H and ^{19}F NMR spectroscopy. The amount of fluorinated products was determined from ^{19}F NMR spectra of the crude reaction mixture using octafluoronaphthalene as additional standard (yields collected in Schemes 1 and 2), while pure products were isolated by TLC (SiO_2, petrol ether : CH_2Cl_2 = 1 : 1) and identified on the basis of the spectroscopic data and comparison with independently synthesized products or the literature. Yields listed below refer to isolated pure products.

***d,l-threo*-1-Fluoro-2-methoxy-1,2-ethane[31] (4, R=Ph):** 39%; oily.

***d,l-erytro*-1-Fluoro-2-methoxy-1,2-ethane[31] (5, R=Ph):** 30%; mp 53—54 °C.

***cis*-2-Fluoro-1-methoxyindane[15] (6a):** 47%; mp 37—38 °C.

***trans*-2-Fluoro-1-methoxyindane[15] (6b):** 32%; oily.

***cis*-1-Fluoro-2-methoxyacenaphthene[15] (7a):** 33%; mp 38-39 °C.

***trans*-1-Fluoro-2-methoxyacenaphthene[15] (7b):** 34%; oily

***cis*-10-Fluoro-11-methoxydibenzo(*a*,*f*)cycloheptan-5-one (8a):** 31%; white crystals (MeOH); mp 149.5—150.5 °C; ^{19}F NMR ($CDCl_3$) $\delta_F = -167.2$ (dd, $J = 52.0$, 18.5 Hz); ^{1}H NMR $\delta_H = 5.9$ (d, $J = 52.0$ Hz, 1H), 4.85 (d, $J = 18.5$ Hz, 1H), 3.3 (s, 3H), and 7.5—8.5 (m, 8H); MS *m/z* 257 ($M^+ + 1$; 16%), 256 (M^+; 85), 255 (10), 241 (16), 236 (25), 225 (18), 224 (45), 221 (37), 209 (16), 208 (12), 197 (90), 196 (68), 195 (23), 194 (100), 193 (84), 183 (22), 178 (31), and 165 (80). Calcd for $C_{16}H_{13}FO_2$: C, 74.99; H, 5.27%. Found: C, 74.88; H, 5.27%

***trans*-10-Fluoro-11-methoxy-dibenzo(*a*,*f*)cycloheptan-5-one (8b):** 23%; oily; ^{19}F NMR ($CDCl_3$) $\delta_F = -163.3$ (dd, $J = 52.0$, 2.5 Hz); ^{1}H NMR $\delta_H = 6.0$ (dd, $J = 52.0$, 5.0 Hz, 1H), 4.95 (dd, $J = 5.0$, 2.5 Hz, 1H), 3.3 (s, 3H), and 7.5—8.5 (m, 8H). HRMS Calcd for $C_{16}H_{13}FO_2$: M, 256.0899. Found : *m/z* 256.0892. MS *m/z* 257 ($M^+ + 1$; 18%), 256 (M^+; 98), 255 (10), 236 (8), 225 (18), 224 (62), 221 (24), 209 (28), 208 (25), 197 (90), 196 (66), 195 (22), 194 (98), 193 (100), 183 (20), 178 (100), and 165 (75).

(±)-1-Methoxy-*r*-1-phenyl-*t*-2-fluoroindane[15] (10a): 54%; oily.

(±)-1-Methoxy-*r*-1-phenyl-*c*-2-fluoroindane[15] (11a): 20%; oily.

(±)-1-Ethoxy-*r*-1-phenyl-*t*-2-fluoroindane[14d] (12a): 55%; mp 67—68 °C.

(±)-1-Ethoxy-*r*-1-phenyl-*c*-2-fluoroindane[14d] (13a): 18%; mp 114—115 °C.

(±)-1-Isopropoxy-*r*-1-phenyl-*t*-2-fluoroindane[14d] (14a): 35%; mp 71—73 °C.

(±)-1-Isopropoxy-*r*-1-phenyl-*c*-2-fluoroindane[14d] (15a): 33%; mp 57—58 °C.

(±)-1-Methoxy-*r*-1-phenyl-*t*-2-fluoro-1,2,3,4-tetrahydronaphthalene[14d] (10b): 19%; oily.

(±)-1-Methoxy-*r*-1-phenyl-*c*-2-fluoro-1,2,3,4-tetrahydronaph-

thalene[14d] **(11b):** 43%; oily.

(±)-1-Ethoxy-*r*-1-phenyl-*t*-2-fluoro-1,2,3,4-tetrahydronaphthalene[14d] **(12b):** 27%; mp 56.5—57.5 °C.

(±)-1-Ethoxy-*r*-1-phenyl-*c*-2-fluoro-1,2,3,4-tetrahydronaphthalene[14d] **(13b):** 40%; mp 70—72 °C.

(±)-1-Isopropoxy-*r*-1-phenyl-*t*-2-fluoro-1,2,3,4-tetrahydronaphthalene[14d] **(14b):** 12%; mp 59.5—61.5 °C.

(±)-1-Methoxy-*r*-1-phenyl-*c*-2-fluorobenzocycloheptane[14d] **(11c):** 61%, oily.

(±)-1-Ethoxy-*r*-1-phenyl-*t*-2-fluorobenzocycloheptane[14] **(12c):** 40%; mp 104—105 °C.

(±)-1-Ethoxy-*r*-1-phenyl-*c*-2-fluorobenzocycloheptane[14d] **(13c):** 29%; mp 98—99.5 °C.

(±)-1-Isopropoxy-*r*-1-phenyl-*t*-2-fluorobenzocycloheptane[14d] **(14c):** 55%; mp 100.5—101.5 °C.

(±)-1-Isopropoxy-*r*-1-phenyl-*c*-2-fluorobenzocycloheptane[14d] **(15c):** 8%; mp 76—77.5 °C.

Synthesis of 2-Fluoro-1-phenylbenzocyclenes (16). Aqueous HBr (40%, 5 mL) was added to the isolated crude reaction mixtures, obtained after fluoro-alkoxylation of benzocyclenes **9**, and then heated under reflux for an hour, extracted with CH_2Cl_2 (40 mL), the organic layer washed with aqueous $NaHCO_3$ (10%) and water, dried and after removing the solvent under reduced pressure and isolation of the product by column chromatography (SiO_2, pentane) 2-fluoro 3-phenyl-1*H*-indene[14c] (**16a**) [71%, mp 35.5—36 °C], 3-fluoro-4-phenyl-1,2-dihydronaphthalene[14c] (**16b**) [68%, mp 47.5—48.5 °C] or 6,7-dihydro-8-fluoro-9-phenyl-5*H*-benzocycloheptene[14c] (**16c**) [65%, mp 90—91 °C] were obtained, respectively.

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