Bull. Chem. Soc. Jpn., **68**, 1655—1660(1995)

Chemistry of Organo Halogenic Molecules. 140.
Role of the Reagent Structure on the Transformations of Hydroxy Substituted Organic Molecules with the *N*-Fluoro Class of Fluorinating Reagents[1)]

Marko Zupan,* Jernej Iskra, and Stojan Stavber

Laboratory for Organic and Bioorganic Chemistry, Department of Chemistry, and “J. Stefan” Institute,
University of Ljubljana, Slovenia

(Received September 5, 1994)

Hydroxy-substituted organic molecules were used as target molecules in investigations of the role of the reagent structure on the reactivity of three types of N–F class fluorinating reagents: 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) F-TEDA (**1a**), *N*-fluorobis(phenylsulfonyl)amine NSF (**1b**), and *N*-fluoropyridinium heptafluorodiborate–pyridine (1/1) NFP (**1c**). Methanol is stable, but hydroquinone is very quickly transformed in acetonitrile to quinone with F-TEDA at room temperature; on the other hand, NSF is less reactive, while oxidation with NFP is achieved only at an elevated temperature; a structure variation of the hydroquinone derivatives did not influence oxidation. Fluorination was achieved with monohydroxy-substituted aromatic compounds; a similar trend concerning the reactivity of N–F reagent (**1**) was also observed in reactions with 1- and 2-naphthol, while 9-phenanthrol gave 10,10-difluoro-9-(10*H*)-phenanthrenone with F-TEDA in acetonitrile and 9,10-phenanthrenequinone with NSF. Dealkylation was observed in a reaction with 4-methoxyphenol; although the thio analogue gave bis(4-methoxyphenyl) disulfide, the reactivity was changed and NSF was more reactive than F-TEDA and NFP.

The reactivity of fluorinating reagents of the F–L type (where L denotes a ligand) strongly depends on the structure of the reagent, the structure of the organic molecule (type of transformation—substitution, addition$\cdots$) and the reaction conditions, where the solvent, catalyst, and temperature are the most important factors.[2,3)] The prediction of the course of introduction of a fluorine atom into an organic molecule is still only a partly solved problem; in order to improve our knowledge concerning the role of the reagent structure in the process of fluorination, as much information as possible is needed concerning several target organic molecules. It is also known that F–L type reagents are usually very strong oxidants. For this reason it is very important to examine the reactivity of organic molecules bearing very sensitive functional groups, one of them being hydroxyl. It has already been demonstrated that reactions with alcohols and phenols strongly depend on the reagent used. Benzyl alcohol was converted with XeF_2 to rearranged products, while the course of the transformation of phenyl-substituted alcohols also depends on their structure.[4)] On the other hand, $CsSO_4F$ transformed benzyl alcohol to benzaldehyde, which was further converted to acyl fluoride,[5)] while the substitution process was observed in various hydroxyalkyl-substituted aromatic molecules.[6,7)] Another type of transformation was recently noticed in reactions of F-TEDA–BF_4 with various alcohols, where efficient conversions to vicinal fluorohydrins were established.[8)] Hydroxy aromatic molecules were also readily transformed mainly to fluoro-substituted products, while a strong tendency for further transformation to α,α-difluoro ketones was established.[9—11)]

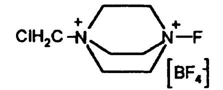
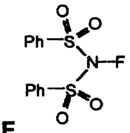
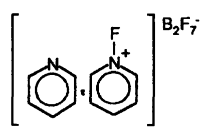
In recent years many new reagents of the N–F class (*N*-fluoro reagent) have been discovered; their reactivity strongly depends on the type of reagent. Three large families differ very much in their behavior[2)] R_1R_2NF type,[12)] *N*-fluoropyridinium and related salts[13)] and $F\text{-}N^+R_1R_2R_3A^-$ type.[14—17)] The following three reagents are now commercially available:[18)] *N*-fluorobis(phenylsulfonyl)amine NSF; *N*-fluoropyridinium heptafluorodiborate–pyridine (1/1) NFP; 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) F-TEDA. Hence, a new *N*-fluoro class of reagents for mild introduction into organic molecules is now more accessible.

An electrochemical investigation of various *N*-fluoro reagents was recently published and several conclusions drawn,[19)] while a direct correlation between the electrochemical behavior and the relative power of the “electrophilic behavior” was suggested,[20)] though this approach was recently criticized.[21)] It was observed that the course of fluorination with the F–L type of reagents is also strongly influenced by the solvent used, and a very different behavior was usually found, depending on whether the reactions were carried out in methylene dichloride or acetonitrile. *N*-Fluoropyridinium salts are considerably more reactive in nonpolar solvents (CH_2Cl_2) than in polar acetonitrile[13] while the completely opposite trend was observed for $CsSO_4F$ reactions.[11] In order to obtain additional information about the role of the ligand part (L) on the reactivity of fluorinating reagents, we found it instructive to study the transformations as well as the effect of a solvent on the reactions of various hydroxyl-group-bearing molecules with three reagents of the *N*-fluoro type.

Results and Discussion

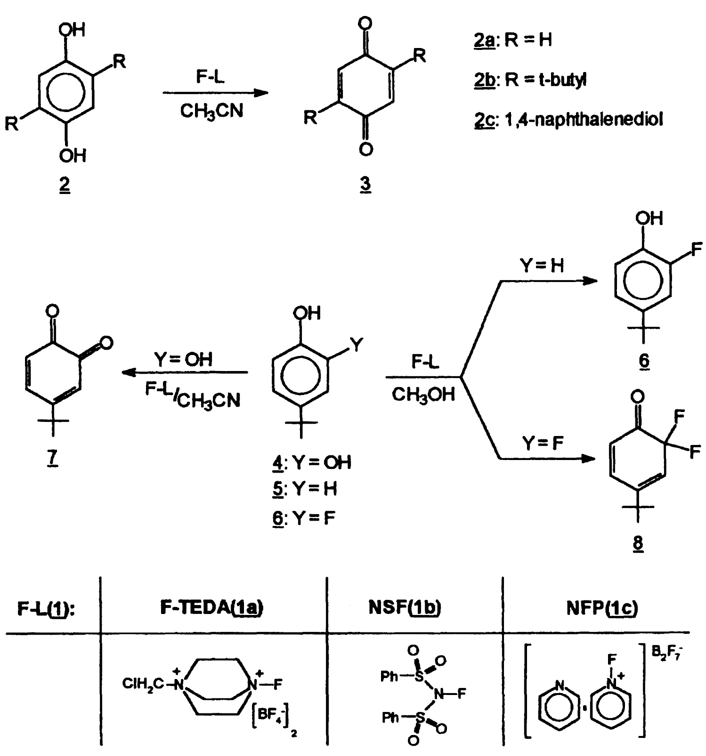
We first studied the stability of 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (F-TEDA, **1a**) in methanol, water, and acetonitrile. It was established that less than a three percent loss of activity occured after 24 h at room temperature. Methanol and water also did not react in acetonitrile, while an immediate interaction was observed with hydroquinone (**2a**) in acetonitrile and complete conversion was achieved in less than two hours. A structural variation of the hydroquinone derivative did not influence the oxidation to quinone with F-TEDA (**1a**), and both the 2,5-di-*t*-butyl derivative (**2b**) and 1,4-naphthalenendiol (**2c**) were completely converted to quinone products (**3b**, **3c**, Scheme 1). However, a very large drop in reactivity toward hydroquinone was observed with *N*-fluorobis(phenylsulfonyl)amine (NSF, **1b**), where after two hours only a 30-percent conversion was achieved. No conversion with *N*-fluoropyridinium heptafluorodiborate–pyridine (1/1) (NFP, **1c**) occured at room temperature after two hours, but significant transformation took place at higher temperatures (Table 1). Umemoto et al. found that *N*-fluoropyridinium salts are more reactive in methylene dichloride than in acetonitrile.[13] Substitution of acetonitrile by methylene dichloride in the case of NFP (**1c**) did not increase the oxidation of hydroquinone, while the same reaction with F-TEDA even showed inhibition; however, complete conversion was achieved after 24 h at room temperature. A reaction in tetrahydrofuran was also inhibited, and a complete conversion of hydroquinone (**2a**) with F-TEDA was observed after a 24-h reaction at room temperature; a very low transformation of hydroquinone was found in a reaction with NSF (**1b**) and NFP (**1c**) under similar reaction conditions. The oxidative properties of F-TEDA were also observed in a reaction with 4-*t*-butyl-1,2-benzenediol (**4**). On the other hand, 4-*t*-butylphenol after a 24-hour reaction at room temperature in acetonitrile with F-TEDA gave a reaction mixture containing two products in a 1 : 1 ratio; also, the fluorodealkylation process was observed, thus giving 4-fluorophenol. Although no dealkylation was found after a 5-hour reaction in methanol under reflux, 2-fluoro derivative (**6**) was also accompanied by up to 15 percent of 2,2-difluoro-4-*t*-butyl-3,5-cyclohexadien-1-one (**8**). Complete conversion to difluoro ketone was observed when pure 2-fluoro-4-*t*-butylphenol (**6**) was fluorinated with F-TEDA (Scheme 2). NSF (**1b**) and NFP (**1c**) were again much less reactive than F-TEDA, and no fluorination products were observed after a five-hour reaction in methanol under reflux, nor after a 24-h reaction at room temperature in acetonitrile.

Table 1. The Effect of Reagent Structure (**1**) on Conversion of Hydroquinone (**2a**)[a]

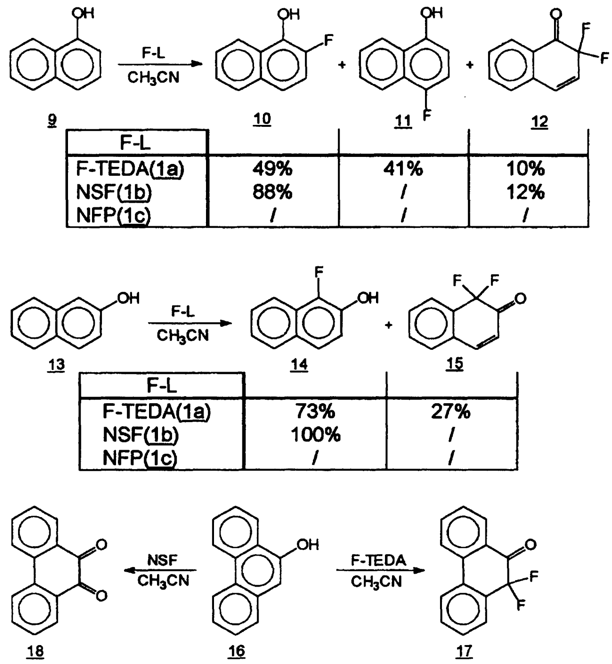
F–L	Time/h	Temp/°C	Conversion/%
 **1a: F-TEDA**	2	20	100
 **1b: NSF**	2	20	30
	3	80	70
 **1c:NFP**	2	20	0
	3	80	60

a) 1 mmol of hydroquinone, 1 mmol of reagent (**1**), 10 ml of acetonitrile.

Fluorinations of naphthols were extensively studied with various types of fluorinating reagents, while the type of products and their distribution strongly depend on the reagent structure (CF_3OF, CF_3COOF, $CsSO_4F$, XeF_2, *N*-fluoropyridinium salts···)[2] and the reactions conditions. 1-naphthol (**9**) is more reactive than 4-*t*-butylphenol; after a three-hour reaction at room temperature in acetonitrile complete conversion was observed with F-TEDA (**1a**), with the product distribution listed in Scheme 2. A similar reaction with NSF (**1b**) gave 70% of fluorinated products; however NFP (**1c**) did not transform 1-naphthol after a 24-h reaction in acetonitrile at room temperature. A similar effect of the reagent structure on fluorination was also observed with 2-naphthol (**13**), which was converted with F-TEDA (**1a**) in acetonitrile to the 1-fluoro derivative (**14**) in 3 h at room temperature; however, **14** was also accompanied by difluoro ketone (**15**). Fluorination with NSF (**1b**) gave 1-fluoro-2-naphthol as the sole product in 30% yield after 3 h under the above-mentioned conditions, while NFP (**1c**) gave no fluorinated products after 24 h at room temperature in acetonitrile. 9-Phenanthrol is even more reactive (**16**), and after a two-hour reaction with F-TEDA in acetonitrile at room temperature only one fluorinated product was present in the crude reaction mixture. This showed in its ^{19}F NMR spectrum a



Scheme 1.



F-L	10	11	12
F-TEDA(1a)	49%	41%	10%
NSF(1b)	88%	/	12%
NFP(1c)	/	/	/

F-L	14	15
F-TEDA(1a)	73%	27%
NSF(1b)	100%	/
NFP(1c)	/	/

Scheme 2.

singlet at −105.3 ppm corresponding to 10,10-difluoro-9-(10*H*)-phenanthrenone (**17**); on the other hand, only an oxidation product was formed after a 24-hour reaction with NSF (**1b**) at room temperature, and 9,10-phenanthrenequinone (**18**) was isolated (Scheme 2).

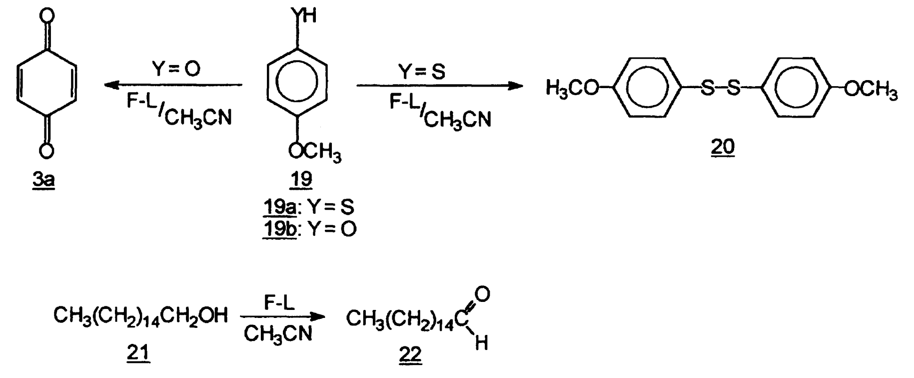
Further, we studied the effect of a heteroatom on a reaction with the N–F class of reagents, and found that F-TEDA readily transformed *p*-methoxyphenol (**19b**) into quinone after demethylation; on the other hand, dimerization was observed with the mercapto analogue (**19a**, Scheme 3). NSF (**1b**) and NFP (**1c**) did not transform the hydroxy derivative (**19b**) into quinone; on the contrary, NSF (**1b**) was found to be even more reactive with *p*-methoxy benzenethiol (**19a**) than was F-TEDA or NFP (Table 2). In a crude reaction mixture obtained after using an equimolar amount of reagent (**1**), the formation of *S*-(4-methoxyphenyl) 4-methoxybenzenthiosulfonate in up to 40% yield was established (Table 2). Under normal reaction conditions all three reagents were dissolved, but when using a smaller amount of solvents the different solubility of the reagents had to be taken into account (solubilities in acetonitrile at room temperature are: F-TEDA 0.12 mmol ml^{-1}, NSF 0.39 mmol ml^{-1}, NFP 0.66 mmol ml^{-1}).

We have already demonstrated that aliphatic alcohols

Table 2. The Effect of Reagent Structure on Conversion of *p*-Methoxybenzenthiol[a)]

Reagent (**1**)	Reaction conditions: Time	Reaction conditions: Ratio	Conversion of **19a**
	h	**1** : **19a**	%
F-TEDA (**1a**)	0.5	0.5 : 1	79
F-TEDA (**1a**)	2	1 : 1	100
NSF (**1b**)	0.5	0.5 : 1	100
NFP (**1c**)	0.5	0.5 : 1	50
NFP (**1c**)	22	1 : 1	78

a) 1 mmol of **19a**, 10 ml of acetonitrile, room temperature.



Scheme 3.

and benzyl alcohol were transformed with $CsSO_4F$ via aldehydes to acyl fluorides,[5] while a rearrangement[4] was observed with XeF_2; for this reason we have finally studied the reaction of 1-hexadecanol (**21**) with F-TEDA in acetonitrile. It was found that after a three-hour reaction under reflux aldehyde (**22**) was formed in high yield, while NSF (**1b**) and NFP (**1c**) were unable to transform it under similar conditions.

The present results again demonstrated how very difficult, or even impossible, it is to predict the reactivity of F–L type reagents, especially on the basis of physicochemical measurements, and that reliable data can be obtained after a careful analysis of the reaction products with several target molecules. Special attention must be paid to the solvent, concentration, catalyst, and reaction temperature, which can give better information about the role of the L part of the reagent.

Experimental

Materials: 1-Chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (F-TEDA), *N*-fluorobis(phenylsulphonyl)amine (NSF), *N*-fluoropyridinium heptafluorodiborate–pyridine (1/1) (NFP), hydroxy, dihydroxy, and mercapto compounds were obtained from commercial sources, and were used without further purification. Methylene dichloride, chloroform, methanol, and acetonitrile were purified by distillation and stored over molecular sieves. ^1H and ^{19}F NMR spectra were recorded with a Varian EM 360L spectrometer with Me_4Si or CCl_3F as an internal standard. IR spectra were recorded with a Perkin–Elmer 727B spectrometer.

Fluorination of Hydroquinone Derivatives: To a solution of 1 mmol dihydroxy compound (**2a**—**c**) in 10 ml of acetonitrile, 1 mmol of reagent (**1a**—**c**) was added and stirred at room temperature or 80 °C for 2, 3, or 24 h. The reaction mixture was poured into water and extracted with methylene dichloride (3×20 ml); the organic phases were then washed with water, dried over Na_2SO_4 and the solvent evaporated under vacuum. The crude reaction mixture was analyzed by ^1H NMR and IR spectroscopy.

***p*-Benzoquinone (3a):** After reacting for two hours at room temperature, the crude reaction mixture was purified by column chromatography (SiO_2, $CHCl_3$) to give *p*-benzoquinone (76 mg, 70%); mp 110—111 °C (lit,[22] mp 113—114 °C); ^1H NMR $\delta=6.9$(s). The effects of the reagent structure and the reaction conditions on the oxidation of hydroquinone are presented in Table 1.

2,5-Di-*t*-butyl-*p*-benzoquinone (3b): After reacting for two hours at room temperature, the crude reaction mixture was purified by column chromatography (SiO_2, $CHCl_3$) to give 2,5-di-*t*-butyl-*p*-benzoquinone (170 mg, 77%); mp 148—150 °C (lit,[22] mp 152—153 °C); ^1H NMR $\delta=1.27$ (s, 9H, CH_3), 6.53 (s, 1H).

1,4-Naphthoquinone (3c): After reacting for three hours at room temperature, the crude reaction mixture was sublimed to give 1,4-naphthoquinone (104 mg, 66%); mp 123—125 °C (lit,[22] 124—125 °C); ^1H NMR $\delta=7.10$ (s, 2H), 7.73—8.43 (m, 4H).

4-*t*-Butyl-*o*-benzoquinone (7): After a one-hour reaction at room temperature, 160 mg of crude product was obtained and purified by column chromatography (SiO_2, $CHCl_3$), and 156 mg of 4-*t*-butyl-*o*-benzoquinone (95%) was isolated; mp 65—66 °C (lit,[23] 69 °C); ^1H NMR $\delta=1.20$ (s, 9H, CH_3), 6.30 (d, 1H), 6.40 (d, 1H), 7.27 (dd, $J=10$ and 1 Hz, 1H).

Fluorination of 4-*t*-Butylphenol (5) and 2-Fluoro-4-*t*-butylphenol (6): To a mixture of 150 mg of 4-*t*-butylphenol (1.0 mmol) and 10 ml of methanol, 354 mg F-TEDA (1.0 mmol) was added and stirred under reflux for 5 h. After the usual work-up procedure, the crude product was separated by preparative TLC (SiO_2, $CHCl_3/CH_3OH$ 5 : 1) and 82 mg (49%) of *2-fluoro-4-t-butylphenol*[11] (**6**): oily product; ^{19}F NMR $\delta=-142.8$ (dd, $J=13$ and 7 Hz); ^1H NMR $\delta=1.2$ (s, 9H, CH_3), 5.6 (s, 1H), 6.7—7.5 (m, 3H); and 23 mg (12%) of *2,2-difluoro-4-t-butyl-3,5-cyclohexadien-1-one*[11] (**8**): oily product; ^{19}F NMR $\delta=-106.3$ (d, $J=7$ Hz); ^1H NMR $\delta=1.2$ (s, 9H, CH_3), 6.2 (m, 2H), 7.27 (d, $J=11$ Hz, 1H); were isolated. 2-Fluoro-4-*t*-butylphenol (1.0 mmol) was also transformed to 2,2-difluoro-4-*t*-butyl-3,5-cyclohexadien-1-one with F-TEDA (1.0 mmol) in 80% yield under the above-mentioned conditions.

Fluorination of 1-Naphthol (9): To a stirred solution of 144 mg of 1-naphthol (1.0 mmol) in 10 ml of acetonitrile, 354 mg of F-TEDA (1.0 mmol) was added and stirred for an additional 3 h at room temperature. After the usual work-up procedure, 144 mg of crude reaction mixture was isolated and the product distribution determined by ^{19}F and ^1H NMR spectroscopy: *2-fluoro-1-naphthol* (**10**):[10] 49% $\delta_F=-143$ (dd, $J=10$ and 6 Hz); *4-fluoro-1-naphthol* (**11**):[10] 41%, $\delta_F=-134$ (dm); *2,2-difluoro-1(2H)-naphthalenone* (**12**):[10] 10%, $\delta_F=-106$ (d, $J=7$ Hz).

Fluorination of 2-Naphthol (13): To a stirred solution of 144 mg of 2-naphthol (1.0 mmol) in 10 ml of acetonitrile, 354 mg of F-TEDA (1.0 mmol) was added and stirred for an additional 3 h at room temperature. After the usual work-up procedure, 150 mg of crude reaction mixture was isolated and the product distribution determined by ^{19}F and ^{1}H NMR spectroscopy: 1-*fluoro*-2-*naphthol* (**14**):[10] 73%, $\delta_F=-154$ (d, $J=7$ Hz); 1,1-*difluoro*-2(1*H*)-*naphthalenone* (**15**):[10] 27%, $\delta_F=-103$ (s).

Fluorination of 9-Phenanthrol (16) with F-TEDA: After 9-phenanthrol (194 mg, 1.0 mmol) was dissolved in 10 ml of acetonitrile, 708 mg of F-TEDA (2.0 mmol) was added over a half-hour period and stirred at room temperature for an additional 2 h. The reaction mixture was poured into water, and extracted with methylene dichloride; the organic phases were then washed with water and dried over sodium sulfate. The crude reaction mixture was purified by preparative TLC (SiO_2, $CHCl_3$–CCl_4 3:1) and 112 mg (49%) of 10,10-difluoro-9(10*H*)-phenanthrenone (**17**) was isolated; mp 99—102 °C (lit;[24] 100—102 °C); ^{19}F NMR $\delta=-105.3$ (s).

Oxidation of 9-Phenanthrol (16): After 9-phenanthrol (**16**, 194 mg, 1.0 mmol) was dissolved in 10 ml of acetonitrile, 318 mg of NSF (**1b**, 1.0 mmol) was added. The reaction mixture was stirred at room temperature for 24 h; the crude reaction mixture was then poured into water and extracted with chloroform. The organic phases were washed with water, dried over sodium sulfate and the solvent evaporated in vacuo. The crude reaction product was analyzed by NMR and IR spectroscopy and purified by preparative TLC (SiO_2, $CHCl_3$); 82 mg (39%) of 9,10-phenanthrenequinone (**18**) was isolated; mp 203—204 °C (lit,[25] mp 205—207 °C); ^{1}H NMR $\delta=7.10$—8.23 (m); IR $\nu=1675$, 1280 cm^{-1}.

Reaction of *p*-Methoxyphenol (19b) with F-TEDA: After *p*-methoxyphenol (**19b**, 124 mg, 1.0 mmol) was dissolved in 10 ml of acetonitrile, 354 mg of F-TEDA (1.0 mmol) was added. The reaction mixture was stirred at room temperature for 2 h; after the usual work-up procedure the crude reaction product was purified by column chromatography (SiO_2, $CHCl_3$) and 68 mg (63%) of *p-benzoquinone* (**3a**): mp 110—111 °C (lit,[22] 113—114 °C); ^{1}H NMR $\delta=6.9$ (s); was isolated.

Reaction of *p*-Methoxybenzenethiol (19a) with F-TEDA: After *p*-methoxybenzenethiol (**19a**, 140 mg, 1.0 mmol) was dissolved in 10 ml of acetonitrile, 354 mg of F-TEDA (1.0 mmol) was added. The reaction mixture was stirred at room temperature for 2 h, then poured into water and extracted with chloroform; the organic phases were washed with water, dried over sodium sulfate and the solvent evaporated under reduced pressure. The components were separated by preparative TLC (SiO_2, $CHCl_3$) and analyzed by IR and NMR spectroscopy: *bis*(4-*methoxyphenyl*) *disulfide* (**20**):[26] 80 mg (58%), mp 37—38 °C (lit,[26] 41—43 °C); ^{1}H NMR: $\delta=3.77$ (s, 3H, CH_3), 6.78 (d, $J=10$ Hz, 2H), 7.47 (d, $J=10$ Hz, 2H); *S*-(4-*methoxyphenyl*) 4-*methoxybenzenethiosulfonate*:[26] 55 mg (35%); mp 89—90 °C (lit,[26] mp 92—94 °C); ^{1}H NMR $\delta=3.90$ (s, 3H, CH_3), 6.87 (d, $J=10$ Hz, 2H), 7.33 (d, $J=10$ Hz, 1H), 7.56 (d, $J=10$ Hz, 1H); IR $\nu=1135$, 1320 cm^{-1}. Bis(4-methoxyphenyl) disulfide was quantitatively transformed into thiosulfonic *S*-ester with F-TEDA in acetonitrile at room temperature. The effects of the reagent structure and the reaction time on the transformation of *p*-methoxybenzenethiol are presented in Table 2. In a reaction with 0.5 mmol of reagent, disulfide was the main product, but was accompanied by up to 15% of thiosulfonic *S*-ester.

Oxidation of 1-Hexadecanol (21): To a suspension of 121 mg of hexadecanol (0.5 mmol, **21**) in 5 ml of acetonitrile, 177 mg of F-TEDA (0.5 mmol) was added and heated under reflux for 3 h. After the usual work-up procedure, the crude reaction product was analyzed by NMR and IR spectroscopy. Isolation after column chromatography (SiO_2, $CHCl_3$) gave 113 mg of *hexadecanal* (94%); mp 36—38 °C (lit,[27] 35 °C), IR $\nu=1710$ cm^{-1}.

The financial support of the Ministry of Science and Technology of the Republic of Slovenia is acknowledged. We are indebted to Dr. G. A. Shia from Allied Signal Chemicals, Buffalo, New York for free samples of NSF and NFP.

References

1) Presented in part at 14th International Symposium on Fluorine Chemistry, Yokohama, 1994.

2) W. A. Sheppard and C. M. Sharts, "Organic Fluorine Chemistry," Benjamin, New York (1969); R. D. Chambers, "Fluorine in Organic Chemistry," Wiley, New York (1973); S. Patai, "The Chemistry of the Carbon–Halogen Bond," Vols. 1 and 2; P. B. D. de la Mare, "Electrophilic Halogenation," Cambridge University Press, Cambridge (1976); S. Patai and Z. Rappoport, "The Chemistry of Functional Groups," "Supplement D, The Chemistry of Halides, Pseudo-Halides and Azides," Part 1 and 2, Wiley, Chichester (1983); R. E. Banks, D. W. Sharp, and J. C. Tatlow, "Fluorine: The First Hundred Years (1886—1986)," Elsevier Sequoia, Lausanne (1986); L. German and S. Zemskov, "New Fluorinating Agents in Organic Synthesis," Springer-Verlag, Berlin (1989); D. H. R. Barton, *Pure Appl. Chem.*, **49**, 1241 (1977); R. H. Hesse, *Isr. J. Chem.*, **17**, 60 (1978); M. Schlosser, *Tetrahedron*, **34**, 3 (1978); M. Cartwright and A. A. Woolf, *J. Fluorine Chem.*, **19**, 101 (1981); M. R. C. Gerstenberger and A. Haas, *Angew. Chem.*, **93**, 659 (1981); S. T. Purrington, B. S. Kagen, and T. B. Patrick, *Chem. Rev.*, **86**, 997 (1986); J. Mann, *Chem. Soc. Rev.*, **16**, 381 (1987); J. A. Wilkinson, *Chem. Rev.*, **92**, 505 (1992).

3) R. Filler, *Isr. J. Chem.*, **17**, 71 (1978); M. Zupan, "Xenon Halide Halogenations in The Chemistry of Functional Groups," "Supplement D: The Chemistry of Halides, Pseudo-Halides and Azides," Part 1 and 2, ed by S. Patai and Z. Rappoport, Wiley, Chichester (1983); M. Zupan, *Vestn. Slov. Kem. Drus.*, (*Suppl.*), **31**, 151 (1984).

4) S. Stavber and M. Zupan, *Tetrahedron Lett.*, **34**, 4355 (1993).

5) S. Stavber, Z. Planinšek, and M. Zupan, *Tetrahedron Lett.*, **30**, 6095 (1989).

6) S. Stavber, I. Košir, and M. Zupan, *J. Chem. Soc., Chem. Commun.*, **1992**, 274.

7) S. Stavber, Z. Planinšek, I. Košir, and M. Zupan, *J. Fluorine Chem.*, **59**, 409 (1992).

8) S. Stavber and M. Zupan, *J. Chem. Soc., Chem. Commun.*, **1994**, 149.

9) S. Stavber and M. Zupan, *J. Chem. Soc., Chem. Com-*

mun., **1981**, 148.

10) S. Stavber and M. Zupan, *J. Org. Chem.*, **50**, 3609 (1985).

11) S. Stavber and M. Zupan, *Tetrahedron*, **48**, 5875 (1992).

12) a) S. Singh, D. D. DesMarteau, S. S. Zuberi, M. Witz, and H. N. Huang, *J. Am. Chem. Soc.*, **109**, 7194 (1987); Z. Q. Xu, D. D. DesMarteau, and Y. Gotoh, *J. Chem. Soc., Chem. Commun.*, **1991**, 179; W. T. Pennington, G. Resnati, and D. D. DesMarteau, *J. Org. Chem.*, **57**, 1536 (1992); b) E. Differding and R. W. Lang, *Tetrahedron Lett.*, **29**, 6087 (1988); E. Differding and H. Ofner, *Synlett*, **1991**, 187; c) F. A. Davis and W. Han, *Tetrahedron Lett.*, **33**, 1153 (1992); F. A. Davis, P. Zhou, and C. K. Murphy, *Tetrahedron Lett.*, **34**, 3971 (1993).

13) T. Umemoto and K. Tomita, *Tetrahedron Lett.*, **27**, 3271 (1986); T. Umemoto, S. Fukami, G. Tomizawa, K. Harasawa, K. Kawada, and K. Tomita, *J. Am. Chem. Soc.*, **112**, 8563 (1990); A. J. Poss, M. Van Der Puy, D. Nalewajek, G. A. Shia, W. J. Wagner, and R. L. Frenette, *J. Org. Chem.*, **56**, 5962 (1991); Y. Naruta, F. Tani, and K. Maruyama, *Tetrahedron Lett.*, **33**, 1069 (1992).

14) R. E. Banks, S. N. Mohialdin-Khaffaf, G. S. Lal, I. Sharif, and R. G. Syvret, *J. Chem. Soc., Chem. Commun.*, **1992**, 595.

15) R. E. Banks, N. J. Lawrence, and A. L. Popplewell, *J. Chem. Soc., Chem. Commun.*, **1994**, 343.

16) R. E. Banks, U. S. Patent 5086178 (1992).

17) G. S. Lal, *J. Org. Chem.*, **58**, 2791 (1993).

18) a) Selectofluor, F-TEDA, 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate), Air Products and Chemicals PLC, UK; b) *N*-fluorobis(phenylsulfonyl)amine, NSF, Allied Signal Inc., Buffalo, New York; c) *N*-Fluoropyridinium heptafluorodibroate–pyridine (1/1), NFP, Allied Signal Inc., Buffalo, New York; Banks et al. indicated that this formula and structure of NFP is false and on the basis of an X-ray study they suggested that this commercially available material is *N*-fluoropyridinium pyridinium tetrafluoroborate trifluorohydroxyborate[14) but in this paper, the original Allied Signal name is used, but comment on the anion structure must be taken into account.

19) E. Differding and P. M. Bersier, *Tetrahedron*, **48**, 1595 (1992).

20) A. G. Gilicinski, G. P. Pez, R. G. Syvret, and G. S. Lal, *J. Fluorine Chem.*, **59**, 157 (1992).

21) K. Sudlow and A. A. Woolf, *J. Fluorine Chem.*, **66**, 9 (1994).

22) S. G. Cohen, *J. Am. Chem. Soc.*, **69**, 1057 (1947).

23) M. Zupan and A. Pollak, *J. Fluorine Chem.*, **7**, 443 (1976).

24) T. B. Patrick, M. H. LeFaivre, and T. E. Koertge, *J. Org. Chem.*, **41**, 3413 (1976).

25) T. L. Ho, T. W. Hall, and C. M. Wong, *Synthesis*, **1973**, 206.

26) G. Palumbo and R. Caputo, *Synthesis*, **1981**, 888.

27) F. Franzen and S. Otto, *Chem. Ber.*, **94**, 1360 (1961).