

# Articles

## Reactions of Alcohols with Cesium Fluoroxysulfate

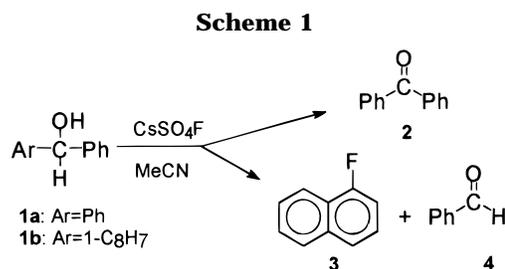
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The reactions of alcohols with cesium fluoroxysulfate ( $\text{CsSO}_4\text{F}$ ) in MeCN suspension were studied, and the role of the structure of the alcohol and the reaction conditions on the course of reaction was determined. Secondary benzyl alcohols bearing a nonactivating aromatic ring were selectively oxidized to the corresponding ketones, while the  $\text{CsSO}_4\text{F}$ -mediated reaction of phenyl-1-naphthylmethanol resulted in the formation of 1-fluoronaphthalene and benzaldehyde. Cyclic and noncyclic secondary alcohols were readily converted to ketones, as well as 1-hydroxybenzocyclohexanes to benzocyclohexanones-1, without any further fluorination or oxidation under the reaction conditions. On the other hand, reactions of primary alcohols with  $\text{CsSO}_4\text{F}$  resulted in the formation of acid fluorides derived from further fluorination of aldehydes. Another type of transformation was observed in the case of alcohols bearing a benzyl functional group attached *geminal* to a hydroxy group, where decarbonylation of reactive intermediates resulting in the formation of benzyl fluoride derivatives became the main process. 2-Phenylethanol was so converted to benzyl fluoride and phenylacetyl fluoride in a 3:1 relative ratio, while 2-phenyl-1-propanol was selectively transformed to 1-phenyl-1-fluoroethane. The presence of the radical inhibitor nitrobenzene in the reaction mixture considerably inhibited conversion of the starting material. The same effect was observed by lowering the solvent polarity. Hammett correlation analysis of the effect of substituents on the reaction rates of oxidation of a set of substituted 1-phenyl-1-ethanols to acetophenones gave the reaction constant  $\rho^+ = -0.32$ , while analysis of analogous data for the transformations of benzyl alcohols to benzoyl fluorides gave the value of  $-0.54$ . A mechanism including radical intermediates was proposed for the transformation of alcohols by  $\text{CsSO}_4\text{F}$ .

Compounds possessing a fluoroxy moiety attract considerable interest among chemists. In spite of their usual high reactivity and moderate stability, fluoroxy compounds are often applied as useful reagents in organic synthesis. The chemistry of these compounds, used as selective fluorination reagents for organic molecules, was reviewed recently.<sup>1</sup> Cesium fluoroxysulfate ( $\text{CsSO}_4\text{F}$ ) is the most stable and easily handled of them and, when some safety precautions are taken into account, can be conveniently used as a benchtop reagent. The organic chemistry of  $\text{CsSO}_4\text{F}$  has been extensively studied during the last decade, leading to the recognition that its reactions with organic compounds strongly depend on the type of organic molecule and the functional groups present. The following types of reactions were observed: fluorofunctionalization of alkenes or alkynes through the addition or addition–elimination process, fluorosubstitution reactions at a saturated, unsaturated, or benzylic carbon atom and at a nitrogen atom, and oxidation or oxygenation of particular functional groups or heteroatoms. It was established that only small variations concerning the structure of the substrate or the reaction conditions are sufficient to change the reaction course drastically and favor one reaction type.<sup>1,2</sup>



Since, like all fluoroxy compounds,  $\text{CsSO}_4\text{F}$  is also a strong oxidant,<sup>3</sup> competition between fluorofunctionalization and oxidation of an organic molecule possessing oxidizable functional groups or heteroatoms can take place.<sup>4,5</sup> In our continued interest in the organic chemistry of  $\text{CsSO}_4\text{F}$ , we now report a more detailed study of its reactions with alcohols.

### Results and Discussion

**Role of the Structure of the Alcohol on the Course of Reaction.** In a typical experiment, described in the Experimental Section, we treated diphenylmethanol (**1a**) with a 20% molar excess of  $\text{CsSO}_4\text{F}$  in acetonitrile suspension and isolated benzophenone (**2**, Scheme 1) in almost quantitative yield, showing that the oxida-

<sup>®</sup> Abstract published in *Advance ACS Abstracts*, June 1, 1997.

(1) Rozen, S. *Chem. Rev.* **1996**, *96*, 1717.

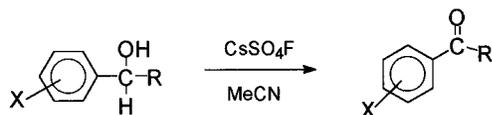
(2) (a) German, L.; Zemskov, S., Eds. *New Fluorinating Agents in Organic Syntheses*; Springer-Verlag: Berlin, 1989. (b) Zupan, M.; Stavber, S. The Role of Reagent Structure in the Mild Introduction of a Fluorine Atom into Organic Molecules. In *Trends in Organic Chemistry*; Council of Scientific Information: Trivandrum, India, 1995; Vol. V, pp 11–36.

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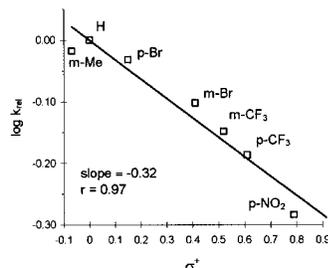
Scheme 2



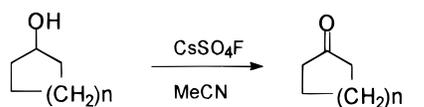
- 5: R=Me  
 6a: R=Ph, X=m-Cl  
 6b: R=Ph, X=m-CF<sub>3</sub>  
 6c: R=Ph, X=p-NO<sub>2</sub>  
 7: R=Et, X=H  
 8: R=c-C<sub>3</sub>H<sub>5</sub>, X=H  
 9: R=CF<sub>3</sub>, X=H

- 10  
 11a  
 11b  
 11c  
 12  
 13  
 14

5	X	k <sub>rel</sub>
a	m-Me	0.96
b	H	1.00
c	p-Br	0.93
d	m-Br	0.79
e	m-CF <sub>3</sub>	0.71
f	p-CF <sub>3</sub>	0.65
g	p-NO <sub>2</sub>	0.52

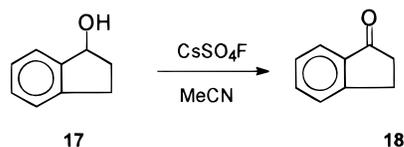


Scheme 3



- 15a: n=1  
 15b: n=2  
 15c: n=3

- 16a-c



17

18



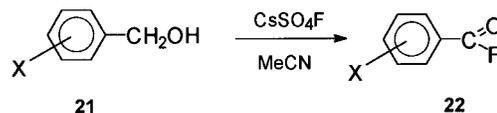
19

20

tion of the benzylic hydroxy group is the exclusive process in this case. A different course of reaction was observed when phenyl(1-naphthyl)methanol (**1b**) reacted with CsSO<sub>4</sub>F under the same reaction conditions, and the fluorodealkylation process, resulting in 1-fluoronaphthalene (**3**) and benzaldehyde (**4**) as the reaction products, was found to be dominant in this case. We further studied the effect of substituents on the benzene ring in secondary benzylic alcohols on the course of the reaction with CsSO<sub>4</sub>F and found that the reaction is directed toward oxidation of the benzylic hydroxy group if the benzene ring is substituted with electron-withdrawing substituents (**5a–6c**, Scheme 2) and towards fluorodealkylation products when strong electron-donating groups are bonded para to the hydroxybenzyl block. Alkyl- and cycloalkyl-substituted benzyl alcohols (**7**, **8**) were also readily transformed to the corresponding ketones, while α-(trifluoromethyl)benzyl alcohol (**9**) was found to be much more stable toward CsSO<sub>4</sub>F under the mentioned reaction conditions and converted to the ketone **14** in less than 50% yield.

Cyclic alcohols (**15**, Scheme 3) were also readily converted to the corresponding ketones **16** with CsSO<sub>4</sub>F in MeCN medium. The resulting carbonyl products were

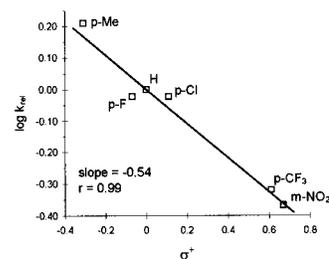
Scheme 4



21

22

21	X	k <sub>rel</sub>
a	p-Me	1.62
b	p-F	0.95
c	H	1.00
d	p-Cl	0.95
e	p-CF <sub>3</sub>	0.48
f	m-NO <sub>2</sub>	0.43



found to be stable under the reaction conditions. No further fluorination to α-fluoro ketones, as observed with some N–F fluorinating reagents under similar reaction conditions,<sup>6</sup> nor the Baeyer–Villiger type of oxidation, expected with reagents possessing similar oxidizing power,<sup>7</sup> took place. Hydroxy-substituted benzocyclohexanes **17** were also selectively transformed to the corresponding benzocyclohexanones **18** and 1-phenyl-2-butanol (**19a**) to 1-phenyl-2-butanone (**20a**). No fluorofunctionalization of the benzylic carbon atom was observed in these cases, in spite of the fact that under the same reaction conditions benzocyclohexanes or alkyl-substituted aromatics could be effectively fluorinated at the benzylic position by CsSO<sub>4</sub>F.<sup>1,2b,8</sup> 2-Octanol (**19b**) was also quantitatively transformed to 2-octanone (**20b**), which was again stable under the reaction conditions.

On the other hand, intermediate products derived from CsSO<sub>4</sub>F-mediated reactions with primary alcohols reacted further, and acid fluorides were isolated as the final result of the reactions, as shown in Scheme 4. Primary benzyl alcohols bearing a nonactivated benzene ring (**21a–f**) were transformed to the corresponding benzoyl fluorides (**22**), while strong donating substituents on the *para* position again favored the fluorodealkylation process. The primary formed aldehyde could be isolated only at short reaction times or a low CsSO<sub>4</sub>F/alcohol molar ratio. Thirty-five percent of benzaldehyde was detected in the crude reaction mixture after 10 min reaction of benzyl alcohol (**21c**) with an equimolar amount of CsSO<sub>4</sub>F, while the relative ratio of aldehyde rose to 85% when a 2-fold excess of starting alcohol was used. After the reaction times ordinarily needed for oxidation of secondary alcohols with an equimolar or excess amount of CsSO<sub>4</sub>F only benzoyl fluorides and the starting benzyl alcohols were detected in the reaction mixtures, thus indicating that the fluorination of aldehydes to acid fluorides<sup>9</sup> is faster than the oxidation of primary alcohols to aldehydes.

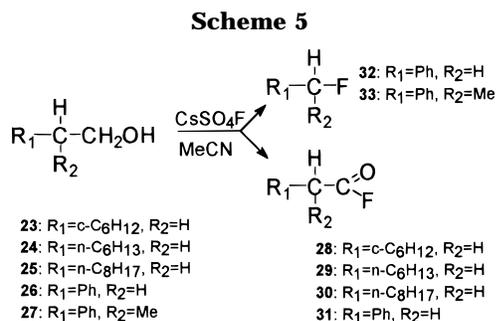
Furthermore, we established the role of the structure of a primary alcohol molecule on the reaction course. Alkyl-substituted primary alcohols (**23**, **24**, Scheme 5) were selectively converted to acid fluorides (**27**, **28**) in high yield, while a benzylic functional group attached *geminal* to the hydroxy interfered in the reaction pathway, causing the decarbonylation of reactive intermedi-

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**Table 1. Effect of the Reaction Conditions on the Transformation of Alcohols with CsSO<sub>4</sub>F<sup>a</sup>**

substrate	solvent	yield <sup>b</sup> (%)
C <sub>6</sub> H <sub>5</sub> CH(Me)OH, <b>5b</b>	MeCN	95; <b>10b</b>
	MeCN/0.1 mmol PhNO <sub>2</sub>	80
	MeCN/1 mmol PhNO <sub>2</sub>	55
	CH <sub>2</sub> Cl <sub>2</sub>	traces
<i>m</i> -CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH(Me)OH, <b>5d</b>	MeCN	93; <b>10d</b>
	MeCN/0.1 mmol PhNO <sub>2</sub>	86
	MeCN/1 mmol PhNO <sub>2</sub>	59
	MeCN/CH <sub>2</sub> Cl <sub>2</sub> 9:1	69
<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OH, <b>21a</b>	MeCN	98; <b>22a</b>
	MeCN/0.1 mmol PhNO <sub>2</sub>	42
	MeCN/1 mmol PhNO <sub>2</sub>	18
	MeCN/CH <sub>2</sub> Cl <sub>2</sub> 9:1	69
	MeCN/CH <sub>2</sub> Cl <sub>2</sub> 4:1	54
	MeCN/CH <sub>2</sub> Cl <sub>2</sub> 3:1	traces
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OH, <b>21c</b>	MeCN	98; <b>22c</b>
	MeCN/0.1 mmol PhNO <sub>2</sub>	65
	MeCN/1 mmol PhNO <sub>2</sub>	26
	MeCN/CH <sub>2</sub> Cl <sub>2</sub> 9:1	79
	MeCN/CH <sub>2</sub> Cl <sub>2</sub> 4:1	53
	MeCN/CH <sub>2</sub> Cl <sub>2</sub> 3:1	0
C <sub>6</sub> H <sub>5</sub> CH(Me)CH <sub>2</sub> OH, <b>26</b>	n-C <sub>6</sub> H <sub>14</sub>	0
	MeCN	91; <b>31</b>
	MeCN/0.1 PhNO <sub>2</sub>	30
	MeCN/1 mmol PhNO <sub>2</sub>	traces
	MeCN/CH <sub>2</sub> Cl <sub>2</sub> 9:1	48
	MeCN/CH <sub>2</sub> Cl <sub>2</sub> 8:1	39
	MeCN/CH <sub>2</sub> Cl <sub>2</sub> 6:1	traces

<sup>a</sup> Standard reaction conditions: 1 mmol of substrate in 2 mL of solvent; inert atmosphere; 2.4 mmol (in the case of **5b** and **5d** 1.2 mmol) of CsSO<sub>4</sub>F; *T* = 35 °C; 1 h. <sup>b</sup> Measured from <sup>1</sup>H (**10a**, **10d**) or <sup>19</sup>F NMR spectra (**22a**, **22c**, **31**) of crude reaction mixtures using anisole or octafluoronaphthalene as internal standard; calculated on starting material.

ates and resulting in the formation of benzyl fluoride derivatives (**30**, **31**). 2-Phenylethanol (**25**) was thus converted to benzyl fluoride (**30**) and phenylacetyl fluoride in a 3:1 relative ratio, while 2-phenyl-1-propanol (**26**) was selectively transformed to 1-phenyl-1-fluoroethane (**31**) and carbon monoxide, as detected by MS analysis of the evolved gas.

**Effect of Radical Scavenger and Solvent.** The important role of the solvent and the presence of various radical scavengers in the reactions of CsSO<sub>4</sub>F with different types of organic molecules, pointed out in several previous reports<sup>1,2b</sup>, was also established in the reactions of CsSO<sub>4</sub>F with alcohols. Nitrobenzene, often used as a radical inhibitor, when added to the reaction mixture while keeping the other reaction parameters constant, reduced the conversion of 1-phenylethanol (**5b**) and its *m*-CF<sub>3</sub> analogue (**5d**) to the corresponding acetophenone by up to 37% (Table 1). The transformation of benzyl alcohol (**21c**) or its *p*-Me derivative (**21a**) was suppressed by more than 80%, while the reaction of 2-phenyl-1-propanol (**26**) was completely inhibited by the presence of an equimolar amount of nitrobenzene. The degree of inhibition of the reaction caused by the presence of a radical scavenger is comparable to those determined

for the reactions of CsSO<sub>4</sub>F with aldehydes<sup>9</sup> in the case of secondary alcohols, while in the case of benzyl alcohol and 2-phenyl-1-propanol the inhibition is twice as strong as for the reactions of CsSO<sub>4</sub>F with the corresponding aldehydes.<sup>9</sup> The conversion of these primary alcohols to acid fluorides or benzyl fluorides, respectively, are also much more influenced by the solvent than the transformation of the analogous aldehydes to the same products,<sup>9</sup> as is evident from the data in Table 1. Less than 25% of CH<sub>2</sub>Cl<sub>2</sub> in the solvent mixture stopped the reaction in the case of **21a,c**, and 15% was sufficient to obtain the same effect in the case of **26**.

**Effect of the Structure of the Alcohol on Reaction Rates.** Applying the competitive technique for determination of relative reactivities expressed by relative rate factors (*k*<sub>rel</sub>),<sup>10</sup> we established that benzyl alcohols are more reactive than alkyl-substituted derivatives. 1-Phenylethanol was found to be twice as reactive as 2-octanol (*k*<sub>rel</sub> = 1.8) and benzyl alcohol to the same degree more reactive than decanol (*k*<sub>rel</sub> = 1.7) or 2-phenyl-1-propanol (*k*<sub>rel</sub> = 2.1). This observation is in contrast to that found for the relative reactivities of the corresponding aldehydes in their reactions with CsSO<sub>4</sub>F, where the reactivity decreased in the order alkyl > aryl > benzyl substituted aldehyde.<sup>9</sup> Correlation analysis using Hammett's relations between reaction rates and substituent parameters afforded values of the reaction constant for the oxidation of a set of secondary (**5**) and primary (**21**) benzyl alcohols with CsSO<sub>4</sub>F. The Hammett correlation plot for the transformation of 1-phenylethanols (**5a-g**) to acetophenones, presented in Scheme 2, showed a satisfactory correlation of relative rate factors with σ<sup>+</sup> substituent constants and gave a straight line with slope ρ<sup>+</sup> = -0.32 and a correlation coefficient of 0.97, while the analysis of analogous data for a set of benzyl alcohols (**21a-f**, Scheme 4) gave the value of -0.54 for the reaction constant and a correlation coefficient of 0.99. The reaction constant ρ<sup>+</sup> for the oxidation of **5** to **10** has the same sign but lower magnitude than those reported for the same reaction using dimethyldioxirane (ρ = -1.57),<sup>11</sup> chromic acid (ρ = -1.16),<sup>12</sup> or chromium trioxide in acetic acid solvent (ρ = -1.01)<sup>13</sup> as oxidants and comparable to those for oxidation by chromium trioxide under basic (ρ = -0.52) or neutral (ρ = -0.37) conditions<sup>13</sup> or by S<sub>2</sub>O<sub>8</sub><sup>2-</sup>-Cu<sup>II</sup> (ρ = -0.27).<sup>14</sup> On the other hand, ρ<sup>+</sup> for the CsSO<sub>4</sub>F-mediated conversion of **21** to **22** is considerably lower than those for the oxidation of benzyl alcohols to benzaldehydes by HNO<sub>3</sub> (ρ = -2.25)<sup>15</sup> or HNO<sub>2</sub> (ρ = -1.70, Yukawa-Tsuno method)<sup>16</sup> and comparable to those found for conversion of benzaldehydes to benzoyl fluorides (ρ<sup>+</sup> = -0.38)<sup>9</sup> by CsSO<sub>4</sub>F.

**Proposed Mechanism.** On the basis of the presented experimental results, the possible reaction pathways of transformation of secondary alcohols to ketones and primary alcohols to acid fluorides by CsSO<sub>4</sub>F are shown in Scheme 6. The electron-transfer process (A), resulting in the formation of cation radical intermediate **32**,

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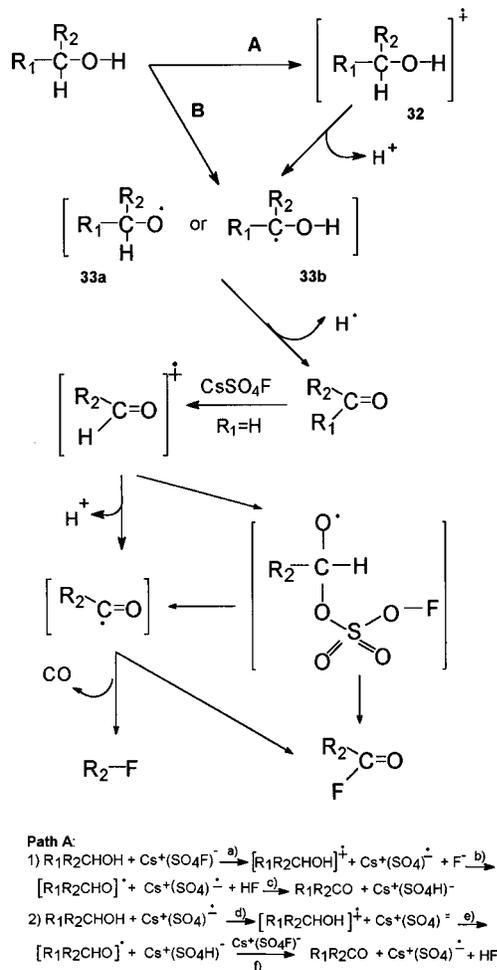
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Scheme 6



followed by proton loss thus forming radical intermediate **33**, which could also be obtained by direct hydrogen radical abstraction from the alcohol molecule (B), are two possible reaction pathways. In both cases, the processes can be mediated by  $SO_4F^-$  (path A1) or  $SO_4^{\cdot-}$  (path A2). The electron-transfer process is generally accepted as the key reaction channel in the oxidation of organic molecules by peroxydisulfate where similar reactive species are involved, and in most cases the same reaction products are formed<sup>14,17</sup> as in the present report. Since the fluoroxysulfate anion is an even stronger oxidant than peroxydisulfate<sup>18</sup> and the ionization potentials of alcohols are between 9 and 10.5 eV, the electron-transfer pathway is the most probable process in these reactions, but direct hydrogen abstraction, suggested in some other oxidation reactions,<sup>11,19</sup> could not be neglected. The electron deficiency in cation-radical intermediate **32** in the case of alkyl-substituted alcohols is located at the oxygen atom, while in the case of benzyl alcohols **32** is additionally stabilized due to resonance over the benzene ring.<sup>19</sup> Proton loss, as the next step, can proceed from the hydroxy group, thus forming alkoxy radical **33a**, or from the  $\alpha$ -hydroxy carbon atom thus forming carbon radical

Table 2. Yields of Isolated Products in the Reactions of Alcohols with  $CsSO_4F$ 

product	isolation method	yield(%)
benzophenone, <b>2</b>	CC	92
1-fluoronaphthalene, <b>3</b>	TLC	48
3'-methylacetophenone, <b>10a</b>	CC	93
acetophenone, <b>10b</b>	CC	90
4'-bromoacetophenone, <b>10c</b>	CC	89
3'-bromoacetophenone, <b>10d</b>	CC	89
3'-(trifluoromethyl)acetophenone, <b>10e</b>	CC	88
4'-(trifluoromethyl)acetophenone, <b>10f</b>	CC	85
4'-nitroacetophenone, <b>10g</b>	CC	83
3'-chlorobenzophenone, <b>11a</b>	CC	88
3'-(trifluoromethyl)benzophenone, <b>11b</b>	CC	87
4'-nitrobenzophenone, <b>11c</b>	CC	82
propiophenone, <b>12</b>	CC	91
cyclopropylphenyl ketone, <b>13</b>	CC	94
$\alpha,\alpha,\alpha$ -trifluoroacetophenone, <b>14</b>	TLC	44
cyclopentanone, <b>16a</b>	GLC	59
cyclohexanone, <b>16b</b>	GLC	62
cycloheptanone, <b>16c</b>	GLC	64
1-indanone, <b>18a</b>	CC	85
1-tetralone, <b>18b</b>	CC	86
1-phenyl-2-butanone, <b>20a</b>	CC	87
2-octanone, <b>20b</b>	CC	87
4'-methylbenzoyl fluoride, <sup>9</sup> <b>22a</b>	TLC	76
4'-fluorobenzoyl fluoride, <sup>9</sup> <b>22b</b>	GLC	49
benzoyl fluoride, <b>22c</b>	CC	76
4'-chlorobenzoyl fluoride, <sup>9</sup> <b>22d</b>	TLC	78
4'-(trifluoromethyl)benzoyl fluoride, <sup>9</sup> <b>22e</b>	GLC	46
3'-nitrobenzoyl fluoride, <sup>9</sup> <b>22f</b>	TLC	74
octanoyl fluoride, <sup>9</sup> <b>27</b>	GLC	50
decanoyl fluoride, <sup>9</sup> <b>28</b>	GLC	50
phenylacetyl fluoride, <sup>9</sup> <b>29</b>	GLC	10
benzyl fluoride, <b>30</b>	GLC	32
1-fluoro-1-phenylethane, <sup>9</sup> <b>31</b>	TLC	78

**33b**, which after hydrogen radical abstraction is then transformed to the final carbonyl product. Both intermediates **33a,b** were postulated and proved during peroxydisulfate-mediated oxidation of alcohols,<sup>14,17a,20</sup> and it was suggested that the initially-formed alkoxy radical rapidly interconverts to the thermodynamically more stable carbon radical. It is interesting that according to our results disproportionation of cation-radical **32** or radical **33**, regularly observed during peroxydisulfate oxidation of similar substrates, did not occur after  $CsSO_4F$ -mediated oxidation. In this case, proton loss from **32** and hydrogen abstraction from **33** are probably considerably faster processes than disproportionation of the same intermediates.<sup>14,20b</sup> In the case of secondary alcohols, oxidation reactions stopped at the ketone formation step, while aldehydes, originally formed from primary alcohols, reacted further following the mechanism already proposed in our previous report,<sup>9</sup> thus resulting in acid fluorides or benzyl fluorides.

Definitive conclusions concerning the reaction pathway of oxidation of alcohols with  $CsSO_4F$  cannot be given, but regarding the strong effect of the radical inhibitor on the reaction course and the magnitude of the reaction constant ( $\rho^+$ ), comparable to values obtained for many radical transformations of alcohols, the main intermediates involved in these reactions must be of a radical nature.

## Experimental Section

<sup>1</sup>H and <sup>19</sup>F NMR spectra were recorded at 60 and 56.4 MHz, respectively. Alcohols from commercial sources were used.

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(18) The  $SO_4F^-/SO_4H^-$  couple has a standard electrode potential of 2.52 V<sup>3</sup>, and after  $F_2$ ,  $XeF_2$  and  $OF_2$  are the strongest oxidants among reagents used in organic synthesis, while the  $S_2O_8^{2-}/2SO_4^{2-}$  couple has a standard electrode potential of 2.01 V.<sup>17a</sup>

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(20) (a) Ledwith, A.; Russell, P. J.; Sutcliff, L. H. *J. Chem. Soc., Perkin Trans. 2* **1973**, 630. (b) Caronna, T.; Citterio, A.; Grossi, L.; Minischi, F.; Ogawa, K. *Tetrahedron* **1976**, *32*, 2741.

CsSO<sub>4</sub>F was prepared by the reaction of water solution of Cs<sub>2</sub>SO<sub>4</sub> with F<sub>2</sub> and handled according to the literature.<sup>21</sup>

**Reactions of Alcohols with CsSO<sub>4</sub>F. General Procedure.** A solution of 2 mmol of alcohol in 4 mL of freshly distilled and dry MeCN was degassed with argon. Then, 600 mg (2.4 mmol), or 1150 mg (4.6 mmol) in the case of primary alcohols, of CsSO<sub>4</sub>F was introduced, and the reaction suspension was stirred under Ar at 30–35 °C for 1 h. After dilution with 60 mL of CH<sub>2</sub>Cl<sub>2</sub>, the insoluble residue was filtered off, and the filtrate washed with saturated aqueous NaHCO<sub>3</sub> (30 mL) and water (30 mL), dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated under reduced pressure. The crude reaction mixtures were analyzed by GLC and <sup>1</sup>H and <sup>19</sup>F NMR spectroscopy. The amounts of the products formed were determined from <sup>1</sup>H or <sup>19</sup>F NMR spectra of the crude reaction mixtures using anisole or octafluoronaphthalene as internal standards and yields calculated on starting material. Products were isolated by column chromatography (SiO<sub>2</sub>, *n*-hexane) or by preparative TLC (SiO<sub>2</sub>, *n*-hexane/CH<sub>2</sub>Cl<sub>2</sub> 4:1) or GLC (OV 101 10%, Chromosorb W A/W 80/100) and identified on the basis of the spectroscopic data and comparison with authentic samples or literature data. The yields collected in Table 2 refer to isolated pure products.

(21) Appelman, E. H. *Inorg. Synth.* **1986**, *24*, 22.

**The Effect of Solvent on the Transformation of Alcohols.** To a solution of 1 mmol of alcohol in 2 mL of solvent (CH<sub>2</sub>Cl<sub>2</sub> or *n*-hexane), or a solvent mixture consisting of MeCN and CH<sub>2</sub>Cl<sub>2</sub>, degassed with argon, was added 300 mg (1.2 mmol) or 575 (2.3 mmol) of CsSO<sub>4</sub>F, and the reaction suspension was stirred under Ar at 35 °C for 2 h. The crude reaction mixtures were isolated and analyzed as cited in the General Procedure. The effect of the solvent on the course of reaction is presented in Table 1.

**The Effect of Radical Inhibitor on the Transformation of Alcohols.** In a degassed solution of 1 mmol of alcohol in MeCN was introduced a corresponding amount of PhNO<sub>2</sub> and CsSO<sub>4</sub>F (1.2 or 2.3 mmol) and the reaction suspension stirred at 35 °C under argon for 1 h. The crude reaction mixture was isolated and analyzed as cited and the effect on the transformation to carbonyl products presented in Table 1.

**Determination of Relative Rate Factors.** The procedure already described in the literature was used.<sup>4,9</sup>

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