product mixture was obtained. NMR yields of this mixture converted to 0.163 g (18%) of **10a** and 0.406 g (38%) of **14a**. Fraction B weighed 0.589 g and consisted of a mixture of condensation products **6** and **16**; NMR yields converted to 0.466 g (23%) of **16** and 0.123 g (7%) of **6**.

Acknowledgment. The authors are pleased to acknowledge support of this work by the National Science Foundation through Grant No. CHE-8513216 and by the Harvey W. Peters Research Center for Parkinson's Disease and Disorders of the Central Nervous System Foundation.

Registry No. **4a**, 5661-14-3; **4b**, 7242-83-3; **4c**, 7242-84-4; **4d**, 3559-04-4; **7a**, 143105-03-7; **7a**-d_3, 143105-04-8; **7b**, 143105-05-9; **7c**, 143105-06-0; **7d**, 143105-07-1; **10a**, 34989-82-7; **10b**, 61798-56-9; **10c**, 84108-97-4; **10d**, 53440-57-6; **14a**, 143105-08-2; **14b**, 143105-09-3; **14c**, 143105-10-6; **14d**, 143105-11-7; $PhSO_2NH_2$, 98-10-2; o-$ClC_6H_4SO_2NH_2$, 6961-82-6.

Reactions of Aldehydes with Cesium Fluoroxysulfate

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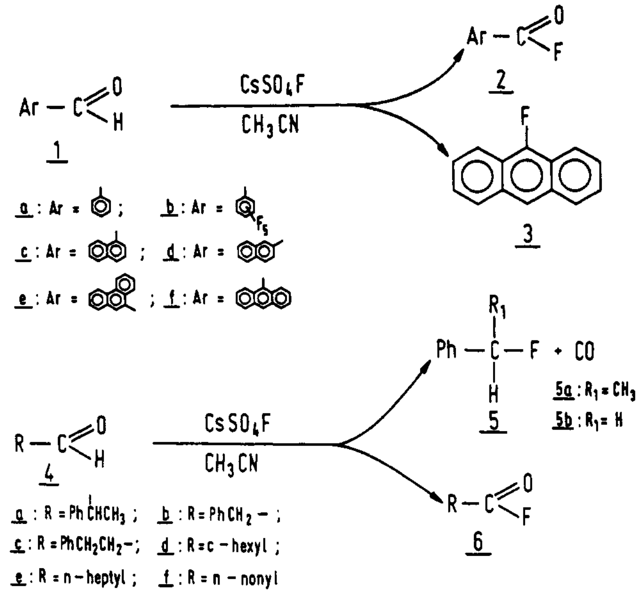
Various aromatic and aliphatic aldehydes reacted at 35–40 °C in CH_3CN with $CsSO_4F$ giving acid fluorides in a good yield. In some cases formation of fluorohydrocarbons was also observed. Hammett correlation analysis of the transformation of various substituted benzaldehydes (p-OCH_3, p-CH_3, p-F, p-CF_3, m-NO_2) gave the reaction constant $\rho^+ = -0.38$. Solvent polarity strongly influenced the conversion of aldehydes into acid fluorides, being in acetonitrile almost quantitative and completely halted in CH_2Cl_2, n-hexane, or tetrahydrofuran. The presence of nitrobenzene, often used as a radical scavenger, considerably reduced the acid fluoride formation. Based on experimental observations was concluded that the main intermediates involved in the conversion of aldehydes into acid fluorides with $CsSO_4F$ must be of a radical nature.

The reactions of cesium fluoroxysulfate ($CsSO_4F$) with organic compounds strongly depend on the type of organic molecules and the functional groups present. Alkenes[1] and alkynes[2] readily reacted with $CsSO_4F$ to yield addition or addition–elimination products, depending on reaction conditions. Fluorofunctionalization of activated aromatics[3] and saturated hydrocarbons,[4] as well as α-carbonyl[5] or benzylic carbon atoms,[6] was also achieved under mild reaction conditions, while molecules containing a sulfur or phosphorus atom was transformed into the corresponding sulfoxides, sulfones, or phosphine oxides,[7] which could be explained by the fact that $CsSO_4F$ possess two reactive centers.[8]

It is known that aldehydes are very sensitive to oxygen and other oxidants transforming into acids or even peracids.[9] Reactions of aldehydes, having an α-hydrogen, with halogens (chlorine or bromine) resulted in α-halo-substituted aldehydes, while there are only few reports on direct conversion of aldehydes to acid chlorides or bromides[10] and none on direct conversion of aldehydes to acid fluorides.

We now report our investigation on the reaction of $CsSO_4F$ with aromatic and aliphatic aldehydes.

Scheme I



Results and Discussion

In a typical experiment 1 mmol of benzaldehyde **1a** was dissolved in 2 mL of freshly distilled and oxygen-free CH_3CN, $CsSO_4F$ (1.1 mmol) was introduced in a solution kept under inert atmosphere, and the reaction suspension was stirred for 1 h at 35–40 °C. The crude reaction mixture, isolated as cited in the Experimental Section, was analyzed and the high-yield formation of benzoyl fluoride as the sole product was confirmed. Furthermore, we have studied the effect of the structure of the aromatic nucleus on the course of the reaction and found that pentafluorobenzaldehyde (**1b**, Scheme I), 1- and 2-naphthyl

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Table I. Fluorination of Aldehydes with $CsSO_4F^a$

substrate	solvent	yield^b (%)
C_6H_5CHO; **1a**	CH_3CN	86; **2a**
	CH_3CN/0.2 mmol of $PhNO_2$	80
	CH_3CN/2 mmol of $PhNO_2$	51
	CH_3CN/CH_2Cl_2 (1:1)	71
	CH_3CN/CH_2Cl_2 (1:9)	6
	CH_2Cl_2	traces
	n-C_6H_{14}	traces
	THF	traces
p-$CH_3C_6H_4CHO$; **7b**	CH_3CN	83; **8b**
	CH_3CN/0.1 mmol of $PhNO_2$	77
$C_6H_5CH_2CHO$; **4b**	CH_3CN	60 (**5b**:**6b** = 1.7:1)^c
	CH_3CN/1 mmol of $PhNO_2$	40 (**5b**:**6b** = 1.7:1)
	CH_3CN/CH_2Cl_2 (9:1)	46 (**5b**:**6b** = 3.5:1)
	CH_3CN/CH_2Cl_2 (1:1)	14
$C_6H_5CH(CH_3)CHO$; **4a**	CH_3CN	84; **5a**
	CH_3CN/1 mmol of $PhNO_2$	65
	CH_3CN/CH_2Cl_2 (4:1)	68

^{a} Standard reaction conditions: 1 mmol of substrate in 2 mL of solvent; inert atmosphere; 1.1 mmol of $CsSO_4F$; T = 35 °C; 1.5 h. ^{b} Measured from ^{19}F NMR spectra of crude reaction mixtures using OFN as additional standard; calcd on starting material. ^{c} Ratios determined by ^{19}F NMR.

aldehydes (**1c**, **1d**), and 9-phenanthryl aldehyde (**1e**) were readily converted into the corresponding (**2a–e**) acid fluorides in a high yield. A different course of the reaction was observed in the case of 9-anthryl aldehyde (**1f**) where 9-fluoroanthracene (**3**) was formed in 35% yield. The role of the structure variations of the aldehyde molecule in the reactions with $CsSO_4F$ is illustrated in Scheme I. 2-Phenylpropanal (**4a**) was readily converted to 1-phenyl-1-fluoroethane (**5a**) and carbon monoxide, as detected by mass spectrometry analysis of evolved gas. Reaction with phenyl acetaldehyde (**4b**) gave a 1.7:1 mixture of benzyl fluoride (**5b**) and phenylacetyl fluoride (**6b**), while aliphatic aldehydes as 3-phenylpropanal (**4c**), cyclohexanecarboxaldehyde (**4d**), octanal (**4e**), and decanal (**4f**) were converted quantitatively to acid fluorides **6c–f**.

The reaction mechanisms of conversion of aldehydes with various oxidation reagents or halogens are still unclear. Two main types of functionalizations are suggested: a free radical and ionic one, the last being more probable in protic, acidic, or basic conditions. We have already demonstrated that the presence of oxygen can effectively change the course of the reactions of $CsSO_4F$ with various organic molecules (acetylenes,[2] alkyl-substituted aromatics[6]), but it can not be used as a radical scavenger in the case of reactions involving aldehydes which are readily converted to carboxylic acids by oxygen. The presence of nitrobenzene, often used as a radical inhibitor, reduced the conversion of benzaldehyde to benzoyl fluoride up to 36%, while the p-methylbenzaldehyde transformation to p-methylbenzoyl fluoride was suppressed up to 22% (Table I). The conversion of 2-phenylpropanal (**4a**) into 1-phenyl-1-fluoroethane (**5a**) was reduced by nitrobenzene for 22%, and the transformation of phenylacetaldehyde (**4b**) into benzyl fluoride (**5b**) and phenylacetyl fluoride (**6b**) was decreased by 28% with no considerable change of the products ratio. The important role of the solvent in the reactions of $CsSO_4F$ with organic molecules, pointed out in several previous reports, was found also in the $CsSO_4F$ reactions with aldehydes. As shown in Table I, the addition of different amounts of dichloromethane to the reaction mixture suppressed the conversion of benzaldehyde into benzoyl fluoride. The use of neat CH_2Cl_2, n-hexane, or tetrahydrofuran as solvents completely stopped the reactions. An even more pronounced effect of the CH_2Cl_2 addition was noticed in the reaction of $CsSO_4F$ with phenyl acetaldehyde (**5b**) where only 10% of CH_2Cl_2 in the solvent mixture considerably changed the products ratio, diminishing phenylacetyl fluoride (**6b**), but not benzyl fluoride (**5b**) formation.

The effect of substituents on the various conversions of substituted benzaldehydes has been intensively studied. The correlation analysis using Hammett's[11] or Taft's[12] and Swain's[13] relations between reaction rates and substituent parameters were generally applied for the evaluation of substituent effects on the reaction course, and from the magnitude and sign of reaction constant (ρ) the valuable information about the nature of reaction center could be obtained and some conclusions on reaction mechanisms were made. However, very different substituent effects on the transformations of substituted benzaldehydes with various reagents into either benzoic acid derivatives, phenoles, or benzoyl halides were observed. In Scheme II three main types of benzaldehydes transformations are shown. For the oxidation reactions an addition process was suggested in the first step, while further migration of the hydrogen atom (as proton, hydride, or radical) strongly depended on reaction conditions. Nevertheless, in all cases the positive sign of the reaction constant (ρ) was found by correlation analysis, their magnitude altering from 0.45 to 1.45, in the case of oxidation of benzaldehydes by Cr(V) and Cr(VI) specia under acidic conditions,[15,16] to 1.83, for the reaction with Mn(VII) under basic conditions.[17] The reaction constants with a negative sign were observed for the phenyl-ring migration process in Baeyer–Villiger reactions of substituted benzaldehydes with peroxymonosulfate ($\rho = -1.7$),[20] as well as with perbenzoic acid in aqueous ethanol ($\rho = -1.6$ to -5.7 depending on pH).[22] Similarly, a very high negative reaction constant (up to -5.5) was established for N-bromobenzamide oxidation of benzaldehydes, and the formation of acylium carbocationic intermediate was thus suggested.[23] Finally, the correlation analysis for the radical intermediates, gave the ρ values altering from -1.13 for the benzoyl chlorides formation with trichloromethyl radicals[10] to -0.49 for the oxidation with perbenzoate radicals in acetic anhydride.[24] The differences in the magnitude of reaction constants could be explained by the different polar nature in transition state as shown in Scheme II.

The effect of substituents on the transformation of benzaldehydes **7a–e** with $CsSO_4F$ is shown in Scheme II. Benzoyl fluorides **8a–e** were formed almost quantitatively, regardless of the substitution of the phenyl ring, and no products of ring fluorination or aryl migration were detected, even in the case of strongly ring-activated substrates, like p-alkoxybenzaldehydes, where at least ring fluorination would be expected as a competitive reaction. Hammett correlation plot for the conversion of benzaldehydes with $CsSO_4F$ presented in Scheme II showed a satisfactory correlation of relative rate factors with σ^+ substituent constants. The straight line is a least-squares fit with slope $\rho^+ = -0.38$ and a correlation coefficient of

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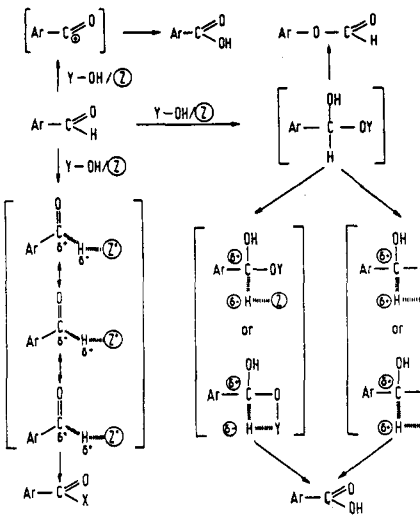
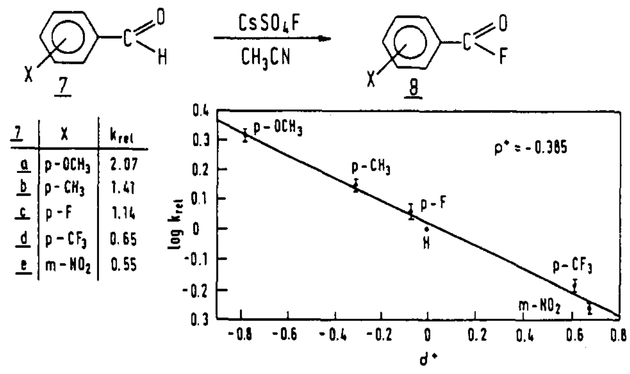
Scheme II. Effect of Reagent and Reaction Conditions on Reaction Constant (ρ) for Transformations of Substituted Benzaldehydes

23	− 5.52	PhCONHBr	Ph−COOOH $^{-}SO_3OOH/H^+$	− 1.6 do − 5.0 − 1.7	22 20
Ref.	ρ = −	Y−OH/Z		ρ = −	Ref.



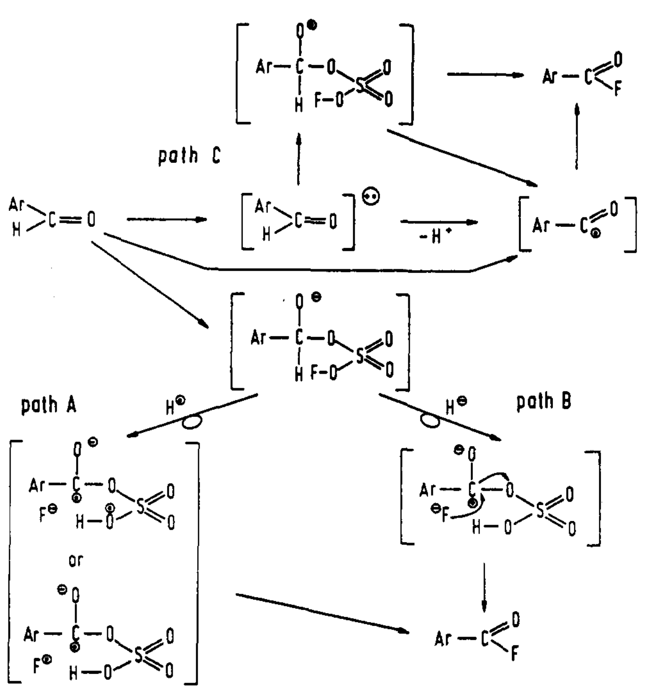
Ref.	ρ = −	Y−OH/Z		ρ = +	Ref.
10	− 1.13	$BrCCl_3/h\nu$	Cr(IV)/H^+	0.97	14
10	− 0.53	SO_2Cl_2	Cr(V)/H^+	0.45	15
10	− 0.54	CCl_3SO_2Cl	Cr(VI)/H^+	1.15	16
24	− 0.49	$PhCOOOH/Ac_2O$	Mn(VII)/OH^-	1.83	17
			Cu(III)/OH^-	0.84	18
			PhCOOOH	1.1 − 1.8	19
			$^{-}SO_3OOH/H^+$	1.81	20
			$HBrO_3$	1.05	21

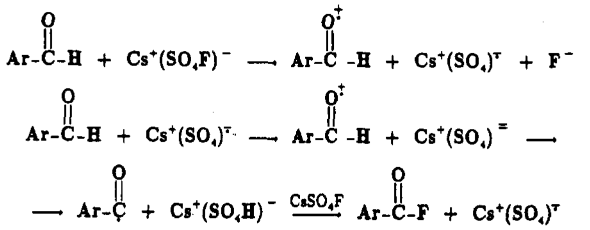


7	X	k_{rel}
a	p-OCH_3	2.07
b	p-CH_3	1.41
c	p-F	1.14
d	p-CF_3	0.65
e	m-NO_2	0.55

0.9955. We have also compared the reactivities of aliphatic and aromatic aldehydes and found that decanal is considerably more reactive than benzaldehyde (k_{rel} = 2.9) and phenyl acetaldehyde (k_{rel} = 3.8).

Scheme III





$$\mathrm{Ar{-}\overset{\overset{\large O}{\|}}{C}{-}H} + \mathrm{Cs^+(SO_4F)^-} \longrightarrow \mathrm{Ar{-}\overset{\overset{\large O^{+\cdot}}{\|}}{C}{-}H} + \mathrm{Cs^+(SO_4)^{-\cdot}} + \mathrm{F^-}$$

$$\mathrm{Ar{-}\overset{\overset{\large O}{\|}}{C}{-}H} + \mathrm{Cs^+(SO_4)^{-\cdot}} \longrightarrow \mathrm{Ar{-}\overset{\overset{\large O^{+\cdot}}{\|}}{C}{-}H} + \mathrm{Cs^+(SO_4)^{=}} \longrightarrow$$

$$\longrightarrow \mathrm{Ar{-}\overset{\overset{\large O}{\|}}{\dot{C}}} + \mathrm{Cs^+(SO_4H)^-} \xrightarrow{\mathrm{CsSO_4F}} \mathrm{Ar{-}\overset{\overset{\large O}{\|}}{C}{-}F} + \mathrm{Cs^+(SO_4)^{-\cdot}}$$

The possible reaction pathways of transformation of aldehydes to acid fluorides with $CsSO_4F$ are shown in Scheme III. The abstraction of the hydrogen radical by $CsSO_4F$ or $CsSO_4^{\cdot-}$ thus forming acylium radical is only one of the probable reaction paths. The possibility of nucleophilic attack of fluoroxysulfate anion to the carbonyl bond must also be taken into account. Adduct could rearrange further in a radical (path A) or scarcely likely ionic (path B) way, while hydrogen atom migration could proceed in at least two ways as shown in Scheme III. Because of the fact that $CsSO_4F$ is known as a very strong oxidant[25] and the ionization potentials of aldehydes are between 8.5 and 9.8 eV, the transformation of aldehyde molecule to cation radical intermediate is also believable. The cation radical could be further transformed to acylium radical by proton loss or attached by fluoroxysulfate anion (path C), and thus formed adduct could be further transformed, similarly, to paths A and B, finally resulting in an acid fluoride formation. However, on the basis of our experimental results, regarding the effect of solvent and radical inhibitor on the reaction course, the decarbonylation process observed in the case of 2-phenylpropanal or α-phenyl acetaldehyde fluorination, and the magnitude as well as the sign of the reaction constant (ρ^+), comparable to values obtained for many radical transformations of aldehydes, we believe that the main intermediates involved in the transformations of aldehydes to acid fluorides by $CsSO_4F$ must be of a radical nature.

Experimental Section

^1H and ^{19}F NMR spectra were recorded at 60 and 56.4 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. Aldehydes from commerical sources were used, and $CsSO_4F$ was prepared according to the literature[3a] and handled in compliance with applicable instructions.[3b]

Fluorination of Aldehydes with $CsSO_4F$. General Procedure. A solution of 1 mmol of aldehyde in 2 mL of freshly distilled and dry CH_3CN was degassed with dry oxygen-free N_2. Then, 275 mg (1.1 mmol) of $CsSO_4F$ was introduced and the reaction suspension was stirred under N_2 at 20–35 °C for 1–2 h and diluted with 40 mL of CH_2Cl_2. The insoluble residue was filtered off. The filtrate was washed with 20 mL of water, dried (Na_2SO_4), and evaporated under reduced pressure. The crude reaction mixtures were analyzed by GLC and ^1H and ^{19}F NMR spectroscopy. The amounts of the fluorinated products formed were determined from ^{19}F NMR spectra of the crude reaction

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mixtures using octafluoronaphthalene (OFN) as internal standard and yields calculated on starting material. Products were isolated by preparative GLC (OV 101 10%, Chromosorb W A/W 80/100), TLC, or column chromatography (SiO_2) and identified on the basis of the spectroscopical data and comparison with authentic samples or literature and in some cases also by conversion to known compounds. The NMR, IR, and MS data for these compounds are available as supplementary material. The yields listed below refer to isolated pure compounds.

Benzoyl fluoride (2a): SiO_2, *n*-pentane; 77%. **Pentafluorobenzoyl fluoride**[26] **(2b)**: GLC, 12.5%, liquid. **1-Naphthalenecarbonyl fluoride**[27] **(2c)**: TLC, 68.5%; mp 67–69 °C (lit.[27] mp 69–70 °C). **2-Naphthalenecarbonyl fluoride**[27] **(2d)**: TLC, 55%; mp 54–56 °C (lit.[27] mp 55–56 °C). **9-Phenanthrenecarbonyl fluoride (2e)**: TLC, 41.5%, mp 112–115 °C; NMR ($CDCl_3$) δ_F +28.5 (s), δ_H 7.7–8.2 (m, 5 H), δ_H 8.7–9.0 (m, 3 H), δ_H 9.0–9.3 (m, 1 H); IR (KBr) ν 1800 cm^{-1}; MS *m/z* 225 (M + 1, 16%), 224 (M, 100), 196 (31), 176 (16). **2e** was converted to 9-Phenanthrenecarboxylic acid, mp 255–257 °C. **9-Fluoroanthracene**[28] **(3)**: TLC, 32%, mp 102–104 °C (lit.[28] mp 102–103 °C). **1-Fluoro-1-phenylethane**[29] **(5a)**: 80%, converted to styrene. **Benzyl fluoride (5b)**: GLC, 19%. **Phenylacetyl fluoride**[30] **(6b)**: GLC, 13.5%, liquid. **3-Phenylpropionyl fluoride**[31] **(6c)**: GLC, 61%, liquid. **Cyclohexanoyl fluoride**[32] **(6d)**: GLC, 54% liquid. **Octanoyl Fluoride**[33] **(6e)**: GLC, 52%, liquid. **Decanoyl fluoride**[33] **(6f)**: GLC, 54%, liquid. ***p*-Methoxybenzoyl fluoride**[34] **(8a)**: TLC, 76% liquid. ***p*-Methylbenzoyl fluoride**[34] **(8b)**: TLC, 77.5%, liquid. ***p*-Fluorobenzoyl fluoride**[34] **(8c)**: GLC, 51%, liquid. ***p*-(Trifluoromethyl)benzoyl fluoride**[34] **(8d)**: GLC, 57%, liquid. ***m*-Nitrobenzoyl fluoride**[34] **(8e)**: TLC, 70.5%, mp 40–42 °C.

The Effect of Solvent on the Fluorination of Aldehydes. To a solution of 1 mmol of aldehyde in a solvent (CH_2Cl_2, THF, or *n*-hexane) or in solvent mixture, consisting of CH_3CN mixed with CH_2Cl_2, degassed with O_2-free N_2, was added 275 mg (1.1 mmol) of $CsSO_4F$, and the reaction suspension was stirred under N_2 at 35 °C for 1 h. The crude reaction mixtures, isolated as citated in the General Procedure, were analyzed by ^{19}F NMR. The effect of solvent on the reaction course is presented in Table I.

Fluorination of Aldehydes in the Presence of Nitrobenzene. In a solution of 1 mmol of aldehyde in dry CH_3CN, degassed with O_2-free N_2, was introduced nitrobenzene. Then $CsSO_4F$ (275 mg, 1.1 mmol) was added and the reaction suspension stirred at 35 °C for 1 h. The crude reaction mixtures was analyzed by ^{19}F NMR. The effect of radical scavenger on the fluorination course is presented in Table I.

Determination of the Relative Rate Factors. One mmol of aldehyde and 1 mmol of its comparative analogue were dissolved in 2 mL of freshly distilled and dry CH_3CN, the solution was degassed with O_2-free dry N_2 and thermostated at 35 °C, and 1 mmol of $CsSO_4F$ was introduced. The reaction suspension was stirred at constant temperature for 1 h. The amounts of products formed were measured from ^{19}F NMR spectra of crude reaction mixtures, using OFN as the additional standard. Applying this known competitive technique, relative reactivities expressed by relative rate factors (k_{rel}) were calculated from the equation[35]

$$k_{rel} = \frac{k_A}{k_B} = \frac{\log (A - X)/A}{\log (B - Y)/B}$$

derived from the Ingold–Shaw relation,[36] where *A* and *B* are the amounts (in mmols) of starting material and *X* and *Y* the amounts of products derived from them.

Registry No. 1a, 100-52-7; **1b**, 653-37-2; **1c**, 66-77-3; **1d**, 66-99-9; **1e**, 4707-71-5; **1f**, 642-31-9; **2a**, 455-32-3; **2b**, 1478-07-5; **2c**, 35424-74-9; **2d**, 37827-83-1; **2e**, 127410-76-8; **3**, 529-85-1; **4a**, 93-53-8; **4b**, 122-78-1; **4c**, 104-53-0; **4d**, 2043-61-0; **4e**, 124-13-0; **4f**, 112-31-2; **5a**, 7100-97-2; **5b**, 350-50-5; **6b**, 370-84-3; **6c**, 458-69-5; **6d**, 1977-87-3; **6e**, 592-94-9; **6f**, 334-47-4; **7a**, 123-11-5; **7b**, 104-87-0; **7c**, 459-57-4; **7d**, 455-19-6; **7e**, 99-61-6; **8a**, 701-53-1; **8b**, 350-42-5; **8c**, 1583-56-8; **8d**, 368-94-5; **8e**, 77976-08-0; H_2, 1333-74-0; $PhNO_2$, 70806-67-6; $CsSO_4F$, 70806-67-6; 9-phenanthrenecarboxylic acid, 837-45-6.

Supplementary Material Available: Tabulated ^1H and ^{19}F NMR, IR, and MS spectroscopical data for compounds **2a–d**, **3**, **6b–f**, and **8a–e** (2 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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