The Effect of Heteroatoms on the Reactions of Organic Molecules with Caesium Fluoroxysulphate

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Abstract: $CsSO_4F$ reacted at room temperature, or at 35 °C in acetonitrile with various heteroatom-containing organic molecules, and three types of transformations have been observed. Fluoro substitution process took place with triphenylmethane, triphenylsilane, triphenylchlorosilane, 4-tert-butylphenol, benzaldehyde, and octanal, thus forming fluorotriphenylmethane, fluorotriphenylsilane, 2-fluoro-4-tert-butylphenol, benzoyl fluoride in high yields. Substitution reaction was accompanied by fluoroaddition process in the case of 2-fluoro-4-tert-butylphenol, where 2,2-difluoro-4-tert-butylcklonexadienon-4,6 was isolated. CsSO₄F easily oxidised secondary alcohols to ketones, and 1,2-dihydroxy-4-tert-butylbenzene to quinone derivate. Oxygenation process was observed in the case of triphenylphosphine, and dibenzotiophene, while ethyl iodide was transformed to ethyliodo(III) difluoride. Solvent plays an important role in these reactions, being successfully performed in CH₃CN, and completely inhibited in CH₂Cl₂, while different shapes of the effect on fluorination of various organic molecules were observed by altering solvent nature by successive mixing of CH₃CN with CH₂Cl₂.

Fluorinating $agents^{1-5}$ (F₂, CF₃OF, CF₃COF, XeF₂, CsSO₄F etc.) represents a class of reagents whose reactivity depends very much on the structure of organic molecules and reaction conditions where solvent, catalyst, and temperature are the most important of them. Prediction of the course of fluorine atom introduction into organic molecules is still only a partly solved problem, but, if we want to improve our knowledge about the role of reagent structure in the course of fluorination, we must get as much information as possible on several target organic molecules. It has already been demonstrated that CsSO₄F is one of the most easy handled and selective fluorinating reagents, while its reactivity depends on structure of organic molecule and reaction conditions⁶⁻⁸, and three main types of functionalisation of organic molecules, as limited examples, have already been achieved: fluorination, oxidation or even oxygenation, and introduction of other functional groups deriveing from solvent, while mixed examples of transformations can be achieved with appropriate organic molecule structure modulation, and variations in reaction conditions.

We now report our further studies on $CsSO_4F$ reactions with organic molecules, with particular attention on the role of various heteroatoms and the solvent on the transformations and reaction course.

 $CsSO_4F$ at 35°C readily reacted with triphenylmethane in CH_3CN (<u>1a</u>, SCHEME <u>1</u>), thus forming fluorotriphenylmethane (<u>2</u>) in good yield, while similar fluoro functionalisation of triphenylsilane (<u>1b</u>) and triphenylchlorosilane (<u>1c</u>) to fluorotriphenylsilane (<u>3</u>) was achieved at room temperature, and only oxygenation process took place with triphenylphosphine (<u>1d</u>). The nature of intermediates in the latter case is not clear yet (direct oxygenation or over the formation of fluorosulphatephosphorine intermediate), but the formation of difluorophosphoranes, observed in the reactions with XeF₂ at -30 °C ⁹, could be exluded, because the stoichiometry of the reaction is one to one for CsSO₄F and triphenylphosphine, and only 10% excess of the reagent is sufficient for quantitative conversion of <u>1d</u> to triphenylphosphine oxide (<u>4</u>).

Sulphides were often used as substrates for examination of the fluorinating reagent nature. Their transformation to difluorosulphoranes¹⁰ or tetrafluorosulphonates¹¹ with CF₃OF has already been demonstrated. Difluorosulphoranes were also isolated in the reaction of XeF₂ with diphenylsulfide at low temperature¹², while rearranged fluoroalkyl derivatives or eliminated products were formed at room temperature¹³. No reaction was observed between dibenzotiophene ($\underline{5}$) and CsSO₄F at -20°C, while reaction at 22°C with 20% excess of reagent gave a mixture of two products: dibenzotiophene-5oxide ($\underline{6}$) and dibenzotiophene-5,5-dioxide ($\underline{7}$) in a 1.2:1 ratio. Complete conversion of dibenzotiophene-5-oxide ($\underline{6}$) into dioxide ($\underline{7}$) was achieved by using only 10% excess of reagent. On the basis of stoichiometry of the reaction the products formation over difluorosuphorane intermediate could be excluded, however at present we are not able to discriminate between two possible types of reactions as shown on SCHEME 1 (direct oxygenation or path over fluorosulphate intermediate).



Furthermore, we have studied reactions of $CsSO_4F$ with oxygen-containing compounds, e.g. alcohols, hydroxy derivative benzenes and aldehydes. Secondary alcohol, 4-tert-butylcyclohexanol, was readily converted to 4-tert-butylcyclohexanone (§, SCHEME 2). 4-tert-Butylphenol was fluoro substituted to 2-fluoro-4-tert-butylphenol (10), while a further fluoro addition-elimination process took place, thus forming 2,2-difluoro-4-tert-butylcyclohexadienon-4,6 (11), and only a trace amount of 2,6-difluoro-4-tert-butylphenol was formed. The introduction of additional hydroxy group into the



substrate molecule completely changed the reaction course and only oxidation process, resulting in 4-tert-butyl-1,2-benzoquinone (9) formation, was observed after the reaction of 1,2-dihydroxy-4-tertbutylbenzene with $CsSO_4F$. Aldehydes are usually easily converted to acids with strong oxidants, however, surprisingly we have found that benzaldehyde, as well as octanal are nearly quantitatively transformed to benzoyl fluoride (12a) or octanoyl fluoride (12b) with $CsSO_4F$. Primary alcohols e.g. benzyl alcohol or octanol, also readily reacted with $CsSO_4F$, but the reaction could not be selectively stopped on its first step, i.e the oxidation to aldehyde, so that the final result was the formation of acid fluorides 12a and 12b and 2.2 mmols of the reagent was necessary for the conversion of mmol of the substrate.

Finally, we have tested the reaction of $CsSO_4F$ with iodo substituted molecules, and found that transformation to iododifluoride derivative took place. Ethyl iodide was transformed with $CsSO_4F$ in acetonitrile to ethyliodo(III) difluoride (13) in good yield, which was confirmed by its further reaction with 1,1-diphenylethen, resulting in the formation of 1,1-diphenyl-1-fluoro-2-iodoethan¹⁴.

Furthermore, we have studied the effect of solvent on fluorination of heteroatomcontaining organic molecules with $CsSO_4F$. We modified the solvent nature by successive mixing of CH_3CN with CH_2Cl_2 , and the effects obtained are shown and compared in FIGURE A-C. The conversion of triphenylsilan to fluoride (A) is less influenced by solvent than the analoque reaction of triphenylchlorosilane, while the fluorination of triphenylmethane was too slow at room temperature, and therefore in this case the reaction was performed at 35 °C. Relative rate factors for these reactions, measured by a competitive technique²⁰, show that triphenylsilane is at least 30-times more reactive than triphenylmethane, and triphenylchlorosilane is 10.8-times more reactive than triphenylmethane in CH_3CN at 35 °C. As is evident from figure B the fluorination of alcohols are very distincly affected by solvent going from aromatic alcohol, over benzylic one to aliphatic derivative. The greatest effect was observed in the case of benzyl alcohol treatment with $CsSO_4F$ in CH_3CN/CH_2Cl_2 mixtures, where already a drop over a 20% share of CH_2Cl_2 stopped the conversion of starting material completely. The curve of fluorinated product yield is also very steep in the case of octanol, while the broken slope of 2-fluoro-4-tert-butylphenol formation indicated that the reaction pathways in cited examples could not be generalized with any doubt. Figure C is a comparative picture of the effects between aldehyde and its analogue alcohol, and it is obvious that the fluorination of aldehydes is considerably less influenced by solvent. We have, so far, no final explanation for the break of benzoyl fluoride slope in comparison with its regularity in the case of actanoyl fluoride, while measured relative rate factor showed that the octanal is three times more reactive than benzaldehyde.

Nevertheless, the present study illustrates again that the structure of organic molecules and solvent play a very important role in the course of the reactions of organic molecules with $CsSO_4F$, however more work is needed on selected types of transformations (fluorosubstitution, fluoroaddition, oxygenation...) in order to get further information on the reaction pathways, which will enable us to drawn more general conclusions concerning reaction mechanisms of $CsSO_4F$ reactions with organic compounds.

FIGURE: THE EFFECT OF SOLVENT AND HETEROATOM-CONTAINING ORGANIC MOLECULE STRUCTURE ON THE REACTIONS WITH CsSO₄F^{a)}



a) Standard reaction conditions: 1 mmol of substrate; 1.1 mmol of $CsSO_4F$; 2 ml of solvent; 1 hour at 20°C. b) Determined from ¹⁹F nmr spectra of isolated crude reaction mixtures, using octafluoronaphthalene as additional standard, and calculated on starting material. c) Reaction temperature 35°C d) 2.2 mmols of $CsSO_4F$ on 1 mmol of substrate.

EXPERIMENTAL SECTION

Ir spectra were recorded with a Perkin-Elmer 277 B spectrometer, ¹H and ¹⁹F NMR spectra with Varian EM-360L at 60 and 56.45 MHz, respectively. Chemical shifts are expressed in ppm from Me_4Si or CCl_3F as internal standards. Mass spectra and high resolution measurements were taken on VG Auto Spec Q spectrometer. TLS was carried out on Merck PCS-Fertigplatten Silicagel F-254. $CsSO_4F$ was prepared according to the literature⁷ and handled in compliance with applicable instructions⁶. Amounts of fluorinated products formed were determined from ¹⁹F nmr spectra of crude reaction mixtures using octafluoronaphthalene as additional standard and yields calculated on starting material.

Fluorination of triphenylmethane $(\underline{1a})$

To a solution of 244 mg (1 mmol) of triphenylmethane (<u>1a</u>) in 2 ml of freshly distilled and dry CH₃CN, degassed with dry oxygen-free N₂, 400 mg (1.6 mmol) of CsSO₄F was added, and the reaction suspension was stirred under N₂ at 35-40°C for 1 hour, and then diluted with 20 ml of CH₂Cl₂. The insoluble residue was filtered off, the filtrate washed with water (20 ml), dried (Na₂SO₄), and evaporated under reduced pressure. The crude reaction mixture was analysed with GLC, ¹H and ¹⁹F nmr spectroscopy, and the conversion of 68% of triphenylmethane to *flurotriphenylmethane*¹⁵ (<u>2</u>) was determined. The pure product <u>2</u> (145 mg (55,3%), m_p=102°-103°C, $\delta_{\rm F}$ =-125 ppm (s), $\delta_{\rm H}$ =7.2 ppm (s)) was isolated by preparative TLC (SiO₂, petrolether:CH₂Cl₂=1:1).

Fluorination of triphenylsilane $(\underline{1b})$ and triphenylchlorosilane $(\underline{1c})$

To a solution of 260 mg (1 mmol) of triphenylsilane in 2 ml of CH_3CN , 275 mg (1.1 mmol) of $CsSO_4F$ was added, and the reaction suspension was stirred at room temperature for 1 hour. After the usual work-up procedure, and analyses of crude reaction mixture an almost quantitative conversion of starting material to *fluorotriphenylsilane* was determined. Purification with column chromatography (SiO₂, n-pethane) gave 240 mg (86 %) of pure product 3 (m_p=61-62°C), identical to the authentic sample. 400 mg (1.6 mmol) of CsSO₄F were used and the reaction temperature was raised to 35°C, in order to obtain the optimal conversion of triphenylchlorosilane to *fluorotriphenylsilane*. 73% of crude product 2 was so formed and purified by preparative TLC (SiO₂, petrolether/CH₂Cl₂ 1:1).

Reaction with triphenylphosphine (1d)

In a suspension of 275 mg (1.1 mmol) $CsSO_4F$ in 2 ml of CH_3CN , 262 mg (1 mmol) of triphenylphosphine (<u>1d</u>) was introduced, and the reactione mixture was stirred at room temperature for 1 hour. After usual work-up procedure, the crude reaction product was crystallized from petrolether, and 240 mg (86 %) of *triphenylposphine oxide* (<u>4</u>), (mp= 156-157°C), identical to the authentic sample, was isolated.

Reaction with dibenzotiophene (5)

In a suspension of 300 mg (1.2 mmol) $CsSO_4F$ in 2 ml of CH_3CN , 184 mg (1 mmol) of dibenzotiophene (5) was introduced, and the reaction mixture was stirred at room temperature for 1 hour. After usual work-up procedure 200 mg of obtained crude reaction mixture was separated by preparative TLC (SiO₂, CHCl₃), and 20.8 mg (0.011 mmol) of starting material, 86.0 mg (0.43 mmol)

of dibenzotiophene-5-oxide¹⁶ (<u>6</u>) ($m_p=186$ °C, $\delta_H=7.0$ -7.9 ppm (m), MS: m/z 202(M⁺+2, 5%), 201(M⁺+1, 15), 200(M⁺, 100), 184 (30), 172 (60), 171(0), 168(15), 139(20); IR: $\nu=1020$ cm⁻¹), and 78.4 mg (0.36 mmol) of dibenzotiophene-5,5-dioxide (<u>7</u>) (mp=227-229 °C), identical to the authentic sample were isolated.

Fluorination of 4-tert-butylphenol and 2-fluoro-4-tert-butyphenol

To a solution of 300 mg (2 mmols) of 4-tert-butylphenol in CH₃CN (4 ml), 600 mg (2.4 mmols) of CsSO₄F were added, and reaction suspension stirred for 1 hour at room temperature. After usual work-up procedure the crude reaction mixture was separated by preparative TLC (SiO₂, petrol ether/CH₂Cl₂ 1:1) and 195 mg (58%) of oily 2-fluoro-4-tert-butylphenol¹⁷ (10): nmr(CDCl₃): $\delta_{\rm F}$ =-142(dd, J=14; 7.5Hz), $\delta_{\rm H}$ =1.3(s,9H), $\delta_{\rm H}$ =5.3(s,1H), $\delta_{\rm H}$ =6.8-7.4(m,3H); MS: m/z: 168(M⁺, 36%), 153(100), 125(50), 77(15), 57(34), 41(45); and 50 mg (13.5%) of 2,2-difluoro-4-tert-butylcohexadienone-4,6 (11): mp=55-56°C; nmr(CDCl₃): $\delta_{\rm F}$ =-103(d,J=6.5Hz), $\delta_{\rm H}$ =1.2(s,9H), $\delta_{\rm H}$ =6.2(m,2H), $\delta_{\rm H}$ =7.2(d,J=12Hz,1H); MS: calcd. for C₁₀H₁₂F₂0 m/z 186.0856, found m/z 186.0860; m/z: 187(M⁺+1, 11%), 186(M⁺,90), 171(75), 158(20), 144(15), 143(100), 127(23), 123(64), 98(60), 77(53), 61(62), 57(28); IR(KBr): $\nu_{\rm CO}$ =1695 cm⁻¹. In a crude reaction mixture a trace amount (not more than 2%) of 2,6-difluoro-4-tert-butylphenol ($\delta_{\rm F}$ =-137.3(d,J=9Hz)) were also noticed, but could not be isolated. 2-Fluoro-tert-butylphenol was also nearly quantitative transformed into 2,2-difluoro-4-tert-butylcyclohexadiene-4,6 (11) with 10% molar excess of CsSO₄F.

Fluorination of benzaldehyde and n-octanal

To a solution of 1 mmol of benzaldehyde, or n-octanal, in 2 ml of CH₃CN, 275 mg (1.1 mmol) of CsSO₄F was added, and the reaction suspension was stirred at room temperature for 1 hour. After the usual work-up procedure, in crude reaction mixtures, 86% of benzoyl fluoride (<u>12a</u>) and 98% of octanoyl fluoride (<u>12b</u>), respectively, were determined. 95 mg (77%) of pure benzoyl fluoride, identical to the authentic sample was isolated by column cromatography, while octanoyl fluoride¹⁸ was purified by preparative GLC (OV 101 10%, Chromosorb W/AW 100/120, T=120°C), and 76 mg (52%) of liquid product ($\delta_{\rm H}$ =0.9 ppm (m, 3H), $\delta_{\rm H}$ =1.2-1.8 ppm (m, 10H), $\delta_{\rm H}$ =2.5 ppm (t, J_{HH}=7Hz, 2Hz), $\delta_{\rm F}$ =44.5 ppm(s); MS: m/z 146(M⁺, 3%), 118(10), 117(10), 103(20), 98(33), 86(25), 85(17), 84(35), 83(20), 82(100), 75(27), 69(37), 57(32), 56(30), 55(63), 47(13), 43(13), 42(27), 41(72)) was isolated.

Fluorination of benzyl alcohol and octanol

To a solution of 1 mmol of benzyl alcohol, or n-octanol, in 2 ml of CH₃CN, 550 mg (2.2 mmol) of CsSO₄F was added during three two-minute intervals, and the reaction suspension was stirred at room temperature for 1 hour. After the usual work-up procedure, 95% of *benzoyl fluoride* (12a) and 95% of *octanoyl fluoride* (12b) respectively, were determined in the crude reaction mixtures.

Oxidation of 4-tert-butylcyclohexanol

To a solution of 156 mg (1 mmol) of 4-tert-butylcyclohexanol in 2 ml of CH_3CN , 300 mg (1.2 mmol) of $CsSO_4F$ was added, and the reaction suspension was stirred at room temperature for 1 hour. After usual work-up procedure 140 mg of crude 4-tert.-butylcyklohexanone (§) was obtained, and 80 mg (52%) of pure product (mp=46-48°C), identical to the authentic sample, was isolated by preparative GLC (OV 101 10%, Chromosorb, T=130°C).

Oxidation of 1,2-dihidroxy-4-tert-butylbenzene

In a suspension of 300 mg (1.2 mmol) $CsSO_4F$ in 2 ml of CH_3CN , 166 mg (1 mmol) of 1,2dihydroxy-4-tert-butylbenzene was introduced, and the reaction suspension was stirred at room temperature for 1 hour. After purification by preparative TLC (SiO₂, CHCl₃) of crude reaction mixture, obtained by usual work-up procedure, 100 mg (61%) of 4-tert-butyl-1,2-benzoquinone¹⁹ (2; m_p=68°-70°C; nmr(CDC₃): $\delta_{\rm H}$ =1.2 ppm (s, 9H), $\delta_{\rm H}$ =6.2 ppm (d, 1H), $\delta_{\rm H}$ =7.2 ppm (dd, J=10 Hz, 2 Hz, 1H), $\delta_{\rm H}$ =6.35 ppm (d, 1H); MS: m/z 164(M⁺, 25%), 121(26), 108(33), 93(100), 91(26), 77(33), 51(40), 41(36)) was isolated.

Fluorination of ethyl iodide

In a suspension of 300 mg (1.2 mmol) $CsSO_4F$ in 2 ml of CH_3CN , 0.5 ml of ethyl iodide was introduced, and the reaction suspension was stirred at room temperature for 1 hour. 90 mg (0.5 mmol) of 1,1-diphenylethen was then added, and the reaction suspension was stirred for an additional hour at room temperature, diluted with CH_2Cl_2 (15 ml), the insoluble residue was filtered off, filtrate washed with water solution of NaHSO₃ (10%, 10 ml), saturated solution of NaHCO₃ (10 ml), and water (10 ml), dried (NaSO₄), and evaporated under reduced pressure. In ¹⁹F nmr spectra of crude reaction mixture 79% of 1,1-diphenyl-1-fluoro-2-iodoethane, identical to independent synthesized product¹⁴, was determined.

The effect of solvent on the fluorination of heteroatom-containing organic molecules

To a solution of 1 mmol of heteroatom-containing organic molecule in a solvent mixture (2 ml), consisting of CH_3CN mixed with CH_2Cl_2 , and degassed with oxygen-free dry N_2 , 275 mg (1.1 mmol) of $CsSO_4F$ was added, and the reaction suspension was stirred under N_2 at 20°C for 1 hour (in a reaction of triphenylmethane the reaction temperature was 35°C, because of very low conversion of starting material at 20°C). After the usual work-up procedure, the yields of fluorinated products, calculated on starting material, were determinated from ¹⁹F nmr spectra of crude reaction mixtures, using octafluoronaphthalene as additional standard. The resulting yields (average of at least three runs) of fluorinated products, obtained after different substrate reactions, as a function of volume % of CH_3CN in solvent mixture are shown and compared in **FIGURE A-C**.

Determination of the relative rate factors

1 mmol of heteroatom-containing organic substrate and 1 mmol of its comparitive analogue were dissolved in 2 ml of freshly distilled and dry CH_3CN , the solution was degassed with oxygen-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 hour. The amounts of products formed were measured from ¹⁹F nmr spectra of crude reaction mixture, isolated by usual work-up procedure, using octafluoronaphthalene as the additional standard. Applying this known competitive technique,

relative reactivities expressed by relative rate factors (k_{rel}) were calculated from the equation²⁰:

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

derived from Ingold-Shaw relation²¹, where A and B are the amounts (in mmols) of starting material and X and Y the amounts of products derived from them.

The following rate factors were established: $k_{1b}/k_{1a} = \text{over 30}$; $k_{1c}/k_{1a} = 10.8$; $k_{\text{octanal}}/k_{\text{benzaldehyde}} = 2.9$

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