Caesium Fluoroxysulphate as a Mild Fluorinating Agent for the Fluorination of Alkoxy-substituted Benzene and Naphthalene Derivatives

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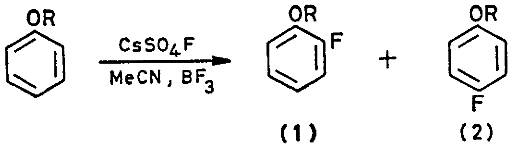
Summary Room-temperature fluorination of alkoxy-substituted benzene derivatives with caesium fluoroxysulphate in the presence of boron trifluoride as catalyst resulted in the formation of *ortho*- and *para*-fluoro-substituted products, the ratio being dependent on the size of the alkoxy-group, while reactions with 2-alkoxynaphthalene derivatives resulted in the formation of 1,1-difluoro-2-oxo-1,2-dihydronaphthalene as well as 1-fluoro-substituted products.

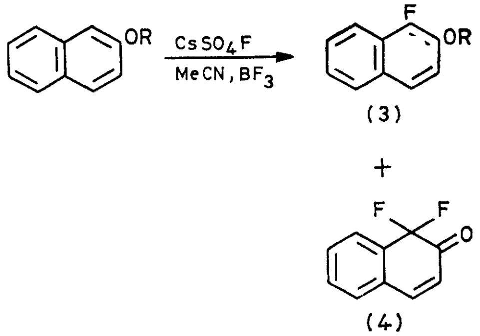
Introduction of fluorine into aromatic molecules is a different problem from the introduction of other halogen atoms.[1] CF_3OF[2] and xenon difluoride[3] are the only mild reagents so far discovered for the direct introduction of fluorine into organic molecules. The high price of xenon difluoride is its greatest disadvantage, while reactions with CF_3OF proceed successfully only with alkoxy-substituted aromatic molecules, with the experimental conditions demanding stringent safety precautions because of the high toxicity of the reagent gas and its extreme reactivity. The recent preparation and characterisation of caesium and rubidium fluoroxysulphates,[4] and their oxidative properties and stability at room temperature made them promising as mild fluorinating agents for organic substrates. However, reaction with toluene in aqueous solution resulted in a complex reaction mixture,[4] which appeared to diminish their potential utility.

We now report that caesium fluoroxysulphate is an easily handled, mild fluorinating agent for alkoxy-substituted benzene and naphthalene derivatives.† In a typical experiment, carried out in a polyethylene vessel, to a stirred suspension of $CsSO_4F$ (1 mmol) in acetonitrile (3 ml), a solution of the aromatic substrate (1 mmol) in acetonitrile (1 ml) was added, and finally a catalytic amount of BF_3 was introduced over the reaction mixture. The mixture was stirred at room temperature for 1.5—6 h, 10 ml of methylene dichloride was added, the unsoluble product filtered off, and the filtrate was washed with water and dried (Na_2SO_4). The solvent was evaporated off *in vacuo*, the mixture was analysed by ^{19}F n.m.r. spectroscopy and the products were isolated by gas chromatography. Reaction with phenol (Scheme) gave 70% of 2- and 4-fluorophenol and 30% of unchanged phenol. Conversion of starting material into products was improved by increasing the amount of caesium fluoroxysulphate from 1 mmol to 1·2 mmol. The yields of fluoro-products were higher, but small amounts of difluoro-phenols were also formed (up to 8%). We have also studied the effect of the alkoxy group on the course of fluorination and found that the amounts of the *para*-isomers are increased with larger substituents (Scheme). In no case did we find evidence for the formation of *meta*-products, and the yields of monofluoro-substituted products were between 70 and 80%.



R	Ratio (**1**) : (**2**)[a]
H	6·2 : 1
Me	2·8 : 1
Bu^n	1·8 : 1
EtCHMe	1·2 : 1

[a] Ratios determined by ^{19}F n.m.r. spectroscopy; total yields 70—80%.



R	Ratio (**3**) : (**4**)[a]
H	83 : 17
Me	74 : 26
Et	72 : 28
Pr^i	62 : 38

[a] Ratios determined by ^{19}F n.m.r. spectroscopy; total yields 60—80%.

Scheme.

Reaction with β-naphthol resulted in the formation of two products (**3**) and (**4**), (**3**) being the main product. The alkoxy group has an important affect on the amount of the ketone (**4**) which is formed (Scheme). The yields of products are also very high (60—80%).

(*Received,* 10*th November* 1980; *Com.* 1205.)

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† $CsSO_4F$ is stable when stored in a dry polyethylene flask at 0 °C, while on contact with a metallic spatula or under mechanical pressure decomposition or even explosion takes place.

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[4] E. H. Appelman, L. J. Basile, and R. C. Thompson, *J. Am. Chem. Soc.*, **1979**, **101**, 3384.