PRELIMINARY NOTE

## ROOM TEMPERATURE FLUORINATION OF AROMATIC MOLECULES WITH CESIUM FLUOROXYSULPHATE

STOJAN STAVBER and MARKO ZUPAN\*

Jozef Stefan Institute and Department of Chemistry, E. Kardelj University of Ljubljana, 61000 Ljubljana (Yugoslavia)

## SUMMARY

Room -temperature fluorination of benzene with cesium fluoroxysulphate in the presence of boron trifluoride as catalyst resulted in the formation of fluorobenzene, while reaction with naphthalene gave 1-fluoro and 2-fluoronaphthalene in the ratio 5:1, the overall yield being between 38 and 42 %. The fluorination of phenanthrene and pyrene should be carried out at higher dilution and needs no catalyst. Phenanthrene gave 9-fluorophenanthrene and 9,9-difluoro-10keto-9,10-dihydrophenanthrene in the ratio 1:6 in a yield of about 70%, while pyrene gave 1-fluoro and 4-fluoropyrene in the ratio 7.5:1.

Introduction of fluorine into aromatic molecules differs markedly from that of other halogens [1]. The availability of reagents convenient for direct, mild introduction of fluorine in to aromatic molecules is limited,  $XeF_2$  [2] and  $CF_3OF$  [3] being two of them. The high price of xenon difluoride is the greatest disadvantage of this reagent, and while reactions with  $CF_3OF$  proceed successfully with aromatic molecules, substituted with electron donating groups, the experimental conditions demand stringent safety precautions because of the high toxicity of the reagent gas and its extreme reactivity. The recent preparation and characterisation of cesium and rubidium fluoro-xysulphate [4], their oxidative properties and stability at room temperature made them promising mild reagents for the fluorination of organic substrates. However, reaction with toluene in aqueous solution resulted in a complex reaction mixture [4], which diminished their utility.

We now report that cesium fluoroxysulphate represents an easy handling mild fluorinating agent for aromatic molecules. In a typical experiment carried out in a polyethylene vessel, we made a suspension of  $CsSO_4F^{*}$  (1 mmol) in acetonitrile (1 ml), a solution of benzene (1 mmol) in acetonitrile (0.5 ml) was added under stirring and finally a catalytic amount of BF<sub>3</sub> was introduced over the reaction



mixture. After 4.5 hours stirring at room temperature, another addition of  $CsSO_4F$  was made (1 mmol) and the stirring continued for another hour. The isoluble product was filtered off and the reaction mixture was analysed by <sup>19</sup>F nmr and vpc. It was found that 30 - 35 % of fluorobenzene was formed. Under similar conditions (30 % excess of  $CsSO_4F$  was used) fluorination of naphthalene gave a mixture of 1- and 2-fluoronaphthalene in the ratio 5 : 1, the overall yield being between 38 - 42 %.

The fluorination of phenanthrene, gave two products as well as greater amounts of polymeric material. The yield of the two products, 9-fluorophenanthrene and 9,9-di-fluoro-10-keto-9,10-dihydrophenanthrene which were formed in the ratio 1:6, was improved by using a greater amount of solvent, i.e. 20 ml of acetonitrile for 1 mmol of phenanthrene, while 2 mmols of  $CsSO_4F$  were added stepwise, i.e. 0.5 mmol per hour. Under such conditions, the overall yield was improved up to 70%. The fluorination of

<sup>\*</sup>CsSO<sub>4</sub>F is a stable compound when stored in a dry polyethylene flask at  $0^{\circ}$ C, while on contact with a metallic spatula or under mechanical pressures decomposition or even explosion takes place.



pyrene needed even an higher dilution to be successful, i.e. 1 mmol of pyrene in 40 ml of acetonitrile, while 1.3 mmol of cesium fluoroxysulphate was added in six parts during 2-hours stirring. After the work-up mentioned above, the formation of two products was established, i.e. 1-fluoropyrene and 4-fluoropyrene in the ratio 7.5 : 1, in overall yield of 40 - 45 %. The reaction needed no catalyst, while reaction under the conditions mentioned for benzene resulted only in the formation of polymeric material. Reaction with anthracene gave, after separation, only anthraquinone, while the mass spectrum of the crude reaction mixture showed the presence of 9.9-difluoro-10-keto-9,10-dihydroanthracene and monofluoroanthracene.

All products were isolated by preparative vpc or tlc, and their structures assigned on the basis of ir, ms,  $^{19}$ F and  $^{1}$ H nmr spectra, which were in agreement with the



literature ones. The search for experimental conditions, leading to higher yields of products and fluorination of other aromatic molecules is now in progress.

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