



Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:

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Potassium Fluoride on Alumina—A New Reagent for Selective-O-Demethylation of Arylalkyl Ethers

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Published online: 24 Sep 2006.

To cite this article: A. S. Radhakrishna, K. R. K. Prasad Rao, S. K. Suri, K. Sivaprakash & B. B. Singh (1991) Potassium Fluoride on Alumina—A New Reagent for Selective-O-Demethylation of Arylalkyl Ethers, *Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry*, 21:3, 379-383, DOI: [10.1080/00397919108016759](https://doi.org/10.1080/00397919108016759)

To link to this article: <http://dx.doi.org/10.1080/00397919108016759>

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**POTASSIUM FLUORIDE ON ALUMINA - A NEW REAGENT FOR
SELECTIVE-O-DEMETHYLATION OF ARYLALKYL ETHERS**

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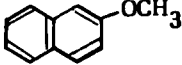
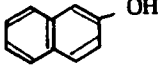
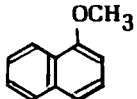
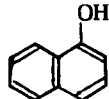
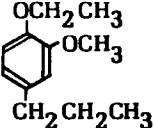
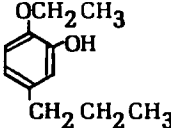
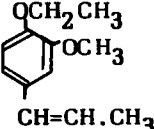

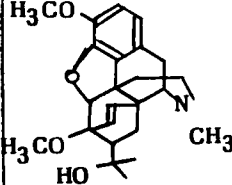
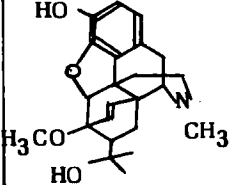
Abstract : Arylalkyl ethers undergo selective O-Demethylation on treatment with potassium fluoride coated on alumina.

Aromatic O-demethylation is a synthetically very useful reaction. There are a number of methods used for dealkylating arylalkyl ethers,¹ which include acidic,² basic,³ hard acid-weak base salts,⁴ lithium iodide under neutral conditions,⁵ etc. Potassium fluoride has been extensively used as a base in organic synthesis.⁶ Recently potassium fluoride coated on various inorganic supports has been shown to bring about the hydrogen bond assisted reactions with greater facility than the unsupported reagent.⁷ We have recently reported the use of KF-alumina as a reagent for isomerization of olefins.⁸

This paper describes the demethylation of aromatic methyl ethers using potassium fluoride coated on alumina.

Potassium fluoride-alumina reagent is simply prepared by mixing the support with an aqueous solution of potassium fluoride and then removing water.⁸ This reagent smoothly demethylated α -Naphthylmethyl ether to α -Naphthol at 210-215°C in 3 h. Under the same conditions use of potassium fluoride or alumina alone as the reagent did not give any phenol.

TABLE

| Sl. No. | Substrate | Conditions | Product | Yield |
|---------|---|--------------|---|-------|
| 1 |  | 5h/210-215°C |  | 80% * |
| 2 |  | 3h/210-215°C |  | 85% |
| 3 |  | 5h/210-215°C |  | 60% |
| 4 |  | 5h/210-215°C |  | 60% |
| 5 |  | 3h/210-215°C |  | 50% |

* Yield based on recovered unreacted ether which has a tendency to sublime to the condenser during the reaction.

To test the generality of the reaction a representative set of aromatic methyl ethers were demethylated (Table). In the examples 3 to 5 cited in the table, no product arising out of N-demethylation or O-deethylation could be detected.

Experimental

Potassium fluoride coated on neutral alumina was the catalyst used in all the reactions; 20 g of $\text{KF}/\text{Al}_2\text{O}_3$ reagent was used per gram of the substrate. Products were characterised by comparison with authentic samples (IR, ^1H -NMR, Glc/TLC). All yields refer to isolated yields based on single experiment and are not optimised.

KF-Alumina Reagent

To a stirred solution of KF (20 g) in 150 ml of water (pH=6.2) is added neutral alumina (60-80 mesh 30 g) in 150 ml of water (pH=7.6) and stirred for $\frac{1}{2}$ h. pH of the mixture at the end of this time is 11.5. Water is then evaporated under reduced pressure in a rotary evaporator keeping the temperature around 60°C. When most of the water has been removed it is heated to 140-150°C and maintained at that temperature under vacuum (5 mm) for 6 h. Yield 50 g.

Demethylation - A Typical Procedure

To a stirred suspension of the $\text{KF}-\text{Al}_2\text{O}_3$ reagent (20 g) dry ethylene glycol (35 ml) is added. The mixture is stirred and heated while distilling the low boilers until an internal temperature of 220°C is attained; cooled to 150°C and

ethylisoeugenol (1 g) added in one lot. The mixture is stirred and heated at 210-215°C for 5 h. The reaction mixture is cooled, diluted with 100 ml of 0.5% sodiumhydroxide solution. Toluene (30 ml) is added and stirred for 15 min. It is filtered and solid washed with 25 ml water and 25 ml Toluene. From the filtrate the organic and aqueous layers are separated. Organic layer contains small amounts of unreacted starting material. Aqueous layer is acidified with 10% HCl and extracted with 3x25 ml of dichloroethane. The combined organic extracts washed with 50 ml water. Dichloroethane layer briefly dried over Na_2SO_4 and then solvent distilled off under reduced pressure to get the phenol.

Demethylation (Example 5)

Reaction is carried out in the same manner as described above. After heating the reaction mixture at 210-215°C for 3 h, it is cooled, diluted with 200 ml water and filtered to remove alumina. The clear filtrate is treated with excess ammonium chloride until precipitation ceases, then extracted with 3x30 ml of chloroform. The combined organic layer washed with 50 ml water and briefly dried over anhydrous sodium sulfate. Solvent distilled off under reduced pressure to get the product.

Acknowledgement

We acknowledge the support received from our analytical laboratory for this work.

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(Received in UK 4 December, 1990)