Potassium Fluoride on Alumina
(KF/Al₂O₃)

Compiled by Mannmohan Chhibber

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Introduction

Potassium fluoride on alumina (KF/Al₂O₃) is a versatile base developed by Ando et al. for alkylation reactions.¹ Over the years the reagent has found applications in a large number of organic reactions such as elimination,² addition,³ condensation,⁴ epoxidation,⁵ palladium-catalyzed coupling⁶ and the synthesis of heterocyclic compounds.⁷ The KF/Al₂O₃ system has been able to replace organic bases in many reactions, but still its enhanced source of basicity as compared to non-supported KF remains a matter of debate in literature.⁸ Recently, Blass has reviewed⁹ KF/Al₂O₃ mediated organic synthesis.

The solid supported reagent has the advantage of being used in solid and solution phase reactions thus facilitating ease of separation from reaction mixture by filtration. In addition, it can be conveniently used for microwave and ultrasound mediated chemical transformations.

Preparation of KF/Al₂O₃

KF/Al₂O₃ is commercially available as a 40 wt.% on alumina. It can also be prepared² by mixing alumina to a KF solution in water and then drying under vacuum at 50–60 °C so as to impregnate the alumina. The traces of moisture are finally removed by drying at 75 °C for several hours under high vacuum.

Abstracts

(A) Sawyer et al. have demonstrated the use of KF/Al₂O₃ and 18-Crown-6 to synthesize diaryl ethers, diarylthio ethers, and diaryl amines via SₐAr type addition reaction of phenol, thiophenol, and aniline to 2-fluorobenzonitrile respectively. The optimization of the above reaction conditions led to the synthesis of compounds, which were unachievable using Ullman coupling. For example, electronically unfavorable 3-chloro benzonitrile can be condensed with 3-methylphenol to give corresponding diaryl ether in 66% yields using KF/Al₂O₃, 18-Crown-6 in DMSO at 140 °C.¹⁰

(B) Glaser coupling reactions to generate diacetylenes using KF/Al₂O₃ with CuCl₂ and solvent free conditions under microwave irradiation have been optimized by Kabalka et al. The use of two different alkynes, however gives a mixture of products.¹¹
(C) Silveira et al. have reported the use of KF/Al₂O₃ for the synthesis of 3,4-dihydroisoquinolines and isoquinolines by desulfonylation of N-sulfonyl-tert-hydroxyisoquinone derivatives. Microwave irradiation (490 W) of the solid-state reaction mixture containing the substrate and base for 10–20 s gives 3,4-dihydroisoquinoline, which on increasing the time leads to the formation of corresponding isoquinoline.¹²

(D) KF/Al₂O₃ selectively desilylates the tert-butyldimethylsilyl protected phenol at room temperature. Acetonitrile as the solvent eliminates the need for an aqueous work up and the use of ultrasound accelerates the reaction thereby reducing reaction times.¹³

(E) Selective O-demethylation of arylalkyl ethers has also been accomplished using KF/Al₂O₃ and dry ethylene glycol in 3–5 h at 210–215 °C in moderate to high yields.¹⁴

References