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Potassium Fluoride Supported on Alumina Induced Aldol Condensation of Fluorene

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Potassium Fluoride Supported on Alumina Induced Aldol Condensation of Fluorene

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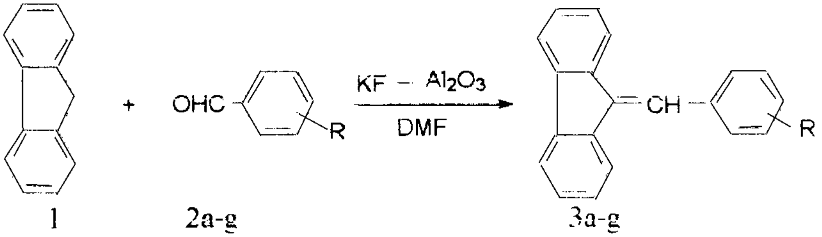
Abstract: In the presence of potassium fluoride supported on alumina as a solid base, Fluorene condensated smoothly with aromatic aldehydes in DMF at 150 ℃ to give dibenzofulvenes in fair yield (44-90%).

The utility of fluoride salts as bases in a variety of synthetic reactions has been recognized in recent years.[1-2] The potassium fluoride supported on alumina has stronger basicity and is considerably more reactive than non supported potassium fluoride. It has been demonstrated that KF-Al_2O_3 is a versatile solid base for various organic reactions, such as aldol condensation,[3-5] Darzens reaction,[3,5] Michael addition reaction,[3,6-8] β -elimination reaction,[3] alkylation on carbon, nitrogen, oxygen and sulfur[9-12] centers, etc. We have successfully used KF-Al_2O_3 as a solid base catalyst to catalyze the aldol condensation of indene and acetophenone with aromatic aldehydes.[13] Our ongoing research program aimed at extending the applications of KF-Al_2O_3 as a solid base in organic synthesis. Here we wish to report the application of

$KF-Al_2O_3$ in the aldol condensation of fluorene with aromatic aldehydes.



R = p-F, p-Cl, p-H, p-CH_3, p-OCH_3, p-$N(CH_3)_2$, m-Cl

The aldol condensation of fluorene with carbonyl compounds have been known to take place under the base catalysts such as sodium alcoholate[14] or sodium hydroxide in the presence of a phase transfer catalyst[15,16]. Now by adding one equivalent of $KF-Al_2O_3$ powder to the reaction mixture, which was suspended in the solution, we carried out the condensation of fluorene with a set of aromatic aldehydes in dimethylformamide at the temperature of 150 C. The experimental results listed in table 1 showed that nearly all fair yields of condensation products dibenzofulvenes were obtained (44-90%). This demonstrated that potassium fluoride supported on alumina is an effective solid base for the aldol condensation of fluorene.

In order to get the best reaction conditions, we have thoroughly studied various reaction parameters by choosing the reaction of fluorene with p-chlorobenzaldehyde as a comparing standard If $KF-Al_2O_3$ was not added to the reaction mixture, the condensation did not take place, nearly the total of unreacted fluorene can be recovered. On the other hand, the molar ratio of $KF-Al_2O_3$ to reactive materials strongly affected the yields of products. The best molar ratio is one equivalent of $KF-Al_2O_3$ to one equivalent of fluorene and aldehyde ($KF-Al_2O_3$/fluorene aldehyde =1:1:1), which gave the highest yield of dibenzofulvene (3b) (90%). Deficient

Table 1 The Data of the Substituted Fulvenes

Entry	R	Yield	m.p	m.p in	Formula	C		H		IR
		(%)	(℃)	lit[14](℃)		calcd	found	calcd	found	(cm^{-1})
3a	p-F	65	118-119	(120)	$C_{20}H_{13}F$	88.56	88.21	4.73	4.81	1597
3b	p-Cl	90	147-148	(149.5)	$C_{20}H_{13}Cl$	82.96	83.19	4.33	4.54	1640
3c	p-H	44	74-75	(74-74)	$C_{20}H_{14}$	94.27	94.45	5.77	5.55	1595
3d	p-CH_3	73	96-97	(97.5)	$C_{21}H_{16}$	93.84	93.99	6.12	6.01	1631
3e	p-CH_3O	85	129-130	(130-131)	$C_{21}H_{16}O$	88.87	88.70	5.69	5.67	1635
3f	p-$N(CH_3)_2$	67	135-136	(135-135.5)	$C_{22}H_{19}N$	88.44	88.85	6.55	6.44	1598
3g	m-Cl	78	89-90	(90.5)	$C_{20}H_{13}Cl$	83.23	83.19	4.41	4.54	1593

(0.6:1:1) and excess (1.25:1:1) of amount of KF-Al_2O_3 both led to the decrease of yields (43% and 63% respectively).

If the reaction was carried out in an aprotic polar solvent e. g. DMF, the temperature was also affected the reaction yield . When the reaction was carried out at 100, 140, 150 ℃ for the same time (10h), the yields of dibenzofulvene (3b) were 56%, 63% and 90% respectively. If the reaction was carried out in ethanol or acetonitrile at their refluxing temperature for the same time (10h) as in the DMF, the yield decreased to 62% or 56%. this results indicated that the propertis of the solvent have some effects. Here it must be mentioned that all the solvents ought to be dried thoroughly, for the moisture greatly diminishes the activity of KF-Al_2O_3 .

We also carried out the condensation reaction of fluorene with p-chlorobenzaldehydes in the presence of potassium carbonate supported on alumina K_2CO_3-Al_2O_3 as a solid base in DMF at 150

C for 10h. as in the reaction using KF-Al_2O_3 as solid base, which gave 76% yield of dibenzofulvene (3b). This means that the activity of KF-Al_2O_3 can be comparing with the activity of the widely used base K_2CO_3.

Thus, in conclusion, it can be said that potassium fluoride supported on alumina is an effective reagent for the aldol condensation of fluorene and our experimental route provides easy and efficient ways to prepare dibenzofulvenes. It is believed that[17,18] KF-Al_2O_3 owes its efficient and versatile reactivity as a heterogeneous base for organic synthesis to at least three possibly mechanisms: dispersion and increased surface area of KF giving co-ordinately unsaturated F^-; liberation of strong base during preparation; and co-operative action of F^- and the hydrated alumina surface.

Experiment Section

Fluorene and aromatic aldehydes are commercial reagents for organic synthesis. DMF, EtOH and CH_3CN are dried by standard methods. The solid base catalyst KF-Al_2O_3 (12.5 mmol KF on 2g alumina) and K_2CO_3-Al_2O_3 (6 mmol K_2CO_3 on 2g alumina) are prepared by reported methods[3,19]. Melting points were determined by using the capillary tube method and are uncorrected. The microanalysis were obtained by using a Carlo Erba model 1106 Elemental Analyzer. IR were recorded as KBr disc on a Nicolet 170 SX IR Spectrometer.

General Procedure:

To a solution of fluorene (0.83g, 5 mmol) and KF-Al_2O_3 (0.80g, 5 mmol) in DMF (8 mL) is added the aromatic aldehyde (5 mmol) . The mixture is stirred at 150 °C for 10 hours. Then the solid catalyst is filtered from the reaction mixture. The organic solution was cooled and poured into water (50mL). A yellow solid product precipitated, which was filtered, washed with water and dried in air. and finally recrystallized from ethanol. The product was ready for analysis.

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