



Synthesis of Herbicides through N-Arylation by using $\text{KF}/\text{Al}_2\text{O}_3$ under solventless and transition metal free condition

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ABSTRACT

The present work describes the synthesis of herbicides through N-arylation by using $\text{KF}/\text{Al}_2\text{O}_3$ under solvent less and transition metal free condition at room temperature.

Keywords: Herbicides, N-arylation, $\text{KF}/\text{Al}_2\text{O}_3$, Supported reagent, Solvent free.

INTRODUCTION

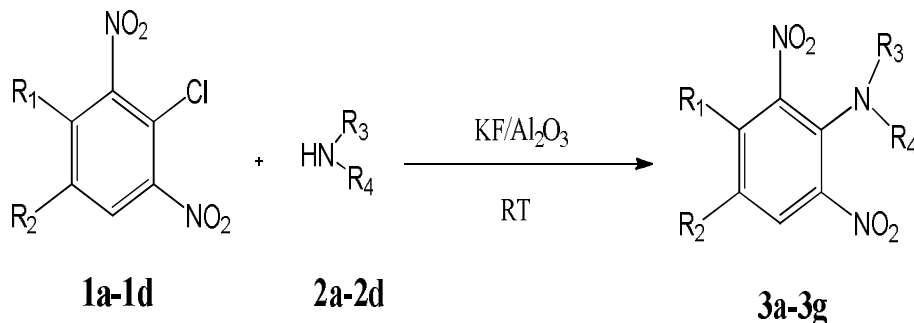
Herbicides are generally known as weed killers. These are the pesticides which are commonly used to kill unnecessary plants. Discriminating herbicides kill particular targets, while the desired crops remain unharmed. They are generally prepared by the following methods; (a) refluxing for hours (b) using solvents[1]. The disadvantage of these methods include drastic conditions, tedious work up, time consuming and use of solvents. Therefore we are interested in simple and eco friendly method for these herbicides. One such approach is use of supported reagents like $\text{KF}/\text{Al}_2\text{O}_3$. $\text{KF}/\text{Al}_2\text{O}_3$ replaces many bases in abundant of reactions[2,3]. It possesses a number of advantages such as selectivity, eco-friendly nature, escaping of cumbersome workup and products can be easily isolated by filtration. In view of these facts we have developed a simple method for the synthesis of herbicides through N-arylation by using $\text{KF}/\text{Al}_2\text{O}_3$ under solventless and transition metal free condition at room temperature. We have previously reported⁴ N-arylation using $\text{KF}/\text{Al}_2\text{O}_3$ and have now applied it for the synthesis of herbicides.

MATERIALS AND METHODS

The melting points were determined using capillary tube and are uncorrected. The FTIR spectra were recorded on Spectrum One Perkin Elmer (US). The ¹H NMR spectra were recorded on a Bruker AVANCE (300 MHz) spectrometer (with TMS as internal reference). ¹³C NMR spectra were recorded on Bruker AVANCE (75MHz) spectrometer. Mass spectra were recorded on API-3000 MD-series (US). Elemental analyses were carried out in EA 3000, Euro Vector, Italy. The purity of the compounds was checked by TLC on pre-coated SiO_2 gel (200mesh).

The starting compounds **1a**[5], **1b**[2], **1c**[6] and **1d**[7] have been synthesized as per literature procedure.

Synthetic Procedure: To a mixture of dry KF (0.3g) and basic Al_2O_3 (0.5g) as solid support add secondary amines (0.005M) and stir it well. Now add activated aryl halide (0.005M) at room temperature for 5 min with continuous stirring. After completion of reaction (Thin layer chromatography) the solid was extracted with chloroform and filtered. The chloroform extract was distilled and residue purified by crystallization/column chromatography.



Scheme 1

N-butyl-N-ethyl-2,6-dinitro-4-(trifluoromethyl)aniline (3a) : m.p.: 65 °C (Lit.[8] 65–66.5 °C). Yield 86%. The spectral data (UV, Mass) was also consistent with the reported data[9,10].

4-methyl-2,6-dinitro-N,N-dipropylaniline (3b) : m.p.: 42 °C (Lit[11]. 40-42 °C). Yield 78%. The spectral data (Mass) was also consistent with the reported data[11].

N-ethyl-N-(2-methylallyl)-2,6-dinitro-4-(trifluoromethyl)aniline (3c) : m.p.: 56 °C (Lit.[12] 54–57 °C). Yield 75%. The spectral data (Mass) was also consistent with the reported data[10].

N-(2-chloroethyl)-2,6-dinitro-n-propyl-4-(trifluoromethyl)aniline (3d) : m.p.: 42 °C (Lit.[12] 42–43 °C). Yield 74%. The spectral data (Mass) was also consistent with the reported data[10].

2,6-dinitro-N¹,N¹-dipropyl-4-(trifluoromethyl)benzene-1,3-diamine (3e) : m.p.: 124 °C (Lit.[1] 124–125 °C). Yield 70%. The spectral data (Mass, ¹H-NMR) was also consistent with the reported data[1].

2,6-dinitro-N,N-dipropyl-4-(trifluoromethyl)aniline (3f) : m.p.: 48 °C (Lit.[13] 47–48 °C). Yield 85%. The spectral data (¹H-NMR, ¹³C-NMR, Mass, UV) was also consistent with the reported data[5,14,15].

4-(dipropylamino)-3,5-dinitrobenzenesulfonamide (3g) : m.p.: 139 °C (Lit.[16] 138–140 °C). Yield 78%. The spectral data (¹H-NMR, ¹³C-NMR, Mass) was also consistent with the reported data[16].

Table 1. Synthesis of herbicides (3a-3g)

Compounds	R ₁	R ₂	R ₃	R ₄
1a, 2a, 3a	H	-CF ₃	-CH ₂ CH ₃	(-CH ₂) ₃ CH ₃
1b, 2b, 3b	H	-CH ₃	(-CH ₂) ₂ CH ₃	(-CH ₂) ₂ CH ₃
1a, 2c, 3c	H	-CF ₃	-CH ₂ CH ₃	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{C}=\text{CH}_2 \end{array}$

1a, 2d, 3d	H	-CF ₃	(-CH ₂) ₂ CH ₃	(-CH ₂) ₂ Cl
1c, 2b, 3e	-NH ₂	-CF ₃	(-CH ₂) ₂ CH ₃	(-CH ₂) ₂ CH ₃
1a, 2b, 3f	H	-CF ₃	(-CH ₂) ₂ CH ₃	(-CH ₂) ₂ CH ₃
1d, 2b, 3g	H	-SO ₂ NH ₂	(-CH ₂) ₂ CH ₃	(-CH ₂) ₂ CH ₃

RESULTS AND DISCUSSION

Compounds (**2a-2d**) smoothly underwent N-arylation with activated halides (**1a-1d**) in presence of KF/Al₂O₃ at room temperature to afford the corresponding N-arylated compounds (**3a-3g**) that are used as herbicides.

APPLICATIONS

This work is useful for the synthesis of herbicides through N-arylation by using KF/Al₂O₃ under solventless and transition metal free condition at room temperature.

CONCLUSIONS

We have successfully synthesized herbicides through N-arylation by using KF/Al₂O₃ under solventless and transition metal free condition at room temperature for 5 min.

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