

Plant Juice Catalysed Synthesis of Substituted Pyrrole through Paal Knorr Reaction

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ABSTRACT

The current research work proposed the novel methodology for the synthesis of N-substituted pyrrole catalysed by juice of Kalanchoe Pinnata plant leaves. The reaction was carried out between hexane 2,5 dione and aniline. This protocol is environmentally benign cost effective and fruitful which has produced the desired product in short reaction time and easy work up. The synthesised compounds has been confirmed by ¹HNMR , IR and C¹³ spectroscopy. The natural abundance, cost effective, non toxic and good to excellent yields are some specific features of this catalyst.

Keywords : Hexane-2, 5-dione , Aniline, Pyrrole, Kalanchoe Pinnata Juice

I. INTRODUCTION

The journey of green synthetic protocol inspired us to introduce the green methodology for the synthesis of Pyrrole using Paal Knorr reaction.[1-5]. The nitrogen heterocyclic compounds like Pyrrole, Pyrazole, Quinoline, Isoquinoline , Triazole plays an important role in human and plant life. The nitrogen heterocyclic compounds are fruitful in context to pharmaceutical, agriculture and industrial perspective. Pyrrole being most versatile heterocyclic compound exclusively found in chlorophyll, vitamin B12 or bile pigments and haemoglobin [6-9]. Due to simple structure and easy synthetic strategy numerous protocols has been introduced including Hantzsch Reaction, Knorr reaction and Paal Knorr reaction[10-13]. Apart from these protocols the green synthetic protocols for synthesis of pyrrole attracted the much attention of

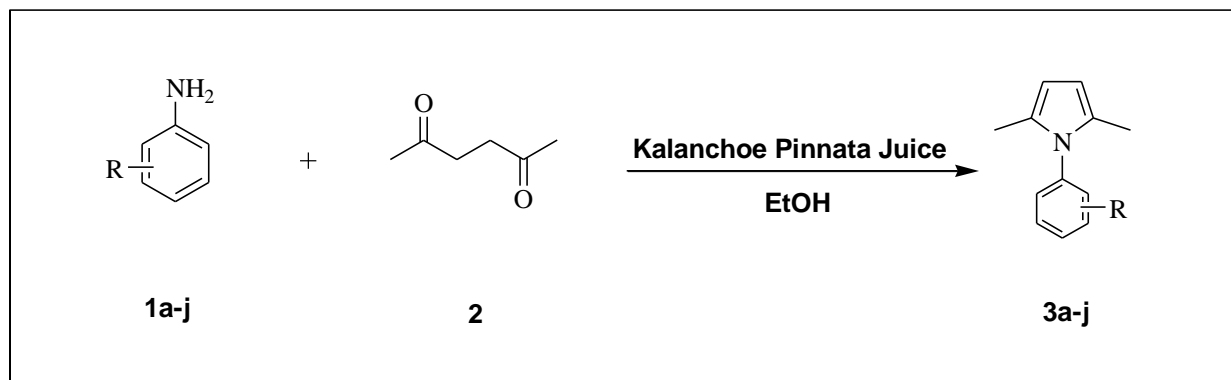
researchers.[14-15] The Paal Knorr reaction is most fruitful synthetic method for synthesis of pyrrole which gives excellent results. By adopting this protocol we have synthesized the Pyrrole by reaction of hexane-2,5-dione with substituted anilines in presence of juice of Kalanchoe Pinnata leaves. The Kalanchoe Pinnata plant belongs to family Kalanchoe which is commonly found in most part of world. The plant is rich in organic acids, flavonoids and terpenoids. The leaves of plant are rich with the organic acids like cinnamic acid, oxalic acid and ascorbic acid. [16-18]

II. METHODS AND MATERIAL

All the chemicals of analytical grade were used for the synthesis of desired product. In this synthesis the aniline (1a-j) and hexane-2,5-dione (2) were treated in presence of Kalanchoe Pinnata juice for the for 1-5 hrs

at 90° C to produce N-substituted Pyrrole (3a-j) Scheme 1 The completion of reaction was observed by TLC method. The mixture was allowed to cool and the diluted with water and DCM. The work up was

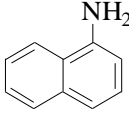
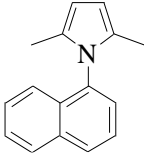
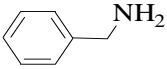
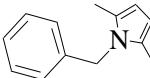
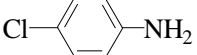
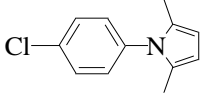
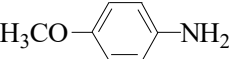
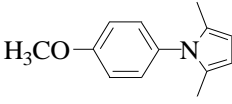
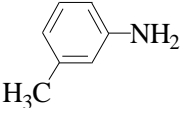
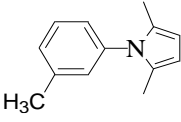
performed by washing with brine and the product was recrystallise with alcohol to get pure product. It is observe that 2 ml of Juice produce excellent result in context to time, yields and work up factors.



Paal-Knorr Synthesis of Pyrrole catalysed by Kalanchoe Pinnata Juice

Table 1 : Synthesis of Substituted Pyrrole By Kalanchoe Pinnata Juice

Entry	Anilines 1a-j	N-Substituted Pyrrole 3a-j	Reaction Time (hr)	Yield(%)
a			04	63
b			03	74
c			02	82
d			4.5	51
e			03	66

f			02	84
g			1.5	93
h			1.3	91
i			01	93
j			1.5	83

III. RESULTS AND DISCUSSION

In our continuous search of green synthetic protocol, we have introduced the plant juice catalysed synthesis of substituted pyrrole and we have obtained good to excellent results as shown in table 1. *Kalanchoe Pinnata* being rich in ascorbic acids, cinnamic acid and oxalic acid acts as green catalyst. The efficiency of this catalyst is monitored by taking 2 ml of juice and results obtained are discussed.

Initially when we performed the reaction of Hexane-2,5-dione with aniline with electron withdrawing group it take more time to give the product (table 1, entry d) But as we change the substrate with simple aniline and aniline with electron donating group it is

revealed that reaction completed in less time and the yield is also enhanced. (table 1, Entry i)

IV. CONCLUSION

This green synthetic protocols is found to be cost effective, environmentally benign and because of natural availability of *Pinnata Kalanchoe* plant. The non toxic, rich in acid and solubility in most solvents are some specific features of this catalyst. The good to excellent yields of the desired product satisfy us to use this protocol for other heterocyclic synthesis through this protocol.

Typical procedure for synthesis of Pyrrole

Anilines 1a-j (0.1 mole) and hexane-2,5-dione (0.1mole) were dissolved in ethanol in 50 ml round bottom flask . To this mixture 2 ml of *Kalanchoe*

Pinnata juice was added and stirred for 01 hr to 05 hrs. After completion of reaction as indicated by TLC, then the mixture was allowed to cool and the diluted with water and DCM. The work up was performed by washing with brine and the product was recrystallise and air dried. In order to get the purity, the product was recrystallised from ethanol-water mixture.

Spectral Data

2,5-Dimethyl-1H-pyrrolyl-1-benzoic acid (3a)

¹HNMR (CDCl₃, 400 MHz): δ 2.07 (s, 6H), 5.86 (s, 2H), 7.38 (d, J= 8.31 Hz, 2H), 8.34 (d, J=8.31 Hz, 2H), 11.1(bs, 1H) LC-MS: m/z: 216 (M+ 1)⁺, ¹³CNMR (CDCl₃, 100 MHz) 170.13, 145.55, 131.77, 129.70, 127.31, 126.21, 107.38, 14.31

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