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ONE POT SYNTHESIS OF 2-AMINO PYRANES USING AMMONIUM CARBONATE AS AN EFFICIENT CATALYST

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ABSTRACT
One pot synthesis of 4-amino pyraneshave been achieved using ammoinium carbonate in aqueous ethanol system. The describe method is useful for the synthesis of pyranes using aromatic aldehydes, malononitrile and dimedone as three component reaction using conventional heating as well as microwave. The method provides simple and easy way for the synthesis of 2-amino pyraneswith good yield.

Keywords: 2-amino pyrane, aldehyde, malononitrile, dimedone, catalysed, ammonium carbonate, conventional, microwave.

INTRODUCTION
Heterocyclic compounds are the very important class of organic compounds. Many naturally occurring compounds contain the heterocyclic rings as core part in them like haemoglobin and chlorophyll. Pyranes are one of the important heterocyclic compounds. These are reported to exhibit many biological properties like anti-oxidant[1], antimicrobial[2], antifungal [3], anti-cancer[4]. These are also reported to have pigment property and agrochemical applications[5].

Multicomponent reactions are the key strategies for the current organic synthesis. After Strecker's synthesis of amino acids[6] the multicomponent reactions were explored. If we look at last few decades then it realises that the number of publications of multicomponent reactions are continuously increasing. The significant benefits of the MCR are short time for the reactions and less steps for the synthesis that leads to good yield of products. These out comings meet to the requirement of green chemistry principles which are demand of future chemistry also i.e. sustainable chemistry.

Most of one pot synthesis 2-aminopyranes utilised three components aldehyde, malononitrile and active methylene group containing compounds like dimedone. Variety of methods and catalysts are reported for its synthesis. Bases such as potassium carbonate[7], caesium carbonate[8], sodium ethoxide[9], sodium bicarbonate[10], meglumine[11], N-methyl morpholine[12], pipyridine[13], triethyl amine[14], potassium tertiary butoxide[15], basic alumina[16] are reported for the 2-amino pyranes. γ-Alumina[17], silica supported sulphuric acid[18] like materials are reported as heterogeneous catalysts. Nano particles like $ZnAl_2O_4$–Bi_2O_3 composite[19], palladium (0)[20], Preysslerheteropoly acid on $Ni_{0.5}Zn_{0.5}Fe_2O_4$ magnetite nanoparticles[21], Nano-titania-supported Preyssler-type heteropolyacid[22], Nano Silica-Bonded 5-N-Propyl-Octahydro-Pyrimido[1,2-A]Azepinium Chloride [23], gold

nanoparticles supported on thiol - functionalized reduced graphene oxide[24], Fe_3O_4 magnetic nanoparticles coated with a copolymer[25], (Fe_2O_3)-MCM-41-supporteddual acidic ionic liquid [26], 4-(40-Diamino-di-phenyl)-sulfone supported onhollow magnetic mesoporous Fe3O4@SiO_2[27], Nano-SiO_2[28] are also reported. Ionic liquids like ionic hydroxides[29], piperidinium acetate[30], amino acid ionic liquids [31], 2-Hydroxyethyl-1-ammonium 3-hydroxypropane-1-sulfonate [32], tetrabutylammonium Chloride[33], salts like $Mg(ClO_4)_2$[34], $Ba(OTf)_2$[35] are also reported. Organic catalysts such as b-Cyclodextrin[36], binaphthyl-modified organocatalyst[37], DBDMH[38], Fructose [39], L-Proline[40- 42], Vitamin B_1[43], urea[44], Vitamin B_{12}[45], are reported for the efficient synthesis of 2-amino pyranes.

Some reported methods are having drawbacks like cost of catalysts or the high conditions for reactions or the difficulty of reaction workups. We earlier reported the simple, expeditious and green process for the Knoevenagel condensation of aldehydes with malononitriles using ammonium carbonate. Ammonium carbonate provided the creation of anions over active methylene groups which arekey for the condensation. Hence we extended the ammonium carbonate use for 2-aminopyrane synthesis.

RESULT AND DISCUSSIONS
Being a salt ammonium carbonate has less solubility in organic solvents but more in water. Our earlier experimentation proved the reactivity of ammonium carbonate in aqueous ethanol medium for organic reaction. Hence we selected the same medium for 2-aminopyrane synthesis. To optimise the reaction condition we selected benzaldehyde as prototype. The 10 mol% ammonium carbonate was added to stirring mixture of

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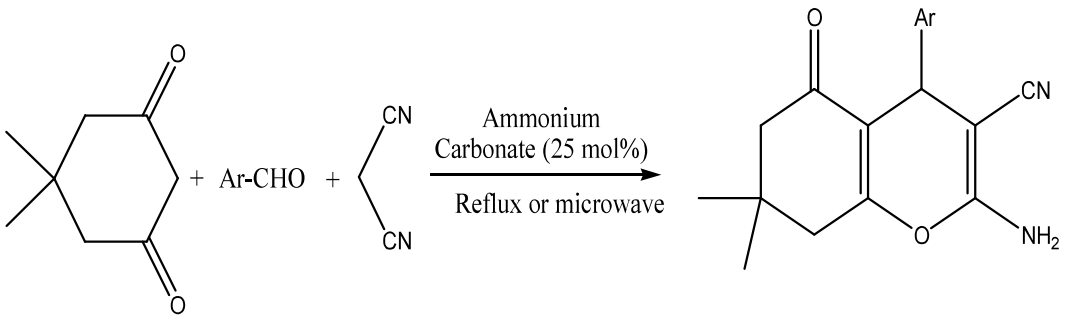
dimedone (1mmol) in 10 ml of aqueous ethanol (1:1) and stirred for 2 minutes. Then benzaldehyde (1mmol) was added and again stirred further 5 minutes. Later malononitrile (1mmol) was added and stirred again. But we got less yield of the product. Hence the reaction was checked at refluxed condition and got 45% of the yield. To increase the yield, 20 mol% of ammonium carbonate was added. This time we got 73% of product. This encouraged us to increase of ammonium carbonate to 25mol% and got 92% yield. Further increase in amount did not increase the product yield significantly. Hence we opted the 25mol% ammonium carbonate for the 2-aminopyrane synthesis. Along with this we tried to use microwave as alternative energy source and found excellent results.

Scheme



1 **2(a-i)** **3** **4(a-i)**

EXPERIMENTAL

All chemicals used were of the synthetic grade. The ethanol and water were distilled before use. The reaction progress was monitored on alumina coated TLC using n-hexane -ethyl acetate (8:2) system. All the melting points were recorded using open capillary method and are uncorrected. A domestic Microwave was used of make Samsung, 230V- 50 Hz, 800 W, M1833N. IR spectra were recorded on Shimadzu IR Affinity 1 instrument using KBrpalates. Proton NMR was recorded on BRUKER Avance II 400 NMR Spectrometer in DMSO d^6 as a solvent. The mass was recorded on WATERS, Q-TOF Micro mass (ESI-MS) in methanol.

General procedure of the synthesis of substituted 2-aminopyranes:

a. Conventional method:

To the stirring mixture of aromatic aldehyde (1mmol) and dimedone (1mmol) in 10 ml of ethanol-water (1:1) system 25mol% of ammonium carbonate was added and stirred for 5 minutes. Then malononitrile (1 mmol) was added to this stirring mixture and refluxed for appropriate time. After the completion of reaction, the mixture was allowed to cool and diluted with 20 ml of ice cold water and filtered. The obtained compound was dried and recrystallized using 80% ethanol in water system.

b. Microwave method:

To the mixture of aromatic aldehyde (1mmol), dimedone (1mmol) and malononitrile (1mmol) 10 ml of ethanol-water (1:1) system, 25mol% of ammonium carbonate was added and stirred. This mixture was then irradiated at 450watt for appropriate time with regular interval to cool the reaction mixture. After completion of reaction, the mixture was cooled and 20 ml of ice cold water was added in it and filtered. The resulting compound was dried and recrystallized using 80% ethanol in water.

Table-2: one pot synthesis of 2-amino pyranes catalysed by ammonium carbonate[a]

Entry	Aldehyde	Product	Yield		Time (Min.)		M. P. (^oC)	
			Reflux	MW	Reflux	MW	Found	Reported
1	4-MeO-C_6H_4	4a	93	94	35	5	201-202	199-200[36]
2	C_6H_5	4b	92	93	25	5	228-229	224-226[36]
3	4-Cl-C_6H_4	4c	94	92	30	4	208-210	210-212[36]
4	4-OH-C_6H_4	4d	84	87	35	5	206-207	208-210[36]
5	4-F-C_6H_4	4e	91	90	30	4	211–212	210-212[36]
6	4-NO_2-C_6H_4	4f	94	91	25	3.5	180–181	177-179[36]
7	3-NO_2-C_6H_4	4g	92	90	30	4	215-216	210-212[36]
8	3,4-Cl-C_6H_3	4h	91	93	25	5	254–256	253-255[36]
9	2-Furan	4i	87	84	40	5	224–225	225-227[36]

[a] experimental conditions: aromatic aldehyde (1mmol), dimedone (1mmol) and malononitrile (1mmol), Solvent - 10 ml of ethanol-water (1:1), ammonium carbonate (25mol%)

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REPRESENTATIVE SPECTRAL DATA

2-amino-4-(4-chlorophenyl)-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-4H-chromene-3-carbonitrile

IR (KBr, cm^{-1}): 3393,3337, 2966, 2213, 1680, 1608, 1372, 1216. ^1H NMR (400 MHz, DMSO-d^6): δ (ppm) 0.94 (s, 3H), 1.00 (s, 3H), 1.15 (m, 1H), 1.96-2.23 (m,3H), 4.17 (s, 1H), 6.4 (s, 2H), 7.14 (d, J = 8 Hz, 2H), 7.31 (d, J = 8 Hz, 2H). Mass: 329 (M+1)

CONCLUSION

The ammonium carbonate in aqueous ethanol system is found to be good for the synthesis of 2-amino pyrane compounds. It provides an easy way for one pot three component reaction in both conventional refluxing and microwave assisted synthesis. The short time reaction and easy workup process are the merits of this reaction.

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