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Microwave Promoted, Sodium Acetate Catalyzed One Pot Synthesis of Poly Functionalized 4H-Pyrans

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A clean and efficient one pot synthesis of 4H-pyran derivatives through condensation of aromatic aldehydes, malononitrile and dicarbonyl compounds under microwave irradiation in presence of Sodium acetate as a catalyst is described.

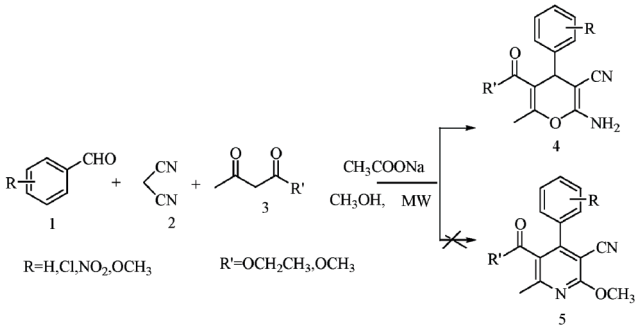
Keywords: Multicomponent reaction; 4H-pyran derivatives; Microwave irradiation; Sodium acetate.

INTRODUCTION

Multi component reactions (MCRs) have emerged as powerful tools in organic, combinatorial and medicinal chemistry.[1] The MCRs strategy offers significant advantages over conventional multi step synthesis due to its flexible, convergent, and atom economical nature.[2] In a true sense, MCRs represent environmentally benign processes by reducing the number of steps, energy consumption and waste production.[3] These features make MCRs well-suited for the construction of diversified arrays of valuable heterocyclic scaffolds. Therefore, great efforts have been and still are being made to find and develop new multi component reactions. Usually, to drive the conversion of MCR, one or two components are excessive and this always leads to the trouble of separating and purifying the target products. Another drawback in MCRs is they can not be planed perfectly in advance and majority of them are accidental. After getting the product the logic and mechanism of the reaction is proposed.

Polyfunctionalized 4H-pyrans constitute a structural unit of a number of natural products[4] and inherent reactivity of the pyran ring is versatile synthons.[5] These 4H-pyrans are isosters of 1,4-dihydro pyridine[6] with potential pharmacological interest and active synthons that have been extensively used in heterocyclic synthesis. In addition, polyfunctionalized 4H-pyrans are biologically interesting compounds which possess various pharmacological activities,[7] e.g. antiallergic[8] and antitumor[9] activities. 4H-pyrans are also useful intermediates for the synthesis of various compounds, such as pyranopyridine derivatives[10] polyazanaphthalenes, pyrano[2,3-d]pyrazoles,[11] pyrano pyrimidines and pyridin-2-ones,[12] with various other biological activities. The 4H-pyrans are synthesized mainly by a three-components coupling reaction of aromatic aldehydes, malononitrile and β-diketones catalyzed by bases like Triethylamine,[13] Piperidine,[14] Rubidium fluoride,[15] Recently, Shestopalov and co-workers[16] have developed a one-pot electrochemical synthesis of title compounds catalyzed by electro generated base with the yields ranged from 60 to 80%. However, many of these procedures suffer from one or more disadvantages such as harsh reaction conditions, prolonged time period, poor yields and use of hazardous and expensive catalysts. Therefore, the development of a clean, high-yielding and environmentally benign approach is still desirable. We wish to report a clean and efficient method for the synthesis of 4H-pyran derivatives in excellent yields through one-pot condensation of aromatic aldehydes, malononitrile and dicarbonyl compounds using sodium acetate as catalysts in methanol as a solvent under microwave irradiations. The reaction is depicted in Scheme I.

Scheme I Synthesis of 4H-pyran derivatives



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RESULTS AND DISCUSSION

4H-pyran derivatives were obtained in excellent yields and in shorter reaction time through the one-pot condensation of aromatic aldehydes (1 mmol), malononitrile (1 mmol) and dicarbonyl compounds (1.1 mmol) using sodium acetate (10 mol %) as catalysts in methanol as a solvent under microwave irradiations (280 W).

The results are summarized in Table 1.

To investigate the reaction in detail a model reaction was carried out by condensing Benzaldehydes, Malonitrile and Ethyl acetoacetate in various solvents and catalyst (10 mol %) such as TBABr, CTAB, K_2CO_3, KH_2PO_4, NH_2PO_4, CH_3COONa, L-Proline (Table 2). The results showed that when Sodium acetate was used as a catalyst its action was more effective than L-Proline, K_2CO_3. In case entries 1, 2, 5 and 6, instead of desired product the intermediate alkylidenemalononitrile with 90%, 85%, 60% and 80% yields was obtained. The results of the reactions are depicted in Table 2.

We have also studied the effect of concentration of catalyst (sodium acetate) under microwave irradiation at 280 W in methanol as a solvent. It was observed that 10 mol% of the catalyst was the optimum quantity to get the desired product in excellent yield. The results are depicted in Table 3. Different aldehydes containing electron-withdrawing, electron releasing substituents and β-diketoesters were used for universal applicability of the method for the synthesis of pyrans. It was found that in all cases, the yields were excellent.

Interestingly in the present study when sodium acetate was used as catalyst in the reaction under microwave irradiation the exclusive product obtained was pyran derivatives. However, earlier Dewen Dong *et al*[17] reported substituted pyridine derivatives. The possible mechanism is depicted in Scheme II. Although the detailed mechanism of the above reaction remains to be fully clarified, the forma-

Table 1. Synthesis of products **4a-4k** under MW (280 W), 10 mol % Sodium acetate as a catalyst

Entry	Product	Ar	R'	Time	M.P		Yield
					Found	Lil.	
1	**4a**	C_6H_5	OCH_2CH_3	4.0	178-179	178-179[21]	90
2	**4b**	4-Cl-C_6H_4	OCH_2CH_3	3.5	171-172	170-172[20]	93
3	**4c**	4-OMe-C_6H_4	OCH_2CH_3	5.5	132-133	136-138[20]	82
4	**4d**	4-NO_2-C_6H_4	OCH_2CH_3	3.5	175-176	176-178[20]	85
5	**4e**	2-Cl-C_6H_4	OCH_2CH_3	4.0	179-181	180-181[20]	91
6	**4f**	2-OMe-C_6H_4	OCH_2CH_3	6.0	142-144	-	80
7	**4g**	3,4,5-$(OCH_3)_3$-C_6H_3	OCH_2CH_3	4.5	181-183	-	88
8	**4h**	2-NO_2-C_6H_4	OCH_2CH_3	3.5	163-165	-	83
9	**4i**	C_6H_5	OCH_3	4.0	172-173	-	87
10	**4j**	2-Cl-C_6H_4	OCH_3	3.5	158-159	161-162[18]	89
11	**4k**	4-NO_2-C_6H_4	OCH_3	3.5	170-172	-	86

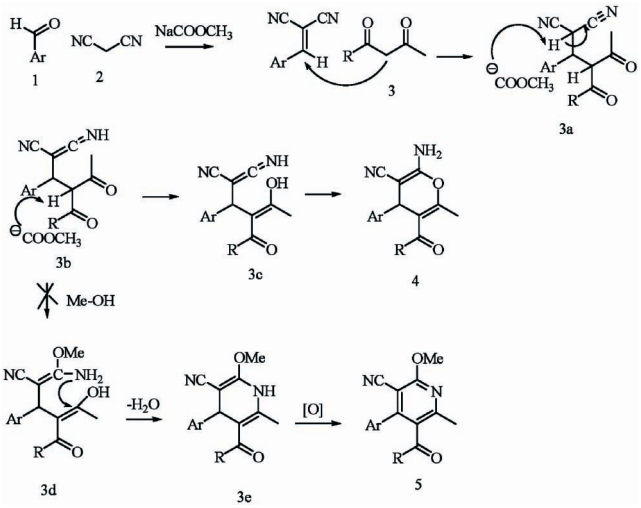
Table 2. A model reaction by condensing Benzaldehydes, Malonitrile and Ethyl acetoacetate in various solvents and catalyst (10 mol %) under microwave irradiation at 280 W

Entry	Catalyst	Solvent	Time (min)	Yield % of Alkylidenemalononitrile	Yield % of 4H Pyrane
1	TBABr	Water	8	90	-
2	CTAB	Water	8	85	-
3	K_2CO_3	Ethanol	8	-	10
4	TBABr+K_2CO_3	Water: Ethanol 30%	8	-	50
5	KH_2PO_4	Water: Ethanol 10%	8	60	-
6	NH_2PO_4	Water: Ethanol 10%	8	80	-
7	CH_3COONa	Ethanol	4	-	78
8	L-Proline	Ethanol	8	-	23
9	L-Proline	–	4	-	10
10	CH_3COONa	Methanol	4	-	90

Table 3. Effect of the concentration of the catalyst in methanol under microwave irradiation at 280 W

Entry	Sodium acetate in mol %	Yield %
1	5	59
2	7	68
3	8	80
4	10	90
5	12	87

Scheme II Proposed mechanism for the formation of 4H pyran



tion of compound **4** could be explained by a possible reaction sequence presented in Scheme II. Compound **4** is expected to proceed via initial condensation of aromatic aldehydes with malononitrile to afford alkylidenemalononitrile which further undergoes in situ Michael addition with ester of active methylene carbonyl moiety to yield the intermediate **3a**, followed by **3b** and **3c**, which is then cyclized to furnished **4**, a desired product. On other hand if **3b** will pick the proton form methanol (Solvent) then route of reaction will be different, and finally the pyridine ring will be formed, which is not possible here. This may be due to low basicity of sodium aceate.

The Absolute configuration was further proved by ^{1}H NMR and ^{13}C NMR. In Case of Pyridine derivative, there is OCH_3 group and should give singlet at about 3.5 ppm. However in ^{1}H NMR spectra of all the compounds this peak are absent so this is clear indication that there is no OCH_3 and ultimately it is pyran ring, not the pyridine ring. Further ^{13}C NMR values for Carbon **2** and carbon **6** are 166 ppm and 157 ppm clearly show that position 2 and 6 belong to pyran ring.

EXPERIMENTAL

All reagents were purchased from Merck and Loba and used without further purification. Melting points were measured in open capillary and are uncorrected. The products were characterized by IR spectra, ^{1}H NMR, ^{13}C NMR and elemental analyses. IR spectra were recorded on Perkin–Elmer FT-IR-1710 instrument. ^{1}H NMR and ^{13}C NMR was recorded on BrukerMSL-300 MHz and Bruker MSL-200 MHz instruments using TMS as an internal standard. Elemental analyses were determined by an elemental analyzer (CHNS-O, EA 1108-elemental analyzer, Carlo Erba instruments). Microwave oven used was LG microwave MOD-MG-1742WE, 2450 MHz and 700 W maximum output.

General procedure for the preparation of 4H-pyrans (4a-4k)

A mixture of aromatic aldehyde (1.0 mmol), malononitrile (1.0 mmol), active methylene compounds (1.1 mmol) and methanol 2 mL were taken in 50 mL beaker followed by addition of sodium acetate (10 mol%). The beaker was covered by watch glass and kept for microwave irradiation at 280 W. Completion of the reaction was monitored by TLC, after completion of the reaction, the reaction mixture was cooled to room temperature and 5 mL of water added and filtered. The residue was collected as a crude product, washed with methanol and recrystallized by absolute ethanol.

Ethyl 6-amino-5-cyano-2-methyl-4-phenyl-4H-pyran-3-carboxylate (4a)

White Solid, m.p. 178-179 ^{o}C; IR (KBr): 927, 2727, 2189, 1674, 1608, 1500, 1457, 1377, 1169, 1060, 965, 722; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.1-7.3 (m, 5H, Ar-H), 4.4 (brs, 2H, NH_2), 4.3 (s, 1H, CH), 4.1 (q, 2H, J = 7.2 Hz, CH_2), 2.2 (s, 3H, CH_3), 1.1 (t, 3H, J = 7.2 Hz, CH_3); $C_{16}H_{16}N_2O_3$: Anal Calc. for C, 67.59; H, 5.67; N, 9.85; Found: C, 67.64; H, 5.75; N, 9.82.

Ethyl 6-amino-4-(4-chlorophenyl)-5-cyano-2-methyl-4H-pyran-3-carboxylate (4b)

White Solid, m.p. 171-172 ^{o}C; IR (KBr): 3405, 3019, 2193, 1083, 1383, 1216, 1065, 925, 770, 669; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.1 (d, 2H, J = 8.1 Hz, Ar-H), 7.3 (d, 2H, J = 8.1 Hz, Ar-H), 4.5 (brs, 2H, NH_2), 4.4 (s, 1H, CH), 4.0 (q, 2H, J = 6.9 Hz, CH_2), 2.2 (s, 3H, CH_3), 1.1 (t, 3H, J = 6.9 Hz, CH_3); $C_{16}H_{15}ClN_2O_3$ Anal. Calc. For C, 60.29; H, 4.74; N, 8.79; Found: C, 60.29; H, 4.79; N, 8.83.

Ethyl 6-amino-5-cyano-4-(4-methoxyphenyl)-2-methyl-4H-pyran-3-carboxylate (4c)

White Solid, m.p. 132-133 °C; IR (KBr): 2929, 2727, 1456, 1377, 1303, 1154, 1076, 964, 722; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.26 (d, 2H, *J* = 7.0 Hz, Ar-H), 7.14 (d, 2H, *J* = 7.0 Hz, Ar-), 4.47 (brs, 2H, NH_2), 4.39 (s, 1H, CH), 4.0 (q, 2H, *J* = 7.2 Hz, CH_2), 3.7 (s, 3H, OCH_3), 2.3 (s, 3H, CH_3), 1.14 (t, 3H, *J*= 7.2 Hz, CH_3); $C_{17}H_{18}N_2O_4$: Anal. Calc. For C, 64.96; H, 5.77; N, 8.91; Found: 64.92; H, 5.81; N, 8.95.

Ethyl 6-amino-5-cyano-2-methyl-4-(4-nitrophenyl)-4H-pyran-3-carboxylate (4d)

Yellow Solid, m.p. 175-176 °C; IR (KBr): 3020, 2197, 1682, 1521, 1348, 1268, 1215, 1062, 760, 669; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.2 (d, 2H, *J* = 8.0 Hz, Ar-H), 7.4 (d, 2H, *J* = 8.0 Hz, Ar-H), 4.7 (brs, 2H, NH_2), 4.6 (s, 1H, CH), 4.1 (q, 2H, *J* = 7.0 HzCH_2), 2.1 (s, 3H, CH_3), 1.1 (t, 3H, *J* = 7.0 Hz, CH_3); $C_{16}H_{15}N_3O_5$: Anal. Calc. For C, 58.36; H, 4.59; N, 12.76; Found: C, 58.32; H, 4.61; N, 12.79.

Ethyl 6-amino-4-(2-chlorophenyl)-5-cyano-2-methyl-4H-pyran-3-carboxylate (4e)

White Solid, m.p. 179-181 °C; IR (KBr): 3405, 3019, 2400, 2193, 1677, 1590, 1215, 1068, 757, 669; ^{1}H NMR (300MHz, $CDCl_3$): δ 7.1-7.2 (m, 4H, Ar-H), 5.0 (s, 1H, CH), 4.4 (brs, 2H, NH_2), 4.0 (q, 2H, *J* = 7.2 Hz, CH_2), 2.2 (s, 3H, CH_3), 1.0 (t, 3H, *J* = 7.2 Hz, CH_3); $C_{16}H_{15}ClN_2O_3$: Anal. Calc. for C, 60.29; H, 4.74; N, 8.79; Found: C, 60.30; H, 4.77; N, 8.84.

Ethyl 6-amino-5-cyano-4-(2-methoxyphenyl)-2-methyl-4H-pyran-3-carboxylate (4f)

White Solid, m.p. 142-144 °C; IR (KBr): 3309, 2900, 2728, 2192, 1688, 1601, 1457, 1377, 1156, 1061, 772, 448; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.8-7.3 (m, 4H, Ar-H), 4.5 (brs, 2H, NH_2), 4.4 (s, 1H, CH), 4.0 (q, 2H, *J* = 7.2 Hz, CH_2), 3.8 (s, 3H, OCH_3), 2.4 (s, 3H, CH_3), 1.1 (t, 3H, *J* = 7.2 Hz, CH_3); ^{13}C NMR ($CDCl_3$): δ 13.86, 18.36, 38.63, 55.12, 60.61, 61.37, 107.72, 112.07, 113.50, 119.8, 129.85, 145.40, 156.81, 157.55, 159.64, 165.82; $C_{17}H_{18}N_2O_4$: Anal. Calc. For C, 64.96; H, 5.77; N, 8.91; Found: C, 64.95; H, 5.79; N, 8.92.

Ethyl 6-amino-5-cyano-4-(3,4,5-trimethoxyphenyl)-2-methyl-4H-pyran-3-carboxylate (4g)

White Solid, m.p. 181-183 °C; IR (KBr): 3341, 2980, 2195, 1702, 1593, 1505, 1461, 1327, 1258, 1055, 434; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.4 (s, 2H, Ar-H), 4.5 (brs, 2H, NH_2), 4.4 (s, 1H, CH), 4.1 (q, 2H, *J* = 7.2 Hz, CH_2), 3.8 (s, 9H, OCH_3), 2.4 (s, 3H, CH_3), 1.1 (t, 3H, *J* = 7.2 Hz, CH_3); ^{13}C NMR ($CDCl_3$): δ 13.98, 18.38, 56.08, 60.71, 62.26, 104.47, 107.86, 137.07, 139.40, 153.23, 156.0, 157.37, 165.88; $C_{19}H_{22}N_2O_6$: Anal. Calc. for C, 60.95; H, 5.92; N, 7.48; Found:C, 60.98; H, 5.95; N, 7.50.

Ethyl 6-amino-5-cyano-2-methyl-4-(2-nitrophenyl)-4H-pyran-3-carboxylate (4h)

Yellow Solid, m.p. 163-165 °C; IR (KBr): 2924, 2727, 2208, 1717, 1682, 1600, 1460, 1377, 1304, 1154, 1065, 965, 722, 446; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.3-7.8 (m, 4H, Ar-H), 5.3 (brs, 2H, NH_2), 4.6 (s, 1H, CH), 4.0 (q, 2H, *J* = 7.2 Hz, CH_2), 2.4 (s, 3H, CH_3), 1.1 (t, 3H, *J* = 7.2 Hz, CH_3); ^{13}C NMR ($CDCl_3$): δ 13.63, 18.43, 32.89, 60.91, 107.24, 118.21, 124.0, 127.87, 130.58, 133.23, 139.09, 149.03, 158.0, 165.02; $C_{16}H_{15}N_3O_5$: Anal. Calc. C, 58.36; H, 4.59; N, 12.76; Found: C, 58.32; H, 4.65; N, 12.79.

Methyl 6-amino-5-cyano-2-methyl-4-phenyl-4H-pyran-3-carboxylate (4i)

White Solid, m.p. 172-173 °C; IR (KBr): 3431, 3223, 2947, 2195, 1689, 1604, 1409, 1342, 1261, 1120, 1061, 951, 744, 583; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.18-7.32 (m, 5H, Ar-H), 4.48 (brs, 2H, NH_2), 4.44 (s, 1H, CH), 3.58 (s, 3H, OCH_3), 2.37 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$): δ 18.46, 38.50, 51.84, 62.08, 107.81, 118.92, 127.33, 128.59, 143.65, 157.60, 157.57, 166.36; $C_{15}H_{14}N_2O_3$: Anal. Calc. C, 66.66; H, 5.22; N, 10.36; Found: C, 66.71; H, 5.30; N, 10.45.

Methyl 6-amino-4-(2-chlorophenyl)-5-cyano-2-methyl-4H-pyran-3-carboxylate (4j)

White Solid, m.p. 158-159 °C; IR (KBr): 3431, 2923, 2727, 2360, 2195, 1675, 1455, 377, 1157, 1063, 722; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.1-7.4 (m, 4H, Ar-H), 5.0 (s, 1H, CH), 4.6 (brs, 2H, NH_2), 3.6 (s, 3H, OCH_3), 2.4 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$): δ 18.40, 35.44, 51.67, 61.02, 106.76, 118.49, 127.28, 128.35, 129.85, 133.01, 140.88, 157.69, 166.11; $C_{15}H_{13}ClN_2O_3$: C, 59.12; H, 4.30; N, 4.19; Found: C, 59.21; H, 4.37; N, 9.15.

Methyl 6-amino-5-cyano-2-methyl-4-(4-nitrophenyl)-4H-pyran-3-carboxylate (4k)

Yellow Solid, m.p. 170-172 °C; IR (KBr): 3402, 3330, 3202, 2955, 2201, 1689, 1605, 1520, 1345, 1065, 865, 731; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.14-8.18 (d, 2H, *J* = 8.0 Hz, Ar-H), 7.34-7.38 (d, 2H, *J* = 8.0 Hz, Ar-H), 4.69 (brs, 2H, NH_2), 4.54 (s, 1H, CH), 3.58 (s, 3H, OCH_3), 2.39 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$): δ 18.69, 13.69, 51.88, 60.72, 106.65, 118.27, 124.03, 128.30, 147.04, 160.95,

157.74, 165.77; $C_{15}H_{13}N_3O_5$: Anal. Calc. for C, 57.14; H, 4.16; N, 13.33; Found: C, 57.20; H, 4.10; N, 13.45.

CONCLUSION

An efficient and environmentally benign strategy for the synthesis of multi functional 4H pyran derivatives is developed. The method offers several advantages including high yield of products, short reaction time, easily availability of catalyst, ease of work-up and low-cost.

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