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Microwave Assisted Urea-Acetic Acid Catalyzed Knoevenagel Condensation of Ethyl Cyanoacetate and 1,3-Thiazolidine-2,4-dione with Aromatic Aldehydes under Solvent Free Condition

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Knoevengel condensation reaction of various aromatic aldehydes with ethyl cyanoacetate and 1,3-thiazolidinone-2,4-diones catalyzed by urea-acetic acid under solvent free condition where olefinic products were obtained in high yield within short reaction time.

Keywords: Knoevengel condensation, Solvent free, Urea-Acetic acid.

INTRODUCTION

Knoevenagel condensation is an important reaction in organic chemistry by which carbon-carbon double bond is formed. One of the product ethyl α-cyanocinnamates is used as an important intermediate for the synthesis of different pharmaceutically important organic compounds and also has application in making paper, dyes, fibers, plastics *etc*. [1]. Other product 5-arylidene derivatives of 4-thiazolidinones are well known in the pharmaceutical industry and have been shown a broad spectrum of biological activities including anti-inflammatory [2a], antibacterial [2b], antiviral [2c], antimicrobial [2d], antifungal [2e] and possess aldose reductase inhibitors [2f], antidiabetic activity [2g-k].

A number of synthetic strategies have been developed for the Knoevengel condensation of aromatic aldehydes and ethyl cyanoacetate. This reaction is catalyzed by organic bases or with variety of catalyst like zeolites [3], $AlPO_4$-Al_2O_3 [4], $LaCl_3 \cdot H_2O$ [5], I_2/K_2CO_3 [6], CTMAB [7], TEBA [8], NH_4OAc-Basic alumina [9], $H_3PW_{12}O_{40}$ [10], NaF and LiCl [11], $MgBr_2 \cdot OEt_2$ [12], $TiCl_4$/Base [13], MgO and ZnO [14], $ZnCl_2$ [15], lipase as a biocatalyst [16], *etc.* The synthesis of 5-arylidene-2,4-thiazolidinediones such as sodium acetate in acetic acid under reflux conditions [17], microwave irradiation [18], piperidine in ethanol [19a], piperidinium acetate in toluene under reflux conditions [19b], piperidinium acetate in DMF under microwave irradiation [20], glycine and sodium carbonate in H_2O under reflux conditions [21], grinding with ammonium acetate in the absence of solvents [22], alum in H_2O [23], Baker's yeast [24], KF-Al_2O_3 under microwave irradiation [25], glycine under microwave irradiation [26], polyethylene glycol-300 [27] and ethylenediamine diacetate [28]. Recently, ionic liquids catalyzed synthesis of 5-arylidene-2,4-thiazolidinediones have also been reported [29,30]. All the above methods have their own advantages but also suffer from one or more disadvantages such as long reaction time, low to moderate yields, tedious work-up procedures, requirement of special apparatus and use of organic solvents.

In present work, urea-acetic acid couple is used as a catalyst for Knoevengel condensation between aromatic aldehydes and compounds with active methylene group like ethyl cyano-acetate (**Scheme-I**) and 1,3-thiazolidinone-2,4-dione (**Scheme-II**) under microwave irradiation. Both are non-toxic, easily available, easy to handle and low cost compounds.

EXPERIMENTAL

Melting points were determined in open capillary tubes and are uncorrected. IR spectra were recorded with a Shimadzu IR-408 spectrometer. ^1H NMR spectra were determined in $CDCl_3$/DMSO-d_6 solution on a Bruker Avance II (400 MHz) NMR spectrometer and TMS was used as a internal standard. Mass spectra were recorded on a WATERS, Q-TOF MICROMASS (LC-MS). Domestic microwave oven (Samsung) was used at Power 600 W.

General procedure for synthesis of ethyl α-cyanocinnamates (3a-n) and 5-arylidine-2,4-thiazolidinediones (5a-l): A mixture of aromatic aldehydes (4.7 mmol), ethyl cyano-acetate (0.531 g, 4.7 mmol) or 1,3-thiazolidinone-2,4-dione (0.550 g, 4.7 mmol) and urea-acetic acid in (0.028 g : 0.028 g, 10 mmol % 1:1) was taken in an Erlenmeyer flask and subjected to microwave irradiation at 600 W at 10 s interval for a specified

time as indicated in Tables 1 and 2. The completion of the reaction was monitored by TLC (20 % ethyl acetate in *n*-hexane). The reaction mixture was cooled to room temperature and treated with cold water the product thus obtained was filtered, dried and recrystallized from ethanol affording pure products.

Physical and spectral data

Ethyl (E)-2-cyano-3-phenyl-2-propenoate (3a): Yield: 96 %; m.p.: 50-51 °C (lit. 50 °C [11]); FTIR (KBr, ν_{max}, cm^{-1}): 2982, 2222, 1725, 1605; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.2 (s, 1H, CH), 7.9 (m, 2H, phenyl), 7.5 (m, 3H phenyl), 4.3–4.4 (q, *J* = 7.12 Hz, 2H, CH_2), 1.3–1.4 (t, *J* = 7.12 Hz, 3H, CH_3); LC-MS: *m/z* (M +1) calcd. for $C_{12}H_{11}NO_2$: 202; found: 202.

Ethyl (E)-2-cyano-3-(3-nitrophenyl)-2-propenoate (3b): Yield: 96 %; m.p.: 130-132 °C (lit. 130 °C [11]); FTIR (KBr, ν_{max}, cm^{-1}): 2987, 2224, 1719, 1605, 1528, 1355; ^1H NMR (400 MHz, DMSO-d_6): δ = 8.49 (s, 1H, CH), 8.9 (s, 1H, phenyl), 8.41 (t, 2H, phenyl), 7.82 (t, 1H, phenyl), 4.4 (q, *J* = 6.8 Hz, 2H, CH_2), 1.4 (t, *J* = 6.8 Hz, 3H, CH_3).

Ethyl (E)-2-cyano-3-(2-chlorophenyl)-2-propenoate (3c): Yield: 92 %; m.p.: 62-64 °C; FTIR (KBr, ν_{max}, cm^{-1}): 2994, 2223, 1731, 1609, 758; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.69 (s, 1H, CH), 8.2 (d, 1H, phenyl), 7.5 (m, 2H, phenyl), 7.4 (m, 1H, phenyl), 4.4 (q, *J* = 7.2 Hz, 2H, CH_2), 1.4 (t, *J* = 7.2 Hz, 3H, CH_3); LC-MS: *m/z* (M +1) calcd. for $C_{12}H_{10}NO_2Cl$: 236; found: 236

Ethyl (E)-2-cyano-3-(3-methoxy 4-hydroxyphenyl)-2-propenoate (3d): Yield: 95 %; m.p.: 112 °C (lit. 114 °C [16]); FTIR (KBr, ν_{max}, cm^{-1}): 3376, 2983, 2940, 2218, 1703, 1575; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.1 (s, 1H, CH), 7.8 (s, 1H, phenyl), 7.4 (d, 1H, phenyl), 7.0 (d, 1H, phenyl), 6.5 (s, 1H, OH), 4.3 (q, *J* = 6.8 Hz, 2H, CH_2), 3.9 (s, 3H, OCH_3), 1.4 (t, *J* = 6.8 Hz, 3H, CH_3).

Ethyl (E)-2-cyano-3-(3-chlorophenyl)-2-propenoate (3e): Yield: 98 %; m.p.: 102-103 °C; FTIR (KBr, ν_{max}, cm^{-1}): 2985, 2221, 1714, 1609, 759; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.1 (s, 1H, CH), 7.9 (d, 2H, phenyl), 7.5 (d, 1H, phenyl), 7.4 (t, 1H, phenyl), 4.4 (q, *J* = 6.8 Hz, 2 H, CH_2), 1.4 (t, *J* = 6.8 Hz, 3H, CH_3).

Ethyl (E)-2-cyano-3-furyl-2-propenoate (3f): Yield: 92 %; m.p.: 94-96 °C (lit. 95 °C [11]); FTIR (KBr, ν_{max}, cm^{-1}): 2988, 2222, 1716, 1620; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.0 (s, 1H, CH), 7.7 (d, 1H, furyl), 7.4 (d, 1H, furyl), 6.6 (t, 1H, furyl), 4.3 (q, *J* = 7.12 Hz, 2 H,CH_2), 1.4 (t, *J* = 7.12 Hz, 3H,CH_3).

Ethyl (E)-2-cyano-3-(4-chlorophenyl)-2-propenoate (3g): Yield: 94 %; m.p.: 90-92 °C (lit. 92-93 °C [11]); FTIR (KBr, ν_{max}, cm^{-1}): 2988, 2221, 1722, 1608, 758; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.2 (s, 1H, CH), 7.9 (d, 2H, phenyl), 7.4 (d, 2H, phenyl), 4.4 (q, *J* = 7.12 Hz, 2H, CH_2), 1.4 (t, *J* = 7.12 Hz, 3H, CH_3).

Ethyl (E)-2-cyano-3-(4-hydroxyphenyl)-2-propenoate (3h): Yield: 90 %; m.p.: 170-172 °C (lit. 168 °C [16]); FTIR (KBr, ν_{max}, cm^{-1}): 3253, 2988, 2231, 1731, 1713; ^1H NMR (400 MHz, DMSO-d_6): δ = 10.5 (s, 1H, OH), 8.1 (s, 1H, CH), 7.9 (d, 2H, phenyl), 6.9 (d, 2H, phenyl), 4.3 (q, *J* = 7.12 Hz, 2H, CH_2), 1.38 (t, *J* = 7.12 Hz, 3H,CH_3) ppm.

Ethyl (E)-2-cyano-3-(2-nitrophenyl)-2-propenoate (3i): Yield: 95 %; m.p.: 118-120 °C; FTIR (KBr, ν_{max}, cm^{-1}): 2995, 2231, 1725, 1603, 1527, 1343; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.7 (s, 1H, CH), 8.3 (s, 1H, phenyl), 7.8 (m, 2 H, phenyl), 7.7 (t, 1H, phenyl), 4.4 (q, *J* = 7.12 Hz, 2H, CH_2), 1.4 (t, *J* = 7.1 Hz, 3H, CH_3). LC-MS: *m/z* (M +1) calcd. for $C_{12}H_{10}N_2O_4$: 247; found: 247.1

Ethyl (E)-2-cyano-3-(4-methoxyphenyl)-2-propenoate (3j): Yield: 90 %; m.p.: 80-82 °C (lit. 86 °C [16]); FTIR (KBr, ν_{max}, cm^{-1}): 2990, 2941, 2841, 2213, 1716, 1585; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.1 (s, 1H, CH), 8.0 (d, 2H, phenyl), 7.0 (d, *J* = 7.0 Hz, 2H, phenyl), 4.3 (q, *J* = 7.12 Hz, 2H, CH_2), 3.8 (s, 3H, OCH_3), 1.3–1.4 (t, *J* = 7.12 Hz, 3H, CH_3).

Ethyl (E)-2-cyano-3-(3,4,5-trimethoxyphenyl)-2-propenoate (3k): Yield: 90 %; m.p.: 98-99 °C; FTIR (KBr, ν_{max}, cm^{-1}): 2981, 2948, 2844, 2218, 1730, 1601, 1577; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.1 (s, 1H, CH), 7.3 (s, 2H, phenyl), 4.4 (q, *J* = 7.12 Hz, 2H, CH_2), 3.96 (s, 3H, CH_3), 3.93 (s, 6H, CH_3), 1.4 (t, *J* = 7.12 Hz, 3H, CH_3). LC-MS: *m/z* (M +1) calcd. for $C_{15}H_{17}NO_5$: 292; found: 292.1.

Ethyl (E)-2-cyano-3-(2-methoxyphenyl)-2-propenoate (3l): Yield: 94 %; m.p.: 70-72 °C (lit. 70 °C [16]); FTIR (KBr, ν_{max}, cm^{-1}): 2988, 2942, 2835, 2223, 1709, 1596; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.7 (s, 1H, CH), 8.3 (d, 1H, phenyl), 7.5 (t, 1H, phenyl), 7.0 (t, 1H, phenyl), 6.9 (d, 1H, phenyl), 4.3–4.4 (q, *J* = 7.12 Hz, 2H, CH_2), 3.9 (s, 3H, OCH_3), 1.3–1.4 (t, *J* = 7.12 Hz, 3H, CH_3).

Ethyl (E)-2-cyano-3-(4-fluorophenyl)-2-propenoate (3m): Yield: 94 %; m.p.: 96-98 °C (lit. 97 °C [16]); FTIR (KBr, ν_{max}, cm^{-1}): 2998, 2224, 1717, 1593, 762; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.2 (s, 1H, CH), 8.0 (t, 2H, phenyl), 7.2 (t, 2H, phenyl,), 4.4 (q, *J* = 7.12 Hz, 2 H, CH_2), 1.4 (t, *J* = 7.12 Hz, 3H, CH_3).

Ethyl (E)-2-cyano-3-(1-naphthyl)-2-propenoate (3n): Yield: 90 %; m.p.: 95-96 °C; FTIR (KBr, ν_{max}, cm^{-1}): 2969, 2223, 1718, 1603; ^1H NMR (400 MHz, $CDCl_3$): δ = 9.1 (s, 1H, CH), 8.3 (d, 1H, Ar), 8.0 (t, 2H, Ar), 7.9 (d, 1H, Ar), 7.6 (m, 3H, Ar),4.4 (q, *J* = 7.12 Hz, 2 H, CH_2), 1.4 (t, *J* = 7.12 Hz, 3H, CH_3); LC-MS: *m/z* (M +1) calcd. for $C_{16}H_{13}NO_2$: 253; found: 253.1

5-(Benzylidene)-1,3-thiazolidine-2,4-dione (5a): Yield: 93 %; m.p.: 240 °C (lit. 240 °C [22]); IR (KBr, ν_{max}, cm^{-1}): 3140, 3031, 2785, 1738, 1688); ^1H NMR (400 MHz, DMSO-d_6): δ = 12.5 (s, 1H, NH), 7.7 (s, 1H, =CH), 7.4-7.5 (m, 5H, Ar); LC-MS: *m/z* (M +1) calcd. for $C_{10}H_7NO_2S$: 206; found: 206

5-[(Furan-2-yl)methylidene]-1,3-thiazolidine-2,4-dione (5b): Yield: 91 %; m.p.: 233-235 °C (lit. 231-233 °C [28]); IR (KBr, ν_{max}, cm^{-1}): 3131, 3031, 2800, 1785, 1685; ^1H NMR (400 MHz, DMSO-d_6): δ = 12.3 (s, 1H, NH), 7.5 (s, 1H, =CH), 7.9 (d, 1H, Ar), 6.9 (d, 1H, Ar), 6.6 (m, 1H, Ar).

5-(3,4,5-Trimethoxybenzylidene)-1,3-thiazolidine-2,4-dione (5c): Yield: 90 %; m.p.: 210 °C; IR (KBr, ν_{max}, cm^{-1}): 3197, 2993, 2949, 1749, 1699; ^1H NMR (400 MHz, DMSO-d_6): δ = 12.55 (s, 1H, NH), 7.71 (s, 1H, =CH), 6.8 (s, 2H, Ar), 3.7 (s, 3H, CH_3). 3.8 (s, 6H, $2CH_3$); LC-MS: *m/z* (M +1) calcd. for $C_{13}H_{13}NO_5S$: 296.1; found: 296.1.

5-[(Naphthalene-1-yl) methylidene]-1,3-thiazolidine-2,4-dione (5d): Yield: 87 %; m.p.: 234-236 °C; IR (KBr, ν_{max}, cm^{-1}): 3120, 3010, 2766, 1742, 1693; ^1H NMR (400 MHz, DMSO-d_6): δ = 12.64 (s, 1H, NH), 8.41 (s, 1H, =CH), 8.1 (d, 1H, Ar), 7.9 (m, 2H, Ar), 7.5-7.6 (m, 4H, Ar).

5-(4-Hydroxybenzylidene)-1,3-thiazolidine-2,4-dione (5e): Yield: 86 %; m.p.: 310 °C (lit. 309-310 °C [28]); IR (KBr, ν_{max}, cm^{-1}): 4302, 3126, 3004, 2790, 1724, 1678; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.35 (s, 1H, NH), 10.21 (s, 1H, OH), 7.6 (s, 1H, =CH), 7.4 (d, 2H, Ar), 6.9 (d, 2H, Ar).

5-(3-Nitrobenzylidene)-1,3-thiazolidine-2,4-dione (5f): Yield: 95 %; m.p.: 188 °C (lit. 187-189 °C [28]); IR (KBr, ν_{max}, cm^{-1}): 3165, 3052, 2772, 1747, 1695, 1534, 1353; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.72 (s, 1H, NH), 7.92 (s, 1H, =CH), 8.4 (t, 1H, Ar), 8.28 (dq, 1H, Ar), 7.98 (d, 1H, Ar), 7.7 (t, 1H, Ar); LC-MS: *m/z* (M +1) calcd. for $C_{10}H_6N_2O_4S$: 251; found: 251

5-(4-Chlorobenzylidene)-1,3-thiazolidine-2,4-dione (5g): Yield: 92 %; m.p.: 228-229 °C (lit. 228 °C [28]); IR (KBr, ν_{max}, cm^{-1}): 3144, 3048, 2763, 1722, 1609; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.57 (s, 1H, NH), 7.74 (s, 1H, =CH), 7.49-7.55(m, 4H, Ar).

5-(2-Nitrobenzylidene)-1,3-thiazolidine-2,4-dione (5h): Yield: 92 %; m.p.: 218-220 °C; IR (KBr, ν_{max}, cm^{-1}): 3155, 3056, 2768, 1741, 1682; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.46 (s, 1H, NH), δ 8.02 (s, 1H, =CH), 8.18 (dq, 1H, Ar), 7.83 (t, 1H, Ar), 7.7-7.6 (m, 2H, Ar).

5-(4-Hydroxy-3-methoxybenzylidene)-1,3-thiazolidine-2,4-dione (5i): Yield: 90 %; m.p.: 195-197 °C (lit. 194-196 °C [23]); IR (KBr, ν_{max}, cm^{-1}): 3486, 3225, 3018, 2783, 1734, 1677; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.33 (s, 1H, NH), 9.82 (s, 1H, Ar-OH), 7.67 (s, 1H, =CH), 7.0 (d, 1H, Ar), 7.03 (dq, 1H, Ar), 6.9 (d, 1H, Ar), 3.87 (s, 3H, CH_3).

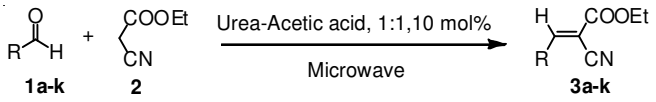
5-(4-Bromobenzylidene)-1,3-thiazolidine-2,4-dione (5j): Yield: 90 %; m.p.: 262-264 °C; IR (KBr, ν_{max}, cm^{-1}): 3148, 3052, 2764, 1749, 1722; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.61 (s, 1H, NH), 7.75 (s, 1H, =CH), 7.6 (d, 2H, Ar), 7.5-7.4 (d, 2H, Ar). LC-MS: *m/z* (M +1) calcd. for $C_{10}H_6NO_2SBr$: 284.9; found: 284.9

5-(3-Chlorobenzylidene)-1,3-thiazolidine-2,4-dione (5k): Yield: 95 %; m.p.: 244-246 °C; IR (KBr, ν_{max}, cm^{-1}): 3166, 3052, 2774, 1745, 1677; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.62 (s, 1H, NH), 7.71 (s, 1H, =CH), 7.54 (s, 1H, Ar), 7.42-7.54 (m, 3H, Ar).

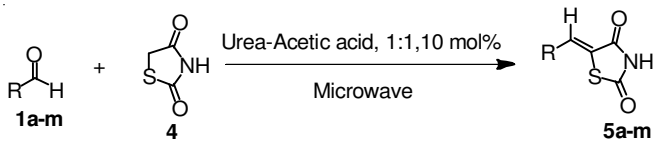
5-(2-Methoxybenzylidene)-1,3-thiazolidine-2,4-dione (5l): Yield: 95 %; m.p.: 260-262 °C; IR (KBr, ν_{max}, cm^{-1}): 3135, 3028, 2769, 1738, 1677; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.53 (s, 1H, NH), 8.00 (s, 1H, =CH), 7.4 (m, 1H, Ar), 7.3 (dq, 1H, Ar), 7.09-7.04 (m, 2H, Ar); LC-MS: *m/z* (M +1) calcd. for $C_{11}H_9NO_3S$: 236; found: 236.1.

RESULTS AND DISCUSSION

In this report a simple, efficient, solvent free and rapid method for microwave-assisted synthesis of ethyl α-cyanocinnamates (**3**) and 5-arylidine-2,4-thiazolidinediones (**5**) is demonstrated. Various aromatic aldehydes (**1**) react with active methylene compounds ethyl cyanoacetate (**2**) and 1,3-thiazolidine-2,4-diones (**4**) catalyzed by urea-acetic acid couple under solvent free microwave irradiation condition (**Schemes I** and **II**). The reaction was rapid completed within 1-2 min and gave desired products in good to excellent yield. It was observed that the reaction does not proceed when performed without urea-acetic or one of them and no effect on increasing in concentration of



Scheme-I: Synthesis of ethyl α-cyanocinnamates



Scheme-II: Synthesis of 5-arylidine-2,4-thiazolidinediones

catalyst from 10 mol % to 20 mol % on the reaction rate as well as yield of the product.

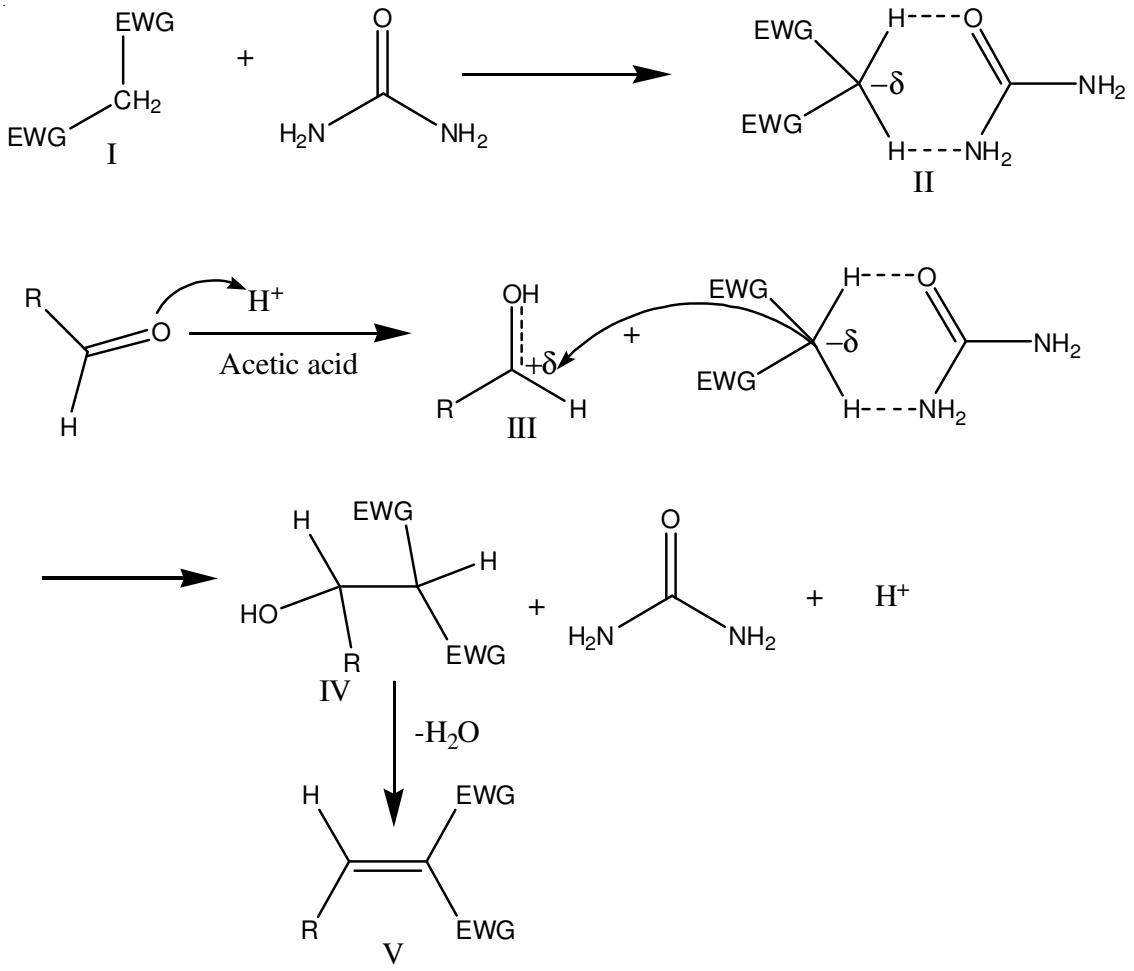
In most of the cases, products (**3a-3n**, Table-1 and **5a-5l**, Table-2) were identified by previously reported melting points and spectroscopic methods and newly synthesized compounds (**3c, 3e, 3i, 3k, 3n** Table-1 and **5c, 5d, 5h, 5j, 5k, 5l** Table-2) are characterized by IR, ^{1}H NMR and LC-MS. The generality of this approach has been demonstrated by the condensation of a wide verity of aromatic aldehydes including electron donating, electron withdrawing groups and carbocyclic, heterocyclic rings with active methylene compounds. It was found that in all cases high yield of product is formed except unsaturated aldehydes.

TABLE-1
KNOEVENAGEL CONDENSATION OF ETHYL CYANOACETATE WITH AROMATIC ALDEHYDES

Entry	R	Time (s)	Yield (%)[a,b]
3a	C_6H_5	50	96
3b	3-$NO_2C_6H_4$	50	96
3c	2-ClC_6H_4	60	92[c]
3d	3-OCH_3,4-OHC_6H_3	60	95
3e	3-ClC_6H_4	70	98[c]
3f	2-Furyl	50	92
3g	4-ClC_6H_4	60	94
3h	4-HOC_6H_4	50	90
3i	2-$NO_2C_6H_4$	50	95[c]
3j	4-$OCH_3C_6H_4$	80	90
3k	3,4,5-$(OCH_3)_3C_6H_2$	80	90[c]
3l	2-$OCH_3C_6H_4$	40	94
3m	4-Fluoro C_6H_4	50	94
3n	2-Naphthyl	60	90[c]
3k	Ph CH=CH	5-6 min	–[d]

[a]Yield of isolated product; [b]Compounds are characterized by IR, ^{1}H NMR, LC-MS and compared with authentic samples; [c]New compounds; [d]No reaction.

The possible mechanism (**Scheme-III**) for microwave assisted urea-acetic acid catalyzed Knoevengel condensation, involves the protonation of carbonyl oxygen of aromatic aldehydes by acetic acid (III) so increasing electrophilicity of carbonyl carbon while urea at high energy act as a base reacts with active methylene compound to forms intermediate (II), active hydrogen of active methylene is pulled toward the more electronegative atoms oxygen and nitrogen result in increase in nucleophilicity of methylene carbon. Then addition of resulting nucleophiles to the carbonyl group of aromatic aldehydes after dehydration gives the final product.



Scheme-III: Possible mechanism for Knoevengel condensation

TABLE-2
KNOEVENGEL CONDENSATION OF 1,3-THIAZOLIDINE-2,4-DIONES WITH AROMATIC ALDEHYDES

Entry	R	Time (min)	Yield (%)[a,b]
5a	C_6H_5	1.5	93
5b	2-Furyl	1.5	91
5c	$3,4,5\text{-}(OCH_3)_3\,C_6H_2$	1.5	90[c]
5d	2-Naphthyl	2.0	87[c]
5e	$4\text{-HO}\,C_6H_4$	2.0	86
5f	$3\text{-}NO_2\,C_6H_4$	1.5	95
5g	$4\text{-Cl}\,C_6H_4$	2.0	92
5h	$2\text{-}NO_2C_6H_4$	1.5	92[c]
5i	$4\text{-OH-3-}OCH_3\,C_6H_3$	1.5	90
5j	$4\text{-Br}\,C_6H_4$	1.5	90[c]
5k	$3\text{-Cl}\,C_6H_4$	2.0	95[c]
5l	$2\text{-}OCH_3\,C_6H_4$	1.5	95[c]
5m	Ph CH=CH	5-6[a]	–[d]

[a]Yield of isolated product; [b]All compounds are characterized by IR, ^{1}H NMR, LC-MS and compared with authentic samples; [c]New compounds; [d]No reaction.

Possible mechanism for microwave assisted urea-acetic acid catalyzed Knoevengel condensation is shown in **Scheme-III**.

Conclusion

In conclusion, microwave assisted, urea-acetic acid catalyzed condensation of active methylene compounds such as ethyl cyanoacetate and 1,3-thiazolidine-2,4-diones with aromatic aldehydes improves in terms of simple workup, short reaction time and good to excellent yield.

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