

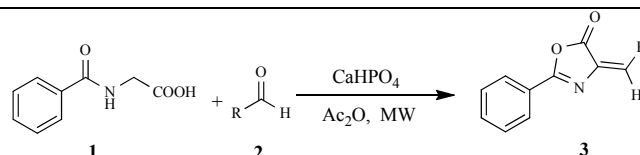
MICROWAVE-ASSISTED EFFICIENT AND MILD SYNTHESIS OF AZLACTONE DERIVATIVES

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A convenient and mild procedure for the synthesis of azlactones in the presence of catalytic amounts of calcium hydrogen phosphate as a green, inexpensive and environmentally benign catalyst has been demonstrated. The present protocol is operationally simple and offers some advantages such as good yields, short reaction time, simple work-up, low cost and reusability of catalyst, which makes this method mild and eco-friendly.



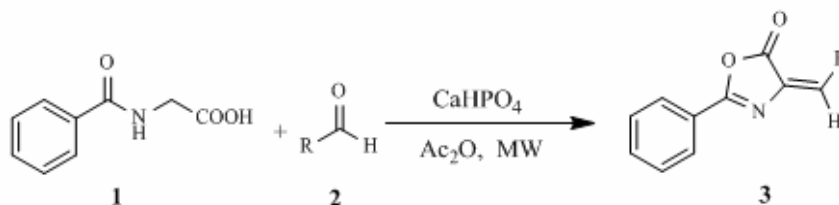
INTRODUCTION

The wide range of biological and pharmaceutical properties are reported for Azlactone derivatives and they have attracted much chemical interest.^{1,2} They are appropriate building blocks and valuable intermediates for the preparation of diverse biologically active molecules, including amino acids,^{3,4} heterocyclic compounds,⁵ and biosensors and photosensitive devices for proteins.⁶ Furthermore, these compounds are pharmaceutically active agent such as anticancer, antitumor, antimicrobial, anti-inflammatory, anti-hypertensive, and inhibitor of central nervous system.⁷⁻¹⁰ After primary synthesis report in 1893 by Erlenmeyer¹¹, several other dehydrating agent and catalysts such as perchloric acid,¹² polyphosphoric acid,¹³ Al₂O₃,¹⁴ supported KF,¹⁵ Bi(OAc)₃,¹⁶ Bi(OTf)₃,¹⁷ Yb(OTf)₃,¹⁸ Ca(OAc)₂,¹⁹ organic-inorganic hybrid polyoxometalates,²⁰ TsCl-DMF²¹ and functionalized magnetic nanocatalyst²² have been employed in azlactones synthesis. However, some of these procedures have some disadvantageous drawbacks, such as long

reaction time, unsatisfactory yields, use of expensive, corrosive and non-reusable catalysts and rigorous work-up procedures. Therefore, the development of a mild, eco-friendly and more convenient method for synthesis of azlactones without using any hazardous solvents and green catalyst is still in demand.

Hydrogen phosphate salts are inexpensive, easily available and safe salts that are used in some organic transformation.²³⁻²⁷ CaHPO₄ is an inexpensive hydrogen phosphate salt that have been found reliable use in industry and life. It is used in powder form in some toothpaste, chewing gums and in food processing industry to act as acidity regulator, anti-caking agent, dough modifier, skeletal repairing, and emulsifier.²⁸⁻³⁰ As a part of our research interest towards the development of efficient one-pot synthetic methodologies in eco-friendly conditions,^{31,32} herein we wish to explore an efficient microwave-assisted synthesis of azlactone derivatives via the one-pot condensation of aldehydes and hippuric acid under solvent-free conditions using CaHPO₄ as an efficient, mild, inexpensive and environmentally benign catalyst (Scheme 1).

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Scheme 1 – The CaHPO₄ catalyzed Erlenmeyer azlactones synthesis.

EXPERIMENTAL

1. Materials and methods

All chemicals were purchased from Merck or Acros chemical companies and used without further purification unless otherwise stated. Tris-aldehyde (4,4',4''-((1,3,5-triazine-2,4,6-triyl)tris(oxy))tribenzaldehyde) was synthesized in laboratory according to reported method.³³ All known compounds were identified by comparison of their melting points and NMR data with the authentic samples. The IR spectra were recorded on a Unicam Galaxy Series FT-IR 5030 spectrophotometer using KBr discs. The ¹H and ¹³C NMR spectra were recorded on a Bruker Avance spectrometer operating at 400 or 300 and 100 or 75 MHz respectively in CDCl₃ with TMS as an internal standard (δ in ppm). Microwave irradiation was carried out in a National Microwave Oven, Model No. NN-K571MF (2450 MHz). Microanalyses were performed by the Elemental Analyzer (Elemental, Vario EL III) at the Arak University. All the reactions were monitored by thin layer chromatography performed on precoated silicagel 60F₂₅₄ plates (Merck) in EtOAc/n-Hexane (1:3) as an eluent.

2. General procedure for the microwave-assisted synthesis of azlactone derivatives Catalyzed by CaHPO₄

The appropriate aldehyde (1 mmol), hippuric acid (1 mmol), Ac₂O (1 ml) and CaHPO₄ as a catalyst (0.2 mmol) was mixed in a test tube. Then, the reaction mixture was irradiated using the microwave oven at a power output of 300W for the appropriate time (Table 2). After completion of the reaction as indicated by TLC, the reaction mixture was cooled to room temperature. 5 ml Cold ethanol/water (1:1) was added and the mixture was stirred for 15 min until a yellow solid precipitated. An aqueous solution of NaHCO₃ (10 ml, 20%) was added, the solid products and the catalyst were filtered. The solid materials were dissolved in hot ethanol to remove the catalyst. The solvent was allowed to cool in room temperature to obtain crude products.

Spectral Data of the Selected Compounds (3a-s)

4-benzylidene-2-phenyloxazol-5(4H)-one (3a): IR (KBr): ν_{\max} = 3070, 1789, 1651, 1552, 1450, 1305, 1158, 760, 657 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ = 2.27 (s, 1 H), 7.42–7.63 (m, 6 H), 8.18–8.21 (m, 4H) ppm. Anal Calcd for C₁₆H₁₁NO₂: C, 77.10; H, 4.45; N, 5.62. Found: C, 77.31; H, 4.53; N, 5.58.

4-(4-methylbenzylidene)-2-phenyloxazol-5(4H)-one (3b): IR (KBr): ν_{\max} = 3065, 1796, 1653, 1607, 1557, 1491, 1298, 1161, 1001, 889, 775 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ = 2.41 (s, 3 H), 7.21–7.34 (m, 3 H), 7.50–7.62 (m, 3H), 8.11–8.19 (m, 4H) ppm. Anal Calcd for C₁₇H₁₃NO₂: C, 77.55; H, 4.98; N, 5.32. Found: C, 77.69; H, 5.08; N, 5.41.

4-(4-nitrobenzylidene)-2-phenyloxazol-5(4H)-one (3i): IR (KBr): ν_{\max} = 3090, 1797, 1655, 1610, 1530, 1520, 1413, 1342, 1298, 1224, 1161, 1107, 981, 846, 775, 686, 559 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ = 8.36 (ABq, 8.4 Hz, 4H), 8.23

(d, J = 8.4 Hz, 2H), 7.7 (t, J = 7.35 Hz, 1H), 7.59 (t, J = 7.35 Hz, 2H), 7.27 (s, 1H) ppm; ¹³C NMR (75 MHz, CDCl₃): 166.7, 165.6, 148.3, 139.3, 136.3, 134.2, 132.7, 129.1, 128.8, 127.5, 124.9, 123.9 ppm. Anal Calcd for C₁₆H₁₀N₂O₄: C, 65.31; H, 3.43; N, 9.52. Found: C, 65.49; H, 3.52; N, 9.43.

4-(4-isopropylbenzylidene)-2-phenyloxazol-5(4H)-one (3j): IR (KBr): ν_{\max} = 3000, 2960, 2870, 1797, 1655, 1604, 1552, 1448, 1327, 1163, 1053, 983, 866, 698, 570 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 8.11 (d, J = 7.2 Hz, 2H), 8.08 (d, J = 6 Hz, 2H), 7.54 (t, J = 5.4 Hz, 1H), 7.46 (t, J = 5.5 Hz, 2H), 7.28 (d, J = 6.3 Hz, 2H), 7.19 (s, 1H), 2.9 (m, 1H), 1.2 (d, J = 5.1 Hz, 6H) ppm; ¹³C NMR (100 MHz, CDCl₃): 167.8, 163.0, 152.8, 133.1, 132.7, 132.0, 131.2, 128.9, 128.2, 127.1, 126.3, 125.7, 34.3, 23.7 ppm. Anal Calcd for C₁₉H₁₇NO₂: C, 78.33; H, 5.88; N, 4.81. Found: C, 78.46; H, 5.95; N, 4.81.

4-(2,4-dichlorobenzylidene)-2-phenyloxazol-5(4H)-one (3k): IR (KBr): ν_{\max} = 3092, 1799, 1655, 1579, 1467, 1383, 1325, 1160, 1140, 1095, 981, 860, 758, 683, 569, 422 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ = 8.92 (d, J = 9.9 Hz, 1H), 8.19 (d, J = 8.1 Hz, 2H), 7.67–7.51 (m, 4H), 7.41 (d, J = 8.4 Hz, 1H), 7.27 (s, 1H); ¹³C NMR (75 MHz, CDCl₃): 165.9, 164.7, 137.2, 137.1, 134.7, 133.9, 133.8, 130.0, 129.8, 129.0, 128.5, 127.6, 125.2, 124.8 ppm. Anal Calcd for C₁₆H₉Cl₂NO₂: C, 60.40; H, 2.85; N, 4.40. Found: C, 60.53; H, 2.90; N, 4.46.

4-(2,6-dichlorobenzylidene)-2-phenyloxazol-5(4H)-one (3l): IR (KBr): ν_{\max} = 3084, 1797, 1759, 1672, 1564, 1427, 1321, 1165, 981, 866, 777, 698 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ = 8.12 (d, J = 7.9 Hz, 2H), 7.62 (t, J = 7.4 Hz, 1H), 7.50 (t, J = 7.5 Hz, 2H), 7.44 (d, J = 8.0 Hz, 2H), 7.37 (s, 1H), 7.33 (t, J = 7.5 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃): δ = 165.8, 164.5, 137.8, 135.1, 133.7, 131.3, 130.4, 128.8, 128.6, 128.2, 126.4, 125.3 ppm. Anal Calcd for C₁₆H₉Cl₂NO₂: C, 60.40; H, 2.85; N, 4.40. Found: C, 60.51; H, 2.91; N, 4.37.

4-(3,4-dimethoxybenzylidene)-2-phenyloxazol-5(4H)-one (3m): IR (KBr): ν_{\max} = 3090, 3001, 2961, 2836, 1784, 1649, 1595, 1452, 1329, 1244, 1140, 1018, 866, 627 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ = 8.16 (s, 1H), 8.11 (d, J = 8 Hz, 1H), 7.49–7.62 (m, 5H), 7.19 (s, 1H), 6.94 (d, J = 8.3 Hz, 1H), 4.03 (s, 3H), 3.96 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ = 167.4, 161.9, 151.8, 148.8, 132.7, 131.6, 130.8, 128.7, 127.7, 127.6, 126.7, 125.6, 110.6, 55.7, 55.6; Anal Calcd for C₁₈H₁₅NO₄: C, 69.89; H, 4.89; N, 4.53. Found: C, 69.84; H, 4.93; N, 4.61.

2-phenyl-4-(3,4,5-trimethoxybenzylidene)oxazol-5(4H)-one (3n): IR (KBr): ν_{\max} = 2999, 2942, 2841, 1784, 1761, 1655, 1578, 1506, 1452, 1329, 1256, 1126, 1003, 966, 851, 687 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ = 8.14 (d, J = 7.8 Hz, 2H), 7.55–7.57 (m, 5H), 7.18 (s, 1H), 3.99 (s, 6H), 3.96 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ = 167.3, 162.9, 153.0, 141.1, 133.1, 132.2, 131.5, 128.9, 128.8, 128.0, 125.5, 109.7, 60.9, 56.0; Anal Calcd for C₁₉H₁₇NO₅: C, 67.25; H, 5.05; N, 4.13. Found: C, 67.34; H, 5.10; N, 4.19.

4-((4,6-bis(4-((Z)-5-oxo-2-phenyloxazol-4(5H)-ylidene)methyl)phenoxy)-1,3,5-triazin-2-yl)oxy) benzaldehyde (3o): IR (KBr): ν_{\max} = 1795, 1701, 1656, 1566, 1500, 1365, 1298, 1211, 1161, 1076, 983, 842, 698, 561 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 7.20–7.63 (m, 14H, ArH and =CH), 8.17 (t, J = 6.6 Hz, 6H, ArH), 8.25 (d, J = 8.4 Hz, 4H, ArH),

9.99 (s, 1H, -CHO) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ = 120.9, 121.0, 121.4, 124.3, 126.9, 127.3, 127.9, 128.8, 128.9, 130.3, 130.7, 132.4, 132.7, 152.1, 154.8, 162.8, 166.3, 172.4, 189.6 ppm.; Anal Calcd for $\text{C}_{42}\text{H}_{25}\text{N}_5\text{O}_8$: C, 69.32; H, 3.46; N, 9.62. Found: C, 69.21; H, 3.55; N, 9.71.

2-phenyl-4-(thiophen-2-ylmethylene)oxazol-5(4H)-one (3q): IR (KBr): ν_{max} = 3091, 790, 1647, 1555, 1460, 1327, 1298, 1153, 1053, 982, 856, 799, 698, 534, 492 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ =8.19 (d, J = 7.8 Hz, 2H), 7.75 (d, J = 7.8 Hz, 1H), 7.64-7.54 (m, 4H), 7.5 (s, 1H), 7.19 (dd, J = 4.2, 4.5 Hz, 1H) ppm; ^{13}C NMR (75 MHz, CDCl_3): δ =166.9, 162.4, 137.6, 135.3, 134.9, 133.1, 130.9, 128.9, 128.3, 127.9, 125.6, 124.8 ppm. Anal Calcd for $\text{C}_{14}\text{H}_9\text{NO}_2\text{S}$: C, 65.87; H, 3.55; N, 5.49; S, 12.56. Found: C, 65.77; H, 3.61; N, 5.43; S, 12.67.

RESULTS AND DISCUSSION

Initially, as a model, the condensation reaction of benzaldehyde, hippuric acid and acetic anhydride was examined in the presence of CaHPO_4 in organic solvents and solvent-free condition under microwave irradiation (Table 1). As shown in Table 1, it was found that microwave-assisted solvent-free condition is a more efficient (Table 1, entry 6) over the organic solvents. When the reaction was carried out in the presence of different amounts of catalyst, the highest yield was obtained with 0.2 mmol (0.03 g) of catalyst under microwave-assisted solvent-free condition after 5 minutes. Increasing the amount of catalyst to 0.4 mmol did not affect the product yield (Table 1, entry 8). Moreover, the catalyst is essential and in the absence of the catalyst, only 20 % of the corresponding azlactone was produced (Table 1, entry 9). The recyclability of CaHPO_4 was investigated. The catalyst was recovered easily by simple filtration, washed with hot ethanol and dried under vacuum and reused in a subsequent reaction. As seen in Table 1, entry 7, the catalyst

showed no substantial reduction in the activity even after four runs.

After optimization of condition for azlactones synthesis and in order to investigate the generality of this procedure, a variety of aromatic aldehydes bearing electron-withdrawing and electron-donating groups and heterocyclic aldehydes were reacted with hippuric acid and Ac_2O in the presence of CaHPO_4 under microwave-assisted solvent-free conditions. The results (Table 2) indicated that the corresponding azlactones were synthesized in 84-95 % isolated yield in 5-10 min. Aliphatic aldehydes were also examined under the same conditions, but the corresponding products were not isolated.

After completion of the reaction, the catalyst was separated by simple filtration and washed several times with ethanol. The reusability of the catalyst was found to be effective up to several cycles without significant loss in the activity (Table 1, entry 7). Products were characterized by FT-IR, ^1H NMR, and ^{13}C NMR analysis.

We synthesized the tris-aldehyde (4,4',4''-((1,3,5-triazine-2,4,6-triyl)tris(oxy))tribenzaldehyde) according to the reported method,³³ then the obtained tripodal reacted with three equimolar hippuric acid to yield the tripodal azlactone under mild condition but unexpectedly the isolated product was dipodal azlactone and only two aldehyde functional group reacted with hippuric acid (Scheme 2 and Table 2). Increasing the reaction time didn't produce the desired tripodal azlactone. The structures of obtained product, 4-(((4,6-bis(4-((Z)-(5-oxo-2-phenyloxazol-4(5H)-ylidene)methyl)phenoxy)-1,3,5-triazin-2-yl)oxy)benzaldehyde (3o), has been approved by its elemental analysis, FT-IR, ^1H NMR and ^{13}C NMR spectral data.

Table 1

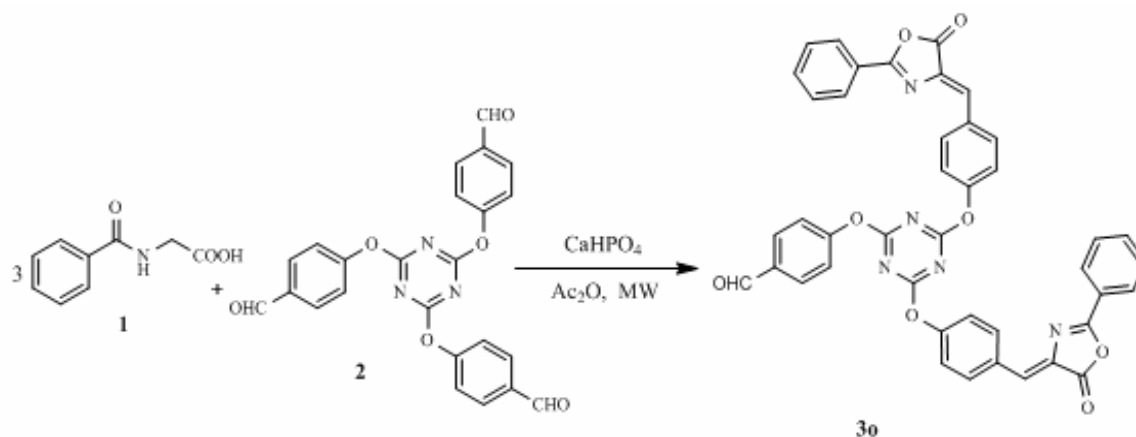
Optimization of reaction conditions for synthesis of azlactones (Table 2, entry 1)^a.

Entry	Catalyst (mmol)	Solvent	Condition	Time (min)	Yield (%) ^b
1	CaHPO_4 (0.2)	THF	Reflux	100	45
2	CaHPO_4 (0.2)	DMF	Reflux	100	61
3	CaHPO_4 (0.2)	CHCl_3	Reflux	100	38
4	CaHPO_4 (0.05)	-	MW	10	54
5	CaHPO_4 (0.1)	-	MW	5	75
6	CaHPO_4 (0.2)	-	MW	5	93
7	CaHPO_4 (0.2)	-	MW	5	93, 87, 85, 82 ^c
8	CaHPO_4 (0.4)	-	MW	5	91
9	-	-	MW	5	20
10	CaHPO_4 (0.2)	-	110 °C	90	81

^a Benzaldehyde (1 mmol), hippuric acid (1 mmol), Ac_2O (1 ml).

^b Isolated yields.

^c Catalyst reused in four consecutive reactions.



Scheme 2 – The synthesis of unexpected dipodal azlactone from tris-aldehyde.

Table 2

Synthesis of azlactone derivatives catalyzed by CaHPO₄ under microwave irradiation

Entry	Aldehyde	Time(min)	Yield (%) ^a	Product	M.P. (°C)	
					Found ^b	Reported [Lit.]
1	C ₆ H ₅ CHO	5	93	3a	169-171	167-168[14]
2	4-MeC ₆ H ₄ CHO	8	88	3b	139-141	143-144[14]
3	4-ClC ₆ H ₄ CHO	8	95	3c	193-194	188-189[22]
4	3-NO ₂ C ₆ H ₄ CHO	8	94	3d	172-174	171-172[22]
5	4-BrC ₆ H ₄ CHO	8	89	3e	194-195	197-199[22]
6	4-N(Me) ₂ C ₆ H ₄ CHO	10	91	3f	215-216	210-211[21]
7	2-ClC ₆ H ₄ CHO	10	92	3g	158-160	160-161[21]
8	4-FC ₆ H ₄ CHO	7	93	3h	187-199	182-185[14]
9	4-NO ₂ C ₆ H ₄ CHO	8	93	3i	232-234	234-236[21]
10	4-(CH ₃) ₂ CHC ₆ H ₄ CHO	10	84	3j	129-130	-
11	2,4-(Cl) ₂ C ₆ H ₃ CHO	8	85	3k	158-160	160-161[21]
12	2,6-Cl ₂ C ₆ H ₄ CHO	7	92	3l	159-160	153-155[22]
13	3,4-(MeO) ₂ C ₆ H ₃ CHO	10	90	3m	153-155	150-152[19]
14	3,4,5-(MeO) ₃ C ₆ H ₂ CHO	8	87	3n	205-208	203-204[22]
15	4,4',4''-((1,3,5-triazine-2,4,6-triyl)tris(oxy))tribenzaldehyde	10	90	3o	190-192	-
16	Pyridine-2-CHO	10	89	3p	161-163	168-169[14]
17	Thiophene-2-CHO	10	92	3q	175-177	170-171[14]
18	5-(Me)-Thiophene-2-CHO	10	90	3r	150-152	145-147 [15]

^a Isolated yields.^b Melting points are not corrected.

CONCLUSIONS

The CaHPO₄ catalyst has been successfully used for microwave-assisted synthesis of Azlactone derivatives via the condensation of hippuric acid with a wide variety of aromatic and

heteroaromatic aldehydes under solvent-free conditions. Furthermore two novel azlactones have been produced and characterized carefully. Short reaction times, removal of the solvent, the simple experimental and work-up procedure combined with the reusability of catalyst and good yields

make this method as a mild and eco-friendly protocol for azlactones synthesis.

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