Title: Vitamin B12: An efficient type catalyst for the one-pot synthesis of 3,4,5-trisubstituted furan-2(5*H*)-ones and *N*-aryl-3-aminodihydropyrrol-2-one-4-carboxylates

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PII: S1001-8417(15)00311-3
DOI: http://dx.doi.org/doi:10.1016/j.cclet.2015.07.025
Reference: CCLET 3402

To appear in: *Chinese Chemical Letters*

Received date: 12-6-2015
Revised date: 7-7-2015
Accepted date: 13-7-2015

Please cite this article as: M. Kangani, M.-T. Maghsoodlou, N. Hazeri, Vitamin B12: An efficient type catalyst for the one-pot synthesis of 3,4,5-trisubstituted furan-2(5*H*)-ones and *N*-aryl-3-aminodihydropyrrol-2-one-4-carboxylates, *Chinese Chemical Letters* (2015), http://dx.doi.org/10.1016/j.cclet.2015.07.025

Graphical Abstract

Vitamin B12: an efficient type catalyst for the one-pot synthesis of 3,4,5-trisubstituted furan-2(5*H*)-ones and *N*-aryl-3-aminodihydropyrrol-2-one-4-carboxylates

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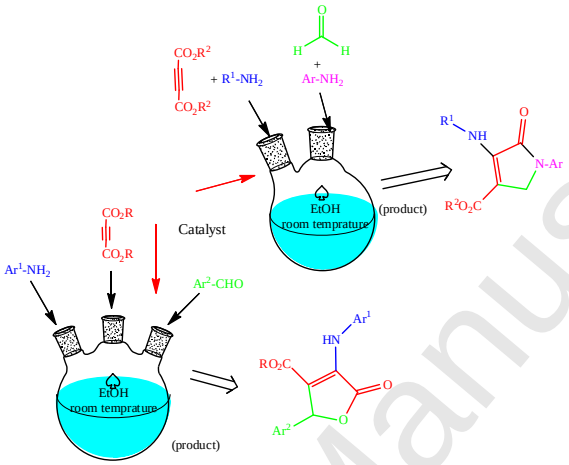

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Original article

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ARTICLE INFO

Article history:
Received 12 June 2015
Received in revised form 7 July 2015
Accepted 13 July 2013
Available online

Keywords:
Vitamin B12
3,4,5-Trisubstituted furan-2(5H)-ones
N-aryl-3-aminodihydropyrrol-2-one-4-carboxylates

ABSTRACT

Vitamin B12 was applied as catalyst for the one-pot three-component synthesis of 3,4,5-trisubstituted furan-2(5*H*)-ones from the condensation between aldehydes, amines and dialkylacetylendicarboxylates at ambient temperature in EtOH. In addition, *N*-aryl-3-aminodihydropyrrol-2-one-4-carboxylates were synthesis using mentioned catalyst at ambient temperature in EtOH from condensation between formaldehyde, amines, and dialkylacetylenedicarboxylates. This methodology has number of advantages such as: use of green and nonhazardous catalyst, clean work up, short reaction times, high yields and no need to column chromatography.

1. Introduction

Vitamin B12, also called cobalamin (Cbl), Cbl has been called nature's most beautiful cofactor and was identified as the anti-pernicious anemia factor from liver in 1948. Cbl shows biological activity in a very small amount. Cbl acts as the cofactor for two enzymes, *i.e.*, methylmalonyl-CoA mutase and methionine synthase, in humans. Both enzymes are important for health. The B 12 content in food is very low. Its greatest abundance is in meat, fish, and milk products; it is generally absent from fruits and vegetables, but nor, an edible green and purple seaweed, is a non-dairy product that contains a significant amount of B12 Cbl found in food is originally from these bacteria, in which the complex molecule is synthesized using at least 25 genes in the Cob operon. Cbl acts as the cofactor for two enzymes present in humans [1] (Fig. 1). The properties and reactivity of vitamin B12 derivatives have been extensively investigated ever since it was shown to possess a cobalt-carbon bond in the biological cofactors adenosyl and methylcobalamin [2-6]. These versatile organometallic complexes are used in a variety of enzymes to catalyze radical rearrangements and methyltransfers. Moreover, vitamin B12 has found use in organic chemistry for carbon-carbon bond formations [7-12].

Furanones are the five-member heterocyclic compounds possessing lactone ring in their structures. These heterocycles are the core structures of many bioactive natural products as well as synthetic drugs such as rubrolide, sarcophine, benfurodilhemisuccinate, *etc.* [13, 14]. 5*H*-Furan-2-onederivatives exhibit many pharmacological and biological activities including antifungal, antibacterial, anti-oxidants, anti-inflammatory, anti-microbial and anti-cancer agents [15–19]. Due to this wide range of abundance and applicability, various approaches toward substituted butenolides have been developed, which involve the use of organo-lithium [20], boronic acids [21,22], transition-metal catalysts such as $Pd(OAc)_2$ [23], Ru [24], Cu(II) [25], AuCl [26], and secondary amines [27]. However, many of these methods involve the use of expensive catalysts and hazardous reagents in stoichiometric amounts. A new route to the synthesis of furan skeletons was developed by Murthy *et al. via* the multi-component reaction of aromatic amines, aldehydes and acetylenic esters, which lead to the preparation of 3,4,5-substituted furan-2(5H)-one derivatives using *β*-cyclodextrin as a catalyst in water [28]. Recently, Nagarapu et al. reported that $SnCl_2$ can efficiently catalyze this reaction [29]. The presence of pyrrol-2-ones (5-lactams or g-lactams) in pharmaceuticals and natural products has continued to stimulate a great deal of interest in the development of new methodologies for their synthesis [30,31]. There are several bioactive natural molecules with a pyrrol-2-one moiety, such as holomycin and thiolutin [32], thiomarinol A4 [33], oteromycin [34], pyrrocidine A [35], quinolactacin C [36], and ypaoamide [37]. On the other hand, dihydropyrrol-2-ones have been successfully used as peptidomimetic [38], HIV integrase [39], herbicidals [40], DNA polymerase inhibitors [41], caspase-3 inhibitors [42] cytotoxic and antitumor agents [43], antibiotics [44], and also inhibitors of the annexin A2-S100A10 protein interaction [45]. Recently, a few methods have been reported for the synthesis of highly substituted dihydropyrrol-2-ones using one-pot, four-component reactions in the presence of catalyst, such as AcOH, I_2, benzoic acid, TiO_2 nanopowder or $Cu(OAc)_2{}^{-}H_2O$ [46–51]. However, some of these methods have drawbacks, such as high temperature and utilize a

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chlorinated solvent. Therefore, the development of a milder and more efficient route for one-pot synthesis of these important heterocycles is still in demand. Thus, in continue of our research on multi-component synthesis [52-55],we herein report a green synthesis of 3,4,5-trisubstituted furan-2(5*H*)-ones and *N*-aryl-3-aminodihydropyrrol-2-one-4-carboxylates using catalytic amount of vitamin B12 as catalyst at ambient temperature in EtOH (Schemes 1 & 2).

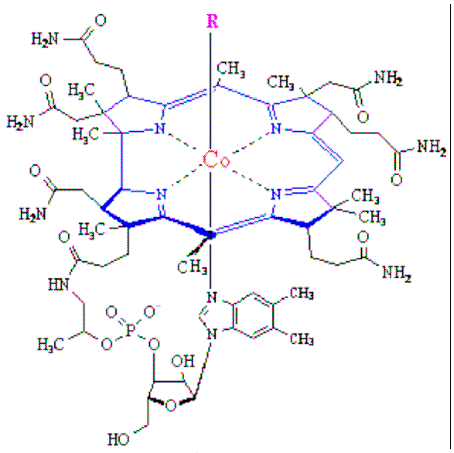


Fig 1. The structure of vitamin B12.

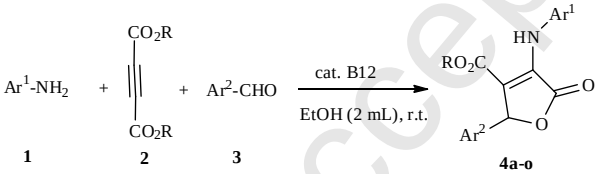
2. Experimental

2.1. Chemistry

Chemicals were purchased from Merck (Darmastadt,Germany), Acros (Geel, Belgium) and Fluka (Buchs, Switzerland), and used without further purification. The Vitamin B12 was purchased from the Sigma-Aldrich company. Melting points were taken on an Electrothermal 9100 apparatus. IR spectra were obtained on a JASCO FT/IR-460 plus spectrometer. The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX-400 Avanve instrument with $CDCl_3$ as solvent and using TMS as internal reference at 400 MHz and 100 MHz, respectively.

2.2 General procedure for the synthesis of 3,4,5-trisubstituted furan-2(5H)-ones

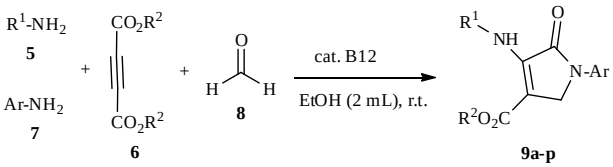
A mixture of amine **1** (1 mmol), dialkylacetylenedicarboxylate **2** (1 mmol), aromatic aldehyde **3** (1mmol) and vitamin B12 (0.001g) in EtOH (2 mL) was stirred at ambient temperature for appropriate time (Scheme 1). After completion of the reaction (monitored by TLC), the water was added to produce solid precipitate, and the precipitate was filtered off and washed with ethanol (3×2 mL) to give the pure product **4**. The structures of the synthesized compounds were characterized by their IR, ^{1}H NMR and ^{13}C NMR spectra and were found to be identical with data described in the literature.



Scheme 1. Synthesis of 3,4,5-trisubstituted furan-2(5H)-ones in the presence of vitamin B12 as catalyst in EtOH at ambient temperature.

2.3 General procedure for the synthesis of N-aryl-3-aminodihydropyrrol-2-one-4-carboxylates

A mixture of amin **5** (1 mmol) and dialkylacetylenedicarboxylate **6** (1 mmol) in EtOH (2 mL) was stirred for 25 min. Next, amine **7** (1 mmol), formaldehyde **8** (37% solution, 1.5 mmol) and vitamin B12 (0.001 g) were added in successively. The reaction mixture was allowed to stir at ambient temperature for appropriate time. After completion of the reaction (monitored by TLC), the water was added to produce solid precipitate, and the precipitate was filtered off and washed with ethanol (3× 2 mL) to give the pure product **9 (**Scheme 2). The structures of the synthesized compounds were characterized by their IR, ^{1}H NMR and ^{13}C NMR spectra and were found to be identical with data described in the literature [47,48].



Scheme 2. Synthesis of *N*-aryl-3-aminodihydropyrrol-2-one-4-carboxylates in the presence of vitamin B12 as catalyst in EtOH at ambient temperature.

Methyl 2,5-dihydro-5-oxo-2-phenyl-4-(phenylamino)furan-3-carboxylate (**4a**): White solid; IR (KBr, cm^{-1}): 3260, 3208, 1702, 1661; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.77 (s, 3 H, OCH_3), 5.76 (s, 1H, benzylic), 7.13 (t, 1H, *J* = 7.3 Hz),7.24–7.31 (m, 7H), 7.52 (d, 2H, *J* = 8 Hz), 8.90 (br, NH, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.3 and 162.7 (CO), 156.3, 136.1, 134.9,129.0, 128.7, 128.6, 127.4, 125.9, 122.3, 112.8 (C of aromatic), 61.6(C of methoxy), 52.1 (C of benzylic).

Methyl 4-(*p*-tolylamino)-2,5-dihydro-5-oxo-2-phenylfuran-3-carboxylate (**4b**): White solid; IR (KBr, cm^{-1}): 3228, 2950, 1706, 1677, 1513; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.27 (s, 3H, CH_3), 3.76 (s, 3H, OCH_3), 5.72 (s, 1H, benzylic),7.09 (d, 2H, *J* = 8 Hz), 7.22–7.270 (m, 5H, aromatic), 7.34 (d, 2H, *J* = 8.4 Hz), 8.86 (br, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.3 and 162.8 (CO), 156.4, 135.8, 135.0, 133.5, 129.6, 128.6,128.5, 127.5, 122.4, 112.6 (C of aromatic), 61.3 (C of methoxy), 52.0 (C of benzylic), 20.9 (C of methyl).

Ethyl 2-(4-cyanophenyl)-2,5-dihydro-5-oxo-4-(phenylamino)-furan-3-carboxylate (**4e**): White solid; IR (KBr, cm^{-1}): 3293 (NH), 2977, 2225 (CN), 1731, 1684,1666, 1500; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.23 (t, 3H, *J* = 7.2 Hz,CH_3), 4.24 (q, 2H, *J* = 7.2 Hz, CH_2), 5.82 (s, 1H, benzylic), 7.17 (t, 1H, *J* = 7.2 Hz), 7.32–7.47 (m, 6H, aromatic), 7.59 (d, 2H, *J* = 8 Hz), 9.03 (br, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.6 and 162.5 (CO), 156.89, 140.8, 135.7, 132.5, 129.2, 128.3, 126.3, 122.1, 118.1,112.6 (C of aromatic), 112.2 (C of CN), 61.6 (C of methoxy), 60.8 (C of benzylic),14.0 (C of ethoxy).

Methyl 2,5-dihydro-5-oxo-1-phenyl-4-(phenylamino)-1*H*-pyrrole-3-carboxylate (**9a**): White solid, IR (KBr, cm^{-1}): 3310 (NH), 1705, 1684, 1645; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.76 (s, 3H, OCH_3), 4.57 (s, 2H, CH_2), 7.16-7.23 (m, 4H, ArH),7.34 (t, 2H, *J* = 8.0 Hz, ArH), 7.42 (t, 2H, *J* = 8.0 Hz, ArH), 7.81 (d, 2H, *J* = 8.0 Hz, ArH), 8.05 (br s,1H, NH).

Ethyl 4-(p-tolylamino)-2,5-dihydro-5-oxo-1-*p*-tolyl-1*H*-pyrrole-3-carboxylate (**9d**): Yellow solid, IR (KBr, cm^{-1}): 3310 (NH), 1707, 1682, 1649; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.25 (t, 3H, *J* = 7.2 Hz, OCH_2CH_3), 2.36 (s, 3H, CH_3), 2.37 (s, 3H, CH_3),4.23 (t, 2H, *J* = 7.2 Hz, OCH_2CH_3), 4.52 (s, 2H, CH_2), 7.06 (d, 2H, *J* = 8.4 Hz, ArH), 7.14 (d, 2H, *J* = 8.0 Hz, ArH), 7.21 (d, 2H, *J* =8.4 Hz, ArH), 7.69 (d, 2H, *J* = 8.8 Hz, ArH), 8.01 (br s, 1H, NH);^{13}C NMR (100 MHz, $CDCl_3$): δ 164.7 and163.7 (CO), 143.1,136.3, 136.2, 134.6, 134.2, 129.6, 128.9, 122.9, 119.1, 102.4(C of aromatic), 48.3 (CH_2-N), 60.2 (C of methoxy), 21.0 (Cof methyl), 20.9 (C of methyl), 14.2 (C of ethoxy).

Methyl 4-(benzylamino)-1-*p*-tolyl-2,5-dihydro-5-oxo-1*H*-pyrrole-3-carboxylate (**9m**): White solid, IR (KBr, cm^{-1}): 3310 (NH), 1704, 1682, 1646; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.34 (t, 3H, *J* = 7.2 Hz, OCH_2CH_3), 4.27 (t, 2H, *J* = 7.2 Hz, OCH_2CH_3), 4.41 (s, 2H, CH_2-N), 5.12 (d, 2H, *J* = 6.4 Hz, CH_2-NH), 6.90 (br s, 1H, NH), 7.28-7.37 (m, 5H, ArH), 7.52 (d, 2H, *J* = 8.8 Hz, ArH), 7.70 (d, 2H, *J* = 8.8 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.6 and 164.3 (CO), 139.5, 136.2, 134.8, 129.6, 128.7, 127.5, 127.3, 119.4, 97.1(C of aromatic),51.0 (C of methoxy), 48.0 and 46.6 (CH_2-N), 20.9 (C of methyl).

3. Results and discussion

The reaction condition was optimized for the synthesis of 3,4,5-substituted furan-2(5*H*)-one derivatives, for this purpose the reaction between benzaldehyde, aniline and dimethylacetylendicarboxylate was chosen as a model system. The reaction was initially carried out in different conditions (Table 1). Since we wanted to present a green and environmentally benign protocol for this experiment, we did not test organic solvents under these conditions.

Table 1
Optimization of the reaction conditions for the synthesis of **4a** in EtOH.[a]

Entry	Catalyst (mo l %)	Time (h)	Isolated yields (%)
1	TiO_2 (10)	10	25
2	$Zn(SO_4)_2$-$7H_2O$ (10)	9	25
3	$Zr(NO_3)_4$ (10)	9	30
4	$ZrCl_4$ (10)	9	50
5	$HClO_4$–SiO_2 (10)	9	20
6	$KHSO_4$ (10)	9	26
7	NH_4HSO_4 (10)	9	40
8	Vitamin B12 (7.35 * 10-5)	2	85

[a] Amounts of material in all reactions: aldehyde (1 mmol), aniline (1 mmol) and DMAD (1 mmol).

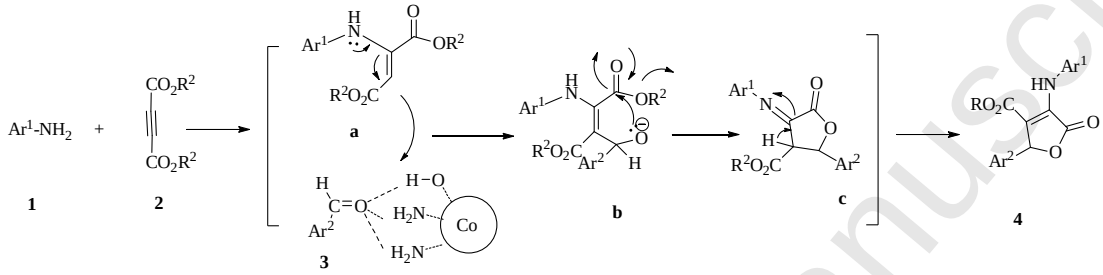
The scope and efficiency of these procedures were explored for the synthesis of a wide variety of substituted 3,4,5-substituted furan-2(5*H*)-ones (Table 2). Generally, the results were excellent in terms of yield and product purity. A series of aromatic aldehydes and amines were investigated (Table 2, products **4a–o**). In all cases, aromatic aldehydes containing electron-donating groups gave shorter times and higher yields than that with electron-withdrawing groups.

Table 2
Synthesis of 3,4,5-substituted furan- 2(5*H*)-ones.

Product	Ar [1]	Ar[2]	R	Time (min)	Isolated yield (%)	mp (°C)	Lit.mp (°C) [Ref]
4a	Ph	Ph	Me	120	85	159-162	159-162 [24]

4b	Ph	4-Me–C_6H_4	Me	60	75	280-282	284-287 [24]
4c	4-Me-C_6H_4	Ph	Me	60	85	179-180	181-183 [24]
4d	4-Cl-C_6H_4	Ph	Me	60	75	148–150	149-152 [24]
4e	4-CN-C_6H_4	Ph	Et	120	80	152–154	152–154 [52]
4f	Ph	4-F-C_6H_4	Me	60	85	290-293	293-295 [25]
4g	Ph	4-Cl-C_6H_4	Me	60	85	167–170	165–166 [53]
4h	Ph	3-NO_2-C_6H_4	Me	90	80	199-202	203-205 [53]
4i	4-OMe–C_6H_4	Ph	Me	60	85	235-238	239-242 [53]
4j	4-NO_2–C_6H_4	Ph	Me	80	80	129-130	130-131[53]
4k	Ph	Ph	Et	60	90	166–168	164–166 [22]
4l	Ph	4-Me–C_6H_4	Et	60	90	119–121	120–121 [22]
4m	4-Me–C_6H_4	Ph	Et	60	85	185-186	188-191 [22]
4n	4-Cl–C_6H_4	Ph	Et	60	80	180-182	184-185 [22]
4o	4-OMe–C_6H_4	Ph	Et	60	80	174-176	174 [22]

A proposed mechanism for the formation of **4** is shown in Scheme 3. There are many reactive sites in the vitamin B12 molecule that can active carbonyl group (Fig.1).



Scheme 3. Proposed mechanism for the one-pot three-component synthesis of 3,4,5-substituted furan-2(5*H*)-ones in the presence of vitamin B12 as green catalyst.

Next, the reaction condition was optimized for the synthesis of *N*-aryl-3aminodihydropyrrol-2-one-4-carboxylates. Formaldehyde, aniline, and dimethylacetylenedicarboxylate were chosen as model compounds. The reaction was initially carried out in different condition (Table 3). As can be seen in Table 3, catalytic amount of vitamin B12 (7.35 * 10-5 mol%) was found to be the most effective catalyst for the reaction at room temperature.

Table 3

Optimization of the reaction conditions for the synthesis of **9a** in EtOH.[a]

Entry	Catalyst (mol%)	Time (h)	Isolated yields (%)
1	TiO_2 (10)	15	25
2	$Zn(SO_4)_2$-$7H_2O$ (10)	15	25
3	$Zr(NO_3)_4$ (10)	12	30
4	$ZrCl_4$ (10)	12	50
5	$HClO_4$–SiO_2 (10)	12	20
6	$KHSO_4$ (10)	15	26
7	NH_4HSO_4 (10)	15	40
8	Vitamin B12 (7.35 * 10-5)	2	75

[a] Amounts of material in all reactions: aniline (2 mmol), DMAD (1 mmol), and formaldehyde (1.5 mmol).

To demonstrate the utility and generality of this method, the various substituted anilines, dimethyl or diethyl acetylenedicarboxylates and formaldehyde were employed successfully to generate the desired *N*-aryl-3-aminodihydropyrrol-2-one-4-carboxylates **9a–h** (Table 4). Encouraged by these results, different polyfunctionalized dihydropyrrol-2-ones **9i–p** were synthesized using two different amines. Aliphatic amines, such as benzyl amine, 1-(pyridin-2-yl)methanamine and *n*-butyl amine, were reacted with dialkylacetylene-dicarboxylates, anilines and formaldehyde to produce the corresponding products in good to high yields.

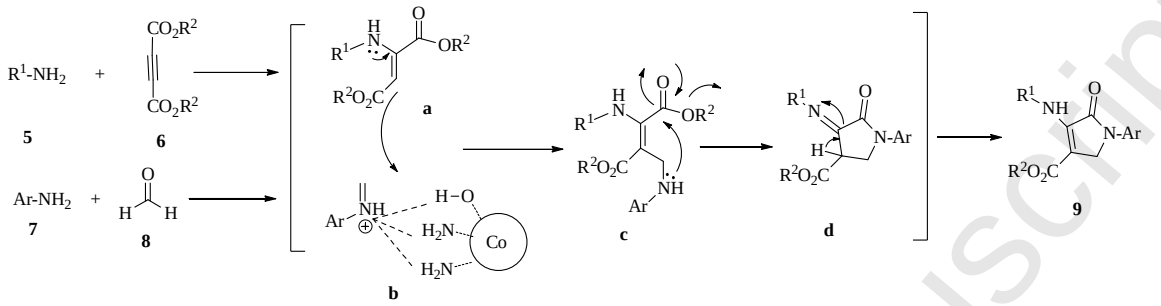
Table 4

Synthesis of *N*-aryl-3-aminodihydropyrrol-2-one-4-carboxylates.

Product	R^1	R^2	Ar	Time (min)	Isolated yield (%)	m.p (°C)	Lit.mp (°C) [Ref]
9a	Ph	Me	Ph	120	75	154–155	155–156 [48]
9b	Ph	Et	Ph	60	85	136–138	138–140 [47]
9c	4-Me-C_6H_4	Me	4-Me-C_6H_4	90	85	177–179	177–178 [48]
9d	4-Me-C_6H_4	Et	4-Me-C_6H_4	60	85	128–130	131–132 [47]
9e	4-OMe-C_6H_4	Et	4-OMe-C_6H_4	120	80	152–154	152–154 [54]
9f	4-F-C_6H_4	Me	4-F-C_6H_4	60	85	163–165	163–165 [53]
9g	4-Cl-C_6H_4	Et	4-Cl-C_6H_4	60	85	167–170	168–170 [53]
9h	4-Br-C_6H_4	Et	4-Br-C_6H_4	90	80	167–169	169–171 [53]

9i	$PhCH_2$	Me	Ph	60	85	136–138	140–141 [47]
9j	$PhCH_2$	Et	Ph	60	80	81 127	129 130 [47]
9k	$PhCH_2$	Me	4-F-C_6H_4	60	90	166–168	166–168 [53]
9l	$PhCH_2$	Me	4-Br-C_6H_4	60	90	119–121	120–121 [48]
9m	$PhCH_2$	Me	4-Me-C_6H_4	60	85	144–146	144–146 [53]
9n	C_5H_4N-2-CH_2	Me	4-Me-C_6H_4	60	80	104–106	106–108 [47]
9o	n-C_4H_9	Me	Ph	60	80	60–62	60 [48]
9p	n-C_4H_9	Et	4-Br-C_6H_4	60	85	94–97	94–96 [53]

On the basis of the above experimental results, together with the related reports, a proposed reaction mechanism for this one-pot, four-component hetero-annulations is illustrated in Scheme 4.



Scheme 4. Proposed mechanism for the one-pot four-commponent synthesis of *N*-aryl-3-aminodihydropyrrol-2-one-4-carboxylates in the presence of vitamin B12 as catalyst.

4. Conclusion

In summary, we report an eco-friendly and straightforward one-pot condensation for the synthesis of 3,4,5-trisubstituted furan-2(5*H*)-ones and *N*-aryl-3-aminodihydropyrrol-2-one-4-carboxylates in the presence of catalytic amount of vitamin B12 as a highly effective ,green and homogenous catalyst. Vitamin B12 is clean, safe, non-toxic, and easy access. Moreover, this method has several other advantages such as, high yields, operational simplicity, clean and neutral reaction conditions, which makes it a useful and attractive process for the synthesis of a wide variety of biologically active compounds.

Acknowledgment

We gratefully acknowledge financial support from the Research Council of the University of Sistan and Baluchestan.

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