A Simple and Convenient Synthesis of 4-Ylidene-5(4*H*)oxazolone Derivatives: Oxazolone Ring Transformation Leading to Other Heterocyclic Structures

Ramadan M. Abdel-Motaleb, Hadeer M. Bakeer, Gammal H. Tamam, and Wael A. A. Arafa*

Department of Chemistry, Faculty of Science, Fayoum University, Fayoum, Egypt
*E-mail: waa00@fayoum.edu.eg

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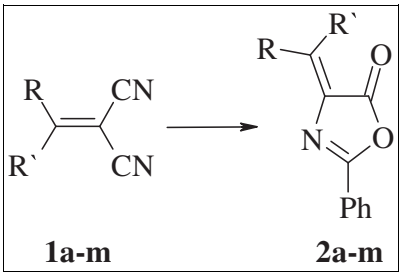

Simple, effective, and high yield synthetic procedure for the synthesis of 4-ylidene-5(4*H*)-oxazolones **2a**–**m** from arylidene-malononitriles under solvent-free conditions is described. The scope of this reaction was investigated, and it was found that the presence of anhydrous sodium acetate gave the corresponding oxazolones in excellent yields. The newly generated oxazolone derivative **2m** underwent ring transformation into pyrroles, imidazoles, pyridazine, and triazines.

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INTRODUCTION

The discovery of novel synthetic routes toward oxazolone derivatives is an area of continued interest for organic chemists. Oxazoles constitute an immensely important member of the aromatic heterocycle family because of their presence in a myriad of bioactive natural products [1–3], role as privileged pharmacophores [4–6], and ability to serve as versatile building blocks in organic synthesis [7–9]. Accordingly, this has led to numerous synthetic methods for constructing this aromatic heterocycle and the continued pursuit of ever more efficient and flexible approaches [8–10]. Many procedures have been developed for the construction of 4-ylidene-5(4*H*)-oxazolone derivatives, but none of these have been extended to be general [11–17]. However, some of these procedures often utilize costly reagents and afford products in only moderate yields. One of the most reported methods since pioneering by Erlenmeyer [18] involves the Knoevenagel condition of aromatic aldehydes with oxazolones. Although the reaction goes well with aldehydes in moderate yield, it failed with ketones. In addition, alternative procedures of condensation of hippuric acid with ketones have been reported [16], but these syntheses suffer from low yields.

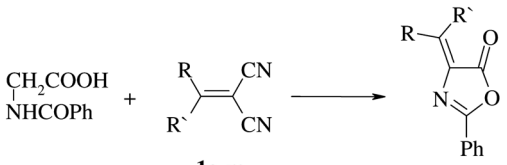
Thus, it is desirable to develop a straightforward, simple, general, environmentally benign, and efficient method for the synthesis of 4-ylidene-5(4*H*)-oxazolones from arylidene-malononitriles under solvent-free conditions.

RESULTS AND DISCUSSION

In this article, we present a new and simple procedure for the synthesis of 4-ylidene-5(4*H*)-oxazolones **2a**–**m** directly from the arylidene-malononitriles **1a**–**m** and hippuric acid in the presence of acetic anhydride and their conversion into nitrogen heterocycles. The synthetic pathways for the target products **2a**–**m**, based on the Retro-Michael reaction, are shown in Scheme 1. Initially, we started the reaction of arylidene-malononitriles **1a**–**m** (1 equiv), hippuric acid (1 equiv), and acetic anhydride (2 equiv) in the absence of any catalyst. This has afforded from poor to reasonable yields of 4-ylidene-5(4*H*)-oxazolones **2a**–**m** (Table 1, condition A).

Better conversions and therefore excellent isolated yields were observed, when anhydrous sodium acetate was used as a catalyst (Table 1, condition B) than condition A. An interpretation of yield enhancement is that sodium acetate might facilitate the generation of the azlactone anion which attacks the arylidene-malononitrile as presented in Scheme 2. A supporting chemical evidence for the suggested mechanism was obtained by treating the mother liquor of the reaction mixture with cooled benzene diazonium chloride solution, which trapped the regenerated malononitrile and furnished the well-known phenylazo-malononitrile. The structures of 4-ylidene-5(4*H*)-oxazolones **2a**–**l** and phenylazo-malononitrile were established on the basis of their IR, ^{1}H NMR spectra, and by comparison with authentic samples prepared according to the reported methods (Table 1).

Scheme 1



1a-m **2a-m**

a, R=C_6H_5; R`=H
b, R=p-$OCH_3C_6H_4$; R`=H
c, R=p-$CH_3C_6H_4$; R`=H
d, R=p-ClC_6H_4; R`=H
e, R=fur-2-yl; R`=H
f, R=thiophen-2-yl; R`=H
g, R=C_6H_5; R`=CH_3
h, R=p-$CH_3C_6H_4$; R`=CH_3
i, R=p-ClC_6H_4; R`=CH_3
j, R=thiophen-2-yl; R`=CH_3
k, R=R`=CH_3
l, R-R`= $(CH_2)_5$
m, R=CH_2CO_2Et, R`=CH_3

The reaction between **1m** and hippuric acid was used as a model system to identify reaction parameters that would provide optimal results. As presented in Table 2, a poor yield (10%) was observed in the absence of anhydrous sodium acetate (entry 1). However, by addition of 0.5 equiv of this catalyst, a moderate yield (60%) was accomplished (entry 2). Most significantly, the use of 1 equiv amount of the catalyst has furnished the highest yield (entry 3). When the reaction time was reduced (entry 4), lower yield of was observed at fixed amount of catalyst (entries 3 and 4). No more improvement in the reaction yield was observed by increasing the amount of anhydrous sodium acetate than 1 equiv (entry 5). On the basis of these results, we recommended the optimized conditions of entry 3 as a protocol to test the generality of the method, and a survey of some selected examples is compiled in Table 1 (condition B).

The successful preparation of **2m** may be regarded as a major application of the new route to oxazolones, given the project usefulness of structurally related heterocycles in medicinal chemistry. Thus, we believed that any new ylidenemalononitriles are expected to react with hippuric acid and afford the corresponding ylideneoxazolones. Herein, a detailed procedure for the synthesis of **2m** accompanied by full characterization data is included.

The ethyl 3-(5-oxo-2-phenyloxazol-4(5*H*)-ylidene)butanoate **2m** was synthesized starting from the reaction of ethyl 4,4-dicyano-3-methylbut-3-enoate **1m** with hippuric acid in the presence of anhydrous sodium acetate. The structure of compound **2m** was deduced from elemental analysis and IR, ^{1}H NMR, and ^{13}C NMR spectroscopies. For example, the IR spectrum displayed absorption bands at 2990 cm^{-1} for C–H aliphatic, 1779 cm^{-1} due to C=O of (oxazolone), and 1732 cm^{-1} corresponding to C=O (ester). The sharp triplet at δ 1.25 in the ^{1}H NMR spectrum was assigned for CH_2CH_3 protons. The CH_3 protons resonated as a sharp singlet at δ 1.97. Another sharp singlet observed at δ 3.15 integrated for two protons was assigned to CH_2–CO_2Et protons. Also, a quartet observed at δ 4.37 attributed for CH_2CH_3 protons. The remaining five aromatic protons of the phenyl moiety appeared as a complex multiplet in the region δ 7.17–7.24. On the other hand, peaks resonated at 10.22, 14.53, 39.85, 62.69, and 162.51, 168.21 ppm in the ^{13}C NMR, assigned for $2CH_3$, $2CH_2$, and 2C=O groups, respectively, confirm the carbon skeleton of compound **2m**. Further, the structure of **2m** was also confirmed by recording its mass spectrum, which showed a molecular ion peak at *m/z* 273. The observed molecular mass is in agreement with the assigned molecular formula, $C_{15}H_{15}NO_4$. Moreover, an additional proof of structure **2m** was obtained from reasonable derivations based on the presence of active methylene group which can be easily reacted with aryl diazonium salts and aldehydes.

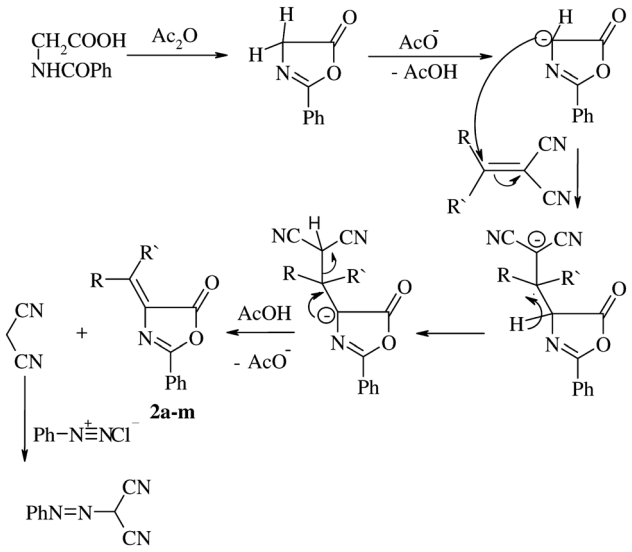
It is well known that the reactions of active methylene with aldehyde lead to the formation of benzylidene derivatives. As depicted in Scheme 3, the analogous reaction of **2m** with benzaldehyde carried out in the presence of

Table 1

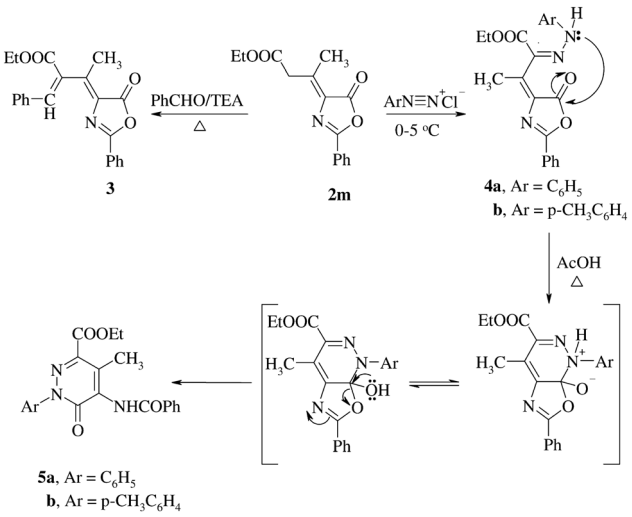
Synthesis of 4-ylidene-5(4*H*)-oxazolones **2a–m** (conditions A and B).

	Condition A		Condition B		M.p. (°C)	
Product No.	Time (min)	Yield (%)	Time (min)	Yield (%)	Found	Reported
2a	60	87	3	90	170	170 [19]
2b	60	95	3	99	165	165 [19]
2c	60	97	3	99	144	145 [20]
2d	60	97	3	98	205	198 [20]
2e	60	89	3	97	170	171 [21]
2f	60	85	3	95	179	177 [22]
2g	60	20	60	85	99	101 [23]
2h	60	18	60	88	119	118–119[23]
2i	60	10	60	90	151	148–150[23]
2j	60	22	60	86	160	158[16]
2k	60	30	60	96	101	99–100[24]
2l	60	28	60	93	137	138[25]
2m	60	10	60	98	237	–

Scheme 2



Scheme 3



triethylamine, under fusion condition, afforded the expected benzylidene derivative **3**. The structure of benzylidene derivative **3** was confirmed on the bases of elemental analysis and spectral data. In the ^{1}H NMR spectrum of compound **3**, the signal belonging to C=CH appeared at 8.52 ppm integrated for one proton. This unusually low field value could be revealed the formation of hydrogen bond between the hydrogen atom of C=CH moiety and nitrogen atom of oxazolone ring. The IR spectrum of compound **3** showed strong absorption bands at 1752 and 1710 cm^{-1} corresponding to two carbonyl groups along with other bands assigned to the introduced functionalities. Furthermore, compound **3** gave stable molecular ion peak in the mass spectrum at *m/z* 361 (14.9%) (M^+) corresponding to $C_{22}H_{19}NO_4$ with a base peak at 91 (100%) due to the formation of tropelium ion.

On the other hand, compound **2m** couples smoothly with diazotized aromatic amines in cold ethanolic sodium acetate solution, and afforded compounds identified as ethyl 3-(5-oxo-2-phenyloxazol-4(5*H*)-ylidene)-2-(2-arylhydrazono) butanoate **4a**,**b** (Scheme 4).

The ^{1}H NMR spectrum of compounds **4a**, for example, displayed no signals belonging to the CH_2 group; instead, new signals due to NH appeared at 8.63 ppm integrated for one proton. The IR spectrum of **4a** displayed absorption band at 3340, for (NH) group, in addition to two carbonyl absorption bands at 1757 and 1711 cm^{-1}. Furthermore, mass spectra of compounds **4a**,**b** showed molecular ion peaks in agreement with their molecular formula.

Interestingly, we found that the latter compounds, **4a**,**b**, could be easily transformed into the desired pyridazine derivatives **5a**,**b** upon short reflux in acetic acid. We reasoned that the reaction possibly takes place *via* nucleophilic attack of nitrogen lone pair on carbonyl of oxazolone followed by rearrangement to furnish the final isolable products **5a**,**b** (Scheme 3). The IR spectrum of compound **5a**, for example, showed an absorption band at 3386 cm^{-1} indicating the presence of NH group. The absorption bands observed at 1718 and 1665 cm^{-1} could be attributed to carbonyl functional groups. The disappearance of absorption band corresponding to carbonyl of

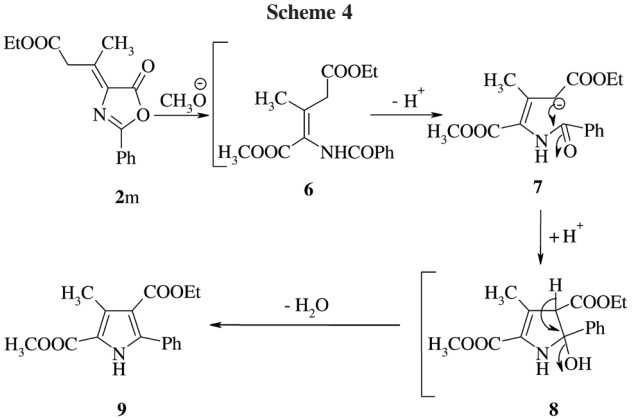
Table 2

Results of the reaction of **1m** with hippuric acid under different conditions.[a]

Entry	Anhydrous NaOAc (equiv)	Time (min)	Yield (%)
1	0	60	10
2	0.5	60	60
3	1	60	98
4	1	3	75
5	1.5	60	98

[a]These experiments were carried out using 1 mmol of **1m** and 1 mmol of hippuric acid in the presence of 2 mmol of acetic anhydride.

Scheme 4



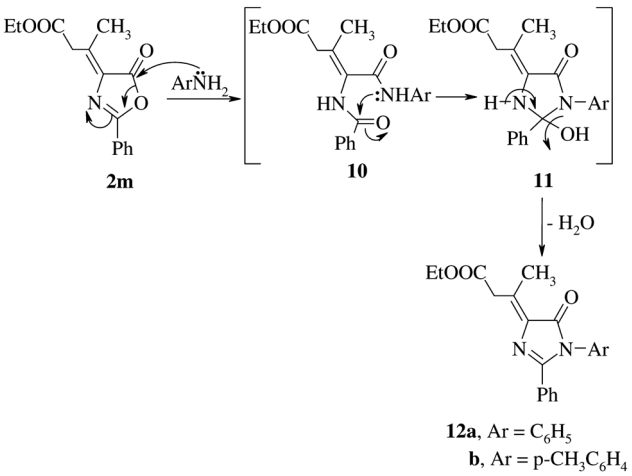
oxazolone ring indicated that the ring transformation occurred. Furthermore, **5a**,**b** gave stable molecular ion peaks in their mass spectra.

Pyrroles are an important class of heterocyclic compounds and are structural units found in a vast array of natural products, synthetic materials, and bioactive molecules [26–28]. Various reactions leading to pyrroles have been reported [29, 30]. It was found that [23, 31] the oxazolone ring opening was performed by the methanolysis in the presence of sodium methoxide. This treatment afforded the corresponding benzamido esters. In contrast to this behavior, methanolysis of ethyl 3-(5-oxo-2-phenyloxazol-4(5*H*)-ylidene)butanoate **2m** in the presence of a catalytic amount of sodium methoxide afforded a product of molecular formula $C_{16}H_{17}NO_4$ (Scheme 4). The IR spectrum of the isolated product showed the presence of NH (3369 cm^{-1}), two carbonyl ester (1725 and 1718 cm^{-1}) and absence of any amide carbonyl absorptions. ^1H and ^{13}C NMR spectra of the obtained product were completely matched with the assigned structure **9**. Furthermore, the highest recorded peak at *m*/*z* 287 (4.1%) represents the molecular ion peak, and the EI fragmentation pattern is completely in accord with the assigned structure. A mechanistic rationalization of the reaction is provided in Scheme 5. We thought that pyrrole derivative **9** could be synthesized from **2m** *via* methanolysis to form the nonisolable intermediate **6** followed by intramolecular ring transformation *via* nucleophilic attack of the active methylene on the amide carbonyl to afford intermediate **8**. Elimination of water molecule from the latter intermediate yields the final isolable product **9** (Scheme 4).

Imidazole derivatives are important five-membered nitrogen-containing heterocyclic compounds, which are widely used in materials science, antitumor activator as well as optical materials [32–34]. Saettone [35] reported that ring transformation of 3,4-disubstituted oxazolones into 5-hydroxyimidazoline-2-ones could be occurred in the presence of amines, while Krieg and Lautenschlager [36] have realized the ring transformation of oxazolone-3-caroxamides into imidazolones by interaction with strong acids.

Similarly, interaction of compound **2m** with primary aromatic amines, namely aniline and *p*-toluidine, in boiling dioxane, afforded imidazolones **12a**,**b**. The IR spectra of derivatives **12a**,**b** displayed absorption bands in the region of 1715–1723 and 1673–1679 cm^{-1} due to carbonyl of ester and cyclic amide, respectively. Also, ^1H NMR (DMSO-d_6) spectrum of compound **12a** showed triplet at 1.27 due to CH_2CH_3, singlet at 1.72 for CH_3, singlet at 3.04 attributed to CH_2, quartet at 4.23 for CH_2CH_3, and two multiplets at 7.32–7.43 and 7.63–7.66 due to 10 ArH. The mass spectra of these compounds were the useful probe to check the formation of the products, as they reveal the presence of peak at *m*/*z* 348 and 362 according to the molecular formula $C_{21}H_{20}N_2O_3$ and $C_{22}H_{22}N_2O_3$, respectively. The plausible mechanism for the synthesis

Scheme 5



of imidazolone derivatives **12a**,**b** involves the nucleophilic attack of nitrogen lone pair on carbonyl of oxazolone in compound **2m**, yielding the nonisolable adducts **10** and **11**. The latter intermediates readily underwent ring cyclization *via* losing of water molecule to yield the stable compounds **12a**,**b** (Scheme 5).

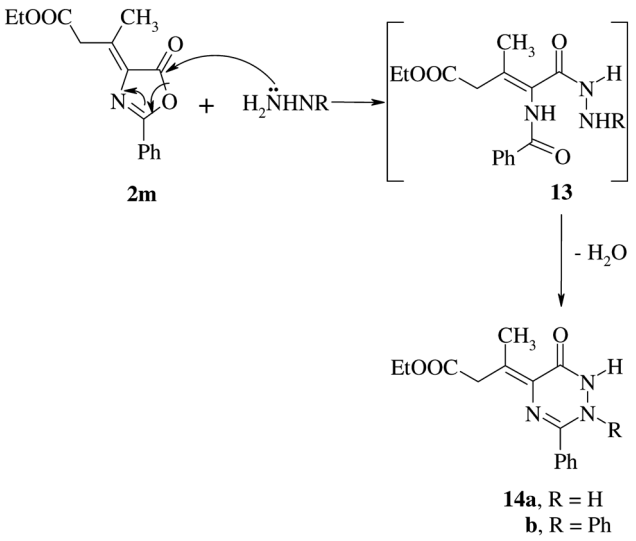
Also, the treatment of the oxazolone derivative **2m** with equimolar amount of hydrazine hydrate (in ethanol at room temperature) or phenyl hydrazine (in boiling ethanol) gave the triazines **14a**,**b**, respectively. The reaction leading to the formation of **14a**,**b** began with heterocyclic ring fission with the formation of the nonisolable hydrazide intermediates **13**, which underwent ring closure *via* elimination of water molecule to afford the final products **14a**,**b** (Scheme 6).

The structure assignment of compounds **14a**,**b** was elucidated on the basis of IR, ^1H NMR, and mass spectra as well as correct elemental analyses. IR of **14b** exhibited absorption bands at 3213 due to NH group and at 1719 and 1666 cm^{-1} due to two carbonyl groups. In the ^1H NMR spectrum of compound **13b**, the signal belonging to NH group appeared at 9.42 ppm resonated for one proton (changeable with D_2O). Furthermore, stable molecular ion peak was observed in the mass spectra of compounds **14a**,**b**.

CONCLUSIONS

In summary, we have demonstrated an efficient procedure, which can be applied to the synthesis of aliphatic and (hetero)-aromatic azlactones in excellent yields. The high yields achieved with this procedure together with the versatility of the synthetic strategy have allowed for a broad range of new substrates to be synthesized, and it should be applicable to many more. In addition, we reported

Scheme 6



novel ring transformations involving oxazolone **2m**, which afforded a new application for the synthesis of interesting heterocyclic derivatives.

EXPERIMENTAL

General. Melting points of the synthesized compounds are determined in open-capillaries on a Stuart electric melting point apparatus and are uncorrected. Reactions are monitored by thin-layer chromatography (TLC) on a silica gel-coated aluminum sheet (silica gel F254). Elemental analyses were performed by the Microanalysis center, Cairo University. Infrared spectra were recorded on Satellite 2000 spectrometer using KBr discs. Mass spectra were determined on GC–MS (QP/000 EX) Shimadzu spectrometer at an ionizing voltage of 70 eV. NMR spectra were recorded on Varin Mercury 300 MHz spectrometer (Chemical shift in ppm down field from TMS as an internal reference).

Synthesis of 4-ylideneoxazolone derivatives 2a–m. ***Method A.*** A mixture of **1** (0.01 mol), hippuric acid (0.01 mol), and acetic anhydride (0.02 mol) was warmed into solution. Heating was then continued on a boiling water-bath for 1 h. Excess acetic anhydride was decomposed with water, and the residue was triturated with methanol. The yellow solid product was filtered off and recrystallized from a proper solvent.

Method B. A mixture of **1** (0.01 mol), hippuric acid (0.01 mol), acetic anhydride (0.02 mol), and anhydrous sodium acetate (0.01 mol) was warmed for 3–60 min (Table 2). Excess acetic anhydride was decomposed with water, and the residue was triturated with methanol. The yellow solid product was filtered off and recrystallized from a proper solvent.

Ethyl 3-(5-oxo-2-phenyloxazol-4(5H)-ylidene)butanoate 2m. Recrystallized from ethanol to afford yellow crystals in 98% yield m.p. 237°C. IR (KBr, ν, cm^{-1}): 2990 (C–H aliph.), 1779, 1732 (C=O). MS: (*m/z*, %): 273 (13.62%). ^{1}H NMR (DMSO-d_6) δ (ppm) 1.25 (3H, t, CH_2CH_3), 1.97 (3H, s, CH_3), 3.15 (2H, s, CH_2), 4.37 (2H, q, $CO_2CH_2CH_3$), 7.17–7.24 (5H, m, ArH). ^{13}C NMR (DMSO-d_6, δ ppm): 10.22 (CH_3), 14.53 (CH_2CH_3), 39.85 (CH_2), 62.69 (CH_2CH_3), 128.73 (oxazole C-4), Ph: [129.48 (C), 129.59 (4CH), 130.00 (CH)], 138.98 (C), 155.78 (oxazole C-2), 162.51 (CO_2Et), 168.21 (oxazole C-5). Anal. $C_{15}H_{15}NO_4$ (273.28) Calcd.: C, 65.92%; H, 5.53%; N, 5.13%. Found: C, 66.13%; H, 5.46%; N, 4.92%.

Synthesis of ethyl 2-benzylidene-3-(5-oxo-2-phenyloxazol-4(5*H*)-ylidene)butanoate 3. A solution of **2m** (0.01 mol) and benzaldehyde (0.01 mol) in the presence of catalytic amount of triethylamine were heated in an oil bath at about 150°C for 1 h. The reaction mixture was treated by methanol. The formed solid was collected by filtration and recrystallized from dioxane to give yellow crystals in 53% yield m.p. 237°C. IR (KBr, ν, cm^{-1}): 1752, 1710 due to (C=O). MS: (*m/z*, %): 361 (M^+) (14.9%). ^{1}H NMR (DMSO-d_6) δ (ppm) 1.31 (3H, t, CH_2CH_3), 2.01 (3H, s, CH_3), 4.20 (2H, q, $CO_2CH_2CH_3$), 7.07–7.34 (5H, m, ArH), 7.50–7.86 (5H, m, ArH), 8.52 (1H. s, C=CH). Anal. $C_{22}H_{19}NO_4$ (361.39) Calcd.: C, 73.12%; H, 5.30%; N, 3.88%. Found: C, 73.44%; H, 5.58%; N, 4.11%.

Synthesis of ethyl 3-(5-oxo-2-phenyloxazol-4(5*H*)-ylidene)-2-(2-arylhydrazono)butanoate 4a,b. A solution of aryl diazonium chloride, namely, phenyl and *p*-tolyl diazonium chloride (0.01 mol) was added gradually while stirring to a cold solution of **2m** (0.01 mol) in ethanol (50 mL) containing sodium acetate trihydrate (5 g). The reaction mixture was left for 1 h. The solid product that formed was collected, washed with water, and dried and recrystallized from a proper solvent.

Compound 4a. Recrystallized from ethanol to give yellow crystals in 65% yield m.p. 211°C. IR (KBr, ν, cm^{-1}): 3340 (NH), 1757, 1711 (C=O). MS: (*m/z*, %): 377 (M^+) (18.7%). ^{1}H NMR (DMSO-d_6) δ (ppm): 1.34 (3H, t, CH_2CH_3), 1.80 (3H, s, CH_3), 4.36 (2H, q, CH_2CH_3), 7.25–7.44 (5H, m, *Ph*N) 7.72–7.77 (5H, m, ArH), 8.63 (1H, s, NH). Anal. $C_{21}H_{19}N_3O_4$ (377.39) Calcd.: C, 66.83%; H, 5.07%; N, 11.13%. Found: C, 67.10%; H, 4.83%; N, 11.30%.

Compound 4b. Recrystallized from dioxane to give yellow crystals in 72% yield m.p. 252°C. IR (KBr, ν, cm^{-1}): 3300 (NH), 1749, 1716 (C=O). MS: (*m/z*, %): 391 (M^+) (34.82%). Anal. $C_{22}H_{21}N_3O_4$ (391.42) Calcd.: C, 67.51%; H, 5.41%; N, 10.74%. Found: C, 67.36%; H, 5.72%; N, 10.50%.

Synthesis of 5a,b. A solution of **4a**,**b** (0.01 mol) in glacial acetic acid (30 mL) was refluxed for 45 min. The solids that separated on concentration and cooling were filtered off and recrystallized from the proper solvent to give compounds **5a,b**.

Ethyl 5-benzamido-4-methyl-6-oxo-1-phenyl-1,6-dihydropyridazine-3-carboxylate 5a. Recrystallized from acetic acid to give yellow crystals in 56% yield m.p. 235°C. IR (KBr, ν, cm^{-1}): 3386 (NH), 1718, 1665 (C=O). MS: (*m/z*, %): 377 (M^+) (6.3%). ^{1}H NMR (DMSO-d_6) δ (ppm): 1.18 (3H, t, CH_2CH_3), 2.12 (3H, s, CH_3), 4.20 (2H, q, CH_2CH_3), 7.12–7.52 (5H, m, *Ph*N), 7.65–7.82 (5H, m, ArH), 8.99 (1H, s, NH). Anal. $C_{21}H_{19}N_3O_4$ (377.39), Calcd.: C, 66.83%; H, 5.07%; N, 11.13%, Found: C, 66.61%; H, 5.20%; N, 11.35%.

Ethyl 5-benzamido-4-methyl-6-oxo-1-(p-tolyl)-1,6-dihydropyridazine-3-carboxylate 5b. Recrystallized from acetic acid to give yellow crystals in 60% yield m.p. 270°C. IR (KBr, ν, cm^{-1}): 3332 (NH), 1711, 1658 (C=O). MS: (*m/z*, %): 391 (M^+) (15.2%). Anal. $C_{22}H_{21}N_3O_4$ (391.42), Calcd.: C, 67.51%; H, 5.41%; N, 10.74%, Found: C, 67.71%; H, 5.21%; N, 11.00%.

Synthesis 4-ethyl 2-methyl 3-methyl-5-phenyl-1*H*-pyrrole-2,4-dicarboxylate 9. A solution of sodium methoxide (0.01 mol) in absolute methanol (50 mL) was added to **2m** (0.01 mol), and the reaction was stirred at room temperature for 10 h. The solvent was removed *in vacuo*; cold water was added

dropwisely to the residue, until the precipitation was complete. The solid that separated out was filtered off and recrystallized from ethanol.

Pale yellow crystals in 54% yield m.p. 156°C. IR (KBr, ν, cm^{-1}): 3369 (NH) 1725, 1718 (C=O). MS: (*m/z*): 287 (M^+) (4.1%). ^1H NMR (DMSO-d_6) δ (ppm) 1.04 (3H, t, CH_2CH_3), 1.60 (1H, b b, NH), 2.16 (3H, s, CH_3), 3.85 (3H, s, $COOCH_3$), 4.52 (2H, q, CH_2CH_3), 7.25–7.61 (5H, m, ArH). ^{13}C NMR (DMSO-d_6, δ ppm): 10.23 (CH_3), 15.71 (CH_2CH_3), 48.82 (OCH_3), 62.51 (CH_2CH_3), pyrrole: [116.55 (C4), 119.79 (C2), 140.13 (C5), 142.51 (C3)], Ph: [127.27, 128.72, 129.34, 131.61], 156.93 (CO_2CH_3), 161.22 ($CO_2C_2H_5$). Anal. $C_{16}H_{17}NO_4$ (287.31). Calcd.: C, 66.89%; H, 5.96%; N, 4.88%. Found: C, 67.03%; H, 5.82%; N, 5.11%.

Synthesis of 12a,b. The oxazolone **2m** (0.01 mol) in dioxane (30 mL) was boiled with aniline or *p*-toludine (0.01 mol) for 5 h. The mixture was cooled and poured into water (100 mL). The solid was filtered off and recrystallized from a proper solvent.

Ethyl 3-(5-oxo-1,2-diphenyl-1H-imidazol-4(5H)-ylidene) butanoate 12a. Recrystallized from dioxane to give yellow crystals in 50% yield m.p. 205°C. IR (KBr, ν, cm^{-1}): 1715, 1673 (C=O). MS: (*m/z*, %): 348 (M^+) (28.2%). ^1H NMR (DMSO-d_6) δ (ppm): 1.27 (3H, t, CH_2CH_3), 1.72 (3H, s, CH_3), 3.04 (2H, s, CH_2), 4.23 (2H, q, CH_2CH_3), 7.32–7.43 (5H, m, ArH), 7.63–7.66 (5H, m, ArH). Anal. $C_{21}H_{20}N_2O_3$ (348.40), Calcd.: C, 72.40%; H, 5.79%; N, 8.04%, Found: C, 72.30%; H, 5.52%; N, 7.87%.

Ethyl 3-(5-oxo-2-phenyl-1-(p-tolyl)-1H-imidazol-4(5H)-ylidene)-butanoate 12b. Recrystallized from DMF to give yellow crystals in 47% yield m.p. 247°C. IR (KBr, ν, cm^{-1}): 1723, 1679 (C=O). MS: (*m/z*, %): 362 (M^+) (34.66%). Anal. $C_{22}H_{22}N_2O_3$ (362.42), Calcd.: C, 72.91%; H, 6.12%; N, 7.73%, Found: C, 72.88%; H, 6.00%; N, 7.47%.

Synthesis of ethyl 3-(6-oxo-3-phenyl-1,6-dihydro-1,2,4-triazin-5(2*H*)-ylidene)butanoate 14a. The oxazolone **2m** (0.01 mol) was suspended in ethanol (50 mL) and treated with hydrazine hydrate (0.01 mol) at room temperature. The mixture was stirred over night at room temperature. The solid product that separated was filtered off and recrystallized from ethanol to give yellow crystals in 50% yield m.p. 230°C. IR (KBr, ν, cm^{-1}): 1725, 1663 (C=O). MS: (*m/z*, %): 287 (M^+) (4.1). Anal. $C_{15}H_{17}N_3O_3$ (287.31), Calcd.: C, 62.71%; H, 5.96%; N, 14.63%, Found: C, 62.98%; H, 5.75%; N, 14.69%.

Synthesis of ethyl 3-(6-oxo-2,3-diphenyl-1,6-dihydro-1, 2,4-triazin-5(2*H*)-ylidene)butanoate 14b. A solution of **2m** (0.01 mol) in ethanol (30 mL) was treated with phenyl hydrazine (0.01 mol), and the reaction mixture was refluxed for 5 h. The solid product obtained after concentration of the solution was collected by filtration and recrystallized from dioxane to give yellow crystals in 58% yield m.p. 277°C. IR (KBr, ν, cm^{-1}): 3213 (NH), 1719, 1666 (C=O). MS: (*m/z*, %): 363 (M^+) (2.8%). ^1H NMR (DMSO-d_6) δ (ppm): 1.12 (3H, t, CH_2CH_3), 1.70 (3H, s, CH_3), 2.65 (2H, s, CH_2), 4.20 (2H, q, CH_2CH_3), 7.53–7.63 (5H, m, *Ph*N), 7.99–8.03 (5H, m, *Ph*C), 9.42 (1H, s, NH). Anal. $C_{21}H_{21}N_3O_3$ (363.41), Calcd.: C, 69.41%; H, 5.82%; N, 11.56%, Found: C, 69.22%; H, 5.75%; N, 11.71%.

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