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Research Article

PYRIDINE AS AN EFFICIENT CATALYST IN SYNTHESIS OF FUSED α-METHYLENE-γ-BUTYROLACTONE DERIVATIVES

Mohammad Rezghi and *Alireza Hassanabadi
Department of Chemistry, Zahedan Branch, Islamic Azad University,
P.O. Box 98135-978, Zahedan, Iran
**Author for Correspondence*

ABSTRACT
A good yield in the synthesis of α-methylene-γ-butyrolactone derivatives is described involving the reaction of acetylenic esters and 4-hydroxy coumarin in the presence of pyridine. This one-pot method is simple and effective under mild conditions.

Keywords: *4-Hydroxycoumarin, Acetylenic Esters, Pyridine, α-Methylene-γ-Butyrolactones*

INTRODUCTION
Chromenes often appears as an important component in both biologically active and natural compounds (Polyakov, 1999; Harbone, 1988). α-Methylene-γ-butyrolactones are important structural unit in natural products and are intermediates in organic synthesis (Petragnani *et al*., 1986; Sarma and Sharma, 1986).
The synthesis of latter uses a procedure first described by Yavari and Hossaini (2006), in which they synthesized a series of α-Methylene-γ-butyrolactones via the phenols and acetylenic esters in the presence of pyridine. In continuation of our previous work, for *N*-vinylation of heterocyclic compounds in the presence of pyridine as a catalyst (Asgharian-Sheykhi *et al*., 2013; Shahraki and Hassanabadi, 2014). In this study, we have used the procedure of Yavari and Hossaini (2006) to synthesize another class of α-Methylene-γ-butyrolactones starting from another enoles such as 4-hydroxycoumarin.

MATERIALS AND METHODS
Melting points were determined with an Electrothermal 9100 apparatus and are uncorrected. Elemental analyses were performed using a Heraeus CHN–O–Rapid analyser. Mass spectra were recorded on a Finnigan-MAT 8430 mass spectrometer operating at an ionisation potential of 70 eV. IR spectra were recorded on a Shimadzu IR-470 spectrometer. ^{1}H and ^{13}C spectra were recorded on Bruker DRX-400 Avance spectrometer in $CDCl_3$ using TMS as the internal standard. Chemicals were purchased from Fluka (Buchs, Switzerland) and were used without further purification.

General Procedure
A mixture of the 4-hydroxy coumarin (1 mmol) and acetylenic esters (1 mmol) in 15 mL of diethyl ether was added dropwise pyridine (0.2 mmol) at room temperature. The reaction mixture was then stirred for 24 h The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography using hexane–ethyl acetate as eluent. The solvent was removed under reduced pressure to afford the product.

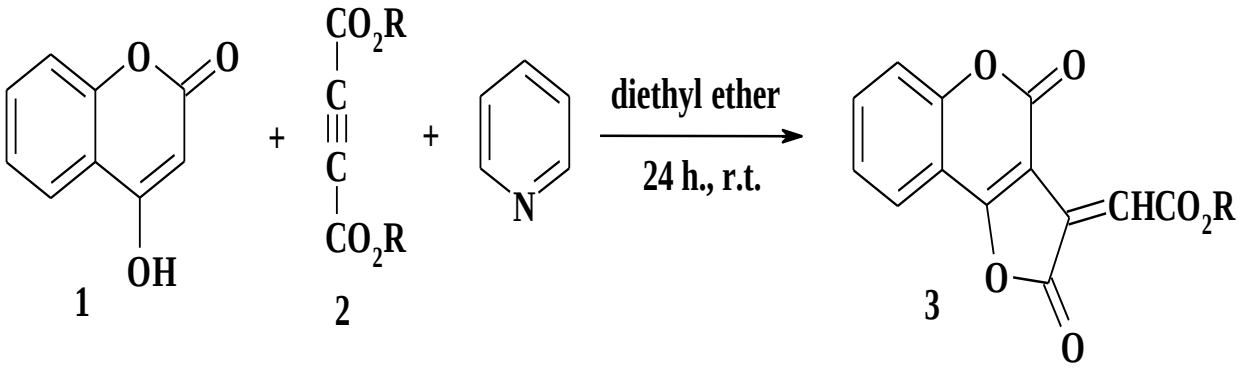
Methyl (2,4-dioxo-4H-furo[3,2,c]chromen-3-ylidene)acetate **(3a):** Yellow powder, yield: 83%, m.p. 130–132 °C, IR (KBr) (ν_{max}/cm^{-1}): 1738, 1663 (C=O), ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ 3.79 (3H, s, OCH_3), 6.90 (1H, s, CH), 7.41 (1H, t, $^{3}J_{HH}$ = 8 Hz, CH of coumarin moiety), 7.60 (1H, d, $^{3}J_{HH}$ = 8 Hz, CH of coumarin moiety), 7.79 (1H, t, $^{3}J_{HH}$ = 8 Hz, CH of coumarin moiety), 8.19 (1H, d, $^{3}J_{HH}$ = 8 Hz, CH of coumarin moiety) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si): δ 52.58 (OCH_3), 110.63 (=CH), 105.80, 116.82, 117.41, 123.17, 124.86, 133.34, 154.37 and 159.28 (carbons of coumarin moiety), 153.55 (C), 162.93, 165.37 and 166.72 (3C=O) ppm. Anal. Calcd for $C_{14}H_8O_6$: C, 61.77; H, 2.96. Found: C, 61.95; H, 2.81 %. MS, *m/z* (%): 272 ($M^{+\cdot}$, 8).

Ethyl (2,4-dioxo-4H-furo[3,2,c]chromen-3-ylidene)acetate **(3b):** Yellow powder, yield: 80%, m.p. 117–119 °C, IR (KBr) (ν_{max}/cm^{-1}): 1735 and 1660 (C=O), ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ 1.18 (3H, t, $^{3}J_{HH}$ =7 Hz, CH_3), 4.15 (2H, q, $^{3}J_{HH}$ =7 Hz, OCH_2), 6.97 (1H, s,

CH), 7.48 (1H, t, $^3J_{HH}$ = 8 Hz, CH of coumarin moiety), 7.63 (1H, d, $^3J_{HH}$ = 8 Hz, CH of coumarin moiety), 7.77 (1H, t, $^3J_{HH}$ = 8 Hz, CH of coumarin moiety), 8.14 (1H, d, $^3J_{HH}$ = 8 Hz, CH of coumarin moiety) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si): δ 13.82 (CH_3), 62.63 (OCH_2), 110.59 (=CH), 105.80, 116.85, 117.53, 123.20, 124.93, 133.28, 154.30 and 159.18 (carbons of coumarin moiety), 153.60 (C), 162.94, 165.26 and 166.71 (3C=O) ppm. Anal. Calcd for $C_{15}H_{10}O_6$: C, 62.94; H, 3.52. Found: C, 63.14; H, 3.60 %. MS, *m/z* (%): 286 ($M^{+\cdot}$, 5).

RESULTS AND DISCUSSION

Reaction of 4-hydroxy coumarin **1** with acetylenic esters **2** in the presence of pyridine as an efficient catalyst, leads to fused α-methylene-γ-butyrolactone derivatives **3** in good yields (Figure 1).



3	R	%Yield* of 3
a	Me	83
b	Et	80

* Isolated yields

Figure 1: Reaction of the 4-hydroxy coumarin 1 and acetylenic esters 2 in the presence of pyridine

When the 4-hydroxy coumarin **1** was added to the acetylenic esters **2** in the absence of pyridine, no product was detected.

The structures of compounds **3a,b** were deduced from their elemental analyses and their IR, ^{1}H NMR, ^{13}C NMR spectra. The mass spectra of these compounds displayed molecular ion peaks at the appropriate *m/z* values.

The ^{1}H NMR spectrum of **3a** exhibited a sharp line at δ = 3.79 ppm for the protons of methoxy group. Aromatic protons resonate between 7.41 and 8.19 ppm as multiplets. The vinylic proton was observed at δ = 6.90 ppm as a sharp singlet. The ^{13}C NMR spectrum of **3a** showed 14 distinct resonances in agreement with the proposed structure. The mass spectrum of **3a** displayed the molecular ion peak at *m/z* = 272. The IR spectrum of compound **3a** also supported the suggested structure. Strong absorption bands were observed at 1738 and 1663 cm^{-1} for the carbonyl groups. A tentative mechanism for this transformation is proposed in Figure 2.

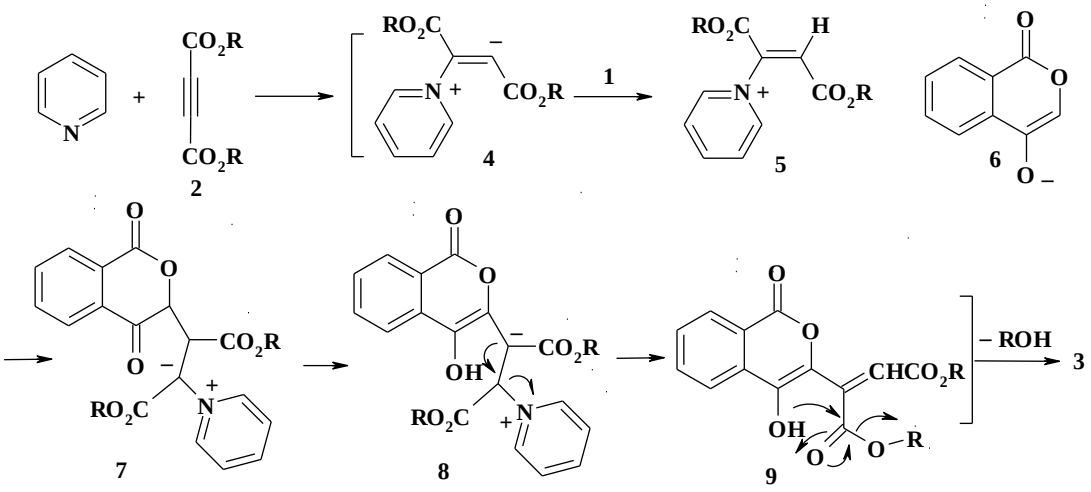


Figure 2: Suggested mechanism for formation of compound 3

On the basis of the well established reactivity of pyridines (Acheson and Taylor, 1960; Yavari *et al.*, 2004), with acetylene carboxylates it is reasonable to assume that the compound **3** arises from initial addition of the pyridine to the acetylenic ester **2** and subsequent protonation of the 1:1 adduct **4** by compound **1**. This adduct is then attacked by the anion of **1** in a Michael fashion to produce **7**. This intermediate is converted to **8** via a proton-shift and **3** is produced by elimination of pyridine (Figure 2).

Conclusion

In summary, we have shown that pyridine is an efficient catalyst which has advantages in the synthesis of α-methylene-γ-butyrolactone derivatives such as simple work-up, and affording good yield. The present method carries the advantage that, not only is the reaction performed under neutral conditions, but the reactants can be mixed without any activation or modification.

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