*Iranian Journal of Organic Chemistry Vol. 4, No. 1 (2012) 775-777*

IranJOC
Iranian Journal of Organic Chemistry

# A novel convenient method for synthesis of new podand derivatives of 4H-pyran-4-one

Mohammad Habibi Joibari[a*], Reza Marandi[b], Gissa Rezaei[b] and Ramin Zafar Mehrabian[a]

[a]*Department of Chemistry, Gorgan Branch, Islamic Azad University, Gorgan, Iran*
[b]*Department of Applied Chemistry, North Tehran Branch, Islamic Azad University, Tehran, Iran*

Received: November 2011; Revised: December 2011; Accepted: January 2012

**Abstract:** 4H-pyran-4-one carboxaldehyde derivatives were synthesized by a simple, fast, efficient, and basic method in good yields. New podand derivatives of 4H-pyran-4-one were prepared by the imination reaction of 2, 6- carboxaldehyde -3, 5-diphenyl-4H-pyran-4-one with 2-aminophenol under controlled condition. The yield of 2-aminophnol podand is 90% and this synthetic podands can use for removal heavy metals as a good adsorbent.

**Keywords:** Synthesis, Podands, 2,6-Bis((E)-(2-hydroxyphenylimino)methyl)-3,5-diphenyl-4H-pyran-4-one.

## Introduction

Functionalized heterocycles are often used for synthesis of target organic compounds in the production of dyes, drugs and a variety of pharmacological applications, 4H-pyran-4-one derivatives comprise an useful class of heterocyclic compounds which are useful as flavoring agent, food preservatives, fungicides, herbicides, anti-HIV drugs [1-6].

Podands are important material in chemistry, many excellent podands are found in nature. Sometime synthetic podands behave like crown ethers and can be complexed with metals and cations [7-9].

Several synthetic routes for 4H-pyran-4-one podands derivatives have been reported in the literatures [10-12]. The synthesis of 2,6-bis((E)-(2-hydroxyphenylimino)methyl)-3,5-diphenyl-4H-pyran-4-one (E2) has not reported.

We wish to report here a convenient, one-pot preparation and safe method with higher yield by reclaimable compound for the synthesis of mono and dicarboxaldehyde derivatives and synthesis the new podands of 4H-Pyran-4-one derivatives.

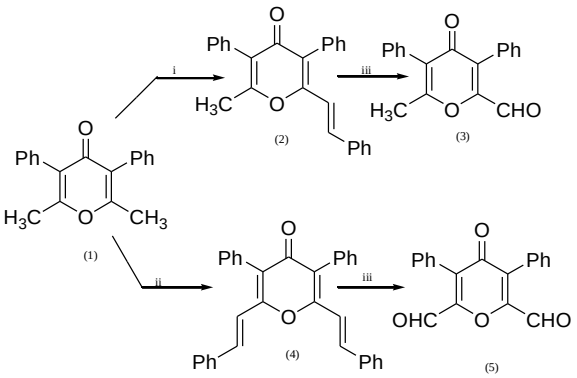
## Results and discussion

In this method for synthesis of reagent compound it is necessary to prepare 4H-Pyran-4-ones dicarboxldehyde derivative. Ghandi and co-workers prepared some mono- and dicarboxlaldehyde derivatives of 4H-pyran-4-one by the condensation of mono and dimethyl derivatives of 4H-pyran-4-one with benzaldehyde, followed by the oxidation of corresponding mono and distryl derivatives in the presence of osmium tetroxide and potassium periodate in yield of 60% overall [13] (Scheme **1**).

In additionaly method, total yield is less than 60%, and the other method, Teimuri and co-workers prepared carboxaldehyde derivatives of 4H-pyran-4-ones from their corresponding bromomethyl derivatives by treatment with silver acetate followed by hydrolysis and oxidation [14, 15]. In all these methods the final product were prepared by four steps with maximum total yield of 57%.

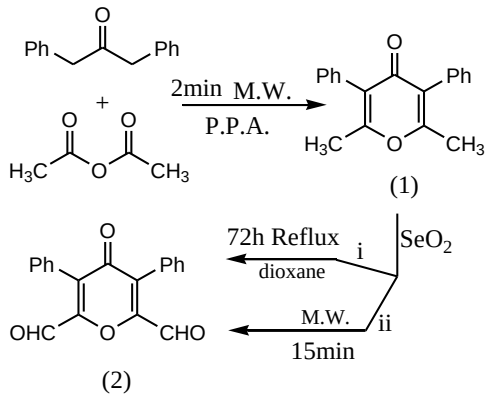
*Corresponding author. Tel: (+98) 171 3332076, E-mail: m_habibi@gorganiau.ac.ir

Selenium dioxide is a useful reagent for methyl groups oxidation in preparation of caerulomycin E [16], dicarboxaldehyde naphthyridine derivatives [17], and 1, 10-dicarboxaldehyde phenathroline [18, 19].



**Scheme 1:** (i) PhCHO, NaOEt, (ii) 2PhCHO, 2NaOEt, (iii) $OsO_4$, $KIO_4$

We synthesize dicarboxaldehyde derivatives of 4H-pyran-4-one by two different methods by using selenium dioxide as a methyl group oxidant with a suitable yield (Scheme **2**).

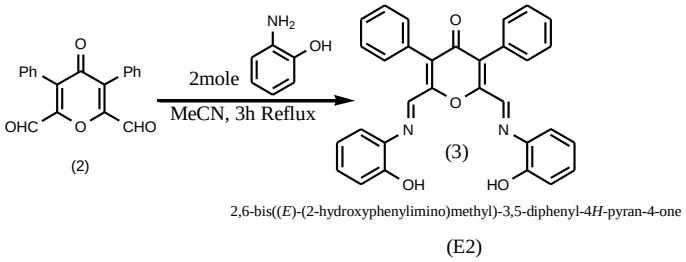


**Scheme 2:** (i) By solvent, (ii) Solvent-free method

In this process selenium dioxide was reduced to selenium which we reclaimed all of selenium by reaction with nitric acid. It seems that selenium reacted with nitric acid and selenous acid ($H_2SeO_3$) produced.

Recently, the wide applicability of microwave irradiation in chemical reaction enhancement is due to the high reaction rate with the formation of more pure cleaner products and simple operation [20-25].

Synthetic dicarboxaldehyde reacted with aminophenol derivatives and new podand derivatives of 4H-pyran-4-one (E2) was prepared with a suitable yield (Scheme **3**).



**Scheme 3:** Preparation of $E_2$ by imination reaction

## Experimental

Melting points were determined with an Electro thermal Instrument model 9100 and are uncorrected. Infrared (FT-IR) spectra were run on a Shimadzu 8010 M Spectrophotometer as KBr disks or as smears between salt plates. The $^1$H *NMR* spectra were recorded on a Varian-EM 390 spectrometer. Chemical shifts are reported in δ (ppm) with TMS as an internal standard. Mass spectra were taken by a Shimadzu MS-QP 1100 EX mass spectrometer. Elemental analyses were performed on a Heareus CHN-0-RAPID analyzer. Starting materials were purchased from commercial sources. Column chromatography was performed using Merck Kieselgel 60 (0.063–0.200 mm). All of the organic solvents used in this study were dried over appropriate drying agents and distilled prior to use.

*Typical procedure for the synthesis of 2,6-dimethyl-3,5-diphenyl-4H-pyran-4-one (1):*

A mixture of 12.5 mL (0.02mol) acetic anhydride and 20 g (0.02 mol) polyphosphoric acid and 2.1 g (0.01mol) of 1,3- diphenyl-2-propanone subjected to microwave irradiation for 2 minutes to achive 2,6-dimethyl-3,5-diphenyl-4H-pyran-4-one(2). The cooled mixture was diluted with ice-water, and was extracted with dichloromethane for several times. The combined organic phase was dried over anhydrous $MgSO_4$ and evaporated under vacuum according to the previously reported procedure [20]. The mixture was recrystalized in absolute ethanol, and 1.93 g (70%) of yellow pale crystal of **(1)** was obtained; mp.202.8 -203.7°C (lit.[19], mp 203.2-203.9°C); 1H NMR (100 MHz, DMSO): δ 2.3 (6 H, s, 2 $CH_3$), 7.25 -7.49 (10H, m, phenyl-H).

*Synthesis of 2,6-dicarboxaldehyde-3,5-diphenyl-4H-pyran-4-one (2) by selenium dioxide:*

A solution of 2.76 g (0.01mol) 2, 6-dimethyl-3, 5-diphenyl-4H-pyran-4-one **(1),** and 3.33 g (0.03mol) $SeO_2$ in 10 mL dioxane was refluxed for 72h under $N_2$. Black precipitate (Se) was collected, and washed

several times by dichloromethane. The organic layer was evaporated under reduced pressure and was separated by column chromatography, and 2.05 g (60%) of pale yellow crystals 2,6- dicarboxaldehyde 3, 5-diphenyl -4H-Pyran-4- one (3) was obtained; mp. 196 -196.9 $^{o}$C, IR (KBr): 3031, 2879, 1708, and 1648 $cm^{-1}$. 1H NMR (DMSO): **δ** 7.40s, 10H, phenyl-H), 9.69 (s, 2H,-CHO). MS (EI, 70 eV): 304 ($M^{+}$). Anal. Calcd. For $C_{19}H_{12}O_4$: C 74.99; H 3.98; Found: C, 75.15; H, 4.08.

*Solvent-free preparation of 2,6-dicarboxaldehyde-3,5-diphenyl-4H-pyran-4-one (2) by selenium dioxide:*

1.38 g (5mmol) of 2,6-dimethyl -3,5-diphenyl -4H-Pyran- 4-one, and 5.55 g (50mmol) of $SeO_2$ was mixed and were reacted with each other under microwave irradiation for 15 min. The mixture was washed several times by dichloromethane, parts of mixture was separated by column chromatography and 1.28 g (75%) of 2,6-dicarboxaldehyde-3,5-diphenyl-4H-pyran-4-one was obtained.

*Synthesis of 2,6-bis((E)-(2-hydroxyphenylimino) methyl)-3,5-diphenyl-4H-pyran-4-one (E2):*

A solution of 2.18 g (0.02mol) 2-aminophenol in 10 mL MeCN was added to A solution of 3.04 g (0.01mol) 2,6-dicarboxaldehyde-3,5-diphenyl-4H-pyran-4-one(3) in 10 mL MeCN and was refluxed for 3h and the yellow precipitate was collected and 4.37g (90%) of yellow precipitate 2,6-bis((E)-(2-hydroxyphenylimino)methyl)-3,5-diphenyl-4H-pyran-4-one (E2) was obtained; mp 237-238.1˚C; IR (KBr): 3379, 3057, 2854, 1613, 1591, 1234, 976,700 and 754 $cm^{-1}$. $^{1}$H NMR (DMSO): δ 6.8 (4H, phenyl-H), 7.0 (4H, phenyl-H), 7.4 (10H, phenyl-H), 8.4 (2H, N=CH). 9.5 (2H, OH), $^{13}$CNMR (DMSO): δ 116.54, 119.67, 123.03, 128.11, 128.69, 128.85, 130.13, 131.01, 131.52, 136.77, 150.64, 151.9, 154.79, 177.06, MS (EI, 70 eV): 486 ($M^{+}$). Anal. Calcd. for $C_{31}H_{22}N_2O_4$: C 76.53; O13.15; H 4.56; Found: C, 76.32; O, 13.18; H, 4.50.

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