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# Synthesis and Properties of 2-Arylmethyldimedones and 3-Arylmethyl-4-hydroxy-quinolin-2(1*H*)-ones

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## Introduction

Previously, we have developed a new type of powerful antioxidants and free radical scavengers – arylmethyl Meldrum`s acids [1]. The activity of these compounds is mainly due to the presence of 1,3-dicarbonyl group and less affected by the substituents in the aryl moiety. In order to evaluate the role of the *β*-diketone fragment we synthesized other cyclic 2-arylmethyl-1,3-dicarbonyl compounds **1a** and **1b** – derivatives of 4-hydroxyquinolin-2(1*H*)-ones and dimedone, respectively.

## Results and Discussions

Typically, cyclic 2-arylmethyl-1,3-dicarbonyl compounds are obtained through Knoevenagel condensation of cyclic 1,3-dicarbonyl compound with aromatic aldehyde, followed by hydrogenation of the formed arylidene derivative. Literature survey shows that such methodology is rarely used for the synthesis of target compounds **1**.

It was intended to realize the aldol condensation of quinolinones **2a** with aromatic aldehydes in pyridine similarly to the method [2] suggested for the synthesis of different 2-arylidene-4-hydroxyquinolin-2(1*H*)-ones. Opposite to the literature [2] data, we obtained only products **3** from tandem Knoevenagel and Michael reaction. In order to find out the conditions applicable for the synthesis of arylidene derivatives **4**, the reaction of 4-hydroxy-6-methoxyquinolin-2(1*H*)-one and vanillin was used as a model system. Unfortunately, corresponding *bis*-adduct **3** was isolated instead of compound **4** in all cases (Table I).

TABLE I
Condensation of 4-Hydroxy-6-methoxyquinolin-2(1*H*)-one and Vanillin

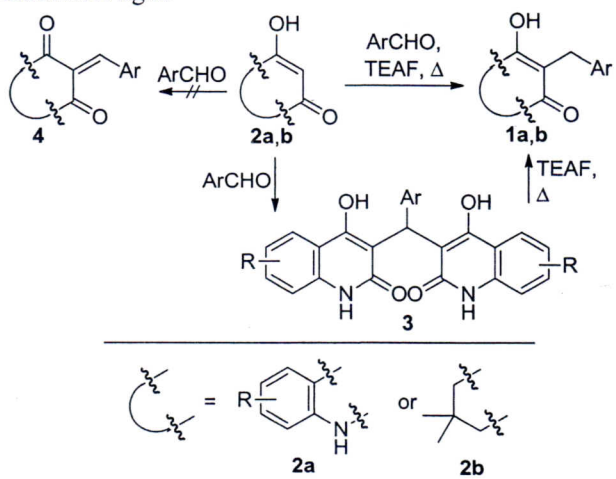
| Entry | Conditions | | Reaction time, h | Yield of comp. **3**, %[a] |
|---|---|---|---|---|
| | Solvent | Temp., °C | | |
| 1 | pyridine | 116 | 4 | 97 |
| 2 | water | 75 | 30[b] | 18 |
| 3 | water | 100 | 23.5 | 54 |
| 4 | trifluoroacetic acid | 78 | 30[b] | 16 |
| 5 | ethanol | 78 | 30[b] | 40 |
| 6 | acetic acid | 118 | 2 | 82 |

[a]The yield was detected in the mixture of products by HPLC.
[b]The reaction was quenched before full conversion of starting compounds.

In order to avoid formation of compounds **3**, the transformation was realized under reductive conditions (Scheme 1) in triethylammonium formate similarly to the methodology described for alkyl Meldrum`s acids [3]. Contrary to the literature [3] data the reactions of quinolin-2-ones **2a** or dimedone (**2b**) with aromatic aldehydes needed high temperature (more than 130 °C). These conditions were appropriate for different substituents both in aldehyde and quinolin-2-one moieties.

Target compounds **1a** can be obtained also by heating of *bis*-quinolin-2-ones **3** in triethylammonium formate. We could not establish whether the compounds **1a** formed directly from arylidene **4** or from *bis*-adduct **3**.

Most of the synthesized compounds **1a** and **1b** were analyzed for their antiradical (DPPH and galvinoxyl tests) and antioxidant (inhibition of oxidation of rapeseed oil methyl esters) properties. It was found out that all quinolin-2-one derivatives **1a** demonstrated weak activity, but the compounds **1a** and **1b** containing syringol and guaiacol moiety in the aldehyde fragment showed remarkably higher antiradical activity. It was observed that dimedone derivatives **1b** are fluorescent, when the solutions of compounds **1b** are exposed to ultraviolet light.




Scheme. 1. Synthesis of target compounds **1**.

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