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Proceeding Paper

Double Condensation of 3-Coumaranone with Aromatic Carbonyl Compounds Catalyzed by Brønsted Hyperacids †

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Abstract: Condensation of two molecule of 3-coumaranone with aromatic carbonyl compounds is catalyzed by PFAT under microwave irradiation, new dicoumararan-3-ones are obtained.

Keywords: hyperacid catalyst; 3-coumaranone; auron; 3,3′-(phenylmethylene) bis (benzofuran-2(3H)-one

1. Introduction

The acidic condensation of 3-coumaranone (benzofuran-2(3*H*)-one) with aromatic carbonyl compounds (aldehydes, diones) conduct to different products depending on the acidity of the catalyst. With poorly Bronsted acid such as clay, aurons (3-benzylideneben-zofuran-2(3*H*)-one and (or) 3-(hydroxyl(phenyl) methyl)benzofuran-2(3H)-on were formed with a microwave activation [1,2].

2. Results and Discussion

We reported herein that double condensation of 3-coumaranone with aromatic carbonyl compounds take place with Brønsted hyperacids. The condensation of 3-coumaranone and 8-hydroxy-3-coumaranone with diones (**2a**-**2d**) and the aldehydes (**2e**,**2f**) were studied in dimethylsulfoxide (DMSO) with pentafluorophenylammonium trifluoromethanesulfonate (PFAT) as catalyst [3] (Figure 1).

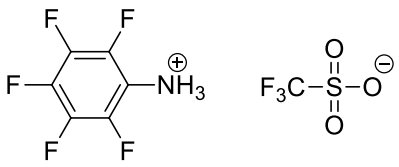

Figure 1. PFAT: pentafluorophenylammonium trifluoromethanesulfonate (PFAT); CAS: 912823-79-1.

New 3,3′-(phenylmethylene)bis(benzofuran-2(3H)-ones (bicoumaranones) were obtained according a condensation reaction (Figure 2), results are reported Table 1. Bicoumaranones) were identified by NMR and mass spectrometry (HRMS).

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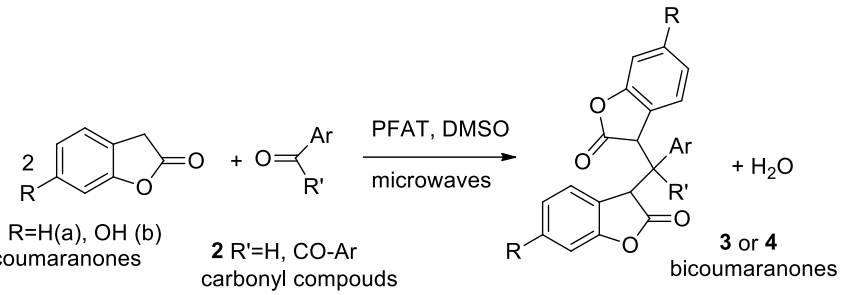
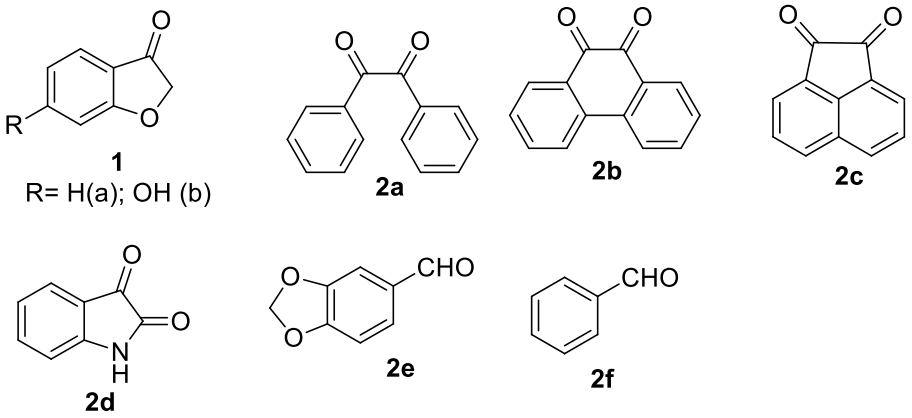


Figure 2. hyperacidic condensation of 3-coumaranones with carbonyl compounds.

Table 1. hyperacidic condensation of 3-coumaranones with carbonyl compounds into bicoumaranones.



Entry	Coumaranone	Carbonyl Comp.	Bicoumaranone	Yield (%)
1	**1a**	**2a**	**3a**	70
2	**1a**	**2b**	**3b**	80
3	**1a**	**2c**	**3c**	78
4	**1a**	**2d**	**3d**	62
5	**1a**	**2e**	**3e**	78
6	**1a**	**2f**	**3f**	75
7	**1b**	**2a**	**4a**	60
8	**1b**	**2d**	**4d**	75

Similar results can be obtained with trifluoromethanesulfonic acid (Triflic acid) [4] without solvent as catalyst under microwave irradiation with a slightly less good yield. To our knowledge, bicoumaran-3-one are only cited in one paper of the litterature as by-product [5].

3. Reaction Mechanism

A reaction mechanism is proposed (Figure 3) involving the addition of a carbocation to an enolic form, this mechanism is very close to that known for the condensation of aldehyde acids with two molecules of 4-hydroxycoumarone to form dicoumarols [6].

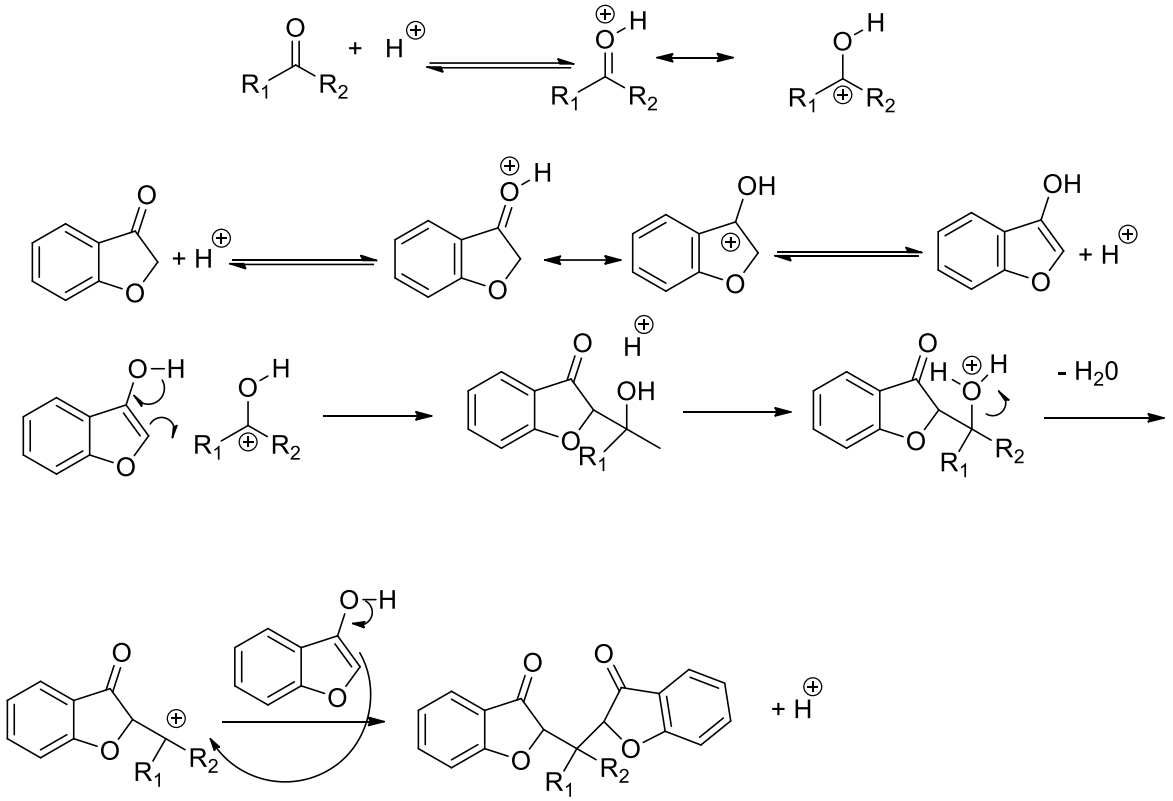


Figure 3. Mecanism proposed for the formation of dicoumaranone from two molecules of 3-coumaranone and one molecule of carbonyl compond.

4. Experimental

4.1. General Information

The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Brüker AC 400 spectrometer at 400 MHz. Samples were recorded in $CDCl_3$ solutions using TMS as an internal standard. The chemical shifts are expressed in δ units (ppm) and quoted downfield from TMS.

Mass spectra were recorded on Xevo G2-XS QTof Waters.

Microwave irradiations were performed at 2450 MHz with an Anton–Paar Monowave 300.

4.2. Starting Reactants

The 6-hydroxybenzofuran-3(*2H*)-one (**1b**) was prepared according to the literature [7]. Benzofuran-3(*2H*)-one (**1a**), benzil (**2a**), phenanthraquinone (**2b**), acenaphthoquinone (**2c**), isatin (2d), piperonal (**2e**) and benzaldehyde (**2f**) are commercial (Alfa).

4.3. Typical Experiment

In a typical experiment **1a** (2 mmol) and **2b** (1 mmol) was dissolved in DMSO (1 mL) with PFAT (0.01 mmol).The mixture was irradiated at 160 °C for 10 min. The mixture become dark red.

Analysis with Xevo G2-XS Qtof Waters: ESI + (M + 23(Na+) = 481.1047 corresponding to $C_{30}H_{18}O_5$; ESI^- (M + 23-H) = 457.1071.

5. Conclusions

Aurones are known for their numerous biological properties, it is likely that these 3,3′-(phenylmethylene) bis(benzofuran-2(3H)-ones have interesting properties which will be studied in the near future.

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