Clay catalysis: solventless condensation of benzofuran-3(*2H*)-one with α, β-dicarbonyl compounds under microwave irradiation. Synthesis of new acyl-aurones.

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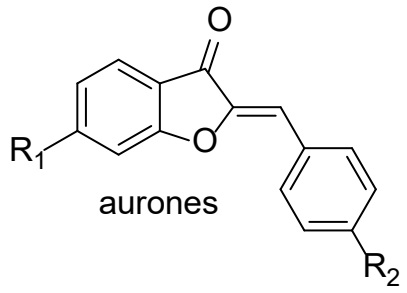
Aurones are natural products and some of aurone derivatives were used recently in medicinal chemistry.

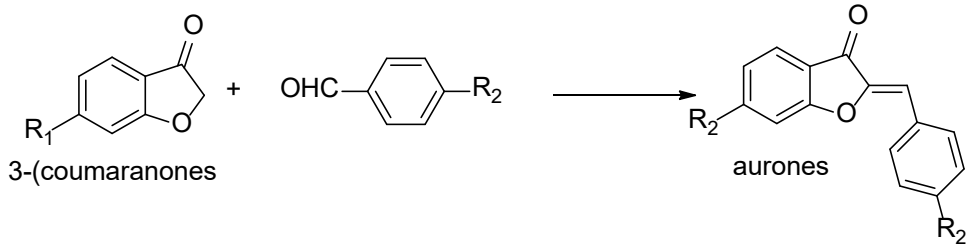


aurones

I.Mazziotti,, G .Petrarolo, C. La Motta. Aurones: A Golden Resource for Active Compounds, *Molecules* **2022**, *27*(1), 2; doi : 10.3390/molecules27010002

G. Sui,T. Li, B. Zhang, R. Wang, H. Hao, W. Zhou, Recent advances on synthesis and biological activities of aurones, *Biorg. Med. Chem.*., **2021**, *29* , 115895; doi :10.1016/j.bmc.2020.115895.

The aurones were generally synthesized by condensation of coumaran -3-one with aldehydes under acido-basic conditions.

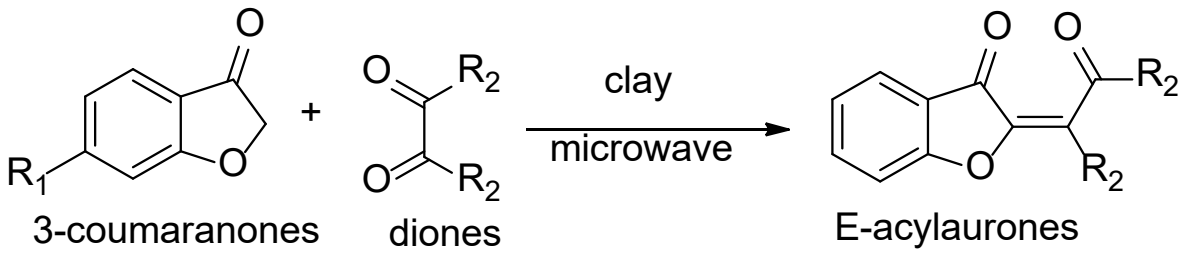


3-(coumaranones aurones

While ketones generally do not condense easily in acidobasic conditions with 3-coumaranones, we report herein that the more electrophilic α–β-dicarbonyl compounds lead to these condensations and conduct to new tetrasubstituted aurones. To our knowledge, the tetrasubstituted aurones described in literature were obtained only by ring formation.

- In order to avoid the benzylic rearrangement of the α,β–dicarbonyl compounds in a basic medium, we have preferred to use acidic catalysis rather than basic one. We have described since 1989 , the clays as good catalysts in solvent-free Knoevenagel reaction under microwave irradiation (Scheme 1).

A. Ben Alloum, B. Labiad, D. Villemin, Application of microwave heating techniques for dry organic reactions. *J. Chem. Soc. Chem. Commun.*, **1989**, 386-387; doi: 10.1039/C39890000386.



Scheme 1: acidic catalysed condensation of 3-coumaranone with α, β-dicarbonyl compounds.

According to these methodology, we have used an equimolar mixture of benzofuran-3(*2H*)-one and dicarbonyl compound absorbed on clay in close tube irradiated by microwave at 2450 MHz in a resonance cavity Anton Paar Monowave 300.

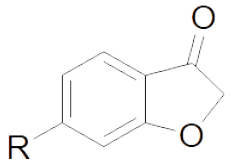
K. Boussafi, D. Villemin, N. Bar, M. Belghosi. Green Synthesis of Aurones and Related Compounds under Solvent-free Conditions., *J. Chem. Res.* **2016** ,*40*, 557-569; doi: 10.3184/174751916X14719593488659.

We have tested the reaction of **1a** with **2a** and with the clays K10, KSF or algerian clay of Maghnia (Maghia) treated with sulphuric acid as catalyst. All these clay conduct to the same yield (80%) after microwave irradiation.

Under these conditions novel acyl-aurones not previously described were obtained according the scheme 1. The irradiation conditions and the yields are reported in Table 1. The new products were characterized by mass spectroscopy and ^{13}C NMR spectroscopy.

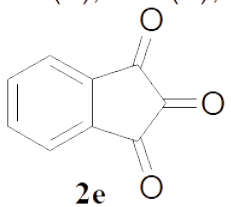
Table 1 : Synthesis of Aurones

Entry	Coumaranone 1a-b	Dicarbonyl 2	Conditions	Yield of 3 (%)
	1a	2a	200°C, 15 min	3a 80
	1a	2b	200°C, 10 min	3a
	1a	2c	200°C, 10 min	3a
	1a	2d	200°C, 10 min	3d
e	1a	2e	200°C, 15 min	3e
f	1b	2a	180°C,10 min	3f
g	1b	2b	180°C, 10 min	3g

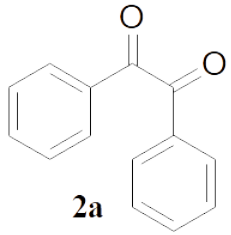


1

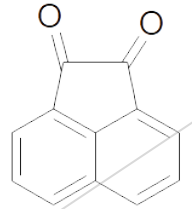
R= H (a); OH (b); OCH_3 (c)



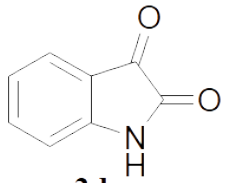
2e



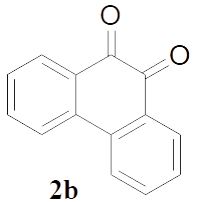
2a



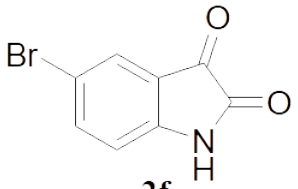
2c



2d

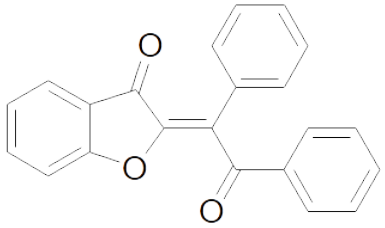


2b

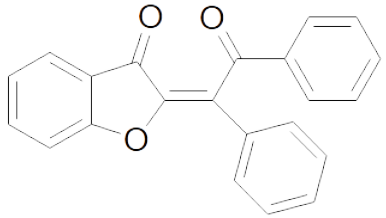


2f

Two stereoisomers can be formed in the acidic catalysed condensation of 3-coumaranone with carbonyl compounds. In the case of aldehydes only the more stable Z-isomer was obtained. In the case of α, β-dicarbonyl compounds, only one **3a** stereoisomer was formed (TLC, NMR)



3A Z isomer



3A E isomer, more stable

- In conclusion, the reaction of dione or trione with coumaranones in the presence of clays conducts under microwave irradiation to acylaurones.
- This reaction allows a simple and easy synthesis of a variety of diones or triones derivatives.
- Only the *E*- isomer of 3a was found.