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ORIGINAL ARTICLE

Microwave-assisted solvent-free one pot synthesis of isobenzofuran-1(3*H*)-ones using sulphamic acid catalyst

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KEYWORDS

Isobenzofuran-1(3*H*)-ones; Sulphamic acid catalyst 2-carboxybenzaldehyde

Abstract Use of sulphamic acid for the synthesis of isobenzofuran-1(3*H*)-ones from 2-carboxybenzaldehyde and substituted cyclic as well as non-cyclic ketones in good yield has been demonstrated. Sulphamic acid proved to be an excellent catalyst for this condensation reaction. Reaction has been carried out by both conventional and microwave methods.

1. Introduction

Isobenzofuran-1(3*H*)-ones forms important class of natural products possessing significant biological properties like antibacterial, anti-convulsant, anti-HIV, anti-asthmatic, antitumor, anti-platelet activities, and anaesthesia (Pedrosa et al., 2006; Zhu et al., 2004; Safari et al., 2007). In particular, 3-substituted phthalides are vital heterocyclic motifs in many bioactive compounds such as iso-coumarins, anthraquinones, anthracyclines, and several alkaloids (Paradkar et al., 1998). 3-Substituted phthalides are easily converted into (a) 3-phenacylidene phthalides, known for their plant growth regulatory activity (Bousquet et al., 2008; Houbin and Dayawan, 1981), (b) 3-alkylidene phthalides, known for their biological importance (Mali et al., 1990) and (c) 3-styryl phthalides which are used as colour formers for heat and pressure-sensitive recording materials importance (Mali and Massey, 1997). The literature survey revealed that 3-phenacylphthalides are synthesized by reacting 2-bromobenzaldehyde with 1,3 dicarbonyl compounds under catalytic conditions in the presence of alkali importance (Lee et al., 1997; Chatterjee et al., 1974). Recently it has been reported that the reaction of phthalaldehydic acid with various aromatic methyl ethers in the presence of TFA provided 3-aryl phthalides in good yields (Paradkar et al., 1998). This observation led us to explore the reaction of 2-carboxybenzaldehyde with acetophenone which gave 3-phenacylphthalide in good yield. Substituted acetophenones and 2-carboxybenzaldehyde gave products which were fully characterized by ^{1}H NMR.

Solid acid catalyst has become one of the most important tools for synthesis and development of sustainable chemical production. These catalysts are economic, active and selective. The combination of solid acid catalyst with microwave irradiation provides more benign processes, very short reaction time, and high product purity with no secondary reactions.

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In continuation of our ongoing research for the development of simple and efficient methods for the synthesis of various heterocyclic compounds (Kokare et al., 2007; Kotharkar et al., 2005; Bahekar and Shinde, 2004; Zambre et al., 2009) herein we have presented a novel, mild and efficient method for the synthesis of isobenzofuran-1(3*H*)-ones using microwave-assisted and conventional method in the presence of sulphamic acid catalyst.

2. Results and discussion

Synthesis of isobenzofuran-1(3*H*)-ones was achieved using Methods A and B. Method A comprises of conventional heating and Method B is microwave-assisted synthesis. Microwave used in the study is Microsynth Lab station of Ethusi Milestone with temperature control (see Scheme 1).

Optimization of reaction in Method A was carried out using different concentrations of sulphamic acid. Effect of different concentrations of sulphamic acid on the yield of final product was studied. From the data in Table 1 it is observed that the use of 20 mol% sulphamic acid was more effective.

Also in Method B optimization was carried out by using different watts at different temperatures. It was observed that maintaining temperature at 80 °C at 1000 W was most favourable.

Using similar conditions different derivatives were synthesized. The yields and time required for the reaction using Methods A and B are summarized in Table 2.

The progress of the reaction was monitored by TLC [solvent system: (ethyl acetate):(hexane) = 1:4]. After completion of the reaction, the reaction mixture was extracted with dichloromethane:water. The pure products were obtained by recrystallization using EtOH with 93–98% yields in Method A and 94–99% in Method B. All the synthesized compounds were characterized by ^{1}H NMR, mass spectrometry (ES-MS).

In conclusion novel and highly efficient methodology for the synthesis of isobenzofuran-1(3*H*)-ones by one pot condensation reaction of acetophenones, phthalaldehydic acid catalysed by sulphamic acid has been established. This method offers several significant advantages such as, high conversions, easy handling, clean reaction profile and shorter reaction times, which makes it a useful and attractive process for the rapid synthesis of substituted isobenzofuran-1(3*H*)-ones.

2.1. Method A

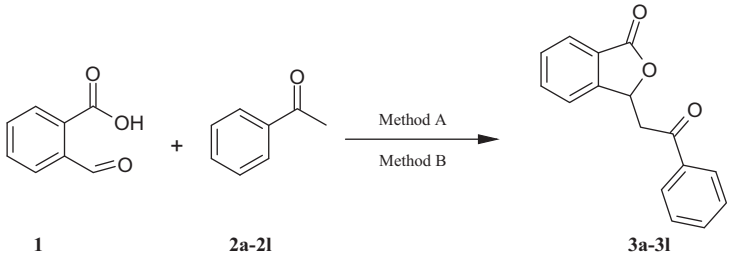
2.1.1. General procedure for conventional synthesis of isobenzofuran-1(3H)-ones (**3a–3l**)

A mixture of 2-carboxybenzaldehyde (10 mmol), ketone (12 mmol) and sulphamic acid (2 mmol) was treated at 120 °C (the reaction mixture turns to liquid) under solvent-free condition for the appropriate time as indicated in Table 1. The progress of the reaction was monitored by TLC [solvent system: (ethyl acetate):(hexane) = 1:4]. After completion of the reaction, the reaction mixture was extracted with dichloromethane:water. The pure products were obtained by recrystallization using EtOH in 93–98% yields. All the synthesized compounds were characterized by ^{1}H NMR, mass spectrometry (ES-MS).

2.2. Method B

2.2.1. General procedure for microwave-assisted synthesis of isobenzofuran-1(3H)-ones (**3a–3l**)

A mixture of 2-carboxybenzaldehyde (10 mmol), ketone (12 mmol) and sulphamic acid (2 mmol) was treated at 80 °C

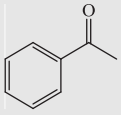
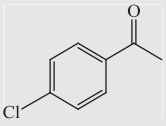
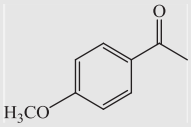
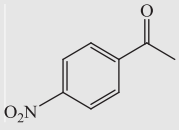
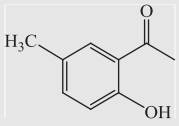
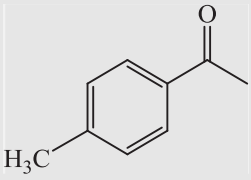
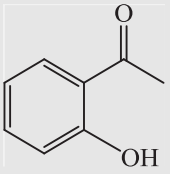
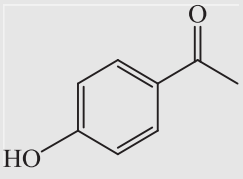
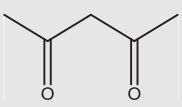


Scheme 1 Synthesis of isobenzofuran-1(3*H*)-ones using sulphamic acid as a novel catalyst under solvent-free condition. Method A: Conventional synthesis: Sulphamic acid catalyst 20 mol%, 105–120 min, 120 °C, solvent free. Method B: Microwave-assisted synthesis: Sulphamic acid catalyst 20 mol%, 2 min, 80 °C solvent free.

Table 1 Synthesis of different isobenzofuran-1(3*H*)-ones using sulphamic acid under solvent-free condition using various mol% of sulphamic acid.

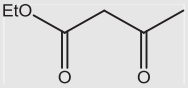
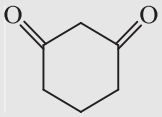
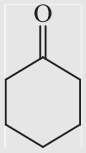
Sr. no.	Sulphamic acid catalyst (mol%)	Reaction time (min)		Yield (%)	
		Conventional	Microwave	Conventional	Microwave
1	50	100	2	98	99
2	40	100	2	98	99
3	30	105	2	98	99
4	20	105	2	98	99
5	10	130	2	92	94

Table 2 Synthesis of different isobenzofuran-1(3*H*)-ones using sulphamic acid under solvent-free condition.

Sr. no.	Reactants	Time (min)		Melting point (°C)		Yield (%)	
		Conventional	Microwave	Observed	Reference	Conventional	Microwave
3a		105	2	145	145	98	99
3b		120	2	146	146	95	97
3c		105	2	220	219	93	95
3d		120	2	209	210	94	95
3e		120	2	134	135	93	95
3f		110	2	149	149	94	96
3g		110	2	154	154	95	96
3h		120	2	170	170	96	96
3i		105	2	104	104	94	94

(*continued on next page*)

Table 2 (*continued*)

Sr. no.	Reactants	Time (min)		Melting point (°C)		Yield (%)	
		Conventional	Microwave	Observed	Reference	Conventional	Microwave
3j		110	2	79	78	94	94
3k		115	2	220	220	97	98
3l		110	2	Oil	Oil	97	98

(the reaction mixture turns to liquid) under solvent-free condition for the appropriate time as indicated in Table 1. The progress of the reaction was monitored by TLC [solvent system: (ethyl acetate):(hexane) = 1:4]. After completion of the reaction, the reaction mixture was extracted with dichloromethane:water. The pure products were obtained by recrystallization using EtOH in 94–99% yields. All the synthesized compounds were characterized by ^{1}H NMR, mass spectrometry (ES-MS).

The representative analytical data for 3-(2-oxo-2-phenylethyl) isobenzofuran-1(3*H*)-ones (**3a**):

^{1}HNMR ($CDCl_3$ – 200 MHz): 8.00–7.66 (m,9H), 6.123–6.043 (t,1H, J = 6.5), 3.864–3.808 (d,1H, J = 17.5), 3.755–3.691 (d,1H, J = 18.1).

ES-MS m/z (%): 252(M + H).

Anal. Calcd for $C_{16}H_{12}NO_3$: C, 76.18; H, 4.79; Found: C, 76.21; H, 4.81.

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