Organic acids as efficient catalysts for microwave-assisted synthesis of xanthenones

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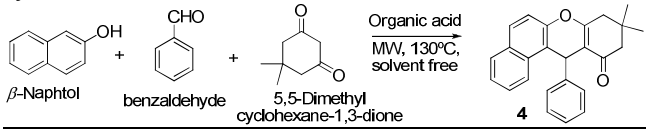
INTRODUCTION

Organocatalysis is a process in which metal-free organic molecules are used to accelerate the rate of chemical reactions.[1] The use of organocatalysts has also been increased due to their low toxicity to the environmental and low sensitivity to oxygen. Natural organic acids (NOA) are biodegradable and thus considered eco- and user-friendly alternatives to synthetic organocatalysts.[2] This work aimed to evaluate oxalic, malonic, succinic and acetic acids as potential organocatalysts for microwave-assisted synthesis of xanthenones under solvent-free conditions.

RESULTS AND DISCUSSION

The efficiency of oxalic, malonic, succinic and acetic acids as catalysts under solvent free and microwave irradiation (MW) was first determined using the reaction described in Table 1.

Table 1. Efficiency of natural organic acids (NOA) for the synthesis of xanthenone **4***,**.

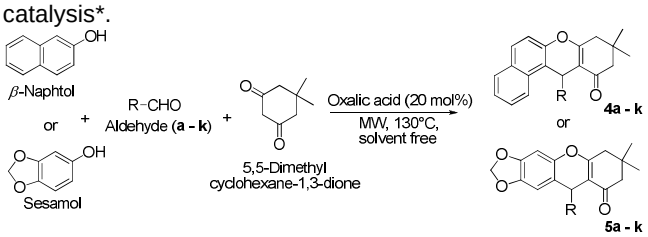


NOA (mol%)	MW (min)	Reaction yield (%)			
		Oxalic acid	Malonic acid	Succinic acid	Acetic acid
5	5	58	9	10	1
5	10	51	35	26	58
10	5	62	16	2	2
10	10	52	21	51	51
20	5	82	17	14	51
20	10	65	54	55	67

*Reagents and conditions: benzaldehyde/β-naphtol/5,5-dimethyl-1,3-cyclohexanedione (molar ratio = 1:1.2:1.5). **Reactions free of NOA furnished **4** in 16% and 20% after 5 and 10 min of MW, respectively. MW: microwave irradiation.

The best yield reaction was achieved when using 20 mol% oxalic acid and 5 min of MW. This condition was further used to obtain a series of xanthenones by varying the aldehyde used (Table 2). A wide range of aromatic aldehydes bearing both electron-donor and electron-withdrawing substituents could successfully be used to provide at least 20 xanthenones from either β-naphtol or sesamol (Table 2).

Table 2. Synthesis of xanthenones under oxalic acid-catalysis*.



Aldehyde (R-CHO)	Phenolic Compound	
	β-naftol	Sesamol
	Yield (%)	Yield (%)
4-NO_2-C_6H_4- (**a**)	80[a]	54[b]
4-F-C_6H_4- (**b**)	72[a]	91[b]
4-Cl-C_6H_4- (**c**)	81[a]	68[b]
2-HO-C_6H_4- (**d**)	91[b]	90[b]
3-HO-C_6H_4- (**e**)	60[b]	50[b]
4-HO-C_6H_4- (**f**)	35[a]	70[b]
4-MeS-C_6H_4- (**g**)	86[a]	79[b]
4-MeO-C_6H_4- (**h**)	70[a]	44[b]
3,4-(MeO)-4-(HO)-C_6H_2- (**i**)	46[a]	62[a]
3-(MeO)-4-(HO)-C_6H_3- (**j**)	55[a]	63[a]
C_6H_5-(**k**)	82[b]	67[a]

*Reagents and conditions: benzaldehyde/phenolic compound/5,5-dimethyl-1,3-cyclohexanedione (molar ratio = 1:1.2:1.5). [a]MW-assisted reaction (10 min). [b]MW-assisted reaction (5 min).

The best time of reaction for obtaining xanthenones from β-naftol was 10 min while sesamol furnished better yields from 5 min reactions regardless the nature of the aldehyde used.

CONCLUSION

A novel approach was developed for the preparation of xanthenones based on the environmentally friendly use of oxalic acid under MW and solvent-free conditions.

ACKNOWLEDGEMENTS

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