Asian Journal of Chemistry Vol. 19, No. 5 (2007), 4121-4123

NOTE

Synthesis of Deoxybenzoins Using Microwave Irradiations under Solvent Free Condition

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Phenols on reaction with arylacetic acid in the presence of polyphosphoric acid (PPA) under microwave irradiation and solvent free condition give deoxybenzoins directly in high yields.

Key Words: Deoxybenzoins, Polyphosphoric acid, Arylacetic acid, Phenols, Microwave irradiation.

Deoxybenzoins are the useful starting materials for the synthesis of compounds such as symmetrical and unsymmetrical stilbenes, dibenzyls and benzils with varying substitutions in the two rings, while 2-hydroxydeoxybenzoins (2-hydroxyphenyl benzyl ketones) are the required intermediates for the synthesis of number of naturally occurring flavonoids[1,2] including isoflavones, isoflavanones, 3-phenyl-4-hydroxycoumarins, α-methyldeoxybenzoins. The required 2-hydroxydeoxybenzoins are generally obtained by Hoesch reaction[3] between phenols and benzyl cyanides. Large attempts have also been made to prepare these intermediates by direct acylation of phenols with phenyl acetic acids in the presence of various condensing reagents which include anhydrous zinc chloride (Nencki reaction)[4], boron trifluoride[5], borontrifluoride etherate[6,7], phosphorous oxytrichloride-zinc chloride[8]. The use of aryl acetic anhydrides in the presence of boron trifluoride etherate has also been made for the synthesis of these compounds[6]. The above listed methods suffer from one or the other limitations of longer reaction periods and poor yields due to formation of mixture of compounds specially in case of polyhydroxy benzenes such as phloroglucinol and pyragallol.

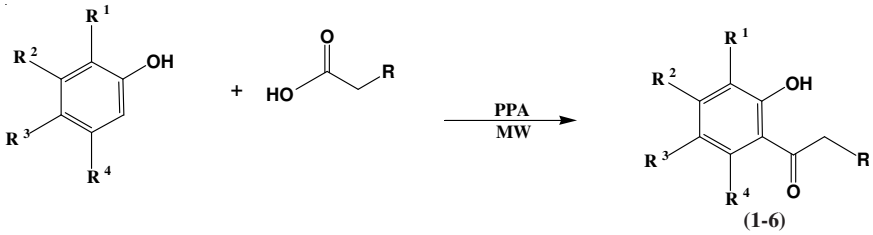
In recent years, organic reactions using microwave (MW) irradiations have gained enormous importance as it accelerates the variety of synthetic transformations[9,10]. Another important feature of this technique is that the reactions can be carried out under solvent free condition thus providing eco-friendly conditions for the reactions.

Here, we wish to report an efficient method for direct acylation of phenols in the presence of polyphosphoric acid (PPA) using microwave irradiation under solvent free conditions. A mixture of resorcinol, phenyl acetic acid and PPA was irradiated in 20 mL loosely stoppered pyrex bottle. The compound obtained after working up was identified as 2,4-dihydroxyphenyl benzyl ketone by its ^{1}H NMR spectra and direct comparison with the authentic sample[11] (Co-IR). Using above procedure differently substituted phenols were reacted with phenyl acetic acid, 4-methoxy phenyl acetic acid to get various substituted 2-hydroxydeoxybenzoines (**1-6**).

The reaction was carried out in a domestic microwave oven (samsung output energy 900 W, frequency 2450 MHz, with temperature control arrangement No. CE 118 KF) using 40 % power for all the experiments and maintaining oven temperature at 40ºC in 20 mL loosely stoppered pyrex bottle.

Preparation of substituted 2-hydroxydeoxybenzoins (1-6)

PPA was prepared in 20 mL loosely stoppred pyrex bottle by subjecting a mixture of P_2O_5 (0.042 mol) and phosphoric acid (0.03 mol) to microwave irradiation (4 × 5 s). To this freshly prepared PPA was added phenol (0.02 mol), phenyl acetic acid (0.025 mol) and the mixture was irradiated in microwave oven for time periods given in the Table-1 (**Scheme-I**).



(1-6)

Scheme-I

TABLE-1
MICROWAVE ASSISTED SOLVENT FREE SYNTHESIS OF DEOXYBENZOINS

Compd. No.	R	R^1	R^2	R^3	R^4	Time (s)	Yield (%)	m.p. (ºC)	Lit. m.p. (ºC)	Ref.
1	C_6H_5	H	OH	H	H	10	90	113-14	114	11
2	C_6H_5	H	OH	H	OH	7	80	163-64	163-65	12
3	C_6H_5	OH	OH	H	H	8	84	140-42	141-42	6
4	C_6H_5	H	H	OH	H	10	82	112-14	113	13
5	$C_6H_4OCH_3(p)$	H	OH	H	H	8	81	156-58	158-59	14
6	$C_6H_4OCH_3(p)$	H	OH	H	OH	7	78	190-91	192-93	15

Completion of the reaction was checked on TLC. Crushed ice was added to the reaction mixture to decompose the excess of PPA. The residue thus obtained was filtered, washed with water and then treated with aqueous sodium bicarbonate solution to remove unreacted acid. The compound was finally crystallized from hot water.

In conclusion, it can be stated that the present method is an highly efficient microwave assisted solvent free protocol for the direct preparation of substituted 2-hydroxydeoxybenzoins of phenols.

ACKNOWLEDGEMENTS

The authors thank to CSIR, New Delhi and M.D. University, Rohtak for providing financial assistance to Suresh Kumar and M.S. Lamba, respectively.

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(*Received*: 3 April 2006; *Accepted*: 14 March 2007) AJC-5528