September 2009 *Volume 5 Issue 3*

Trade Science Inc.

Organic CHEMISTRY

An Indian Journal

Short Communication

OCAIJ, 5(3), 2009 [357-359]

Solvent free synthesis of aromatic diether from 7-Hydroxy coumarin without catalyst under microwave irradiation

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Received: 3rd July, 2009 ; Accepted: 13th July, 2009

ABSTRACT

7-Hydroxy coumarin reacts remarkably fast with many phenols and alkyl halides under microwave irradiation which results in aromatic diethers. Irradiation of the mixtures in a domestic microwave oven leads in a remarkable short time (60-400 sec.) to the desired O-alkyl derivatives of 7-Hydroxy coumarin. The procedure is simple, rapid, efficient and is an alternative for the use of inorganic carrier and organic solvent for microwave irradiation.

KEYWORDS

7-Hydroxy coumarin;
Alkyl halides;
Phenols and diether.

1. INTRODUCTION

Microwaves are a powerful reliable energy source that may be adapted to many applications. It has been reported that microwaves will provide the organic chemist with the right tools and knowledge to be able to effectively apply microwave energy to any synthetic route[1]. Microwave heating and its application in organic chemistry for the reactions in 'dry' media is currently developed successfully and in the past few years there has been a tremendous interest in this area[2-5]. Remarkable decrease in reaction times and in some cases cleaner reaction and better yields have been reported with microwave irradiation[6]. Reactions under dry conditions (i.e., in the absence of a solvent, on solid support with or without catalysts) were originally developed in last eighties[7]. Synthesis without solvents under microwave irradiation offers several advantages[8]. The absence of solvent reduces the risk of hazardous explosions when the reaction takes place in a closed vessel in an oven. During microwave induction of reactions under dry conditions the reactants adsorbed on the surface of alumina, silica gel and clay absorb the microwaves where as the support does not. Consequently, such supported reagents efficiently induce reactions under safe and simple conditions with domestic microwave ovens instead of specialized commercial microwave systems that require sealed Teflon bombs[9].

The reaction between phenols and alkyl halides a series of PTC has been reported in an aqueous solution of sodium hydroxide in the absence of organic solvent[10]. Copper catalyzed diaryl ether synthesis of cesium carbonate as a base has been reported[11]. Phenols have been alkylated using the alkyl halide/cesium carbonate/acetonitrile system[12].

Synthesis of alkyl phenyl ethers has been carried out using fluoride ion[13]. Microwave irradiation has been used

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for the rapid synthesis of a variety of compounds[14-18].

Thermal conductivity of various materials is important, in conventional heating, employing an external heat source. The conductive heating results in long equilibrium time and absolute control over the reaction become difficult. Conversely, in microwave heating the microwaves are coupled directly with molecules in reaction mixture leading to rapid rise in temperature and the container is not heated.

As this process is independent of the thermal conductivity of the reactor (vessel) materials, the result is an instantaneous localized superheating of anything that will react to dipole rotation or ionic conduction, the two fundamental mechanisms for transferring energy from microwaves to the reaction mass being heated. Microwaves transfer energy in 10^{-9} s with each cycle of electromagnetic energy. The kinetic molecular relaxation from this energy is approximately 10^{-5} s. This means that the energy transfers faster than the molecules can relax, which results in non-equilibrium conditions and high instantaneous temperatures that affect the kinetics of the system. Further, microwaves do not influence the orientation of those collisions, nor the activation energy. An increase in temperature causes greater movement of molecules which leads to a greater number of energetic collisions. This leads to enhancement in reaction rates and product yields[19]. Aromatic ethers can be obtained from phenols and halide under microwave irradiation in absence of any inorganic carrier and organic solvent. This method is very simple, rapid and affords good yields of aromatic ethers[20]. O-alkylation's of phenolic compounds is a versatile approach to aryl ether. These compounds are the basis of many pharmaceutical templates that are used in dry discovery with conducting heating these reactions can take anywhere from one to seven days for completion. Microwave enhanced transformations of a polymer bound base (PTBD) with phenols occur in less than 30 minutes[21]. Ether is important intermediates in organic synthesis. They are useful as pesticides, fungicides and selective herbicides for the control of various noxious weeds[22,23].

2. EXPERIMENTAL

Melting points were determined in open capillaries in Paraffin bath and are uncorrected. IR spectra were recorded in KBr disc on a Perkin Elmer spectrometer for all products 1H-NMR spectra were recorded on NMR spectrometer in $CDCl_3$ using chloroform an internal standard. The mass spectra were recorded on GCMS-QP 2010 mass spectrometer. All the reagents used were of AR grade and were used without further purification. The reactions were carried out in microwave oven. (CE2977 Samsung)

All compounds were characterized by modern spectral and elemental techniques.

d. ^{1}H NMR : ($CDCl_3$, δ ppm) :2.39 (s, -CH_3), 6.05 (s, Ar-OCH_2CH_2O-Ar), 8.09(s, Ar-OH), 6.66-7.50 (m, Arom) ES/MS: m/z 312.

e. ^{1}NMR : ($CDCl_3$, δ ppm) :2.38 (s, -CH_3), 6.04 (s, Ar-OCH_2CH_2O-Ar), 6.79-7.45 (m, Arom) ES/MS: m/z 341.

J. ^{1}H NMR : ($CDCl_3$, δ ppm) :2.38 (s, -CH_3), 6.06 (s, Ar-OCH_2CH_2O-Ar), 6.81-8.80 (m, Arom) ES/MS: m/z 347

n. ^{1}H NMR : ($CDCl_3$, δ ppm) :2.38 (s, -CH_3), 6.08 (s, Ar-OCH_2O-Ar), 6.66-7.50 (m, Arom) ES/MS: m/z 298.

t. ^{1}H NMR : ($CDCl_3$, δ ppm) :2.39 (s, -CH_3), 6.04 (s, Ar-OCH_2O-Ar), 6.77-7.58 (m, Arom) ES/MS: m/z 333.

3. RESULTS AND DISCUSSION

Under microwave irradiation, number of phenols reacts remarkably fast with 7-Hydroxy coumarin and alkyl halide to give aromatic diethers.The results are summarized in TABLE 1.

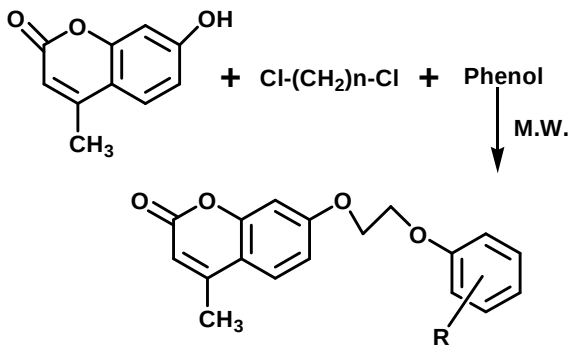

TABLE 1 : Physical data of the synthesized compounds

Entry	Phenol	n	W and T required for reaction*		Yield (%)	M.P. (°C)
			W	Sec.		
a	3- Hydroxy pyridine	2	600	65	72	128
b	Resorcinol	2	600	82	70	82
c	Picric acid	2	600	55	68	123
d	Hydroquinone	2	600	247	83	158
e	O-nitro phenol	2	600	65	74	171
f	2-naphthol	2	600	75	75	110
g	P-nitro phenol	2	600	360	68	112
h	1-naphthol	2	600	80	74	86
i	Salicylic acid	2	600	114	70	109
j	8-Hydroxy quinoline	2	600	73	72	80
k	3-Hydroxy pyridine	1	600	210	72	112
l	Resorcinol	1	600	100	73	149
m	Picric acid	1	600	60	66	131
n	Hydroquinone	1	600	300	69	143
o	O-nitro phenol	1	600	80	70	182
p	2-naphthol	1	600	160	72	116
q	P-nitro phenol	1	600	420	65	89
r	1-naphthol	1	600	60	69	90
s	Salicylic acid	1	600	270	66	123
t	8-Hydroxy quinoline	1	600	65	68	161

***Where W and T indicate watts and time, respectively.**

4. CONCLUSIONS

The present investigation we have been developed simple and economical one step procedure for the diether of 7-hydroxy coumarin that occurs under mild conditions using inexpensive reagents and microwave oven as the irradiation source. Moreover, our method of diether synthesis is superior to other methods. We use coumarin, alkyl halides and phenols as starting materials instead of Inorganic carriers and organic solvents. This makes the procedure simple, convenient and safe. On the other hand, this study leads to a better understanding of O- alkylation of 7-hydroxy coumarin derivatives.

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