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# Fast Synthesis of Benzofurans from Coumarins

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**Abstract**

Heterocyclic nucleus forms the basic of most of the medicinal compounds. Instead of using classical method. It is proposed to carry out the synthesis of heterocyclic compounds by ring transformation that may involve ring contraction, ring retention and ring expansion in five, six and seven membered heterocycles containing oxygen, sulphur and nitrogen. Special attention would be paid to apply the principles of green chemistry while carrying out these ring transformations e.g., choice of safer reagents, use of green catalysts and phase-transfer catalysts whenever necessary. Here a new solid support, Zinc oxide is used. Employing microwave incluced synthesis whenever possible, minimizing the use of toxic solvents. Benzofurans have been achieved from coumarins by ring contraction reaction in single step. Microwave irradiation has been used to shorten the reaction time and to improve the yield.

*Key words :* Ring contraction, Benzofurans, Coumarins, Microwave, Zinc Oxide as new solid support, Green Chemistry, Medicinal Compounds.

## Introduction

**B**enzofuran derivatives are a major group of biologically active heterocycles which are usually important constituents of plant extracts used in medicinal chemistry for their various biological activities.[1-3] Due to their diverse activities, much attention has been paid to synthetic strategies to access these systems, and a number of methods have been developed.[4] Pyrolysis of 2-pyrone at 900-1000°C in a stream of nitrogen leads to ring contraction into furan. The yield[5] of furan is, however, low (15%). On the other hand pyrolysis of coumarin under the same conditions gives, surprisingly, a very high yield (85%) of benzofuran. In the present paper, we report the same reaction, i.e., the conversion of coumarins (1a-c) into benzofurans (2a-c) by ring transformation reaction (Scheme-1) under microwave irradiation. It is solid state reaction. For solid state reaction, the reaction is to perform on a solid support[6] (no solvent) which couples

effectively with microwaves. Silica and alumina are the common solid supports, but we have used a new solid support, zinc oxide.

Organic transportations carried out under microwave irradiation offer several advantages; these require shorter reaction time, involve very small amount of solvent, and the products obtained are in higher yield.[7-8]

**Experimental**

Reactions were carried out under atmospheric pressure in an open vessel adapted to a microwave oven. All compounds were identified by IR and $^1$H NMR and gave satisfactory result in comparison with authentic samples. Boiling point of benzofuran is in good agreement with literature data (Table-1).Purity of the compound was checked by TLC. IR spectra were recorded on a Perkin Elmer 157 spectrometer. $^1$H NMR spectra were recorded in acetone / $CCl_4$ on a Bruker WM 400 MHz spectrometer using TMS as an internal reference.

*Benzofurans (2a - c) :*

Coumarin (1a - c) (0.05 mol) was ground with zinc oxide (5g) and the mixture irradiated with microwave at 40% (320 W) level in a Kenstar OM-20 ESP (800 W) unmodified domestic oven operating at 2450 MHz for the time indicated in Table-1. The reaction product was extracted with two 100 ml portions of ether and the ether removed on a rotatory evaporator. The residue was distilled and benzofuran collected as a fraction of b.p. as indicated in Table 1.

***Benzofuran (2a)***

| | | | | |
|---|---|---|---|---|
| lemental analysis | : | Cal. for $C_8H_6O$ | : | C, 81.35%<br>H, 5.08% |
| | | Found | : | C, 81.28%<br>H, 5.02% |
| IR | : | $\upsilon_{max}$ / $cm^{-1}$ | : | 3170, 3125, 1600<br>1580, 1150, 1075 |
| $^1$H NMR | : | $\delta_H$ (Acetone) | : | 7.79 ($C_2$-H), 6.77 ($C_3$-H),<br>7.64 ($C_4$-H), 7.23 ($C_5$-H)<br>7.30 ($C_6$-H), 7.52 ($C_7$-H) |

***5-Methoxybenzofuran (2b)***

| | | | | |
|---|---|---|---|---|
| Elemental analysis | : | Cal. for $C_9H_8O_2$ | : | C, 72.97%<br>H, 5.40% |
| | | Found | : | C, 72.97%<br>H, 5.35% |
| IR | : | $\upsilon_{max}$ / $cm^{-1}$ | : | 3175, 3120, 1605, 1580,<br>1265, 1150, 1070 |
| $^1$H NMR | : | $\delta_H$ ($CCl_4$) | : | 7.48 ($C_2$-H), 6.54 ($C_3$-H),<br>6.89 ($C_4$-H), 3.75 ($OCH_3$ at $C_5$),<br>6.57 ($C_6$-H), 7.28 ($C_7$-H) |

***6-Methoxybenzofuran (2c)***

| | | | | |
|---|---|---|---|---|
| Elemental analysis | : | Cal. for $C_9H_8O_2$ | : | C, 72.97%<br>H, 5.40% |
| | | Found | : | C, 72.88%<br>H, 5.30% |
| IR | : | $\upsilon_{max}$ / $cm^{-1}$ | : | 3165, 3120, 1600, 1575,<br>1260, 1150, 1065 |
| $^1$H NMR | : | $\upsilon_H$ ($CCl_4$) | : | 7.42 ($C_2$-H), 6.56 ($C_3$-H),<br>7.32 ($C_4$-H), 6.75 ($C_5$-H),<br>3.75 ($OCH_3$ at $C_6$), 6.92 ($C_7$-H) |

**Results and Discussion**

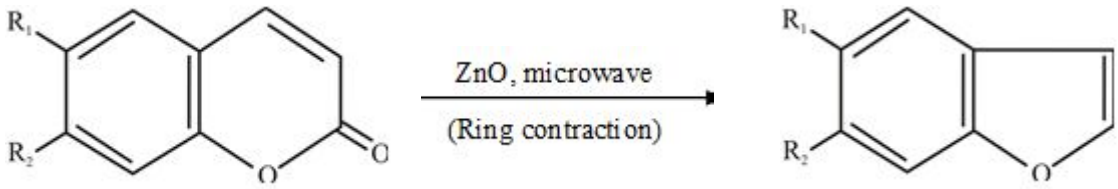
The reactions (Scheme-1) were usually completed within 10 min. which otherwise require very strong heating[5]. The other method of synthesis of benzofuran also requires in total 11 hours of heating under reflux.[7]

The special attention to this paper is to use of zinc oxide powder as solid support instead of alumina or silica. Generally alumina or silica is used for solid surface reaction under microwave irradiation. Here, zinc oxide has been used as a new solid surface. It is not hazardous while silica and alumina are hazardous to human while inhaling beyond the limit. The zinc oxide powder can be reused[9] upto three times after simple washing with dichloromethane.

In summary, the method of the synthesis of benzofuran has been notably improved in the light of green chemistry.

Table 1. Results of synthesis of benzofurans

| | Experimental | | | Literature | |
|---|---|---|---|---|---|
| Compound | Time/min. | Yield% | B.P./$^{o}$C | Yield% | B.P./$^{o}$C |
| 2a | 8 | 91 | 172 | 85[3] | 174[6] |
| 2b | 9 | 88 | 184 | - | - |
| 2c | 9 | 87 | 208 | - | - |




1a-C 2a-C

1a : $R_1$ = H, $R_2$ = H
1b : $R_1$ = $OCH_3$, $R_2$ = H
1c : $R_1$ = H, $R_2$ = $OCH_3$

2a : $R_1$ = H, $R_2$ = H
2b : $R_1$ = $OCH_3$, $R_2$ = H
2c : $R_1$ = H, $R_2$ = $OCH_3$

Scheme - 1

**Conclusion**

It is extremely important that the products designed to be synthesized should be biodegradable. It is necessary to have accurate and reliable sensors, monitors and other analytical methodologies to assess the hazards that may be present in the process stream. The benzofuran is synthesized by green chemical method. The interest in heterocyclic compounds due to their special medicinal properties. The FTIR studies, $^{1}$H NMR and elemental analysis indicated the formation of benzoforan and its derivatives.

*Scope of future work :*

Benzofuran compounds are a class of compounds that are ubiquitous in nature. Numerous studies have shown that most benzofuran Compounds have strong biological activities such as anti-tumor, antibacterial, anti-oxidative and antiviral activities. Owing to these biological activities and potential applications in many aspects, benzofuran compounds have attracted more and more attention of chemical and pharmaceutical researches worldwide, making these substances potential natural drug lead

compounds.

In view of medicinal value, the reported benzofuron compounds may be subjected to sensitive test. The synthesis is one-step-process, yield is very high and it has been achieved in few minutes. Use of microwave irradiation enabled the saving of time and energy which may result in diminishing the cost of product.

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