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Der Chemica Sinica, 2015, 6(11):32-36

Pelagia Research Library
ISSN: 0976-8505
CODEN (USA) CSHIA5

Synthesis, characterization and biological study of aryl benzyl ethers using micelles as a phase transfer catalyst

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ABSTRACT

A new versatile and environmental friendly approach for the synthesis of phenolic ethers by condensing dihydric phenols with benzyl/p-nitro benzyl bromide in a MeOH-water medium using anionic micelles NaLS(Sodium Lauryl Sulphate) as a phase transfer catalyst at room temperature. All the synthesized ethers were characterized by analytical and spectral methods. Their biological study had also been carried out to find out the ability of micelles to control the activity of phenolic ethers.

Key words: Dihydric phenols, benzylbromide, anionic micelles, biological activity.

INTRODUCTION

Aromatic ethers and their derivatives have been studied extensively over the past decade. Day by day aromatic ethers are frequently applied for the betterment of human welfare. The importance of aromatic ethers is due to its versatile nature. A large number of aryl ethers and their derivative find applicability in agriculture, engineering and biochemistry[1]. Due to their great flexibility and structural aspects a wide range of aryl ethers have been synthesized and their functional aspects were studied. The linkage C-O-C in ether compounds has a significant role in the drug action[2]. For example diphenyl ethers and their halo derivatives have agrochemical uses such as herbicide and fungicides. Similarly, phenolic ethers find application in chemical engineering, as food colouring material, perfumes and additive of polymers[3]. Some of the ethers are used as synthetic reagent in organic reactions.

Micellar catalyzed reaction under room temperature are attractive offering reduced pollution, low cost and offer high yields with simple process and handling[4]. The salient features of this method are shorter reaction times, simple reaction conditions and enhancements in yields[5]. In this paper we have described the synthesis, physicochemical characterization and biological activities of benzyl phenyl ethers derived from dihydric phenols with benzyl/p-nitrobenzyl bromide and triethyl amine.

MATERIALS AND METHODS

All the reagents and solvents used were of labeled on the data shown in laboratory grade. Elemental analyses were performed on Carlo Ebra 1108 analyzer. Melting points were determined on a Mel-Temp melting point apparatus and are uncorrected. Infrared spectra were recorded on a perkin Elmer FT-IR spectrophotometer in wave number

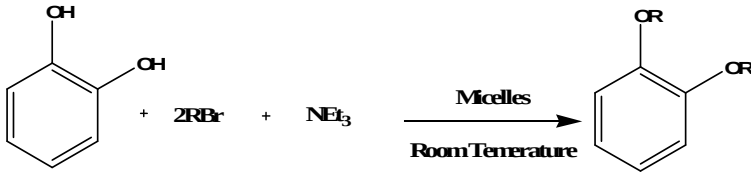
region 4000-400cm^{-1}. ^{1}H NMR spectra were recorded on a Bruker WH 500 spectrometer employing TMS as internal reference and $CHCl_3$ – d_1 as solvent. Thin layer chromatography (TLC) was carried out on silica gel plate (Fluka-Kieselgel, 0.2 mm thickness).

Preparation of micelles

2.08 X10^{-3} mol dm^{-3} of Sodium Lauryl Sulphate(NaLS) was dissolved in MeOH-water medium (70:30 v/v). This solution was stirred for 2 hours. This micellar solution was used as the medium for the reactions.

Synthesis of aryl benzyl ethers

2 moles of benzyl/4-nitrobenzyl bromide, 2 moles of triethylamine and 1 mole of dihydric phenol(s) are dissolved in minimum amount of methanol. It is then added slowly in required amount of micellar solution. The solution was stirred well for 30 minutes at room temperature. The solid product obtained was filtered, washed with water and petroleum ether several times and dried under reduced pressure in a desiccators. The purity of the synthesized compounds were checked by TLC using $CHCl_3$,ethyl acetate(1:3) as eluent. The solid products were crystallized from ethyl acetate. This is shown in Scheme -1



Scheme -1

According to the scheme we obtained 6 different products corresponding to different *o*, *m* and *p* – biphenols and alkyl halides. The formed products are shown in Fig-1

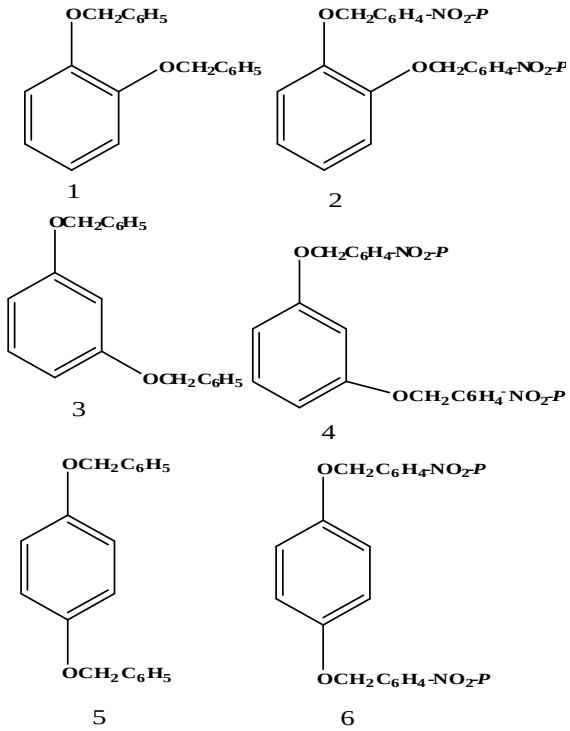


Fig-1

RESULTS AND DISCUSSION

Analytical Study

The prepared compounds elemental analysis and physical studies were carried out and it is shown in Table-1

Table -1: Analytical and physical data of the compounds 1-6

Compd No.	Molecular formula	R	Rf	Yield %	M.P	Elemental analysis		
						C	H	N
1	$C_{20}H_{18}O_2$	$-CH_2C_6H_5$	0.49	77	74-76	82.69(Cal) 82.59 (Found)	6.18(Cal) 6,12(Found)	-
2.	$C_{20}H_{18}O_2$	$-CH_2C_6H_5$	0.48	75	123-125	82.71(Cal) 82.64 (Found)	6..30Cal) 6,23(Found)	-
3.	$C_{20}H_{18}O_2$	$-CH_2C_6H_5$	0.46	78	116-117	82.74(Cal) 82.69 (Found)	6.32(Cal) 6,.28(Found)	-
4.	$C_{20}H_{16}N_2O_6$	$-CH_2C_6H_4O_2$-*p*	0.51	79	80-81	63.12(Cal) 63.20(Found)	7.30(Cal) 7.22(Found)	4,21(Cal) 4.12(Found)
5.	$C_{20}H_{16}N_2O_6$	$-CH_2C_6H_4O_2$-*p*	0.47	81	109-111	63.18(Cal) 63.10(Found)	7.39(Cal) 7.32(Found)	4,27(Cal) 4.21(Found)
6.	$C_{20}H_{16}N_2O_6$	$-CH_2C_6H_4O_2$-*p*	0.53	77	120-121	63.17(Cal) 63.24(Found)	7.36(Cal) 7.29(Found)	4,25(Cal) 4.16(Found)

Spectral studies

The prepared samples were characterized by IR, NMR and Mass spectra. The results of the spectra l data were discussed in the following section.

FT-IR Spectra

The data of the IR spectra of phenyl ethers are listed in Table- 2. The band appearing at 1220 cm-1 due to C-O-C ether linkage[6] in compound (1a-3a). Compounds (1b-3b) show this band at 1248-1258 cm^{-1}. This slight increase may be due to the presence of electron withdrawing $-NO_2$ group at the para position of phenyl rng. The absorption frequency of nitro group occurs at 1333-1356cm^{-1}.

Table-2 : IR spectra of compounds (1-6)

Compd No.	Aromatic C-H	Aliphatic C-H	C=C	C-O-C	C-NO_2
1	3090	2968	1547	1227	-
2	3068	2945	1535	1248	845,1350
3.	3080	2932	1528	1210	-
4.	3104	2956	1519	1258	833,1341
5	3008	2928	1585	1225	-
6.	3075	2919	1578	1254	828,1329

^1H & ^{13}C NMR Spectra

^1H NMR spectrum showed a singlet at 5.13- 5.21 ppm due to methylene proton $-CH_2$-O of benzyl phenyl ether. The other chemical shift values are found to be comparable to the reported values of similar compounds[7]. The $-CH_2$-O moves further to down field 5.30-5.42 for the compounds 1b-3b, may be due to the presence of electron withdrawing nitro group at *para* position of phenyl ring.^{13}C NMR Spectra showed a singlet at 66-74 ppm, due to $-OCH_2$ of benzyl ether. The NMR data are shown in Table-3 & 4.

Table-3: ^1H NMR data of compounds (1-6)

Compound No.	Aliphatic H ($-O-CH_2$)	Aromatic H (CH_2-Ar)	Aromatic H (O-Ar)
1.	5.17 s	7.53-8.03m	7.15-7.35m
2.	5.31 s	7.91-8.20m	7.10-7.69m
3.	5.13 s	7.98-8.03m	7.20-7.56m
4.	5.50 s	7.81-7.95m	7.19-7.67m
5.	4.98 s	7.56-7.97m	7.26-7.57m
6.	5.35 s	7.39-7.85m	6.93-7.48m

Table-4: ^{13}C NMR data of compounds (1-6)

Compond No	Aromatic carbon	Ipso carbon	-CH_2-O
1.	128	138	70
2	130	144	72
3	129	140	66
4	127	139	73
5	131	135	71
6	129	142	74

Biological activity

The in vitro biological activity of the investigation phenyl ether was tested against the bacteria bacillus cereus, two gram positive Staphylococcus aureus and two gram negative Aeromonas hydrophilla by disc diffusion method [8],[9] using nutrient agar as medium and chloromphenicol, gentamycin as control. The antifungal activities of the compounds were also tested by the well diffusion method [10],[11] against the fungi Aspergillus niger and candida albigans, potato dextrose agar as the medium and miconozole as control. The stock solution was prepared by dissolving the compounds in DMSO. The zone of inhibition was developed at which the concentration was noted and is shown in Table-5.

Table- 5: Anti-microbial screening data for the compounds (1-6)

Compd No	*Bacillus cereus* (Gram +ve)	*Staphylococcus Aureus* (Gram +ve)	*Aeromonas Hydrophilla* (Gram –ve)	*Proteus Mirabilis* (Gram –ve)	*Aspergillus Niger*	*Candida Albicans*
1	11 12	14 17	18 20	13 17	15 17	12 15
2	11 22	14 18	17 20	10 17	15 13	14 18
3	10 12	13 17	16 20	12 16	09 17	12 16
4	21 23	11 17	12 16	13 17	11 17	12 17
5	10 12	12 17	13 15	11 14	13 16	11 14
6	11 18	14 17	18 20	13 17	15 17	12 19

CONCLUSION

Based on various physicochemical and spectral analysis, it is possible for us to confirm the structures of the synthesized compounds. In the protocol, we observed better yields in a shorter period compared to the reactions carried out in conventional methods. Among the compounds , 1b and 3b show significant activity against *B.Cereus, S. aureus* and *A.niger*. Other compounds show feeble activity against *proteus mirabilis* and *candida albicans*. In conclusion, we have described an efficient and elegant method of synthesis of phenyl ethers using micellar medium as a phase transfer catalyst. Further, this method is facile, mild and simple one.

Acknowledgement

The authors are thankful to IIT Madras, Chennai, for providing analytical support.

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