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Environmentally Benign Synthetic Protocol for O-Alkylation of *β*-Naphthols and Hydroxy Pyridines in Aqueous Micellar Media

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ABSTRACT

Ultrasonic and microwave-assisted practical methods have been developed for the O-alkylation of aryl (*β*-naphthols) and Heteroaryl (hydroxy pyridines) in aqueous surfactant media in good to excellent yields. The developed methods are simple, efficient, economical and environmentally safe. Our novel methods describe a set of green methods to Williamson synthesis.

Keywords: Ultrasonically Assisted; Microwave Assisted; Green Chemistry; Micelles; *β*-Naphthols; Heteroaryl Hydroxy Compounds; Alcohols

1. Introduction

The discovery, development and identification of biologically active compounds gained lot of importance in the recent years. Even though there are considerable number of adverse effects, chemists always tried to design a drug possessing maximum therapeutic application and minimum toxicity. Organic ethers are one of the most important classes of chemicals which have significant applications as herbicides, disinfectors, pharmaceuticals, plasticizers, solvents, drug intermediates and as solvents in organic synthesis. They are also used as important precursors for polymers and fragrances [1,2]. Literature survey shows that Williamson synthesis is probably one of the most common classical methods being used for the preparation of symmetrical and unsymmetrical ethers [3-11].

A good number of homogeneous Bronsted acids or Lewis acid based transition metals have also been reported as catalysts in the etherification of alcohols [5-9]. However, these systems exhibited some drawbacks including their deactivation through decomposition by the water formed during the course of reaction. In many cases these methods also reveal the accumulation of significant amount of acid at the end of reaction due to the hydrolysis of Lewis acid catalysts such as metal oxide, which upon neutralization gives considerable amount of salts. The acid waste, residual catalyst and salt material may cause several environmental problems when they are dispossed off, and some of them may be toxic. Difficulties such as catalyst recovery for reuse and neutralization of the reaction mixture also make the process tedious. Literature survey shows some reports on the use of phase transfer, polymer and clay supported catalysts for the synthesis of symmetrical and unsymmetrical ethers [12-18]. Another general root for the synthesis of organic ethers is Mitsunobu reaction, which uses either PPh_3 or polymer bound PPh_3 as catalyst. Triphenyl phosphene is highly sensitive to water and toxic in nature, and the reaction demands inert and dry conditions [18-22]. Recent publications of Kumaraswamy *et al*. [20], Deababratha and coworkers [21,22] provide excellent bibliography and information on the synthesis of aryl, heteroaryl ethers derived from various roots.

Noteworthy drawbacks encountered in many conventional methods necessitated the search for an appropriate reaction system to enhance reaction conversion and less environmental pollution. Combinatorial synthesis has brought lot of revolution in the recent trends of organic synthesis. Many chemical reactions with organic substances conducted in the laboratory as well as in industry need organic solvents as reaction media, even though water is safe, benign, environmentally friendly and cheap compared with organic solvents. The necessity of organic solvents as reaction media in the industry sector and academic institutions [23,24], could be attributed to probably for two important reasons: 1) most of the organic substances are insoluble in water and soluble in apolar organic solvents and 2) many organic substrates,

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reagents and catalysts are decomposed or deactivated in aqueous medium. In spite of all these factors, the goal is to develop a novel catalytic system that uses water as a solvent for a wide range of reactions. A perusal of literature indicated that surfactants have been used to promote a variety of synthetic organic reactions. It is believed that surfactants form micelles in protic solvents such as water which act as micro reactors to enhance the reaction rates and afford very good to excellent yields of end products [25-27]. Our preliminary studies in this direction ended up fruitful results when we have performed the title reactions in aqueous micellar media. Thus, in this study, we have used a variety of anionic (SDS), cationic (CTAB) and non-ionic (Tx-100) micellar media. The first drawback of water as a solvent (the solubility) is overcome by the use of aqueous solutions of surfactants, which solubilised all the reactants.

Green or sustainable chemistry has now attained the status of a major scientific discipline, and the studies in this area have led to the development of cleaner and relatively benign chemical processes with many new technologies being developed each year. Encouraged by the "Green Chemistry strategies" of Paul Anastas and Warner [28], we have made an attempt to develop synthetic protocols for etherification reactions. Ultrasonic waves are the one of the most important tools to assist and trigger chemical reactions. Rate accelerations have been noticed in many sluggish reactions [29-35]. Thus the ultrasonically assisted reactions (USAR) became a part of green chemical reactions. The other part of non-conventional energy sources to trigger a chemical reaction is the use of microwaves [36-40]. Microwaves are electromagnetic radiation with a frequency range from 300 to 300,000 MHz, with free space wavelengths of 1 m to 1 mm. Microwaves don't have any effect on molecular bonds or electron clouds like other parts of electromagnetic radiation such as infrared (IR) or the uv-visible radiations. The energy of microwaves is so low that only molecular rotation could be induced. In the present study we were successful to develop an acid free and solvent free synthetic protocols for etherification of phenols and hydroxy pyridines by replacing H_2SO_4 with a variety of micelle forming surfactants such as sodium dodecyl sulphate (SDS), cetyl trimethyl ammonium bromide (CTAB) and Triton-X 100 (Tx-100) with and without using water as reaction medium. We were also successful to conduct ultrasonically assisted (USAR) and microwave assisted reactions (MWAR).

2. Experimental Details

2.1. Typical Experimental Procedure for Etherification of *β*-Naphthols under Conventional Conditions

To a stirred solution of methanol (0.64 g, 20 mmol) and 0.1 M micellar solution (10 mL) was added substituted *β*-naphthol (1.44 g, 10 mmol) and heated up to reflux and the progress of the reaction was monitored by TLC. After the completion of reaction, the reaction mixture was diluted with dichloromethane (10 mL), and separated from aqueous layer. The organic layer was then washed with water (3 × 5 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to afford the crude product. The crude product was purified by column chromatography (silica gel, 100 - 200 mesh) using EtOAc-hexane (1:9) as eluent to obtain the desired product.

2.2. Typical Experimental Procedure for Ultrasonically-Assisted Etherification (USAS) Etherification of *β*–Naphthols

To a solution of methanol (0.64 g, 20 mmol)) and 0.1 M micellar solution (10 mL) was added substituted *β*-naphthol (1.44 g, 10 mmol) at room temperature, and sonicated at 40˚C in an ultrasonic bath. The ultrasonic bath had a frequency of 33 kHz and electric power rating of 100 W. The reaction was carried out in a round bottom flask of 50 mL capacity equipped with a mechanical agitator and the flask was suspended at the centre of the ultrasonic bath. The final products were isolated by absorbing the reaction mixture into silica gel and purifying it by column chromatography using ethyl acetate/hexane gradient.

2.3. Typical Experimental Procedure for Microwave Irradiated Etherification (MWAR) Etherification of *β*-Naphthols

To a solution of methanol (0.64 g, 20 mmol)) and 0.1 M micellar solution (10 mL) was added substituted *β*-naphthol (1.44 g, 10 mmol) and these mixtures were heated in a controlled microwave synthesizer (Biotage Initiator + SP Wave model, 0 - 200 W at 2.45 GHz, capped at 60 W during steady state) for few minutes (attains temperature 120˚C and 1 bar pressure). The final products were isolated by absorbing the reaction mixture into silica gel and purifying it by column chromatography using ethyl acetate/hexane gradient.

3. Spectroscopic Data

2-*Methoxynaphthalene*: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.91 (s, 3H), 7.15 - 7.17 (d, J = 8.8 Hz, 1 H), 7.29 - 7.36 (m, 2H), 7.43 - 7.47 (m, 1H), 7.72 - 7.77 (m, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 55.6, 105.9, 113.7, 124.4, 126.2, 127.8, 128.2, 129.1, 129.9, 133.2, 153.8; IR (KBr) 3067, 3008, 2963, 1632, 1599, 1477, 1462, 1452, 1440, 1398, 1391, 1368, 1262, 1218, 1197, 1173, 1152, 1141, 1118, 1031, 1017, 963, 948, 874, 838, 818, 753, 743, 622, 481, 470 cm^{-1}; MS (EI) *m/z* 159.2 $(M)^+$.

2-*Ethoxynaphthalene*: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.46 (t, J = 7.2 Hz, 3H), 4.127 (d, J = 6.8 Hz, 2H), 7.14 - 7.15 (d, J = 8.8 Hz, 1H), 7.28 - 7.39 (m, 2H), 7.39 - 7.43 (m, 1H), 7.69 - 7.75 (m, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.8, 64.1, 106.5, 118.9, 123.4, 126.2, 126.7, 128.2, 129.1, 129.2, 133.6, 156.8; IR (KBr) 3067, 2984, 2940, 2876, 1829, 1601, 1579, 1511, 1457, 1440, 1395, 1390, 1367, 1358, 1350, 1269, 1259, 1185, 1166, 1144, 1122, 1046, 1020, 958, 928, 873, 823, 762, 719, 623, 477 cm^{-1}; MS (EI) *m/z* 173.2 $(M)^+$.

2-*Propoxynaphthalene*: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.06 (t, J = 6.0 Hz, 3H), 1.83 - 1.86 (m, 2H), 4.01 (t, 2H), 7.10 - 7.14 (m, 2H), 7.30 - 7.41 (m, 2H), 7.69 - 7.74 (m, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 10.5, 22.6, 69.4, 106.6, 119.1, 123.4, 126.2, 126.6, 127.6, 128.8, 129.3, 134.6, 156.7; IR (KBr) 3060, 2976, 2934, 2908, 2878, 1948, 1904, 1832, 1628, 1600, 1513, 1479, 1467, 1448, 1441, 1392, 1371, 1357, 1270, 1260, 1216, 1146, 1121, 1046, 1024, 1017, 1017, 986, 958, 916, 842, 819, 770, 746, 727, 727, 645, 623, 474; MS (EI) *m/z* 187 cm^{-1}. 10 $(M)^+$.

2-*Isopropoxynaphthalene*: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.45 (d, J = 6.0 Hz, 6H), 4.66 - 4.82 (m, 1H), 7.13 - 7.18 (m, 2H), 7.28 - 7.48 (m, 2H), 7.68 - 7.82 (m, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 22.0, 69.8, 108.4, 119.7, 123.4, 126.2, 126.6, 127.6, 128.8, 129.3, 134.6, 155.7; IR (KBr) 3580, 2981, 2936, 2876, 1948, 1904, 1832, 1628, 1600, 1581, 1510, 1468, 1440, 1388, 1373, 1356, 1334, 1216, 1188, 1171, 1137, 1118, 1019, 974, 941, 900, 871, 842, 814, 675, 645, 623, 532 cm^{-1}; MS (EI) *m/z* 187.10 $(M)^+$.

1-*Chloro*-2-*methoxynaphthalene*: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.03 (s, 3H), 7.25 (d, J = 8.6 Hz, 1H), 7.37 - 7.52 (m, 1H), 7.53 - 7.61 (m, 1H), 7.79 - 7.69 (m, 2H), 8.25 (d, J = 8.6 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 57, 105.9, 113.7, 124.4, 126.2, 127.8, 128.2, 129.1, 129.9, 133.2, 153.8; IR (KBr) 3430, 3049, 2972, 2948, 2846, 2541, 1948, 1763, 1625, 1590, 1505, 1469, 1355, 1337, 1273, 1246, 1187, 1148, 1068, 1018, 985, 894, 865, 804, 764, 740, 657, 588, 532 cm^{-1}; MS (EI) *m/z* 192 $(M)^+$.

1-*Bromo*-2-*methoxynaphthalene*: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.04 (s, 3H), 7.28 (d, J = 8.6 Hz, 1H), 7.39 - 7.53 (m, 1H), 7.53 - 7.61 (m, 1H), 7.76–7.89 (m, 2H), 8.23 (d, J = 8.6 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 57.1, 105.9, 113.7, 124.4, 126.2, 127.8, 128.2, 129.1, 129.9, 133.2, 153.8; IR (KBr) 3430, 3045, 2970, 2941, 2841, 1620, 1594, 1500, 1466, 1454, 1351, 1334, 1270, 1245, 1185, 1153, 1134, 1061, 1021, 968, 890, 855, 803, 761, 743, 708, 644, 579, 516 cm^{-1}; MS (EI) *m/z* $(M\text{-}H)^+$ 236.10.

1-*Iodo*-2-*methoxynaphthalene*: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.03 (s, 3H), 7.22 (d, J = 9.0 Hz, 1H), 7.34 - 7.42 (m, 1H), 7.50 - 7.56 (m, 1H), 7.75 (d, J = 8.6 Hz, 1H), 7.84 (d, J = 9.0 Hz, 1H), 8.15 (d, J = 8.6 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 57.3, 87.8, 113.0, 124.4, 128.2, 128.3, 130.4, 131.3, 130.0, 135.7, 156.7; IR (KBr) 3042, 3006, 2969, 2937, 2838, 1617, 1587, 1551, 1497, 1451, 1423, 1346, 1328, 1263, 1242, 1181, 1153, 1132, 1058, 1021, 959, 887, 801, 761, 743 cm^{-1}; MS (EI) *m/z* 285.06 $(M)^+$.

1-*Bromo*-2-*ethoxynaphthalene*: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.38 - 1.41 (t, J = 6.8 Hz, 3H), 4.13 - 4.14 (q, J = 6.8 Hz, 2H), 7.15 - 7.17 (d, J = 8.8 Hz, 1 H), 7.29 - 7.36 (m, 2H), 7.43 - 7.47 (m, 1H), 7.78 - 7.83 (m, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 22.8, 64.6, 105.9, 113.7, 124.4, 126.2, 127.8, 128.2, 129.1, 129.9, 133.2, 153.8.

1-*Bromo*-2-*propoxynaphthalene*: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.03 (t, J = 7.5 Hz, 3H), 1.80 - 1.86 (m, 2H), 4.51 (t, 7.5 Hz, 2H), 7.10 - 7.14 (m, 2H), 7.30 - 7.41 (m, 2H), 7.69 - 7.74 (m, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 10.5, 22.6, 78.4, 113.6, 123.4, 126.2, 126.6, 127.6, 128.8, 129.3, 131.3, 132.6, 154.7; MS (EI) *m/z* 266.04 $(M)^+$.

1-*Bromo*-2-*isopropoxy naphthalene*: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.45 (d, J = 6.0 Hz, 6H), 4.61 - 4.87 (m, 1H), 7.28 (d, J = 8.6 Hz, 1H), 7.39 - 7.53 (m, 1H), 7.53 - 7.61 (m, 1H), 7.76 - 7.85 (m, 2H), 8.23 (d, J = 8.6 Hz, 1H); ^{13}C NMR (50 MHz, CDCl3) δ 22.0, 69.8, 108.4, 119.7, 123.4, 126.2, 126.6, 127.6, 128.8, 129.3, 134.6, 155.7; IR (KBr) 3580, 2981, 2936, 2876, 1948, 1904, 1832, 1628, 1600, 1581, 1510, 1468, 1440, 1388, 1373, 1356, 1334, 1216, 1188, 1171, 1137, 1118, 1019, 974, 941, 900, 871, 842, 814, 675, 645, 623, 532 cm^{-1}; MS (EI) *m/z* 266.10 $(M)^+$.

4-*Methoxy pyridine*: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.84 (s, 3H), 6.81 (d, J = 8.6 Hz, 2H), 8.43 (d, J = 8.6 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 55.1, 109.9, 151.4, 165.4, MS (EI) *m/z* 110.3$(M)^+$, (B.P.168.2˚C).

3-*Methoxy pyridine*: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.84 (s, 3H), 7.34 (t, J = 8.65, J = 4.75 Hz, 1H), 7.38 (d, J = 8.65 Hz, 1H); 8.19 (d, J = 4.75 Hz, 1H); 8.32 (s, 1H); MS (EI) *m/z*110.3$(M)^+$, (B.P.168.4˚C).

2-*Methoxy pyridine*: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.94 (s, 3H), 6.72 (d, J = 8.65 Hz, 1H); 6.82 (t, J = 8.65, J = 4.75 Hz, 1H), 7.59 (t, J = 8.65, J = 4.75 Hz 1H); 8.18 (d, J = 4.75 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 53.1, 110.9, 116.4, 138, 147,165.4,MS (EI) *m/z* 110.3 $(M)^+$, (B.P.142.5˚C).

4-*Ethoxy pyridine*: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.34 (q, 2H), 3.94 (t, 3H), 6.81 (d, J = 8.4 Hz, 2H), 8.43 (d, J = 8.4 Hz, 2H); MS (EI) *m/z* 123.8$(M)^+$, (B.P.165˚C)

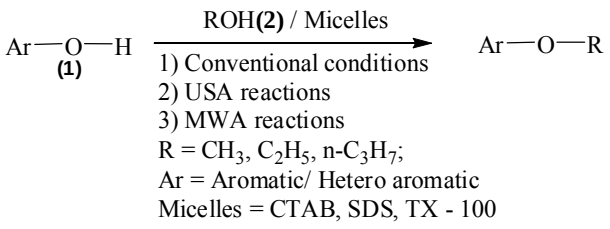
6-*Methoxypicolinaldehyde*: ^{1}H NMR (400 MHz, DMSO) δ 3.971 (s, 3H), 6.986 (d, J = 8.3Hz, 1H), 8.108 - 8.136 (m, 1H), 8.770 (d, J = 2.5 Hz, 1H); 9.968 (s, 1H); MS (EI) *m/z* 137.9$(M)^+$.

5-*Bromo*-2-*methoxypyrimidine*: ^{1}H NMR (400 MHz, DMSO) δ 3.915 (s, 3H), 8.765 (s, 2H); MS (EI) *m/z* 188.9 $(M)^+$.

4. Results & Discussion

Aryl ethers, heteri aryl ethers in general and Naphthalene derivatives such as alkoxy naphthalenes in particular have been identified as one of the best ranges of potent antimicrobials effective against wide range of human pathogens. They occupy a central place among medicinally important compounds due to their diverse and interesting antibiotic properties with minimum toxicity. Synthesis of alkoxy naphthalenes under Williamson's conditions (refluxing in sulfuric acid and organic solvent) is widely used method for the synthesis of aryl ethers. But this method required several hours (≥20 h) at relatively high temperature. Even though there are some reports to modify the drastic conditions of these reactions, many of them exhibited long reaction times, accumulation of unwanted by-products, which ultimately involved tedious work up procedures. Aqueous surfactants are environmentally benign, non-flammable and possesses remarkable ability to catalyze chemical transformations between some insoluble organic reactants. Encouraged by this aspect we have conducted etherification of *β*-naphthol and hydroxy pyridine reactions in aqueous micellar media (**Scheme 1**). For this purpose we have used easily available in the laboratory bench top chemicals sodium dodecyl sulfate (SDS, anionic), cetyl trimethyl ammonium bromide (CTAB, cationic) and Triton X-100 (Tx-100, non-ionic) surfactants to generate micelles in water. However, for comparison, we have also conducted etherification reactions under Williamson's classical conditions in acidic media (**Tables 1** and **2**).

Results obtained under acidic and acid-free micellar conditions are compiled in **Tables 1** and **2**, which clearly indicate highly significant rate accelerations followed by very good yield of end products. Catalytic activity of different micelles is in the order: CTAB > SDS > Tx-100. It is believed that micelles themselves act as micro reactors. The catalytic effect of the micellar solution of CTAB may be attributed to the hydrophobic nature of organic substrates. In micellar solution, organic substrates are pushed away from water molecules towards the hydrophobic core of micelle droplets thus inducing efficient collisions between organic substrates which eventually enhance the reaction rate and result in rapid reactions in water. The hydrophobic interior of the micelles swiftly excludes the water molecules generated during the reaction, thus shifting the equilibrium towards the desired product that ultimately leads to an increase in the reaction yield [41-43]. This explanation is schematically represented in **Figures 1** and **2**.



Scheme 1. Etherification of 2-naphthol and hydroxy pyridine in aqueous micellar media.

Ultrasonic-assisted organic synthesis (USAOS) is a powerful and green approach which is being used to accelerate synthesis of organic compounds. Recent literature reports in USAOS (sonochemical synthesis) indicated that it is an environmentally benign synthesis, which minimized the use of the precious metal catalysts and led to the development of new eco-friendly protocols [29-35]. It offered the synthetic chemist a method of chemical activation which uses equipment which is relatively inexpensive. The driving force for sonochemistry is cavitation and so a general requirement is that at least one of the phases of the reaction mixture should be a liquid. The chemical effects of ultrasound do not come from a direct interaction with molecular species but arises from acoustic avitation the formation, growth, and implosive collapse of bubbles in a liquid. The observed rate and yield enhancements observed in the present study (**Tables 3** and **4**) could be attributed to ultrasonic cavitation effect.

Results obtained under microwave assisted synthesis (MWAS) micellar conditions are compiled in **Tables 5** and **6**, which clearly indicate highly remarkable rate accelerations (reaction times reduced from several (⩾20) to few minutes), followed by high yields. This dramatic rate enhancement could be attributed to bulk activation of molecules, which is believed to be due to rapid superheating of the polar solvents and pressure effects [36-40].

5. Conclusion

In conclusion, this paper reports Ultrasonic- and microwave-assisted O-alkylation of *β*-naphthols in aqueous micellar media. It describes catalytic activity of different micelles is in the order: CTAB > SDS > Tx-100. The reaction times were drastically reduced to one to two hours under sonication and few minutes under microwave conditions from several hours of classical reactions. Thus, the present protocols show rate accelerations associated with high products yields, when compared with

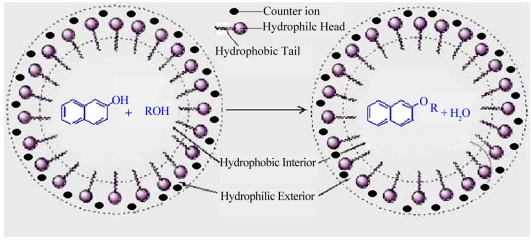


Figure 1. Schematic diagram representing the role of micelles in aqueous media.

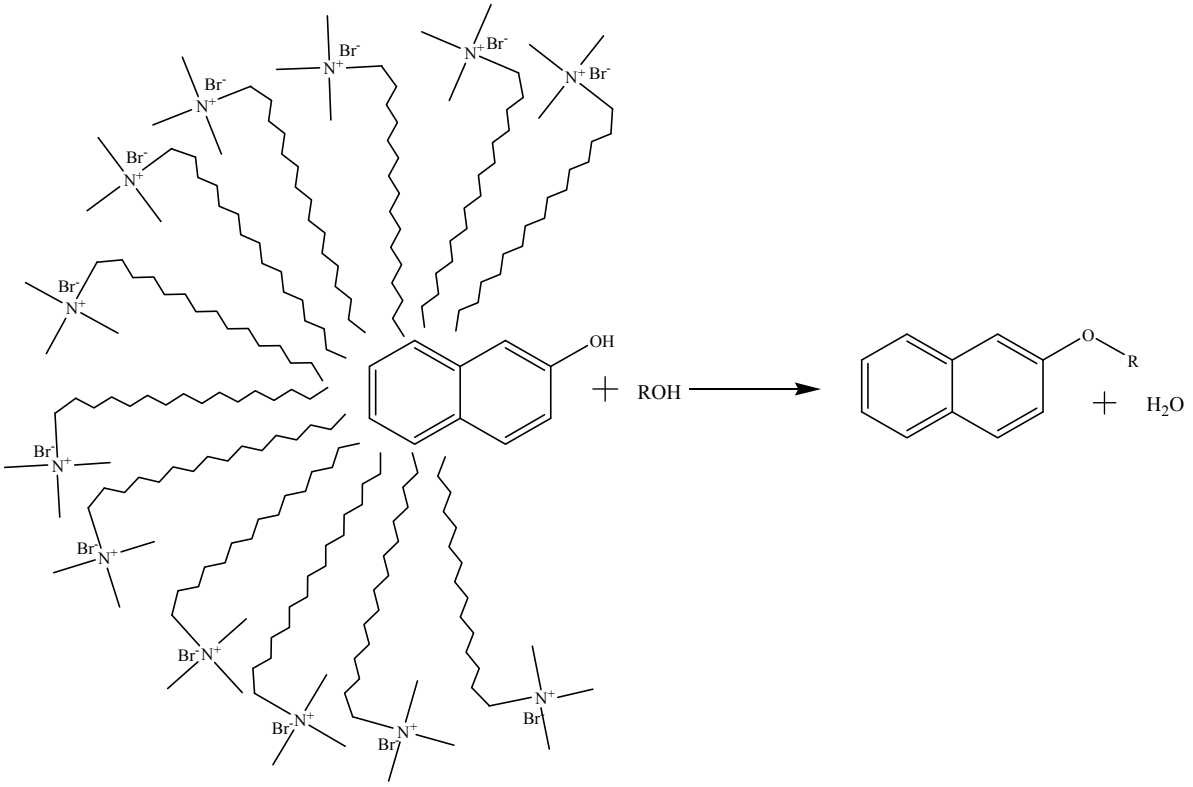


Figure 2. Schematic diagram representing the role of CTAB in aqueous media.

Table 1. Micellar mediated O-alkylation of *β*-naphthols under acidic and acid-free conditions.

Reactants		$H_2SO_4^a$		CTAB		SDS		Tx-100		M.P/B.P (˚C)
1	**2**	Time (h)	% Yield	Time (h)	% Yield	Time (h)	% Yield	Time (h)	% Yield	
β-Naphthol	MeOH	20	91	1.1	96	2.0	86	3.0	91	70 - 71
	EtOH	20	91	2.3	92	2.4	89	3.3	91	35 - 37
	1-PrOH	20	93	2.4	94	2.3	96	3.4	86	37 - 39
	2-PrOH	20	90	2.1	93	2.1	88	3.1	90	-
1-Bromonaphthalen-2-ol	MeOH	20	22	1.1	90	2.0	86	4.0	85	80 - 81
	EtOH	20	17	1.4	88	2.5	85	4.2	83	64 - 66
	1-PrOH	20	13	2.3	84	2.6	84	4.3	80	-
	2-PrOH	20	13	1.3	93	2.4	84	4.1	79	37 - 39
1-Chloronaphthalen-2-ol	MeOH	20	7	1.2	90	2.0	79	4.0	78	64 - 65
	EtOH	20	9	1.3	88	2.4	86	4.2	79	56 - 58
	1-PrOH	20	2	2.3	79	2.1	73	4.1	72	-
	2-PrOH	20	9	1.1	79	2.2	74	3.4	74	-
1-Iodonaphthalen-2-ol	MeOH	20	0	1.4	45	1.4	40	1.4	45	87 - 89
	EtOH	20	0	2.0	43	2.2	39	2.0	38	35 - 37
	1-PrOH	20	0	3.0	41	3.4	36	3.0	39	37 - 39
	2-PrOH	20	0	1.5	49	2.0	43	1.5	41	-

[a]Etherification of derivatives of *β*-naphthol, W. A. Davis, J. Chem. Com, 1900.

Table 2. Micellar mediated O-alkylation of hydroxy pyridines under conventional conditions.

Reactants		CTAB		SDS		Tx-100	
1	**2**	Time (h)	% Yield	Time (h)	% Yield	Time (h)	% Yield
2-Hydroxy pyridine	MeOH	1.3	89	2.0	85	3.1	86
	EtOH	2.4	90	2.5	87	3.4	87
	1-PrOH	2.5	90	2.5	86	3.4	82
	2-PrOH	1.5	90	2.3	87	3.3	89
3-Hydroxy pyridine	MeOH	1.2	91	2.1	85	3.5	82
	EtOH	2.5	89	2.5	84	4.3	81
	1-PrOH	2.4	85	2.5	83	4.3	80
	2-PrOH	1.5	89	2.3	85	4.2	79
4-Hydroxy pyridine	MeOH	1.5	91	2.1	88	4.2	81
	EtOH	2.5	88	2.5	85	4.4	83
	1-PrOH	2.3	88	2.4	83	4.4	82
	2-PrOH	1.5	89	2.3	84	4.1	81
5-Bromopyrimidin-2-ol	MeOH	1.3	91	2.1	87	3.4	89
	EtOH	1.5	89	2.5	87	4.3	87
	1-PrOH	2.4	89	2.5	86	4.3	86
	2-PrOH	1.5	91	2.3	84	4.2	86
6-Hydroxypicolinaldehyde	MeOH	1.3	92	2.1	88	4.2	89
	EtOH	1.5	88	2.5	86	4.3	89
	1-PrOH	2.3	87	2.4	85	4.3	84
	2-PrOH	1.5	88	2.3	87	4.1	86

Table 3. Ultrasonically-assisted O-alkylation of hydroxy pyridines under solvent-free conditions.

Reactants		CTAB		SDS		Tx-100	
1	**2**	Time (min)	% Yield	Time (min)	% Yield	Time (min)	% Yield
2-Hydroxy pyridine	MeOH	90	90	100	89	110	85
	EtOH	120	91	130	86	130	84
	1-PrOH	120	90	130	87	130	85
	2-PrOH	110	90	120	88	125	84
3-Hydroxy pyridine	MeOH	95	90	100	87	120	88
	EtOH	120	89	130	85	140	90
	1-PrOH	125	88	125	88	140	88
	2-PrOH	115	91	120	87	130	90
4-Hydroxy pyridine	MeOH	100	92	114	89	120	89
	EtOH	120	89	130	87	140	89
	1-PrOH	120	89	130	88	140	85
	2-PrOH	110	90	120	88	130	86
5-Bromopyrimidin-2-ol	MeOH	95	93	110	89	115	87
	EtOH	120	89	125	87	130	89
	1-PrOH	115	89	130	88	130	86
	2-PrOH	115	91	125	88	125	87
6-Hydroxypicolinaldehyde	MeOH	90	89	110	87	120	89
	EtOH	115	88	125	86	135	88
	1-PrOH	115	87	125	88	135	86
	2-PrOH	110	89	120	86	130	88

Table 4. Ultrasonically-assisted O-alkylation of *β*-naphthols under solvent-free conditions.

Reactants		$H_2SO_4^a$		CTAB		SDS		Tx-100		M.P/B.P (˚C)
1	**2**	Time (min)	% Yield	Time (min)	% Yield	Time (min)	% Yield	Time (min)	% Yield	
β-Naphthol	MeOH	150	91	90	94	100	95	110	89	70 - 71
	EtOH	190	91	140	96	90	92	150	89	35 - 37
	1-PrOH	200	93	150	91	160	87	170	94	37 - 39
	2-PrOH	150	90	130	92	130	90	140	89	-
1-Bromonaphthalen-2-ol	MeOH	130	89	85	91	110	86	120	88	80 - 81
	EtOH	160	89	140	89	140	86	142	90	64 - 66
	1-PrOH	165	94	145	88	155	89	145	88	-
	2-PrOH	145	89	135	94	125	87	135	91	37 - 39
1-Chloronaphthalen-2-ol	MeOH	130	87	114	92	114	89	120	89	64 - 65
	EtOH	170	89	140	89	100	89	140	89	56 - 58
	1-PrOH	180	88	150	89	130	89	160	83	-
	2-PrOH	160	91	130	90	160	89	130	84	-
1-Iodonaphthalen-2-ol	MeOH	150	89	110	68	115	65	120	65	87 - 89
	EtOH	172	89	120	69	140	63	145	68	35 - 37
	1-PrOH	180	82	130	66	135	61	130	69	37 - 39
	2-PrOH	160	84	115	69	120	69	120	61	-

[a]Etherification of derivatives of *β*-naphthol, W. A. Davis, J. Chem. Com, 1900.

Table 5. Microwave-assisted O-alkylation of *β*-naphthols under solvent-free conditions.

Reactants		$H_2SO_4^a$		CTAB		SDS		Tx-100		M.P/B.P (˚C)
1	**2**	Time (min)	% Yield	Time (min)	% Yield	Time (min)	% Yield	Time (min)	% Yield	
β-Naphthol	MeOH	20	92	04	91	06	89	09	95	70 - 71
	EtOH	34	94	06	93	08	89	15	92	35 - 37
	1-PrOH	38	90	08	91	13	94	15	87	37 - 39
	2-PrOH	25	87	05	95	10	89	12	90	-
1-Bromonaphthalen-2-ol	MeOH	25	94	05	88	09	88	10	86	80 - 81
	EtOH	36	97	11	90	15	85	16	86	64 - 66
	1-PrOH	38	92	15	88	14	87	16	89	-
	2-PrOH	28	87	10	91	15	88	16	87	37 - 39
1-Chloronaphthalen-2-ol	MeOH	25	94	08	89	09	89	12	88	64 - 65
	EtOH	28	96	10	89	12	86	13	88	56 - 58
	1-PrOH	30	89	12	89	15	88	18	82	-
	2-PrOH	26	91	10	89	11	90	14	84	-
1-Iodonaphthalen-2-ol	MeOH	26	86	08	65	12	60	15	65	87 - 89
	EtOH	28	95	10	63	11	69	13	68	35 - 37
	1-PrOH	26	89	10	61	12	66	13	69	37 - 39
	2-PrOH	25	88	09	69	12	63	14	61	-

Table 6. Microwave-assisted O-alkylation of hydroxy pyridines under solvent-free conditions.

Reactants		CTAB		SDS		Tx-100	
1	**2**	Time (min)	% Yield	Time (min)	% Yield	Time (min)	% Yield
2-Hydroxy pyridine	MeOH	05	94	06	91	07	91
	EtOH	07	94	08	91	12	93
	1-PrOH	07	92	13	90	12	88
	2-PrOH	06	93	10	90	11	90
3-Hydroxy pyridine	MeOH	05	92	08	89	10	89
	EtOH	09	91	11	86	12	89
	1-PrOH	10	89	11	88	12	88
	2-PrOH	08	92	10	87	11	88
4-Hydroxy pyridine	MeOH	05	92	08	88	10	88
	EtOH	10	93	12	89	13	89
	1-PrOH	10	91	12	88	13	84
	2-PrOH	08	89	10	89	11	85
5-Bromopyrimidin-2-ol	MeOH	05	92	06	89	07	89
	EtOH	07	89	08	87	10	89
	1-PrOH	07	89	10	88	10	85
	2-PrOH	06	90	09	88	09	86
6-Hydroxypicolinaldehyde	MeOH	05	92	07	89	09	89
	EtOH	09	89	10	87	11	89
	1-PrOH	09	89	10	88	11	85
	2-PrOH	06	90	09	88	10	86

the similar reactions performed under classical conditions. Water is not only an inexpensive and environmentally benign solvent, but also plays an important role in reactivity and selectivity. Surfactants catalyze the reaction efficiently with short reaction times without using any harmful organic reagents and solvents.

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