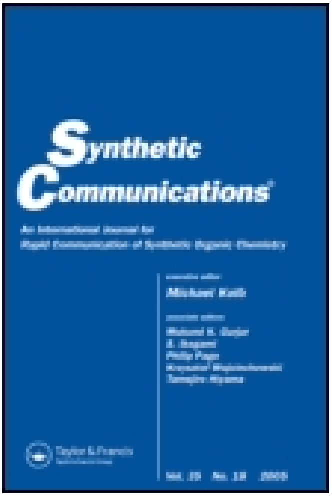

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Synthesis of 8-Quinolinyl Ethers Under Microwave Irradiation

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SYNTHESIS OF 8-QUINOLINYL ETHERS UNDER MICROWAVE IRRADIATION

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Abstract: A simple. rapid and efficient procedure for the synthesis of 8-quinolinyl ethers via microwave irradiation is reported.

Ethers are important intermediates in organic synthesis. Some aromatic ethers such as 2,4-dichlorophenyl 4-nitrophenyl ether, 2,4-dichlorophenyl 3-methoxy-4-nitrophenyl ether, 4-nitrophenyl 2-nitro-4-trifluoromethylphenyl ether and heteroanalogues of diphenyl ether such as 3-(substituted phenoxy)-pyridazines have been found to be useful as pesticides, fungicides and as selective herbicides for the control of various noxious weeds.[1-2]

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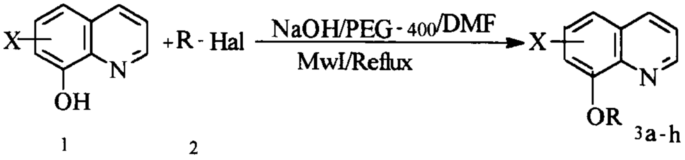
Ethers are generally prepared by the Williamson reaction and the related alkylation of phenols to give aromatic ethers is well known[3]. The phase transfer catalysis technique has been successfully applied to the Williamson ether synthesis[4,5] However, the reaction time is long.

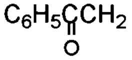
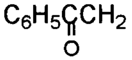
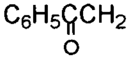
In recent years interest has been shown in the study of microwave assisted organic reactions[6], and some important reviews have been published[6,7]. A new microwave batch reactor (MBR) has been developed for organic synthesis or kinetic studies on the 20-100ml scale, with upper operating limits of 260 ℃ and 10MPa (100 atm)[8]. Microwave irradiation has also been applied to several organic reactions[6]. However, few pracical applications have been devised for aromatic ether synthesis[9,10]. Recently, we have reported the synthesis of aromatic ethers without organic solvent and inorganic carrier under microwave irradiation[11]. But so far, there have not yet been any reports on the synthesis of 8-quinolinyl ethers under microwave irradiation.

We now report on the synthesis of 8-quinolinyl ethers 3 from 8-hydroxyquinolines 1 and organic halides 2 under microwave irradiation. This method is very simple,



Scheme 1

Table1 The Reaction Condition and Yields of 3a-h

Produst				Irrdiation Conditions	Yield
No	X	R	Hal	time/power	%
3a	H	 $C_6H_5\underset{\overset{\|}{O}}{C}CH_2$	Br	700w/3min+375w/10min	91
3b	H	p-$O_2NC_6H_5$	Cl	750w/3min+750w/12min	54
3c	H	$C_6H_5CH_2$	Cl	750w/3min+750w/4min	87
3d	H	p-$O_2NC_6H_5$ CH_2	Cl	750w/3min+300w/8min	86
3e	5.7-di-Cl	$C_6H_5CH_2$	Cl	750w/3min+300w/8min	78
3f	5.7-di-Br	$C_6H_5CH_2$	Cl	750w/3min+300w/10min	76
3g	5.7-di-Cl	 $C_6H_5\underset{\overset{\|}{O}}{C}CH_2$	Cl	750w/3min+300w/10min	80
3h	5.7-di-Br	 $C_6H_5\underset{\overset{\|}{O}}{C}CH_2$	Cl	750w/3min+300w/12min	78

and affords good yields for the synthesis of 8-quinolinyl ethers. The reactions are shown in Scheme 1 and the results are summarized in Table 1.

The effect of the irradiation power on the formation of 8-quinolinyl ethers was studied. The results show that the power suitable for reaction of 8-hydroxyquinolines and NaOH is 750W, and power suitable for reaction of 8-quinolinyl salt with halides is 300W, The Table 1 show that the yield of 3a is 91%. Under the same conditions but power is 600W, the yield of 3a is only 63%. We also investigated the effect of different methods on the reaction of 8-hydroxyquinolines with halides under microwave irradiation. Experimental results show that the 8-quinolinyl ethers are not formed using the one-pot reaction.

EXPERIMENTAL

IR spectra were measured for KBr discs using an Alpha centauri FT-IR spectrophtometer. ‘HNMR spectra (80 MHz) were recorded in $CDCl_3$ using an FT-80 spectrometer. Microanalyses were measured using a Carlo Erba 1106 microelemental analyser. Microwave irradiations are carried out with an improvemental microwave oven Galanz WP 750 B at 2450 MHz.

General procedure: A mixture of the 8-hydroxyquinoline (5.5mmol), solid sodium hydroxide (0.6g, 15mmol), PEG-400 (0.10g, 0.25mmol) and DMF (10ml) was irradiated in 750W for 3 minute. Then, organic halide (8mmol) in DMF (5ml) was added. The reaction mixture was irradiated in the specified power for the specified time. After cooling down at room temperature, the reaction mixture were filtered and the solid was washed with DMF (3 × 5ml) and organic phase were speparated. Finally the DMF was removed at reduced pressure, then acidification with 20% aqueous HCl and the solid were filtered. The product purified by recrystallization from CH_3CH_2OH or CH_3 CH_2OH -$CH_3COOC_2H_5$.

3a: M. P. 161-162 ℃. ‘H-NMR: 6.03(s,2H, CH_2), 7.57-8.07 (m, 9H, Ar-H), 8.90-9.13(q, 2H, Ha, Hb). IR v(KBr): 1265, 1470, 1542, 1598, 1626, 1700, 2921. MS(m/e): 263(M^+). Anal. Calcd. (found) for $C_{17}H_{13}NO_2$: C, 55.57(77.50); H, 4.94(5.02); N, 5.32(5.41).

3b: M. P. 162-163 ℃. ‘H-NMR: 6.96-8.96(m, 9H, Ar-H). IR v(KBr): 1251, 1338, 1504, 1558, 1592. MS(m/e): 266 (M^+). Anal. Calcd. (found) for $C_{15}H_{12}N_2O_3$: C, 67.67(67.60); H, 3.75 (3.71); N, 10.52(10.39).

3c: M. P. 60-61 ℃. ‘H-NMR: 5.46(s, 2H, CH_2). 6.9-7.5(m, 9H, Ar-H), 8.19 (q, 1H, Hb), 8.98 (q, 1H, Ha). IR v(KBr): 1263, 1470, 1566, 1594, 1612, 2849, 2919. MS(m/e): 235 (M^+). Anal. Calcd. (found) for $C_{16}H_{13}NO$: C, 81.70 (81.58); H, 5.75 (5.85); N, 5.96(5.99).

3d: M. P. 91-92 ℃. ‘H-NMR: 5.64(s, 2H, CH_2). 7.64-8.36 (m, 8H, Ar-H), 8.87-9.13 (q, 2H, Ha,Hb). IR v(KBr): 1271, 1342, 1473, 1515, 1598, 1633, 2916. MS(m/e): 280 (M^+). Anal. Calcd. (found) for $C_{16}H_{12}N_2O_3$: C, 68.57 (68.52); H, 4.29 (4.13);10.00(9.95).

3e: M. P. 91-92 ℃. ‘H-NMR: 5.48(s, 2H, CH_2). 7.26-7.64(m, 7H, Ar-H), 8.51 (q, 1H, Hb), 9.03 (q, 1H, Ha). IR v(KBr): 1093, 1238, 1456, 1559, 1579, 1599. MS(m/e): 303 (M^+). Anal. Calcd. (found) for $C_{16}H_{11}Cl_2NO$: C, 63.36 (63.75); H, 3.63 (3.30); N, 4.60(4.46).

3f: M. P. 111-112 ℃. ¹H-NMR: 5.50(s, 2H, CH_2). 7.26-7.74(m, 7H, Ar-H), 8.51 (q, 1H, Hb), 9.02 (q, 1H, Ha). IR v(KBr): 1040, 1230, 1542, 1572, 1596. MS(m/e): 393 (M^+). Anal. Calcd. (found) for $C_{16}H_{11}Br_2NO$: C, 48.85 (48.86); H, 2.80 (2.73); N, 3.56(3.70).

3g: M. P. 105-106 ℃. ¹H-NMR: 5.50(s, 2H, CH_2). 7.26-7.70(m, 7H, Ar-H), 8.52-9.04 (q, 2H, Ha,Hb). IR v(KBr): 1238(C-O-C). MS(m/e): 332 (M^+).

3h: M. P. 117-118 ℃. ¹H-NMR: 5.52(s, 2H, CH_2). 7.25-7.76(m, 7H, Ar-H), 8.52-9.02 (q, 2H, Ha,Hb). IR v(KBr): 1232(C-O-C). MS(m/e): 421 (M^+).

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