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A Tandem Scalable Microwave-Assisted Williamson Alkyl Aryl Ether Synthesis under Mild Conditions

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An efficient tandem synthesis of alkyl aryl ethers, including valuable building blocks of dialdehyde and dinitro groups under microwave irradiation and solvent free conditions on potassium carbonate as a mild solid base has been developed. A series of alkyl aryl ethers were obtained from alcohols in excellent yields by following the Williamson ether synthesis protocol under practical mild conditions. Scale up ability of this practical procedure is shown by the preparation of some of the valuable dialdehydes up to 50 mmole from alcohols. The method is simple, rapid, straight-forward and holds potential for further application in organic synthesis and industrial requirements.

Keywords: Tandem, scalable, Williamson ether synthesis, Alkyl tosylate, Microwave irradiation, Bis-2-nitrophenoxy akyl ether, Bis-2-formylphenoxy alkyl ether

INTRODUCTION

Alkyl aryl ethers are important solvents and synthetic building blocks for the production of fragrances, cosmetics, pharmaceuticals and dyestuffs with emphasis on derivatives of phenols, naphthols and dihydroxybenzenes [1]. The most three important methods in ether formation includes: (1) the Williamson ether synthesis [2], (2) the Mitsunobu reaction [3], and (3) the Ullmann condensation [4-9]. Among them, the Williamson´s procedure seems to be the most straight-forward way, that provides the best generality for the preparation of both symmetric and unsymmetrical ethers [1,10]. Although, the Williamson ether synthesis in solution has been well-known for almost 160 years, there are a few useful procedures available for direct conversion of phenols into aromatic ethers, without requirement of pre-formation of the corresponding phenoxide ions or other reactive groups [11,12].

Nevertheless, these reactions are usually performed by using organic solvents [13], phase-transfer catalysts [14,15], high temperature [1], strong bases [16,17], undesirable solvents [17,18], narrow substrate scopes [19], or noncommercial sophisticated catalysts [20], with long reaction times [21], and also harsh reaction conditions, which limits the attractiveness of some of these methods, especially for large-scale or industrial applications.

Since 1990s, a global movement to environmental protection and more economically beneficial approach in scientific and industrial researches has been emerged, which is known as green chemistry [22]. Therefore, alternative methods that are more compatible with the green chemistry protocol are still needed. Herein, we wish to introduce a more practical and greener version of the noncatalytic Williamson ether synthesis by using microwave irradiation and solvent-free conditions to prepare alkyl aryl ethers from alcohols.

EXPERIMENTAL

General

All reagents were purchased from Aldrich or SD Fine Chemicals and were used without further purification. Products were separated and purified by different chromatographic techniques and were identified by the

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*Corresponding author. E-mail: m.javaherian@scu.ac.ir comparison of their Melting point and NMR with those reported for the authentic samples. FT-IR Spectra (neat) were recorded on BOMEM Inc. 450 instrument. NMR Spectra were recorded on Bruker Avance DPX (400 MHz) in $CDCl_3$ and D_2O with TMS as internal standard for protons and solvent signals as internal standard for carbon spectra. Chemical shift values are reported in δ (ppm) and coupling constants are given in Hz. The progress of all reactions was monitored by TLC on 2 × 5 cm pre-coated silica gel-60 F-254 plates of thickness of 0.25 mm (Merck). The chromatograms were visualized under UV 254-336 nm or by immersion in tanks of common chemical visualizer such as DNP, $H_2SO_{4(conc.)}$, I_2, *etc.*

Method A: Preparation of Alkyl Aryl Ethers by the Reaction of Phenols with Alkyl Tosylates on K_2CO_3 Using MW Irradiation

An agate mortar was charged with K_2CO_3 (5 g), ethyl tosylate (20 mmol, 4.00 g), resorcinol (12 mmol, 1.32 g) and DMF (1 ml). After mixing them by a pestle under a fume hood with safety cares, the mixture was transferred in a pyrex beaker (200 ml) and put inside the microwave oven and exposed to irradiation (500 W) for 2 min. Upon completion the reaction, monitored by TLC (n-hexane/ EtOAc, 4:1, V/V) the reaction vessel was cooled to room temperature and the mixture was stirred with potassium hydroxide solution (50%, 50 ml) to eliminate the excess of resorcinol. Then, the product was extracted by n-hexane (3 × 50 ml) and washed with H_2O (2 × 50 ml) to omit the remainder of DMF. The solvent was dried by anhydrous $CaCl_2$ and evaporated by vacuo-rotary. The desired 1,3-diethoxybenzene was obtained in 95% yield, exclusively (Table 1, entry 16).

Method B: One-pot Preparation of Alkyl Aryl Ethers from Alcohols and Phenols

In a typical procedure, a mixture of 1-octanol (10 mmol, 1.57 ml) and finely powdered KOH (50 mmol, 2.8 g) was vigorously grinded in an agate mortar for 5 min. Then, K_2CO_3 (5 g) and tosyl chloride (15 mmol, 2.86 g) were added and grinded fully by a pestle. An exothermic reaction ensued, and was almost completed, immediately as confirmed by TLC (n-hexane/ EtOAc, 4:1, V/V). To eliminate the remaining TsCl, the finely powdered KOH (10 mmol, 0.56 g) was added again, and ground, thoroughly, until complete elimination of TsCl, according to TLC monitoring. Then, phenol (15 mmol, 1.41 g) and DMF (1 ml) were added to the above mixture and mixed thoroughly. The reaction mixture was transferred to a pyrex beaker (200 ml) and placed inside the microwave oven and irradiated for 40 s. Upon completion the reaction, monitored by TLC (n-hexane/EtOAc, 4:1, V/V), the reaction vessel was cooled to room temperature. The desired product was extracted by n-hexane (3 × 50 ml) and washed with H_2O (2 × 50 ml). The solvent was dried by anhydrous $CaCl_2$ and evaporated by vacuo-rotary. 1-Phenoxyoctane was obtained in 93% yield (Table 2, entry 1).

Attention: It should be noted that, for the reaction of oligoethylne glycols and benzylic alcohols with TsCl, after completion the reaction, according to TLC monitoring, KOH or *t*-BuOH/MW was used to remove the remainder of TsCl [22]. In addition, to prepare methyl and ethyl tosylates, methanol and ethanol were used in three folds compared to TsCl until the consumption of all of the TsCl was investigated [23].

Method C: Microwave Irradiation for the Synthesis of Bis-2-nitro and Bis-2-formylphenoxy Alkyl Ethers in DMF

o-Nitrophenol (2 mmol, 0.27 g), dried K_2CO_3 (3 mmol, 0.40 g) and DMF (2 ml) were placed in a two necked reaction flask (25 ml) and placed inside the cavity of microwave instrument, operated at 90 ºC for 10 min. Then, the diethylene glycol ditosylate (1 mmol, 0.414 g) was added and the mixture was irradiated by MW for 75 min. Water (10 ml) was added and extracted with diethyl ether (2 × 30 ml). The organic layer was separated, dried with anhydrous Na_2SO_4 and evaporated in vacuum. The crude product was purified by short column chromatography (n-hexane/EtOAc, 4:1) and obtained in 84% yield (Table 3, entry 2).

Method D: Large Scale Preparation of Bis-2-formylphenoxyalkyl Ethers

Diethylene glycol (50 mmol, 5.30 g) and dry K_2CO_3 (25 g) were vigorously grinded for 5 min. Tosyl chloride (75 mmol, 14.30 g) was added and grinded for 10 min. MW irradiation at 180 W accelerate the reaction rate

Table 1. Preparation of Alkyl Aryl Ethers by the Reaction of Phenols with Alkyl Tosylates on K_2CO_3 Using MW Irradiation

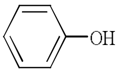
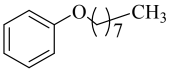
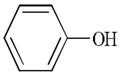
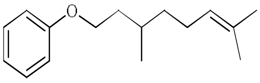
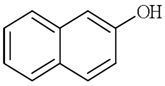
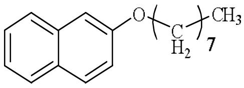
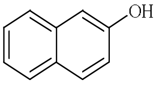
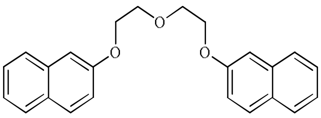
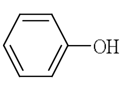
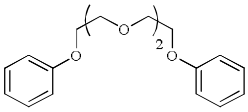
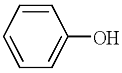
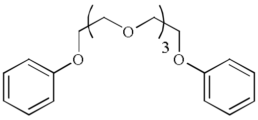
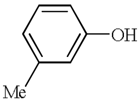
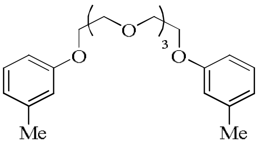
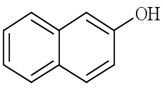
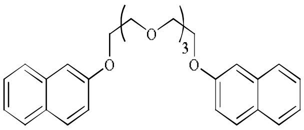
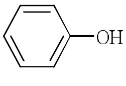
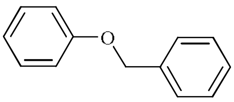
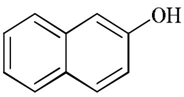
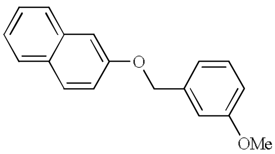
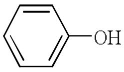
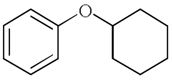
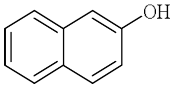
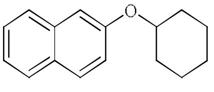
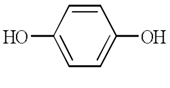
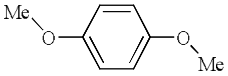
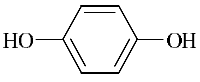
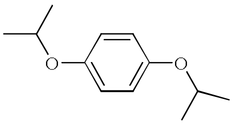
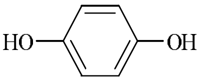
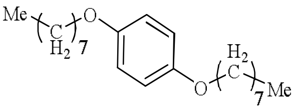
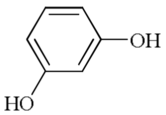
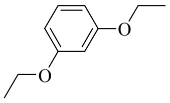
Entry	Phenol	Ether	Time (min)	Yield[f] (%)
1			4	96[a]
2			2	97[a]
3			2	97[b]
4			3	96[a]
5			2	97[c]
6			2	93[d]
7			2	96[d]
8			2	90[d]
9			1	94[b]
10			1	92[b]
11			2	96[c]

Table 1. Continued

12			3	88[c]
13			2	95[d]
14			2	81[e]
15			2	91[e]
16			2	95[e]

power of MW irradiation: [a]200 W, [b]300 W, [c]400 W, [d]500 W, [e]1000 W, [f]The reactions were carried out under solvent free condition (method A) and yields refer to isolated products.

Table 2. Results of One-pot Preparation of Alkyl Aryl Ethers from Alcohols and Phenols

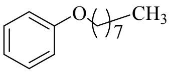
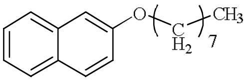
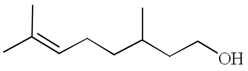
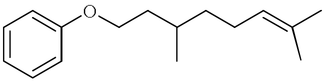
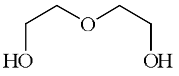
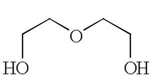
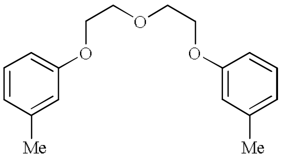
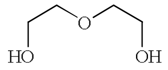
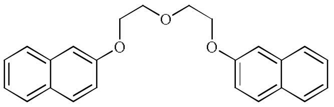
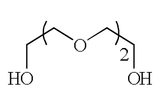
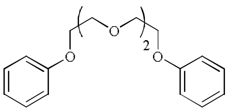
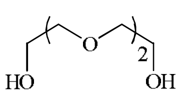
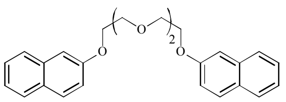
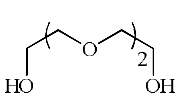
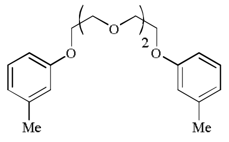
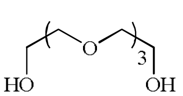
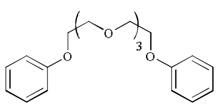
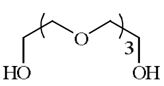
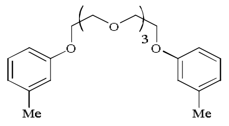
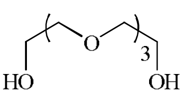
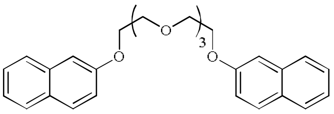
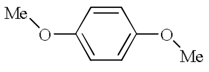
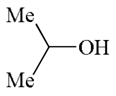
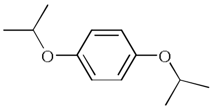
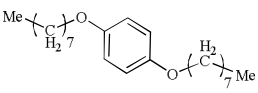
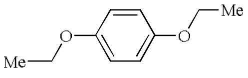
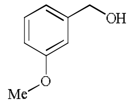
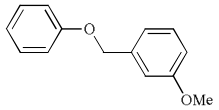
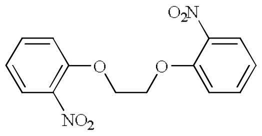
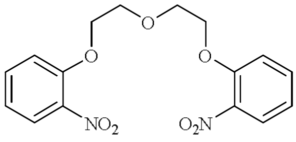
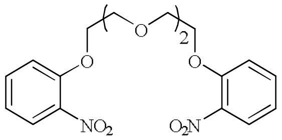
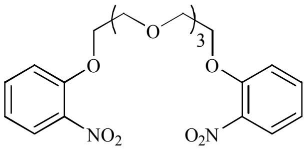
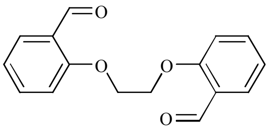
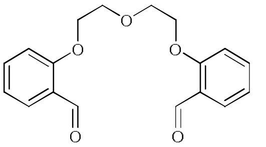
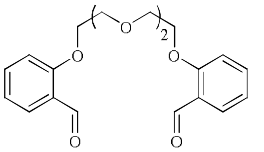
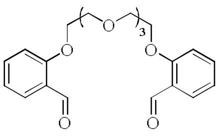
Entry	Alcohol	Ether	Time (min)	Yield (%)[c]
1	$CH_3(CH_2)_6CH_2OH$		40 s	93[a]
2	$CH_3(CH_2)_6CH_2OH$		50 s	94[a]
3			1.5	92[a]
4			2	95[b]
5			2	97[b]

Table 2. Continued

6			2	90[a]
7			1	96[b]
8			2	92[b]
9			2	95[b]
10			2	93[b]
11			2	96[b]
12			2	90[b]
13	CH_3OH		2	96[b]
14			2	85[a]
15	$CH_3(CH_2)_6CH_2OH$		2	93[a]
16	C_2H_5OH		2	94[b]
17			2	95[b]

Power of MW irradiation: [a]1000 W, [b]500 W, [c]The reactions were carried out under solvent free condition (method B) and yields refer to isolated product.

Table 3. Results on Microwave-assisted Rapid Synthesis of Bis-2-nitro and Bis-2-formylphenoxy Alkyl Ethers

Entry	Product	Time (min)	Yield (%)[a]	Yield (%)[b]
1		80	79	85
2		75	84	93
3		75	81	87
4		80	73	80
5		80	88	86
6		90	85	83
7		110	80	76
8		130	74	70

[a]The reactions were carried out under solvent free condition(method A) and yields refer to isolated product. [b] Yields refer to isolated product in DMF (method C).

dramatically. The progress of reaction was monitored by TLC (n-hexane/EtOAc, 4:1, V/V). The remainder of tosyl chloride was removed by wetting the reaction mixture with *t*-BuOH and irradiated in a MW oven (900 W) for 2 min. Then, salicyaldehyde (100 mmol, 12.20 g) was added to the reaction mixture and grinded for 5 min. After half an hour irradiation in a microwave oven (180 W), H_2O (50 ml) was added and the product was extracted with diethyl ether (2 × 40 ml). The organic layer was dried with anhydrous Na_2SO_4 and evaporated by vacuo-rotary. The crude product was purified by short column chromatography (n-hexane/EtOAc, 4:1) and obtained in 72% yield (Table 4, entry 1).

2-Octyloxynaphthalene; (Table 1, Entry 3). IR (neat, cm^{-1}): *v* 745, 787, 835, 1119 (C-O stretch.), 1178 (aliphatic C-O stretch.), 1217, 1258 (C-O stretch.), 1389, 1465, 1512, 1601 (aromatic C=C stretch.), 1629, 2855, 2927, 3058 (aromatic C-H stretch.); ^{1}H NMR (400 MHz, $CDCl_3$ δ/ppm): 1.03 (3H, t, *J* = 4 Hz, $-CH_2-C\underline{H}_3$), 1.43-1.67 (10H, m), 1.92 (2H, m), 4.11 (2H, t, *J* = 8 Hz, $-O-C\underline{H}_2-CH_2-$), 7.17-7.84 (7H, m).; ^{13}C NMR (100 MHz, $CDCl_3$, *δ*/ppm): 14.34 ($-CH_2-\underline{C}H_3$), 22.87 ($-O-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-\underline{C}H_2-CH_3$), 26.32 ($-O-CH_2-CH_2-\underline{C}H_2-CH_2-CH_2-CH_2-CH_2-CH_3$), 29.45 ($-O-CH_2-CH_2-CH_2-CH_2-\underline{C}H_2-CH_2-CH_2-CH_3$), 29.59 ($-O-CH_2-CH_2-CH_2-\underline{C}H_2-CH_2-CH_2-CH_2-CH_3$), 32.04 ($-O-CH_2-CH_2-CH_2-CH_2-CH_2-\underline{C}H_2-CH_2-CH_3$), 67.83 ($-O-\underline{C}H_2-CH_2-$), 106.41, 119.15, 123.44, 126.27, 127.72, 129.01, 129.33, 134.76, 157.20 ($=\underline{C}-O$).

Cyclohexyloxybenzene; (Table 1, Entry 11). IR (neat, cm^{-1}): *v* 691 (mono subst. oop), 753 (mono subst. oop), 967, 1050 (C-O stretch.), 1170 (aliphatic C-O stretch.), 1239 (C-O stretch.), 1372, 1453, 1493, 1599 (aromatic C=C stretch.), 2857, 2936, 3032 (aromatic C-H stretch.); ^{1}H NMR (400 MHz, $CDCl_3$ δ/ppm): 1.27-2.39 (10H, m), 4.24 (1H, q, *J* = 8 Hz, $-O-C\underline{H}$-cyclohex), 6.92-7.31 (5H, m, Ar $\underline{H}$).; ^{13}C NMR (100 MHz, $CDCl_3$, *δ*/ppm): 23.85, 25.68, 31.87, 75.27 ($=C-O-\underline{C}$-cyclohex), 116.03, 120.46, 129.47, 157.75 ($=\underline{C}-O$).

2-(2-Phenoxyethoxy)ethoxy)benzene; (Table 2, Entry 4). IR (neat, cm^{-1}): *v* 691(mono subst. oop), 752 (mono subst. oop), 950, 1060 (C-O stretch.), 1134 (aliphatic C-O stretch.), 1300 (C-O stretch.), 1358, 1497, 1599 (aromatic C=C stretch.), 1699 (overtone bands), 1776 (overtone bands), 1834 (overtone bands), 1931 (overtone bands), 2874, 2928, 3040 (aromatic C-H stretch.); ^{1}H NMR (400 MHz, $CDCl_3$ δ/ppm): 3.98 (4H, t, *J* = 6 Hz, $-O-C\underline{H}_2-CH_2-O-Ar$), 4.20 (4H, t, *J* = 6 Hz, $-O-CH_2-C\underline{H}_2-O-Ar$), 6.99-7.38 (10H, m, Ar $\underline{H}$); ^{13}C NMR (100 MHz, $CDCl_3$, *δ*/ppm): 67.81 ($-O-CH_2-\underline{C}H_2-O-Ar$), 70.70 ($-O-\underline{C}H_2-CH_2-O-Ar$), 114.72, 120.99, 129.82, 158.83 ($=\underline{C}-O-CH_2-CH_2-O-$).

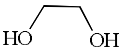
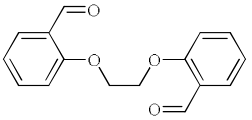
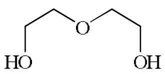
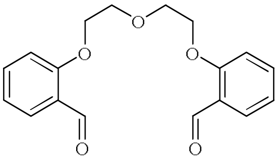
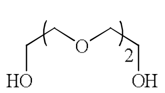
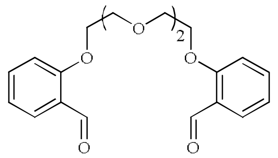
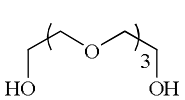
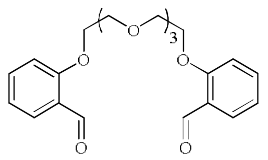
2,2'-((Oxybis(ethane-2,1-diyl))bis(oxy))dinaphthalene; (Table 2, Entry 4). IR (neat, cm^{-1}): *v* 690, 765, 965, 1130 (C-O stretch.), 1217, 1255 (C-O stretch.), 1470, 1600 (aromatic C=C stretch.), 1629, 2872, 2948, 3058 (aromatic C-H stretch.); ^{1}H NMR (400 MHz, $CDCl_3$ δ/ppm): 4.05 (4H, t, *J* = 8 Hz, $-O-C\underline{H}_2-CH_2-O-Ar$), 4.32 (4H, t, *J* = 8 Hz, $-O-CH_2-C\underline{H}_2-O-Ar$), 7.19-7.96 (14H, m, Ar $\underline{H}$).; ^{13}C NMR (100 MHz, $CDCl_3$, *δ*/ppm): 67.50 ($-O-CH_2-\underline{C}H_2-O-Ar$), 69.99 ($-O-\underline{C}H_2-CH_2-O-Ar$), 106.81, 119.07, 123.73, 126.40, 126.83, 127.69, 129.46, 134.52, 156.75 ($=\underline{C}-O-CH_2-CH_2-O-$).

1,2-Bis(2-phenoxyethoxy)ethane; (Table 2, Entry 7). IR (neat, cm^{-1}): *v* 691 (monosubst. oop), 754 (monosubst. oop), 932, 1128 (aliphatic C-O stretch.), 1246 (C-O stretch.), 1353, 1496, 1599 (aromatic C=C stretch.), 1697 (overtone bands), 1776 (overtone bands), 1844 (overtone bands), 1932 (overtone bands), 2870, 2918, 3063 (aromatic C-H stretch.); ^{1}H NMR (400 MHz, $CDCl_3$ δ/ppm): 3.78 (4H, s, $-O-C\underline{H}_2-C\underline{H}_2-O-$), 3.88 (4H, t, *J* = 8 Hz, $-O-CH_2-CH_2-O-C\underline{H}_2-CH_2-O-Ar$), 4.15 (4H, t, *J* = 8 Hz, $-O-CH_2-CH_2-O-CH_2-C\underline{H}_2-O-Ar$), 6.94-7.33 (10H, m, Ar $\underline{H}$); ^{13}C NMR (100 MHz, $CDCl_3$, *δ*/ppm): 67.30 ($-O-CH_2-CH_2-O-CH_2-\underline{C}H_2-O-Ar$), 69.84 ($-O-CH_2-CH_2-O-\underline{C}H_2-CH_2-O-Ar$), 70.66 ($-O-\underline{C}H_2-\underline{C}H_2-O-CH_2-CH_2-O-Ar$),, 114.64, 120.88, 129.48, 158.80 ($=\underline{C}-O-CH_2-CH_2-O-$).

1,2-Bis(2-(m-tolyloxy)ethoxy)ethane; (Table 2, Entry 9). IR (neat, cm^{-1}): *v* 690 (meta subst. oop), 783 (meta subst. oop), 957, 1132 (C-O stretch.), 1291 (C-O stretch.), 1453, 1490, 1603 (aromatic C=C stretch.), 2872, 2920, 3036 (aromatic C-H stretch.); ^{1}H NMR (400 MHz, $CDCl_3$ δ/ppm): 2.29 (6H, s, $Ar-C\underline{H}_3$), 3.63 (4H, s,$-O-C\underline{H}_2-C\underline{H}_2-O-$), 3.76 (4H, t, *J* = 6 Hz, $-O-CH_2-CH_2-O-C\underline{H}_2-CH_2-O-Ar$), 4.00 (4H, t, *J* = 6 Hz, $-O-CH_2-CH_2-O-CH_2-C\underline{H}_2-O-Ar$) 6.53-7.26 (8H, m, Ar $\underline{H}$).; ^{13}C NMR (100 MHz, $CDCl_3$, *δ*/ppm): 21.49 ($Ar-\underline{C}H_3$), 67.22 ($-O-CH_2-CH_2-O-CH_2-\underline{C}H_2-O-Ar$), 70.28 ($-O-CH_2-CH_2-O-\underline{C}H_2-CH_2-O-Ar$), 70.76 ($-O-\underline{C}H_2-\underline{C}H_2-O-CH_2-CH_2-O-Ar$), 111.51, 115.47, 121.65, 129.21, 139.22, 158.91 ($=\underline{C}-O-CH_2-CH_2-O-$).

2,2'-((((Oxybis(ethane-2,1-diyl))bis(oxy))bis(ethane-2,1-diyl))bis(oxy))dinaphthalene; (Table 2, Entry 12). IR (neat, cm^{-1}): *v* 690, 765, 965, 1120 (C-O stretch.), 1255 (C-

Table 4. Results on Scalable Ability (50 mmol) of Tandem Synthesis of Dialdehydes

Entry	Diol	Dialdehyde	Yield (%)[a]
1			69
2			72
3			66
4			64

[a]Yields refer to isolated product.

O stretch.), 1461, 1511, 1596 (aromatic C=C stretch.), 1629, 2874, 3058 (aromatic C-H stretch.); ^{1}H NMR (400 MHz, CDCl$_3$ δ/ppm): 3.80 (8H, s, Ar-O-CH$_2$-CH$_2$-O-C$\underline{H}_2$-C$\underline{H}_2$-O-C$\underline{H}_2$-C$\underline{H}_2$-O-CH$_2$-CH$_2$-O-Ar), 3.94 (4H, t, *J*= 8 Hz, Ar-O-CH$_2$-C$\underline{H}_2$-O-CH$_2$-CH$_2$-O-CH$_2$-CH$_2$-O-C$\underline{H}_2$-CH$_2$-O-Ar), 4.25 (4H, t, *J* = 8 Hz, Ar-O-C$\underline{H}_2$-CH$_2$-O-CH$_2$-CH$_2$-O-CH$_2$-CH$_2$-O-CH$_2$-C$\underline{H}_2$-O-Ar), 7.17-7.81 (14H, m, Ar $\underline{H}$).; ^{13}C NMR (100 MHz, CDCl$_3$, *δ*/ppm): 67.46 (Ar-O-$\underline{C}$H$_2$-CH$_2$-O-CH$_2$-CH$_2$-O-CH$_2$-CH$_2$-O-CH$_2$-$\underline{C}$H$_2$-O-Ar), 70.62 (Ar-O-CH$_2$-$\underline{C}$H$_2$-O-CH$_2$-CH$_2$-O-CH$_2$-CH$_2$-O-$\underline{C}$H$_2$-CH$_2$-O-Ar), 71.25 (Ar-O-CH$_2$-CH$_2$-O-$\underline{C}$H$_2$-$\underline{C}$H$_2$-O-$\underline{C}$H$_2$-$\underline{C}$H$_2$-O-CH$_2$-CH$_2$-O-Ar), 106.80, 119.09, 123.97, 126.42, 126.85, 127.71, 129.31, 134.58, 156.83 (=$\underline{C}$-O-CH$_2$-CH$_2$-O-).

1,4-Dimethoxybenzene; (Table 2, Entry 13). IR (neat, cm^{-1}): *ν* 690, 825 (para subst. oop), 1046 (C-O stretch.), 1105 (aliphatic C-O stretch.), 1232 (C-O stretch.), 1465, 1509, 1598 (aromatic C=C stretch.), 1847 (overtone band), 1963 (overtone band), 2066, 2833, 2929, 2998, 3050 (aromatic C-H stretch.); ^{1}H NMR (400 MHz, CDCl$_3$ δ/ppm): 3.74 (6H, s, Ar-C$\underline{H}_3$), 6.87 (4H, s, Ar $\underline{H}$).; ^{13}C NMR (100 MHz, CDCl$_3$, *δ*/ppm): 55.74 (Ar-$\underline{C}$H$_3$), 114.67 (-$\underline{C}$H=C-O-CH$_3$)., 153.79 (=$\underline{C}$-O-CH$_3$).

1-Methoxy-3-(phenoxymethyl)benzene; (Table 2, Entry 17). IR (neat, cm^{-1}): *ν* 691, 786, 881, 1040 (C-O stretch.), 1078, 1158 (aliphatic C-O stretch.), 1255 (C-O stretch.), 1379, 1493, 1596 (aromatic C=C stretch.), 2835, 2937, 3032 (aromatic C-H stretch.); ^{1}H NMR (400 MHz, CDCl$_3$ δ/ppm): 3.96 (3H, s, Ar-C$\underline{H}_3$), 5.19 (2H, s, CH$_3$-O-Ar-C$\underline{H}_2$-O-Ar), 7.06-7.53 (9H, m, Ar $\underline{H}$).; ^{13}C NMR (100 MHz, CDCl$_3$, *δ*/ppm): 55.27 (Ar-$\underline{C}$H$_3$), 69.90 (CH$_3$-O-Ar-$\underline{C}$H$_2$-O-Ar), 113.65, 115.11, 119.87, 120.19, 129.70, 130.04, 139.01, 159.06 (=$\underline{C}$-O-CH$_2$-Ar), 160.13 (CH$_3$-O-$\underline{C}$=CH-).

1,2-Bis(2-nitrophenoxy)ethane; (Table 3, Entry 1). IR (KBr, cm^{-1}): *ν* 511, 665, 753 (*ortho* subst. oop), 850, 931, 1047 (C-O stretch.), 1154 (aliphatic C-O stretch.), 1281 (C-O stretch.), 1362 (-NO$_2$ sym. stretch.), 1523 (-NO$_2$ asym. stretch.), 1606 (aromatic C=C stretch.), 2872, 2937, 3101(aromatic C-H stretch.); ^{1}H NMR (400 MHz, CDCl$_3$ δ/ppm): 4.65 (4H, s, Ar-O-C$\underline{H}_2$-C$\underline{H}_2$-O-Ar), 7.16-7.86 (8H, m, Ar $\underline{H}$).; ^{13}C NMR (100 MHz, Acetone-d$_6$, δ/ppm): 68.4 (Ar-O-$\underline{C}$H$_2$-$\underline{C}$H$_2$-O-Ar), 115.5, 121.0, 124.9, 134.1 (=$\underline{C}$-NO$_2$), 140.2, 152.5 (=$\underline{C}$-O-CH$_2$-CH$_2$-O-).

2,2'-((Oxybis(ethane-2,1-diyl))bis(oxy))bis(nitrobenzene); (Table 3, Entry 2). IR (KBr, cm^{-1}): v 515, 664, 849, 923, 1046 (C-O stretch.), 1088, 1128 (aliphatic C-O stretch.), 1264 (C-O stretch.), 1356 (-NO$_2$ sym. stretch.), 1525 (-NO$_2$ asym. stretch.), 1610 (aromatic C=C stretch.), 2879, 2926, 3083 (aromatic C-H stretch.); ^{1}H NMR (400 MHz, CDCl$_3$ δ/ppm): 4.02 (4H, t, J = 6.4 Hz, Ar-O-CH$_2$-C$\underline{H}_2$-O-C$\underline{H}_2$-CH$_2$-O-Ar), 4.30 (4H, t, J = 6.4 Hz, Ar-O-C$\underline{H}_2$-CH$_2$-O-CH$_2$-C$\underline{H}_2$-O-Ar), 7.00-7.85 (8H, m, Ar $\underline{H}$).; ^{13}C NMR (100 MHz, CDCl$_3$, δ/ppm): 69.7 (Ar-O-$\underline{C}$H$_2$-CH$_2$-O-CH$_2$-$\underline{C}$H$_2$-O-Ar), 69.7 (Ar-O-CH$_2$-$\underline{C}$H$_2$-O-$\underline{C}$H$_2$-CH$_2$-O-Ar), 115.0, 120.6, 125.59, 134.2 (=$\underline{C}$-NO$_2$), 140.0, 152.2 (=$\underline{C}$-O-CH$_2$-CH$_2$-O-).

1,2-Bis(2-(2-nitrophenoxy)ethoxy)ethane; (Table 3, Entry 3). IR (KBr, cm^{-1}): v 516, 665, 738, 778 (ortho subst. oop), 854, 920, 1037 (C-O stretch.), 1085, 1127 (aliphatic C-O stretch.), 1163, 1281 (C-O stretch.), 1354 (-NO$_2$ sym. stretch.), 1523 (-NO$_2$ asym. stretch.), 1611 (aromatic C=C stretch.), 2875, 2931, 3080 (aromatic C-H stretch.); ^{1}H NMR (400 MHz, CDCl$_3$ δ/ppm): 3.77 (4H, s, Ar-O-CH$_2$-CH$_2$-O-C$\underline{H}_2$-C$\underline{H}_2$-O-CH$_2$-CH$_2$-O-Ar), 3.93 (4H, t, J = 6.8 Hz, Ar-O-CH$_2$-C$\underline{H}_2$-O-CH$_2$-CH$_2$-O-C$\underline{H}_2$-CH$_2$-O-Ar), 4.28 (4H, t, J = 6.8 Hz, Ar-O-C$\underline{H}_2$-CH$_2$-O-CH$_2$-CH$_2$-O-CH$_2$-C$\underline{H}_2$-O-Ar), 7.01-7.84 (8H, m, Ar $\underline{H}$).; ^{13}C NMR (100 MHz, CDCl$_3$, δ/ppm): 69.2 (Ar-O-$\underline{C}$H$_2$-CH$_2$-O-CH$_2$-CH$_2$-O-CH$_2$-$\underline{C}$H$_2$-O-Ar), 69.5 (Ar-O-CH$_2$-CH$_2$-O-$\underline{C}$H$_2$-$\underline{C}$H$_2$-O-CH$_2$-CH$_2$-O-Ar), 71.0 (Ar-O-CH$_2$-$\underline{C}$H$_2$-O-CH$_2$-CH$_2$-O-$\underline{C}$H$_2$-CH$_2$-O-Ar), 114.9, 120.5, 125.5, 134.1(=$\underline{C}$-NO$_2$), 140.0, 152.3 (=$\underline{C}$-O-CH$_2$-CH$_2$-O-).

2,2'-((((Oxybis(ethane-2,1-diyl))bis(oxy))bis(ethane-2,1-diyl))bis(oxy))bis(nitrobenzene); (Table 3, Entry 4). IR (neat): v 521, 605, 667, 743 (ortho subst. oop), 852, 937, 1043 (C-O stretch.), 1133 (aliphatic C-O stretch.), 1280 (C-O stretch.), 1354 (-NO$_2$ sym. stretch.), 1525 (-NO$_2$ asym. stretch.), 1604 (aromatic C=C stretch.), 2875, 3077 (aromatic C-H stretch.); ^{1}H NMR (400 MHz, CDCl$_3$ δ/ppm): 3.73 (4H, s, Ar-O-CH$_2$-CH$_2$-O-C$\underline{H}_2$-C$\underline{H}_2$-O-CH$_2$-CH$_2$-O-Ar), 3.89 (4H, t, J = 6.8 Hz, Ar-O-CH$_2$-C$\underline{H}_2$-O-CH$_2$-CH$_2$-O-C$\underline{H}_2$-CH$_2$-O-Ar), 4.25 (4H, t, J = 6.8 Hz, Ar-O-C$\underline{H}_2$-CH$_2$-O-CH$_2$-CH$_2$-O-CH$_2$-C$\underline{H}_2$-O-Ar), 3.67 (4H, t, J = 6.8 Hz), 6.99-7.81 (8H, m, Ar $\underline{H}$).; ^{13}C NMR (100 MHz, CDCl$_3$, δ/ppm): 69.1 (Ar-O-$\underline{C}$H$_2$-CH$_2$-O-CH$_2$-CH$_2$-O-CH$_2$-$\underline{C}$H$_2$-O-Ar), 70.6 (Ar-O-CH$_2$-CH$_2$-O-$\underline{C}$H$_2$-$\underline{C}$H$_2$-O-CH$_2$-CH$_2$-O-Ar), 71.0 (Ar-O-CH$_2$-$\underline{C}$H$_2$-O-CH$_2$-CH$_2$-O-$\underline{C}$H$_2$-CH$_2$-O-Ar), 115.0, 120.5, 125.5, 134.1 (=$\underline{C}$-NO$_2$), 140.0, 152.2 (Ar-O-$\underline{C}$H$_2$-CH$_2$-O-CH$_2$-CH$_2$-O-CH$_2$-$\underline{C}$H$_2$-O-Ar).

2,2'-(Ethan-1,2-diylbis(oxy))dibenzaldehyde; (Table 3, Entry 5). IR (KBr, cm^{-1}): v 752 (*ortho* subst. oop), 1045 (C-O stretch.), 1248 (C-O stretch.), 1598 (aromatic C=C stretch.), 1690 (-C=O stretch.), 2760 (Fermi resonance), 2869, 3050 (aromatic C-H stretch.); ^{1}H NMR (400 MHz, CDCl$_3$ δ/ppm): 4.55 (4H, s, Ar-O-C$\underline{H}_2$-C$\underline{H}_2$-O-Ar), 7.07-7.11 (4H, t, J = 8 Hz), 7.57- 762 (2H, m, Ar $\underline{H}$), 7.85-7.87 (2H, q, Ar $\underline{H}$), 10.46 (2H, s, -C$\underline{H}$O).; ^{13}C NMR (100 MHz, CDCl$_3$, δ/ppm): 67.4 (Ar-O-$\underline{C}$H$_2$-$\underline{C}$H$_2$-O-Ar), 112.7, 121.7, 127.4 (=$\underline{C}$-CHO), 128.6, 136.0, 160.7 (=$\underline{C}$-O-CH$_2$-CH$_2$-O-), 189.46 (-$\underline{C}$HO).

2,2'-((Oxybis(ethane-1,2-dil))bis(oxy))dibenzaldehyde; (Table 3, Entry 6). IR (KBr, cm^{-1}): v 758 (*ortho* subst. oop), 1047 (C-O stretch.), 1093 (aliphatic C-O stretch.), 1240 (C-O stretch.), 1595 (aromatic C=C stretch.), 1685 (-C=O stretch.), 2882, 2940, 3100 (aromatic C-H stretch.); ^{1}H NMR (400 MHz, CDCl$_3$ δ/ppm): 4.03 (4H, t, J = 6.8 Hz, Ar-O-CH$_2$-C$\underline{H}_2$-O-C$\underline{H}_2$-CH$_2$-O-Ar), 4.30 (4H, t, J = 6.8 Hz, Ar-O-C$\underline{H}_2$-CH$_2$-O-CH$_2$-C$\underline{H}_2$-O-Ar), 7.0 (4H, m, Ar $\underline{H}$), 7.5 (2H, m, Ar $\underline{H}$), 7.8 (2H, q, Ar $\underline{H}$), 10.5 (2H, s, -C$\underline{H}$O).; ^{13}C NMR (100 MHz, CDCl$_3$, δ/ppm): 69.9 (Ar-O-$\underline{C}$H$_2$-CH$_2$-O-CH$_2$-$\underline{C}$H$_2$-O-Ar), 71.3 (Ar-O-CH$_2$-$\underline{C}$H$_2$-O-$\underline{C}$H$_2$-CH$_2$-O-Ar), 112.8, 121.1, 125.0 (=$\underline{C}$-CHO), 128.4, 135.8, 161.1(=$\underline{C}$-O-CH$_2$-CH$_2$-O-), 189.7(-$\underline{C}$HO).

2,2'-(((Ethane-1,2-diylbis(oxy))bis(ethane-2,1-diyl))bis(oxy))dibenzaldehyde; (Table 3, Entry 7). IR (KBr, cm^{-1}): v 750 (*ortho* subst. oop), 1002, 1049 (C-O stretch.), 1123 (aliphatic C-O stretch.), 1244 (C-O stretch.), 1291, 1595 (aromatic C=C stretch.), 1680 (-C=O stretch.), 2868, 2912, 3100 (aromatic C-H stretch.); ^{1}H NMR (400 MHz, CDCl$_3$ δ/ppm): 3.47 (4H, s, Ar-O-CH$_2$-CH$_2$-O-C$\underline{H}_2$-C$\underline{H}_2$-O-CH$_2$-CH$_2$-O-Ar), 3.90 (4H, t, J = 6.9 Hz, Ar-O-CH$_2$-C$\underline{H}_2$-O-CH$_2$-CH$_2$-O-C$\underline{H}_2$-CH$_2$-O-Ar), 4.22 (4H, t, J = 6.9 Hz, Ar-O-C$\underline{H}_2$-CH$_2$-O-CH$_2$-CH$_2$-O-CH$_2$-C$\underline{H}_2$-O-Ar), 6.96 (4H, m, Ar $\underline{H}$), 7.48 (2H, m, Ar $\underline{H}$), 7.78 (2H, q, Ar $\underline{H}$), 10.50 (2H, s,-C$\underline{H}$O).; ^{13}C NMR (100 MHz, CDCl$_3$, δ/ppm): 68.2 (Ar-O-$\underline{C}$H$_2$-CH$_2$-O-CH$_2$-CH$_2$-O-CH$_2$-$\underline{C}$H$_2$-O-Ar), 69.5 (Ar-O-CH$_2$-CH$_2$-O-$\underline{C}$H$_2$-$\underline{C}$H$_2$-O-CH$_2$-CH$_2$-O-Ar), 70.9 (Ar-O-CH$_2$-$\underline{C}$H$_2$-

O-CH_2-CH_2-O-$\underline{C}H_2$-CH_2-O-Ar), 112.9, 120.9, 125.0 (=$\underline{C}$-CHO), 128.1, 135.9, 161.2 (=$\underline{C}$-O-CH_2-CH_2-O-), 189.8 (-$\underline{C}$HO).

2,2'-((((Oxybis(ethane-2,1-diyl))bis(oxy))bis(ethane-2,1-diyl))bis(oxy))dibenzaldehyde;(Table 3, Entry 8). IR (KBr, cm^{-1}): v 755 (*ortho* subst. oop), 1002, 1055 (C-O stretch.), 1131 (aliphatic C-O stretch.), 1250 (C-O stretch.), 1300, 1605 (aromatic C=C stretch.), 1685 (-C=O stretch.), 2750 (Fermi resonance), 2850, 2922, 3050 (aromatic C-H stretch.); ^{1}H NMR (400 MHz, $CDCl_3$ δ/ppm): 3.65 (4H, t, J = 6.4 Hz, Ar-O-CH_2-CH_2-O-$C\underline{H}_2$-CH_2-O-CH_2-$C\underline{H}_2$-O-CH_2-CH_2-O-Ar), 3.75 (4H, t, J = 6.4 Hz, Ar-O-CH_2-CH_2-O-CH_2-$C\underline{H}_2$-O-$C\underline{H}_2$-CH_2-O-CH_2-CH_2-O-Ar), 3.9 (4H, t, J = 6.4 Hz, Ar-O-CH_2-$C\underline{H}_2$-O-CH_2-CH_2-O-CH_2-CH_2-O-$C\underline{H}_2$-CH_2-O-Ar), 4.25 (4H, t, J = 6.4 Hz, Ar-O-$C\underline{H}_2$-CH_2-O-CH_2-CH_2-O-CH_2-CH_2-O-CH_2-$C\underline{H}_2$-O-Ar), 6.96 (4H, m, Ar $\underline{H}$), 7.48 (2H, m, Ar $\underline{H}$), 7.78 (2H, q, Ar $\underline{H}$), 10.50 (2H, s,-C$\underline{H}$O).; ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 63.6 (Ar-O-$\underline{C}H_2$-CH_2-O-CH_2-CH_2-O-CH_2-CH_2-O-CH_2-$\underline{C}H_2$-O-Ar), 69.5 (Ar-O-CH_2-CH_2-O-$\underline{C}H_2$-$\underline{C}H_2$-O-$\underline{C}H_2$-$\underline{C}H_2$-O-CH_2-CH_2-O-Ar), 70.9 (Ar-O-CH_2-$\underline{C}H_2$-O-CH_2-CH_2-O-CH_2-CH_2-O-$\underline{C}H_2$-CH_2-O-Ar), 112.8, 120.9, 125.0 (=$\underline{C}$-CHO), 128.2, 135.9, 161.24 (=$\underline{C}$-O-CH_2-CH_2-O-), 189.8 (-$\underline{C}$HO).

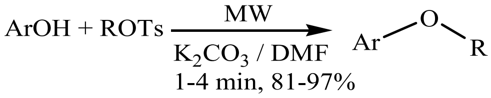
RESULTS AND DISCUSSION

The preparation of sulfonate esters from alcohols is an effective way to introduce a reactive leaving group within an alkyl chain of alkylating agent. As reported in our previous work, various types of alkyl tosylates were efficiently prepared as the proper alkylating agents from their corresponding alcohols, in high yields under solvent-free conditions by grinding the reactants on K_2CO_3 surface [23]. Clearly, the prepared alkyl tosylate is a susceptible substrate for further nucleophilic substitution reactions, due to presence of tosylate group as one of the best leaving group in organic chemistry. Microwave heating has been widely recognized as an efficient synthetic tool. Its benefits such as increasing chemical yields and reaction rates and also enhancing selectivity and reactivity have been well documented [24,25]. According to our contiguous project in preparing and exploiting the alkyl tosylates, we tried to synthesize alkyl aryl ethers, our target compounds, by microwave-heating [23,26]. It was found that treatment of alkyl tosylates with different phenols on K_2CO_3 as a mild basic surface, followed by the radiation of reaction mixture within a MW oven in a short period of time, the corresponding alkyl aryl ethers were prepared in high yields and good purities, (Scheme 1, Table 1).

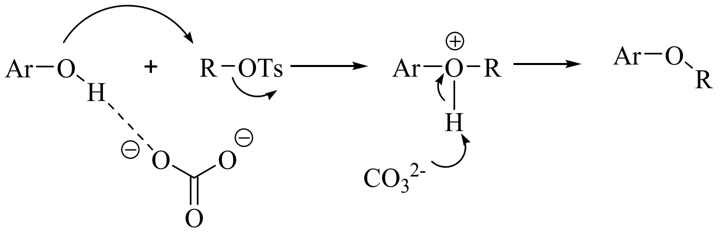
So far, most microwave protocols developed for the preparation of aryl ethers have involved a large excess of strong bases such as sodium or potassium hydroxide to deprotonate the relatively acidic hydrogen of phenol, often in aqueous medium [27,28]. Under thermal conditions, use of K_2CO_3, has been occasionally reported, but these reactions often suffer from long reaction times [29]. Mechanistically, it can be proposed that the reaction is a S_N2-type *O*-alkylation. K_2CO_3, as a mild and convenient basic solid support plays an important role that can help the polarization of phenolinc hydroxyl group, and enhancing its nucleophilicity toward alkyl tosylate. Also, neutralization of oxonium intermediate can be supposed, (Scheme 2).

It is believed that in the most of the times, solvent-free MW reactions absorption is mainly dependent on the polarity of system [29]. Similarly, we found that in these S_N2-type reactions, at least one liquid component is needed, too. Thus, to evaluate the scope of solvent effect and thermal behavior induced by MW radiations, four different conditions were examined: (1) without addition of any solvent to the mixture, (2) addition a small amount of a polar protic solvent such as C_2H_5OH or CH_3OH, (3) addition a small amount of a polar aprotic solvent such as THF, DMSO, DMF, and finally, (4) addition a few drops of butylmethylimidazolium bromide (BMIM) as an ionic solvent.

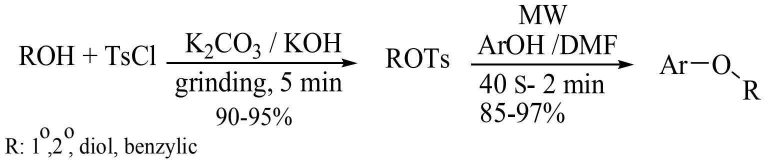
In two first approaches, the reactions proceeded slowly, but in the presence of polar aprotic solvents and BMIM the reactions were developed efficiently. Therefore, it seems that the weak solvation of reactants and facilitating the S_N2 displacement by a polar aprotic solvent may be the main reason. While DMF, DMSO and BMIM showed good results, to obtain the optimized reaction conditions, DMF as the most efficient was our solvent of choice. We reasoned that the coincidence of DMF in S_N2 reactions and dielectric MW-heating can cause to make the reaction medium homogeneous as well as absorb extra microwave energy that exceeds heat transfer and mobility of the involved species. It should be noted that although longer radiation times or



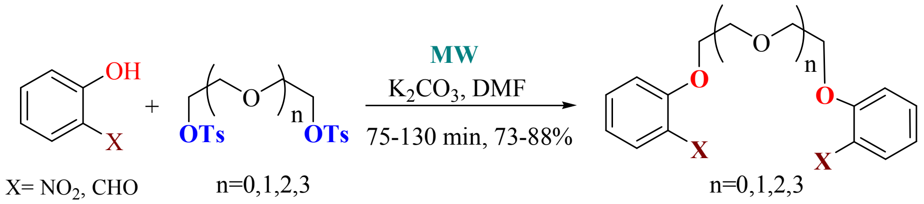
Scheme 1. Preparation of alkyl aryl ethers by MW irradiation



Scheme 2. A proposed mechanism for the reaction of phenols with alkyl tosylates on K_2CO_3 surface



Scheme 3. One pot preparation of alkyl aryl ethers from alcohols and phenols



Scheme 4. Microwave-assisted rapid synthesis of bis-2-nitro and bis-2-formylphenoxy alkyl aryl ethers

more intensive conditions was employed, the reactions in the presence of THF were not completed that can be attributed to its less dielectric constant ($\varepsilon = 7.6$) in comparison to DMF ($\varepsilon = 36.7$) and DMSO ($\varepsilon = 46.7$).

Ideally, in organic synthesis, reducing synthetic steps in a true sequential procedure is convenient from time, material, workup, and wholly cost standpoint. So, we next investigated the one pot preparation of alkyl aryl ethers *via in situ* formation of alkyl tosylates from their corresponding alcohols. Then, in a tandem manner, the reaction of the prepared alkyl tosylate with a phenol under microwave irradiation was examined (Scheme 3, Table 2).

Needless to say, this reaction pathway, as well as, the previous one, afforded all of the transformations successfully. As shown in Tables 1 and 2, to investigate the general applicability of this method, a series of different kinds of alkyl tosylates 1°, cyclic, benzylic, mono and disubstituted have been reacted with different mono and diphenolic compounds. Results indicated a dramatic reduction in reaction times and enhancement of yields in comparison to conventional thermal processes. In continuation of our ongoing projects to improve the synthesis and application of alkyl tosyaltes, initially, it was decided to prepare simple alkyl aryl ethers from monohydroxyphenols and monotosylates. Encouragement by these excellent results, at second step the reaction of oligoethylene glycol ditosylates such as, di, tri and tetraethylene glycol ditosylates, as valuable building blocks, with monophenolic reactants were examined that presented the convenience and capability of this method. In the third step, the reaction of diphenolic reactants like hydroquinone and resorcinol with monotosylate substrates were carried out. Clearly, all of the approaches were successfully applied in high yields and short times.

Notably, it should be pointed out that dihydroxybenzenes such as catechol and polyethylene glycol ditosylates or dihalides are important starting synthetic building blocks for the preparation of macrocyclic polyehters, namely benzocrown ethers. It is well-known that benzocrown ethers are interesting class of host compounds on the basis of their ability to bind strongly and selectively with inorganic and organic cations and some neutral substrates [31]. Therefore, this procedure fits in a more comprehensive project for us and it is an incipient work to improve methods for introducing benzocrown ethers in near future.

In continuation of our studies, we broadened our interest to the reaction of *o*-nitrophenols and salicyaldehyde with oligoethylene glycol ditosylates to prepare the corresponding nitropodands that are valuable starting materials for synthesizing 10-membered and larger dibenzoazo and azoxy crown ethers and crypatands as ion carriers in ion-selective membranes and ether linked dialdehydes as precious precursors for aza-crown ethers and cyclophanes synthesis through Schiff base-ligand complexes [32-36]. Notably, there were no any meaningful differences between the yields of reactions in solution and solvent free conditions (Scheme 4, Table 3).

In conjunction with our research, to elucidate the capability of this project in scaling up of producing ethers, a tandem reaction up to 50 mmol of oligoethylene glycols and salicyaldeheyde were also conducted that produced their corresponding 2-formylethers in high yields (Table 4).

We also performed a comparative study between this work and others reported in the literature (Table 5). Results show that our method is comparable with other methods in terms of yields, reaction times and simplicity of procedure.

CONCLUSIONS

In summary, it can be claimed that we have developed a simple and rapid method of microwave-assisted alkylation of phenols according to the general Williamson ether synthesis procedure using K_2CO_3 as a mild, cheap and environmentally compatible base. Consequently, following aspects can be referred: high-yields, scale up ability, short reaction times, profiting by both solvent-free conditions and MW technique simultaneously, simplicity in process, handling and workup with no needs of any catalyst, eco-friendly and environmentally acceptable from the green chemistry standpoints, running the reactions in a true one-pot without pre-formation of reactants prior to addition, no side reactions or by-products. It is envisaged that a general procedure has been introduced that may be potentially applicable in a number of chemical and medicinal industries.

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