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RESEARCH ARTICLE

Microwave-promoted pseudo-thia-Fries rearrangement of aryl benzylsulfonates; highly reactive benzyl cation generation

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Aryl benzylsulfonates undergo so-called pseudo-thia-Fries rearrangement under microwave irradiation. Benzylated phenolic compounds have been obtained with the loss of 'SO_2' from the starting materials.

Keywords: Aryl benzylsulfonates; Microwave irradiation; Benzyl cation generation; Pseudo-thia-Fries rearrangement; Microwave-induced acid generator (MIAG)

1. Introduction

Molecules that generate acid upon exposure to radiation have been extensively investigated in microlithography [1, 2]. The photodissociation of sulfonate esters has been widely used to generate acids. Several classes of sulfonate esters have been utilized as photo acid generators (PAGs) in chemically amplified photoresists [3]. These include the *o*-nitrobenzyl [4] and *p*-nitrobenzyl [5] sulfonate esters that, *via* different photochemical mechanisms, undergo C−O bond cleavage to generate sulfonic acid.

Recently, we have reported the thia-Fries rearrangement of aryl *p*-toluenesulfonates supported on a new medium ($ZnCl_2$: $AlCl_3$: SiO_2) under solvent-free conditions with microwave dielectric heating [6]. The ortho-directed sulfonyl moiety was the exclusive product of this reaction. Moreover, these compounds undergo photo-Fries rearrangement, in which the sulfonyl group migrates to ortho and para positions of the phenol ring (scheme 1) [7].

It was believed that the mechanism of the photo-Fries rearrangement of sulfonate esters was analogous to the carboxylates [8], *i.e.* homolytic cleavage of the S−O bond to form a radical pair [ArO• •SO_2R], in the solvent cage, which then undergoes intramolecular coupling or cage escape. During our investigation of aryl *p*-toluenesulfonates [6], we observed that the irradiation of the aryl benzylsulfonate esters under the same reaction conditions of

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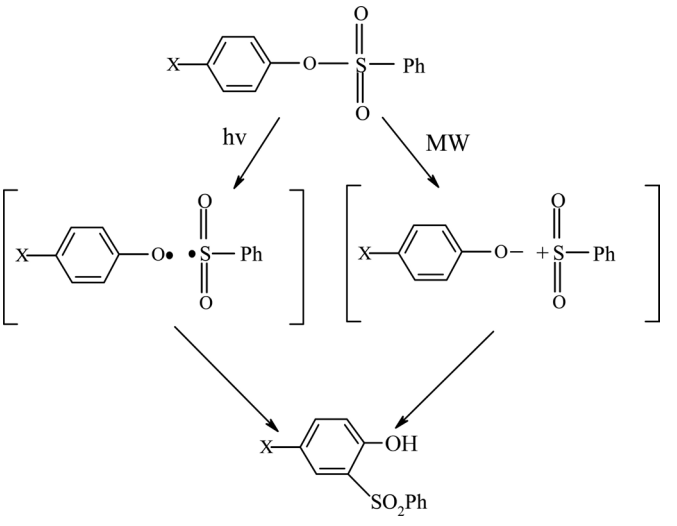
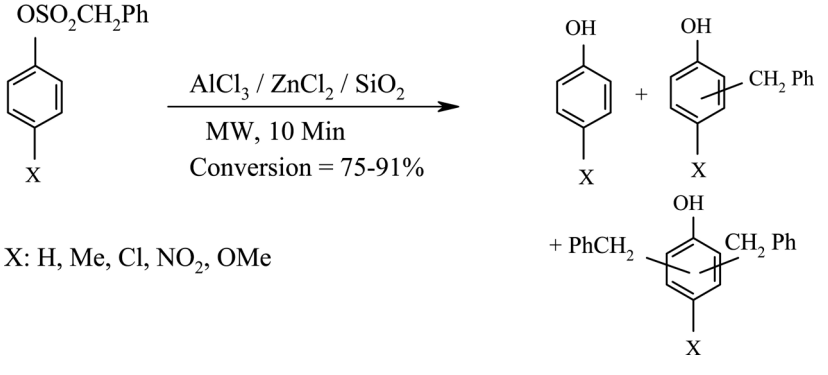


SCHEME 1

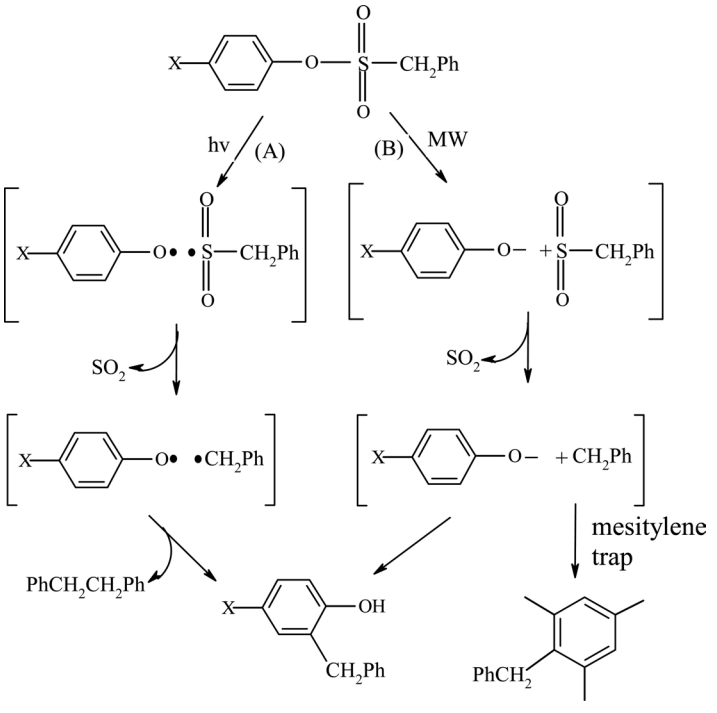
aryl *p*-toluenesulfonates did not proceed by the same reaction pathway. Conversely, alkyl sulfonates showed no Fries-type rearrangement in the presence of either $AlCl_3$ or $ZnCl_2$ in refluxing nitrobenzene [9]. Spectroscopic analysis and GC-MS of the reaction products indicate that aryl benzylsulfonates produce benzylated phenolic compounds with loss of "SO_2" under microwave irradiation (schemes 2 and 3 below). A similar reaction has been observed by photolytic irradiation of these compounds, which generate "SO_2" *via* a pseudo-thia-Fries type rearrangement (scheme 3 below). Therefore, they have been called photo acid generators (PAGs) [10]. We report here the results of our work on the microwave-promoted pseudo-thia-Fries rearrangement of aryl benzylsulfonates.



SCHEME 2

2. Results and discussion

When *p*-tolyl benzylsulfonate as a model compound was mixed with the support (1:3 w/w) [6] and subjected to microwave irradiation for 10 min (the optimized time for thia-Fries rearrangement of the aryl *p*-toluenesulfonates) there was 75.6% conversion of the starting sulfonate. Analysis of the reaction products by ^{1}H NMR showed no intramolecular hydrogen-bonded signal at 9–11 ppm, which would correspond to the H-bond of a phenolic hydroxyl group



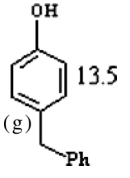
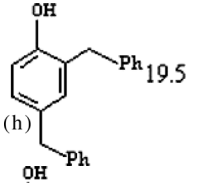
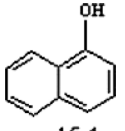
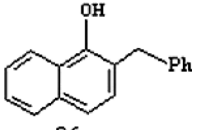
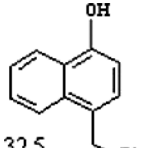
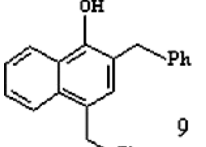
SCHEME 3 Proposed mechanism of the pseudo-thia-Fries rearrangement.

with a sulfinyl moiety, as we have observed for the products of aryl *p*-toluenesulfonates (scheme 1). In addition, the IR spectroscopy of the products showed no absorption for a sulfone. Moreover, GC-MS analysis suggested that the products could be the benzylated phenolic compounds. Finally, the structure of the products was confirmed by comparison of their spectroscopic data with those of authentic samples [11]. Table 1 shows that the benzylated phenols were the exclusive product of this reaction. To examine the effect of electron-donating and electron-withdrawing substituents on phenolic portion of the molecules, different starting materials were prepared and subjected to microwave irradiation under optimized conditions. The results are summarized in table 1.

In all cases the ortho-directed monobenzylated phenol was the main reaction product. Phenyl benzylsulfonate (table 1, entry 5) gave the monobenzylated phenol as the major reaction product (38% ortho + 13.5% para) along with a mixture of dibenzylated phenol (34%). When X = Cl (table 1, entry 2) the ortho-directed monobenzylated derivative was the major product of the reaction (53.5%) along with a small amount of the *ortho*-dibenzylated compound (10%). The presence of a methoxy group, serving as a strong electron-donating group on the aryl moiety (table 1, entry 3), activates the aromatic ring and the tribenzylated derivative (7%) was also observed as a minor product. *p*-Nitrophenyl benzylsulfonate (table 1, entry 4) gave only poor yield of monobenzylated compound (29%). In this case hydrolysis of the starting sulfonate ester was the main reaction product (71%). Finally, naphthyl benzylsulfonate (table 1, entry 6) behaves as other aromatic compounds and gave mono- and dibenzylated naphthols, but with higher conversion (90.8%).

The photo-Fries rearrangement of phenyl benzylsulfonate has been reported [10]. A radical mechanism has been proposed, *i.e.*, homolytic cleavage of S−O bond, desulfonylation of the benzyl sulfonyl radical and, finally, the reaction of the benzyl radical with different species presented in the reaction media. The radical mechanism proposed for the thia-Fries reaction was confirmed by transient spectra and by the detection of diphenylethane, which is formed by the combination of two benzyl radicals (scheme 3, pathway A).

Table 1. Microwave-promoted pseudo-thia-Fries rearrangement of aryl benzyl sulfonates.

Entry	X	(% distribution of the products) (a)	(b)	(c)	(d)	(e)	(f)	Conversion (%)
1	CH_3	41.4	32.2	3.8	16.1	6.5	–	75.6
2	Cl	36.5	53.5	–	10	–	–	78.5
3	OMe	15.5	21	17.5	13	26	7	87.5
4	NO_2	71	29	–	–	–	–	70
5	H	14.5	38	 13.5 (g)	14.5	 19.5 (h)	–	85
6	 15.4	 36 (i)	 32.5 (j)	 9 (k)				90.8

In our case, the microwave-induced rearrangement products of the phenyl benzylsulfonate ester were the mono- and dibenzylated phenolic compounds, resulting from loss of "SO_2" from the starting sulfonates. We believe that the active benzyl cation is formed by the heterolytic cleavage of the S−O bond, followed by the loss of "SO_2" from the benzyl sulfonyl cation species, which undergoes a pseudo-thia-Fries rearrangement to form ortho- and para-directed isomers of benzylated phenols (scheme 3, pathway B). To the best of our knowledge, this is the first report on the microwave-induced generation of active benzyl cation. GC-MS analysis of the crude reaction mixture failed to detect any trace of diphenylethane that would support a radical reaction mechanism. Conversely, when the reaction was carried out in the presence of an excess of mesitylene as a benzyl cation scavenger, benzylated mesitylene was obtained in good yield (36%), a result that supports the cationic mechanism. To demonstrate the microwave effect on the efficiency of this methodology, we also carried out the reaction under classical heating. When benzyl *p*-tolyl sulfonate (table 1, entry 1) was mixed with the support and heated to about 240 °C (the temperature that the reaction medium reached under microwave irradiation) for 10 min in an oil bath, only tarry materials were obtained due to decomposition of the starting material. The reaction also did not proceed in the absence of support under microwave irradiation, confirming the efficiency of the support for the success of this type of reaction.

In conclusion, an $AlCl_3$–$ZnCl_2$ mixture supported on silica gel is an efficient medium for pseudo-thia-Fries rearrangement of aryl benzylsulfonates under microwave irradiation. These materials are benzyl cation generators under these reaction conditions and we name these compounds microwave-induced acid generators (MIAG). This method has the following advantages: (a) the medium is readily available; (b) the reaction is fast and solvent free; (c) a wide range of aryl or naphthyl sulfonates are rearranged by this medium; and finally (d) ease of the work-up.

3. Experimental

The microwave oven used for this work was a National (1550 W) at 2450 MHz (100% power for all reactions). FTIR spectra were recorded as KBr pellets on a Nicolet spectrometer (Magna 550). A Bruker (DRX-500 Avance) NMR was used to record the ^{1}H NMR spectra. For GC-MS, GC: HP6890 Column: HP-5 (30 m × 0.25 mm × 0.2 μm) MSD: HP 5793. The support was prepared as described in ref. 12.

3.1 *General procedure for preparation of aryl benzylsulfonates*

To an ice-cooled stirred solution of phenol (6 mmol) and Et_3N (5.25 mmol) in anhydrous acetone (50 mL), a solution of benzylsulfonyl chloride (5.25 mmol) in anhydrous acetone was dropwise added over about 10 min. After 2–3 h, the reaction mixture was filtered and the acetone was evaporated. The so-obtained solid residue was then dissolved in CH_2Cl_2 (50 mL) and washed with water (2 × 25 mL). The organic phase was subsequently dried over $CaCl_2$ and the solvent was evaporated under reduced pressure. The product was recrystallized from ethanol.

3.2 *General procedure for the reaction of aryl benzylsulfonate under microwave irradiation*

To a solution of the sulfonate ester (1 g) in dry CH_2Cl_2 (15 mL), the support (3 g) was added and mixed well. After evaporation of the solvent the solid was subjected to microwave irradiation for 10 min. Then, the mixture was cooled to room temperature and washed with CH_2Cl_2 (2 × 50 mL). The benzylated phenol derivatives were then purified on a silica-gel column, eluting with a mixture of hexane and ethyl acetate.

3.3 *Selected spectroscopic data for the compounds*

2,6-Dibenzyl-4-methylphenol (liquid) (***1d***). ^{1}H NMR ($CDCl_3$) δ (ppm): 2.4 (3H, s, CH_3), 4.1 (4H, s, CH_2), 4.65 (1H, s, OH), 7–7.6 (12H, m, aromatic); IR (ν cm^{-1}): 3562 (OH), 3023, 2915; MS *m/z* (%) (rel. intensity) 288 ($M^{+\bullet}$, 73), 209 (100), 197(47), 165 (26), 91 (29).

2,4-Dibenzyl-1-naphthol (liquid) (***6k***). ^{1}H NMR ($CDCl_3$) δ (ppm): 4.17 (2H, s, CH_2), 4.43 (2H, s, CH_2), 5.13 (1H, s, OH), 7.1–8.2 (15H, m, aromatic); IR (ν cm^{-1}): 3392 (OH), 3023, 2923; MS *m/z* (%): 324 ($M^{+\bullet}$, 100), 246 (27), 233 (31), 215 (45), 202 (32), 91 (38).

2-Benzyl-1-naphthol (liquid) (***6i***). ^{1}H NMR ($CDCl_3$) δ (ppm): 4.01 (2H, s, CH_2), 5.4 (1H, s, OH), 7.81 (11H, m, aromatic); MS *m/z* (%): 234 ($M^{+\bullet}$, 86), 215 (26), 156 (100), 128 (60), 91 (24).

4-Benzyl-1-naphthol. Mp 115–119 °C (hexane–toluene) (***6j***): ^{1}H NMR ($CDCl_3$) δ (ppm): 4.39 (2H, s, CH_2), 5.23 (1H, s, OH), 6.79 (1H, d, $J = 7.58$ Hz, CH), 7.21 (1H, d, $J = 7.01$ Hz, CH), 7.20–7.30 (5H, m, C_6H_5), 7.49 (2H, m, 2CH), 7.94 (1H, q, CH), 8.25 (1H, q, CH); IR (KBr disk) (ν cm^{-1}): 3346 (OH), 2923, 1600; MS *m/z* (%): 234 ($M^{+\bullet}$, 100), 215 (28), 202 (26), 157 (36), 128 (32), 91 (22).

2,3,6-Tribenzyl-4-methoxyphenol (liquid) (***3f***). ^{1}H NMR ($CDCl_3$) δ (ppm): 3.76 (3H, s, OCH_3) 4.05 (6H, t, $3CH_2$), 4.30 (1H, s, OH), 6.73 (1H, s, CH), 7.09–7.37 (15H, m, $3C_6H_5$); IR (ν cm^{-1}): 3538 (OH), 2930, 3023, 2838; MS *m/z* (%): 394 ($M^{+\bullet}$, 100), 315 (60), 225 (21), 207 (12), 165 (13), 115 (11), 91 (61).

2,6-Dibenzyl-4-methoxyphenol (liquid) (***3d***). ^{1}H NMR ($CDCl_3$) δ (ppm): 3.75 (3H, s, OCH_3) 3.98 (4H, s, $2CH_2$), 4.27 (1H, s, OH), 6.63 (2H, s, 2CH), 7.23–7.34 (10H, m, $2C_6H_5$); IR (ν cm^{-1}): 3538 (OH), 2923, 2838; MS *m/z* (%): 304 ($M^{+\bullet}$, 100), 225 (94), 165 (11), 115 (20), 91 (43).

2,5-Dibenzyl-4-methoxyphenol (liquid) (***3e***). ^{1}H NMR ($CDCl_3$) δ (ppm): 3.79 (3H, s, OCH_3), 3.95 (2H, s, CH_2), 4.02 (2H, s, CH_2), 4.46 (1H, s, OH), 6.52 (1H, s, CH), 6.7 (1H, s, CH), 7.24–7.38 (10H, m, and $2C_6H_5$); IR (ν cm^{-1}): 3530 (OH), 2923, 2840, 1207, 1023; MS *m/z* (%): 304 ($M^{+\bullet}$, 100), 165 (15), 115 (20), 91 (58).

2-Benzyl 4-nitrophenol (***4b***). ^{1}H NMR (acetone) δ (ppm): 4.15 (2H, s, CH_2), 7.18–7.86 (8H, m, aromatic), 9.2 (1H, s, OH); IR (ν cm^{-1}): 3469 (OH), 1523 (NO_2), 1345 (NO_2.); MS *m/z* (%): 229 ($M^{+\bullet}$, 100), 207 (37), 165 (35), 152 (37), 78 (50).

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