# Efficient Synthesis of Sodium Aryloxymethanesulfonates Using Microwave Irradiation†

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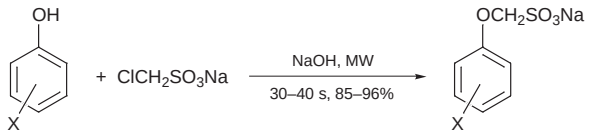
A very simple, efficient and rapid method is described for the synthesis of sodium aryloxymethanesulfonates using microwave irradiation.

Sodium phenoxymethanesulfonate[1] and its derivatives are important intermediates in organic synthesis and are applied widely for the preparation of α-chloroanisole and its derivatives.[2,3] The Barber method, which involves treatment of sodium chloromethanesulfonate[4] with phenol in the presence of base at 200–220 °C for 4 h, is the usual method for their synthesis.[2] In recent years, the application of microwave irradiation has rapidly increased owing to short reactions times and operational simplicity.[5] Condensation reactions of phenols with halides, epichlorohydrine[7] and chloroacetic acid[8] have recently been reported by the microwave technique.

Here, we report that sodium phenoxymethanesulfonate and its derivatives can be obtained from condensation of phenols and sodium chloromethanesulfonate under microwave irradiation in the absence of any inorganic carrier or organic solvent. This method is very simple and the reaction times are very short (Scheme 1).




**Scheme 1**

The presence of a few drops of water is very important for this reaction since in the absence of water the yield of sodium phenoxymethanesulfonate was found to be very low. Presumably, the major effect is that water couples efficiently with the microwaves and also acts as a solvent for the reaction. The results obtained from condensation of different phenols and sodium chloromethanesulfonate are shown in Table 1.

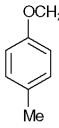
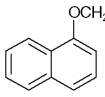
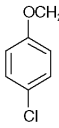
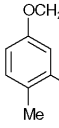
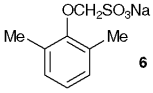
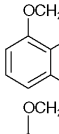
A number of features of this reaction under microwave irradiation should be noted, a substantial increase in the yields and decrease in the reaction times are observed in comparison with the usual thermal method at $> 200$ °C. Second, the presence of substituents with different electronic and steric effects did not affect the rate and yield of this reaction and third, the use of solvents such as DMSO and DMF are avoided, so making the present method very simple and environmentally safer.

## Experimental

Chemicals were purchased from Fluka, Aldrich and Merck. Thin layer chromatography (TLC) on commercial plates of silica gel 60 $F_{254}$ was used to monitor the progress of the reactions. Yields refer to isolated products after purification. Products were characterized by comparison of their physical data (mp, IR and NMR spectra) with samples prepared by the known method.[2]

*Typical Procedure for the Preparation of Sodium Phenoxymethanesulfonate.*—To a mixture of phenol (0.012 mol, 1.12 g), sodium chloromethanesulfonate (0.01 mol, 1.52 g) and sodium hydroxide (0.015 mol, 0.6 g) in an Erlenmeyer flask were added four drops of water at room temperature. The reaction mixture was thoroughly mixed and then placed in a microwave oven (200 W) for 35 s. After cooling to room temperature, 50 ml water was added and the unreacted phenol was extracted with 20 ml diethyl ether at pH 5 (acidification *via* aqueous 0.5 M HCl). The aqueous solution was boiled until the volume was reduced to 10–15 ml and then cooled. The resulting precipitate was filtered off and washed subsequently

**Table 1** Condensation of phenols with sodium chloromethanesulfonate under microwave irradiation

| Entry | Substrate | Product | Irradiation conditions *t*/s (power/W) | Yield[a] (%) | Yield[b] (%) |
|---|---|---|---|---|---|
| 1 | Phenol |  **1** | 35(200) | 92 | 61 |
| 2 | *p*-Cresol |  **2** | 40(100) | 95 | 77 |
| 3 | 1-Naphthol |  **3** | 30(200) | 93 | 50 |
| 4 | *p*-Chlorophenol |  **4** | 40(100) | 92 | 78 |
| 5 | 3,4-Dimethylphenol |  **5** | 30(200) | 93 | 83 |
| 6 | 2,6-Dimethylphenol |  **6** | 40(200) | 92 | 75 |
| 7 | 2,3-Dichlorophenol |  **7** | 30(200) | 90 | 82 |
| 8 | 2-Allylphenol |  **8** | 40(200) | 90 | 80 |
| 9 | Sodium salicylate |  **9** | 40(200) | 85 | 25 |
| 10 | 2-Methoxylphenol |  **10** | 40(200) | 96 | 79 |

[a] Yields obtained using microwave method. [b] Yields obtained using the Barber method.[2]

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† This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1999, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

with cooled water, methanol and then diethyl ether. The obtained product **1** was recrystallized from ethanol and dried at room temperature (1.78 g, 92%). $R_f$ (EtOH) = 0.6, $\delta_H$ (DMSO-$d_6$, 250 MHz) 4.35 (s, 2H, $OCH_2$), 6.9 (m, 5H, Ph).

*Selected* $^1$H NMR *Data* (DMSO-$d_6$ 250 MHz).—**2**: $\delta$ 2.2 (s, 2H, $CH_3$), 4.4 (s, 2H, $OCH_2$), 6.8 (m, 4H, $C_6H_4$). **3**: $\delta$ 4.7 (s, 2H, $OCH_2$), 7.3–7.8 (m, 7H, $C_{10}H_7$). **4**: $\delta$ 4.5 (s, 2H, $OCH_2$), 7.1–7.3 (dd, 4H, $C_6H_4$). **5**: $\delta$ 2.1 (s, 3H, $CH_3$), 2.8 (s, 3H, $CH_3$), 4.5 (s, 2H, $OCH_2$), 7.3–6.5 (m, 3H, $C_6H_3$). **6**: 2.2 (s, 6H, 2 $CH_3$), 4.4 (s, 2H, $OCH_2$), 7.3–6.8 (m, 3H, $C_6H_3$). **9**: $\delta$ 4.4 (s, 2H, $OCH_2$), 6.9–7.1 (dd, 4H, $C_6H_4$). **10**: $\delta$ 3.4 (s, 3H, $OCH_3$), 4.3 (s, 2H, $OCH_2$), 6.9–6.6 (m, 4H, $C_6H_4$).

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