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PHASE TRANSFER CATALYZED SYNTHESIS OF O-ETHOXYPHENOL UNDER MICROWAVE IRRADIATION

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ABSTRACT: o-Chlorophenol reacted with ethanol in the presence of sodium hydroxide and phase transfer catalyst under microwave irradiation and gave o-ethoxyphenol conveniently within a few minutes, and the isolated yield of o-ethoxyphenol vary from 69% to 82%.

o-Ethoxyphenol attracts interest for its fragrance and as an intermediate in the synthesis of ethyl vanillin and other perfumes. In general, it is prepared from o-alkylation of phenolate of catechol with ethyl halide in the presence of phase transfer catalyst such as tetrabutylammonium bromide,^{1,2} or the reaction of sodium phenolate of catechol with ethanol in the presence of triphenylphosphine and

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tetrachloromethane,³ dealkylation of 1,2-diethoxybenzene with water on and aluminosilicate catalyst,⁴ or cleaving of methylenedioxybenzene with methyl magnesium iodide.⁵ Recently, it was conveniently synthesized by selenium compounds catalyzed Baeyer–Villiger oxidation of aromatic aldehyde.⁶ In our laboratory, it is prepared smoothly and firstly by direct reaction of o-chlorophenol with ethanol in the presence of sodium hydroxide and various kinds of phase transfer catalysts within a few minutes under microwave irradiation. The reaction goes rather faster and more smoothly than that under the conventional heating. Microwave in organic synthesis has been developed successfully in several publications⁷⁻¹².

The results are summarized in Table 1. The results show that microwave irradiation does promote and accelerate the reaction of o-chlorophenol with ethanol, the rate enhancement is 240-fold and the yield is greatly increased from 24% to 82%. As could be expected, the role of phase transfer catalysts is indispensable, PEG 400 and PEG 800 are found to be most efficient. The products were fully characterized by IR, GC/MS and ¹H NMR spectroscopy.

EXPERIMENTAL

General considerations: ¹H-NMR spectra were recorded on a Bruker AC-90 spectrometer, using TMS as internal standard; IR spectra were measured using a Perkin-Elmer Model 580B; GC/MS(EI) spectra were performed on a HP 5890 series

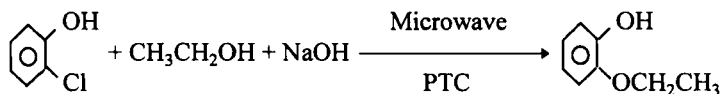


Table 1. Reaction of o-Chlorophenol with Ethanol under Microwave Irradiation

Entry	Catalyst	Conventional Heating		Microwave Irradiation	
		Time (min)	Yield(%) ^a	Time(min)	Yield(%) ^a
1	none	480	14	2	63
2	PEG 400	480	24	2	82
3	PEG 800	480	22	2	78
4	PEG 1500	480	19	2	71
5	benzyltrimethylammonium chloride	480	18	2	70
6	cetyltrimethylammonium bromide	480	18	2	69
7	triethylamine	480	20	2	73
8	tributylamine	480	21	2	74

a. product isolated

II gas chromatography coupled with a HP 5972 mass selective detector. Column Chromatography was carried out on silica gel (70–230 mesh). Microwave irradiations were carried out with a commercial oven (700 W, 2450MHz).

General procedure: A typical experiment procedure as follows: 2 mmol (0.26g) o-chlorophenol, 2 mmol (0.08g) sodium hydroxide, 10 mmol (1.0ml) absolute ethanol and 0.2 mmol (0.08g) PEG 400 were placed in a 10 ml Pyrex tube and sealed off. In a conventional synthesis, the sealed tube in an ethanol atmosphere (78°C) and heated for

8h. In a microwave irradiation synthesis, the sealed tube protected by a Teflon tube is placed in a domestic microwave oven (700W) and heated for 2 minutes. The product is isolated by column chromatography through a short column of silica gel and identified to be o-ethoxyphenol, 24% yield with conventional heating, but 82% with microwave irradiation. b.p. 93-95°C/8 mmHg, m.p. 28°C. IR (film) ν 3520, 2980, 1590, 1500, 1260, 1040, 740. MS (EI): m/z 138 (M^+). 1H NMR ($CDCl_3$) δ 1.40 (3H, t, CH_3), 4.05 (2H, t, CH_2O), 5.70 (1H, s, OH), 6.85 (4H, m, C_6H_4). Anal. Calcd. for $C_8H_{10}O_2$: C, 69.60; H, 7.25. Found: C, 69.75; H, 7.17.

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