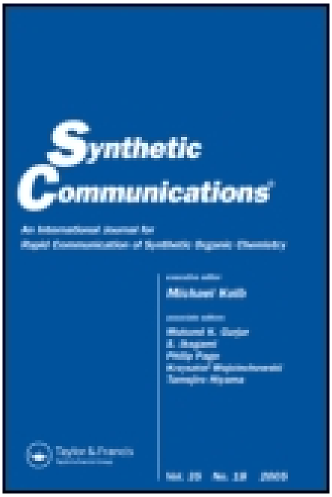

Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Phase Transfer Catalyzed Synthesis of O-Ethoxyphenol Under Microwave Irradiation

Jun Pang [a] , Zuwei Xi [a] , Guoying Cao [a] & Yuncheng Yuan [b]

[a] Dalian Institute of Chemical Physics, Chinese Academy of Sciences , Dalian, 116023, P. R. China

[b] School of Chemical Engineering, Dalian University of Technology , Dalian, 116012, P. R. China

To cite this article: Jun Pang , Zuwei Xi , Guoying Cao & Yuncheng Yuan (1996) Phase Transfer Catalyzed Synthesis of O-Ethoxyphenol Under Microwave Irradiation, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 26:18, 3425-3429, DOI: 10.1080/00397919608003747

To link to this article: http://dx.doi.org/10.1080/00397919608003747

SYNTHETIC COMMUNICATIONS, 26(18), 3425-3429 (1996)

PHASE TRANSFER CATALYZED SYNTHESIS OF O-ETHOXYPHENOL UNDER MICROWAVE IRRADIATION

Jun Pang*, Zuwei Xi and Guoying Cao

Dalian Institute of Chemical Physics, Chinese Academy of Sciences

Dalian 116023, *P.R.China*

Yuncheng Yuan

School of Chemical Engineering, Dalian University of Technology

Dalian 116012, *P.R.China*

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

---

* *To whom correspondence should be addressed.*

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 publications[7-12].

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 ^{1}H NMR spectroscopy.

EXPERIMENTAL

General considerations: ^{1}H-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

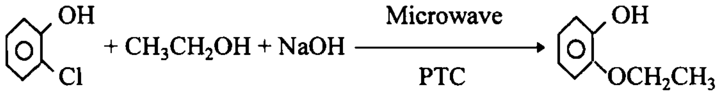

Table 1. Reaction of o-Chlorophenol with Ethanol under Microwave Irradiation

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) υ 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.

Acknowledgment. This work was supported by the National Nature Science Foundation of China (NO 29272038).

References

1. V.Z. Sharf, L. Kh. Freidlin, O.M.Kholmer and I.M.Lebedev. Maslob. , *Zhir. Prom.* , 1962, 28, 35.
2. Yuan Qun, Shen Xueqiang and Xu Ying, *Chinese Journal of Applied Chemistry*, 1989, 6,42.
3. Furukawa Isao and Hashimoto Shizunobu, *Nippon Kakaku Kaishi*, 1983, 7, 1099.
4. Cerveny Libor, Marhoul Antonio and Ruzicka Vlastimil, *Chem. Prum.* , 1975, 25, 75.
5. Cabiddu Salvatore, Vaccioni Antonio and Secci, Mario, *Gazz. Chim. Ital.* , 1968, 98, 800.
6. Syper Ludwik, *Shnthesis*, 1989, 3, 167.
7. Gedye, R.; Smith, F., Westaway, K.; Ali, H.; Baldisera, L.; Laberge, L.; Rousell,J; *Tetrahedron Lett.*, 1986, 27(3), 279-82.
8. Giguere, R.J.; Namen, A. M.; Lopze, B.O.; Arepally, A.; Ramos,D.E.; *Tetrahedron Lett.* , 1987, 28(52), 6553-6.

9. Yuan Yuncheng , Gao Dabin and Jiang Yulin, *Synth. Commun.* , 1992, 22, 2117.

10. Yuan Yuncheng, Jiang Yulin and Gao Dabin , *Synth. Commun.* , 1992, 22, 3109.

11. Yuan Yuncheng , Jiang Yulin and Pang Jun , *Gazz. Chim. Ital.* , 1993, 9, 519.

12. Jiang Yulin , Pang Jun and Yuan Yuncheng , *Chin. Chem. Lett.* , 1994, 1, 29.

(Received in the USA 24 April 1996)