

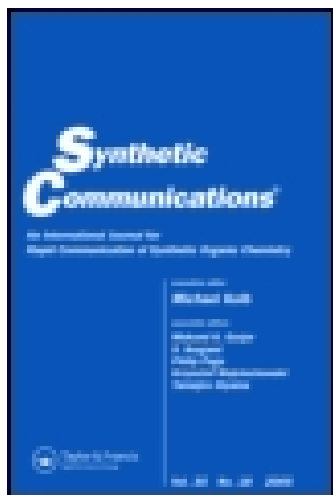
This article was downloaded by: [Carnegie Mellon University]

On: 30 October 2014, At: 05:16

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954

Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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/lcyc20>

Ethoxylation of *o,p*-Nitrochlorobenzene Using Phase Transfer Catalysts by Microwave Irradiation

Yuan Yuncheng^a, Gao Dabin^b & Jiang Yulin^a

^a School of Chemical Engineering, Dalian University of Technology, Dalian, 116012, China

^b Department of Chemical Engineering, Dalian University, Dalian, 116012, China

Published online: 23 Sep 2006.

To cite this article: Yuan Yuncheng, Gao Dabin & Jiang Yulin (1992) Ethoxylation of *o,p*-Nitrochlorobenzene Using Phase Transfer Catalysts by Microwave Irradiation, *Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry*, 22:14, 2117-2119, DOI: [10.1080/00397919208021346](https://doi.org/10.1080/00397919208021346)

To link to this article: <http://dx.doi.org/10.1080/00397919208021346>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and

are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at <http://www.tandfonline.com/page/terms-and-conditions>

Ethoxylation of *o*, *p*-Nitrochlorobenzene Using Phase Transfer Catalysts by Microwave Irradiation

Yuan Yuncheng^a, Gao Dabin^b, and Jiang Yulin^a

^aSchool of Chemical Engineering, Dalian University of Technology, Dalian 116012, China

^bDepartment of Chemical Engineering, Dalian University, Dalian 116012, China

Abstract

Microwave irradiation is very efficient to accelerate the rate of ethoxylation of *o*, *p*-nitrochlorobenzene. The enhancement of reaction rate is 144–240fold.

Key Words microwave irradiation – acceleration – *o*, *p*-nitrochlorobenzene – *o*, *p*-nitrophenetole, ethoxylation

Nucleophilic substitutions of aryl halides are generally difficult. They require severe conditions and give rather low yields. They will be improved, however, in the case when substrates are activated by electronwithdrawing substituents^{1–3}. It was found that by microwave irradiation *o*, *p*-nitrochlorobenzene can be rapidly ethoxylated in comparison with the conventional process. Typical results are shown in Table 1.

Microwave irradiation has been applied in organic synthesis in recent years^{4–8}. The results in Table 1 show that microwave irradiation does accelerate the reaction of *o*, *p*-nitrochlorobenzene and chlorobenzene with ethanol. As could be expected, the role of phase transfer catalysts is indispensable. PEG400 and PEG1500 are most efficient. HTMAB and BTMAC are unstable under such conditions. Without a base the reaction could not

Table1. Reaction of Aryl Chlorides with Ethanol in Microwave Oven (420w)

Entry	Aryl Chloride	Catalyst	Reaction Time (min)	Yields (%)
1	I ^a	—	2	14
2	I	—	6	19
3	I	—	10	24
4	I	PEG20,000 ^d	2	19
5	I	PEG800	2	35
6	I	PEG400	2	99
7	I	PEG1,500	2	99
8	I	HTMAB ^e	2	57
9	I	BTMAC ^f	2	51 ^g
10	I ^b	—	2	28
11	I	PEG400	2	99
12	II ^c	PEG400	10	9 ^h

^ap-nitrochlorobenzene, ^bo-nitrochlorobenzene, ^cchlorobenzene, ^dpolyethylene glycol, ^ehexadecyltrimethylammonium bromide, ^fbenzyltrimethylammonium chloride, ^gby conventional heating reaction time was 8hrs and the enhancement of reaction rate is 240-fold, ^hreaction rate enhancement is 144.

take place. Reaction time is not so crucial. Under similar conditions, however, chlorobenzene is rather unreactive due to the absence of electronwithdrawing substituents.

Typical Experimental Procedure: 313mg (2mmol) p-nitrochlorobenzene, 460mg (10mmol) ethanol, 80 mg (2mmol) sodium hydroxide, and 0.2 mmol phase transfer catalyst were placed in a 10ml pyrex tube and sealed. The tube being protected by a device⁹ was placed in a microwave oven and heated for 2 minutes. The tube was rapidly cooled by cold air and poured into cold water to remove the salts produced. The weight of p-nitrophenetole isolated was 301mg.

Acknowledgment

The authors appreciate the work done by Mr. Yang Conggui and Ms. Liu Chunhua.

References

1. Loupy A. , Philippon N. , Pigeon P. , Sansoulet J. and Galons H. *Synthetic Communication*, 1990, 20, 2855—2864.
2. Miller J. , in "Nucleophilic aromatic substitutions", Ed. Elsevier Amsterdam, 1968.
3. Krumenacker L. and Ratton S. , L' actualite' Chimique, June—July 1986, 29.
4. Gedye R. N. , Smith F. , Westaway K. , Ali H. , Baldisern L. , Laberge L. and Rousell J. *Tetrahedron Lett.* , 1986, 27, 279—282.
5. Gedye R. N. , Smith F. E. and Westaway K. C. , *Can. J. Chem.* , 1988, 66, 17—26.
6. Georges B. , Andre Mustapha M. , *Tetrahedron*, 1990, 46, 5167—5176.
7. Didier V. , Mekki L. and Abdelkrim B. A. , *Chem. Ind. (London)*, 1991, 5, 176.
8. Didier V. , and Abdelkrim B. A. , *Synthetic Communication*, 1991, 21, 63—68
9. Raymond J. G. , Terry L. B. and Scolt M. D. *Tetrahedron Lett.* , 1986, 27, 4945—4948.

(Accepted in USA 24 March, 1992)