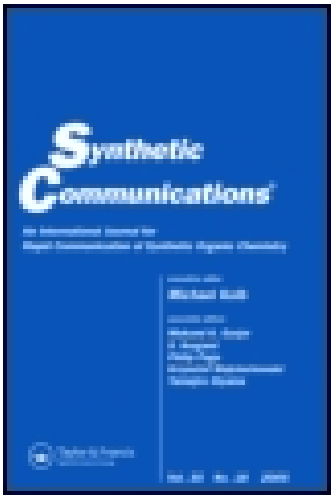

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Ethoxylation of o,p-Nitrochlorobenzene Using Phase Transfer Catalysts by Microwave Irradiation

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

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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	II	PEG400	2	99
12	II[c]	PEG400	10	9[h]

[a]p— nitrochlorobenzene, [b]o— nitrochlorobenzene, [c]chlorobenzene, [d]polyethylene glycol, [e]hexadecyltrimethylammonium bromide, [f]benzyltrimethylammonium chloride, [g]by conventional heating reaction time was 8hrs and the enhancement of reaction rate is 240—fold, [h]reaction 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 device[9] 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.

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