

Microwave-induced Selective Mercuration of 1,4-Naphthoquinone†

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An efficient mercuration of 1,4-naphthoquinone at the C-2 position is reported using arylmercury(II) chloride under microwave irradiation.

Recently there has been much interest in the use of microwave irradiation in synthesis¹ owing to substantial reductions in reaction times. In continuation of our earlier work^{2–6} on microwave-assisted synthesis it was thought worthwhile to synthesize the mercury-containing 1,4-naphthoquinone under microwave activation. The microwave procedure for the mercuration owes its importance to the fact that the reaction is completed in 2–4 min with improved yields when compared to conventional heating which requires 12–13 h. A comparative study in terms of yield and reaction time is also reported (Table 2) using conventional heating.

Experimental

Mps (uncorrected) were recorded on an Electrothermal apparatus. The purities of the compounds were checked on silica-coated Al plates (Merck).

General Procedure for the Synthesis of Arylmercury(II) Chloride 1a–e. Mercury(II) acetate (0.01 mol) was added to a mixture of DMF (10 ml) and benzene/toluene/chlorobenzene/bromoben-

zene/anisole (0.1 mol) in a 100 ml beaker and the mixture was irradiated in a microwave oven for 1.0–1.5 min at 2450 MHz. The contents were concentrated *in vacuo* to remove most of the unreacted benzene/toluene/chlorobenzene/bromobenzene/anisole and DMF. To this, EtOH (15 ml) was added. A boiling aqueous solution of NaCl (0.01 mol) was added slowly with stirring when a white precipitate separated out. The solid obtained was filtered off, washed with water, dried and recrystallized from acetone. The melting points were comparable to the reported mps^{7–11} and are given in (Table 1).

General Procedure for the Synthesis of 2-[arylmercury(II)]-1,4-naphthoquinone 2a–e. **Method A (thermal).** To a solution of 2 (0.01 mol in 15 ml acetone) anhydrous K₂CO₃ (2 g) and arylmercury(II) chloride (0.01 mol) were added (Scheme 1). The reaction mixture was stirred under reflux for a specified time (Table 2). It was then cooled and filtered to remove the inorganic salt; excess of solvent from the clear filtrate was evaporated under reduced pressure. The solid obtained was filtered off, dried and recrystallized from acetone–light petroleum (bp 40–60°C).

Method B (microwave irradiation). To a solution of 2 (0.01 mol) in *N,N*-dimethylacetamide anhydrous K₂CO₃ (2 g) and arylmercury

Table 1 Arylmercury(II) chlorides produced

Compound	R	Reaction time		Mp (T/°C)		% Yield	
		Lit./h	M.W.I. ^a /min	Found	Lit.	Lit.	M.W.I. ^a
1a	H	3.0 ^b	1.0	256–258	258 ^b	80 ^b	90
1b	4-Me	4.0 ^c	1.0	237	238–239 ^c	75 ^c	80
1c	4-Cl	4.5 ^d	1.5	208–210	210 ^d	70 ^d	80
1d	4-Br	5.0 ^e	1.5	248–249	250 ^e	60 ^e	75
1e	4-OMe	5.0 ^f	1.5	247–248	250 ^f	55 ^f	65

^aM.W.I. = microwave induced. ^bRef. 7. ^cRef. 8. ^dRef. 9. ^eRef. 10. ^fRef. 11.

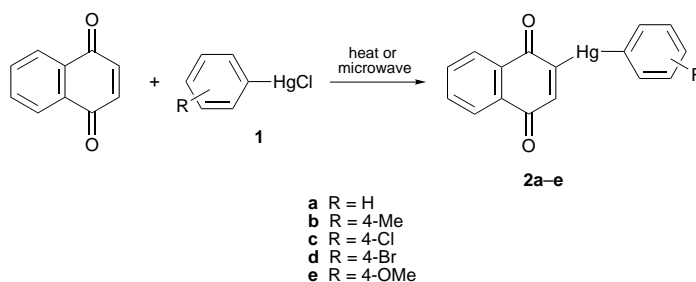


Table 2 Comparison of reaction times and yields obtained using microwave-induced (M.W.I.) and classical method

Compound	R	Mol. formula	% Yield (time/min)		Mp(T/°C)
			M.W.I.	Classical method	
2a	H	C ₁₆ H ₁₀ HgO ₂	85 (2)	80 (12)	210
2b	4-Me	C ₁₇ H ₁₂ HgO ₂	78 (2.3)	69 (13)	200–202
2c	4-Cl	C ₁₆ H ₉ ClHgO ₂	70 (2.3)	68 (12)	212–213
2d	4-Br	C ₁₆ H ₉ BrHgO ₂	65 (2.5)	60 (12)	195
2e	4-OMe	C ₁₇ H ₁₂ HgO ₃	64 (3)	60 (13)	188–190

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†This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1998, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

(II) chloride (0.01 mol) were added in a 100 ml beaker. The beaker was irradiated in a microwave oven for 2.0–3.0 min at 2450 MHz. The reaction mixture was cooled and filtered to remove the inorganic salt. Excess of solvent was evaporated under pressure.

The solid obtained was filtered off, dried and recrystallized from acetone–light petroleum (bp 40–60°C).

Received, 28th July 1997; Accepted, 22nd September 1997
Paper E/7/05428I

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