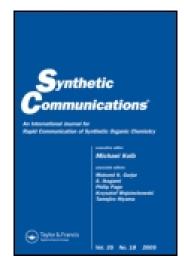
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## Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:

http://www.tandfonline.com/loi/lsyc20

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Published online: 23 Sep 2006.

To cite this article: Prem Kr. Singh & Rajinder N. Khanna (1993) Selective Halogenation of 1,4-Benzoquinones and 1,4-Naphthoquinones with Copper(II) Halide Adsorbed on Alumina, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 23:15, 2083-2089, DOI: 10.1080/00397919308018601

To link to this article: <a href="http://dx.doi.org/10.1080/00397919308018601">http://dx.doi.org/10.1080/00397919308018601</a>

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## SELECTIVE HALOGENATION OF 1,4-BENZOQUINONES AND 1,4-NAPHTHOQUINONES WITH COPPER(II) HALIDE ADSORBED ON ALUMINA

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**ABSTRACT:** 1,4-Benzoquinone or 1,4-naphthoquinone and their derivatives have been halogenated selectively at quinonoid positions with copper(II) halide adsorbed on neutral alumina followed by refluxing in halobenzene to give mono- di-, tri- and tetra-haloquinones.

Quinones are electron carriers in biological systems and are used as oxidants and dehydrogenating reagents in synthetic organic chemistry. Halo-1,4-naphthoquinones have recently been used effectively for the synthesis of naturally occurring anthroquinones. In industry, they are used as inhibitors for polymerisation and as fireproof dyes for wooden materials. Haloquinones also possess anthelmintic, bactericidal, fungicidal and insecticidal properties. In recent years, copper(II) halides adsorbed on alumina have been used for the halogenation of alkoxybenzenes, phenols and aromatic

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hydrocarbons<sup>9</sup>. It has been reported that halogenation with this reagent occurs only with those organic compounds having ionisation potential (IP) higher than 7.55 eV.

In the present communication, we are reporting the use of copper(II) halide adsorbed on alumina for the direct halogenation of 1,4-benzoquinones (IP = 9.68 eV)<sup>10</sup> and 1,4-naphthoquinones (IP = 9.21 eV)<sup>10</sup> in halobenzene solvent. The reaction proceeds with a high degree of regioselectivity and the halogenation preferably takes place at quinonoid positions.

In a typical procedure 1,4-naphthoquinone (4, 1.0 mmol) is at 128°C with copper(II) chloride adsorbed on alumina (5.0 mmol) in chlorobenzene for 22h to give 2-chloro-1,4-naphthoquinone (14, yield 80%). The compound was identified by elemental analysis, NMR, mass and comparison with an authentic sample 11. 1,4-Benzoquinone (1) under similar condition gave three products (8, 9 and 10). In the case of 2-methyl-1,4-naphthoquinone (5) using copper(II) chloride/alumina gave two products namely, 2-trichloromethyl-1,4-naphthoquinone (15)and 3-chloro-2-chloromethyl-1,4naphthoguinone (16), showing that chlorination took place at quinonoid position as well as at the methyl group (Table I). When copper(II) bromide was used in place of copper(II) chloride in bromobenzene, the corresponding bromo products were obtained as summarised in Table II.

TABLE-I

Reaction of 1,4-benzoquinones and 1,4-naphthoquinones with copper(II) chloride/alumina in chlorobenzene.

bq (1) 6/110		ime/Temp h/°C	. Products	γields (%)	M.P. °C	Spectral data NMR/Mass
chloro bq (9)  111. 2,5-dichloro 50 257 bq (10)  2-Methyl bq 7/128  1. 5,6-dichloro 40 100-5 2-methyl bq (11)  11. 5-chloro-2- 60 102 methyl bq (12)  2,6-Dimethoxy 6/128 bq (3)  12. 43-chloro-2,6- 60 151 dimethoxy bq (13)  13. 2-chloro nq 80 112 (14)  2-Methyl nq 20/128 1. 2-trichloro 40 145 methyl nq (15)  11. 3-chloro 2-chloromethyl nq (16)  11. 3-chloro 2-chloromethyl nq (16)	/110	/110		20	236	no peak/248(M <sup>+</sup> +2, 132%),246(M <sup>+</sup> ),
bq (10)  2-Methyl bq 7/128  i. 5,6-dichloro 40 100-5 2-methyl bq (11)  ii. 5-chloro-2- 60 102 methyl bq (12)  2,6-Dimethoxy 6/128				30	175	7.5(s)/212(M <sup>+</sup> +2; 99%) 210(M <sup>+</sup> )
2-methy1 bq (11)  ii. 5-chloro-2- methy1 bq (12)  2,6-Dimethoxy 6/128				50	257	7.32(s)/178(M <sup>+</sup> +2;66%),
ii. 5-chloro-2- methyl bq (12)  2,6-Dimethoxy 6/128 bq (3)  nq (4)  22/128  2-chloro nq (14)  2-methyl nq (14)  2-methyl nq (15)  3-chloro- 2-chloromethyl- nq (16)  6-Methyl nq 12/128  3-chloro-6- 60 90	/128	/128	i. 5,6-dichloro	40	100-5	2.25(d,3H,J=2Hz,-CH <sub>3</sub> ),
methyl bq (12)  2,6-Dimethoxy 6/128 *3-chloro-2,6- 60 151 bq (3) dimethoxy bq (13)  nq (4) 22/128 2-chloro nq 80 112 (14)  2-Methyl nq 20/128 i. 2-trichloro- 40 145 (5) ii. 3-chloro- 60 116 2-chloromethyl- nq (16)			2-methyl bq (11	)		7.35(m,1H,C <sub>3</sub> -H)/ 192(M <sup>+</sup> +2,66%),190(M <sup>+</sup> )
methyl bq (12)  2,6-Dimethoxy 6/128 *3-chloro-2,6- 60 151 bq (3) dimethoxy bq (13)  nq (4) 22/128 2-chloro nq 80 112 (14)  2-Methyl nq 20/128 i. 2-trichloro- 40 145 (5) ii. 3-chloro- 60 116 2-chloromethyl- nq (16)			ii. 5-chloro-2-	60	102	2.1(s,3H,-CH <sub>3</sub> ),6.6(s,
bq (3) dimethoxy bq (13)  nq (4) 22/128 2-chloro nq 80 112 (14)  2-Methyl nq 20/128 1. 2-trichloro- methyl nq (15)  11. 3-chloro- 2-chloromethyl- nq (16)  6-Methyl nq 12/128 3-chloro-6- 60 90						1H,C <sub>3</sub> -H),6.8(s,1H,C <sub>6</sub> -H)/158(M <sup>+</sup> +2.33%),
nq (4) 22/128 2-chloro nq 80 112 (14)  2-Methyl nq 20/128 1. 2-trichloro- 40 145 (5) methyl nq (15)  11. 3-chloro- 60 116 2-chloromethyl- nq (16)	/128	/128	*3-chloro-2,6-	60	151	3.75 and 4.05(2s,6H,
(14)  2-Methyl nq 20/128			dimethoxy bq ()	3)		2X-CH <sub>3</sub> ) 5.85(s,1H,C <sub>5</sub> -H) 204(M <sup>+</sup> +2,33%),202(M <sup>+</sup> )
(5) methyl nq (15)  11. 3-chloro- 60 116 2-chloromethyl- nq (16)  6-Methyl nq 12/128 3-chloro-6- 60 90	2/12	2/128		80	112	7.28(s,1H, C <sub>3</sub> -H),7.78- 7.98(m,2H,C <sub>6,7</sub> -H), 8.12-8.33(m,2H,C <sub>5,8</sub> -H) 194(M*+2,33%)J92(M*)
2-chloromethyl- nq (16) 6-Methyl nq 12/128 3-chloro-6- 60 90	0/12	0/128		40	145	7.6(s,1H.C <sub>3</sub> -H),8.07- 8.27(m,2H,C <sub>6,7</sub> -H), 8.42-8.63(m,2H,C <sub>5,8</sub> -H) 276(M <sup>*</sup> +2,33%),274(M <sup>+</sup> )
o newy ny			2-chloromethyl-		116	4.9(s,2H,-CH <sub>2</sub> -),8.25- 8.27(m,2H,C <sub>6,7</sub> -H),8.4- 8.61(m,2H,C <sub>5,8</sub> -H)/ 242(M <sup>+</sup> +2,66%),240(M <sup>+</sup> )
	12/12	12/128		60	90	2.6(s,3H,-CH <sub>3</sub> ),7.55(s, 1H,C <sub>2</sub> -H),7.92(brd,1H, J=8Hz;C <sub>7</sub> -H),8.28(brs, 1H,C <sub>5</sub> -H),8.39(d,1H, J=8Hz,C <sub>8</sub> -H)/208(M <sup>+</sup> +2,
5-Hydroxy nq(7) No reaction						33%),206(M <sup>+</sup> )

nq = 1,4-naphthoquinone; bq = 1,4-benzoquinone.
\*Purified by preparative thin layer chromatography.

TABLE-II

Reaction of 1,4-benzoquinones and 1,4-naphthoquinones with copper(II) bromide/alumina in bromobenzene

Reactants	Time/Temp. h/°C	Mode of separation	Products	Yields (%)	M.P.	Spectral data
ng (4)	22/18	CC(pet ether)	2-bromo nq (18)	40	131	NMR: 7.55(s, 1H, C <sub>3</sub> -H), 7.66-7.8(m, 2H, C <sub>6,7</sub> -H), 7.9-8.25(m, 2H, C <sub>5,8</sub> -H).
2-Methyl nq (5)	26/128	CC(pet ether)	3-bromo-2- methyl nq (19)	80	181	NMR: 2.4(s, 3H, -CH <sub>3</sub> ), 7.0- 7.9(π, 2H, C <sub>6,7</sub> -H), 8.0- 8.2(π, 2H, C <sub>5,8</sub> -H)
5-Hydroxy nq (7)	42/128	ptlc(benzene-pet. ether) 2-bromo-5- hydroxy nq	) 2-bromo-5- hydroxy nq (20)	04	130	NMR: 7.1(s, 2H, C <sub>3</sub> -H), 7.15-7.3(m, 1H, Ar-H), 7.6(m, 2H, Ar-H), 11.83(s, 1H, -0H chelated)
ng = 1,4-naphthoqui	inone; bq =	bq = 1,4-benzoquinone; cc =	cc = column chromatography;	phy;		

ptic Preparative thin layer chromatography.

Experimental procedure: Melting points were measured on sulphuric acid bath and uncorrected and are expressed in °C. NMR spectra were recorded on a Perkin Elmer R-32NMR spectrophotometer (90 MHz) with TMS as the internal standard and CDCl<sub>3</sub> as solvent. Notations used are as follows s, singlet; d, doublet; br, broad; dd, double doublet and Ar, aromatic.

Alumina supported copper(II) chloride<sup>7</sup>: Copper(II) chloride dihydrate (5.0 g) was dissolved in methanol (30 ml) and neutral alumina (10 g) was added in one portion. The methanol was removed by evaporation and the resulting reagent dried under vacuum at 100°C for 5h.

Alumina supported copper(II) bromide<sup>9</sup>: To a solution of copper(II) bromide (10 g) in distilled water (30 ml), neutral alumina (20 g) was added at room temperature. The mixture was evaporated using rotatry evaporator at 80°C under reduced pressure. The resulting reagent was dried under vacuum at 100°C for 15 h.

General experimental procedure: A 50 ml round bottom flask was charged with copper(II) halide (5.0 mmol) supported on alumina and quinone (1 mmole) dissolved in anhydrous halobenzene (10 ml), and the mixture was stirred vigorously using calcium chloride guard tube at 110-128°C for 6-42 h. The mixture was filtered and the residue obtained upon evaporation of the filtrate was subjected to column

chromatography (silica gel, pet. ether) or ptlc to purify the compound.

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(Received in UK 18 January 1993)