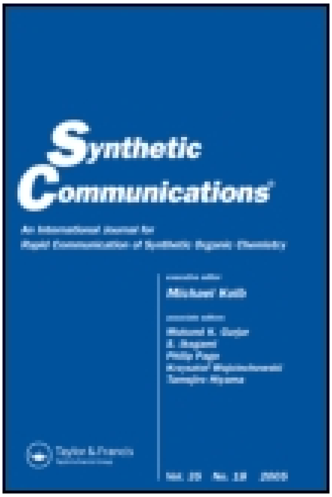

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SELECTIVE HALOGENATION OF 1,4-BENZOQUINONES AND 1,4-NAPHTHOQUINONES WITH COPPER(II) HALIDE ADSORBED ON ALUMINA

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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[1] have recently been used effectively for the synthesis of naturally occurring anthroquinones. In industry, they are used as inhibitors for polymerisation[2] and as fireproof dyes for wooden materials[3]. Haloquinones also possess anthelmintic[4], bactericidal[4], fungicidal[5] and insecticidal[6] properties. In recent years, copper(II) halides adsorbed on alumina have been used for the halogenation of alkoxybenzenes[7], phenols[8] and aromatic

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hydrocarbons[9]. 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)[10] and 1,4-naphthoquinones (IP = 9.21 eV)[10] 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 heated 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-1,4-naphthoquinone (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.

Reactants	Time/Temp. h/°C	Products	Yields (%)	M.P. °C	Spectral data NMR/Mass
bq (1)	6/110	i. 2,3,5,6-tetra chloro bq (8)	20	236	no peak/248(M^+ +2, 132%),246(M^+),
		ii. 2,3,5-tri-chloro bq (9)	30	175	7.5(s)/212(M^++2; 99%) 210(M^+)
		iii. 2,5-dichloro bq (10)	50	257	7.32(s)/178(M^++2;66%), 176(M^+)
2-Methyl bq (2)	7/128	i. 5,6-dichloro 2-methyl bq (11)	40	100-5	2.25(d,3H,J=2Hz,-CH_3), 7.35(m,1H,C_3-H)/ 192(M^++2,66%),190(M^+)
		ii. 5-chloro-2-methyl bq (12)	60	102	2.1(s,3H,-CH_3),6.6(s, 1H,C_3-H),6.8(s,1H,C_6-H)/158(M^++2.33%), 156(M^+)
2,6-Dimethoxy bq (3)	6/128	*3-chloro-2,6-dimethoxy bq (13)	60	151	3.75 and 4.05(2s,6H, 2X-CH_3) 5.85(s,1H,C_5-H)/ 204(M^++2,33%),202(M^+)
nq (4)	22/128	2-chloro nq (14)	80	112	7.28(s,1H, C_3-H),7.78-7.98(m,2H,$C_{6,7}$-H), 8.12-8.33(m,2H,$C_{5,8}$-H)/ 194(M^++2,33%),192(M^+)
2-Methyl nq (5)	20/128	i. 2-trichloro-methyl nq (15)	40	145	7.6(s,1H.C_3-H),8.07-8.27(m,2H,$C_{6,7}$-H), 8.42-8.63(m,2H,$C_{5,8}$-H)/ 276(M^++2,33%),274(M^+)
		ii. 3-chloro-2-chloromethyl-nq (16)	60	116	4.9(s,2H,-CH_2-),8.25-8.27(m,2H,$C_{6,7}$-H),8.4-8.61(m,2H,$C_{5,8}$-H)/ 242(M^++2,66%),240(M^+)
6-Methyl nq (6)	12/128	3-chloro-6-methyl nq (17)	60	90	2.6(s,3H,-CH_3),7.55(s, 1H,C_2-H),7.92(brd,1H, J=8Hz;C_7-H),8.28(brs, 1H,C_5-H),8.39(d,1H, J=8Hz,C_8-H)/208(M^++2, 33%),206(M^+)
5-Hydroxy nq(7)		No reaction			

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. °C	Spectral data
nq (4)	22/18	CC(pet ether)	2-bromo nq (18)	40	131	NMR: 7.55(s, 1H, C_3-H), 7.66-7.8(m, 2H, $C_{6,7}$-H), 7.9-8.25(m, 2H, $C_{5,8}$-H).
2-Methyl nq (5)	26/128	CC(pet ether)	3-bromo-2-methyl nq (19)	80	131	NMR: 2.4(s, 3H, -CH_3), 7.0-7.9(m, 2H, $C_{6,7}$-H), 8.0-8.2(m, 2H, $C_{5,8}$-H)
5-Hydroxy nq (7)	42/128	ptlc(benzene-pet. ether)	2-bromo-5-hydroxy nq (20)	40	130	NMR: 7.1(s, 2H, C_3-H), 7.15-7.3(m, 1H, Ar-H), 7.6(m, 2H, Ar-H), 11.83(s, 1H, -OH chelated)

nq = 1,4-naphthoquinone; bq = 1,4-benzoquinone; cc = column chromatography;

ptlc = 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 $CDCl_3$ as solvent. Notations used are as follows s, singlet; d, doublet; br, broad; dd, double doublet and Ar, aromatic.

Alumina supported copper(II) chloride[7]: 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[9]: 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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