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PARA-PREFERENTIAL ANODIC CHLORINATION OF ALKOXYBENZENES

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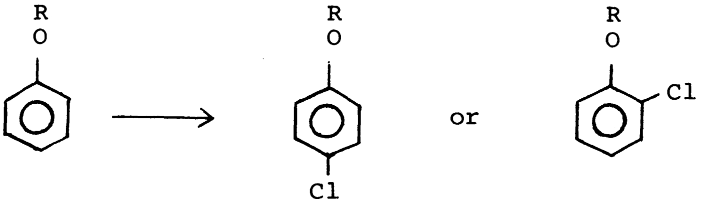
Anodic chlorination of methoxy- and ethoxybenzenes yielded p-alkoxychlorobenzenes preferentially. The p-/o- ratios were 34.5 in N,N-dimethylacetamide-LiCl and 17.1 in N,N-dimethylformamide-LiCl. In the former case, the current efficiency for producing p-chloromethoxybenzene was 95.8% at Pt anode.

Chlorination of alkoxybenzenes **1** with chemical reagents, e.g., dichloramine-T-HCl-AcOH-(Ag),[1)] hypochlorite-organic solvents,[2,3)] $NaClO_4$-H_2SO_4,[4)] and SO_2Cl_2-metal chlorides,[5,6)] provides a mixture of o- and p-chloro isomers in the p-/o- ratio of 4 or less. Taking advantage of the environment of α-cyclodextrin's (α-CD) cavity, p-preferential chlorination of **1** with hypochlorous acid in the presence of α-CD[7)] as well as methylated α-CD[8)] has also been reported. Recently, Osa and coworkers[9,10)] have investigated the electrochemical chlorination of methoxybenzene with a α-CD modified electrode, giving the p-/o- ratio of 25.

Regiopreferential anodic bromination of methoxybenzene in AcOH-H_2O-bromides systems has been developed successfully,[11)] but product selective chlorination has not been reported yet. In this communication, we report highly para-preferential chlorination of alkoxybenzenes by electrolysis in N,N-dimethylacetamide-(DMA)- and N,N-dimethylformamide(DMF)-LiCl systems.



1a: R = CH_3 2a: R = CH_3 3a: R = CH_3
1b: R = C_2H_5 2b: R = C_2H_5 3b: R = C_2H_5

The electrolysis of **1** (0.005 mol in the anolyte) at a constant anode potential was carried out using a H-type cell with a sintered glass diaphragm, fitted with a Pt anode, a graphite cathode, and the reference electrode(SCE). Both anolyte and catholyte contained LiCl (0.0125 mol) in 30 ml of the solvent, respectively. After being passed 965 C (2F/mol of **1**) of electricity, usual work-up afforded the chlorinated products, whose constituents were determined by vpc analysis.

As shown in Table 1, p-alkoxychlorobenzenes **2** could obtained preferentially in both DMA and DMF in the anode potential range between 1.0 and 1.5 V vs. SCE.

Table 1. Results of anodic chlorination of (1a) and (1b), 30°C.

Solvent	Yield (%)			p-/o-
	(1a)	(2a)	(3a)	
DMF	-	94.4	5.5	17.1
DMA	-	95.8	2.8	34.5
MeOH	40.0	43.6	12.7	3.4
FA	85.0	8.3	1.3	6.4

Solvent	Yield (%)			p-/o-
	(1b)	(2b)	(3b)	
DMF*	5.5	88.0	7.4	11.9
MeOH	19.5	49.2	15.8	3.2

* Formamide

Supporting electrolyte: LiCl, Anode(Pt): 1.3 V vs. SCE, Electricity: 965 C.

The electrolysis using Pt electrode provided **2** in good yield in contrast to the cases of graphite and DSA[12)] electrodes. Before having passed 965 C of electricity, o,p-dichloroalkoxybenzenes were not obtained. The yield and p-/o- ratio decreased with increase of water content in the electrolysis media and with replacement of LiCl for NH_4Cl as an electrolyte. No significant influence of temperature was encountered in 30-50°C.

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References and Notes

1) B. Jones and E. N. Richardson, J. Chem. Soc. **1956**, 3939.
2) D. R. Harvey and R. O. C. Norman, J. Chem. Soc. **1961**, 3604.
3) V. L. Heasley, G. E. Heasley, D. M. Ingle, P. D. Davis, and T. L. Rold, J. Org. Chem. **38**, 2549(1973).
4) K. Paluch, J. Baran, and J. Otto, Rocz. Chem. **46**, 509(1972); C.A. **77**, 19285h (1972).
5) W. D. Watson, J. Org. Chem. **39**, 1160(1974).
6) W. D. Watson, U.S.P. 3920757(18 Nov. 1975).
7) R. Breslow and P. Campbell, J. Amer. Chem. Soc. **91**, 3085(1969).
8) R. Breslow, H. Kohn, and B. Siegel, Tetrahedron Lett. **1976**, 1645.
9) T. Matsue, M. Fujihira, and T. Osa, J. Electrochem. Soc.**126**, 500(1979).
10) T. Matsue, M. Fujihira, and T. Osa, Bull. Chem. Soc. Jpn. **52**, 3692(1979).
11) H. Tanaka, T. Shiroi, T. Yamanaka, and S. Torii, Preprint 37th Meeting Chem. Soc. Jpn. II. p. 1015(1978).
12) Dimensionally Stable Anode. RuO_x coated on Ti.

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