PARA-PREFERENTIAL ANODIC CHLORINATION OF ALKOXYBENZENES Yoshiharu MATSUDA and Hiroyasu HAYASHI Faculty of Engineering, Yamaguchi University Tokiwadai, Ube, Yamaguchi 755

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)} NaClO₄-H₂SO₄,⁴⁾ and SO₂Cl₂metal chlorides,^{5,6)} provides a mixture of o- and p-chloro isomers in the p-/oratio of 4 or less. Taking advantage of the environment of \checkmark -cyclodextrin's (\checkmark -CD) cavity, p-preferential chlorination of 1 with hypochlorous acid in the presence of \checkmark -CD⁷⁾ as well as methylated \checkmark -CD⁸⁾ has also been reported. Recently, Osa and coworkers^{9,10)} have investigated the electrochemical chlorination of methoxybenzene with a \checkmark -CD modified electrode, giving the p-/o- ratio of 25.

Regiopreferential anodic bromination of methoxybenzene in AcOH-H₂O-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.



The electrolysis of $1 \\ (0.005 \text{ mol in the anolyte})$ 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 workup 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.

Colvert	Yield (%)			
Solvent	(la)	(2a)	(3a)	p-/o-
DMF	-	94.4	5.5	17.1
DMA	-	95.8	2.8	34.5
МеОн	40.0	43.6	12.7	3.4
FA	85.0	8.3	1.3	6.4
••••••••••••••••••••••••••••••••••••••	Yield (%)			
Solvent	(1b)	(2b)	(3b)	p-/o-
DMF*	5.5	88.0	7.4	11.9
МеОН	19.5	49.2	15.8	3.2

Table 1. Results of anodic chlorination of (la) and (lb), 30°C.

* 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 DSA¹²⁾ 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_ACl 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. <u>38</u>, 2549(1973).
- 4) K. Paluch, J. Baran, and J. Otto, Rocz. Chem. <u>46</u>, 509(1972); C.A. <u>77</u>, 19285h (1972).
- 5) W. D. Watson, J. Org. Chem. <u>39</u>, 1160(1974).
- 6) W. D. Watson, U.S.P. 3920757(18 Nov. 1975).
- 7) R. Breslow and P. Campbell, J. Amer. Chem. Soc. <u>91</u>, 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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