μm) (30 g), employing CHCl$_3$ as the eluting solvent. Appropriate fractions were pooled and evaporated to obtain **4b**: 400 mg, 2.84 mmol, 35%; mp 54–56 °C (lit.[8a] mp 57–58 °C). The ^{1}H NMR and mass spectrum of this compound were superimposable with those of the authentic **4b** (vide supra). (Note: The only other compound isolated in this reaction was the unreacted starting material.)

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Selective Chlorination of Toluene by Anodic Oxidation

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Chlorotoluenes are commerically produced by toluene and chlorine in the presence of a Lewis acid catalyst and a cocatalyst.[1] Since *p*-chlorotoluene has a higher market value than its ortho isomer, numerous attempts to develop processes with high para to ortho isomer ratio (para/ortho) can be found in the patent literature. There is, however, little success, and para/ortho is seldom over 1.0.[2,3]

Electrochemical oxidation of chloride ions in the presence of toluene can also yield chlorotoluenes.[6,7] Gourcy, Simonet, and Jaccaud[10] reported that when tetraethylammonium chloride or lithium chloride was oxidized at a platinum anode in acetonitrile at constant current, toluene was monochlorinated with para/ortho ranging from 0.63 to 1.0. The applied potential range was 1.5 to 2.3 V vs. Ag/Ag$^+$ (0.1 M). If the experiment was done with large excess of a Lewis acid, a para/ortho ratio of 1.8 could be achieved. Osa, Fujihira, Matsue, and Yamauchi[11] claimed that by using an anode made of a carbonaceous material with cyclodextrin or a derivative thereof bonded onto its surface, toluene could be electrochemically chlorinated with para/ortho as high as 4.7. Cyclodextrin, however, is expensive, and the three-step electrode preparation is not trivial. We report that by oxidizing lithium chloride with an *unmodified* platinum electrode at a *constant potential of 1.0 or 1.1 V* vs. Ag/Ag$^+$ (0.01 M) in acetonitrile, toluene can be chlorinated with relatively high para selectively, with no Lewis acid being required.

Experimental Section

All the experiments were done in a divided cell with a glass frit separator, and the cell was placed in a constant-temperature bath. The working electrode was a 2.2-cm^2 platinum sheet, and a stainless-steel counterelectrode was used. Electrolysis was done at a constant potential set by a Princeton Applied Research 178 potentiostat. Potentials were measured against a Ag/Ag$^+$ (0.01 M) reference electrode unless specified. The anodic compartment contained 100 mL of an acetonitrile solution and 200 mg of lithium chloride[12] and in most cases 0.1 M supporting electrolyte (Table I). The content of the cathodic compartment was 60 mL. Acetonitrile was purified by distillation over P_2O_5. Glassware, lithium chloride, and supporting electrolytes were dried in an oven before use. Electrolysis was stopped when the desired number of Faradays per mole of toluene was passed. About 80% of the acetonitrile was distilled off with a 24-in. Vigreux column. The residue was partitioned with dichloromethane and water. The organic extracts were combined and dried, and the solvent was removed by distillation. Yield and isomer ratio were determined by a 30-m J and W fused silica capillary column. The GC internal standard was *o*-xylene. The structure of the chlorotoluenes was confirmed by GC–mass spectroscopy.

Results and Discussions

The results are summarized in Table I. *p*-Chlorotoluene to *o*-chlorotoluene ratios varied from 1.7 to 3.0. Less than 1% *m*-chlorotoluene was observed. Lithium perchlorate or tetraethylammonium fluoroborate was added in most cases to increase the conductivity. Only trace amounts (<2%) of benzyl chloride and dichlorotoluenes were detected by GLC when the toluene conversion was about 45%. The *p*-chlorotoluene selectivity increases when the reaction temperature decreases. Para selectivity is only observed in acetonitrile. When toluene was chlorinated by anodic oxidation of lithium chloride in dimethylformamide, the product mixture showed a *p*-chlorotoluene to *o*-chlorotoluene ratio of 0.77. The two isomers ratio was 0.66 in dimethylacetamide. With methanol as solvent, the para/ortho ratio was 1.0.

The first half-wave potential ($E_{1/2}$) of LiCl and toluene in acetonitrile are 0.7[15] and 1.98 V,[16] respectively. In our case, electrolysis was done at 1.0 or 1.1 V, and the chlorinating species must come from the oxidation of chloride ions. Chlorine radicals probably are not involved because they are known to react with toluene to give side-chain substitution and ring addition products[17] whereas we ob-

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[1] Gelfand, S. In "Kirk-Othmer Encyclopedia of Chemical Technology", 3rd ed.; Wiley: New York, 1979; Vol. 5, pp 821–822.

[2] The following patents claimed a para/ortho ratio of about 1.0: (a) Buckholtz, H. E.; Bose, A. C. U.S. Patent 4 024 198, May 1977; *Chem. Abstr.* **1977**, *87*, 134446*e*. (b) Graham, J. C. U.S. Patent 4 031 142, June 1977. (c) Graham, J. C. U.S. Patent 4 031 147, June 1977. (d) Lin, H. C. U.S. Patent 4 069 263, Jan 1978; *Chem. Abstr.* **1978**, *88*, 190351*C*. (e) Lin, H. C. U.S. Patent 4 069 264, Jan 1978; *Chem. Abstr.* **1978**, *88*, 120761*n*. (f) Lin, H. C.; Robota, S. U.S. Patent 4 250 122, Feb 1981; *Chem. Abstr.* **1981**, *95*, 24504*e*. (g) Graham, J. C. U.S. Patent 401 373, March 1977; *Chem. Abstr.* **1977**, *87*, 5605*s*. (h) Di Bella, E. P. U.S. Patent 403 1144, June 1977; *Chem. Abstr.* **1977**, *87*, 134449*h*. (i) British Patent 1153746, May 1969. (j) British Patent 1163927, Sept 1969. (5) Japan Patent 81/110630, Sept 1981; *Chem. Abstr.* **1982**, *96*, 34810*m*. (l) Saito, R.; Hattori, T.; Kawasuchi, T. Japanese Patent 75/34009, Nov 1975; *Chem. Abstr.* **1976**, *84*, 89792*q*.

[3] When a *stoichiometric amount* of ferric chloride was used as the chlorinating agent, para/ortho ratios as high as 9.0 could be obtained.[4,5]

[4] Sawazai, K.; Fujii, H.; Dehura, M. German Patent 2230369, Jan 1973; *Chem. Abstr.* **1973**, *78*, 84004*a*.

[5] Japan Patent 74/76828, July 1974; *Chem. Abstr.* **1976**, *85*, 46167*t*.

[6] (a) Rifi, M. R.; Covitz, F. H. "Introduction to Organic Electrochemistry"; Marcel Dekker: New York, 1974; pp 296–301. (b) Simonet, J. In "Organic Electrochemistry, An Introduction and a Guide", 2nd ed.; Baizer, M. M., Lund, H., Eds.; Marcel Dekker: New York, 1983; pp 863–865.

[7] Cohen, Dawson, and Crosland[8] reported that anodic oxidations of hydrochloric acid with toluene at refluxing temperature gave *p*-chlorotoluene as the major product. The authors distilled the para isomer out, and *o*-chlorotoluene was left in the residue. The boiling points of *p*-chlorotoluene and *o*-chlorotoluene, however, are 162 and 157–159 °C, respectively.[9] We repeated the experiment and *p*-chlorotoluene to *o*-chlorotoluene to benzyl chloride ratio was 23:51:26.

[8] Cohen, J. B.; Dawson, M. H.; Crosland, P. F. *J. Chem. Soc.* **1905**, *87*, 1034–1037.

[9] West, R. C., Ed. "CRC Handbook of Chemistry and Physics", 62nd ed.; CRC Press, Inc.: Cleveland, OH, 1981.

[10] Gourcy, J.; Simonet, J.; Jaccaud, M. *Electrochimica Acta* **1979**, *24*, 1039–1046.

[11] Osa, T.; Fujihira, M.; Matsue, T.; Yamauchi, T. U.S. Patent 4 269 674, May 1981.

[12] Lithium chloride was only partially soluble in acetonitrile.

[13] Solvent effects on the isomer distribution in the chlorination of toluene was studied by Stock and Himoe.[14] In acetonitrile, para/ortho = 1.6. The reaction rate, however, was relatively slow, and the reaction was only done for kinetic investigation. Conversion of toluene was very low.

[14] Stock, L. M.; Himoe, A. *Tetrahedron Lett.* **1960**, 9–13.

[15] Kolthoff, I. M.; Coetzer, J. F. *J. Am. Chem. Soc.* **1957**, *79*, 1852–1858. Potentials in the paper were measured vs. standard calomel electrode (SCE). They are converted to potentials vs. Ag/Ag$^+$ (0.01 M) for discussion convenience.

[16] Siegerman, H. In "Technique of Electroorganic Synthesis"; Weinberg, N. L., Ed.; Wiley: New York, 1975; Part II, p 690.

Table I. Reaction Conditions and Results of Toluene Anodic Chlorination with Lithium Chloride in Acetonitrile

reaction conditions				result				
toluene, mM	supp[a] electrolyte	appl pot., V	temp, °C	Faradays mol^{-1}	toluene[b]	*o*-chlorotoluene[b]	*p*-chlorotoluene[b]	para/ortho
4.7	Et_4NBF_4	1.1	25	2.2	43.0	17.7	35.3	2.0
4.7	Et_4NBF_4	1.1	0	2.2	47.0	16.0	36.0	2.2
9.2	Et_4NBF_4	1.1	−20	2.0	74.5	5.4	15.5	2.9
4.7	$LiClO_4$	1.1	25	1.3	81.5	5.5	11.0	2.0
18.4	Et_4NBF_4[c]	1.1	25	1.6	71.0	10.0	17.0	1.7
9.2	Et_4NBF_4[d]	1.0	25	2.0	44.5	15.6	35.0	2.2
9.2	[e]	1.1	−20	0.6	92.0	1.4	4.2	3.0
9.2	Et_4NBF_4	1.5	25	1.35	64.0	15.0	16.0	1.1
9.2	Et_4NBF_4	1.1	25	0.5	only isomer ratio determined			2.0
9.2	Et_4NBF_4	1.1	25	1.0	only isomer ratio determined			2.0
9.2	Et_4NBF_4	1.1	25	1.5	only isomer ratio determined			2.0
9.2	Et_4NBF_4	1.1	25	2.0	45.0	16.7	33.0	2.0
9.2	Et_4NBF_4[f]	1.1	25	2.2	45.0	17.6	34.1	1.9

[a] The anodic compartment contained acetonitrile saturated with LiCl. [b] Yield percentage was based on toluene used. [c] Reagent grade acetonitrile, salts were not dried. [d] One gram of aluminum oxide was added to the anodic compartment. [e] No additional supporting electrolyte was used. [f] One gram of sodium carbonate was added to the anodic compartment.

served very little benzyl chloride.

Our process gives a higher percentage of *p*-chlorotoluene than constant-current electrolysis at 1.5–2.3 V vs. Ag/Ag$^+$ (0.1 M). It is known that anodic oxidation of LiCl in acetonitrile involves the first $E_{1/2}$ at 0.7 V (eq 1) and the second $E_{1/2}$ at 1.3 V (eq 2).

$$6Cl^- \xrightarrow{-4e} 2Cl_3^- \tag{1}$$

$$2Cl_3^- \xrightarrow{-2e} 3Cl_2 \tag{2}$$

The constant-current case may involve a different chlorinating intermediate from that in our case. An electrolysis at 1.5 V indeed gives a para/ortho of 1.1. The *N*-chloroacetonitrillium ion (CH_3CN^+Cl) is a possible electrophilic species generated at low potential oxidation.[18,19] High para selectivity observed in acetonitrile might be caused by steric interference between the methyl group and large *N*-chloroacetonitrilium ion.[21]

In one case, when reagent grade acetonitrile was used and the cell and supporting electrolyte were not dried in an oven before use, the para/ortho ratio was 1.7. Hypochlorous acid, which comes from chlorine and water (eq 3), as the reacting intermediate should be a minor pathway.

$$Cl_2 + H_2O \rightarrow HOCl + HCl \tag{3}$$

Hypochlorous acid chlorinates toluene in water to give predominately *o*-chlorotoluene.[21] The increase of the para/ortho ratio by the residual water indicates hypochlorous acid might be an undesired chlorinating species. Slightly higher para selectivity was observed when aluminum oxide was added to the anodic compartment.

The ratio of the two product isomers is independent of their initial concentration. An experiment monitored at 0.5, 1.0, 1.5, and 2.0 Faradays/mol showed a constant para/ortho ratio of 2.0. Although the anolyte became acidic during the reaction, an experiment run in the presence of a weak base (sodium carbonate) did not show any significant difference.

Anodic oxidation of lithium chloride in acetonitrile in the presence of toluene at 1.1 V provides a unique procedure to synthesize chlorotoluenes with high para selectivity. Since no corrosive chemicals or expensive reagents are required, this can be a good method for *p*-chlorotoluene production.

Acknowledgment. I am indebted to Prof. Larry L. Miller for helpful discussions and criticisms.

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(17) Kharasch, M. S.; Berkman, M. G. *J. Org. Chem.* **1941**, *6*, 810–817.

(18) *N*-Iodoacetonitrilium ion (CH_3CN^+I) was proposed by Miller and co-workers as an anodic aryl iodination species: Miller, L. L.; Kujawa, E. P.; Campbell, C. B. *J. Am. Chem. Soc.* **1970**, *92*, 2821–2825. Miller, L. L.; Watkins, B. F. *J. Am. Chem. Soc.* **1976**, *98*, 1515–1519.

(19) Chlorine was added to a chloride-containing acetonitrile solution in an attempt to prepare the acetonitrile adduct. (This experiment was suggested by a reviewer.) To 100 mL of acetonitrile saturated with lithium chloride and chlorine was added 9.2 mM toluene. The mixture was stirred at room temperature. GC analysis showed the ratio of *p*-chlorotoluene to *o*-chlorotoluene to be 1.7. The reaction, however, was slow, and only 6% toluene was converted after 5 h.

(20) If this is the case, reaction in trimethylacetonitrile, with $(CH_3)_3CCN^+Cl$ as the electrophilic species, might result in even greater preference for the para position. (This experiment was suggested by one of the reviewers.) Lithium chloride, however, is insoluble in trimethylacetonitrile. No chlorination was observed when an experiment was done in trimethylacetonitrile.

(21) de la Mare, P. B. D.; Harvey, J. T.; Varma, S. *J. Chem. Soc.* **1958**, 2756–2759.