Electrochemically induced aromatic nucleophilic substitution

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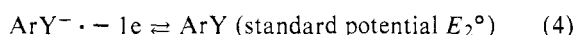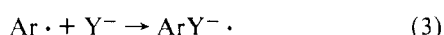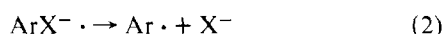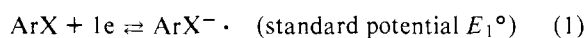# Electrochemically Induced Aromatic Nucleophilic Substitution

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Contribution from the Laboratoire d'Electrochimie de l'Université de Paris VII, 2, Place Jussieu, 75221 Paris Cedex 05, France. Received July 12, 1977
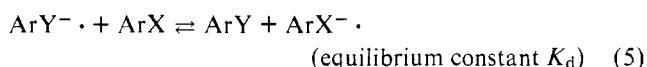
Abstract: Electrochemistry can be used to induce aromatic nucleophilic substitutions by setting up the electrode potential at the reduction level of the substrate in the presence of a nucleophile. With thiolates as nucleophiles, substitution of halogeno derivatives of benzophenone, benzonitrile, and naphthalene occurs catalytically. In the case of cyanide the process is not entirely catalytic; a part of the desired product has to be obtained from further separate oxidation of its anion radical. The reaction mechanism involves the formation of the anion radical at the electrode and its further decomposition into a neutral electrophilic radical which reacts on the nucleophile yielding the anion radical of the substituted product. In the catalytic case, oxidation of the last species may occur by solution electron exchange with the substrate and/or at the electrode. The main competing reactions to substitution are H· atom abstraction from the solvent by the neutral radical or its further reduction through electron transfer at the electrode or in the solution.

The electrochemical reduction of aryl or hetaryl halides, ArX, first yields an anion radical which then decomposes more or less rapidly according to the nature of the halogen and of the Ar group. As compared to the initial anion radical the radical Ar· has lost an electron doublet and a negative charge, hence being more reducible and possessing a greater electrophilic character at the carbon where the halogen was bound. At the same time Ar· is a good hydrogen atom abstractor. The possibility of electrochemically inducing aromatic substitutions of the $S_{RN}1$ type is based on the first of these properties. The chemical aspects of $S_{RN}1$ reactions have been widely investigated and discussed by Bunnett and co-workers[1] and by others.[2,3] Two remarkable features of these reactions are their selectivity and the fact that they do not require activation of the substrate by electron-withdrawing substituents.[4]

The electrochemical inducement of such reactions consists in setting up the electrode potential at the level of the reduction of ArX in the presence of the nucleophile Y⁻, thus initiating the following reaction sequence:

$$ArX + 1e \rightleftarrows ArX^- \cdot \quad \text{(standard potential } E_1°) \quad (1)$$

$$ArX^- \cdot \rightarrow Ar \cdot + X^- \quad (2)$$

$$Ar \cdot + Y^- \rightarrow ArY^- \cdot \quad (3)$$

$$ArY^- \cdot - 1e \rightleftarrows ArY \quad \text{(standard potential } E_2°) \quad (4)$$

and/or

$$ArY^- \cdot + ArX \rightleftarrows ArY + ArX^- \cdot$$
$$\text{(equilibrium constant } K_d) \quad (5)$$

If $E_2° < E_1°$ reaction 5 is in favor of the right-hand side $((RT/F) \ln K_d = E_1° - E_2°)$. Oxidation of the ArY⁻· anion radical into the final substituted product occurs spontaneously in solution. It may also take place concurrently at the electrode. Electrochemistry then appears as a means to actually catalyze the overall substitution reaction:

$$ArX + Y^- \rightarrow ArY + X^-$$
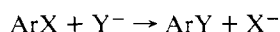
Accordingly the net charge passed through the cell during the reaction must, in principle, be zero.

If, on the contrary, $E_2° > E_1°$, a part of the ArY⁻· anion radical may not be reoxidized spontaneously. Obtention of the totality of ArY then requires part of the reoxidation to be carried out separately.

In a previous preliminary communication[5] we have demonstrated the possibility of an electrochemical catalysis of $S_{RN}1$ reactions on the example of 4-bromobenzophenone with benzenethiolate as the nucleophile. The purpose of the present paper is to describe the extension of such catalytic processes to other substrates and other nucleophiles, to report examples of partially catalytic electrochemical inducements of the reaction, and to discuss the mechanistic implications of these observations.

Results

Haloaromatics in which electrophilicity of the neutral radical Ar· is activated by an electron-withdrawing group (4-bromobenzophenone (**1**), 4-bromobenzonitrile (**2**), 4-iodobenzonitrile (**3**) as well as unactivated compounds (1-bromonaphthalene (**4**) were investigated (Scheme I). Two kinds of nucleophiles were used, thiolates and cyanide ions. They will be discussed separately.

Thiolates as Nucleophiles. In order to increase both their solubility and their reactivity the thiolates were used as tetrabutylammonium salts or as sodium salts associated with a crown ether.

Polarography and cyclic voltammetry can be employed to evaluate the occurrence of the substitution process. An example where the substitution is fast and complete is provided by the reaction of phenyl thiolate on 4-bromobenzophenone: upon increasing additions of PhS⁻ the voltammogram of the starting material is converted finally into that of the substitution product.[5] A typical example of incomplete transformation is the reaction of the same nucleophile on 1-bromonaphthalene (**4**) in acetonitrile (ACN). The polarograms of the starting material and of the final product are shown in Figure 1. The reduction of **4** involves a first two-electron wave featuring Br⁻ expulsion and naphthalene formation and a successive one-
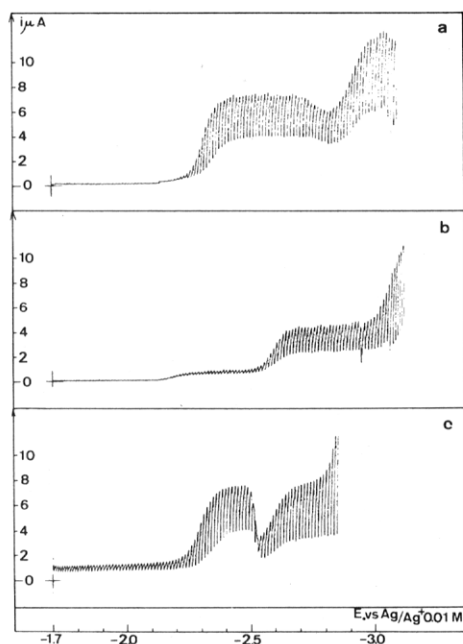
Scheme I

	R	
	Br	1
	SPh	7
	S-t-Bu	8
	SMe	9
	CN	10
	Br	2
	I	3
	SPh	11
	Br	4
	SPh	5
	CN	6
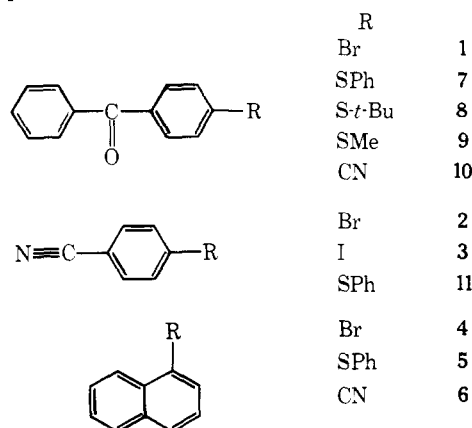
Figure 1. Polarograms of (a) 4-bromonaphthalene, (b) 4-phenylthio-naphthalene, and (c) bromonaphthalene + 10^{-1} M PhS$^-$ in ACN + 0.1 M NEt$_4$ClO$_4$. Concentration of substrates: 10^{-3} M.

electron wave along which naphthalene is reduced into its anion radical. Phenylthionaphthalene (**5**) exhibits a single one-electron wave corresponding to reduction into its anion radical. Figure 1c clearly shows the formation of **5** upon addition of PhS$^-$ to **4** as revealed by the appearance of the wave of **5** in a dip located on the plateau of the first wave of **4**. That the formation of **5** is not total is shown by the fact that the first and second waves of **4** have not completely disappeared. Analysis of the solution indicates that there is no appreciable spontaneous reaction of PhS$^-$ on **4**. The formation of **5** in the polarographic experiment thus occurs in the diffusion layer and

not in the bulk of the solution. Cyclic voltammetry (CV) provides an even clearer picture of the reaction (Figure 2) since reversibility of the waves can additionally be tested. The fast and irreversible character of the electrochemical cleavage of the C–Br bond at the first wave of **4** is evidenced by its CV irreversibility (Figure 2a). There is no tendency toward reversibility when raising the sweep rate even up to several kilovolts per second. The one-electron formation of the anion radicals of naphthalene and **5** gives rise to a reversible wave even at low sweep rates (Figures 2a and 2b). Addition of 0.1 M PhS$^-$ to **4** results (Figure 2c) in a decrease of the first wave and the appearance of the reversible wave of **5** at -2.60 V. At the same time, the wave of the remaining naphthalene becomes irreversible owing to the addition of about 3% of water together with PhS$^-$. Upon cycling between -2.80 and -2.0 V at 2.7 V s^{-1} the first wave of **4** entirely disappears, the CV pattern featuring then only the **5**/**5**$^-$· reversible couple (Figure 2d). At lower sweep rates diffusion from the bulk of the solution makes the first wave of **4** reappear.

The CV characteristics of the other substrates and substitution products are given in Table I. Upon addition of the nucleophiles the cyclic voltammogram of the substrate shows the appearance of the wave of the substitution product in each case. Depending upon the substrate, the solvent, and the nature and concentration of the nucleophile the resulting CV patterns are of the type obtained with 4-bromobenzophenone + PhS$^-$ or of that obtained with 1-bromonaphthalene and PhS$^-$.

Controlled Potential Electrolyses and Coulometry. They were carried out on a mercury pool working electrode the potential of which was set at the level of the first reduction wave of the substrate. The electrolyses durations were of the order of 10 min. It has been carefully checked by high-pressure liquid chromatography that the substitution reaction does not take place spontaneously under the conditions used. GPC and HPLC were employed to determine the yields in substitution (ArY) and hydrogenolysis (ArH) products. The results are given in Table II, which also shows the consumption of electricity in faradays per mole of consumed starting material.
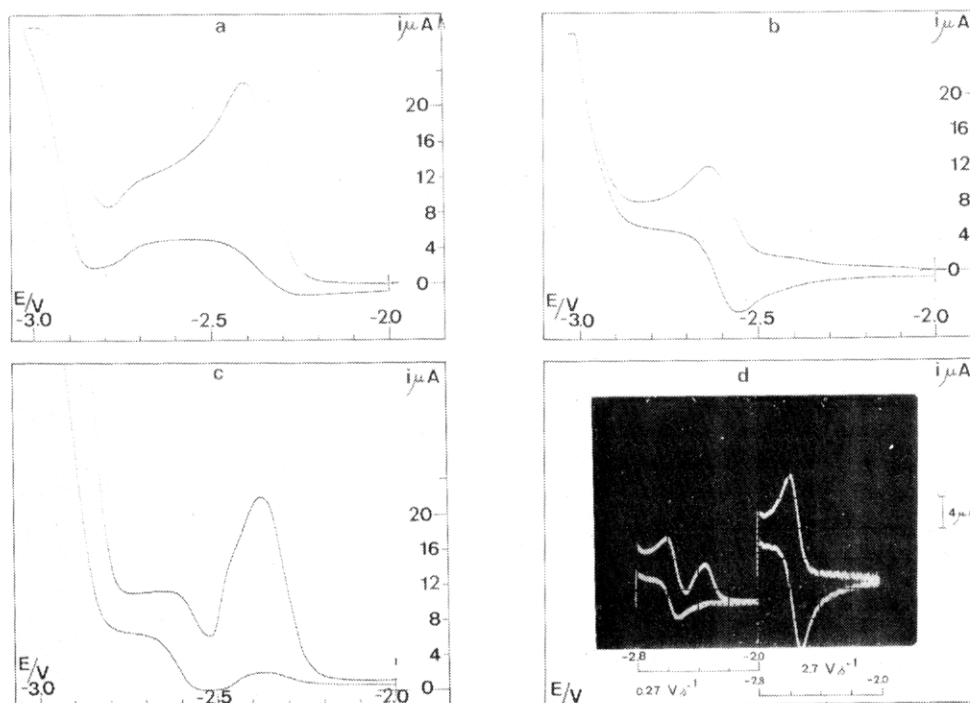
Figure 2. Cyclic voltammetry of (a) 4-bromonaphthalene, (b) 4-phenylthionaphthalene, (c) 4-bromonaphthalene + 10^{-1} M PhS$^-$ in ACN + 0.1 M NEt$_4$ClO$_4$, and (d) cyclic voltammetry between -2.8 and -2.0 V under the same conditions as for (c). Substrate concentration: 10^{-3} M. Sweep rate 0.2 V s^{-1} for (a), (b), and (c) and 0.27 and 2.7 V s^{-1} for (d). Stationary mercury working electrode. All potentials referred to the Ag/Ag$^+$ 0.01 M electrode.

Table I. Cyclic Voltammetry of the Substrates and Substitution Products

Compd	Solvent	Peak potential, V vs. Ag/0.01 M Ag$^+$ (number of electrons exchanged, reversibility)		
1	ACN	-1.88 ($\simeq 2$, irr)	-2.00^a (1, rev)	-2.30^a (1, irr)
1	Me$_2$SO	-1.75 ($\simeq 2$, irr)	-2.00^a (1, rev)	-2.46^a (1, irr)
7	ACN		-1.95^b (1, rev)	-2.26^b (1, irr)
7	Me$_2$SO		-1.89^b (1, rev)	-2.35^b (1, irr)
8	Me$_2$SO		-2.15^b (1, rev)	-2.55^b (1, irr)
9	ACN		-2.15 (1, rev)	-2.32 (1, irr)
10	ACN		-1.74 (1, rev)	-2.12 (1, irr)
2	ACN	-2.17 (2, irr)	-2.74^a (1, rev)	
3	ACN	-1.82 (2, irr)	-2.74^a (1, rev)	
11	ACN		-2.31 (1, rev)	-2.81 (1, irr)
4	ACN	-2.36 (2, irr)	$-2.92^{a,b}$ (1, rev)	
5	ACN		-2.61 (1, rev)	
6	Me$_2$SO		-2.09 (1, rev)	-2.72 (1, irr)

^{a} Waves of the corresponding ArH. ^{b} These waves are affected by water addition (addition of PhSNBu$_4$ involves addition of water). The reduction process tends to become two-electron and irreversible (hydrogenation).

These results suggest the following remarks: (1) there is a definite relationship between the yield in substitution product and the number of faradays per mole: when the yield is good, consumption of electricity is very low, reflecting the catalytic character of the electrochemical process. (2) Tetrabutylammonium salts appear as better reagents than the sodium salts used in conjunction with a crown ether. In the case of 1 and

PhS$^-$ we also used dicyclohexyl-18-crown-6 and [2.2.2]-cryptate.[6] (3) Me$_2$SO is a better solvent than ACN. (4) In the case of benzonitriles, the bromo derivative leads to strikingly better yields than the iodo.

Cyanide as the Nucleophile. The case of cyanide differs from that of thiolates since the standard potential of the substituted product is now less negative than the reduction potential of the substrate. This last potential is itself less negative than the standard potential of the substrate. We are therefore in a situation where $E_2° < E_1°$, i.e., where a not entirely catalytic process may take place.

Cyclic voltammetry of the cyanide substitution of 4-bromobenzophenone is shown in Figure 3. When 0.1 M CNNEt$_4$ is added to a 10^{-3} M solution of 1 the first cathodic scan shows a decrease of the first wave of 1. The formation of the anion radical of 10 is evidenced by the appearance of the anodic peak of 10 on the reversal of the first cycle. This is confirmed by the observation of the cathodic peak of 10 during the cathodic part of the second cycle. Cycling repeatedly between -1.4 and -2.0 V at 0.4 V s^{-1} results in the reversible pattern of 10 to be the only present in the voltammogram. It is also noted that during the first cycle the anodic trace crosses the cathodic trace showing the existence of a reduction current during the anodic scan.

In the case of bromonaphthalene a similar behavior was observed. However, the wave of cyanonaphthalene was much lower.

Controlled potential scale electrolyses of 1 at -1.7 V in the presence of cyanide followed by air oxidation of the 4-cyanobenzophenone anion radicals gave a good yield of the substituted product (Table II). Electrochemical reoxidation, either shifting the potential to -1.4 V after reductive production of the anion radical, or carrying out the experiment in an undivided cell with a platinum anode, also led to 4-cyanobenzophenone, although in a somewhat smaller yield. The formation of the anion radical of 10 was also checked by ESR: running the electrolysis of a 2×10^{-3} M solution of 1 in the presence of 10^{-1} M CNNEt$_4$ in the cavity of the ESR spectrometer on a platinum grid cathode at -2.0 V vs. SCE gave the same spectrum as obtained with a 2×10^{-3} M solution of 10 at -1.70 V vs. SCE.

Table II. Results of the Electrolyses

| Substrate and concn	Nucleophile and concn	Solvent	Electrolysis potential, V vs. Ag/Ag$^+$	No. of faraday/ mol	ArY, %	ArX, %	ArH, %
1 10^{-2} M	PhSNBu$_4$ 10^{-1} M	ACN	-1.8	0.2	(7) 95	0	3
1 10^{-2} M	PhSNa + dB18C6^a 2×10^{-2} M	ACN	-1.8	0.65	(7) 38	0	17
1 10^{-3} M	PhSNa + dB18C6^a 3×10^{-2} M	Me$_2$SO	-1.8	1.4	(7) 40	0	29
1 10^{-3} M	t-BuSNBu$_4$ 10^{-1} M	Me$_2$SO	-1.8	0.3	(8) 60	0	0
1 10^{-2} M	CH$_3$SNBu$_4$ 10^{-1} M	ACN	-1.9	1.7	(9) 5	0	75
1 10^{-2} M	CNNEt$_4$ 1 M	ACN	-1.7	0.25	(10) 95	0	3
2 10^{-2} M	PhSNBu$_4$ 10^{-1} M	ACN	-2.1	0.2	(11) 80	4	10
3 10^{-2} M	PhSNBu$_4$ 10^{-1} M	ACN	-1.7	1.5	(11) 20	0	80
4 10^{-2} M	PhSNBu$_4$ 10^{-1} M	Me$_2$SO	-2.2	0.3	(5) 100	0	0
4 10^{-2} M	PhSNBu$_4$ 10^{-1} M	ACN	-2.2	1.2	(5) 32	0	40
4 10^{-3} M	CNNEt$_4$ 10^{-1} M	Me$_2$SO	-2.2	0.5	(7) 0	45	55

^{a} dB18C6 = dibenzo-18-crown-6.

In the case of bromonaphthalene, although cyclic voltammetry indicates the formation of a small amount of the anion radical of **6,** practically no substitution product was found in preparative scale electrolysis.

Discussion

In the case where a good yield of substitution product was obtained (**1** and **2** with PhSNBu$_4$ in ACN and **4** with PhSNBu$_4$ in Me$_2$SO) the coulometric and cyclic voltammetry results clearly show the validity of the reaction mechanism involving a nucleophilic attack of the Ar· radical in the reaction sequence 1–5. Indeed a radical–radical coupling mechanism involving reactions 1 and 2 followed by

$$Ar· + Y^- \leftrightharpoons Ar^- + Y·$$

$$Ar· + Y· \rightarrow ArY$$
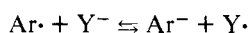
would lead to the balance equation

$$ArX + 1e + 0.5Y^- \rightarrow 0.5Ar^- + 0.5ArY + X^-$$
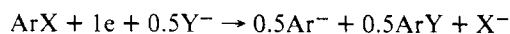
i.e., would correspond to the consumption of 1 faraday/mol and to a yield of only 50% in substitution product.

Reoxidation of the ArY$^-$· anion radical into ArY at the electrode (eq 4) or in solution (eq 5) are competing processes the ratio of which depends on the rate of the anion radical cleavage (eq 2).[7] If reaction 2 is very fast Ar· may be formed and attacked by Y$^-$ close enough to the electrode so that ArY$^-$· may be able to diffuse back to the electrode and be oxidized there before having time to be oxidized in solution by ArX. If reaction 2 is slow, oxidation of ArY$^-$· in ArY will occur essentially in solution.

The other results obtained with thiolates show that the catalytic substitution process may be concurred by other reaction paths. One of these is H-atom abstraction from the solvent SH and Ar· yielding the unsubstituted product ArH[8] and S·. This is clearly seen by comparing the results obtained (Table II) with Me$_2$SO and ACN in the case of **4** + PhS . The better yield obtained with the first solvent can indeed be explained by the fact that Me$_2$SO is a poorer H atom donor than ACN.[9,10] This seems to be also the reason why lower yields are obtained when using a sodium salt in conjunction with a crown ether or a cryptate instead of a tetraalkylammonium salt. The ultimate fate of S· is to be further reduced into S$^-$ at the electrode or in solution, S$^-$ being then able to react as a nucleophile on Ar· giving rise to a series of substitution products or on the activating group, e.g., the carbonyl, of the substrate.[11]

Another competing route is the further reduction of Ar· into Ar$^-$ followed by proton abstraction from solvent or residual water. This reaction can again occur at the electrode or in the solution:

$$Ar· + 1e \rightleftarrows Ar^-$$

$$Ar· + ArX^- \rightarrow Ar^- + ArX$$

$$Ar^- + H_2O(SH) \rightarrow ArH + OH^-(S^-)$$
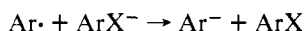
This is likely to be the reason why iodobenzonitrile gives rise to much less substitution than bromobenzonitrile under the same conditions (Table II). In both cases the reaction of the nucleophile with Ar· is fast enough to overcome the H atom transfer as well as the reduction in solution as shown by the excellent yield obtained with bromobenzonitrile. However, the decomposition of the anion radical is faster in the case of the iodo derivative than in the case of the bromo. The Ar· radical can then diffuse back and be reduced at the electrode before having time to react on the nucleophile.

In the case of cyanation, the substitution process is not entirely catalytic owing to the fact that the anion radical of the
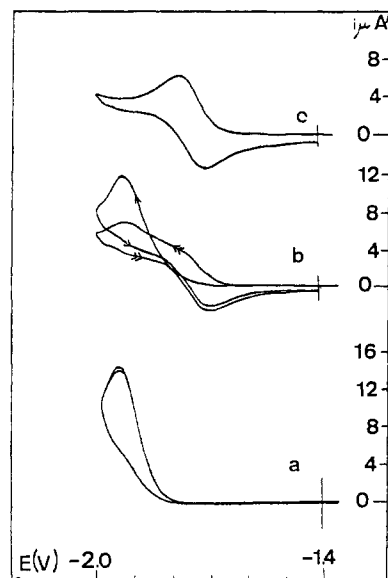

Figure 3. Cyclic voltammetry on the first wave of (a) 4-bromobenzophenone, (b) 4-bromobenzophenone + 0.1 M CNNEt$_4$ (←, first cycle; ↞, second cycle), (c) 4-cyanobenzophenone. Concentration of 4-bromo- and 4-cyanobenzophenone 10^{-3} M. Supporting electrolyte: 0.1 M NEt$_4$ClO$_4$. Sweep rate: 0.4 V s^{-1}. Reference electrode Ag/Ag$^+$ 0.01 M.

cyano-substituted product is electrochemically stable toward the electrode at the reduction potential of the starting material and also toward the starting halogeno compound itself as far as solution electron transfer is concerned ($K_d < 1$ in eq 5). It must, however, be realized that this does not prevent catalysis from occurring to some extent. Indeed, although the solution electron transfer (eq 5) is not thermodynamically in favor of the right-hand side, it can be driven toward the formation of ArY by the succeeding decomposition of ArX$^-$· (reaction 2) provided that this is sufficiently fast. ArY may thus be formed spontaneously in the solution and be only partially reduced at the electrode if electrolysis time is short.

The observation, in CV, of a reduction process occurring during the anodic scan leading to crossing of the anodic and cathodic traces confirms this interpretation. ArY is indeed formed in solution, as described above, and builds up as time elapses during the cathodic and the anodic scan. A part of it diffuses back to the electrode and gives rise to a reduction current up to a potential positive to the reduction potential of ArX.[12]

As a conclusion of the present study, electrochemistry appears as a valuable means for inducing nucleophilic aromatic substitutions. Its two main advantages over chemical means are as follows. (1) The electrode potential can be set up at a suitable value to induce the substitution without leading to a further reduction of the substituted product. Alternatively, the electrochemical study can be used to select a redox couple fulfilling these requirements. (2) The analysis of current-potential curves and coulometry under conditions where substitution occurs in the vicinity of the electrode allows a relatively easy characterization of the reaction mechanism. A more detailed analysis of this problem, particularly of the competition between substitution and side reactions, is currently under investigation in this laboratory.

Experimental Section

Chemicals. ACN was distilled before use on calcium hydride. Me$_2$SO was purchased from SNPA (pharmaceutical quality) and used without further purification. The starting compounds 1–4 were of commercial origin.

4-Phenylthiobenzophenone (**7**) was prepared by a Friedel–Crafts reaction between diphenyl sulfide and benzoyl chloride.[13]

4-Thio-*tert*-butylbenzophenone (**8**) was prepared by a Friedel–Crafts reaction between phenyl *tert*-butyl sulfide[14] and benzoyl chloride in a manner similar to ref 15. The yield was, however, very low (less than 5%) and the product had to be purified by preparative GLC on a 3% OV-17 column. The product obtained is an oily compound identified through its NMR [δ 1.27 (s, 9 H), 7.0–8.3 (m, 9 H)] and its mass spectrum [molecular peak at m/e 270 (4) and 214 (2), 105 (100), 91 (4), 77 (56), 51 (14)]. The main product of this reaction is 4-mercaptobenzophenone. It should be noted that as stated in ref 14 **8** cannot be prepared by reaction of **1** with *tert*-butylthiolate.

4-Methylthiobenzophenone (**9**) was prepared by reaction of thioanisole and benzoyl chloride in the presence of $AlCl_3$.[16]

4-Cyanobenzophenone (**10**) was prepared according to ref 17 by reaction of 4-cyanobenzoyl chloride with benzene in the presence of $AlCl_3$.

4-Cyanodiphenyl sulfide was obtained by reacting **3** (0.01 mol) with sodium phenylthiolate (0.01 mol) in refluxing acetonitrile for 2 h. The solvent was evaporated and the resulting solid extracted with boiling petroleum ether. After recrystallization from petroleum ether, white crystals were obtained, mp 39–40 °C (lit.[18] mp 39–40 °C).

1-Naphthyl phenyl sulfide (**5**) was obtained according to ref 19 from 0.13 mol of 1-bromonaphthalene and 0.13 mol of sodium thiophenate in boiling dimethylformamide. The reaction time was 46 h. The product thus obtained was purified by preparative GLC on an OV-17 column.

1-Cyanonaphthalene (**6**) is a commercial product.

Tetrabutylammonium phenylthiolate and tetrabutylammonium *tert*-butylthiolate were prepared by mixing stoichiometric amounts of the thiol with a 40% aqueous solution of tetrabutylammonium hydroxide in the solvent to be used and drying the resulting solution on 4 Å molecular seive (remaining water content 3% by Karl Fischer titration).

Sodium phenylthiolate and sodium *tert*-butylthiolate were prepared by mixing stoichiometric amounts of the thiol with sodium methylate in methanol and evaporating the solvent. All these thiolates are partly oxidized in solution to the corresponding disulfides. These last compounds were reduced back to the thiolates by a preelectrolysis (for example, diphenyl sulfide is electrolyzed in acetonitrile at $E = -1.2$ V Ag/Ag^+).[20]

Tetraethylammonium methylthiolate was obtained by electrochemical reduction of dimethyl disulfide ($E = -2.4$ V; reference Ag/Ag^+; solvent acetonitrile: supporting electrolyte; 10^{-1} M tetraethylammonium perchlorate; the resulting solution is dark brown) immediately before adding the substrate.

Tetraethylammonium cyanide was prepared by the method of Andreades and Zahnow.[21]

Dibenzo-18-crown-6 and dicyclohexyl-18 crown-6 were prepared by the Pedersen method[22] while the [2.2.2]cryptate was a commercial compound (Merck).

All the compounds prepared gave correct elemental analysis and NMR and mass spectra.

Electrochemical Instrumentation and Procedures. Instrumentation and procedures for polarography and cyclic voltammetry have been described elsewhere.[23,24] All the potentials of this paper are referred to the Ag/Ag^+ 0.01 M electrode in the solvent used. The cell used for coulometric measurements had a 40-cm^2 mercury pool as working

electrode and the counter electrode was a platinum spiral. They were separated by a Nafion 125 membrane (Du Pont Co.). The volume of the solution was 25–50 mL, the maximal current 50–100 mA, and the electrolysis time about 10 min. The electrolyses were followed in situ by polarography or cyclic voltammetry.

Analysis of the Electrolyzed Solutions. The resulting solutions were analyzed by polarography, cyclic voltammetry, and GLC on a 1.50 m 3% OV-17 column on 100/120 Varaport, the detection begin by flame ionization, with reference to authentic samples prepared as described above.

Blanks of the Reaction. It was carefully checked by high-pressure liquid chromatography (Varian 8500, 50 cm Vydac RP column, elution with water–methanol mixtures) that the reactions are not spontaneous. Mixtures were prepared exactly as for the electrolyses and injected at regular intervals on the chromatograph; both the constancy of the concentration of the starting material and the absence of the substitution product were checked.

References and Notes

(1) (a) J. K. Kim and J. F. Bunnett, *J. Am. Chem. Soc.*, **92**, 7463, 7464 (1970); (b) R. A. Rossi and J. F. Bunnett, *ibid.*, **96**, 112 (1974); (c) *ibid.*, **94**, 683 (1972); (d) *J. Org. Chem.*, **38**, 3020 (1973); (e) J. F. Bunnett and B. F. Gloor, *ibid.*, **38**, 4156 (1973); (f) R. A. Rossi and J. F. Bunnett, *ibid.*, **37**, 3670 (1972); (g) *ibid.*, 1407 (1973); R. A. Rossi, R. H. de Rossi, and A. F. Lopez, *J. Am. Chem. Soc.*, **98**, 1252 (1976).
(2) R. Kumar and P. R. Singh, *Tetrahedron Lett.*, 613 (1972).
(3) (a) J. F. Wolfe, J. C. Greene, and T. Hudlicky, *J. Org. Chem.*, **37**, 3199 (1972); (b) J. V. Hay, T. Hudlicky, and J. F. Wolfe, *J. Am. Chem. Soc.*, **97**, 374 (1975); J. V. Hay and J. F. Wolfe, *J. Am. Chem. Soc.*, **97**, 3702 (1975).
(4) J. A. Zoltewicz, *Top. Curr. Chem.*, **59**, 33 (1975).
(5) J. Pinson and J. M. Savéant, *J. Chem. Soc., Chem. Commun.*, 933 (1974).
(6) J. M. Lehn and J. P. Sauvage, *J. Am. Chem. Soc.*, **97**, 6700 (1975).
(7) C. Amatore and J. M. Savéant, *J. Electroanal. Chem.*, in press.
(8) L. Nadjo and J. M. Savéant, *J. Electroanal. Chem.*, **30**, 41 (1971).
(9) D. E. Bartak, K. J. Houser, B. C. Rudy, and M. D. Hawley, *J. Am. Chem. Soc.*, **94**, 7526 (1972).
(10) D. E. Bartak and W. C. Danen, *J. Org. Chem.*, **35**, 1206 (1970).
(11) F. M.'Halla, J. Pinson, and J. M. Savéant, submitted.
(12) A similar phenomenon has been observed in the electrochemical reduction of malononitrile in DMF: L. S. R. Yeh and A. J. Bard, *J. Electrochem. Soc.*, **124**, 189 (1977).
(13) W. Dilthey, L. Neuhaus, E. Reis, and W. Schommer, *J. Prakt. Chem.*, **124**, 81 (1930).
(14) V. N. Ipatieff, H. Pines, and B. S. Friedman, *J. Am. Chem. Soc.*, **60**, 2731 (1938).
(15) V. Hnesova Seidlova, Z. Sedivy, and M. Protiva, *Cesk. Farm.*, 308 (1962).
(16) M. P. Balfe, R. E. Dabby, and J. Kenyon, *J. Chem. Soc.*, 382 (1951).
(17) P. Zuman, O. Exner, R. F. Rekker, and W.Th. Nauta, *Collect. Czech. Chem. Commun.*, **33**, 3213 (1968).
(18) M. Sanesi and M. Lazzarone, *Ric. Sci., Sez. A*, **3**, 299 (1963).
(19) J. H. Uhlenbroek, *Recl. Trav. Chim. Pay-Bas*, **80**, 1057 (1961).
(20) B. Persson and B. Nygärd, *J. Electroanal. Chem.*, **56**, 373 (1974).
(21) S. Andreades and E. W. Zahnow, *J. Am. Chem. Soc.*, **91**, 4181 (1969).
(22) C. J. Pedersen, *Org. Synth.*, **52**, 66 (1972).
(23) J. M. Savéant and Su Khac Binh, *Bull. Soc. Chim. Fr.*, 3549 (1972).
(24) J. M. Savéant and Su Khac Binh, *Electrochim. Acta*, **20**, 21 (1975).