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Electroreductive aromatization of imines and diimines

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4-Methyl-4-trichloromethyl-*p*-quinone-(1)-arylimines (**1a**–**1d**) undergo the cathodic elimination of a trichloromethyl group to give the corresponding *N*-tolylarylamines (**2a**–**2d**), whose yields were strongly dependent on the kind of electrode materials. The yield of **2a** increased in the sequence: Hg < Pt < glassy carbon < graphite felt of Toyoubo Corp (GF-T) < graphite felt of National Electric Carbon Corp (GF-N). Modification of GF-T with zinc or bismuth was effective in giving **2a** in a higher yield. Similarly, electroreduction of 1,1-bis [*p*-(4-methyl-4-trichloromethyl-2,5-cyclohexadienone-(1)- iminyl) phenyl]cyclohexane (**3a**) and -4- methylcyclohexane (**3b**) gave 1,1-bis[4-*N*-*p*-tolylaminophenyl]- cyclohexane (**4a**) and -4-methylcyclohexane (**4b**) by the elimination of two trichloromethyl groups together with 1-[4-*N*-*p*-tolylamino- phenyl]-1-[*p*-(4-methyl-4-trichloromethyl-2,5-cyclohexadienone-(1)-iminyl)phenyl]cyclohexane (**5a**) and -4-methylcyclohexane (**5b**) as by-products.

Keywords: *aromatization*, *imines*, *diimines*

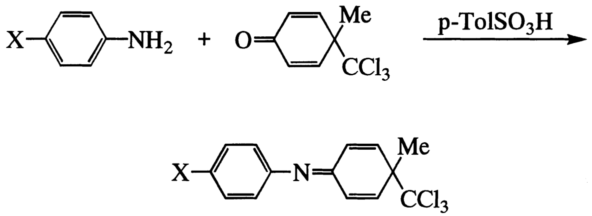
1. Introduction

Preceding work has shown that treatment of 4-methyl-4-trichloromethyl-*p*-quinone-(1)-arylimines (**1a**–**1d**) with zinc powder in acetic acid gives the corresponding *N*-tolylarylamines (**2a**–**2d**) in 50–70% yields, that is, an aromatization is achieved [1]. The imine **1** is synthesized by a condensation of 4-methyl-4-trichloromethyl-*p*-quinone with arylamines [2]. Therefore, this method is a convenient *N*-tolylation of aromatic amines. The present paper deals with an electroreductive aromatization reaction of **1a**–**1d** brought about by **2a**–**2d**. Furthermore, the electrosyntheses of 1,1-bis(4-*N*-*p*-tolyl-aminophenyl) cyclohexane (**4a**) and -4-methylcyclohexane (**4b**) from 1,1-bis[*p*-(4-methyl-4-trichloromethyl-2,5-cyclohexadienone-(1)-iminyl)phenyl] cyclohexane (**3a**) and -4-methylcyclohexane (**3b**) were conducted. Further tolylation of **4a** by *p*-iodotoluene led to the formation of 1,1-bis(4-*N*,*N*-di-*p*-tolylaminophenyl)cyclohexane (**6a**) [3], which has been successfully used as a hole-conduction and injection-agent in an organic electroluminescent diode [4].

2. Experimental details

The imines **1a**–**1d** were prepared by a condensation of 4-methyl-4-trichloromethyl-*p*-quinone with arylamines in the presence of *p*-toluenesulfonic acid according to the published method [2].

Similarly, the diimines **3a**–**3b** were prepared from *N*-magnesium bromine salt of 1,1-bis(4-*p*-aminophenyl) cyclohexane or 1,1-bis(4-*p*-aminophenyl)-4-methylcyclohexane and 4-methyl-4-trichloromethyl-*p*-quinone [2].



1a - 1d

a : X = MeO, **b** : X = Me, **c** : X = PhO, **d** : X = H

Chart 1.

The substrates prepared were identified by their physical properties, NMR and M/S spectra. They showed ^1H and ^{13}C NMR, and M/S consistent with the structures assigned. All NMR spectra were observed with an EX-400 spectrometer and mass spectra were measured with an Shimadzu GCMS, QP-1000.

Voltammetry and macroelectrolysis were carried out using the same experimental setup and procedures as reported in the previous papers [5, 6]. All the voltammograms were taken in acetonitrile (MeCN) containing 0.1 M tetraethylammonium *p*-toluenesulfonate (Et_4NOTs), all the potentials being quoted against a Ag/0.1 M $AgNO_3$ in MeCN (Ag/Ag^+) electrode. The controlled potential and current macroelectrolyses were carried out in MeCN containing 0.1 M Et_4NOTs at room temperature. Phenol, benzoic acid, and acetic acid were used as proton donors. The

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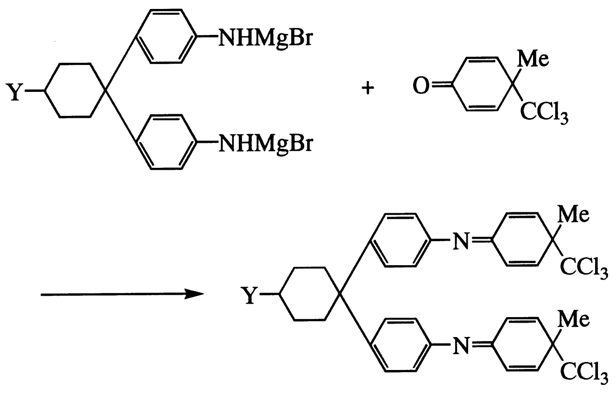


3a - 3b

a : Y = H, **b** : Y = Me

Chart 2.

electrolytic cell for macroelectrolysis comprised three separate compartments. A mercury pool (~7.0 cm^2), a platinum flag (1.5 cm × 2 cm), a glassy carbon rod(GC, 5 mm dia. × 4 cm), graphite felt of National Electric Carbon Corp., WDF (GF-N, 1.5 cm × 0.5 cm × 0.5 cm), and graphite felt of Toyoubo Corp., KF-1500 (GF-T, 1.5 cm × 0.5 cm × 0.5 cm) were used as cathode materials. Furthermore, GF-N and GF-T electrodes modified with zinc or bismuth were used. These electrodes are referred to herein as Zn or Bi/GF-N and Zn or Bi/GF-T electrodes, respectively. The Zn/GF-N and Zn/GF-T electrodes were prepared by plating zinc on the interior surface of the graphite felt block from 0.2 M $ZnSO_4$ aqueous solution by controlled current electrolysis (current: 20 mA, charge passed: 50 C). Bi/GF-N and Bi/GF-T electrodes were similarly prepared by plating bismuth from a 4.9 M HCl solution of 0.3 M $BiCl_3$ by controlled current electrolysis (current: 50 mA, charge passed: 100 C).

The macroelectrolysis of imines **1a**–**1d** finished when the TLC spot of the substrate disappeared. In the case of diimines **3a**–**3b**, the electrolysis was stopped after a total charges of 8–10 F mol^{-1} was passed. The electrolysed solution was carefully distilled under reduced pressure and the residue was extracted with ethyl ether. After working-up in the normal manner, the crude products were separated via preparative TLC to give pure products, which were subjected to ^{1}H NMR and ^{13}C NMR, and M/S for characterization of the products. Each product showed ^{1}H and ^{13}C NMR, and M/S consistent with the structure assigned.

Impurities in the graphite felts (GF-T and GF-N) were analysed by X-ray fluorescence (Rigaku, 3370E). Their surface morphology was examined using a scanning electron microscope (Jeol, JSM-5300).

3. Results and discussion

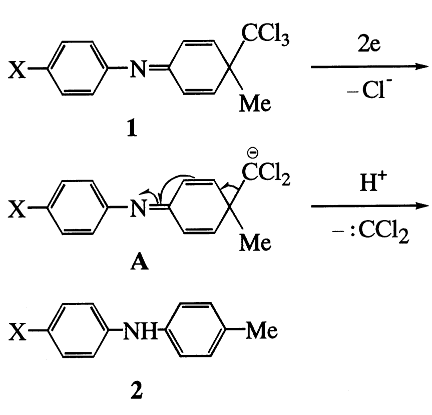
The imines **1a**–**1d** exhibited a reduction wave of half-wave potential −1.99 to −2.03 V, dependent on the kind of *p*-substituent group. The controlled potential macroelectrolyses of **1a** at different cathodes were conducted in the presence of proton donors. These results are listed in Table 1, with the coulometric *n*-values. The *n*-values were obtained from the amount of the substrate added and the quantity of electricity passed until the electrolysis finished. Table 1 shows that the kind of cathode material had a large influence on the yield of **2a** the highest yield being obtained by the use of GF-N electrode among the cathodes used. The yield of **2a** was also affected by phenol, benzoic acid, and acetic acid as proton donors, increasing in that order. The macroelectrolysis of **1a** at Pt was likewise carried out in the absence of a proton donor. Although the result was not included in the Table, 4-hydro-4-methyl-*p*-quinone-(1)-*p*-methoxyphenylimine was obtained in 18% yields together with **2a** (8% yield). The *n*-values obtained were considerably larger than the theoretical value of 2 and the smaller *n*-value tends to lead to the larger yield.

Table 1. Controlled potential macroelectrolysis of ***1a*** *at −2.3 V (vs Ag/Ag$^+$) in MeCN containing 0.1* M *Et_4NOTs*

*Cathode material**	*Proton donor (Equiv.)*	*n-Value*	*Yield of* **2a** */%*
Pt	phenol (4.0)	5.2	24
Pt	benzoic acid (4.0)	4.7	34
Pt	acetic acid (4.0)	5.6	43
Pt	acetic acid (20.)	14.8	38
Hg	acetic acid (4.0)	5.5	25
GC	acetic acid (4.0)	5.5	48
GF-N	phenol (4.0)	3.2	54
GF-N	benzoic acid (4.0)	2.7	72
GF-N	acetic acid (4.0)	2.7	77

*GC: glassy carbon, GF-N: graphite felt of National Electric Carbon Corporation.

The electroreductive aromatization reaction is likely to occur through the following mechanism, the trichloromethyl group leaving as dichlorocarbene. Although the fate of the intermediate **A** was not ascertained, a similar dichlorocarbene has been proposed in the nonelectrochemical aromatization reaction of 4-dichloromethyl-4-methyl-2,5-cyclohexadiene-1-one [7].



Scheme 1.

Table 2. Controlled current macroelectrolyses of **1a–1d** *at different graphite felt cathodes (1.5 cm × 0.5 cm × 0.5 cm) in acetonitrile containing 0.1 M Et_4NOTs in the presence of acetic acid (4 equiv.)*

Substrate	*Cathode material**	*Current* /mA	*n-Value*	*Product yield* /%
1a	GFN	10	2.5	**2a** (82)
1a	GFN	20	2.5	**2a** (85)
1a	GFN	30	2.5	**2a** (82)
1a	GFT	20	2.4	**2a** (60)
1a	Zn/GFT	20	2.5	**2a** (83)
1a	Bi/GFT	20	2.5	**2a** (79)
1a	Zn/GF-N	20	2.5	**2a** (86)
1b	GF-N	20	2.5	**2b** (89)
1c	GF-N	20	2.5	**2c** (78)
1d	GF-N	20	2.4	**2d** (78)

* GF-N: graphite felt of National Electric Carbon Corporation.
GF-T: graphite felt of Toyoubo Corporation.

Products **2a**–**2d** exhibited no reduction wave within the cathodic limitation of the electrolyte. Thus, a series of controlled current macroelectrolyses of **1a**–**1d** were carried out at different graphite felt cathodes. These results are summarized in Table 2. No influence of the current on the product yield was found in the range 10 to 30 mA. The imines **1a**–**1d** all undergo cathodic elimination with the loss of the trichloromethyl group to give the corresponding *N*-tolylarylamines **2a**–**2d** in 78–89% yields in the case of the GF-N electrode. This electrolysis gave **2** in higher yields than a treatment with zinc powder in acetic acid [1]. The use of GF-T as a cathode material in the electroreduction of **1a** gave **2a** in a low yield of 60%.

Table 3. Analysis of impurities in each graphite felt by X-ray fluorescence (wt %)

Graphite felt	*Element*							
	P	*S*	*Ca*	*Si*	*K*	*Na*	*Mg*	*Cl*
GF-N*	–	0.1	trace	trace	trace	–	–	–
GF-T†	4.6	0.1	0.3	0.1	trace	0.2	0.1	0.4

* GF-N: graphite felt of National Electric Carbon. Corporation.
† GF-T: graphite felt of Toyoubo Corporation.

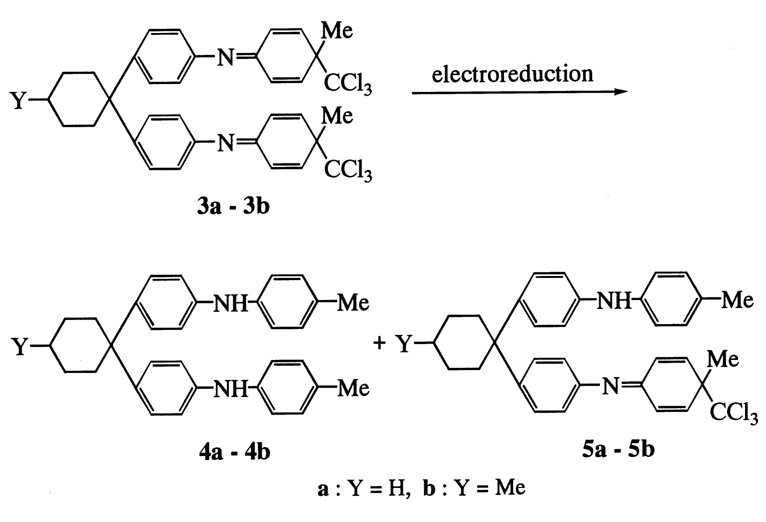
To examine the difference in the yield of **2a** between GF-N and GF-T electrodes, the impurities in GF-N and GF-T were analysed by X-ray fluorescence. As can be seen from Table 3, a marked difference occurred in the amounts of P, that is, no detection for GF-N but 4.6 wt% for GF-T. This difference in the P impurity may lead to the difference in the yield of **2a**. Moreover, a difference such as shown in Fig. 1. was observed in SEM micrographs of GF-N and GF-T surfaces, that is, the GF-N surface is much more smooth, but the GF-T surface is fluffy. The use of Zn or Bi/GF-T electrodes prepared by plating zinc or bismuth caused a significant improvement in the yield of **2a.** With a Zn/GF-N electrode, however, such a Zn plating effect was not realized (see Table 2). The poor yields of **2** using of the GF-T electrode and such an effect of Zn plating can not be explained.

Table 4 summarizes electroreduction of **3a** and **3b** using different graphite felt electrodes at a constant

Table 4. Controlled current macroelectrolyses of **3a** *and* **3b** *at different graphite felt (GF) cathodes (1.5 cm × 0.5 cm × 0.5 cm) with 20 mA in acetonitrile containing 0.1 M Et_4NOTs in the presence of acetic acid (8 equiv.)*

Substrate	*Cathode**	*Charge* /F mol^{-1}	*Conversion* /%	*Product yield†* /%	
3a	GF-N	8.0	84	**4a** (56)	**5a** (11)
3a	GF-T	9.0	97	**4a** (43)	**5a** (5)
3a	Zn/GF-N	8.4	97	**4a** (52)	**5a** (7)
3a	Bi/GF-N	9.7	90	**4a** (53)	**5a** (8)
3a	Bi/GF-T	10.0	95	**4a** (48)	**5a** (6)
3b	GF-N	10.1	81	**4b** (52)	**5b** (5)
3b	GF-T	8.6	97	**4b** (52)	**5b** (8)
3b	Zn/GF-N	11.0	81	**4b** (47)	**5b** (13)
3b	Zn/GF-T	10.5	83	**4b** (49)	**5b** (9)

* GF-N: graphite felt of National Electric Carbon Corporation.
GF-T: graphite felt of Toyoubo Corporation.
† The yields of **4** and **5** were calculated by dividing the amounts of **4** and **5** by the amount of **3** consumed, respectively.



Scheme 2.

current of 20 mA. The electrolysis was terminated after about 8–10 F mol^{-1} were passed. The conversion was calculated using the difference between the substrate contents of the catholyte before and after electrolysis. The yield of each product was calculated by dividing the amount of product by the amount of substrate consumed.

Electroreduction of **3a** and **3b** led to formation of 1,1-bis[4-*N*-*p*-tolylaminophenyl]cyclohexane (**4a**) and -4-methylcyclohexane (**4b**) by the elimination of two trichloromethyl groups together with half-aromatization products, 1-[4-*N*-*p*-tolylaminophenyl]-1-[*p*-(4-methyl-4-trichloromethyl-2,5-cyclohexadienone-(1)-iminyl)phenyl]cyclo-hexane (**5a**) and -4-methylcyclohexane (**5b**) by the elimination of a trichloromethyl group (Scheme 2). The yields of **4a** and **4b** were low compared with these of **2a**–**2d** (see Tables 2 and 4). The yields of **4a** and **4b** were not improved even using GF electrodes modified with Zn or Bi metal, that is, a Zn or Bi plating effect, such as in the cases of the electrolysis of **1a**–**1d**, was not observed.

Although the product yield was not so high, it is noticed that such an electroreductive aromatization is a convenient way for *N*-tolylation of aromatic amines **3a–3b** which were prepared from 4-methyl-4-trichloromethyl-*p*-quinone and *N*-magnesium bromine salt of 1,1-bis(4-*p*-aminophenyl)cyclohexene or 1,1-bis(4-*p*-amino-phenyl)-4-methylcyclohexene.

4. Conclusion

The present work relating to preparation of 1,1-bis(4-*N*,*N*-di-*p*-tolylaminophenyl)cyclohexane (**6a**), which is the typical electron transporting agent in the organic electroluminescent diode, leads to the following conclusions:

(i) 4-Methyl-4-trichloromethyl-*p*-quinone-(1)-arylimines (**1a**–**1d**) undergo cathodic elimination of a trichloromethyl group to give the corresponding N-tolylarylamines (**2a**–**2d**). Their yields are strongly dependent on the kinds of electrode material and proton donors. The yield of **2a** increases in the sequence: Hg < Pt < glassy carbon < graphite felt of Toyoubo Corp. (GF-T) < graphite felt of National Electric Carbon Corp. (GF-N) and phenol < benzoic acid < acetic acid for the proton donor.

(ii) The modification of GF-T with zinc or bismuth is effective in giving **2a** with a higher yield.

(iii) Electroreduction of 1,1-bis [*p*-(4-methyl-4-trichloromethyl-2,5-cyclohexadienone-(1)-iminyl) phenyl]cyclohexane (**3a**) and -4-methylcyclohexane (**3b**) affords 1,1-bis[4-*N*-*p*-tolylaminophenyl]-cyclohexane (**4a**) and -4-methylcyclohexane (**4b**) by the elimination of two trichloromethyl groups in moderate yields. It is known that further tolylation of **4a** by *p*-iodotoluene leads to the formation of **6a**.

(iv) The yields of **4a** and **4b** were not improved even using GF electrodes modified with Zn or Bi metal.

(v) The present electroreductive aromatization is a promising method for *N*-tolylation of aromatic amines.

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