ORGANIC LETTERS

2006
Vol. 8, No. 3
411−414

Construction of Electrocatalytic Electrodes Bearing the Triphenylamine Nucleus Covalently Bound to Carbon. A Halogen Dance in Protonated Aminotriphenylamines

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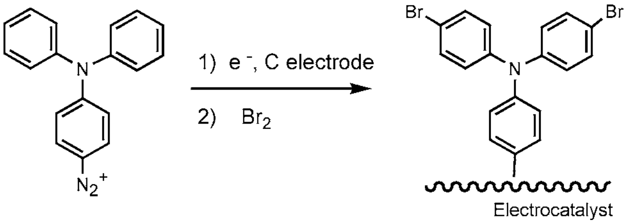
Received October 21, 2005

ABSTRACT



The triarylamine nucleus has been attached to a carbon fiber electrode by diazotization of an aminotriphenylamine followed by electrochemical reduction. The resulting electrodes can electrocatalyze the oxidation of organic substrates. In acid, 4-amino-4′,4′′-dibromotriphenylamine undergoes dismutation into a mixture of amines containing from 0 to 3 bromine atoms.

A major theme in modern electrochemistry is the modification of the surfaces of electrodes to make them more selective toward certain components of solutions or otherwise enhance their redox properties. For example, many groups have attached enzymes or other biomolecules, redox-active groups, or other functional groups to electrodes to enhance their reactivity and specificity.[1,2] In such studies, the surface-modified electrode is often able to catalyze redox processes at potentials lower than those necessary at unmodified electrodes, permitting the use of milder conditions. A variety of methods have been described for attaching materials to electrode surfaces.[2] A concern in many such procedures is eventual loss of the coating by, for example, solubilization, desorption, or hydrolysis of the linking group. Pinson, Savéant, and co-workers have described an elegant, general, and efficient procedure for covalent bonding of aryl groups to an electrode by electrochemical reduction of an aryldiazonium ion at the electrode.[3] Aryl radicals are produced and bind efficiently to the electrode in this process. The bonding apparently involves true chemical bonds; consequently, the resulting modified electrode is highly stable against loss of the compactly packed monolayer of aryl groups. A variety of aryl groups have been attached to carbon, silicon, and metal surfaces by this procedure.[4] An obvious use of such electrodes is for electrocatalysis. We report the first example of an electrode modified in this fashion which can effect electrocatalytic oxidation of organic substrates.

The radical cation of 4,4′,4′′-tribromotriphenylamine (**1**) is a versatile oxidant which has been shown to be an efficient electrocatalyst, e.g., for deprotection of dithioacetals to acetals or aldehydes, depending on electrolysis conditions, and benzylic ethers to aldehydes.[5] Steckhan developed polymers containing the triarylamine nucleus.[5c] Our procedure for synthesizing the necessary aminotriphenylamine

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[1] (a) Bartlett, P. N.; Cooper, J. M. *J. Electroanal. Chem.* **1993**, *362*, 1. (b) Bianco, P. *Rev. Mol. Biotech.* **2002**, *82*, 393. (c) Gorton, L. *Electroanalysis* **2000**, *7*, 23.

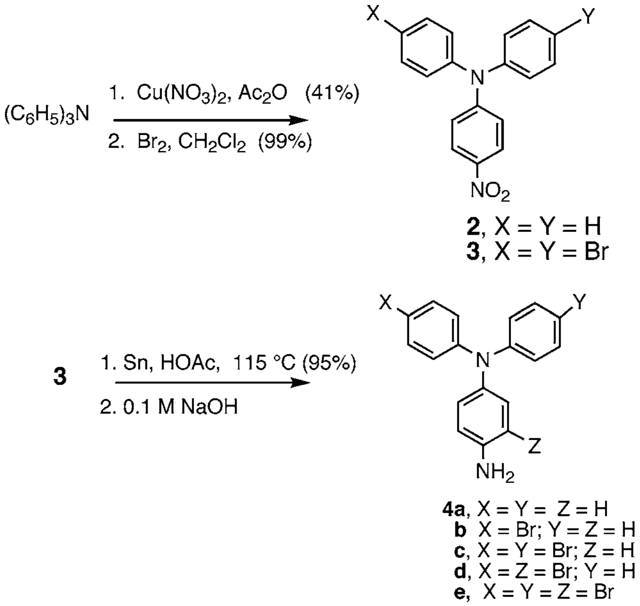
[2] (a) Wrighton, M. S. *Science* **1986**, *231*, 32. (b) Downard, A. J. *Electroanalysis* **2000**, *12*, 1085. (c) Murray, R. W. *Technique Chem.* **1992**, *22*, 1. (d) Wang, J. *Analytical Electrochemistry*, 2nd ed.; Wiley-VCH: New York,, 2000; pp 118, 121.

[3] Allongue, P.; Delamar, M.; Desbat, B.; Fagebaume, O.; Hitmi, R.; Pinson, J.; Saveant, J.-M. *J. Am. Chem. Soc.* **1997**, *119*, 201.

[4] (a) Pinson, J.; Podvorica, F. *Chem. Soc. Rev.* **2005**, *34*, 429. (b) Coulon, E.; Pinson, J. *J. Org. Chem.* **2002**, *67*, 8518.

10.1021/ol052558n CCC: $33.50

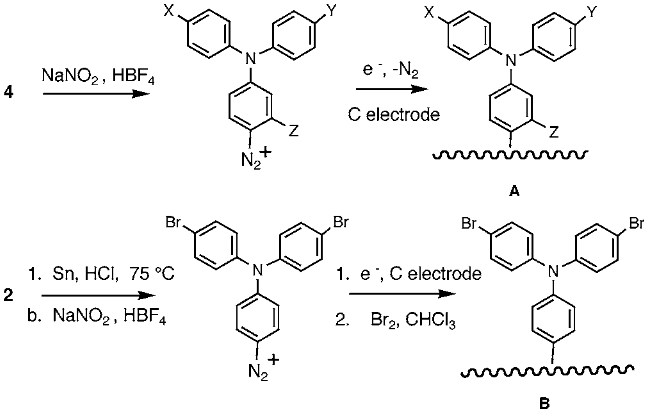
Scheme 1. Halogen Dance in 4-Aminotriphenylamines



moiety for subsequent attachment to an electrode is shown in Scheme 1. 4-Nitrotriphenylamine (**2**) was synthesized by reaction of triphenylamine with $Cu(NO_3)_2$ in acetic anhydride at room temperature, a reagent system which we have used previously to nitrate reactive arenes.[6] Compound **2** could readily be obtained in pure form (54% crude yield; 41% isolated yield), free of the corresponding dinitro (8%) and trinitro (38%) congeners, by medium-pressure liquid chromatography. Addition of **2** to a solution of Br_2 in CH_2Cl_2 at room temperature afforded the corresponding dibromide (**3**)[7] (99% yield; homogeneous by TLC and capillary chromatography). Reduction of **3** by tin in acetic acid at reflux, followed by treatment with 0.1 M NaOH, afforded a mixture of 4-aminotriphenylamine (**4a**) (4%). 4-amino-4′-bromotriphenylamine (**4b**) (6%), 4-amino-4′,4″-dibromotriphenylamine (**4c**) (42%), an isomer of **4c**, probably 4-amino-3,4′-dibromotriphenylamine (**4d**) (13%), and 4-amino-3,4′,4″-tribromotriphenylamine (**4e**) (32%). When the reaction was carried out at 75 °C, **4c** was formed in 87% yield, together with tribromide **4e** (12%) and monobromide **4b** (1%). (We will return to this dismutation process later). The amines are too sensitive in air to permit chromatographic separation of **4c** from the other amines. Diazotization of the mixture of amines produced at 75 °C with $NaNO_2$ in aqueous HBF_4 at 0 °C afforded a mixture of the solid diazonium tetrafluoroborates, which could be isolated by filtration of the cold solution. The yield of diazonium species is about 65%, ascertained by pyrolysis of the dry salt to afford 4-fluoro-4′,4″-dibromotriphenylamine as the major product.[8]

Electrode Modification. Pinson has shown that it is possible to attach aryl radicals to a variety of forms of carbon.[4] Carbon fibers were chosen here because of their relatively high surface area.[2d] The triphenylamine moiety was attached to the carbon electrode as shown in Scheme 2. A carbon fiber electrode consisting of a strand of pressed graphite fibers was chosen for attachment of the triphenylamine moiety. Cyclic voltammetry of an aqueous solution of the mixture of diazonium salts showed the expected[1] irreversible peak at −0.37 V vs Ag0.1 M $AgNO_3$ (the potential of this electrode is +0.35 V vs SCE). The electrode was then immersed in a solution of the diazonium salts, which were reduced and the corresponding aryl radical attached to the electrode, at controlled potential (by a single potential step from −0.2 to −0.6 V) until the current had decreased to zero. After repeated washing with organic solvents, the cyclic voltammogram shown in Figure 1 was obtained by repetitive scanning from 0 to +1.2 V. An oxidation wave was observed at ca. +0.9 V. (Compound **1**

Scheme 2. Construction of Modified Electrodes Bearing an Attached Triphenylamine Nucleus



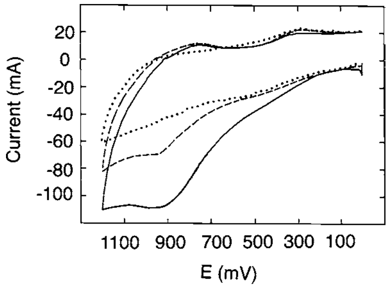


Figure 1. Repetitive cyclic voltammetry on carbon fiber electrode A (l = 1 cm) in acetonitrile/0.1 M TBAHFP: solid line, scan 1; dashed line, scan 2; dotted line, scan 3.

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(5) (a) Brinkhaus, K. H. G.; Steckhan, E.; Schmidt, W. *Acta Chem. Scand.* **1983**, *37B*, 499. (b) Schmidt, W.; Steckhan, E. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 673. (c) Wend, R.; Steckhan, E. *Electrochim. Acta* **1997**, *42*, 2027.

(6) Yamato, T.; Fujita, K.; Kamimura, H.; Tashiro, M.; Fry, A. J.; Simon, J.; Ochterski, J. *Tetrahedron Lett.* **1995**, *51*, 9851.

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(8) Roe, A. *Org. React.* **1949**, *5*, 193.

exhibits a reversible couple at 0.75 V.) The magnitude of the current decreased during the first few scans and then remained constant but even after a number of such scans the anodic current remained substantially greater than at an unmodified electrode. This electrode bearing several different triarylamino groups is designated here as electrode A.

Electrocatalysis. The cyclic voltammogram of 1,2-bis(trimethylsilyl)-1,2-diphenylethane (**5**) in acetonitrile at an unmodified electrode is shown as a solid line in Figure 2.

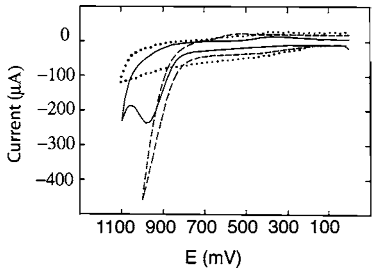
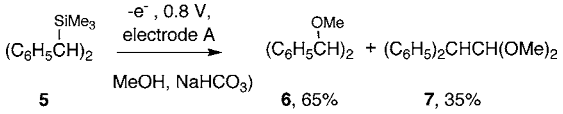


Figure 2. Cyclic voltammetryin 0.1 M TBAHFP/acetonitrile: (a) solid line, 1,2-bis[trimethylsilyl-1,2-diphenylethane (**5**) (1.5 mM) at an unmodified carbon electrode; (b) dotted line, a modified electrode A in the solvent without **5**; (c) dashed line, same as (b) but in the presence of 1.5 mM **5**.

An anodic peak is observed at ca. +1.0 V for the direct oxidation of **5**. The dotted line represents the behavior of electrode A in a 0.1 M solution of tetrabutylammonium hexafluorophosphate (TBAHFP) in acetonitrile. The dashed line represents the voltammetric response after addition of **5** (1.5 mM) to the solution. A severalfold increase in the anodic current is observed at potentials in the range 0.8−0.9 V, affording clear evidence for catalytic oxidation of **5** by the attached triarylamine moiety. It should be noted that because the carbon fibers we use are larger and less smooth than typical electrodes for analytical voltammetry, these voltammograms are not as well-defined as those at smaller electrodes. Preparative-scale electrolysis at +0.8 V of **5** (0.3 g) in methanol containing solid $NaHCO_3$ at a larger carbon electrode (1 cm^2) modified in the same fashion afforded a 65:35 mixture of 1,2-dimethoxy-1,2-diphenylethane (**6**) and 1,1-dimethoxy-2,2-diphenylethane (**7**) in 95% yield (Scheme 3). Addition of $NaHCO_3$ ensured that **7** is a primary product and not formed by acid-promoted pinacolic rearrangement of **6**. These are the same products in the same ratios as from the direct electrolysis.[7] We have discussed the formation of **7** previously.[9] Similar electrocatalytic behavior was observed with 3,4-dimethoxybenzyl alcohol, which is converted to the corresponding aldehyde by the electrocatalyst.[5a]

Scheme 3. Electrocatalytic Oxidation of 1,2-Bis(trimethylsilyl)-1,2-diphenylethane at Electrode A



It was not possible to separate the mixture of amines **4** before diazotization because of the ready oxidation of these substances in air. The presence of tri- and monobromo-substituted triphenylamine components presumably accounts for the broadness of the anodic peak in Figure 1 and the observed peak potential of ca. 0.9 V; the parent substance **1** has an oxidation potential of ca. 0.75 V. A second method was therefore devised for attachment of the 4,4′-dibromotriphenylamine nucleus to carbon. 4-Nitrotriphenylamine (**2**) was reduced with tin and hydrochloric acid, diazotized, and electrochemically attached to a carbon fiber electrode surface as previously described for the mixture of amines **4**. Pinson has shown that it is possible to carry out a variety of chemical reactions on the aryl rings in these modified electrodes.[4] The electrode was therefore immersed for 2 min in a 1 M solution of Br_2 in chloroform to afford electrode B (Scheme 2, second equation). Bromination at positions ortho to the central nitrogen atom of the triarylamine nucleus is presumably sterically blocked in this modified electrode. The oxidation potential of such electrodes is ca. 0.7 V, i.e., 0.2 V less positive than those prepared from **4** (Figure 3). Apparently, this is because only two bromine atoms are introduced by this method. This electrode again showed electrocatalytic behavior, even in a solution of only 1.5 mM **5** (the limit of its solubility) (Figure 4). These experiments demonstrate the feasibility of chemical attachment of the triarylamine nucleus to carbon electrodes. The procedure used here will permit tuning the redox potential of the catalytic electrode by varying the number and electronic nature of the groups on the triphenylamine nucleus.

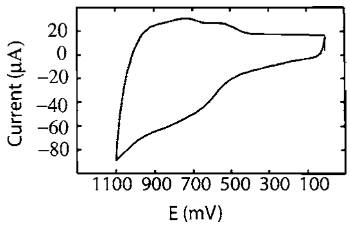


Figure 3. Cyclic voltammetry at carbon fiber electrode B ($l = 1$ cm) in acetonitrile/0.1 M TBAHFP.

The formation of amines **4a**−**e** upon reduction of the dibromide **3** calls for comment. The literature contains a number of so-called *halogen dance* reactions in which a halobenzene is converted into a mixture of substances containing anywhere from 0 to 3 halogen atoms. Many such processes have involved intermediate aryl carbanions.[10] Certain of these have been electrochemically induced.[10c,d] Some halogen dances involve reaction of an aryl halide with

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(10) (a) Bunnett, J. F. *Acc. Chem. Res.* **1972**, *5*, 139. (b) Duan, X.-F.; Zheng, Z.-B. *Heterocycles* **2005**, *65*, 2005. (c) Mubarak, M. S.; Peters, D. G. *J. Electroanal. Chem.* **1997**, *435*, 47. (d) Mubarak, M. S.; Peters, D. G. *J. Org. Chem.* **1996**, *61*, 8074.

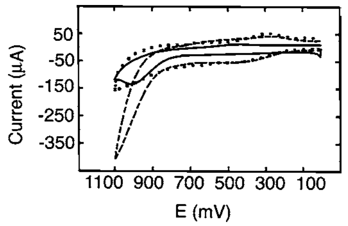
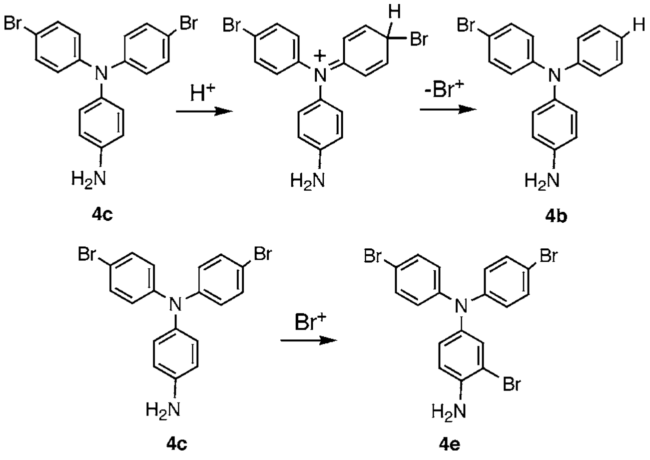


Figure 4. Cyclic voltammetry in 0.1 M TBAHFP/acetonitrile: (a)-solid line, 1,2-bis(trimethylsilyl)-1,2-diphenylethane (**5**) (1.5 mM) at an unmodified carbon electrode; (b) squares, a modified electrode B in the solvent without **5**; (c) dashed line, same as (b) but in the presence of 1.5 mM **5**.

strong Lewis acids.[11] The dismutation to afford **4a**−**e** that takes place upon Sn/HCl reduction of **3** seems to be related to the latter. A likely mechanism is shown in Scheme 4. The reaction presumably takes place on the protonated aminotriphenylamine. Protonation at the 4-amino group (probably the most basic site) does not offer an obvious path for halogen loss. On the other hand, protonation at the 4′-carbon atom is assisted by electron donation from the central nitrogen, as is clear from the high reactivity of this site toward electrophilic substitution (recall that nitration of triphenylamine, even at room temperature, affords almost 40% of the trinitro derivative). Loss of Br^+ from the protonated amine would then lead to monobromide **4b** and, upon repetition of the sequence, **4a**. Halogenation by Br^+ would afford tribromide **4e** and the isomeric dibromide **4d**.

Scheme 4. Mechanism of the Halogen Dance



Acknowledgment. This work was supported by the National Science Foundation (CHE-0411699) and by Wesleyan University.

Supporting Information Available: Experimental procedures for synthesis of compounds and modification of electrode surfaces. This material is available free of charge via the Internet at http://pubs.acs.org.

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