Electrolysis of Tetrakis(4-N,N-dimethylaminophenyl)methane – Fragmentation of a Tetraarylmethane under Oxidative Conditions

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Upon anodic oxidation tetrakis(4-N,N-dimethylaminophenyl)methane (3) fragments to give the stable species crystal violet (6), $N,N,N',N'$-tetramethyl benzidine radical cation (8) and Michler’s hydrol blue (12) that can be readily identified by their characteristic UV/vis absorption bands.

Introduction

The design of nanometer-sized molecular materials with three-dimensional highly symmetrical building blocks has recently aroused considerable interest [1]. Tetrahedral core units with suitable functionality at their vertices are attractive starting points for the construction of diamond-like rigid-rod molecular architectures and dendrimers with spherical topologies [2]. Among several structural motifs with tetrahedral symmetry tetraarylmethanes are of particular interest [3]. The sp³-hybridized center links four substituents with extended π-systems in the sense of a homon conjugation, simultaneous mutual orthogonality, and high degeneracy of the molecular orbitals of the conjugated chains [4]. Molecular electronic devices based upon the electronic communication of conjugated substructures have become increasingly important in the rapidly developing field of molecule based electronics [5]. In particular, tetrakis(aryl)methane structures 1 bearing redox active fragments on the tetrahedral scaffold could display an interesting electronic and electrochemical behavior favorable for future electronic applications as hole or electron transporters or as emitters in OLEDs (organic light emitting diodes) or OFETs (organic field effect transistors) [6].

Recently, we could show that electron deficient tetrakis(pyrimidylarylene) methanes (1: REDOX = 5-R-pyrimidin-2-yl) display a cooperative reduction behavior between the individual branches of the tetrahedra [7]. According to cyclic voltammetry quasi reversible redox cycles indicate an electrochemically mediated bispirocyclization that can be performed repeatedly in several cycles. This interesting feature prompted us also to consider electron rich substituents, the most fundamental being the dimethylamino group. Here we wish to report the synthesis and the electrochemical behavior of tetrakis(4-N,N-dimethylaminophenyl)methane.

Results and Discussion

Tetrakis(4-N,N-dimethylaminophenyl)methane (3) is prepared in a straightforward manner by a permethylation [8] of tetrakis(aminophenyl)methane [9] (2) under the conditions of a reductiveamination of formaldehyde with sodium borohydride in 87% yield (Scheme 1).

With this tetra-donor substituted tetra(aryl)methane in hand the electronic properties were investigated by regarding the cyclic voltammetry be-

behavior of a dichloromethane solution of 3 (Fig. 1). In multi-sweep experiments and even at high scan rates neither reversible nor quasi-reversible electron-transitions were found in the anodic region but an irreversible oxidation wave at $E_{p,ox}^\text{ox} = 673 \text{ mV}$ indicating a decomposition of an initially formed cationic species. Most peculiar, the electrolyte solution turned blue and remained persistent even after prolonged standing under air.

Therefore, an electrolysis of a dichloromethane solution of 3 was performed and the UV/vis spectra of the resulting solution was studied (Fig. 2). Like fingerprints, three electrolysis products could be identified due to their characteristic absorption bands. The absorption at 621 nm can be assigned unambiguously to the cation of Michler's hydrol blue (12), [10] the transition at 587 nm arises from the longest wavelength absorption band of crystal violet (6),[11] and bands arising from vibrational fine structures at 474, 458, 439, and 420 nm stem from the stable radical cation of N,N',N'-tetramethyl-benzidine (8) [12].

The detection of these fragmentation products, however, allows an insight into the electrolysis of aminosubstituted tetra(aryl)methanes and their formation can be mechanistically rationalized as follows (Scheme 2).

The anodic oxidation of 3 gives rise to the formation of the radical cation 4. Now, two different fragmentation pathways explain the formation of the stable species 6, 8 and 12. Path A commences with an $\alpha$-cleavage at the central carbon atom giving rise to the formation of radical 5 and the first stable specimen, the tris(A-N,N-dimethylaminophenyl)carbenium ion 6. The radical 5 is very likely to dimerize to furnish the benzidine 7 that is instantaneously oxidized at the anode to give the highly stabilized radical cation 8 [13]. Pathway B begins with a bispirocyclization of 4 to furnish the isomeric radical cation 9 where the radical and the cation are spatially separated but well stabilized by two mutually orthogonal dimethylamino substituted cyclohexadienyl systems. The release of the ring strain by opening the three-membered ring furnishes the radical cation 10 where the radical now is efficiently stabilized by two 4-N,N-dimethylaminophenyl fragments. Fragmentation of 10 in the sense of an $\alpha$-cleavage at the central carbon atom produces the benzidine 7 that is further oxidized to give the radical cation 8 (see pathway A) and the highly reactive radical cation 11 that can easily abstract a hydrogen atom from

Fig. 1. Cyclic voltammogram of 3 in the anodic region (dichloromethane, 20 °C, scan rate = 100 mV/s, supporting electrolyte: N°Bu$_4^+$PF$_6$Z).
Fig. 2 UV/vis spectrum of the electrolyte after the electrolysis of 3 and identified products (dichloromethane, 20 °C, potential: 800 mV; time: 180 min; supporting electrolyte: N°Bu₄PF₆⁻).

the surrounding dichloromethane solvent shell to furnish the bis(N,N-dimethylamino) benzhydryl cation 12.

This mechanistic rationale of the electrochemical fragmentation of 3 is additionally supported by the appearance of the crystal violet (6) as the basis peak in the fragmentation pattern of the mass spectrum of 3. Furthermore, the molecular peak of the radical cation 4 (or 9 or 10) at m/z 492 is found with a relative intensity of 25% indicating a relative persistence of 4 and its isomers 9 and 10. Finally, even the reactive intermediate 11 can be detected at m/z 252 with a relative intensity of 9%.

As a consequence for the design of fragmentation stable tetra-donor electrophores a partial electronic decoupling between the redox active branches on the tetraarylmethane scaffold has to be seriously considered. This could be achieved by attaching electron-rich moieties such as ferrocenes, phenothiazines or carbazoles to the tetrahedral vertices.

Conclusion

The tetrakis(dimethylamino) substituted tetra(aryl)methane scaffold displays an interesting fragmentation pattern upon anodic oxidation. However, for the design of fragmentation stable tetraarylmethanes with redox-addressable subunits a significant electronic decoupling of the inner phenylene bridges has to be taken into account. Thus, tetrakis(aryl)methane structures 1 bearing redox active fragments are very promising candidates for electronic manipulations of nanometer sized molecules. Syntheses and investigations of tetraarylmethanes with further electrophores are currently under way.

Experimental Section

Reagents and solvents were purchased reagent grade and used without further purification. THF was dried and distilled according to standard procedures [14]. Tetrakis(aminophenyl)methane 2 was prepared according to a literature procedure [9]. - TLC: silica gel plates (60 F²₅₄ Merck, Darmstadt). Melting points (uncorrected values): Reichert-Jung Thermovar. - ¹H and ¹³C NMR spectra: Bruker ARX 300, CDCl₃. The assignments of quaternary C, CH, CH₂ and CH₃ have been made by using DEPT spectra. - IR: Perkin Elmer Lambda 3. - UV/vis: Beckman DK-2-A, Beckman UV 5240 and Perkin Elmer Models Lambda 16. - MS: Finnigan MAT 90 and MAT 95 Q. - Elemental analysis was carried out in the Microanalytical Laboratory of the Institut für Organische Chemie, Ludwig-Maximilians-Universität München.
Scheme 2. Mechanistic rationale for the electrochemical fragmentation of 3.

**Electrochemistry:** Cyclic voltammetry experiments (EG & G potentiostatic instrumentation) were performed under argon in dry and degassed dichloromethane at room temperature and at scan rates of 100, 250, and 500 mVs⁻¹. The electrolyte was 0.10 M Bu₄NPF₆. The working electrode was a 1 mm platinum disk, the counter electrode was a platinum wire, and the reference electrode was a Ag/AgCl electrode. The potential of Fc/Fc⁺ was determined in dichloromethane (E₁/₂ = 450 mV).

**Tetrakis(4-N,N-dimethylaminophenyl)methane (3)**

In a solution of 1.1 g of conc. sulfuric acid in 3 ml of water were dissolved 0.72 g (24 mmol) of paraformaldehyde under cautious warming. After cooling to room temp, this solution was diluted with 10 ml of THF. To this mixture was slowly added a suspension of 0.38 g (1.00 mmol) of tetrakis(4-aminophenyl)methane 2 and 1.10 g (28.0 mmol) of sodium borohydride in 30 ml of THF under simultaneous stirring. After the addition sodium hydroxide was added until the mixture became alkaline. The solution was decanted and water and chloro-
form were added to the residue. The combined organic phases were washed with water and dried with anhydrous sodium sulfate. After filtration through a short plug of celite gel the solvents were removed in vacuo and the residue was recrystallized from chloroform/methanol to give 0.43 g (87%) of 3 as beige needles. M. p. > 350 °C. – UV/vis (CH2Cl2): λmax (lgε) = 268 nm (4.74). – IR (KBr): ν = 2796, 1609, 1513, 1348, 949, 814, 576 cm⁻¹. – ¹H NMR (300 MHz, CDCl3): δ = 2.90 (s, 24 H, (Me₂ NC₆H₄)₃C+), 6.61 (d, J = 9.0 Hz, 8 H, CH=C-N), 7.06 (d, J = 9.0 Hz, 8 H, CH=CH=C-N). – ¹³C NMR (75 MHz, CDCl3): δ = 40.6 (CH₃), 111.3 (CH), 131.7 (CH), 136.8 (Cquat.), 148.1 (Cquat.). – MS (70 eV, EI): m/z (%): 492 (M⁺, 25), 372 ((Me₂NC₆H₄)₂C⁺, 100), 252 ((Me₂NC₆H₄)C⁺, 9). – C₃₃H₄₀N₄ (492.7): calcd. C 80.45, H 8.18, N 11.37; found C 80.40, H 8.18, N 11.29.

**Electrolysis of 3**

A solution of 5 mg (0.01 mmol) of 3 in 20 ml of dry and degassed chloromethane containing N⁵Bu⁺PF₆⁻ (0.1 M) as supporting electrolyte was prepared at room temperature. In the electrolysis cell were placed 10 ml of this solution under a blanket of argon and the anodic potential was set to 800 mV for 180 min. After that time the deep blue solution was transferred to the UV/vis spectrometer and the spectrum was recorded.

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