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Synthesis and Study of the Anodic Behavior of 1,3,4,6-Tetraaryl-2 λ 4 δ 2 -thieno[3,4-c]thiophenes

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SYNTHESIS AND STUDY OF THE ANODIC BEHAVIOR OF 1,3,4,6-TETRAARYL- $2\lambda^4\delta^2$ -THIENO[3,4-c]THIOPHENES

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Two heterocyclic compounds based on the thieno[3,4-c]thiophene structure with four aryl substituents were prepared and their behavior in electrooxidation studied. These tetraarylthieno[3,4-c]thiophenes were synthesized in three steps starting from 1,3-dibenzoylmethane in the case of 1,3,4,6-tetraphenyl- $2\lambda^4\delta^2$ -thieno[3,4-c]thiophene **1a** and from 1,3-bis(4'-methoxyphenyl)propane-1,3-dione in the case of 1,3,4,6-tetrakis(4'-methoxyphenyl)- $2\lambda^4\delta^2$ -thieno[3,4-c]thiophene **1b**, a new compound. Both cyclic and hydrodynamic voltamperometric analyses indicate two reversible one-electron oxidation stages for compound **1b**, while for compound **1a** only the first stage is reversible. The preparative electrooxidation of the two compounds results in the opening of one thiophene ring giving rise to γ -keto-thioketones.

Keywords: Cation radical; electrooxidation; thieno[3,4-c]thiophene; thioketone; thiophene

INTRODUCTION

It is known that the biphenyl linkage has a stabilizing effect on cation radicals derived from methoxylated aromatics, especially when included in a cyclic system such as fluorene, dibenzofuran, and even more dibenzothiophene.^{1a} This stabilizing effect is even greater with two sulfur bridges as in dibenzo[bc,fg][1,4]dithiapentalene. Actually the preparation, by anodic oxidation, of the mixed valence salt, bis(2,3,4,6,7,8-hexamethoxydibenzo[bc,fg][1,4]dithiapentalenium) perchlorate (Scheme 1) was successful.^{1b}

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SCHEME 1

That is why we thought that compounds with the same heterocyclic moiety, that is, thieno[3,4-c]thiophene with four substituents instead of the two condensed benzene rings as represented on the chemical scheme 2 below, could also lead to stable cation radicals by electrooxidation.



SCHEME 2

In fact, the chemical oxidation of 1,3,4,6,-tetraphenylthieno[3,4-c]thiophene **1a**, by action of silver tetrafluoroborate or aluminium chloride in dichloromethane at -73° C leads to a cation radical.² Also, the reaction of potassium with this same compound in dimethoxyethane at -30° C gives the anion radical.²

The chemical oxidation of 1,3,4,6-tetrakis(isopropylsulfanyl)thieno[3,4-c]thiophene³ by iodine in hexane at -30° C affords as well a cation radical. On the other hand its oxidation using nitrosonium tetrafluoroborate (NOBF₄) in acetonitrile at -30° C gives a dication.³

Only a few substituted thieno[3,4-c]thiophenes have been synthesized in a stable form. We mention 1,3,4,6-tetraphenylthieno[3,4-c]thiophene,⁴ 1,3,4,6-tetra(2-thienyl)thieno[3,4-c]thiophene,⁵ 1,3,4,6-tetrakis(alkylsulfanyl)thieno[3,4-c]thiophene,⁶ and 1,3-dibromo-4,6-dicyanothieno[3,4-c]thiophene.⁷ For the present study, a new one was synthesized: 1,3,4,6-tetrakis(4'-methoxyphenyl)thieno[3,4-c]thiophene **1b**.

Handling and using 1,3,4,6-tetraarylthieno[3,4-c]thiophenes 1 is difficult because they easily undergo oxidation in solution, with opening of one thiophene ring, under the effect of light and aerial oxygen;^{4,8} this requires manipulation away from light, in degassed solution, and under nitrogen atmosphere.

SYNTHESIS OF 1,3,4,6-TETRAARYL- $2\lambda^4\delta^2$ -THIENO[3,4-c]THIOPHENES

1,3,4,6-Tetraphenyl-2 $\lambda^4 \delta^2$ -thieno[3,4-c]thiophene 1a

The first step is the coupling reaction in the presence of sodium iodide of brominated dibenzoylmethane⁹ into 1,4-diphenyl-2,3-dibenzoylbutane-1,4-dione.¹⁰ The reaction of phosphorus pentasulfide with this tetrabenzoylethane in refluxing pyridine gives directly 1,3,4,6-tetraphenyl- $2\lambda^4\delta^2$ -thieno[3,4-c]thiophene **1a**.

This method is faster than the one described in the literature,⁴ which needs two additional steps.

1,3,4,6-Tetrakis(4'-methoxyphenyl)- $2\lambda^4\delta^2$ -thieno[3,4-c]thiophene 1b

The method used is the same as the one described above for the synthesis of compound **1a**, but needs a previous preparation of 1,3-bis(4'-methoxyphenyl)propane-1,3-dione (or dianisoylmethane) by condensation of 4-methoxyacetophenone with methyl 4-methoxybenzoate in the presence of sodium hydride¹¹ (An = p.MeO-C₆H₄):

An-CO-CH₃ + MeO-CO-An
$$\xrightarrow{\text{NaH,DMSO/ether}}$$

An-CO-CH₂-CO-An (56%) $\xrightarrow{\text{+Br}_2, \text{CH}_2\text{Cl}_2}$
Pyridine, -5°C

Anodic Behavior

1) Voltammetry.

a) Cyclic voltammetry. Cyclic voltammetry measurements were carried out from solutions of tetraarylthieno[3,4-c]thiophenes $1, 2.5 \times 10^{-3}$ M in



FIGURE 1 Cyclic voltammogrammes of 1,3,4,6-tetraarylthieno[3,4-c]-thiophenes 1a and 1b (c = 2.5 mM), Pt anode (reference Ag/0.01 M Ag⁺, v = 100 mVs^{-1}) in CH₂Cl₂- 0.1 M nBu₄NPF₆.

 $CH_2Cl_{2^-}$ 0.1 M nBu₄NPF₆ (CH₂Cl₂ was used because of the insolubility of compounds 1 in acetonitrile); a platinum anode (A = 0.785 mm²) was used as a working electrode, and Ag/0.01 M Ag⁺ as a reference electrode.

Figure 1a represents the voltammogramme of 1,3,4,6-tetraphenylthieno[3,4-c]thiophene **1a** at a scan rate of 100 m Vs⁻¹; the curve shows clearly the full reversibility of the first peak at 0.27 V; it was found to be a purely reversible one-electron process (Epa-Epc = 60 mV). The second oxidation peak, which appears at 1.10 V, is irreversible.

The cyclic voltammogramme relative to the oxidation of 1,3,4,6tetrakis(4'-methoxyphenyl)thieno[3,4-c]thiophene 1b (Figure 1b) shows the presence of two reversible one-electron redox couples respectively at 0.05 V and 0.72 V, E_{pa} - E_{pc} being equal to about 60 mV and the ratio of peak currents (i_{pc}/i_{pa}) being close to 1. The presence of a methoxy substituent in the para position of the benzene ring makes compound **1b** much more easily electrooxidizable than compound **1a**. b) Hydrodynamic voltammetry. At a concentration of 1.25×10^{-3} M, in CH₂Cl₂- 0.1 M nBu₄NPF₆ as well, on a polished platinum rotating disc electrode, compound **1a** presents two waves of oxidation having different heights. However compound 1b shows two oxidation waves of equal heights (Figure 2). The half-wave potentials are 0.26, 1.12 V for 1a and 0.035, 0.72 V for 1b, versus Ag/0.01 M Ag⁺ reference electrode.

The current intensity is proportional to the square root of the rotation rate of the electrode (Figure 3). This confirms that the electrooxidation



 $\begin{array}{l} \textbf{FIGURE 2} \quad Intensity versus potential plots of \textbf{1a} (a) and \textbf{1b} (b) (c = 1.25 \text{ mM}), \\ at a rotated-disk platinum electrode (diameter: 2 mm), in CH_2Cl_{2^-} 0.1 \text{ M} \\ nBu_4NPF_6 (reference Ag/0.01 \text{ M Ag}^+) at different rotation rates (in revolutions per second) 1) 500, 2) 750, 3) 1000, 4) 1500, 5) 2000, 6) 2500. Scan rate: 5 mVs^{-1}. \end{array}$

of compounds 1a and 1b is a fully diffusion controlled process. 12 Besides, potential variations of the two waves of compound 1b as a function of the decadic logarithm of the ratio $i_{\rm lim}$ -i/i are parallel lines of 80 mV slope.



FIGURE 3 Intensity of the limiting current (i_{lim}) as a function of the square root of the angular velocity of the disc (in radians per second) $\omega^{1/2}$ of the rotated-disc platinum electrode (diameter: 2 mm), at the potentials of 0.50 V for a solution 1.25 mM of **1a** (a) and 0.25 (for i_1): first wave (solid line), and 1.00 V (for i_2): second wave (dashed line), of a solution 1.25 mM of **1b** (b).



FIGURE 4 EPR spectra recorded: a) during the anodic oxidation of **1a**, at a platinum microanode, in $CH_2Cl_{2^-}$ 0.2 M nBu_4NBF_4 (i = 30 μ A); and b) just after the end of the electrolysis of **1a**.

2) Macroscale electrolyses. The preparative electrolyses were conducted in a three-compartment H-shaped cell, on a platinum foil anode (total area: 16 cm²) in $CH_2Cl_{2^-}$ 0.1 M nBu_4NPF_6 with Ag/0.01 M Ag⁺ as a reference electrode.

The preparative electrolysis at the first oxidation step of 1,3,4,6tetraphenylthieno[3,4—c]thiophene **1a** ($\mathbf{E} = 0.25$ V) in the presence of a soluble base, such as 2,6-lutidine, leads exclusively to γ -keto-thioketone **2** by opening of the ring, after consumption of 2 F × mol⁻¹ (despite anolyte degassing and protection of the electrolysis cell from light). An ESR spectrum was recorded during the electrooxidation of **1a**, in order to observe its variation under our experimental conditions, such as microcell, equipped of a platinum microanode, in CH₂Cl₂- 0.2 M nBu₄NBF₄ with a current intensity of 30 μ A. The signal assigned to the cation radical species appeared first alone and progressively decreased (Figure 4) up to a colorless solution.



SCHEME 3

The following mechanism is proposed for the formation of γ -keto-thicketone **2**.



Anodic oxidations of 1,3,4,6-tetrakis(4'-methoxyphenyl)thieno[3,4c]thiophene **1b** carried out, both at the potential of the first peak and at the potential of the second peak, in the same conditions as **1a**, gave the same kind of γ -keto-thioketone **3** (characterized by IR and mass spectrometry):





CONCLUSION

In spite of the similarities of the structure between dibenzodithiapentalene and tetraarylthieno[3,4-c]thiophene 1, it is not possible to obtain stable cation radical salts by electrooxidation, because of the high tendency to the opening of one of the cycles.

EXPERIMENTAL

General Methods

The reaction progress and purity of samples were checked by T.L.C. on silica gel plates (Merck, 5714). Purification of starting materials and electrolysis products was carried out by silica gel column chromatography (Merck, 7736). The proton NMR spectra were recorded at 60 MHz, with TMS as an internal reference, in $CDCl_3$.

Starting Materials

1,3,4,6-Tetraphenyl- $2\lambda^4\delta^2$ -thieno[3,4-c]thiophene 1a

1° 1,3-Diaryl-2-bromopropane-1,3-dione. This compound was synthesized according to the procedure of Garg G. H.:⁹ bromination of an ice-cold mixture of dibenzoylmethane and pyridine in dichloromethane: m.p. 94°C (methanol) (lit.:⁹ 92–93°C).

 2° 1,4-Diphenyl-2,3-dibenzoylbutane-1,4-dione. It was prepared by the catalytic coupling,¹⁰ at room temperature for 12 h, of 1,3-diary1-2-bromopropane-1,3-dione in the presence of potassium iodide in acetone: m.p. 210°C (lit.:¹⁰ 204–208°C).

 3° 1,3,4,6-Tetraphenyl- $2\lambda^4\delta^2$ -thieno[3,4-c]thiophene **1a**. Under a nitrogen atmosphere, a mixture of 1,4-diphenyl-2,3-dibenzoylbutane-1,4-dione (3.0 g, 6.7 mmol) in pyridine (30 ml) with phosphorus pentasulfide (3.0 g, 13.5 mmol) was refluxed for 2 h. A red violet color appeared. After cooling, the reaction mixture was poured onto ice. The filtration and recrystallization in acetic anhydride of the precipitate gave red crystals of 1,3,4,6-tetraphenyl- $2\lambda^4\delta^2$ -thieno[3,4-c]thiophene **1a** (700 mg, 23%): m.p. 245°C (lit.:⁴ 245–247°C).

1,3,4,6-Tetrakis(4'-methoxyphenyl)- $2\lambda^4\delta^2$ - thieno[3,4-c]thiophene 1b

1° 1,3-Bis(4'-methoxyphenyl)-2-bromopropane-1,3-dione. This compound was prepared according to reference:⁹ bromination of an ice-cold solution of 1,3-bis(4'-methoxyphenyl)propane-1,3-dione¹⁰ in dichloromethane for 30 mins: m.p. $95-96^{\circ}C$.

 2° 1,4-Bis(4'-methoxyphenyl)-2,3-bis(4'-methoxybenzoyl)butane-1,4-dione. To a solution of 1,3-bis(4'-methoxyphenyl)-2-bromopropane-1,3-dione (8.5 g, 23.5 mmol) in acetone (20 mL), was added dropwise a solution of sodium iodide (14.1 g, 94 mmol) in acetone (23 mL). Then, after stirring for 12 h at room temperature, the reaction mixture was diluted with dichloromethane, washed twice with an aqueous solution of sodium sulfate. After usual work-up and recrystallization in acetic acid, were isolated 3.5 g (53%) of 1,4-bis(4'-methoxyphenyl)-2,3-bis(4'-methoxybenzoyl)butane-1,4-dione: m.p. 222°C (AcOH); NMR (CDCl₃) δ OMe 3.80 (s, 12H), δ CH 6.66 (s, 2H), δ Ar 6.82–6.99–7.95–8.11 (A₂X₂ system, J_{AX} = 9 Hz, 16H); MS m/z 566 (C₃₄H₃₀O₈).

3° 1,3,4,6-Tetrakis(4'-methoxyphenyl)-2λ⁴δ²-thieno[3,4-c]thiophene **1b**. A mixture of 1,4-bis(4'-methoxyphenyl)-2,3-bis(4'-methoxybenzoyl)butane-1,4-dione (3.0 g, 5.3 mmol) in pyridine (30 mL) and phosphorus pentasulfide (3 g) was refluxed for 2 h under a nitrogen atmosphere. A violet red color appeared. After cooling, the reaction mixture was poured onto ice. The filtration and recrystallization in acetic anhydride of the precipitate gave 0.650 g (22%) of red crystals of thienothiophene **1b**: m.p. 263–264°C (Ac₂O); NMR (CDCl₃) δ OMe 3.80 (s, 12H), δ Ar 6.70–6.85–7.16–7.31 (A₂X₂ system, J_{AX} = 9 Hz, 16H); MS: m/z 564 (C₃₄H₂₈O₄S₂). Anal: calc: C 70.92; H 4.93; O 10.88; S 12.28. Found: C 72.31; H 4.99; O 11.33; S 11.35.

Macroscale Electrolyses

Macroscale electrooxidations were carried out at room temperature, with bubbling nitrogen, in a three-compartment H-shaped cell. The intermediate compartment (useful volume: 5 mL) was used to minimize the mixing of the catholyte (V: 30 mL) and anolyte (V: 65 mL); the compartments were separated by two glass-frits (inside diameter: 2 cm). The anode was a platinum foil (total area: 16 cm²), the cathode a graphite rod (diameter: 1 cm) and reference electrode Ag/0.01 M Ag⁺ in MeCN. A volume of 100 mL CH₂Cl₂- 0.1 M nBu₄NPF₆ was divided among the three compartments and salt bridge. Between 0.5 and 1 mmol of tetraarylthienothiophene was added into the anodic compartment, in the presence of 2 mmol of 2,6-lutidine, which was closed by a silicone stopper. The electrolysis was carried on until the intensity dropped to zero.

Anodic Oxidation of 1,3,4,6-Tetraphenyl- $2\lambda^4\delta^2$ -thieno[3,4-c]thiophene 1a

Compound **1a** (444 mg, 1 mmol) was oxidized at a platinum anode, in CH_2Cl_2 —nBu₄NPF₆ 0.1 M in the presence of 2,6-lutidine (0.23 mL, 2 mmol), at a potential of 0.25 V; a green coloration appeared. After 24 h, at the end of the electrolysis, the electricity consumption was about 2 Faradays per mole. The anolyte was diluted with dichloromethane (250 mL) and washed with a 1% aqueous solution of acetic acid (100 mL), decanted off, washed with water (4 × 50 mL), and dried over Na₂SO₄. After usual work-up, the residue was purified by chromatography on silica gel (dichloromethane 50/cyclohexane 50) to give a green compound, 2,5-diphenyl-4-benzoyl-3-thiobenzoylthiophene **2** (430 mg, 93%): m.p. 120°C (lit.:³ 115°C). IR (KBr) ν_{CO} 1650, ν_{CS} 1225 cm⁻¹. NMR (CDCl₃) δ Ar 7.08–7.60 (m, 16H) and 7.62–7.85 (m, 4H). MS m/z 460 (C₃₀H₂₀OS₂).

Anodic Oxidation of 1,3,4,6-Tetrakis(4'-methoxyphenyl)- $2\lambda^4\delta^2$ -thieno[3,4-c]thiophene 1b

Compound **1b** (282 mg, 0.5 mmol) was oxidized, at a platinum anode in CH₂Cl₂- nBu₄NPF₆ 0.1 M at a potential of 0.05 V (another run, at a potential of 0.70 V led to the same result) for 24 h; a green coloration appeared. After 24 h, at the end of the electrolysis, the electricity consumption was about 2 Faradays per mole. The anolyte was diluted with dichloromethane (150 mL), washed with water (4 × 50 mL), and dried over Na₂SO₄. After the usual work-up, the residue was purified by chromatography on silica gel (dichloromethane 50/cyclohexane 50) to give a green compound, 2,5-bis(4'-methoxyphenyl)-4-benzoyl-3-thiobenzoylthiophene **3** (150 mg, 66%): m.p. 181°C. IR (KBr) ν_{CO} 1640, ν_{CS} 1160 cm⁻¹. NMR (CDCl₃) δ Ar 7.08–7.60 (m, 16H) and 7.62–7.85 (m, 4H). MS m/z 516 (C₃₄H₂₈OS₂).

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