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Electrosynthesis of Mono- and Bisthianthrenium Salts[1a]

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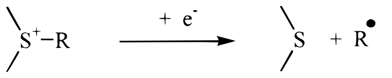
Introduction

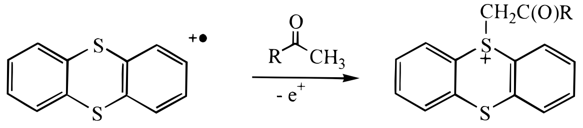
Over the last several years we have been involved with the development of simple organic-based reducing agents as replacements for the commonly used tin hydrides, especially for the formation of α-carbonylalkyl radicals.[2] Normally these radicals are generated from the corresponding halide or selenide since direct hydrogen atom abstraction next to a carbonyl group by oxyl radicals is too slow to be of synthetic utility. Recent work by Savéant has demonstrated that alkyl radicals are formed by the concerted dissociative reduction of sulfonium salts (reaction 1).[3] Since the sulfonium salts are easily reduced (i.e., voltammetric peak potentials are near −1 V vs SCE), this reaction represents a potential facile and chemoselective route to alkyl radicals.



(1)

One simple approach to the synthesis of a suitable sulfonium precursor is the reaction of thianthrene radical cation ($\mathbf{1}^{\bullet+}$) with a ketone (reaction 2).[4,5] Shine and coworkers originally reported the formation of mono- and bisthianthrenium salts from reaction of $\mathbf{1}^{\bullet+}$, prepared by chemical oxidation of **1**, with ketones and alkenes.[4j,k,5b]

While the formation of these sulfoniums by chemical oxidation is facile, in principle, $\mathbf{1}^{\bullet+}$ can be prepared in situ by electrochemical oxidation. Furthermore, voltammetric analysis can provide some insights into the kinetics and mechanism of the reaction. Here, we demonstrate the utility of the electrosynthetic approach with the reactions of two ketones and two alkenes leading to the formation monothianthrenium ($\mathbf{2}^{+}$, $\mathbf{3}^{+}$) and bisthianthrenium salts ($\mathbf{4}^{2+}$, $\mathbf{5}^{2+}$). We also report, for the first time, a single-crystal X-ray structure of the bisthianthrenium salt ($\mathbf{4}^{2+}$). Mechanistic aspects of the reactions of $\mathbf{1}^{\bullet+}$ from voltammetric analysis are briefly discussed.



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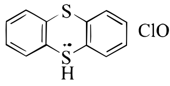
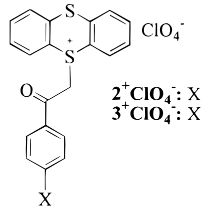
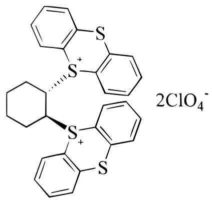
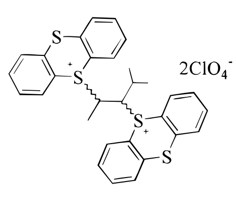

$\mathbf{1}^{+\bullet}$ **ClO$_4^-$**


$\mathbf{2}^{+}$**ClO$_4^-$**: X = CH$_3$
$\mathbf{3}^{+}$**ClO$_4^-$**: X = H


$\mathbf{4}^{2+}$**(ClO$_4^-$)$_2$**


$\mathbf{5}^{2+}$**(ClO$_4^-$)$_2$**

Results and Discussion

The voltammogram of **1** in acetonitrile consists of two reversible oxidation waves corresponding to the formation of $\mathbf{1}^{\bullet+}$ and thianthrenium dication ($\mathbf{1}^{2+}$), respectively. The latter reacts with traces of water present in acetonitrile to give the sulfoxide, which has two oxidation waves at more positive potentials.[6] The voltammogram in Figure 1a shows the first reversible oxidation wave of thianthrene in acetonitrile at $E^\circ = 1.10$ V vs SCE.[6] In the presence of added 4-methylacetophenone (120 mM, Figure 1b) the oxidation wave of thianthrene increases in height at the expense of the corresponding reduction wave. At higher concentrations of 4-methylacetophenone (400 mM, Figure 1c) the oxidation wave is approaching 2 electrons per molecule and is chemically irreversible (typical of an ECE/DISP type process). A new reduction wave appears at ca. −0.8 V (Figure 1b,c). From the voltammogram it is possible to estimate a second-order rate constant for the reaction of the ketone with the

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(6) By going to the second oxidation wave of thianthrene and scanning back to the negative potential, a reduction wave corresponding to the formation of thianthrenesulfoxide is observed. However, the peak potential and half-width of the wave are clearly different from those observed in the presence of added ketones.

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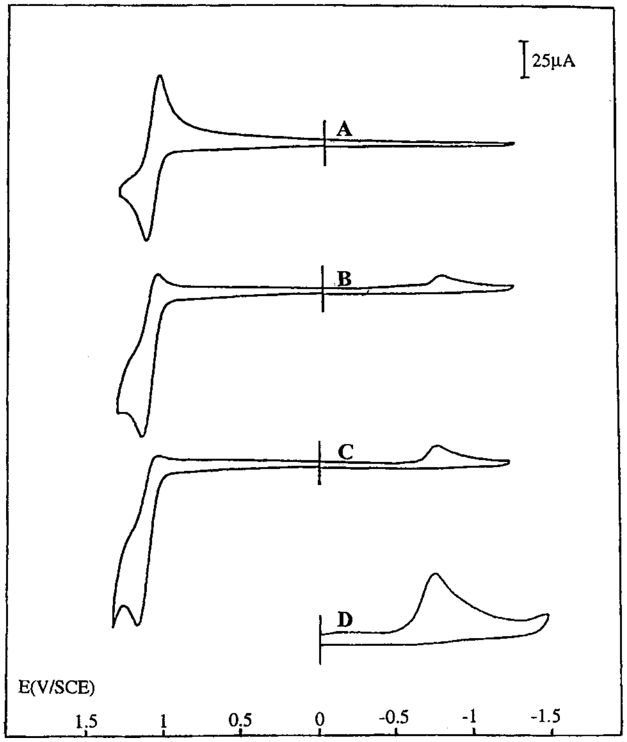

Figure 1. Cyclic voltammograms of thianthrene (**1**, 2 mM) in CH_3CN with $^{n}Bu_4NClO_4$ (0.1 M) as supporting electrolyte, on a glassy carbon electrode (scan rate, $v = 0.20$ V s^{-1}, 20 °C), with (A) 0 mM; (B) 120 mM; (C) 400 mM 4-methylacetophenone; (D) voltammogram of electrosynthesized $\mathbf{4^{2+}(ClO_4^-)_2}$ under same conditions.

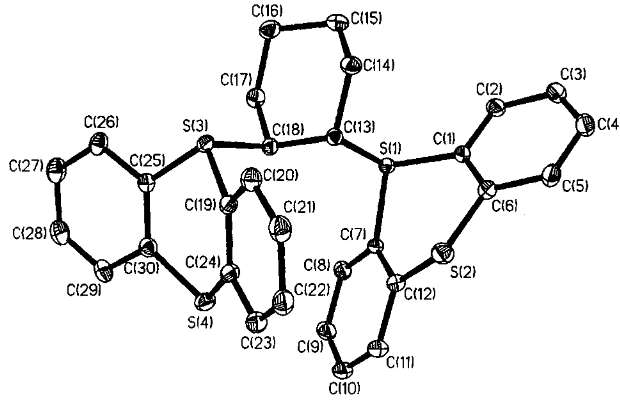

Figure 2. ORTEP diagram of $\mathbf{4^{2+}(ClO_4^-)_2}$ (hydrogen atoms are omitted for clarity). Selected bond distances and angles: S(1)−C(1) = 1.756(2) Å, S(1)−C(7) = 1.760(2) Å, S(1)−C(13) = 1.858(2) Å, S(3)−C(18) = 1.859(2) Å, S(3)−C(19) = 1.762(2) Å, S(3)−C(25) = 1.764(2) Å, C(13)−C(18) = 1.535 Å; C(1)−S(1)−C(7) = 103.77(11)°, C(1)−S(1)−C(13) = 102.98(10)°, C(7)−S(1)−C(13) = 100.71(10)°, C(18)−S(3)−C(19) = 103.63(10)°, C(18)−S(3)−C(25) = 100.31(10)°, C(19)−S(3)−C(25) = 103.90(11)°, S(1)−C(13)−C(18) = 103.24(14)°, S(3)−C(18)−C(13) = 108.57(15)°.

radical cation.[7] Controlled potential electrolysis of **1** in acetonitrile (using $NaClO_4$ (0.1 M) as the supporting electrolyte)[8] at 1.15 V vs SCE led to a gradual decrease in the two electron oxidation wave and an increase in the reduction wave at −0.8 V. The electrolysis was stopped when approximately 90% of starting thianthrene was consumed. The product α-(thianthrenium)-4-methylacetophenone perchlorate ($\mathbf{2^{+}ClO_4^-}$) was isolated and characterized by ^{1}H and ^{13}C NMR.

The voltammogram of pure $\mathbf{2^{+}ClO_4^-}$ shown in Figure 1d, exhibits an irreversible reduction wave which corresponds to the reduction wave observed in Figure 1b,c. Analysis of this broad wave leads to a transfer coefficient, α, of about 0.3 and is consistent with a dissociative process (eq 1) as described in the literature.[3] Similarly, electrolysis in the presence of acetophenone resulted in the formation of α-thianthrenium acetophenone perchlorate ($\mathbf{3^{+}ClO_4^-}$). Since benzophenone does not react under identical reaction conditions and since the products $\mathbf{2}^+$ and $\mathbf{3}^+$ contain a newly formed C−S bond, we conclude (as suggested by Shine[5b]) that small amounts of enol present in the solution are actually the reactive species.

Voltammetry in the presence of cyclohexene resulted in the loss of some reversibility of the one electron oxidation wave associated with **1**. As the electrolysis progressed, the oxidation wave decreased in height and a new reduction wave appeared at $E = -0.490$ V (vs SCE). However, in contrast to reactions with acetophenone, the overall reaction with cyclohexene corresponded to the consumption of only one electron per molecule. Electrolysis in the presence of 4-methyl-2-propene also gave similar results. The products were isolated (see Experimental Section) and identified by ^{1}H and ^{13}C NMR to be $\mathbf{4^{2+}(ClO_4^-)_2}$ and $\mathbf{5^{2+}(ClO_4^-)_2}$, respectively. In this case it appears that the intermediate distonic radical cation is trapped by $\mathbf{1}^{\bullet+}$ (see below).

Shine and co-workers have previously synthesized $\mathbf{4^{2+}(ClO_4^-)_2}$ by reaction of $\mathbf{1}^{\bullet+}$ perchlorate salt with cyclohexene in acetonitrile.[3k] These authors also noted that solutions of $\mathbf{4^{2+}(ClO_4^-)_2}$ in acetonitrile slowly decomposed. However, in the present study, we find this is not the case, and we were able to grow crystals of $\mathbf{4^{2+}(ClO_4^-)_2}$ from acetonitrile. This may be a result of having accumulated fewer byproducts in the electrochemical synthesis compared to the chemical oxidation approach.

Iwai and Shine[3j] reported the formation and reactions of $\mathbf{4^{2+}(ClO_4^-)_2}$ with CN^-, $C_6H_6S^-$, and I^- in DMSO. They pointed out that the interpretation of their reactivity data was complicated, as neither the configuration nor the conformation of $\mathbf{4^{2+}(ClO_4^-)_2}$ was known. However, they suggested for a number of cogent reasons that the configuration of $\mathbf{4^{2+}(ClO_4^-)_2}$ was likely *trans*. The single-crystal X-ray structure of $\mathbf{4^{2+}(ClO_4^-)_2}$ confirms the *trans* configuration of the two thianthrene rings. It is evident from Figure 2 that the cyclohexane ring adopts a chair conformation, with the two thianthrene moieties being attached to C(13) and C(18) in a *trans* configuration. The distances and angles in the cyclohexane and the aromatic rings are typical for aliphatic and aromatic systems, respectively. As is typical for sulfonium salts, there is significant pyramidalization about the sulfur atoms S(1) and S(3). S(1) is lying 0.780(2) Å above the base of pyramid defined by C(1), C(7), and C(13), while S(3) is 0.568(2) Å above the pyramidal base. The C−S−C angles are all less than tetrahedral. It is noteworthy that the

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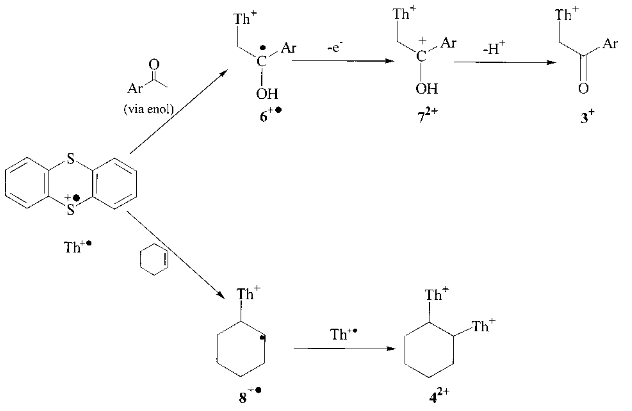
[7] From the voltammetric experiments and using a digital simulation of the reactions in Scheme 1, we have deduced the values of rate constant for reaction of thianthrene radical cation with acetophenone and 4-methylacetophenone as 6 and 90 M^{-1} s^{-1}, respectively. A more detailed report of the kinetics of these reactions with a wide range of ketones and alkenes is in preparation and will be reported separately.

[8] $NaClO_4$ was used as supporting electrolyte because of its low solubility in CH_2Cl_2, which aided (see Experimental Section) in the isolation of products from the reaction mixture.

Scheme 1



thianthrene moieties adopt a butterfly conformation, with angles between the planes defined by the aromatic rings being 35.1° (for S(1)/S(2)) and 34.3° (for S(3)/S(4)). The perchlorate anions and the acetonitrile molecule, present as solvent of crystallization, are well separated from the thianthrene dications.

Our proposed mechanism for the observed reactions of ketones and alkenes with thianthrene radical cation is shown Scheme 1. It is important that this mechanism also gives some insight into the reason for the chemical selectivity (either mono- or bisthianthrenium salts) of the process. The electrochemically generated thianthrene radical cation $\mathbf{1}^{\bullet+}$ reacts with the enol form of the ketone or an alkene to give a distonic radical cation $\mathbf{6}^{\bullet+}$ or $\mathbf{8}^{\bullet+}$. The distonic radical cation $\mathbf{6}^{\bullet+}$ readily undergoes oxidation by reaction with $\mathbf{1}^{\bullet+}$ (DISP) to form the dication $\mathbf{7}^{2+}$, which deprotonates to yield the ketothianthrenium salt, consuming two electrons in the process. Since the concentration of the enol form of acetophenones is very small in solution, the reaction requires high concentrations of ketones.[7] The reactions of aliphatic ketones are slow and give low yields. However, the reactions of the corresponding enol ethers are facile. These results will be reported separately.

The reaction of cyclohexene with $\mathbf{1}^{\bullet+}$ leads to consumption of only one electron, suggesting that the initially produced distonic radical cation, $\mathbf{8}^{\bullet+}$, reacts with $\mathbf{1}^{\bullet+}$ to give a bissulfonium salt. This difference in reactivities of ketones and alkenes with thianthrene radical cation is probably due to the relative ease of oxidation of $\mathbf{6}^{\bullet+}$ compared to the secondary alkyl radical of $\mathbf{8}^{\bullet+}$.[9] Typically secondary alkyl radicals have standard oxidation potentials in the range of 0.5 V vs SCE, while ketyl radicals have potentials of ca. −0.5 V vs SCE.[9,10] The presence of a the thianthrenium group b to the radical center will shift both standard potentials in a positive direction. It is likely that the oxidation of $\mathbf{8}^{\bullet+}$ will not be thermodynamically feasible. On the other hand oxidation of $\mathbf{6}^{\bullet+}$ by $\mathbf{1}^{\bullet+}$ is still expected to be exergonic. In general, when electron transfer is energetically favored, that pathway prevails.[11]

In conclusion, we have demonstrated that preparative electrolysis offers a convenient method for the synthesis and isolation of mono- and bisthianthrenium salts. It is proposed that the selectivity to mono- or bisthianthrenium is governed by the oxidation potential of the intermediate distonic radical cation.

Experimental Section

Materials. Thianthrene, 4-methylacetophenone, acetophenone, 4-methyl-2-propene, and sodium perchlorate were commercially available (Aldrich) and were used as received. Tetrabutylammonium perchlorate (TBAP) was recrystallized from ethyl acetate/hexane (9:1) before use. Acetonitrile (BDH, OmniSolv) was refluxed and distilled over CaH_2 before use. ^1H and ^{13}C NMR spectra were obtained at 400 MHz, and the chemical shifts are reported relative to tetramethylsilane.

Cyclic Voltammetry. Experiments were carried out using an EG&G model 173 potentiostat with model 179 coulometer and a model 175 universal programmer. Measurements were made in a standard three-electrode cell with a 3 mm diameter glassy carbon working electrode and a platinum wire as counter electrode. The reference electrode consisted of a silver wire in a solution of acetonitrile/$n Bu_4NClO_4$ (0.1 M) separated from the solution by a cracked glass seal. Samples were purged with Ar prior to each measurement. Ferrocene ($E° = 0.44$ V vs SCE, in CH_3CN) was used as an internal reference. All potentials are reported with respect to SCE.

General Procedure for Electrolysyntheis of Thianthrenium Salts. The preparative scale electrolyses were carried out at 1.15 V vs SCE in a 100 mL cell with a graphite felt (6 mm) working electrode and Pt wire counter electrode. The working electrode was separated from the cathodic compartment by means of a glass frit. Solutions were kept under an argon stream during the electrolysis. $NaClO_4$ was used as supporting electrolyte because of its low solubility in CH_2Cl_2, which aided in the isolation of reaction products from the reaction mixture. The reaction mixture was concentrated to 5 mL on a rotary evaporator, and $NaClO_4$ was precipitated by addition of CH_2Cl_2 (50 mL). The filtrate was concentrated (ca. 10 mL), and addition of excess diethyl ether afforded product thianthrenium salt as a white solid. The crude product was recrystallized from acetonitrile/diethyl ether at −4 °C to afford pure thianthrenium salt as a white crystalline solid (yield > 90%), which was characterized by ^1H NMR ($CDCl_3$) and single-crystal X-ray diffraction studies. The spectral data for mono- and bisthianthrenium salts prepared in this study are summarized below.

9-(4-Methylacetophenone)thianthrenium perchlorate ($\mathbf{2}^+ClO_4^-$): ^1H NMR ($CDCl_3/CD_3CN$) δ 8.32 (dd, 2H, $J = 7.80$, 1.50 Hz), 7.76 (t, 4H, $J \sim 8$ Hz), 7.69 (t, 2H, J 8.1 Hz), 7.63 (t, 2H, J 8.1 Hz), 7.56 (t, 1H, J 7.50 Hz)) 7.39 (t, 2H, J 8.30 Hz), 5.60 (s, 2H), 2.3 (s, 3H); ^{13}C NMR ($CDCl_3/CD_3CN$): δ 136.8, 135.5, 135.2, 134.6, 133.2, 130.5, 130.0, 129.2, 128.9, 117.1, 116.7, 50.1.

9-(Acetophenone)thianthrenium perchlorate ($\mathbf{3}^+ClO_4^-$): ^1H NMR ($CDCl_3/CD_3CN$) δ 8.42 (dd, 2H, $J = 7.80$, 1.50 Hz), 7.84 (t, 4H, $J \sim 8$ Hz), 7.79 (t, 2H, J 8.1 Hz), 7.63 (t, 2H, J 8.1 Hz), 7.56 (t, 1H, J 7.50 Hz)) 7.39 (t, 2H, J 8.30 Hz), 5.60 (s, 2H); ^{13}C NMR ($CDCl_3/CD_3CN$) δ 136.80, 135.58, 135.23, 134.73, 133.67, 130.54, 130.13, 129.26, 129.06, 117.15, 117.04, 116.65.

1,2-Bis(5-thianthrenium)cyclohexane diperchlorate ($\mathbf{4}^{2+}(ClO_4^-)_2$): ^1H NMR ($CDCl_3/CD_3CN$) δ 8.33 (d, 4H, $J = 8.01$ Hz), 7.97 (dd, 4H, $J = 8.01$; 1.54 Hz), 7.83 (td, 4H, $J = 8.02$, 1.40 Hz), 7.75 (td, 4H, $J = 7.50$, 1.56 Hz), 4.51 (s (br), 2H), 2.41 (m, 4H), 2.14 (m, 4H).

2,3-Bis(5-thianthrenium)-4-methylpentane diperchlorate ($\mathbf{5}^{2+}(ClO_4^-)_2$): ^1H NMR ($CDCl_3/CD_3CN$) δ 8.35 (d, 4H, $J = 7.76$ Hz), 7.81 (dd, 4H, $J = 7.94$, 1.55 Hz), 7.73 (td, 4H, $J = 7.18$, 1.40 Hz), 7.65 (td, 4H, $J = 7.45$, 1.53 Hz), 4.59 (t, 1H, $J = 1.60$ Hz), 4.36 (m, 1H), 2.81 (m, 1H), 1.56 (t, 6H, $J = 6.8$ Hz), 1.12 (d, 3H, 1.57 Hz); ^{13}C NMR ($CDCl_3/CD_3CN$) δ 136.80, 135.71, 135.54, 134.56, 133.50, 131.63, 130.82, 63.52, 54.60, 28.22, 28.29, 21.72, 19.28.

Single-Crystal X-ray Crystallography of $\mathbf{4}^{2+}(ClO_4^-)_2$: A suitable crystal was mounted on a Siemens SMART diffractometer (graphite monochromator Mo Kα X-ray). Crystal data for $\mathbf{4}\cdot CH_3CN$: $C_{64}H_{58}Cl_4N_2O_{16}S_8$, $M = 1509.40$, colorless plates, crystal size = 0.5 × 0.3 × 0.1 mm; monoclinic space group $P2_1/c$; $a = 18.1222(2)$ Å, $b = 22.3330\ (4)$ Å, $c = 16.4101(2)$ Å, $\beta =$

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93.5470(10)°, $U = 6628.77(11)$ Å^3, $Z = 4$, $D_c = 1.512$ g cm^{-3}, $F(000) = 3120$, μ(Mo Kα) = 0.501 mm^{-1}; 75 380 data were collected with $2\theta_{\max} = 550$ at −100 °C, and merged to give 17 140 unique data ($R_{\text{int}} = 0.0373$). The structure was solved by direct methods and refined on F^2 data using Siemens SHELXTL program suite. All non-hydrogen atoms were refined with anisotropic temperature factors. Hydrogen atoms were included at calculated positions with fixed isotropic temperature factors. The refinement converged at $R = 0.0446$, $wR = 0.1026$ for $I > 2\sigma(I)$ data ($R = 0.0685$, $wR = 0.1209$ for all data).

Supporting Information Available: X-ray analysis for $\mathbf{4^{2+}(ClO_4^-)_2}$ including a summary of crystallographic parameters, atomic coordinates, bond lengths, and bond angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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