

## The Direct Electrochemical Synthesis of Tin(II) Derivatives of Aromatic 1,2-Diols, and a Study of their Oxidative Addition Reactions

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The electrochemical oxidation of anodic tin in non-aqueous solutions of aromatic diols  $R(OH)_2$  ( $=$  1,2-dihydroxybenzene, 2,3-dihydroxynaphthalene, tetrabromo-1,2-dihydroxybenzene, or 2,2'-dihydroxybiphenyl) gives rise to  $Sn(O_2R)$  species in high yield. When 1,10-phenanthroline (phen) is present in the cell,  $Sn(O_2R)(phen)$  is obtained. Such adducts, and salts of  $[SnX(O_2R)]^-$  anions ( $X = Br$  or  $I$ ), can also be prepared directly from the  $Sn(O_2R)$  compounds. The latter also undergo oxidative addition reactions with  $I_2$ , to give  $Sn^{IV}I_2(O_2R)$ , and with the substituted *o*-quinones  $O_2C_6X_4$  ( $X = Cl$  or  $Br$ ) to give the corresponding catecholates  $Sn^{IV}(O_2R)(O_2C_6X_4)$ .

The method of direct electrochemical synthesis consists in essence of oxidizing a metal anode in an organic solution containing the appropriate ligand or ligand precursor to produce the appropriate metal–ligand derivative. In addition to experimental simplicity and high yield, one advantage of this technique is that the products are often those of the metal in a low oxidation state, since the starting point is the element itself. Examples of such syntheses include chromium(III) bromide,<sup>1</sup> tin(II) and lead(II) thiolates,<sup>2</sup> hexahalogenodigallate(II) anions,<sup>3</sup> thorium di-iodide,<sup>4</sup> copper(I) thiolates,<sup>5</sup> and indium(I) thiolates.<sup>6</sup> By an extension of the recent preparation of zinc and cadmium diolates,<sup>7</sup> we have now synthesized tin(II) derivatives of substituted aromatic 1,2-diols, and of 2,2'-dihydroxybiphenyl; adducts of these  $Sn(O_2R)$  species with halide or bidentate nitrogen donors can also be easily prepared electrochemically. The oxidative addition reactions of  $Sn(O_2R)$  compounds have also been briefly investigated in the course of these studies.

The previous routes to such tin(II) compounds involve more laborious procedures than those described here. The formation of  $Sn(O_2C_6H_4)$  by the long heating of catechol (1,2-dihydroxybenzene) with tin–copper alloy under hydrogen at high pressure [7.5 h, 128 atm (atm  $\approx 10^5$  Pa)] has been reported by Zuckerman,<sup>8</sup> and this and other diols react with  $SnO$ – $Cu$  mixtures under pressure (typically 12 h, 200 °C, 120 atm), or on long refluxing with  $SnO$ – $Cu$  in xylene.<sup>9</sup> 1,2-Dihydroxyphenyl compounds also react with tin(II) chloride and sodamide ( $NaNH_2$ ) to give  $Sn(O_2R)$  derivatives.<sup>10a</sup> The coordination chemistry and redox reactions of these tin(II) compounds do not appear to have been investigated.

### Experimental

Tin metal (Alfa), aromatic diols, 2,2'-dihydroxybiphenyl, tetrahalogeno-*o*-quinones, 2,2'-bipyridine (bipy), and 1,10-phenanthroline (phen) (Aldrich) were used as supplied. Solvents were dried and distilled before use, and stored over drying agents.

Tin analysis was by atomic absorption spectrophotometry, and inorganic halogen analysis by the Volhard method;<sup>10b</sup> total halogen analysis by the Oakdale–Thompson method<sup>10c</sup> did not give reproducible results. Microanalysis on selected compounds was performed by Guelph Chemical Laboratories. Proton and <sup>13</sup>C n.m.r. spectra were recorded on a Bruker AC 300 L spectrometer. Infrared spectroscopy involved the use of samples as KBr discs with a Nicolet 5DX instrument. Conductivities were measured in a standard platinum electrode cell, standardized with 1 mol dm<sup>-3</sup> aqueous  $KNO_3$ .

*Electrochemical Synthesis.*—The method of preparing  $Sn(O_2R)$  compounds essentially followed that used in previous work from this laboratory.<sup>1–7,11</sup> The solution phase was contained in a 100-cm<sup>3</sup> tall-form beaker; a tin rod (diameter 0.95 cm) formed the anode of the cell, and a platinum wire coil was the cathode. Details of solution composition, electrochemical conditions, etc. are given in Table 1. The diols used were 1,2-dihydroxybenzene (catechol), 2,3-dihydroxynaphthalene, tetrabromo-1,2-dihydroxybenzene, and 2,2'-dihydroxybiphenyl. As the electrolysis proceeded, hydrogen gas evolved at the cathode, and a solid formed at the anode; this material gradually deposited in the cell, and at the end of the experiment

Table 1. The electrochemical preparation of  $Sn(O_2R)$  and  $Sn(O_2R)(phen)$  compounds

| Diol <sup>a</sup> | Solution composition <sup>b</sup> |          | Time of electrolysis <sup>c</sup> (h) | Metal dissolved (mg) | Mass of product (g) | Yield <sup>d</sup> (%) | $E_F/mol F^{-1}$ |
|-------------------|-----------------------------------|----------|---------------------------------------|----------------------|---------------------|------------------------|------------------|
|                   | diol (g)                          | phen (g) |                                       |                      |                     |                        |                  |
| $C_6H_4(OH)_2$    | 0.17                              | —        | 2.0                                   | 180                  | 0.3                 | 94                     | 0.51             |
| $C_6H_4(OH)_2$    | 0.21                              | 0.35     | 2.5                                   | 225                  | 0.58                | 75                     | 0.51             |
| $C_{10}H_6(OH)_2$ | 0.27                              | —        | 2.25                                  | 200                  | 0.42                | 89                     | 0.50             |
| $C_{10}H_6(OH)_2$ | 0.27                              | 0.31     | 2.0                                   | 190                  | 0.65                | 89                     | 0.54             |
| $C_6Br_4(OH)_2$   | 0.66                              | —        | 2.0                                   | 185                  | 0.69                | 82                     | 0.52             |
| $C_6Br_4(OH)_2$   | 0.66                              | 0.28     | 2.0                                   | 190                  | 0.9                 | 80                     | 0.54             |
| $C_{12}H_8(OH)_2$ | 0.57                              | —        | 4.0                                   | 365                  | 0.90                | 96                     | 0.51             |
| $C_{12}H_8(OH)_2$ | 0.33                              | 0.33     | 2.25                                  | 210                  | 0.73                | 85                     | 0.52             |

<sup>a</sup>  $C_6H_4(OH)_2 =$  1,2-dihydroxybenzene,  $C_{10}H_6(OH)_2 =$  2,3-dihydroxynaphthalene,  $C_6Br_4(OH)_2 =$  tetrabromo-1,2-dihydroxybenzene, and  $C_{12}H_8(OH)_2 =$  2,2'-dihydroxybiphenyl. <sup>b</sup> In acetonitrile (50 cm<sup>3</sup>) containing  $NEt_4ClO_4$  (20 mg). <sup>c</sup> All experiments run at 20 V and 40 mA. <sup>d</sup> Based on mass of metal dissolved.

**Table 2.** Analytical results for Sn(O<sub>2</sub>R) and related products

| Compound  | Colour        | Sn (%) |       | Halogen (%) |       |
|---|---------------|--------|-------|-------------|-------|
|   |               | Found  | Calc. | Found       | Calc. |
| <i>(i)</i> O <sub>2</sub> R = O <sub>2</sub> C <sub>6</sub> H <sub>4</sub>    |               |        |       |             |       |
| Sn(O <sub>2</sub> R) <sup>a</sup>   | Colourless    | 52.4   | 52.3  |             |       |
| Sn(O <sub>2</sub> R)(phen)  | Yellow        | 29.1   | 29.2  |             |       |
| [PPh <sub>4</sub> ][SnBr(O <sub>2</sub> R)]                                   | Pale yellow   | 18.6   | 18.4  | 12.4        | 12.4  |
| [NBu <sub>4</sub> ][SnI(O <sub>2</sub> R)]                                    | Yellow        | 19.8   | 19.9  | 21.4        | 21.3  |
| SnI <sub>2</sub> (O <sub>2</sub> R)(bipy)                                     | Orange        | 18.6   | 18.6  | 39.7        | 39.9  |
| Sn(O <sub>2</sub> R)(O <sub>2</sub> C <sub>6</sub> Br <sub>4</sub> )(bipy)    | Yellow-beige  | 14.9   | 14.7  |             |       |
| Sn(O <sub>2</sub> R)(O <sub>2</sub> C <sub>6</sub> Cl <sub>4</sub> )(bipy)    | Yellow-beige  | 18.7   | 18.9  |             |       |
| <i>(ii)</i> O <sub>2</sub> R = O <sub>2</sub> C <sub>10</sub> H <sub>6</sub>  |               |        |       |             |       |
| Sn(O <sub>2</sub> R) <sup>b</sup>   | Colourless    | 43.0   | 42.9  |             |       |
| Sn(O <sub>2</sub> R)(phen)  | Yellow        | 26.1   | 26.0  |             |       |
| [PPh <sub>4</sub> ][SnBr(O <sub>2</sub> R)]                                   | Cream         | 17.3   | 17.1  | 11.4        | 11.5  |
| [NBu <sub>4</sub> ][SnI(O <sub>2</sub> R)]                                    | Yellow        | 19.8   | 19.6  | 18.6        | 18.4  |
| [NBu <sub>4</sub> ][SnI(O <sub>2</sub> R)(phen)]                              | Yellow        | 14.3   | 14.4  | 15.0        | 15.4  |
| SnI <sub>2</sub> (O <sub>2</sub> R)(bipy)                                     | Orange        | 17.4   | 17.3  | 36.8        | 37.0  |
| Sn(O <sub>2</sub> R)(O <sub>2</sub> C <sub>6</sub> Br <sub>4</sub> )(bipy)    | Green-beige   | 13.7   | 13.9  |             |       |
| Sn(O <sub>2</sub> R)(O <sub>2</sub> C <sub>6</sub> Cl <sub>4</sub> )(bipy)    | Orange-yellow | 16.8   | 16.9  |             |       |
| <i>(iii)</i> O <sub>2</sub> R = O <sub>2</sub> C <sub>6</sub> Br <sub>4</sub> |               |        |       |             |       |
| Sn(O <sub>2</sub> R)  | Cream-yellow  | 22.0   | 21.9  |             |       |
| Sn(O <sub>2</sub> R)(phen)  | Orange        | 16.6   | 16.4  |             |       |
| [PPh <sub>4</sub> ][SnBr(O <sub>2</sub> R)]                                   | Yellow        | 12.5   | 12.3  |             |       |
| [NBu <sub>4</sub> ][SnI(O <sub>2</sub> R)]                                    | Yellow        | 13.2   | 13.1  |             |       |
| SnI <sub>2</sub> (O <sub>2</sub> R)(bipy)                                     | Yellow        | 12.4   | 12.5  |             |       |
| Sn(O <sub>2</sub> R) <sub>2</sub> (bipy)                                      | Gold-yellow   | 10.8   | 10.6  |             |       |
| Sn(O <sub>2</sub> R)(O <sub>2</sub> C <sub>6</sub> Cl <sub>4</sub> )(bipy)    | Green-yellow  | 12.8   | 12.6  |             |       |
| <i>(iv)</i> O <sub>2</sub> R = O <sub>2</sub> C <sub>12</sub> H <sub>8</sub>  |               |        |       |             |       |
| Sn(O <sub>2</sub> R)  | Colourless    | 39.3   | 39.2  |             |       |
| Sn(O <sub>2</sub> R)(phen)  | Orange        | 24.9   | 24.6  |             |       |
| [PPh <sub>4</sub> ][SnBr(O <sub>2</sub> R)]                                   | Cream-yellow  | 16.8   | 16.5  | 11.3        | 11.1  |
| SnI <sub>2</sub> (O <sub>2</sub> R)(bipy)                                     | Golden yellow | 16.9   | 16.7  | 35.5        | 35.6  |
| Sn(O <sub>2</sub> R)(O <sub>2</sub> C <sub>6</sub> Cl <sub>4</sub> )(bipy)    | Yellow        | 17.1   | 16.9  |             |       |
| Sn(O <sub>2</sub> R)(O <sub>2</sub> C <sub>6</sub> Br <sub>4</sub> )(bipy)    | Yellow        | 13.7   | 13.5  |             |       |

<sup>a</sup> Found: C, 31.6; H, 1.70. C<sub>6</sub>H<sub>4</sub>O<sub>2</sub>Sn requires C, 31.8; H, 1.80%. <sup>b</sup> Found: C, 43.8; H, 2.25. C<sub>10</sub>H<sub>6</sub>O<sub>2</sub>Sn requires C, 43.4; H, 2.20%.

was collected by filtration, washed with acetonitrile (5 cm<sup>3</sup>) and then diethyl ether (5 cm<sup>3</sup>), and dried *in vacuo*.

When the cell solution contained both R(OH)<sub>2</sub> and phen (Table 1), the product which precipitated, and which was collected and dried in the manner just described, was the appropriate 1:1 adduct.

Analytical results for all products are presented in Table 2.

**Adducts of Sn(O<sub>2</sub>R) Compounds.**—(i) When Sn(O<sub>2</sub>R) compounds prepared electrochemically were subsequently treated with either phen or bipy, the product was the 1:1 adduct, identical in the case of phen to the materials prepared by the direct method. In a typical experiment, bipy (0.16 g, 1.02 mmol) was added to a suspension of Sn(O<sub>2</sub>C<sub>6</sub>H<sub>4</sub>) (0.23 g, 1.00 mmol) in acetonitrile (20 cm<sup>3</sup>). The colourless solid immediately became golden-yellow. After a period of stirring (4 h, room temperature), the solid was collected, washed with benzene and then acetonitrile, and dried *in vacuo*; yield of Sn(O<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)(bipy) 0.35 g, 92%. Analogous reactions had yields in this same order.

(ii) A suspension of Sn(O<sub>2</sub>C<sub>6</sub>H<sub>4</sub>) (0.35 g, 1.54 mmol) in acetonitrile (20 cm<sup>3</sup>) was treated with a solution of PPh<sub>4</sub>Br (0.65 g, 1.54 mmol) in the same solvent (20 cm<sup>3</sup>). The colourless solid gradually turned yellow over *ca.* 1 h. The stirring was continued overnight, after which the solid was collected, washed with acetonitrile and then diethyl ether, and dried *in vacuo*; yield of [PPh<sub>4</sub>][SnBr(O<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)] 0.90 g, 91%. Similar reactions

involving other Sn(O<sub>2</sub>R) compounds gave the corresponding products in yields of 85% or better.

(iii) Addition of a solution of NBu<sub>4</sub>I (0.37 g, 1 mmol) in acetonitrile (20 cm<sup>3</sup>) to Sn(O<sub>2</sub>C<sub>6</sub>H<sub>4</sub>) (0.23 g, 1 mmol) gave a yellow solution. After 4 h, the mixture was filtered to remove impurities and *ca.* 90% of the solvent evaporated *in vacuo*; addition of diethyl ether (10 cm<sup>3</sup>) to the remaining liquid caused precipitation of a yellow solid, which was collected, washed with diethyl ether and dried *in vacuo*; yield of [NBu<sub>4</sub>][SnI(O<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)] 0.54 g, 90%.

(iv) An analogous reaction between a solution of NBu<sub>4</sub>I (0.37 g, 1 mmol) in CH<sub>3</sub>CN (20 cm<sup>3</sup>) and Sn(O<sub>2</sub>C<sub>10</sub>H<sub>6</sub>)(phen) (0.46 g, 1 mmol) gave the yellow-orange [NBu<sub>4</sub>][SnI(O<sub>2</sub>C<sub>10</sub>H<sub>6</sub>)(phen)] in 88% yield.

**Oxidation of Sn(O<sub>2</sub>R) Compounds.**—(i) Sn(O<sub>2</sub>C<sub>6</sub>H<sub>4</sub>) (0.40 g, 1.76 mmol) was suspended in acetonitrile (20 cm<sup>3</sup>), and a mixture of iodine (0.45 g, 1.76 mmol) and bipy (0.27 g, 1.76 mmol) in acetonitrile (20 cm<sup>3</sup>) added. The white solid immediately turned orange; stirring was continued overnight, and the resultant solid collected, washed, and dried as in other experiments; yield of SnI<sub>2</sub>(O<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)(bipy) 0.98 g, 88%. Analogous results were obtained with 2,3-dihydroxynaphthalene and tetrabromo-1,2-dihydroxybenzene derivatives.

(ii) Sn(O<sub>2</sub>C<sub>6</sub>H<sub>4</sub>) (0.48 g, 2.1 mmol) was dissolved in acetonitrile (20 cm<sup>3</sup>) and bipy (0.33 g, 2.1 mmol) added. A

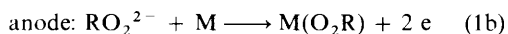
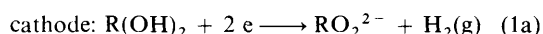
period of stirring (2 h) was followed by the addition of *o*-O<sub>2</sub>C<sub>6</sub>Cl<sub>4</sub> (0.52 g, 2.1 mmol) in the same solvent. An immediate change of colour to orange was observed; after 4 h stirring, the solid, which by then had become beige, was collected, washed, and dried *in vacuo*. The product is the bipy complex of the oxidative adduct Sn(O<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)(O<sub>2</sub>C<sub>6</sub>Cl<sub>4</sub>); yield 1.25 g, 94%. Parallel results were obtained with derivatives of other 1,2-diols, and the oxidative addition reaction was also identified when these substrates were treated with tetrabromo-*o*-quinone.

(iii) CH<sub>3</sub>I (0.23 g, 1.59 mmol, 0.15 cm<sup>3</sup>) was stirred with a suspension of Sn(O<sub>2</sub>C<sub>6</sub>H<sub>4</sub>) (0.36 g, 1.59 mmol) in acetonitrile (20 cm<sup>3</sup>) for 6 h at room temperature. The solid recovered at the end of this period was identified as the original Sn(O<sub>2</sub>C<sub>6</sub>H<sub>4</sub>). A similar conclusion emerged from a similar experiment involving CH<sub>3</sub>I and Sn(O<sub>2</sub>C<sub>12</sub>H<sub>8</sub>).

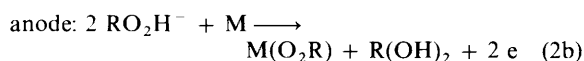
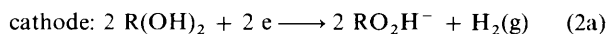
(iv) Sn(O<sub>2</sub>C<sub>6</sub>H<sub>4</sub>) (0.16 g, 0.69 mmol) was suspended in a solution of diphenyl disulphide (0.15 g, 0.69 mmol) in toluene (20 cm<sup>3</sup>) for 6 h at room temperature. The solid recovered was the initial Sn(O<sub>2</sub>C<sub>6</sub>H<sub>4</sub>), as was the case when Sn(O<sub>2</sub>C<sub>10</sub>H<sub>6</sub>) was treated with an equimolar quantity of diphenyl diselenide.

## Results and Discussion

*Electrochemical Synthesis.*—The anodic oxidation of tin in the presence of aromatic 1,2-diols is a simple and efficient route to compounds which can otherwise only be obtained by rather cumbersome methods. Although the experiments were conducted on a relatively small scale, there is little difficulty in producing larger quantities either by using larger cells or by running several cells in series. The electrochemical efficiency, defined as moles of metal dissolved per Faraday of charge, is  $0.52 \pm 0.02$  mol F<sup>-1</sup> for the synthesis of both Sn(O<sub>2</sub>R) and Sn(O<sub>2</sub>R)(phen) compounds, showing clearly that adduct formation occurs *via* a process occurring after the anodic formation of Sn(O<sub>2</sub>R). This *E*<sub>F</sub> value is capable of two interpretations. In the simplest, one has the sequence (1) so that



current is carried by the catechol dianion. The alternative, (2), involves the loss of only one hydrogen atom, with the resultant monoanions migrating and eventually reacting at the anode in pairs. The same choice of mechanisms also exists in



systems involving the direct electrochemical synthesis of  $\alpha,\omega$ -dithiolato derivatives of divalent metals from HS(CH<sub>2</sub>)<sub>*n*</sub>SH,<sup>12</sup> and studies to identify the species generated at the cathode of such cells are planned. This point aside, the mechanism is in keeping with earlier work on electrochemical synthesis.

The products were characterized analytically, and by i.r. and n.m.r. spectroscopy. These results are discussed below. The physical properties of Sn(O<sub>2</sub>C<sub>6</sub>H<sub>4</sub>) prepared electrochemically are identical with those reported by Cocks and Zuckerman,<sup>9</sup> and similar to those of the other Sn(O<sub>2</sub>R) compounds obtained in this work. All are stable to atmospheric exposure, to heat, and to hydrolysis, they do not melt below *ca.* 300 °C, and they are insoluble in common organic solvents other than strong bases such as pyridine, triethylamine, or dimethyl sulphoxide. These properties, along with the Lewis acid properties (see below) suggest cross-linking by O → Sn donation to give a homopolymer in the solid state. Solvation would then be responsible for the solubility in basic solvents.

*Adducts of Sn(O<sub>2</sub>R).*—Given the physical properties of these tin(II) compounds, and the preparative methods hitherto available, it is perhaps not surprising that the chemistry of these compounds has not been previously investigated. Tin(II) halides are both acceptors and donors, and we find that this ambivalence also applies to Sn(O<sub>2</sub>R) compounds. Both bipy and phen form 1:1 complexes with each of the four 1,2-diolates prepared, and with PPh<sub>2</sub>Br and NBu<sup>n</sup><sub>4</sub>I we obtained the anionic complexes [SnX(O<sub>2</sub>R)]<sup>-</sup> (X = Br or I). These salts are electrolytes in dimethyl sulphoxide, acetonitrile, or nitromethane (Table 3). It seems probable that the structure of the [SnX(O<sub>2</sub>R)]<sup>-</sup> anions is similar to that<sup>13</sup> of [GeI(acac)]<sup>-</sup> (acac = acetylacetonate), and some degree of association in solution could well be responsible for the slight lowering of the conductivity from the normal value in the case of some of these salts in dimethyl sulphoxide. The anion [SnI(O<sub>2</sub>C<sub>10</sub>H<sub>6</sub>)(phen)]<sup>-</sup> presents an interesting problem, in that this is apparently a five-co-ordinate tin(II) complex. The significance or otherwise of the lone pair on tin(II) in these compounds has not been established, but it is worth noting that the structural evidence<sup>14</sup> on the homoleptic Sn(OR)<sub>2</sub> compounds (R = 2,4,6-tri-*t*-butylphenyl or 4-methyl-2,6-di-*t*-butylphenyl) suggests that this may be an important steric feature of the parent Sn(O<sub>2</sub>R) compounds.

*Oxidation of Sn(O<sub>2</sub>R).*—Whatever the stereochemical influence of the non-bonding pair of electrons on tin, there can be no doubt about their participation in the reaction with iodine, where the product is the six-co-ordinate tin(IV) complex SnI<sub>2</sub>(O<sub>2</sub>R)(bipy) (or phen). Equally, in the reaction with *o*-O<sub>2</sub>C<sub>6</sub>X<sub>4</sub> (X = Cl or Br), the basic process is clearly that of

Table 3. Molar conductivities of salts of [SnX(O<sub>2</sub>R)]<sup>-</sup> anions

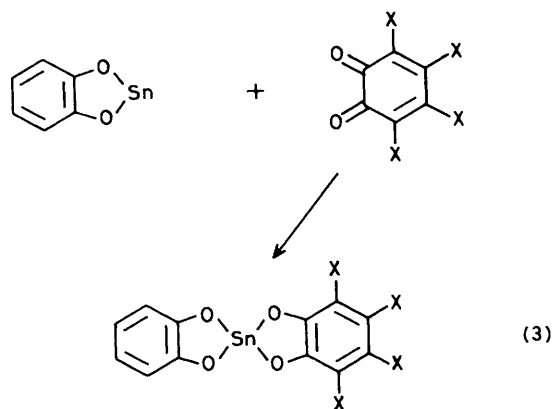
| Compound  | Solvent <sup>a</sup>               | Molar conductivity (ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup> ) | Standard values of 1:1 electrolytes <sup>b</sup> (ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup> ) |
|---|------------------------------------|---|---|
| [PPh <sub>4</sub> ][SnBr(O <sub>2</sub> C <sub>6</sub> H <sub>4</sub> )]                    | (CH <sub>3</sub> ) <sub>2</sub> SO | 44  | 50–70   |
| [NBu <sup>n</sup> <sub>4</sub> ][SnI(O <sub>2</sub> C <sub>6</sub> H <sub>4</sub> )]        | CH <sub>3</sub> CN                 | 132   | 120–160   |
| [PPh <sub>4</sub> ][SnBr(O <sub>2</sub> C <sub>10</sub> H <sub>6</sub> )]                   | CH <sub>3</sub> NO <sub>2</sub>    | 92  | 75–95   |
| [NBu <sup>n</sup> <sub>4</sub> ][SnI(O <sub>2</sub> C <sub>10</sub> H <sub>6</sub> )]       | (CH <sub>3</sub> ) <sub>2</sub> SO | 53  | 50–70   |
| [NBu <sup>n</sup> <sub>4</sub> ][SnI(O <sub>2</sub> C <sub>10</sub> H <sub>6</sub> )(phen)] | (CH <sub>3</sub> ) <sub>2</sub> SO | 42  | 50–70   |
| [PPh <sub>4</sub> ][SnBr(O <sub>2</sub> C <sub>6</sub> Br <sub>4</sub> )]                   | (CH <sub>3</sub> ) <sub>2</sub> SO | 46  | 50–70   |
| [NBu <sup>n</sup> <sub>4</sub> ][SnI(O <sub>2</sub> C <sub>6</sub> Br <sub>4</sub> )]       | (CH <sub>3</sub> ) <sub>2</sub> SO | 48  | 50–70   |
| [PPh <sub>4</sub> ][SnBr(O <sub>2</sub> C <sub>12</sub> H <sub>8</sub> )]                   | (CH <sub>3</sub> ) <sub>2</sub> SO | 50  | 50–70   |
| [NBu <sup>n</sup> <sub>4</sub> ][SnI(O <sub>2</sub> C <sub>12</sub> H <sub>8</sub> )]       | CH <sub>3</sub> CN                 | 140   | 120–160   |

<sup>a</sup> Concentration *ca.* 1 mmol dm<sup>-3</sup>. <sup>b</sup> Values from W. J. Geary, *Coord. Chem. Rev.*, 1971, 7, 81.

**Table 4.** Representative  $^1\text{H}$  and  $^{13}\text{C}$  n.m.r. spectra of  $\text{Sn}(\text{O}_2\text{R})$  compounds in  $[\text{}^2\text{H}_6]$ dimethyl sulphoxide; resonances in p.p.m. from  $\text{SiMe}_4$ 

| Compound   | $^1\text{H}$ *    | Assignment  | $^{13}\text{C}$      | Assignment         |
|--|-------------------|---|----------------------|--------------------|
| 1,2- $\text{C}_6\text{H}_4(\text{OH})_2$                             | 7.8(br) (2)       | OH  | 145.58               | $\text{C}^{1,2}$   |
|  | 6.8(m) (4)        | aryl  | 119.83               | $\text{C}^{4,5}$   |
|  |                   |   | 116.13               | $\text{C}^{3,6}$   |
| $\text{Sn}(o\text{-O}_2\text{C}_6\text{H}_4)$                        | 6.54(m) (2)       | aryl  | 155.71               | $\text{C}^{1,2}$   |
|  | 6.38(m) (2)       |   | 116.34               | $\text{C}^{4,5}$   |
| $\text{Sn}(o\text{-O}_2\text{C}_6\text{H}_4)(\text{phen})$           | 9.18(m) (2)       | $\left. \begin{array}{l} \text{H}^2, \text{H}^9 \\ \text{H}^4, \text{H}^7 \\ \text{H}^5, \text{H}^6 \\ \text{H}^3, \text{H}^8 \end{array} \right\} \text{phen}$ | 114.69               | $\text{C}^{3,6}$   |
|  | 8.66(m) (2)       |   |                      |                    |
|  | 8.06(m) (2)       |   |                      |                    |
|  | 7.88(m) (2)       |   |                      |                    |
|  | 6.2—6.5(m) (4)    |   | $\text{O}_2\text{R}$ |                    |
| $\text{SnI}_2(o\text{-O}_2\text{C}_6\text{H}_4)(\text{bipy})$        | 8.80(m) (2)       | $\left. \begin{array}{l} \text{H}^{3,3'} \\ \text{H}^{4,4'} \\ \text{H}^{5,5'} \\ \text{H}^{6,6'} \end{array} \right\} \text{bipy}$                             | 149.52               | $\text{C}^{3,3'}$  |
|  | 8.54(m) (2)       |   | 147.28               | $\text{C}^{1,1'}$  |
|  | 8.22(m) (2)       |   | 141.30               | $\text{C}^{4,4'}$  |
|  | 7.71(m) (2)       |   | 126.33               | $\text{C}^{6,6'}$  |
|  | 6.66(m) (2)       | $\text{O}_2\text{R}$  | 122.81               | $\text{C}^{5,5'}$  |
|  | 6.46(m) (2)       |   |                      |                    |
| 2,3- $\text{C}_{10}\text{H}_6(\text{OH})_2$                          | 9.53(s) (2)       | OH  | 150.03               | $\text{C}^{1,2}$   |
|  | 7.58(m) (2)       | aryl  | 117.45               | $\text{C}^{4,5}$   |
|  | 7.18(m) (2)       |   | 113.50               | $\text{C}^{3,6}$   |
|  | 7.13(s) (2)       |   | 147.04               | $\text{C}^{2,3}$   |
|  |                   |   | 129.01               | $\text{C}^{4a,8a}$ |
|  |                   |   | 125.74               | $\text{C}^{1,4}$   |
|  |                   |   | 123.10               | $\text{C}^{5,8}$   |
|  | 109.79            |   | $\text{C}^{6,7}$     |                    |
| $\text{Sn}(2,3\text{-O}_2\text{C}_{10}\text{H}_6)$                   | 7.45(m) (2)       | aryl  | 158.09               | $\text{C}^{2,3}$   |
|  | 6.99(m) (2)       |   | 128.78               | $\text{C}^{4a,8a}$ |
|  | 6.67(s) (2)       |   | 124.83               | $\text{C}^{1,4}$   |
|  |                   |   | 120.72               | $\text{C}^{5,8}$   |
|  |                   |   | 107.61               | $\text{C}^{6,7}$   |
| $[\text{PPh}_4][\text{SnBr}(2,3\text{-O}_2\text{C}_{10}\text{H}_6)]$ | 7.98—7.69(m) (20) | $\text{PPh}_4$  |                      |                    |
|  | 7.27(m) (2)       | $\text{O}_2\text{R}$  |                      |                    |
|  | 6.90(m) (2)       |   |                      |                    |
|  | 6.68(s) (2)       |   |                      |                    |
|  |                   |   |                      |                    |
| $\text{SnI}_2(2,3\text{-O}_2\text{C}_{10}\text{H}_6)(\text{bipy})$   | 8.82(m) (2)       | $\left. \begin{array}{l} \text{H}^{3,3'} \\ \text{H}^{4,4'} \\ \text{H}^{5,5'} \\ \text{H}^{6,6'} \end{array} \right\} \text{bipy}$                             | 150.52               | $\text{C}^{3,3'}$  |
|  | 8.57(m) (2)       |   | 147.49               | $\text{C}^{1,1'}$  |
|  | 8.29(m) (2)       |   | 140.86               | $\text{C}^{4,4'}$  |
|  | 7.76(m) (2)       |   | 126.10               | $\text{C}^{6,6'}$  |
|  | 7.48(m) (2)       | $\text{O}_2\text{R}$  | 122.53               | $\text{C}^{5,5'}$  |
|  | 7.0—7.1(m) (4)    |   | 151.04               | $\text{C}^{2,3}$   |
|  |                   |   | 128.62               | $\text{C}^{4a,8a}$ |
|  |                   |   | 125.26               | $\text{C}^{1,4}$   |
| 1,2- $\text{C}_6\text{Br}_4(\text{OH})_2$                            | 10.2(vbr)         | OH  | 121.77               | $\text{C}^{5,8}$   |
|  | —                 | no OH   | 107.23               | $\text{C}^{6,7}$   |
| $\text{Sn}(o\text{-O}_2\text{C}_6\text{Br}_4)$                       | 8.72(m) (2)       | $\left. \begin{array}{l} \text{H}^{3,3'} \\ \text{H}^{4,4'} \\ \text{H}^{5,5'} \\ \text{H}^{6,6'} \end{array} \right\} \text{bipy}$                             |                      |                    |
|  | 8.43(m) (2)       |   |                      |                    |
|  | 8.03(m) (2)       |   |                      |                    |
|  | 7.54(m) (2)       |   |                      |                    |
|  |                   |   |                      |                    |
| $\text{SnI}_2(o\text{-O}_2\text{C}_6\text{Br}_4)(\text{bipy})$       | 8.82(m) (2)       | $\left. \begin{array}{l} \text{H}^{3,3'} \\ \text{H}^{4,4'} \\ \text{H}^{5,5'} \\ \text{H}^{6,6'} \end{array} \right\} \text{bipy}$                             |                      |                    |
|  | 8.57(m) (2)       |   |                      |                    |
|  | 8.24(m) (2)       |   |                      |                    |
|  | 7.72(m) (2)       |   |                      |                    |
|  |                   |   |                      |                    |
| $(\text{C}_6\text{H}_4\text{OH-2})_2$                                | 9.30(br) (2)      | OH  |                      |                    |
|  | 7.3—6.9(m) (8)    | aryl  |                      |                    |
| $\text{Sn}(2,2'\text{-O}_2\text{C}_{12}\text{H}_8)$                  | 7.2—6.8(m) (8)    | aryl  |                      |                    |
|  | 9.07(m) (2)       | phen  |                      |                    |
|  | 8.46(m) (2)       |   |                      |                    |
|  | 7.96(m) (2)       |   |                      |                    |
|  | 7.76(m) (2)       |   |                      |                    |
| $\text{SnI}_2(2,2'\text{-O}_2\text{C}_{12}\text{H}_8)(\text{bipy})$  | 7.11—6.8(m) (8)   | aryl  |                      |                    |
|  | 8.84(m) (2)       | bipy  |                      |                    |
|  | 8.58(m) (2)       |   |                      |                    |
|  | 8.40(m) (2)       |   |                      |                    |
|  | 7.87(m) (2)       |   |                      |                    |
| $\text{Sn}(2,2'\text{-O}_2\text{C}_{12}\text{H}_8)(\text{phen})$     | 7.1—6.8(m) (8)    | aryl  |                      |                    |

\* s = Singlet, m = multiplet, br = broad. Numbers in parentheses show relative integrated intensities.



oxidative addition although the final isolated product is in the form of an adduct with bipy. Reaction (3) is exactly parallel to that of tin(II) halides with these same tetrahalogeno-o-quinones,<sup>15</sup> as demonstrated by the spectroscopic evidence discussed below. In the case of  $\text{SnX}_2$ , the conclusion is also buttressed by X-ray crystallographic studies.

In contrast, we did not observe any reaction between typical  $\text{Sn}(\text{O}_2\text{R})$  compounds and  $\text{CH}_3\text{I}$ , although this latter substance does react<sup>16</sup> with  $\text{SnI}_2$ , under conditions much more severe than those used in our work. Similarly, the oxidative addition of  $\text{SnPh}_2$  to  $(\text{PhCH}_2\text{S})_2$  to give  $\text{SnPh}_2(\text{SCH}_2\text{Ph})_2$ <sup>17</sup> is not paralleled by any reaction between  $\text{Sn}(\text{O}_2\text{R})$  and  $\text{Ph}_2\text{S}_2$  or  $\text{Ph}_2\text{Se}_2$  under the conditions used. Further studies of these systems are planned.

**Spectroscopic Results.**—The identification of the  $\text{Sn}(\text{O}_2\text{R})$  compounds, and of their derivatives, depends on both analytical and spectroscopic evidence. The i.r. spectra of all the compounds studied demonstrate the absence of  $\nu(\text{O}-\text{H})$  of the parent diols, observed at  $3\,200\text{--}3\,400\text{ cm}^{-1}$ ;  $\nu(\text{C}-\text{O})$ , at ca.  $1\,280\text{--}1\,230\text{ cm}^{-1}$  in the parent diols, is observed at  $1\,254$  ( $\text{R} = o\text{-O}_2\text{C}_6\text{H}_4$ ),  $1\,257$  ( $\text{R} = 2,3\text{-O}_2\text{C}_{10}\text{H}_6$ ),  $1\,222$  ( $\text{R} = o\text{-O}_2\text{C}_6\text{Br}_4$ ), and  $1\,249 + 1\,212\text{ cm}^{-1}$  ( $\text{R} = \text{O}_2\text{C}_{12}\text{H}_8$ ) in the tin(II) compounds. In the adducts with bipy or phen, we also observed the characteristic i.r. spectrum of these complexed ligands. With the products of the reaction of  $\text{Sn}(\text{O}_2\text{R})$  with  $o\text{-O}_2\text{C}_6\text{X}_4$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ), the most important observation is that  $\nu(\text{C}=\text{O})$  of the *o*-quinone, at ca.  $1\,700\text{ cm}^{-1}$ , is absent in every case, being replaced by bands at  $1\,430\text{m} + 1\,240\text{s cm}^{-1}$  in the  $\nu(\text{C}-\text{O})$  manifold; similar results have been observed in the  $\text{SnX}-o\text{-O}_2\text{C}_6\text{X}_4$  systems.<sup>15</sup>

The  $^1\text{H}$  and  $^{13}\text{C}$  n.m.r. spectra of a number of compounds are presented in Table 4, with assignments which follow those in previous work.<sup>15</sup> These results are selected as representative examples only, with the results for compounds of a given group of diolato complexes being essentially identical. The  $^1\text{H}$

assignments for bipy are based on the work of Castellano *et al.*<sup>18</sup> and those for phen on that of Dove and Hallett.<sup>19</sup> The  $^{13}\text{C}$  values and assignments agree reasonably well with those of Holmes *et al.*<sup>20</sup> for  $o\text{-O}_2\text{C}_6\text{H}_4^{2-}$  and  $2,3\text{-O}_2\text{C}_{10}\text{H}_6^{2-}$  complexes of silicon(IV), although their numbering system is different from that used here.

While some of the detailed assignments may be open to revision, there is no doubt that both classes of n.m.r. spectra confirm the presence of the appropriate  $\text{RO}_2^{2-}$  ligand, and of the neutral bidentate donor. Taken together with the i.r. evidence, the formulation of the products of the electrochemical preparations, of the  $\text{Sn}(\text{O}_2\text{R})$  adducts, and of the oxidative addition products, is well established.

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