

## Hydrogen Bonded Molecular Complexes of Cyclic Carboxyaryl Sulfonium Salts with Chlorides: Syntheses and Molecular Structures

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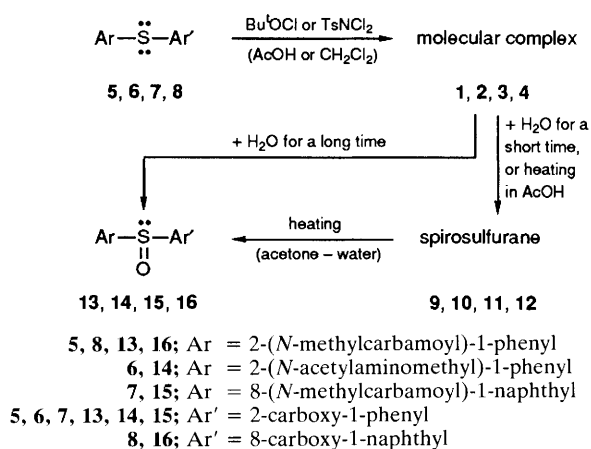
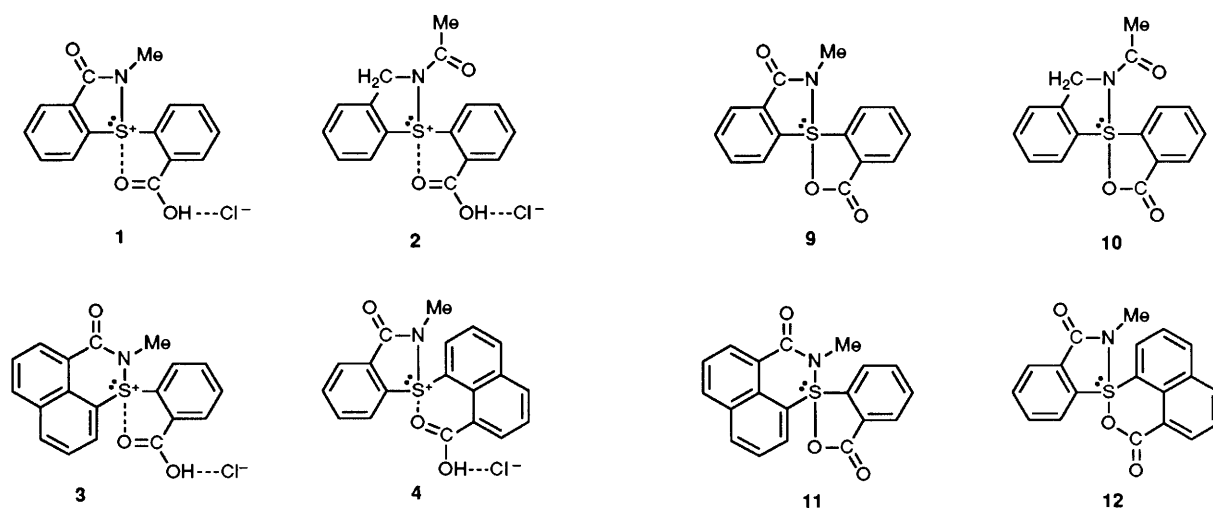
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Intermediates of spiro-sulfurane formations are prepared from carboxyaryl sulfides with chlorinating agents; the molecular structures determined by X-ray diffraction show distorted trigonal bipyramidal geometry about the sulfur atom with  $S^+ \cdots O=$ ,  $S^+ \cdots Cl^-$  and  $O-H \cdots Cl^-$  interactions.

In an earlier paper we suggested a mechanism for the formation of diaryldiacloxy-spiro-sulfuranes from the corresponding carboxyaryl sulfides with halogenating agents, citing kinetic evidence for the existence of chlorosulfonium salt types of intermediates in the first step of the reaction.<sup>1</sup> We have also reported on stable intermediates characteristic for

the subsequent steps with preparations and molecular structures of a monocyclic sulfonium salt type showing strong  $S^+ \cdots O=$  intramolecular interactions.<sup>2,3,4</sup> In this paper we present the syntheses and some reactions of the species **1-4** which can be regarded as intermediates in the last stage of spiro-sulfurane formations from carboxyaryl sulfides with



Scheme 1

chlorinating agents. Their molecular structures determined by X-ray diffraction possess relatively strong  $\text{S}^+\cdots\text{O}=\text{C}, \text{OH}\cdots\text{Cl}^-$  and weak  $\text{S}^+\cdots\text{Cl}^-$  intramolecular interactions.

1-(2'-Carboxyphenyl)-2,3-dihydromethyl-3-oxo-2,1-benzazathiol-1-ium chloride **1**, 1-(2'-carboxyphenyl)-2-acetyl-3*H*-2,1-benzazathiol-1-ium chloride **2**, 1-(2'-carboxyphenyl)-2,3-dihydromethyl-3-oxo-1,2-naphtho[1,8-*d,e*]thiazin-1-ium chloride **3** and 1-(8'-carboxynaphthyl)-2,3-dihydromethyl-3-oxo-2,1-benzazathiol-1-ium chloride **4** were prepared from the corresponding sulfides **5**, **6**, **7** and **8**, respectively, with a slight excess of *tert*-butyl hypochlorite or dichloramine-T in dry AcOH (**1**, **2**) or in  $\text{CH}_2\text{Cl}_2$  (**3**, **4**) at room temperature for 4 h (yields: 21% for **1**, 85–95% for **2–4**). The solid products were isolated from the reaction mixture by filtration (in the cases of **1** and **4** after addition of diethyl ether).<sup>†</sup>

<sup>†</sup> All new products gave satisfactory microanalyses. The molecular structures of spirosulfuranes **9**, **10**, **11** and **12** as determined by X-ray diffraction method show slightly distorted trigonal bipyramidal geometry about the sulfur, and will be published elsewhere.

**Selected spectroscopic data:** IR[ $\nu(\text{C}=\text{O})/\text{cm}^{-1}$  KBr]: for **1**: 1708vs, 1632vs; for **2**: 1692vs, 1650vs; for **3**: 1695vs, 1660vs, for **4**: 1711vs, 1645vs; for **9**: 1691vs, 1648vs; for **10**: 1668vs, 1633vs; for **11**: 1662vs, 1639vs; for **12**: 1691vs, 1630vs;  $\nu(\text{S}=\text{O})/\text{cm}^{-1}$  (KBr) for **13**: 1028vs; for **14**: 1015vs; for **15**: 1021vs; for **16**: 985vs. <sup>1</sup>H NMR (80 MHz): for **1** ( $\text{CD}_3\text{OD}$ ):  $\delta$  3.50 (s, Me); for **2** ( $\text{CD}_3\text{OD}-[2\text{H}_6]\text{DMSO}$ ):  $\delta$  2.54 (s, Me), 5.74 (q,  $\text{CH}_2$ ,  $J$  14 Hz); for **3** ( $\text{CD}_3\text{OD}$ ):  $\delta$  3.70 (s, Me); for **4** ( $\text{CDCl}_3-\text{CD}_3\text{OD}$ )  $\delta$  3.08 (s, Me); for **9** ( $\text{CD}_3\text{OD}$ ): 2.90 (s, Me); for **10** ( $\text{CD}_3\text{OD}-[2\text{H}_6]\text{DMSO}$ ):  $\delta$  2.46 (s, Me), 5.55 (s,  $\text{CH}_2$ ); for **11** ( $\text{CD}_3\text{OD}$ ):  $\delta$  3.64 (s, Me); for **12** ( $\text{CDCl}_3-\text{CD}_3\text{OD}$ ):  $\delta$  2.90 (s, Me).

Crystals of the molecular complexes **1**, **2**, **3** and **4** are stable at room temperature, but on contacting water or aqueous  $\text{KHCO}_3$  solution they immediately transform as a solid product into the corresponding spirosulfuranes **9**, **10**, **11** and **12**, respectively, due to the nucleophilic attack of the carbonyl oxygen on the sulfonium centre with loss of the preformed hydrogen chloride (after immediate drying *in vacuo* over  $\text{P}_2\text{O}_5$ , yield 50–95%). Similar transformations can be observed when **1**, **2**, **3** and **4** are boiled in dry AcOH for 1.5 h (after evaporation of the solvent, yield 100% for pure spirosulfuranes **9–12**).<sup>‡</sup>

Both the molecular complexes **1–4** and the spirosulfuranes **9–12** hydrolyse in aqueous solutions into the corresponding sulfoxides **13–16**, respectively; (i) by adding equal volumes of water to the saturated solutions of **1**, **2**, **3** and **4** in dry methanol then allowing to stand at 25 °C for 2 days, (ii) by boiling the solutions of **9**, **10**, **11** and **12** in 8:1 acetone–water for 2 h. These observations support experimentally the assumption that the sulfoxide formation from sulfide proceeds through sulfonium salt and sulfurane species having trigonal bipyramidal arrangements about the central sulfur atom (*cf.* ref. 5).

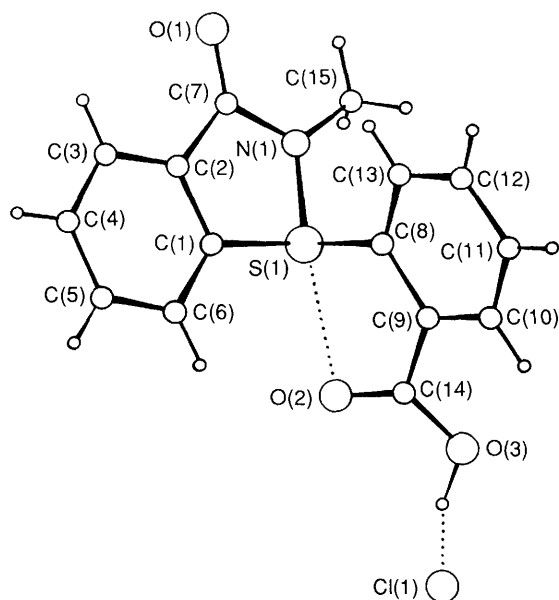
The molecular structures of **1** and **3** as determined from single crystal X-ray diffraction<sup>‡</sup> are shown in Figs. 1 and 2 with

<sup>‡</sup> Single crystals for X-ray analysis both of **1** and **3** were obtained by crystallization from methanol–diethyl ether solvent mixture with *m.p.s* 318–319 °C and 170–190 °C (decomp.), respectively.

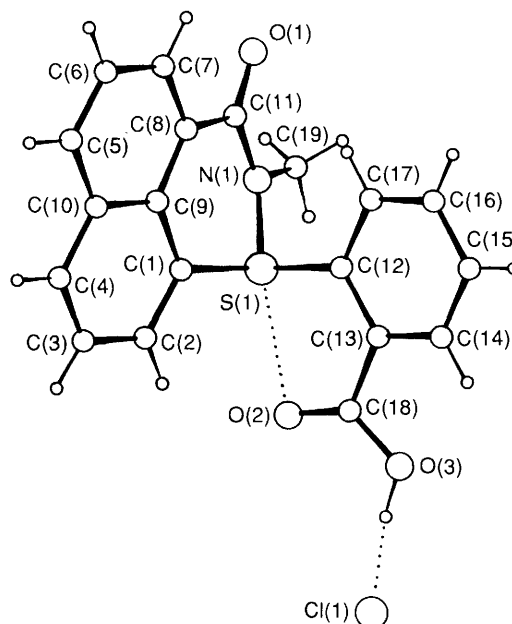
**Crystal data** for **1**:  $\text{C}_{15}\text{H}_{12}\text{ClNO}_3\text{S}$ ,  $M = 321.8$ , monoclinic, space group  $Cc$  (no. 9),  $a = 14.804(2)$ ,  $b = 7.879(2)$ ,  $c = 12.618(2)$  Å,  $\beta = 103.03(1)^\circ$ ,  $U = 1433.8(8)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.49$  g cm<sup>-3</sup>, monochromated Cu-K $\alpha$  radiation,  $\lambda = 1.54184$  Å,  $\mu = 38.1$  cm<sup>-1</sup>. Data were collected on an Enraf-Nonius CAD-4 diffractometer in the range  $1.5^\circ < \theta < 75.0^\circ$ . The structure was determined by direct methods and refined by full-matrix least-squares analysis. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were introduced in idealized positions except H[O(3)] which was located on a difference Fourier map and added to the structure factor calculations. The final  $R$  values were  $R = 0.040$ ,  $R_w = 0.054$  for 1232 reflections with  $I > 3\sigma(I)$  and for 1388 unique reflections  $R_{\text{tot}} = 0.051$ .

For **3**:  $\text{C}_{19}\text{H}_{14}\text{ClNO}_3\text{S}$ ,  $M = 371.9$ , monoclinic, space group  $P2_1/c$  (no. 14),  $a = 11.101(1)$ ,  $b = 9.638(1)$ ,  $c = 16.007(1)$  Å,  $\beta = 105.29(1)^\circ$ ,  $U = 1652.0(5)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.495$  g cm<sup>-3</sup>,  $\mu = 33.9$  cm<sup>-1</sup>. Data collection was performed on a CAD-4 using the same conditions as given above. Lorentz polarization and a linear decay correction were applied. The structure was determined by direct methods and refined by full-matrix least-squares analysis to a final  $R = 0.062$ ,  $R_w = 0.095$  for 2639 reflections taken with  $I > 3\sigma(I)$  and  $R_{\text{tot}} = 0.089$  for 3621 unique reflections. The hydrogen atoms were located on difference Fourier maps and added to the structure factor calculations, but their positions were not refined.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



**Fig. 1** Perspective view of a molecule of **1** with numbering scheme for non-hydrogen atoms. Selected interatomic distances (Å) and angles (°): S(1)–N(1) 1.695(4), S(1)–C(1) 1.767(4), S(1)–C(8) 1.824(4), C(14)–O(3) 1.321(5), C(14)–O(2) 1.224(6), S(1)···O(2) 2.512(4), S(1)···Cl(1) 3.399(2), O(3)···Cl(1) 2.903(4), and O(2)···S(1)–N(1) 172.6(3); C(1)–S(1)–C(8) 100.9(3), Cl(1)···S(1)–C(8) 176.7(2) and Cl(1)···H[O(3)]–O(3) 163.7(7).‡



**Fig. 2** Perspective view of a molecule of **3** with numbering scheme for non-hydrogen atoms. Selected interatomic distances (Å) and angles (°): S(1)–N(1) 1.655(2), S(1)–C(1) 1.769(4), S(1)–C(12) 1.817(4), C(18)–O(3) 1.310(4), C(18)–O(2) 1.208(5), S(1)···O(2) 2.638(2), S(1)···Cl(1) 3.385(1), O(3)···Cl(1) 2.913(3), and O(2)···S(1)–N(1) 166.4(2); C(1)–S(1)–C(12) 104.4(3), Cl(1)···S(1)–C(12) 154.7(1) and Cl(1)···H[O(3)]–O(3) 166.5(5).‡

selected interatomic distances and angles. X-Ray structure analyses of **1** and **3** revealed distorted trigonal bipyramidal geometries about the central sulfur atom (disregarding the chloride anion) with relatively strong S<sup>+</sup>···O=, OH···Cl<sup>−</sup>, and weak S<sup>+</sup>···Cl<sup>−</sup> close contacts (sums of van der Waals radii for S and O 3.25 Å,<sup>6</sup> for S and Cl 3.59 Å<sup>7</sup>). The interactions between sulfur and chloride are practically ionic. The geometric parameters for −C(O)OH···Cl<sup>−</sup> moieties of **1** and **3** show strongly hydrogen bonded structures, similar to those found in betaine hydrochloride.<sup>8</sup>

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