Reactions of 1,3-benzodithiole-2-thione and ethylene trithiocarbonate with benzyne generated from 2-carboxybenzenediazonium chloride: preparation of novel bicyclic sulfonium salts by trapping 1,3-dipolar cycloaddition intermediates

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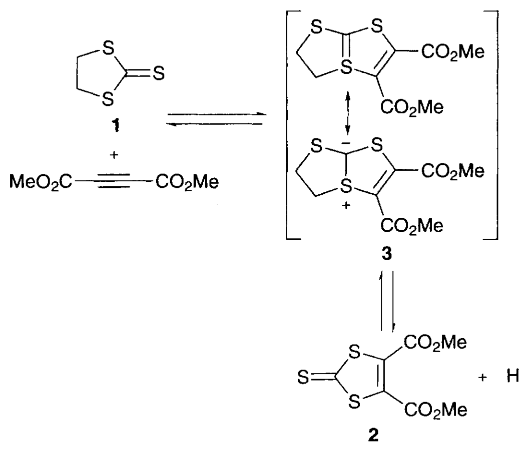
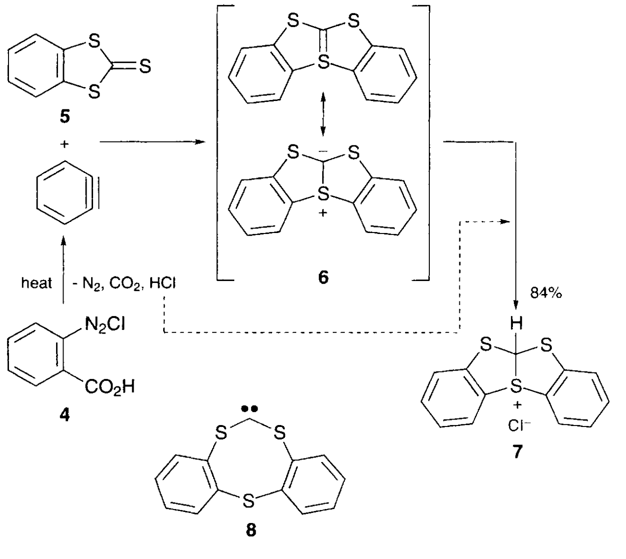
The reaction of benzyne, generated from 2-carboxybenzenediazonium chloride 4, with 1,3-benzodithiole-2-thione gives the novel bicyclic sulfonium chloride 7 by trapping of the 1,3-dipolar cycloaddition intermediate 6 with hydrogen chloride which when treated with ethylene trithiocarbonate affords 7 in one-pot in good yields.

It has long been known that dimethyl acetylenedicarboxylate (DMAD) reacts with ethylene trithiocarbonate **1** to give ethylene and the 1,3-dithiole-2-thione derivative **2**.[1] Although the reaction had been recognized as a 1,3-dipolar cycloaddition, no discrete intermediate had been proposed until Lakshmikantham and Cava suggested that the bicyclic 'tetravalent' sulfur heterocycle (a sulfonium ylide) **3** is initially produced, and that this unstable species then either reversibly reverts to the starting materials or irreversibly collapses to give the observed products.[2] There are also a large number of reactions which are synthetically important that may proceed *via* a similar mechanism.[3] However, tetravalent sulfur intermediates such as **3** have not been spectroscopically detected nor chemically trapped, though the reaction of **1** with bromocyanoacetylene afforded a thioacetyl bromide derivative which derived from the ring-opening of the initial adduct.[3i] Here we report that the reaction of 1,3-benzodithiole-2-thione **5** with benzyne, generated from 2-carboxybenzenediazonium chloride **4**,[4] allowed us to trap chemically such an intermediate to give the novel bicyclic sulfonium salt **7**, from which a number of new eight-membered ring compounds, trithiocins, are derived.

The reaction of benzyne with **5** should lead to the intermediate **6** by analogy with the reaction of **1** with DMAD. Thiabenzenes are species in which one of the carbon atoms of the benzene or benzene derivative is replaced by a tetravalent sulfur atom. Many are stable at low temperatures and can be fully characterized spectroscopically.[5] With this in mind, the two five-membered rings of **6** each of which possesses a formal cyclic 6π-electron structure corresponding to a thiathiophene, might be stabilized in their own right. In addition, the two plausible decomposition pathways of **6**, (reversion to the starting materials and carbon–sulfur bond cleavage leading to the carbene **8**), are seemingly unfavourable endothermic processes. These factors make the lifetime of **6** longer and thus enabled us to chemically trap **6**. We found that **6** was effectively trapped by hydrogen chloride to give the sulfonium salt **7** when the reaction of **5** with benzyne was carried out using the diazonium salt **4** as the benzyne precursor. Thus, heating **5** with a slight excess of **4** in refluxing 1,2-dichloroethane gave the sulfonium salt **7** in over 84% yield with an 8% recovery of compound **5**. The salt **7** corresponded to the adduct of **6**; hydrogen chloride was produced by the decomposition of compound **4**.† More important synthetically is the reaction of **1** with **4**; heating **1** with 2 equiv. of **4** in 1,2-dichloroethane under reflux in the presence of propylene oxide‡ directly afforded compounds **5** and **7** in 15 and 62% yields, respectively. This reaction enables compound **7** to be easily prepared in one-pot in large quantities.§ These observations revealed that the initial adduct **9**, formed from **1** and benzyne, decomposed to ethylene and **5** more quickly than it was trapped by hydrogen chloride to give the sulfonium salt **10**, while **6**, produced by the reaction of **5** with benzyne, is a more long-lived species and was captured by hydrogen chloride to produce **7**.¶

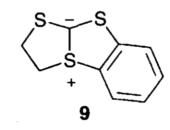
The sulfonium salt **7** is a crystalline stable compound and possesses a novel bicyclic system. Its structure was determined unequivocally spectroscopically and also by the chemical transformations described below. The salt **6** is an isomer of the carbenium salt **11** that possesses a cyclic 10π-electron structure,





though formal, satisfying Hückel's ($4n + 2$) rule and is a hitherto unknown, higher analogue of the 1,3-dithiolium ion. Although no indication for the presence of the equilibrium between **7** and **11** was obtained by ^{1}H and ^{13}C NMR, compound **7** chemically behaved as the equivalent of **11** to give new eight-membered ring compounds, the trithiocin derivatives. Thus, reduction of **7** with sodium borohydride resulted in carbon–sulfur bond cleavage to give the dibenzotrithiocin **12**[‖] in 95% yield. Attempted isolation of **6** by the deprotonation of **7** with base (pyridine, Et_3N, potassium *tert*-butoxide and BuLi) at low temperatures was unsuccessful but gave compound **14**[‖] as faint yellow crystals with a high mp and poor solubility in common organic solvents, in varying yields. For example, treatment of **7** with potassium *tert*-butoxide in THF afforded **14** in 84% yield. The formation of **14** may involve the initial formation of **6** by deprotonation, the nucleophilic attack by **6** on **7**, followed by concomitant carbon–sulfur bond cleavage of the both reactants and then deprotonation. Compound **14** is a higher analogue of tetrathiafulvalenes and might serve as a precursor for the preparation of molecular devices. Alkaline hydrolysis of **7** afforded the eight-membered sulfoxide **13**[‖] in 95% yield, which is converted to **12** on reduction with a low-valent titanium reagent in 95% yield. The formation of **13** indicated that the hydroxide ion first attacks on the sulfonium sulfur atom which is then followed by carbon–sulfur bond cleavage.

$$\mathbf{1} + \mathbf{4}\ (2\ \text{equiv}) \xrightarrow[\text{reflux}]{\text{Cl(CH}_2\text{)}_2\text{Cl, propylene oxide}} \mathbf{5}\ (15\%) + \mathbf{7}\ (62\%)$$



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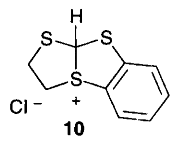

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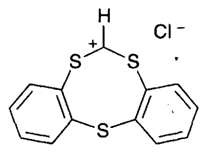

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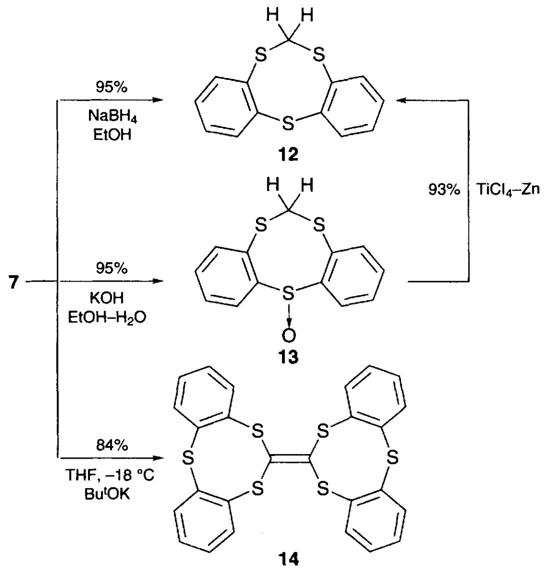

Footnotes

† The intermediate ylide produced by reaction of dimethyl sulfide with benzyne, generated by treatment of *o*-bromochlorobenzene with BuLi, is trapped with perchloric acid to give dimethylphenylsulfonium perchlorate.[6]

‡ Propylene oxide has been used as the scavenger of hydrogen chloride generated from **4**. However, the yield of **7** was not much influenced by the presence of propylene oxide probably because the reaction of hydrogen chloride with **6** is much faster than that with propylene oxide, while a considerable acceleration of the decomposition of **4** to benzyne was observed by addition of propylene oxide.

§ A mixture of 8.54 g (62.7 mmol) of **1**, 23.14 g (125.4 mmol) of **4**, and propylene oxide (25 cm^3) in 1,2-dichloroethane (800 cm^3) was heated under reflux for 2 h. The resulting yellowish orange mixture was evaporated under reduced pressure and the residue was triturated with CH_2Cl_2 (100 cm^3) to give **1** (11.50 g, 62%) as near-white solid. Chromatographic purification of the filtrate gave **5** (2.77 g, 15%). Caution should be exercised in the handling of **4** because of its explosive nature. *Selected physical and spectroscopic data* for **7**: mp 193–195 °C (dec); colourless needles (from AcOH); ^{1}H NMR (CF_3CO_2D, 400 MHz) δ_H 7.62 (4 H, m), 7.76 (2 H, m), 7.90 (1 H, s, methine) and 8.00 (2 H, m); ^{13}C NMR (CF_3CO_2D, 100 MHz) δ_c 74.18 (d, methine), 124.74 (s), 127.23 (d), 131.00 (d), 132.14 (d), 137.81 (d) and 145.85 (s); MS *m/z* 298 (M^+, Cl = 37), 296 (M^+, Cl = 35), 216, 189, 187 and 184.

¶ The reaction of **1** with benzyne, generated by thermolysis of diphenyliodonium-2-carboxylate or by oxidation of 1-aminobenzotriazole, afforded the dithiole **5** in low yields (9 and 13%).[1] The low yields of **5** show that **5** further reacts with benzyne to give **6**, which, in the absence of an appropriate trapping agent, collapsed to give a complex mixture. Thus, the reaction of **5** with benzyne, generated by decomposition of benzenediazonium-2-carboxylate, gave a complex mixture from which any products could not be isolated in a pure form.

‖ *Selected physical and spectroscopic data* for **12**: mp 157–158 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ_H 4.76 (2 H, broad s, CH_2) and 7.13–7.64 (8 H, m); ^{13}C NMR ($CDCl_3$, 50 MHz) δ_C 39.5 (CH_2), 128.3 (CH, overlapping of two signals), 133.2 (CH), 134.4 (C), 136.2 (CH) and 139.6 (C). For **13**: mp > 220 °C (dec); ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 3.48 (1 H, d, J = 15.2 Hz, CH_2), 4.66 (1 H, d, J = 15.2 Hz, CH_2), 7.32–7.36 (2 H, m), 7.52–7.58 (4 H, m) and 8.19 (2 H, d, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 45.3 (CH_2), 124.1 (CH), 129.5 (C), 130.8 (CH), 136.0 (CH) and 155.6 (C); IR (KBr) ν/cm^{-1} 1067 (SO). For **14**: mp 385–386 °C (dec); ^{1}H NMR (Me_2SO-[$^2H_6$], 400 Hz) δ_H 7.30–7.33 (m), 7.45–7.47 (m) and 7.58–7.60 (m) (intensity ratio, 2 : 1 : 1); UV–VIS (CH_2Cl_2) λ_{max} (ε) 340 nm (16750); IR (KBr) ν/cm^{-1} 1615, 1562, 1472, 1442, 1245, 1035, 842 and 748; MS *m/z* 520 (M^+), 304, 228.

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