Reaction of Cyclic Polysulfides. Oxidation of 6b,9a-Dihydroacenaphtho[1,2-*d*][1,2,3]trithiole

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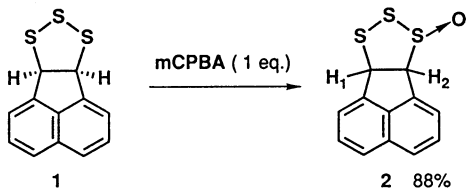
Synopsis. The treatment of 6b,9a-dihydroacenaphtho[1,2-*d*][1,2,3]trithiole with 1 equiv of *m*-chloroperbenzoic acid (mCPBA) affords the corresponding oxidized product, 6b,9a-dihydroacenaphtho[1,2-*d*][1,2,3]trithiole 7-oxide, as the sole product in 88% yield, whereas the oxidation using *N*-halosuccinimide gives 6b,9a-dihydroacenaphtho[1,2-*d*][1,2,3]trithiole 7,7-dioxide via 6b,9a-dihydroacenaphtho[1,2-*d*][1,2,3]trithiole 7-oxide. Moreover, the reaction with chloramine T gives a 1,3,2-dithiazolidine derivative in satisfactory yield.

Recently the attention of many organosulfur chemists has been directed to the chemical behavior of cyclic polysulfides[1] because some biologically active compounds involving pentathiepin or trithiole ring in the molecule were found in marine-natural products.[2] We have also studied the chemistry of cyclic polysulfides extensively in exploring several novel methods for the synthesis of these cyclic polysulfides such as benzopentathiepin and the related compounds.[3] Some new routes to sulfur-containing heterocyclic compounds from the cyclic polysulfides have been developed in the past few years.[4] In our continuous studies in this field, we have found the formation of a new cyclic polysulfide, 6b,9a-dihydroacenaphtho[1,2-*d*][1,2,3]trithiole (**1**), which is regarded as a good model for studying the chemical behavior of trithiolanes, upon treating 5*H*-benzo[*e*][1,2,3,4]tetrathiepin or 6*H*-benzo[*f*][1,2,3,4,5]pentathiocin with acenaphthylene.[5] Since, so far, only one example of oxidation of trithiolanes has been reported,[6] many problems still remain to be resolved, for example, the regio- and chemoselectivity in the reaction of cyclic polysulfides involving trithiolanes with a variety of oxidizing agents. In this paper, we wish to report some interesting oxidation of **1** with several oxidizing agents such as mCPBA, *N*-halosuccinimide (NXS), and chloramine T.

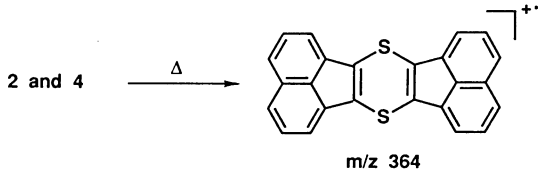
Results and Discussion

The treatment of **1** with 1 equiv of mCPBA at room temperature for 3 h gave an oxidized product, 6b,9a-dihydroacenaphtho[1,2-*d*][1,2,3]trithiole 7-oxide (**2**), regio- and chemospecifically in 88% yield (Scheme 1).[6,7] The unsymmetrical structure of **2** was confirmed spectroscopically. Thus, ^{1}H NMR spectra for two methine protons showed two sets of doublet peaks at δ=6.10 and 5.72 and the ^{13}C NMR spectra also appeared as twelve peaks based on twelve unequivalent carbons. For the mass spectra of **2**, an unexpected peak appeared at *m*/*z* =364 corresponding to diacenaphtho[1,2-*b*:1′,2′-*e*][1,4]dithiin which was formed by thermal decomposition–dimerization of **2** under the mass measurement conditions (Scheme 2).[8] The IR spectrum of **2** showed a characteristic absorption for –S–SO–group at 1075 cm^{-1}. The oxidation of **1** using 2 equivs of mCPBA or further oxidation of **2** with 1 equiv of mCPBA followed by hydrolysis resulted in the formation of 1,2-acenaphthenedisulfinic acid and generation of hydrogen sulfide as shown in Scheme 3. It is reasonable to consider that the second oxidation of **2** occurred at 3-position to give intermediate **A**, since the sulfur atom of 9-position in **2** is electron-rich compared to the central sulfur and mCPBA is an electrophilic oxidizing agent.

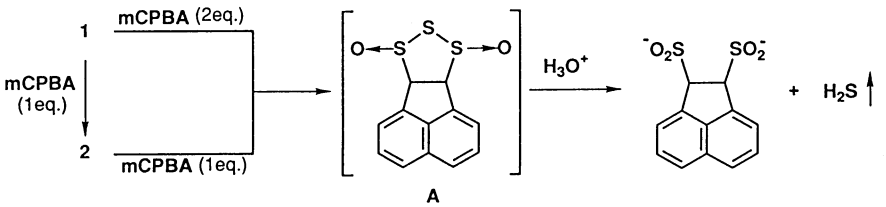


Scheme 1.

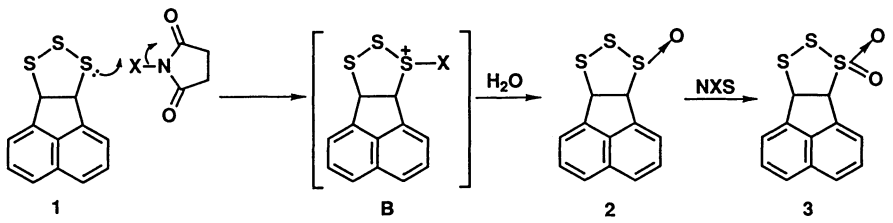
Some interesting results were obtained by the oxidation of **1** with *N*-halosuccinimide (NXS),[9] which is also regarded as an electrophilic halogenation agent. Thus, the oxidation of **1** with 1 equiv of *N*-bromosuccinimide (NBS) at room temperature for 3 h followed by hydroly-

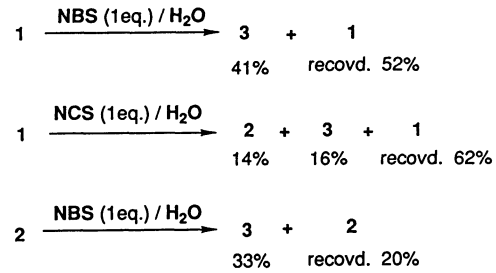


Scheme 2.



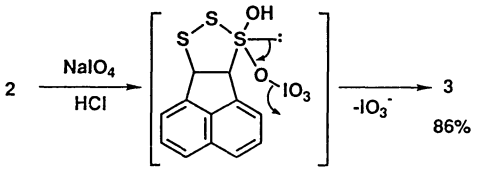
Scheme 3.





Scheme 4. *N*-Halosuccinimide (NXS) oxidation of **1**.

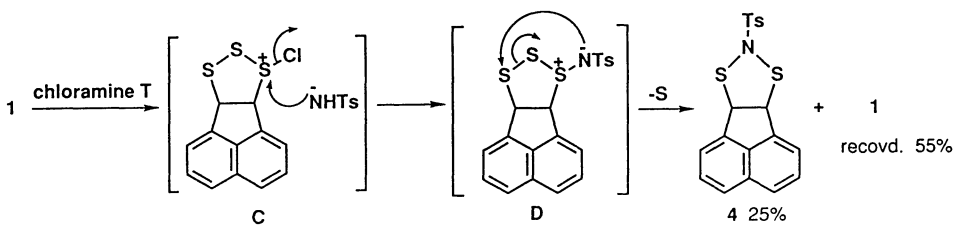
sis gave 6b,9a-dihydroacenaphtho[1,2-*d*][1,2,3]trithiole 7,7-dioxide (**3**) in 41% yield as shown in Scheme 4. Two characteristic absorptions for -S-SO_2- group were observed at 1320 and 1120 cm^{-1} and two doublet peaks of ^1H NMR for **3** also appeared at δ=5.80 and 5.25 due to two methine protons, to evidence the formation of the 7,7-dioxide **3**. Furthermore, interestingly, the treatment of **2**, which was formed from **1** by oxidation using mCPBA, with 1 equiv of NBS resulted in the production of **3** in 33% yield and **2** was recovered in 20% yield. Similarly, the reaction of **1** with *N*-chlorosuccinimide (NCS) gave two oxidized products, **2** and **3**, in yields of 14 and 16%, respectively, recovering **1** in 62% yield. This result suggests that the first oxidation of **1** with NXS proceeds electrophilically to give **2**,[9] and further oxidation of **2** occurs at the electron-poor sulfinyl sulfur atom. It is generally well-known that the oxidation of sulfide to sulfoxide with NXS proceeds by nucleophilic attack of the sulfur atom toward the halogen atom to form a halosulfonium ion,[9] which is hydrolyzed to give the corresponding sulfoxide. It is very interesting that further oxidation of **2** with NXS gave the 7,7-dioxide **3** only. To consider the plausible reaction pathway, a possibility of the intermolecular disproportionation of **2** to give **1** and **3**, was examined by treating the 7-oxide **2** with aq hydrobromic acid, but the expected 7,7-dioxide **3** was not obtained. On the other hand, the reaction of **2** with hydrobromic acid in the presence of succinimide did not afford the 7,7-dioxide **3**. Moreover, **1** was not formed at all in the reactions of **2** with NBS. Accordingly, such intermolecular disproportionation is elimi-



Scheme 5.

nated. The treatment of **2** with sodium periodate, a typical nucleophilic oxidizing agent, afforded the 7,7-dioxide **3** in a high yield (Scheme 5). This result suggests apparently that the sulfinyl sulfur atom in **2** is most electron-poor. This is also supported by the result from MNDO calculation for **2**.[10] Therefore, it should be noted that the 7,7-dioxide **3** is obtained by oxidation of **1** or **2** with a typical electrophilic oxidizing agent, NXS. Since, up to date, such oxidation of cyclic polysulfides containing more than two sulfur atoms in the ring has never been studied, our present result provides the first example of direct formation of *S,S*-dioxide of the terminal sulfur from trithiolane using NXS.

The treatment of **1** with 1 equiv of chloramine T at room temperature for 3 h gave 1,3,2-dithiazolidine **4** in 25% yield as shown in Scheme 6.[11] Furthermore, the reaction of **1** with *p*-toluensulfonamide in the presence of 1 equiv of NBS or NCS also afforded 1,3,2-dithiazolidine **4** in 12% yield.[12] The plausible reaction pathway is illustrated in Scheme 6. Based on the above-mentioned results obtained in the reaction using mCPBA and NXS, it is obvious that initial halogenation



Scheme 6.

occurs at 1-position on trithiolane ring to give a halosulfonium intermediate **C**. Sequentially, sulfilimine intermediate **D** formed by the imination of halosulfonium intermediate **C** extrudes the central sulfur atom by intramolecular nucleophilic substitution to give product **4**.[13] Since, to our knowledge, such dithiazolidine compound involving -S-N-S- bond has never been synthesized so far, some peculiar reactivity and versatility in the structural and synthetic chemistry are expected.

Experimental

General: ^{1}H NMR spectra were obtained on a Hitachi R-22, 90 MHz spectrometer. ^{13}C NMR spectra were obtained on a Varian XL-GEM 200. These spectra were obtained in $CDCl_3$. IR spectra were recorded on a Hitachi 295 spectrophotometer. MS spectra were obtained on a Hitachi M-2000 operating in the EI mode with ionization energy of 20 eV. Elemental analyses were performed on a Yanagimoto MT-3. All melting points were obtained by capillary method (Aldrich Ltd.) and are uncorrected.

Oxidation of 1 with mCPBA: To a solution of the **1** (124 mg, 0.5 mmol) in 2.5 ml of CH_2Cl_2 at 0 °C was slowly added 1 equiv of 87% mCPBA (98 mg, 0.5 mmol) in 2.5 ml of CH_2Cl_2. After completion of the addition, the solution was stirred for 3 h at room temperature. The resulted precipitate (*m*-chlorobenzoic acid) was filtered off and the filtrate was washed with 10% aq sodium hydrogensulfite followed by 10% aq sodium hydrogencarbonate and brine. The CH_2Cl_2 layer was dried over sodium sulfate and the solvent was then evaporated under vacuum. The crude product was chromatographed on silica gel using $CHCl_3$ as an eluent to give 116 mg (88%) of **2**.

6b,9a-Dihydroacenaphto[1,2-*d*][1,2,3]trithiole 7-oxide **2**: Pale yellow needles (from $CHCl_3$-hexane, 1/1), mp 148 °C (decomp); ^{1}H NMR, δ=7.40—7.96 (m, 6H), 6.10 (d, J=5.4 Hz, 1H), 5.72 (d, J=5.4 Hz, 1H); ^{13}C NMR, δ=141.1, 139.3, 133.4, 131.0, 129.5, 128.5, 126.1, 125.4, 122.0, 121.5, 92.3, 65.1; IR (KBr) 2920, 1590, 1490, 1360, 1075, 820, 780 cm^{-1}; MS m/z 364 (10%), 332 (100), 290 (10), 248 (M^+, 6). Found: C, 54.27; H, 2.96%. Calcd for $C_{12}H_8OS_3$: C, 54.52; H, 3.05%.

Oxidation of 1 with *N*-Halosuccinimide: To a solution of **1** (124 mg, 0.5 mmol) in 2.5 ml of 70% aq 1,4-dioxane was added 1 equiv of *N*-halosuccinimide (NXS) (X=Br or Cl, 0.5 mmol) in 5 ml of 1,4-dioxane. The solution was stirred for 3 h at room temperature and then washed with brine. The organic layer dried over sodium sulfate was concentrated under reduced pressure. The residue was chromatographed on silica gel using $CHCl_3$ as an eluent to give 46 mg (33%) of **3**.

6b,9a-Dihydroacenaphto[1,2-*d*][1,2,3]trithiole 7,7-dioxide **3**: Yellow needles (from $CHCl_3$-hexane, 1/1), mp. 189 °C (decomp); ^{1}H NMR δ=7.40—7.83 (m, 6H), 5.80 (d, J=5.4 Hz, 1H), 5.25 (d, J=5.4 Hz, 1H); IR (KBr) 2930, 1320, 1180, 1150, 1120, 780 cm^{-1}; MS m/z 281 (M^++1, 100%). Found: C, 54.59; H, 2.96%. Calcd for $C_{12}H_8O_2S_3$: C, 54.52; H, 3.05%.

Oxidation of 2 with Sodium Periodate: To a solution of **2** (132 mg, 0.5 mmol) in 2.5 ml of 1,4-dioxane containing a few drops of concd hydrochloric acid was added 1 equiv of sodium periodate (107 mg, 0.5 mmol) in 2.5 ml of water. The solution was stirred for 3 h at room temperature. The reaction mixture was poured into water and extracted with $CHCl_3$ (3×10 ml). The organic layer was washed with saturated aqueous sodium thiosulfate (1×15 ml) and dried over sodium sulfate. After evaporation of $CHCl_3$ under vacuum, the remained crude product was chromatgraphed on silica gel using $CHCl_3$ as an eluent to give 121 mg (86%) of **3**.

Oxidation of 1 with Chloramine T: To a solution of **1** (124 mg, 0.5 mmol) in 2.5 ml of $CHCl_3$ at room temperature was slowly added 1.1 equiv of chloramine T in CH_3OH (2.5 ml) and then the solution was stirred for 3 h. After washing of the solution with 10% aq NaOH and brine, the organic layer was dried over sodium sulfate and concentrated under vacuum. The residue was chromatographed on silica gel using $CHCl_3$ as an eluent to give 48 mg (25%) of **4**.

8-Tolylsulfonyl-6b,9a-dihydroacenaphto[1,2-*d*][1,3,2] dithiazole **4**: Colorless cubics (from acetone- hexane, 1/1), mp 187 °C (decomp); ^{1}H NMR δ=7.18—8.15 (m, 10H), 5.69 (s, 2H), 2.69 (s, 3H); IR (KBr) 1340, 1150 cm^{-1}; MS m/z 364 (25%), 332 (100), 248 (48), 184 (95) (The peak at m/z=364 corresponds to diacenaphtho[1,2-*b*:1′,2′-*d*][1,4]dithiin).[8] Found: C, 58.85; H, 3.79; N, 3.24%. Calcd for $C_{19}H_{15}NO_2S_3$: C, 59.20; H, 3.92; N, 3.63%.

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