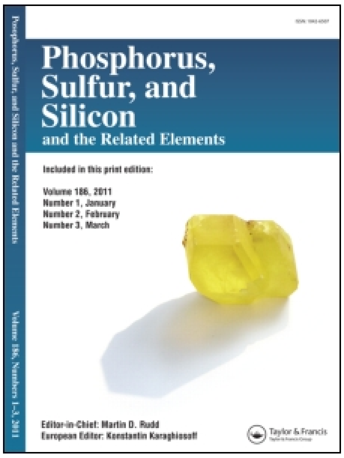

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FORMATION AND GC-MS CHARACTERIZATION OF UNUSUAL CYCLIC SULFIDES

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FORMATION AND GC-MS CHARACTERIZATION OF UNUSUAL CYCLIC SULFIDES

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In connection with another project involving the cleavage of the thiirane ring of cyclohexene episulfide in the presence of trifluoromethylthiocopper, the presence of several unusual cyclic sulfides (5–10, Fig. 1) was observed both in the reaction product and the starting material itself. The formation of these compounds has been rationalized on the presence and participation of the thiyl radical species. Details pertaining to their formation and characterization based on their mass spectral fragmentation behavior are presented in this communication.

Keywords: cyclohexene episulfide; thiirane ring cleavage; unusual cyclic sulfides; trifluoromethylthiocopper; thiyl radical

INTRODUCTION

Sulfur containing compounds occur ubiquitously in nature and play a vital part in endowing and/or modifying the biological properties and potency of natural products such as vitamins, antibiotics, coenzymes, enzyme-mediated reactions, etc. All this has manifested in a sustained interest in the chemistry and synthesis of sulfur containing organic compounds and also in concerted efforts to incorporate sulfur in medicinal compounds. The chemistry, preparation and reactions of cyclohexene sulfide (**1**) have been reviewed[1]. The most commonly employed procedure

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for the preparation of the thiiranes appears to be the reaction of epoxides with sulfur transfer agents such as thiocyanate and thiamides[2a] or carbon disulfide in the presence of catalysts[2b], or potassium thiocyanate[3]. A useful modification of this procedure involves the use of silica supported potassium thiocyanate[4]. Addition of iodocyanate to cycloalkenes is reported to give cyclic thiiranes[5]. Although the mechanism is somewhat obscure, olefin-elemental sulfur interactions have led to the formation of thiiranes[6]. Diazoalkanes have been reacted with elemental sulfur to give thiiranes[7a]. Tetrathia- and pentathia derivatives have been thermally prepared from elemental sulfur in the presence of triirondodecacarbonyl[7b]. Low yields of the thiiranes using sensitized photolysis of olefins and either carbonyl sulfide[8] or isothiocyanate have been reported[9]. In this context, it is interesting to note that the thermally induced transfer of sulfur from stilbene sulfide to cyclohexene has been described[10]. Imidosulfenyl chlorides react with olefins to form thiiranes[11]. *In situ* generated trimethylsilylsulfenyl bromide reacts analogously with olefins[12]. Cyclodehydration of mercaptoethanols with orthocarbonates in the presence of catalytic amounts of acids at room temperature also furnishes thiiranes[13].

Another stereospecific thiirane synthesis takes advantage of the enhanced affinity of the phosphorus atom for oxygen[14]. This novel approach to thiiranes is said to involve pentacoordinated phosphorus species. However, the treatment of epoxides with sulfur containing reagents[3c–d and 15] and the reaction of sulfur monochloride with olefins[15]are the only procedures that have been exploited commercially. Sulfur monochloride has been postulated to undergo disproportionation to various species of polysulfur dichlorides[15]. This contention, in a sense, appears to be supported by the isolation of mono-, di- and trisulfides[15]. The synthesis of bi- and tricyclic polysulfides in moderate to poor yields by mixing dilute solutions of 1,2-cyclohexanedithiol and polysulfur dichloride in anhydrous ether and carbon disulfide, appears to further lend support to the postulated disproportionation of sulfur monochloride[16]. The preparation of the Tricyclictetrathia derivative (**10**) has been described[17]. While the bicyclic derivative (**11**) was obtained from the reaction of the dithiol with chlorosulfuranes [S_xCl_2 (X = or > 2)], the bicyclic compound (**12**) was prepared from sulfur dichloride[18]. The hexathia-compounds (**13**) has also been reported[17].

Dimerization of cyclohexene sulfide in the presence of ceric ammonium nitrate in refluxing CCl_4 has furnished perhydrodibenzo tetrathione in 70% yield (**10**)[18]. Pyrolysis of the polymeric material obtained from distillation of the reaction mixture of cyclohexene sulfide with alkaline mercaptoethanol yielded a small amount of decahydroanthracene[19]. In fact, Houk and Whitesides[17] have synthesized cis- and trans-isomers of **10** via the oxidation of their respective precursors, namely cis- and trans-1,2-cyclohexanedithiol (19). Pyrolysis of cyclohexene sulfide at 210° C yielded a complex mixture of compounds consisting of: (**a**) dicylcohexyl sulfide (**14**), (**b**) cyclohexyl phenyl sulfide (**15**), (**c**) dicyclohexyl disulfide (**16**), (**d**) 1,2,3-trithiaperhydrindan (**5**), (**e**) cyclohexanethiol (**17**), (**f**) cyclohexyl cyclohexeneyl sulfide (**18**) and (**g**) benzene (**19**). This formation of sulfur compounds has been attributed to the attack of sulfur radical species on cyclohexene. Evidently cyclohexyl phenyl sulfide and benzene are formed by the sulfur catalyzed dehydrogenation of the cyclohexene moiety with sulfur being extruded during the course of the reaction. Extrusion of sulfur from sulfur containing organic compounds is a common occurrence[20].

In connection with another project involving the cleavage of the thiirane ring of cyclohexene sulfide (**1**) with F_3CSCu (**2**), the presence of several unusual sulfur containing compounds was detected in the reaction mixture[21]. However, many of them were unexpected and their presence was tentatively attributed to the strarting material itself. To substantiate this, a thorough GC-MS analysis of the starting material was conducted and the above inference was found to be correct. Based on the mass spectral fragmentation behavior, seven sulfur containing compounds (**4–10, Fig. 1**) and one non-sulfur containing compound have been characterized and their formation has been rationalized by invoking the presence and participation of sulfur radical species and reactions. The probable mechanism of the formation of the various products and their mass spectral fragmentation behavior are presented in this paper.

RESULTS AND DISCUSSION

The mass spectral fragmentation of cyclohexene sulfide (**1**) has been described [8]. The mass spectral breakdown appears, in part, to resemble the fragmentation of methylcyclohexane and cyclohexane[22]. The second major product is cyclohexene (**3**, $M^+ = 82$, 21.6%). Its mass spectrum has been discussed[22]. Evidently, this is thermally formed from cyclohexene sulfide (**1**). Its mode of formation is explained in **Fig. 2**. The third major component is either methylcyclohexane or cycloheptane ($M^+ = 98$, 6.9%), the origin of which is not known at the present time. The presence of an unknown component, with the retention time of 3.23 min. was also detected. The highest peak seen in its mass spectrum occurs at m/z=131. Although peaks with m/z = 114 (cyclohexene sulfide) and m/z = 82 (cyclohexene) are seen, this by itself was not of much help in deducing its structure. Both cis- and trans-1,2-cyclohexanedithiol (**4**) are known[23]. Their mass spectra have been recorded[23]. 1,2,3-Trithiaperhydrindan (**5**) has been reported to be one of the products of the photochemical reaction of cyclohexene and elemental sulfur[6b]. It is also formed when dilute solutions of 1,2-cyclohexanedithiol and sulfur dichloride are mixed[8a]. Its partial mass spectrum has been given[6b]. The formation and partial mass spectrum of tetrathiadecalin (**6**) have been described[6b]. The same is true of dodecahydrothianthracene (**7**)[10, 21]. Two isomeric compounds having the structure of decahydrodibenzo[c,f]-[1,2,5]trithiepin (**8**) have been cited [24]. The fragmentation of decahydro-dibenzotetrathiocin (**9**), an isomer of the known decahydrodibenzo[1.2.5.6]tetrathiocin (**10**) is interesting. The first peak (m/z = 178) represents the loss of cyclohexene sulfide moiety. The remaining part of the spectrum is similar to that of 1,2,3-trithiaperhydrindan (**5**). It is, in fact, this observation that led to its proposed structure. Compounds of this type are difficult to synthesize, for polymers are usually formed under the conditions employed for their synthesis. The synthesis of decahydrodibenzo[1.2.5.6]-tetrathiocin (**10**) and its partial mass spectrum have been published[18]. The fragmentation of this compound is essentially different from that of its isomer (**9**). The formation of the compounds described in **Fig. 1** involves the active participation of the sulfur radical species. **Fig. 2** endeavors to rationalize the presence and participation of the sulfur radicals. The proposed photochemical and thermal dismutation of the carbon-sulfur and sulfur-sulfur bonds have precedence[25]. The sulfur-cyclohexyl diradical proposed in **Fig. 2** has been implicated in the photochemical reaction of elemental sulfur with cyclohexene [6c].

Recently, we have characterized tri-, tetra-, penta- and hexasulfides[26] formed in the reaction of the disulfide with organometallic reagents and the reaction of hydrogen sulfide with sulfenyl chloride derivative. Compounds **8** and **9** (**Fig. 2**) have not been previously identified as arising from either the photochemical or thermal reaction with elemental sulfur and cyclohexene[6] or the reaction of cyclohexene sulfide (**1**) with

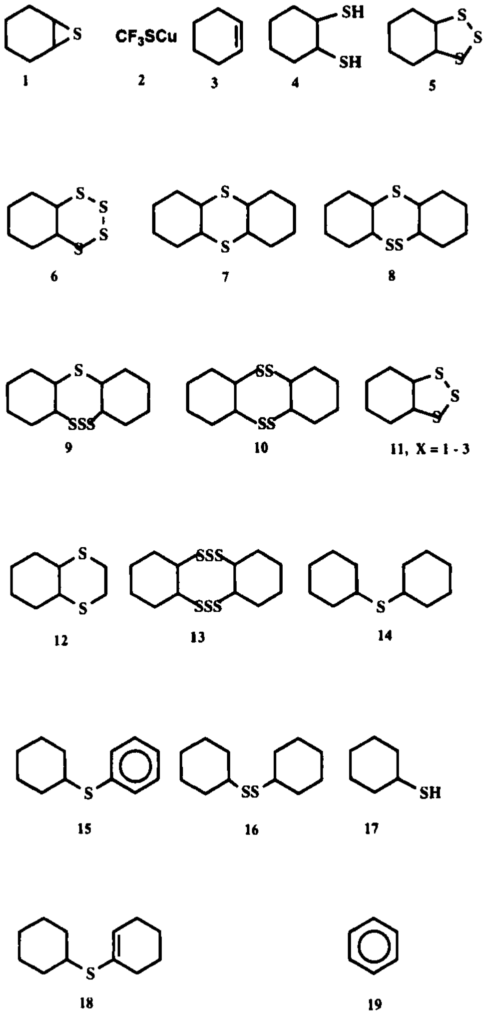

FIGURE 1

dichlorosulfuranes[14a]. The postulated mechanism of the formation of the compounds cited in **Fig. 2** is based on the following considerations:

1) Many of the substitution reactions on sulfur have been suggested to occur via a cascade of addition-elimination reactions rather than a one-step displacement[27a].

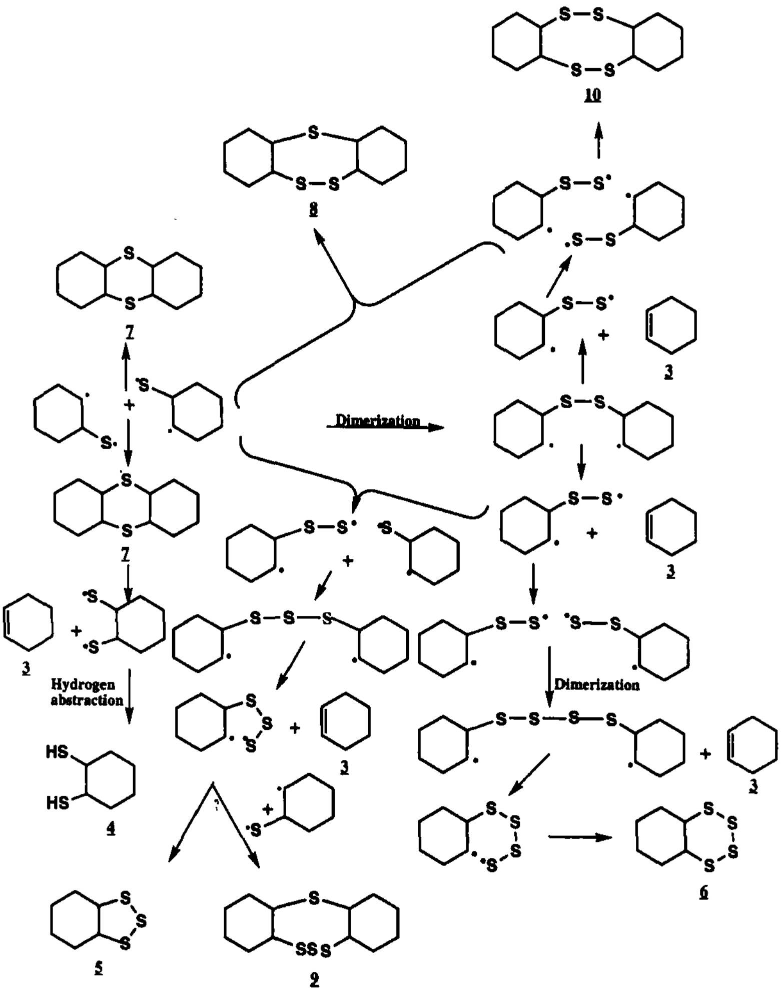

FIGURE 2 Compounds characterized by GC-MS analysis are underlined

2) There are precedents for thiaphilic addition and electron sharing by radicals with sulfur singly bonded to carbon[27b].

3) The formation of thiyl, perthiyl and sulfuranyl radicals has been invoked to rationalize the products formed from the thermolysis of trisulfides[27c].

TABLE I Mass Spectral Fragmentation of Compounds Cited in the Text

Mass Spectral Fragmentation of Cyclohexene sulfide (**1**): M^+ = 114 (100%); 99 (M-CH_3); 85 (M- C_2H_5); 81 (M-HS); 80 (H_2S); 79 (C_6H_7); 77 (C_6H_5); 67 (99-S); 60 (C_2H_4S); 58 (C_2H_2S); 54 (C_4H_6); 53 (C_4H_5) and 51 (C_4H_3).

Mass Spectral Fragmentation of 1,2-Cyclohexanedithiol (**4**): M^+ = 148; 115 ($C_6H_{11}S$); 114 (M-H_2S); 101 (C_5H_9S); 85 (114-C_2H_5); 81 (C_6H_9, 100%); 73 (C_3H_5S); 60 (C_2H_4S); 53 (C_4H_5) and 45 (CSH).

Mass Spectral Fragmentation of 1,2,3-Trithiaperhydrindan (**5**): M^+ = 178; 114 (M-2S); 99 (C_5H_7S or 114- CH_3); 85 (114-C_2H_5 or 114-CH_2); 81 (C_6H_9, 100%); 79 (C_6H_7); 77 (C_6H_5) and 53 (C_4H_5).

Mass Spectral Fragmentation of Tetrathiadecalin (**6**): M^+ = 210; 178 (M-S); 146 (M-2S); 128 (M- C_6H_{10} or S_4); 114 (146-S); 113 (146-HS); 85 (113-C_2H_4); 81 (C_6H_9, 100%); 79 (C_6H_7); 67 (C_5H_7); 54 (C_4H_6); 53 (C_4H_5) and 47 (SCH_3).

Mass Spectral Fragmentation of Dodecahydrothianthracene (**7**): M^+ = 228; 185 (M- C_3H_7); 146 (M-C_6H_{10}); 114 (C_6H_{10} S); 85 (114 C_2H_5); 81 (C_6H_9, 100%); 79 (C_6H_7); 71 (C_3H_3S); 67 (C_5H_7); 55 (C_4H_7); 53 (C_4H_5) and 47 (SCH_3).

Mass Spectral Fragmentation of Decahydrodibenzo[c,f][1,2,5]trithiepin (**8**): M^+ = 260; 227 (M-HS); 195 (M-HS_2); 178 (M- C_6H_{10} S); 146 (C_6H_{10} S_2); 115 ($C_6H_{11}S$); 86 (115-C_2H_5); 81 (C_6H_9, 100%); 71 (C_3H_3S); 67 (C_5H_7); 53 (C_4H_5) and 47 (SCH_3).

Mass Spectral Fragmentation of Decahydrodibenzotetrathiocin (**9**): M^+ = 292; 178 (M-$C_6H_{10}S$, 100%); 113 (C_6H_9S); 85 (113-C_2H_4); 81 (C_6H_9, or 113-S) and 67 (C_5H_7).

Mass Spectral Fragmentation of Decahydrodibenzo[1.2.5.6]tetrathiocin (**10**): M^+ = 292; 227 (M-HS_2); 210 (M- C_6H_{10}); 195 (M-HS_3); 178 (M-$C_6H_{10}S$); 146 (C_6H_{10} S_2); 114 ($C_6H_{10}S$); 81 (C_6H_9, 100%); 67 (C_5H_7) and 53 (C_4H_5).

EXPERIMENTAL PART

All solvents were dry and freshly distilled prior to use. The reactions were carried out in a flame-dried, argon gas-purged 10 or 25 ml three-necked flask equipped with a magnetic stirrer, gas inlet-adaptors and a reflux condenser carrying a dry ice/ acetone cooled trap. The temperature of the coolant passing through the condenser was maintained at –20 °C. Mass spectra were obtained using a Finnigan TSQ-7000 GC/MS/MS equipped with a 30 m × 0.25 mm. i.d. DB-5 capillary column (J and W Scientific, Folsom, CA). The oven temperature was ramped from 60–270° C at 15° C/min. The injection temperature was 250°, interface temperature 250° C, source temperature 150°, electron energy 70 eV and emission current 300 µA. Data was obtained in the electron ionization mode with a mass range of 60–450 da (0.7 sec/scan). Routine GC analyses were accomplished with a Hewlett-Packard 5890A gas chromatograph equipped with a J and W Scientific 30 m × 0.53 mm i.d. DB-5 column (J and W Scientific, Folsom, CA).

SUMMARY

A number of cyclic compounds containing multi-sulfur atoms have been identified by their GC-MS fragmentation patterns. It is conceivable that these compounds have their genesis in autocatalyzed free radical reactions in the presence of ordinary light. There are precedents for this contention[25b].

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