# Cyclopenta-1,2,3-dithiazoles and Related Compounds

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Cyclopentanone oxime reacts with $S_2Cl_2$ at 4 °C in tetrahydrofuran containing a base, or in dimethylformamide, to give deep-violet crystals of the 10π-heteroaromatic trichlorocyclopenta-1,2,3-dithiazole **7** without isolable intermediates; other 1,2,3-dithiazoles (**2**, **4**, **10**, 12, 13 and **15**) are readily formed similarly.

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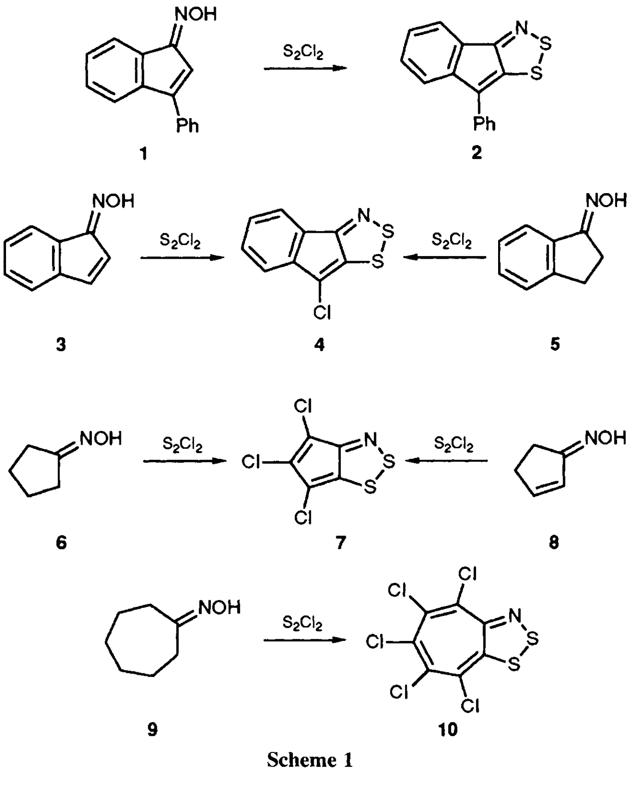
We recently described the formation of the deep-red indeno-1,2,3-dithiazole **2** in a thermolytic rearrangement reaction.[1] We now report an independent synthesis of **2** by treatment of 3-phenylinden-1-one oxime **1** with disulfur dichloride, $S_2Cl_2$, by analogy with the conversion of 2,4-di-*tert*-butylcyclopentadienone oxime with $S_2Cl_2$ into the corresponding 1,2,3-dithiazole-3-oxide (Scheme 1).[2] In our reaction the desired, deoxygenated, product **2** was formed directly (58%) from oxime **1** and $S_2Cl_2$ in boiling tetrahydrofuran (THF). In the presence of ethyldiisopropylamine (Hünig's base) in THF at 4 °C for 72 h the yield of **2** increased to 90%.

This simple, high-yielding, one-step conversion of an oxime into a 1,2,3-dithiazole seemed worthy of further investigation, for its potential synthetic utility and for the interest of the cyclopentadithiazole structure (*cf.* **7**) which could be a 10π-aromatic system, isoelectronic with azulene (*cf.* **16**). Extensive delocalisation in **2** is suggested by its deep-red colour and its high thermal stability.

Indenone oxime **3** similarly gave a 1,2,3-dithiazole with an excess of $S_2Cl_2$, but now the unsubstituted position in the cyclopentadiene ring was chlorinated to give compound **4** as a red crystalline solid; none of the unchlorinated product was detected. In THF at 4 °C for 48 h in the presence of Hünig's base the yield of **4** was 60%. This $S_2Cl_2$ reaction could be extended to more saturated oximes; thus, similar treatment of indanone oxime **5** gave the same chloroindenodithiazole **4** in even higher yield (80%).

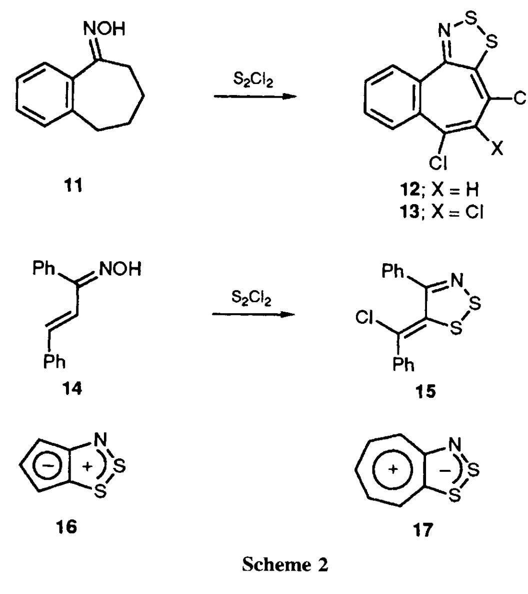
The $S_2Cl_2$ reaction was therefore attempted on the fully saturated cyclopentanone oxime **6**, either with Hünig's base in THF or with no added base in dimethylformamide (DMF), both at 4 °C for 72 h. In each case the fully unsaturated and chlorinated cyclopenta-1,2,3-dithiazole **7** was formed (*ca.* 25%) as deep-violet crystals, and again no intermediate products could be isolated. In this remarkable reaction a simple saturated oxime has been converted, by the formation of seven new bonds, into the highly functionalised heteroaromatic compound **7**. Similar treatment of the unsaturated oxime **8** gave the same product in the same yield. Longer reaction times reduced the yield of dithiazole **7** which was decomposed by $S_2Cl_2$, as were all the dithiazoles reported here. With just one equiv. of $S_2Cl_2$, to form the heterocyclic ring, together with an excess of *N*-chlorosuccinimide, compound **7** was formed in undimished, but not significantly improved, yield (26%).



Scheme 1

In view of the extensive sequence of oxidation and chlorination involved in the formation of **7** from cyclopentanone oxime, it was of interest to see if a similar but longer sequence would result from cycloheptanone oxime **9**, though now the analogous product, **10**, is potentially a 12π-antiaromatic species. When oxime **9** was treated with $S_2Cl_2$ and Hünig's base in THF at 4 °C for 3 days di-, tri-, tetra- and the red penta-chloro (**10**) derivatives of the fully unsaturated cyclohepta-1,2,3-dithiazole were indeed formed but could be isolated only in very low yields (2–5%) after repeated chromatography of the complex reaction mixture. In the presence of an excess of *N*-chlorosuccinimide the pentachloro compound **10** was isolated in 14% yield, together with 7% of the tetrachloro derivative. These yields are not unreasonable in view of the extensive linear reaction sequence, where conversion of the oxime **9** into dithiazole **10** involves the formation of ten new bonds. When two of the cycloheptanone ring positions were blocked by benzo fusion the oxime-$S_2Cl_2$ reaction was much cleaner: benzocycloheptanone oxime **11** gave the orange–red dichloro product **12** (35%) and, in the presence of an excess of *N*-chlorosuccinimide the red trichloro derivative **13** (29%) (Scheme 2).

In an acyclic example of this reaction benzylidene acetophenone oxime **14** in DMF or in THF with Hünig's base, reacted faster than the cyclic oximes, but in substantially the same way to give the monocyclic dithiazole **15** as an orange crystalline



Scheme 2

compound. Again deoxygenation, dehydrogenation and chlorination have all occurred, in modest overall yield (22–23%).

Even though yields are variable, this oxime–$S_2Cl_2$ reaction provides ready access to the relatively rare 1,2,3-dithiazole ring system;[3] its mechanism will be discussed in our full paper. As well as forming the heterocyclic ring, $S_2Cl_2$ must also function as a chlorinating agent, the initial chlorination steps being followed by dehydrochlorination until the fully unsaturated ring system is constructed; then the free carbocyclic positions can be chlorinated. This will be facilitated by the combined ability of the two dithiazole sulfur atoms to activate all such positions by electron release. Polarisation of the cyclopenta–dithiazole as shown in **16** will favour complete chlorination of the electron-rich ring (as in products **4** and **7**) without isolation of less chlorinated species. The reverse polarisation of the cyclohepta–dithiazole **17** would retard electrophilic substitution, thus allowing the isolation of incompletely chlorinated intermediates, such as the di-, tri-, and tetra-chloro compounds mentioned above, and compound **12**. Preliminary work suggests that the chemistry of these polychloro compounds is controlled by the polarisation shown in **16** and **17**.

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