Cyclopenta-1,2-dithioles and cyclopenta-1,2-thiazines from new molecular rearrangements

Oleg A. Rakitin,[a] **Charles W. Rees**[b] **and Tomás Torroba**[c]

[a] *N. D. Zelinsky Institute of Organic Chemistry, Academy of Sciences, Leninsky Prospect, 47, Moscow B-334, Russia*
[b] *Department of Chemistry, Imperial College of Science, Technology and Medicine, London, UK SW7 2AY*
[c] *Departamento de Química Orgánica, Facultad de Veterinaria, Universidad de Extremadura, 10071 Cáceres, Spain*

The cyclobutanone oxime 6 reacts with disulfur dichloride to give two unexpected 10π pseudoazulenes in low yield: the dark blue cyclopenta-1,2-dithiole 7 and the orange cyclopenta-1,2-thiazine 8; the benzo derivative 14 of this oxime gives the analogous benzo product 15 together with the methylene indene 16 in high yield; mechanisms based on abnormal Beckmann rearrangements are proposed for the formation of all of these products.

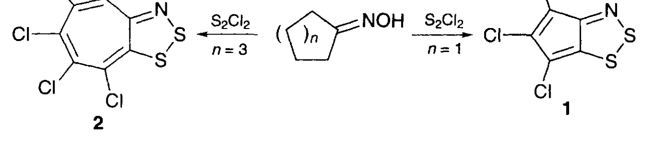
We have previously described a remarkably extensive transformation of simple saturated oximes with disulfur dichloride, S_2Cl_2, into fully unsaturated and chlorinated heteroaromatic systems.[1] Thus, cyclopentanone oxime gave the deep violet 4,5,6-trichlorocyclopenta-1,2,3-dithiazole **1** with S_2Cl_2 and Hünig's base in THF at 4 °C; the addition of *N*-chlorosuccinimide (NCS) supplemented the (spontaneous) ring chlorination and improved the yield of **1**. Similarly, cycloheptanone oxime gave the red pentachlorocycloheptadithiazole **2**. A detailed mechanism was proposed for these reactions based upon the activation to chlorodeprotonation of all the carbocyclic ring positions by the sulfur atoms, and evidence was presented for the 10π and 12π delocalised electronic structures of **1** and **2** respectively.[1]

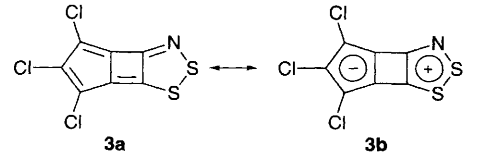
We hoped to extend this reaction to the synthesis of the novel tricyclic species **3**, a heterocyclic derivative of the unknown hydrocarbon **4**[2] and isoelectronic with the dianion of **4**. Compound **3** can also be considered as an analogue of biphenylene with two 6π aromatic rings fused to a four-membered ring, **3b**.

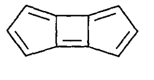
By analogy with compounds **1** and **2** above, compound **3** could possibly be formed from *cis*-bicyclo[3.2.0]heptan-6-one oxime **5**,[3] or its unsaturated derivative **6**,[3] and S_2Cl_2. When oxime **5** was treated with S_2Cl_2, Hünig's base, and NCS in THF a dark blue crystalline compound **7** was obtained in low yield. With the unsaturated oxime **6**, or its *O*-trimethylsilyl derivative, compound **7** was again formed in similar yield, together with a less polar orange crystalline compound **8**. NMR spectroscopy and mass spectrometry showed **7** to be $C_7Cl_3NS_2$ with seven different carbon atoms and the infrared spectrum showed a cyano group at 2218 cm^{-1}. The dark blue compound was confirmed as 4,5,6-trichlorocyclopenta-1,2-dithiole-3-carbonitrile **7** by X-ray structure determination.[4] Thus the 10π pseudoazulene[5] system **7** was formed, by an extensive rearrangement, rather than the expected 12π system **3**. The only other example of this ring system is the air-sensitive 4,6-di-*tert*-butylcyclopenta-1,2-dithiole.[6]

Compound **8**, C_7Cl_5NS, did not have a cyano group, suggesting that the nitrogen was part of a heterocyclic ring; on mechanistic grounds and by analogy with compound **15** (see below), it was assigned the 10π aromatic pentachlorocyclopenta[*d*]-1,2-thiazine structure **8**, a hitherto unreported pseudoazulene system. Despite considerable variation in the oxime–S_2Cl_2 reaction conditions, the yields of **7** (up to 13%) and of **8** (up to 7%) were always low.

The simplest mechanism for the conversion of **6** into **7** and **8** would appear to involve initial ketoxime fragmentation, of the abnormal (second order) Beckmann type,[7] presumably induced by S_2Cl_2. The two possible cyclobutane ring opening processes† would give the isomeric nitriles **9** and **11**. The former (Scheme 1) could react with S_2Cl_2 to give the dithiole ring which by chlorination and dehydrochlorination could give the unsaturated system **10** which can be fully chlorinated by S_2Cl_2 and NCS in the carbocyclic ring; all positions of this ring are activated by electron release from the dithiole sulfur atoms,







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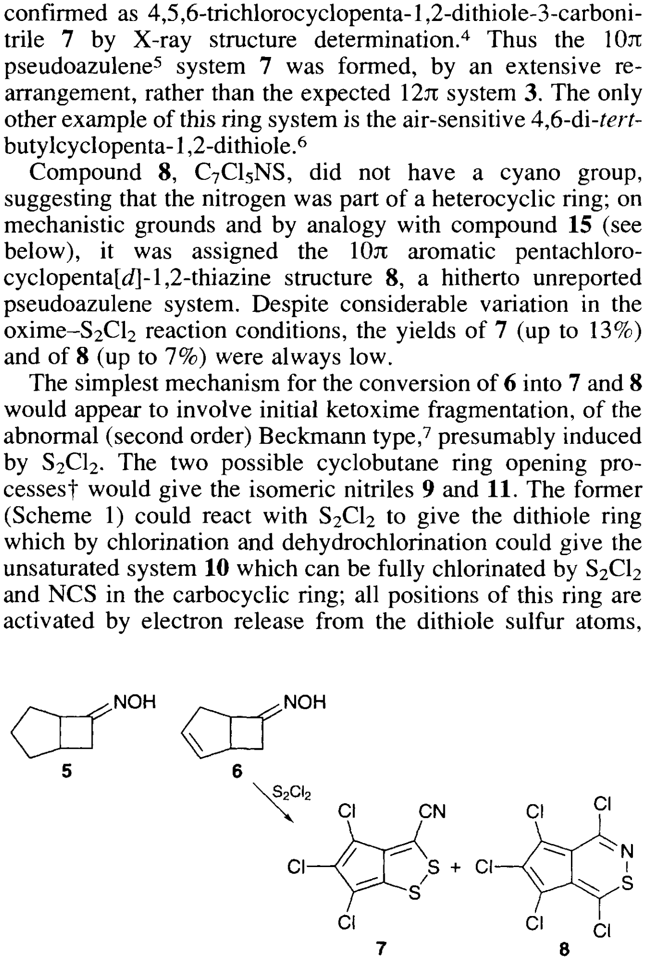
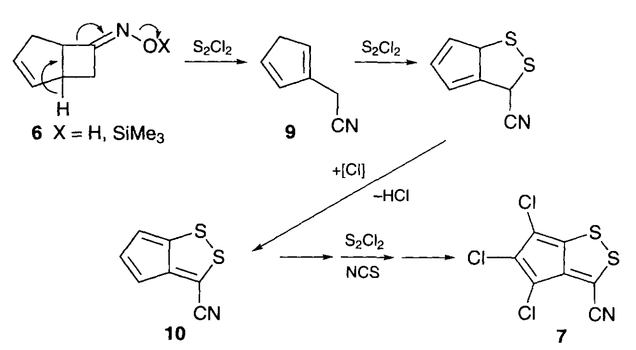
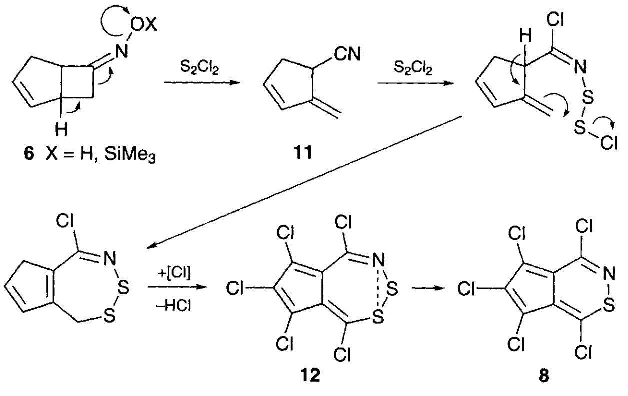
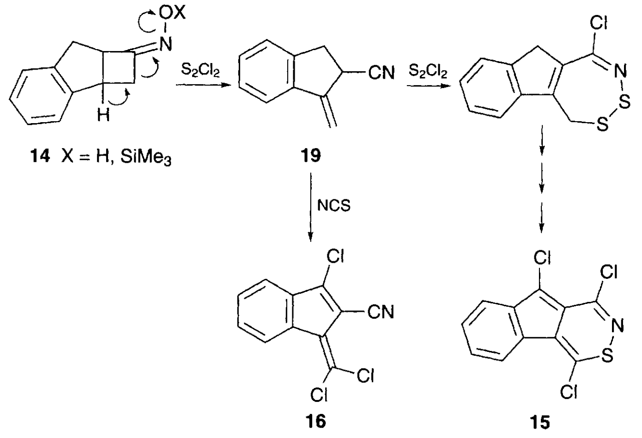




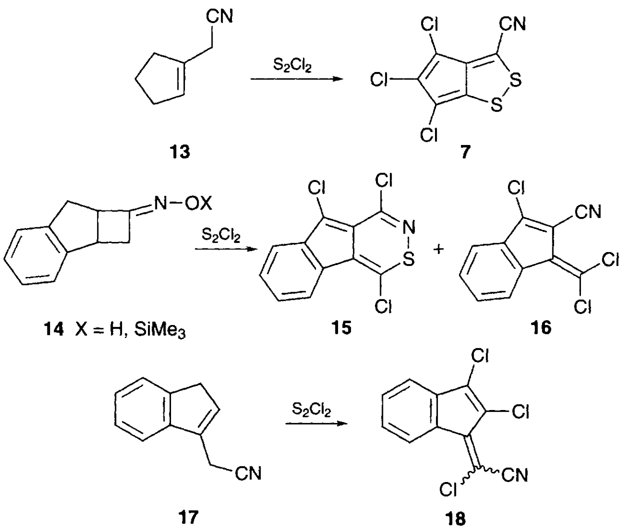
Scheme 1



Scheme 2



Scheme 3



exactly as proposed[1] for the formation of **1** and **2** above. The isomeric nitrile **11** could react with S_2Cl_2 (Scheme 2) to give the seven-membered dithiazepine ring which, by the previous dehydrogenation and chlorination sequence would give the fully chlorinated product **12**. This is a 12π system which by electrocyclization of the 7-membered ring to a fused 6–3 system, followed by loss of sulfur would give the observed product **8**.

Given the cyclopentadithiole structure for product **7** a more rational synthesis would start from 1-cyanomethylcyclopentene **13**.[10] Treatment of this with S_2Cl_2, Hünigs base and NCS in THF did indeed give compound **7**, though in very low yield (3%).

We next investigated the reaction of the benzo analogue **14** of oximes **5** and **6** with S_2Cl_2. Two stable yellow crystalline compounds **15** and **16** were formed from the oxime and its *O*-trimethylsilyl derivative. One of these, $C_{11}H_4Cl_3NS$, was the benzo analogue **15** whose structure was confirmed by X-ray crystallography.[4] The second product, $C_{11}H_4Cl_3N$, was assigned structure **16** on spectroscopic grounds. It is isomeric with, and spectroscopically very similar to, the pair of isomers **18** produced from 1-cyanomethylindene **17**[11] and S_2Cl_2 under the same conditions.

The formation of the two products **15** and **16** from the oximes **14** can be rationalised as shown in Scheme 3. Ring opening of the oximes, as before, gives the key intermediate **19**. This could add S_2Cl_2 to the cyano group to give product **15**, by exactly the same sequence of reactions as shown in Scheme 2. Alternatively it could directly undergo the chlorination–dehydrochlorination sequence, with S_2Cl_2 and NCS, as demonstrated above for **17** → **18**, to give product **16**. In agreement with this mechanism the formation of **16** (78%) is favoured over **15** (10%) by the presence of NCS at the beginning of the reaction, whilst addition of NCS after 72 h favours **15** (45%) over **16** (25%). The yields of the benzo compounds **15** and **16** were much higher than for **7** and **8** from the bicyclic oximes **5** and **6**, giving combined yields of 70, 88 and 95% depending upon the precise experimental conditions.

Strikingly and unexpectedly, all of the products **7**, **8**, **15** and **16** showed birefringence upon melting in a hotstage polarising microscope, and further evidence is being sought for liquid crystallinity in these and related compounds.

We thank the Direcci6n General de Investigaci6n Científica y Técnica of Spain (DGICYT Project No. PB93-0414 and SAB94-0169), Consejería de Educaci6n de la Junta de Extremadura y Fondo Social Europeo (EIA94-43), INTAS (93-624) and the Royal Society for financial support, the Wolfson Foundation for establishing the Wolfson Centre for Organic Chemistry in Medical Science at Imperial College, and Dr D. J. Williams for the X-ray structure determinations.

Footnote

† An analogous Beckmann fission of fused cyclobutanone oximes to give cyanomethyl compounds was first demonstrated in 1980,[8] and a few other examples have since been reported.[9]

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Received, 1st November 1995; Com. 5/07197F