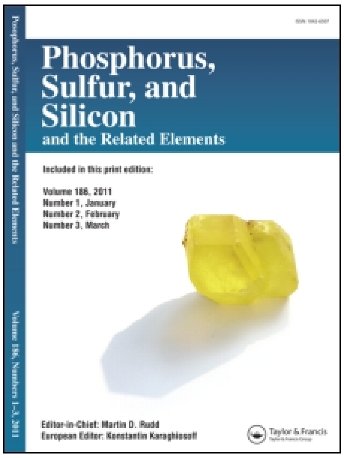

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Reactions of 1,2-Dithiolium Salts and 1,2-Dithiole-3-Thiones with Metal Cyclopentadienides

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REACTIONS OF 1,2-DITHIOLIUM SALTS AND 1,2-DITHIOLE-3-THIONES WITH METAL CYCLOPENTADIENIDES

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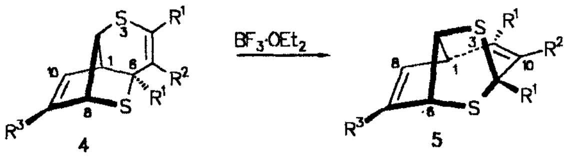
Abstract The reactions indicated in the title lead to a scission of the S,S-bond in the 1,2-dithiole ring followed by an intramolecular Diels Alder addition. By-products are formed by substitution and condensation reactions.

1,2-Dithiolium salts react readily with nucleophiles. The reaction pathway observed depends on the nature of the nucleophile and on the nature of the substituents R in the 3- and 5-position of the 1,3-dithiole ring.

We studied reactions of several 1,2-dithiolium perchlorates with alkali or thallium salts of cyclopentadiene, tert.-butyl cyclopentadiene and di-tert.-butyl cyclopentadiene. The results were rather unexpected. The first step with 3,5-diaryl-1,2-dithiolium salts at -78°C is most probably a clear cut cleavage of the S,S-bond in the 1,2-dithiolium salt by the cyclopentadienide leading to the intermediate **3**. **3** can equilibrate by 1,5H shifts giving rise to the more stable tautomers **3b** and **3c**, in which the sulfur is bound to an sp^2 carbon atom. Due to the short life time of **3a**, this process is not observed. Instead an intramolecular Diels-Alder reaction of the cyclopentadiene ring with the thiocarbonyl group takes place immediately yielding the tricyclic compound **4**. At room temperature, **4** has only a limited stability and rearranges to the isomeric structure **5** by a 1.3 shift of the S(7) - C(6) single bond. This process can be accelerated by small amounts of Lewis acids such as boron trifluoride diethyl ether at -40°C. Higher temperatures favour side reactions. Even chromatographic purification of **4** on silica gel at room temperature gives rise to partially rearranged product.

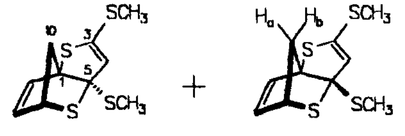


1-H : 3.1 ppm
2-H : 3.3 ppm
8-H : 4.5 ppm

1-H : 4.0 ppm
2-H : 4.9 ppm
6-H : 5.0 ppm

The ^{1}H-NMR pattern for the bridgehead atoms 1-H, 2-H and 8-H or 6-H respectively are quite different in **4** and **5** and rather characteristic for each skeleton. Thus in the primary adduct **4** the hydrogen atoms 1-H and 2-H show complex resonance signals at relatively high field about 3.1 and 3.3 ppm. Both signals are shifted dramatically to rather low field about 4.0 and 4.9 ppm in the rearranged product **5**. The proposed structures **4** and **5** have been confirmed by an X-ray analysis for the isomer obtained from tert.-butyl cyclopentadiene and 4-methyl-3,5-diphenyl-1,2-dithiolium salt.

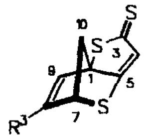
By similar reactions were prepared:



exo (20%) 11 endo (80%)

10-H_a : 2.05 ppm
10-H_b : 1.91 ppm
$J_{a,b}$: 8.7 Hz

10-H_a : 2.25 ppm
10-H_b : 2.13 ppm
$J_{a,b}$: 9.0 Hz



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10-H_a : 2.35 ppm
10-H_b : 2.10 ppm
C-S : 228 ppm