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SYNTHESIS OF LARGE C–S–N HETEROCYCLES FROM [Cp₂TiS₇NR] AND AROMATIC BIS-SULFENYL CHLORIDES (R = H, Me) ^[1]

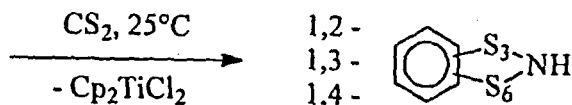
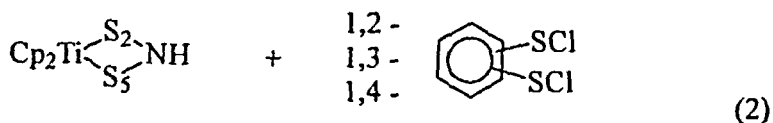
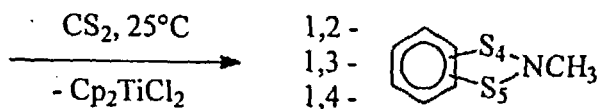
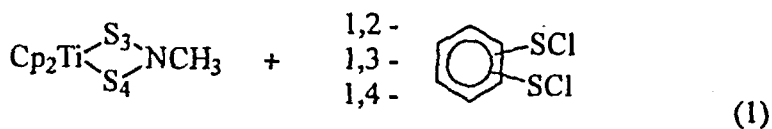
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The three isomeric benzene bis-sulfenyl chlorides C₆H₄(SCl)₂ react with [Cp₂TiS₇NR] (R = H, Me) to give large sulfur-rich heterocycles C₆H₄S₉NR.

Keywords: C–S–N heterocycles; titanocene complexes

Sulfur homocycles S_n (n = 6 – 20) exist in many different conformations.^[2] NMR studies of conformational isomerizations require a suitable heteroatom as a probe. Selenium substitution seems to be ideal but introduces thermal instability^[3] and often requires long recording times due to diminished solubility. Therefore, we have synthesized large sulfur-rich heterocycles containing C and N as heteroatoms starting from the recently

prepared metallacycles $[\text{Cp}_2\text{Ti}(\mu\text{-S}_2)(\mu\text{-S}_5)\text{NH}]$ and $[\text{Cp}_2\text{Ti}(\mu\text{-S}_3)(\mu\text{-S}_4)\text{NMe}]$ with $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ¹⁴. These complexes react with difunctional sulfenyl chlorides to yield heterocycles with (N)H or Me as additional NMR probes. The three isomeric 1,2-, 1,3-, and 1,4-benzene bis-sulfenyl chlorides have been used. The reactions are carried out at 25°C in CS_2 solution:



The obtained products $\text{C}_6\text{H}_4\text{S}_9\text{NH}$ and $\text{C}_6\text{H}_4\text{S}_9\text{NMe}$ (three isomers each; yields 15-20% after TLC purification) form yellow oils which slowly decompose at 25°C with formation of insoluble products. The new heterocycles have been characterized by elemental analyses, EI-MS, infrared and Raman spectroscopy, as

well as by NMR spectra. The mass spectra exhibit the molecular ions with low intensity. The vibrational spectra give evidence for the substitution pattern of the aromatic ring and show the presence of SS and, in three cases, NH bonds.

The ^1H NMR spectra ($\text{CDCl}_3/\text{CS}_2$; 23°C) are most interesting: The NH derivatives yield relatively narrow singlets for the hydrogen atoms linked to N. The chemical shifts of these peaks strongly depend on the ring size. The twelve-membered ring of 1,2- $\text{C}_6\text{H}_4(\mu\text{-S}_3)(\mu\text{-S}_6)\text{NH}$ has its signal at 5.670 ppm, while the NH protons of the thirteen- and fourteen-membered rings of the 1,3- and 1,4-derivatives occur at 5.020 and 4.660 ppm, respectively. This *upfield* shift with increasing ring size is contrasted by the *downfield* shift observed for the methyl protons of the species $\text{C}_6\text{H}_4(\mu\text{-S}_4)(\mu\text{-S}_5)\text{NMe}$: The resonances for the 1,2-, 1,3-, and 1,4-derivatives are observed as sharp singlets at 3.190, 3.310, and 3.330 ppm, respectively.

These sharp singlets indicate that in all cases either only one conformer is present in solution or, more likely, that rapid ring inversion (pseudorotation) takes place at ambient temperature. Dynamic NMR studies at low temperatures are in progress. For other bicyclic S-N derivatives of benzene see ref. 5.

Acknowledgments

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