

NOVEL CYCLOPENTADIENO-1,3-DITHIOLS

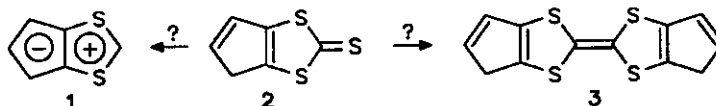
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This paper is dedicated to Professor E.C. Taylor on the
 occasion of his 70th birthday.

Abstract - The synthesis of 5-methylcyclopentadieno-1,3-dithiol-2-thione (16) and some related reactions are described.

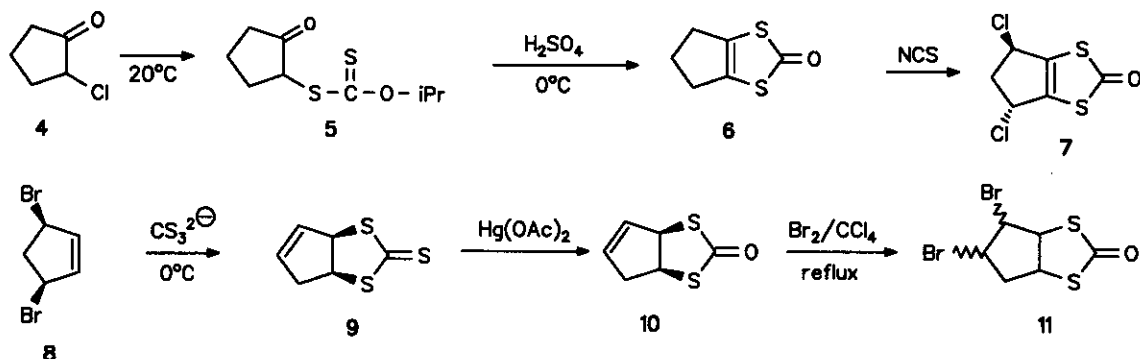
The cyclopentadieno-1,3-dithiol-2-thione (2) is a versatile heterocyclic compound that might be converted into a number of interesting derivatives, e.g. the pseudoazulene (1) or the tetrathiafulvalene (3). We have studied several approaches to 2 and tried its conversion into 1 and 3.



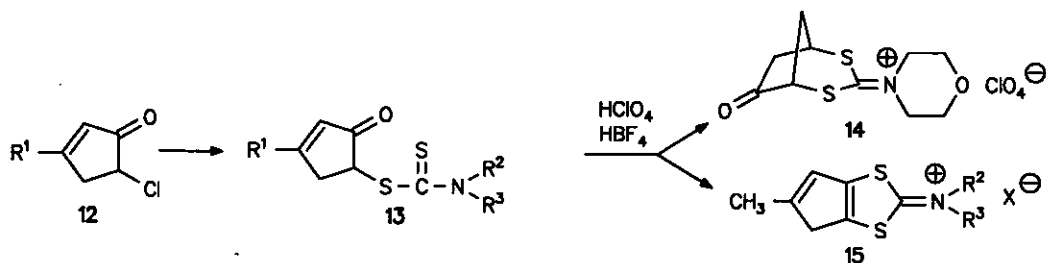
The condensation of 2-chlorocyclopentanone (4) with potassium isopropyl xanthate in acetone lead to the formation of 5 (50% yield), which was cyclized in conc. sulfuric acid at 0°C to give the 1,3-dithiol (6) (92%). We did not succeed in monohalogenating 6. Dichlorination to 7 (58%) could be achieved with *N*-chlorosuccinimide catalyzed by diphenyl diselenide.¹ All attempts, however, failed to eliminate one mol of hydrogen chloride from 7. Mild bases did not attack 7 whereas strong bases decomposed it completely.

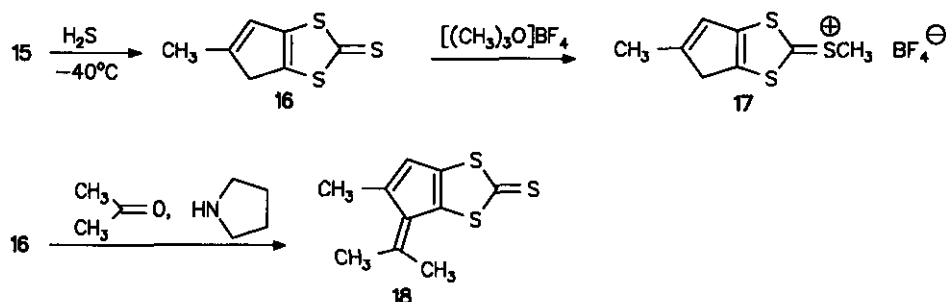
The readily available *cis*-3,5-dibromocyclopentene (8)² reacted with sodium trithiocarbonate in DMF to give the *cis*-1,3-dithiol-2-thione (9) (58%), which was desulfurized by mercuric acetate to form 10 (75%) and brominated to give 11 (95%, mixture of stereo isomers). Once again dehydrobromination

reactions of **11** were unsuccessful, either no reaction or decomposition was observed.

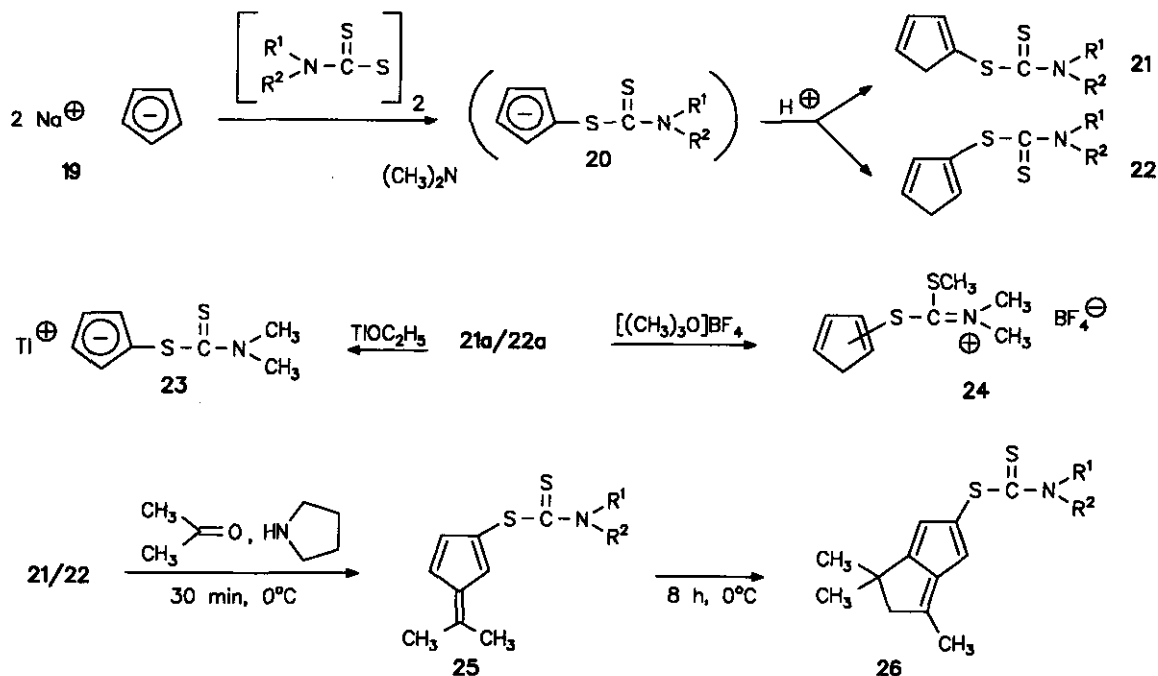


The experiments carried out so far indicated that the starting material should already carry the double bond missing in **6** or **10**. Unfortunately the corresponding 5-halo-2-cyclopentenones (**12**) are difficult to obtain. The chloro derivatives have been prepared from acetylenes and α,β -unsaturated acid chlorides under AlCl_3 -catalysis in fair yields.^{3,4} Condensation of **12** with alkali dithiocarbamates gave rise to **13** (>80%). The cyclization of **13** was effected by strong acids such as ethereal tetrafluoroboric acid (54%) or aqueous perchloric acid (70%). If position 3 in **13** is unsubstituted ($\text{R}^1=\text{H}$) a Michael addition was observed and **14** (90%, 2 h, 20°C in 70% HClO_4) was formed exclusively. If position 3 in **13** is substituted ($\text{R}^1=\text{CH}_3$) an elimination of water occurred leading to the iminium salts (**15**) (**15a**: $\text{R}^2=\text{R}^3=\text{CH}_3$, $\text{X}=\text{BF}_4$, 83%; **15b**: $\text{R}^2/\text{R}^3=\text{morpholine}$, $\text{X}=\text{ClO}_4$, 59%). These could be sulfhydrolysed at -40°C to give the 5-methylcyclopentadieno-1,3-dithiol-2-thione (**16**) (86%, mp 124-127°C) as yellow crystals. By a subsequent methylation the dithiolium tetrafluoroborate (**17**) was obtained.





Deprotonation experiments of the salts (15) or (17) did not lead to stable pseudoazulenes of type (1) but rather to decomposition products. The deep red colour observed after the addition of base might indicate the transitory formation of **1**. We have also been unable to convert **16** into a tetrathiafulvalene of type (3). Desulfurization experiments with triphenylphosphine or trimethylphosphite⁶ as well as reductions of **15**⁷ with subsequent condensation reactions failed. A formation of fulvenes, however, is possible as indicated by the isolation of **18** (90%, orange crystals, mp 126–128°C).



Sodium cyclopentadienide (19) cleaves thiuram disulfides; after acidification a mixture of the tautomeric cyclopentadienes (21) and (22) (ratio about 4:1) was isolated (21a/22a: $R^1 \approx R^2 = CH_3$, 64%, mp 58-69°C; 21b/22b: $R^1/R^2 =$ morpholine, 72%, mp 114-116°C). We have been unsuccessful to effect oxidative cyclizations of 21a/22a or its stable thallium salt (23) to iminium salts of type (15). The reaction mixtures obtained only indicated extensive decomposition.

The iminium salt (24) was isolated after alkylation of 21a/22a with trimethyloxonium tetrafluoroborate. Its deprotonation did not yield a fulvene like compound by an intramolecular condensation but rather methyl dithiocarbamate by rupture of the cyclopentadiene-sulfur bond. The reaction of 21/22 with acetone/pyrrolidine lead to the dihydropentalenes (26) (30-40%), shorter reaction times allowed the isolation of the fulvenes (25) (90-98%).

ACKNOWLEDGEMENTS

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REFERENCES AND NOTES

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