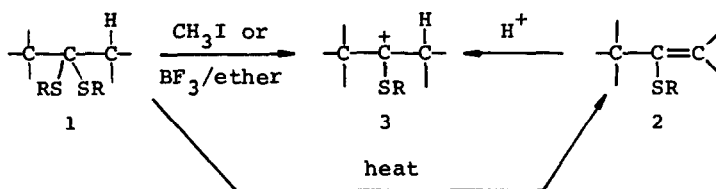


THE FACILE CYCLIZATION OF THIOACETALS AND VINYL SULFIDES WITH BUILT-IN NUCLEOPHILIC CENTRE VIA ALKYLTHIO CARBONIUM INTERMEDIATES¹

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As part of a general program we became interested in the use of alkylthio stabilized carbonium ions 3 with built-in nucleophilic centre for the synthesis of substituted thiacycloalkanes and alkylthio cycloalkanes.

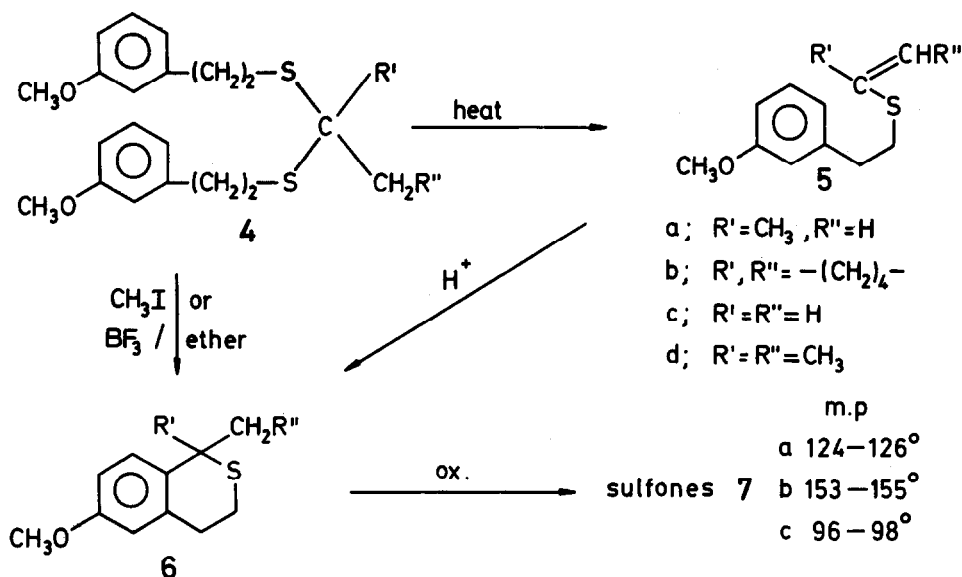


The pyrolysis of the readily accessible thioacetals 1 to the corresponding vinyl thioethers 2 is known since long³. Some of the factors governing this conversion have been studied by Campaigne and co-workers⁴.

We have found that both 1 and 2 can serve as precursors for the synthesis of a wide variety of cyclic compounds and we wish to report our preliminary results on the cyclization of the thioacetals 4a-d, derived from 2-(m-methoxyphenyl) ethanethiol⁵ and acetone, cyclohexanone, acetaldehyde or methyl ethylketone, respectively⁶.

The pyrolysis of the thioacetals 4a and b to the vinyl sulfides 5a and b, respectively, proceeds smoothly on a single passage through any GLC column at 200-250°, and can easily be automatized to a preparative scale. The eliminated thiol is collected as the first fraction on all columns used by us. Pyrolysis of compound 4c led to a reaction mixture consisting of components of which we have not been able to establish the structures thus far. Thioacetal 4d gave rise to a mixture of the three possible isomeric vinyl sulfides in a ratio of terminal to non-terminal olefines of 14 : 86. The two non-terminal isomers were present in roughly equal quantities⁷.

When the vinyl sulfide 5a, 5b or the isomer mixture 5d is stirred with HClO₄ (70%) at r.t. for 2-3 hr, the cyclized products 6a, b and d, respectively, are isolated in a quantitative yield on dilution with water, neutralization and extraction with organic solvents.



The conversion from **4** a-d to **6** a-d is effected by stirring a benzene solution of **4** at r.t. with 1.2-2 eq. of CH_3I (BF_3/ether was used for **4c**) and is complete after reaction times varying from 3-20 days.

The compounds **6** a-d have been characterized by oxidation to the corresponding sulfones **7** a-d.

All new compounds gave a satisfactory combustion analysis and their structures were in accordance with spectral data. Further applications of the cyclization reaction will be reported in due course.

Footnotes and references:

1. Taken in part from: H.R. Reus, forthcoming Thesis, Amsterdam.
2. To whom all correspondence should be addressed.
3. A. Sporzyński, Arch.Chem.Farm. **3**, 59 (1936); CA **32**, 8359 (1938), L.B. Turner, CA **31**, 1038 (1937).
4. E. Campaigne and J.R. Leal, J.Amer.Chem.Soc. **76**, 1272 (1954).
5. Prepared as described by G.G. Urquhart, e.a., Org.Synth. **21**, 36 (1946) for the synthesis of $n\text{-C}_{12}\text{H}_{25}\text{SH}$.
6. Prepared following the procedure described by E. Baumann, Ber. **18**, 883 (1885)
7. Partial overlap of the NMR signals prevented the establishment of the cis/trans ratio with sufficient accuracy.