

The Syntheses of a *gem* Dithiol under Mild Conditions

BENGT MAGNUSSON

Department of Organic Chemistry, Chemical Institute, University of Uppsala, Sweden

Preparation of *gem* dithiols has been limited in the past to the reaction of carbonyl compounds with hydrogen sulphide under various conditions. These conditions, however, are rather critical and temperature, pressure and reaction time must be carefully adjusted for each ketone or aldehyde. Certain aldehydes give good yields under moderate pressures (30–50 atm)¹, while other carbonyl compounds require pressures of 7 500–8 500 atm. Chloral, highly fluorinated ketones and aldehydes, and other carbonyl compounds which form stable *gem* diols do not form *gem* dithiols under pressure. Instead *gem* ol-thiols are obtained, sometimes in good yields². 1,3-Diphenyl-2,2-dimercaptopropane was prepared in 80 % yield by Carmack by simply passing hydrogen sulphide and hydrogen chloride at ordinary pressure into a cold ethanol solution of dibenzylketone³. Unfortunately, this simple method does not seem to be generally applicable, as attempts by the author to apply it to phenylacetone, dibenzylacetone, α -tetralone, 2-indanone, anthrone, xanthone, and fluorenone have all failed due to the formation of trimers or polymers of the thioketones, or total lack of reaction.

Many attempts have also been made to reduce duplodithioketones to *gem* dithiols, but the duplodithioketones are very stable compounds and it is not possible to reduce them with tin and hydrochloric acid. When

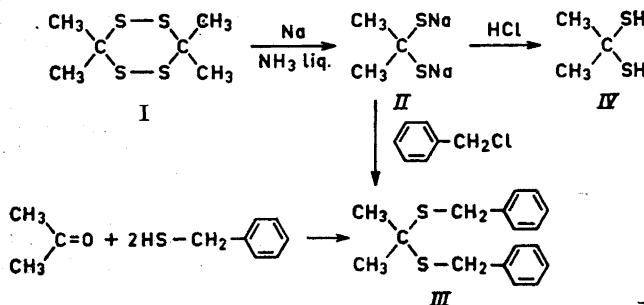
they are boiled for an extended period a faint odor of mercaptane is certainly perceptible, but under these conditions the *gem* dithiols are not stable.

Lithium-aluminium hydride splits up the tetrathiane ring, but *gem* dithiols are not stable in alkaline medium. Furthermore, one of the *gem* SH-groups is substituted by hydrogen⁴. Reduction with hydrogen and Raney-nickel was not tried, because the Raney-nickel would cause desulphuration of the tetrathiane ring, as would even copper powder do in boiling dioxane. Moreover, the nickel catalyst would have been poisoned by the sulphur.

Experiments with Carmacks dithiol showed, however, that its disodium salt was stable in ethanol solution at -70° and that it was possible to react this salt with methyl iodide. Therefore attempts were made to reduce duplodithioacetone⁴ I with sodium in liquid ammonia. This attempt was successful. The presence of the *gem* dithiol was established by adding benzylchloride to the reaction mixture. β,β -Bis-benzylmercaptopropane III was isolated in 80 % yield. It was identical with a specimen prepared from acetone and benzylmercaptane according to Fromm *et al.*⁵

The free dithiol IV could be isolated by removing the ammonia in vacuum after the reduction with sodium. The solid disodium salt II was dispersed in cold ether and hydrogen chloride was passed into the reaction mixture until the *gem* dithiol was set free. From the ether solution, IV was obtained in 30 % yield after one distillation. It was further purified by sublimation at 0.1 mm. Crystal flakes with a melting point of $6-8^\circ$ were obtained. (lit. $4-8^\circ$)¹. (Found: C 33.98; H 7.56; S 58.21. Calc. for $C_2H_6S_2$: C 33.29; H 7.45; S 59.26).

The compound gives a yellow precipitate with lead acetate in ethanol, which turns



red within one second and is rapidly decomposed to black lead sulphide.

These experiments exclude structures of duplodithioacetone with one thioether bond and one trisulphide bond.

Further they point to a new method to obtain *gem* dithiols.

The author is indebted to Professor A. Fredga for his encouraging interest in this work.

1. Cairns, T. L., Evans, G. L., Larchar, A. W. and McKusick, B. C. *J. Am. Chem. Soc.* **74** (1952) 3982.
2. Harris, Jr, J. F. *J. Org. Chem.* **25** (1960) 2259.
3. Berchold, G. A., Edwards, B. E., Campaigne, E. and Carmack, M. *J. Am. Chem. Soc.* **81** (1959) 3184.
4. Magnusson, B. *Acta Chem. Scand.* **13** (1959) 1031.
5. Fromm, E., Forster, A. and v. Scherschewitski, B. *Ann.* **394** (1912) 343.

Received February 23, 1962.

Studies on Peroxy Compounds XXII* Preparation of 2,3,4,5,4',5'- Hexahydro-2,2'-dithienyl

CURT BERGLUND and SVEN-OLOV
LAWESSON

Department of Organic Chemistry, Chemical
Institute, University of Uppsala,
Uppsala, Sweden

2-Benzoyloxy tetrahydrothiophene, I, was first prepared in 1957 by Horner and Jürgens¹. The starting materials were benzoylperoxide and tetrahydrothiophene. Besides I, tetrahydrothiophene sulphoxide, benzoic acid and the anhydride of benzoic acid were obtained.

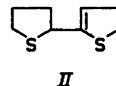
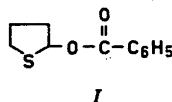
Sosnovsky^{2,3} prepared I by reacting tetrahydrothiophene with *t*-butyl perbenzoate in the presence of cuprous bromide. In that case no oxidation of the sulphide

* Part XXI. Lawesson, S.-O., Dahlén, M. and Frisell, C. *Acta Chem. Scand.* **16** (1962). *In press.*

** Present address: Department of Chemistry, University of Aarhus, Aarhus, Denmark.

Acta Chem. Scand. **16** (1962) No. 3

did occur. By pyrolysis of I for 2 h at 110°C a yield of 80 % of 2,3-dihydrothiophene was obtained. In another experiment Sosnovsky heated I in *t*-butanol under reflux for 100 h and isolated a quantitative yield of benzoic acid and a dimer of dihydrothiophene with a b.p. of 90°C/0.5 mm Hg, $n_D^{25} = 1.6006$. Mol. wt. 179. Nothing was said about the structure of the dimer. The present authors had at the same time⁴ performed this reaction. When we pyrolyzed I at 160–170°C for 2 h no 2,3-dihydrothiophene could be detected but a 45 % yield of the dimer was obtained. B.p. 88–90°C/0.2 mm Hg, $n_D^{20} = 1.6023$. Mol. wt. 168. Although 2,3-dihydrothiophene certainly is an intermediate in our case, the dimerization compound is the final product.



Gas chromatographic analysis showed one peak, indicating a single compound. I.R. measurements showed a double bond and elementary analyses agreed well with the formula, C₈H₁₂S₂. The dimer was desulphurated with Raney Ni and the hydrocarbon formed was octane which was shown by gas chromatographic analysis. The N.M.R. spectrum of the dimer was also taken and the relative intensities of the bands were 1:1:10, corresponding to one ethylenic, one tertiary and ten methylenic hydrogens. The configuration of the dimer was thus fixed to be II.

A full paper of these and related results is being prepared.

We wish to thank Prof. A. Fredga for his interest in this investigation. Financial support from *Magnus Bergvalls stiftelse* and *Lucidol Division, Wallace & Tiernan, Inc., Buffalo, N.Y. U.S.A.* are also acknowledged.

1. Horner, L. and Jürgens, E. *Ann.* **602** (1957) 135.
2. Sosnovsky, G. *J. Org. Chem.* **26** (1961) 281.
3. Sosnovsky, G. *Tetrahedron* **18** (1962) 15.
4. Lawesson, S.-O. and Berglund, C. *Tetrahedron Letters* **2** (1960) 4.

Received March 12, 1962.