The Syntheses of a gem Dithiol under Mild Conditions

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Preparation of gem dithiols has been limited in the past to the reaction of carboxyl 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 carboxyl compounds require pressures of 7500–8500 atm. Chloral, highly fluorinated ketones and aldehydes, and other carboxyl compounds which form stable gem diols do not form gem dithiols under pressure. Instead gem ol-thiols are obtained, sometimes in good yields ². 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 dibenzylketone ³. Unfortunately, this simple method does not seem to be generally applicable, as attempts by the author to apply it to phenylacetonitrile, 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 hydrogen ⁴. 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 Carmack's 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 duplodithiocetone ⁴ 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° were obtained. (l lit. 4–8°). (Found: C 33.98; H 7.56; S 58.21. Calc. for C₇H₈S₂: C 33.29; H 7.45; S 59.26).

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

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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.

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Studies on Peroxy Compounds

XXII * Preparation of 2,3,4,5,4',5'-Hexahydro-2,2'-dithienyl

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2-Benzoyloxy tetrahydrothiophene, I, was first prepared in 1957 by Horner and Jürgens 1. The starting materials were benzoylperoxide and tetrahydrothiophene. Besides I, tetrahydrothiophene sulfoxide, 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 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, \( n_D^2 = 1.6006 \). Mol. wt. 179. Nothing was said about the structure of the dimer. The present authors had at the same time performed this reaction. When we pyrolyzed I at 180—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, \( n_D^2 = 1.6023 \). Mol. wt. 168. Although 2,3-dihydrothiophene certainly is an intermediate in our case, the dimerization compound is the final product.

\[ \text{I} \]

\[ \text{II} \]

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, \( \text{C}_8\text{H}_{12}\text{S}_2 \). 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.

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