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Dithiaspiroheptaan

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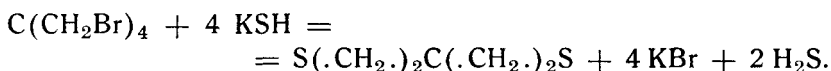
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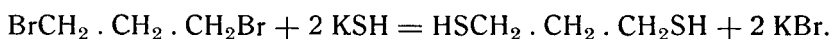
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Summary.

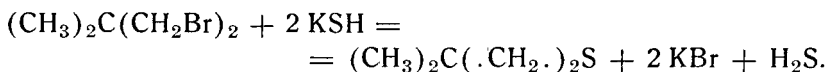
As Schurink ascertained, the reaction of carbontetramethylbromide with potassium hydrosulphide in alcoholic solution yields dithia-2,6spiro-4heptane, and not carbontetramethanethiol (tetra-thiopentaerythritol):



Autenrieth and Wolff followed the same method in preparing propanedithiol-1,3 from dibromo-1,3propane:



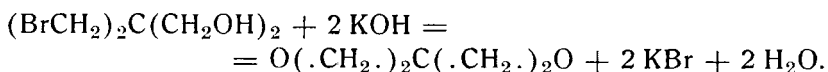
The first reaction was again studied carefully, but no trace of mercaptan could be detected. The reaction was carried out also with dimethyl-2,2dibromo-1,3propane; only the cyclic sulphide and no mercaptan resulted:



Hence the quaternary carbon atom causes the closure of the ring and prevents the mercaptan to be formed, especially when the quaternary carbon atom already forms part of another thiacyclobutane-nucleus.

Methods of preparation were elaborated for dithiaspiroheptane and for dimethylthiacyclobutane.

Dioxa-2,6spiro-4heptane (internal ether of pentaerythritol) was prepared by the action of potassium hydroxide on dibromo-methyl-2,2propanediol-1,3:



The monosulphoxide, the disulphoxide, the sulphoxidesulphone and the disulphone of dithiaspiroheptane were prepared by oxidation of this compound; the monosulphone by reduction of the sulphoxide-sulphone.

These oxides combine with mercuric chloride except the disulphone; the resulting compounds were analysed and described.

The disulphoxide also reacts readily with other salts. A number of combinations with chlorides of bivalent metals were prepared. By recrystallisation of a similar combination with cobalt *d*-campher-sulphonate from absolute alcohol the disulphoxide could be resolved (M_D^{18} of the chloroplatinate in water = -10°).

The optical activity is important for the following reasons:

1. The disulphoxide does not contain any asymmetrical carbon or sulphur atom; the optical activity is due to a pure molecular enantiomorphy.

2. The given method may be applied to other compounds which do not combine with acids and bases.

3. The enantiomorphy of one of the dioxides of dithiaspiroheptane proves that it is the disulphoxide; the other one must be the monosulphone.

4. Enantiomorphy of the disulphoxide is impossible if the position of the methylene groups round the spiro-carbon atom is plane or pyramidal; hence the optical activity proves that the position is tetrahedral or bisphenoidal.

The reaction of dithiaspiroheptane with bromine and iodine yielded a tetrabromide and a tetraiodide. By bromination in benzene and hydrolysis of the intermediary product a dibromodisulphoxide was obtained.

Dithiaspiroheptane does not react with water or alcoholic ammonia at 200° . Hence it seems to be more resistant than thiacyclobutane, which is converted into an acyclic compound.

The reaction with methyl iodide yields a monocyclic sulphonium iodide, the structure of which could be established.

Similar derivatives were obtained from dimethylthiacyclobutane. Dioxaspiroheptane combines with corrosive sublimate, but does not react with iodine nor with methyl iodide.
