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Vorming van spiranen bij de bereiding van thioacetalen en hun röntgenografisch onderzoek

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XII. SUMMARY.

The condensation of 1,3-dichloroacetone with monothioglycol gave rise to the formation of a spirocyclic compound of formula 1 (scheme p. 87). Its structure was proved by the reaction of monothioglycol sodium $\text{NaSCH}_2\cdot\text{CH}_2\text{OH}$ with dichloroacetone.

When a compound can give a thioacetale as well as an ordinary acetale, the former will result. In our case the sulphur atoms are attached to the spiro-carbon atom. Therefore we must conclude that the first stage of the reaction is the loss of hydrogen chloride.

The behaviour of dithioglycol and monothioglycol towards 1,3-dichloroacetone is the same; glycol does not lead to a spirane. In this case no hydrogen chloride splits off and an ordinary acetale, ethylidene-1,3-dichloroacetone, is formed. The activity of a SH group is sufficient to react with the chlorine atoms of dichloroacetone, while a OH group is not enough reactive.

When continuing our experiments we observed that the 2,6-dibromocyclohexanone gave rise to spiranes, in the same way as 1,3-dichloroacetone did. In the case of two 1,3-dimercaptanes, spiranes with two rings of seven atoms were formed.

Whilst dichloroacetone possesses twice the group $-\text{CO}\cdot\text{CH}_2\text{Cl}$, chloroacetyl chloride contains one such group besides a very reactive chlorine atom. Only with dithioglycol it forms a spirane.

The interaction of phosgene with glycol and the thioglycols leads to a carbonate and thiocarbonates.

One aromatic dithiol, o.dimercaptobenzene, was involved in the research; with 1,3-dichloroacetone no definite product was formed, while chloroacetyl chloride gave rise to a spirane. The condensations of dithioglycol with chloroacetyl chloride and phosgene succeeded at room temperature; o.dimercaptobenzene only reacts in boiling dioxane or in a closed tube at 160° . The cause of this difference is not the greater distance of the sulphur atoms in the aromatic compound, but their immobility.

In the second part of this thesis a description is given of the

crystalline structure of some of our spiranes, as determined with the aid of the "retigraph" and a Sauter goniometer. The theory of the retigraph was given besides the method of working with it. With this instrument one can photograph a lattice-plane of the reciprocal lattice of a crystal in its real form. Therefore the indication of the reflections becomes easy and, because a whole layer line is photographed on the film, a good survey of these reflections is obtained.

In the case of four spiranes (scheme p. 87: 1, 2, 3, 4) the space group was determined. Only the spirane 1 proved to possess the twofold axis we should attribute to it on account of stereochemical considerations.

The spirane 2 forms twins along the plane (100). When the crystal is turned around the c-axis, a "retigram" of an odd layer line shows the lattice planes of the reciprocal lattice of each twin; the net lines of one twin, parallel to the b axis, just lie between those of the other, so that it seems as if only one lattice is present. An even layer line around the c axis being photographed, the lattices of the twins coincide, and no sign of the twinning is seen. The crystallographic constants thus answer to the relation $c/a = 4 \cos \beta$.

Finally the crystals of some of the other spiranes were described.