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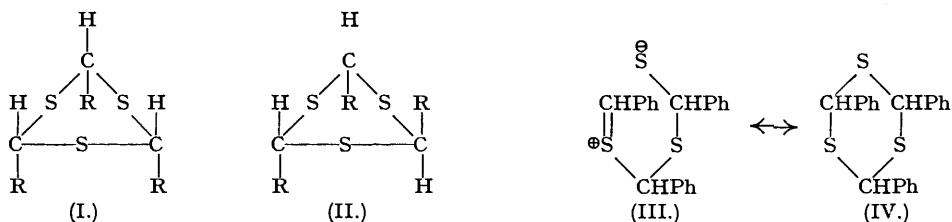
Organic Sulphur Compounds. Part XXX. The Stereochemistry of Trimeric Thioaldehydes. By ALEXANDER SCHÖNBERG and MOHAMED ZAKI BARAKAT.

THIOALDEHYDES are not stable as monomers, so very little is known about them; but many are known in trimeric form, *e.g.*, thioformaldehyde, thioacetaldehyde, and thiobenzaldehyde (Müller, *J. pr. Chem.*, 1927, **116**, 175; Baumann and Fromm, *Ber.*, 1889, **22**, 2600; *Ber.*, 1891, **24**, 1419, 1431, 1441). These are believed to be derivatives of 1 : 3 : 5-trithian (I; R = H), and their reactions agree with such a structure.

Some of the trimeric thioaldehydes have been prepared in only one form, but Wörner (*Ber.*, 1896, **29**, 139) enumerates sixteen which exist in two forms, known as α - and β -forms, the latter being the more stable.

According to Baumann and Fromm (*Ber.*, 1891, **24**, 1429), the existence of the two forms is due to stereoisomerism [compare (I) and (II)]. Some of the trimeric thioaldehydes are readily converted catalytically into their isomers; *e.g.*, trithioanisaldehyde, m. p. 127°, is changed into its isomer, m. p. 183°, in less than a minute on treatment of its solution in benzene with a few crystals of iodine at room temperature, and the change of α - into β -trithiobenzaldehyde is almost as rapid (Baumann and Fromm, *loc. cit.*, pp. 1441, 1435). When α -trithiobenzaldehyde is treated with acetyl chloride, crystals of the β -form begin to separate before the α -form is completely dissolved (Suyver, *Rec. Trav. chim.*, 1905, **24**, 400). The α -form of trithioacetaldehyde is converted into the β -form at room temperature in the presence of traces of iodine (*idem, ibid.*, p. 387).

These ready changes of trimeric thioaldehydes from one isomer to the other seem to us not to be in accordance with Baumann and Fromm's hypothesis. In the cyclic series interconversion of *cis-trans*-isomers takes place *readily* only when there is a possibility of tautomerism, *e.g.*, with menthone and camphoric acid (Shriner, Adams, and Marvel in Gilman's "Organic Chemistry," New York, 1938, p. 399; Wagner-Jauregg in Freudenberg's "Stereochemie," Leipzig and Vienna, 1932, p. 860); but with the compounds in question there is no such possibility. Current theory demands that in molecules such as (I) and (II) the ring structures do *not* restrict the freedom of rotation around the single



bonds between the atoms of the ring (Gilman, *op. cit.*, p. 395), but it is evident that there is no justification for such an assumption, so, in order to support Baumann and Fromm's stereochemical conception, one would have to assume that the catalyst may cause reversible depolymerisation and thus bring about the observed change of one form into the other. This would be an *ad hoc* hypothesis without experimental evidence, for the 1 : 3 : 5-trithians are stable even to strong alkalis and acids.

To explain the existence of α - and β -forms of trimeric thioaldehydes and the ready conversion of the former into the latter, the following theory is advanced. The three carbon atoms and the three sulphur atoms in these 1 : 3 : 5-trithian molecules do not lie in one plane, but may be regarded as "boat" and "chair" structures, the interconversion then being readily explained. According to this explanation, the α - and the β -form of trithioacetaldehyde, for example, are either both *cis*- or both *trans*-forms; the isomeric change is due to a change of the "boat" into the "chair" structure or *vice versa*. This new theory demands a greater number of isomers than have, so far, been isolated, but it is not thereby necessarily invalidated, for other isomers (γ -forms) have occasionally been described, which have been attributed *inter alia* to polymorphism or the occurrence of eutectic mixtures.

In harmony with the new theory is the fact that the molecule of trithioformaldehyde in benzene solution and in the crystal contains, not a planar but a puckered six-membered ring (Sachse's chair ring) (Moerman and Wiebenga, *Z. Krist.*, 1937, **97**, 330).

The "chair" and the "boat" form of cyclohexane have not been isolated, but the cyclohexane and the 1 : 3 : 5-trithian ring system differ, the latter but not the former being capable of resonance, (III) \leftrightarrow (IV) (only two resonating structures are drawn), so the two possible forms of cyclohexane and its simple derivatives are not stabilised by resonance.

The similarity between the cyclohexane ring and the trithian ring which is frequently stressed is only formal, in contrast to the real similarity between the thiophen and the benzene ring. This may be seen from a comparison of the m. p.s, benzene (5.5°), thiophen (-30°), cyclohexane (6°), and trithioformaldehyde (215°).—FOUAD I UNIVERSITY, ABBASSIA, CAIRO. [Received, October 24th, 1944.]