The Polymeric Nature of a Supposed Simple Mercury Ring Compound

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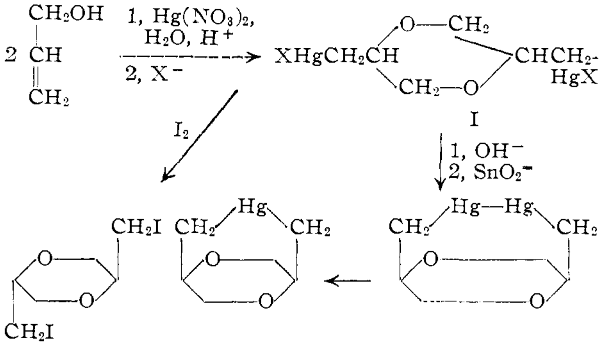
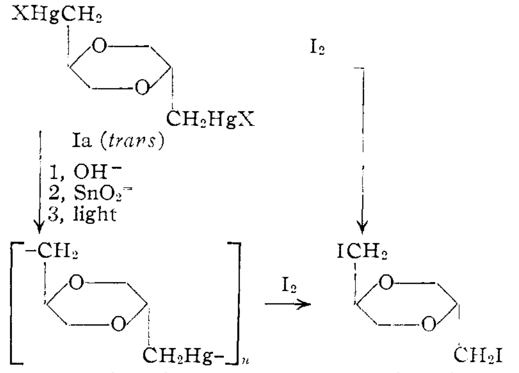
The "diepiiodohydrin" obtained by Sand[1] by the reaction of iodine with a bis-(iodomercurimethyl)-*p*-dioxane (I) has been shown by us[2] to be *trans*-2,5-*bis*-(iodomethyl)-*p*-dioxane (II). This assignment of configuration is in apparent conflict with the claim of Sand[3,1] that the corresponding bromo derivative[4] of I could be reduced by stannite ion to a dimercury bicyclic ring compound III which decomposed in the presence of light to a new bicyclic compound IV containing a single mercury atom in one ring. A dioxane such as IV would of necessity have a *cis*-dimethylenemercury bridge, and since it was obtained by mild reagents and conditions from I, that compound also would be *cis*. If I is *cis*, it would not be expected to yield II (*trans*) on mild iodination. The supposed sequence of Sand's reactions is given in Fig. 1. It is difficult to believe that IV, which must be *cis*, and II, which we have shown to be *trans*, could both be obtained under mild reaction conditions from I. We therefore thought that the structure assigned to IV must be incorrect, even though it has been accepted by several authorities[5] who have reviewed Sand's work. Although Sand uses the objective "vorläufig" in one portion of his paper to describe the mercury ring formula of IV, his reviewers present the ring formula without qualification.



II (*trans*) IV (*cis*) III (*cis*)

Fig. 1.

We can find no record that the molecular weight of IV was ever determined. We have prepared the supposed IV and found its molecular weight to be about 5×10^3. Since it is polymeric, it could be either *cis* or *trans*. On treatment of the supposed IV with iodine we obtained *trans*-2,5-bis-(iodomethyl)-*p*-dioxane. These facts indicate that the supposed IV is polymeric and *trans* and that its formula should be represented by IVa. The latter would be expected to yield II on iodination. Our interpretation of the reactions is given in Fig. 2.



IVa (*trans*) II (*trans*)

Fig. 2.

We wish to point out that the hypothetical monomer IV requires a C–Hg–C bond that is not linear. Grdenic[6] in refuting another structure of Sand's,[3] maintains that such compounds do not exist. In any event, a structure that requires an angular C–Hg–C bond should be postulated only when based on firm experimental evidence.

The question of the structure and configuration of compounds such as Ia is assuming considerable importance in the study of protein structure. For example, Edsall[7] and his co-workers in an elegant research have measured the equilibrium constant for the dimerization of human serum mercapto albumin with this type of compound and found it to be 50,000 times greater than the corresponding equilibrium constant for the dimer formed by simple mercuric salts. They ascribe this difference to the closer approach and consequent deformation of protein molecules necessary when the mercuric ion is used. Their explanation is consistent with our assignment of structure and configuration for Ia, since the greatest separation of mercury atoms and minimum deformation of protein molecules would be possible in the case of the *trans*-2,5-isomer.

Experimental

Poly-*trans*-2,5-*p*-Dioxanedimethylenemercury (IVa).—This material was prepared according to the directions of Sand[3] for the preparation of "mercuriverbindung $C_6H_{10}O_2Hg$" (IV). 0.170 g. of this material dissolved in 18.4 g. of benzene depressed the freezing point of benzene by 0.10°: mol. wt. about 5×10^3; calcd. for monomer 3.14×10^2.

Iodination of IVa.—To 2.23 g. of poly-*trans*-2,5-*p*-dioxanedimethylenemercury (IVa) was added 12 ml. of water, 4.92 g. of iodine and 8 g. of potassium iodide. The mixture was heated on a steam-bath for 18 hours. To the cooled mixture was then added aqueous sodium bisulfite to destroy excess iodine. It was extracted with 40 ml. of chloroform and upon evaporation of the extract 1.67 g. (64%) of *trans*-2,5-bis-(iodomethyl)-*p*-dioxane was obtained. Recrystallized from benzene it melted at 158° and did not depress the m.p. of authentic *trans*-2,5-bis-(iodomethyl)-*p*-dioxane.

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