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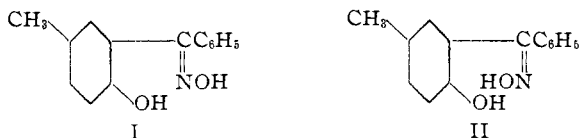
 COMMUNICATIONS TO THE EDITOR
 

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 STEREOISOMERIC *o*-HYDROXYBENZOPHENONE  
OXIMES

Sir:

We have found, in the extension of earlier experiments on the chemical behavior accompanying hydrogen bonding [Blatt, *THIS JOURNAL*, **60**, 205 (1938)], that bonded *o*-hydroxybenzophenone oximes, such as (I), readily form characteristic sparingly soluble copper derivatives, whereas stereoisomeric non-bonded oximes such as (II) do not.



The reaction is extremely sensitive, and the differentiation between stereoisomers is sharp. With the oxime (I) the limit of sensitivity is between 0.0001 g. and 0.00001 g. of oxime per cc. of solution, using an ethereal solution of the oxime and shaking with an excess of saturated aqueous copper acetate. Taking the mean of these two values, the limiting concentration of the oxime is approximately 0.0001 molar. The non-bonded isomer (II) forms no insoluble copper derivative at a concentration as high as 0.025 g. per cc., which is some five hundred-fold greater than the minimum concentration necessary with the bonded isomer. These experiments open a new approach to the problem of the structure of chelate metallic derivatives; they will be reported in detail at a later date, together with the conclusions to which they lead.

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 CRYSTALLINE D-ALTROSAN<sup>1</sup>

Sir:

Several years ago it was stated [Richtmyer and Hudson, *THIS JOURNAL*, **57**, 1721 (1935)] that "crystalline D-altrose is converted by hot hydrochloric acid from  $[\alpha]^{20}_D + 34$  to  $-98^\circ$ ; this

(1) Publication authorized by the Surgeon General, U. S. Public Health Service.

is accompanied by partial loss of reducing power, presumably due to the formation of an anhydro-D-altrose to the extent of 57% at equilibrium." At that time we attempted to isolate the assumed anhydro-altrose by oxidizing the altrose component of this equilibrium mixture (*ca.* 12 g.) with bromine water in the presence of barium benzoate [Hudson and Isbell, *ibid.*, **51**, 2225 (1929)], removing the benzoic acid, barium, and bromine in the customary way, and the D-altroic acid as its calcium salt; the anhydro-altrose remained and was concentrated to a sirup with the expected high levorotation. After three years in a desiccator the sirup began to crystallize, and from it has been obtained 2.5 g. of a new compound. This substance, from a consideration of its composition, rotation, and lack of reducing action toward Fehling's solution, must be the desired anhydride of altrose, and accordingly is named D-altrosan. It is readily soluble in water and in methyl alcohol, sparingly soluble in absolute ethyl alcohol. It was recrystallized as colorless, transparent prisms by allowing its methyl alcohol solution to evaporate in a desiccator over granular calcium chloride. The melting point of D-altrosan in a capillary tube appeared to be about  $135^\circ$ , after considerable preliminary sintering; however, a microscopic examination indicated that the probable melting point lies between  $80$  and  $90^\circ$ , the tiny melted particles being too viscous to coalesce until the higher temperature is reached. The rotation of D-altrosan,  $[\alpha]^{20}_D - 215^\circ$  in water (*c*, 1), is close to the  $-220^\circ$  estimated "from the rotation of D-altrose ( $+32^\circ$ ) and the value  $-98^\circ$  for the equilibrium mixture containing 43% D-altrose." Heated for two and one-half hours at  $98-100^\circ$ , a solution of D-altrosan in *N* hydrochloric acid (*c*, 1) became strongly reducing toward Fehling's solution, and changed in rotation to  $[\alpha]^{20}_D - 109.1^\circ$ ; calculated as altrose, this value becomes  $-98.2^\circ$ , in perfect agreement with the rotation  $-98.2^\circ$  previously reported for D-altrose heated with acid under the same conditions. *Anal.*<sup>2</sup> Calcd. for  $C_6H_{10}O_5$ : C, 44.44; H, 6.22. Found: C, 44.46; H, 6.30.

The study of D-altrosan, and particularly the

(2) Through the kindness of Dr. W. T. Haskins of this Laboratory.