

state was a function of crystal size and ranged from 60 to 95 per cent when the crystal size varied from a few tenths of a millimetre to three millimetres on edge. The crystals were approximately cubic in shape. This type of observation has led us to conclude that the hexavalent state of the radiosulphur that normally occurs in neutron-irradiated potassium chloride is due in part at least to oxidation by oxygen that has been occluded in the crystals. At first sight this type of argument seems to be incompatible with the observation on rubidium chloride¹; however, it should be pointed out that if the above picture is correct, the chemical state of the sulphur should be dependent on the prior history of the crystals. If the crystals were made in such a way that oxidizing materials were excluded, then one might expect to find the sulphur in the -2 state.

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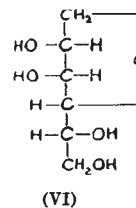
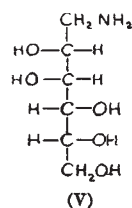
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Jan. 18.

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² Koski, W. S., *J. Amer. Chem. Soc.*, **71**, 4042 (1949).

Deamination of Certain Amino Derivatives of Sugars and Sugar Alcohols

It has already been observed¹ that the deamination of certain amino-sugar derivatives leads to the formation of ethylene oxide anhydro sugars. Thus, when 2-amino 4 : 6-benzylidene α -methyl-2-deoxyaltroside was treated with nitrous acid in acetic acid solution, deamination proceeded rapidly and smoothly and 2 : 3-anhydro 4 : 6-benzylidene α -methylalloside was precipitated. Similarly, the relatively insoluble 2 : 3-anhydro 4 : 6-benzylidene α -methylmannoside was obtained when 3-amino 4 : 6-benzylidene α -methyl-3-deoxyaltroside was deaminated. It might be argued that these two examples are exceptional cases, since both the anhydro sugar derivatives were precipitated during the deamination of the amines from which they were derived, and their formation may be due primarily to their insolubility. Such a possibility has now been eliminated, because several new cases of the formation of ethylene oxide anhydro sugar derivatives from amino-sugars have been observed in which all the reactants and products remained in solution during



the reaction. Thus, deamination of 6-amino 1 : 2-*iso*-propylidene 6-deoxyglucose (I) in acetic acid solution gives 5 : 6-anhydro-1 : 2-*iso*propylidene glucose (II), and that of 4-amino 1 : 6-anhydro 4-deoxy- β -D-mannose² (III) under similar conditions furnishes 1 : 6-3 : 4-dianhydro- β -D-talose (IV). In this case the deamination is accompanied by Walden inversion at C₄.

Experiments on the deamination of carbohydrate amino-derivatives have also been extended to the sugar alcohol series. Thus 1-amino-1-deoxysorbitol was shown to give rise to 1 : 4-anhydrosorbitol by Bashford and Wiggins³, and now the deamination of 1-amino-1-deoxymannitol (V) has been carried out and found to result in the formation of 1 : 4-anhydro-mannitol (VI). Studies on the deamination of the 2-amino-2-deoxysorbitol, obtained by the catalytic hydrogenation of glucosamine, have been commenced. An anhydrohexitol, isolated as its tetra-acetate, was obtained (found : C, 50.6; H, 5.9; OAc, 51.6. C₁₄H₂₀O₉ requires C, 50.6; H, 6.0; OAc, 51.8 per cent). This, by analogy with the work of Levene⁴ on the deamination of 2-aminohexosaminic acids, is most probably a 2 : 5-anhydrohexitol which, if Walden inversion accompanies the deamination, will be 2 : 5-anhydromannitol, or if no such inversion of configuration occurs at C₂, will be 2 : 5-anhydro-sorbitol. Efforts are being made to decide this question.

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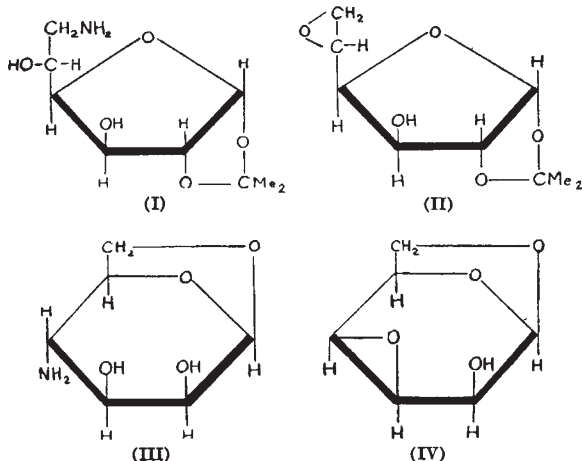
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Nov. 28.

¹ Wiggins, L. F., *Nature*, **157** 300 (1946).

² James, Mrs. S. P., Smith, F., Stacey, M., and Wiggins, L. F., *J. Chem. Soc.*, 625 (1946).

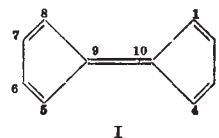
³ Bashford, V. G., and Wiggins, L. F., *J. Chem. Soc.*, 299 (1948).

⁴ Levene, P. A., "Hexosamines and Mucoproteins" (Longmans, Green and Co., Ltd., 1925).



Fulvalene

IN a recent paper¹ dealing with the theoretical treatment of the chemistry of some non-benzenoid hydrocarbons, some unexpected results were obtained for the as yet unknown hydrocarbon fulvalene (I).



The π -electron densities, q , of fulvalene have been computed², and it is found that position 2 has a lower charge than position 1. In spite of this the calculated atomic polarization energies³, A'_n , which may be considered to be approximations to the relative activa-