

## Short Communications

The Structure of Some  
Salts of 2:6-Dimethyl- $\gamma$ -pyrone  
(2:6-Dimethyl-4H-pyran-4-one)

HÅKON HOPE

Universitetets kjemiske institutt,  
Blindern-Oslo, Norway

It was first shown by Collie and Tickle <sup>1</sup> that 2:6-dimethyl- $\gamma$ -pyrone (DM $\gamma$ P) has the property of uniting with various acids to form stable crystalline salts. Since this discovery a considerable amount of work has been done to determine the mechanism of the salt formation (for references see <sup>2</sup>). It is now a widely accepted theory that the proton from the acid is added to the carbonyl oxygen, and that at the same time the pyrone ring acquires an aromatic character. From X-ray data <sup>3</sup> it is known that the free DM $\gamma$ P ring may be described roughly as a system containing two C—C double bonds (C<sub>2</sub>—C<sub>3</sub> and C<sub>5</sub>—C<sub>6</sub>) and two C—C single bonds.

Determination of the crystal structures of some of the DM $\gamma$ P salts will probably give the information which is needed to decide whether these ideas are correct or not. Structure analyses of some of the salts have therefore been started. Up to this time the salts DM $\gamma$ PHBr, DM $\gamma$ PHBr.H<sub>2</sub>O, DM $\gamma$ PHBr.2H<sub>2</sub>O, and DM $\gamma$ PHCl.H<sub>2</sub>O have been investigated by X-ray methods.

The salts were prepared by adding dry HBr (HCl) to a solution of DM $\gamma$ P in benzene or ether <sup>4</sup>. The precipitate was collected on a glass filter and dried *in vacuo*. The anhydrous salts were found to be hygroscopic and had to be kept in a desiccator over a drying agent.

Anhydrous DM $\gamma$ PHBr was crystallized by cooling a solution in a mixture of ether and methanol (1:1). The description given by Collie and Tickle <sup>1</sup> is somewhat ambiguous, as the crystals prepared according to their method contain water of crystallization. The crystals are monoclinic, with a marked tendency towards twin formation.

Space group:  $P2_1/c$ Cell dimensions:  $a = 6.89 \text{ \AA}$ ;  $b = 15.52 \text{ \AA}$ ; $c = 15.51 \text{ \AA}$  $\beta = 94.9^\circ$  $Z = 8$  gives  $\rho_{\text{calc}} = 1.65$ g/cm<sup>3</sup> $\rho_{\text{obs}} = 1.64 \text{ g/cm}^3$ 

The monohydrate DM $\gamma$ PHBr.H<sub>2</sub>O was prepared by exposing anhydrous DM $\gamma$ PHBr to air until one mole of H<sub>2</sub>O per mole of the salt had been taken up. It was crystallized in the same manner as the anhydrous salt. The crystals are triclinic plates, also with a tendency to twin formation.

Space group:  $P\bar{1}$  (assumed)Cell dimensions:  $a = 7.00 \text{ \AA}$ ;  $b = 8.33 \text{ \AA}$ ; $c = 9.47 \text{ \AA}$  $\alpha = 109.9^\circ$ ;  $\beta = 92.9^\circ$ ; $\gamma = 106.0^\circ$  $Z = 2$  gives  $\rho_{\text{calc}} = 1.50$ g/cm<sup>3</sup> $\rho_{\text{obs}} = 1.50 \text{ g/cm}^3$ 

A Fourier projection along the  $a$  axis has been completed, which confirms the assumed space group.

The dihydrate DM $\gamma$ PHBr.2H<sub>2</sub>O was prepared by evaporating a solution of the salt in methanol, to which a little water had been added. The crystals are orthorhombic plates. The chloride DM $\gamma$ PHCl.H<sub>2</sub>O is isomorphous with the corresponding HBr salt, and was prepared in a similar manner.

More detailed structure determinations of the substances mentioned are under way.

This investigation has been sponsored partly by Alf Bjerckes legat, and partly by the United States Air Force Development Command under contract AF 61 (052) -71.

1. Collie, J. N. and Tickle, T. *J. Chem. Soc.* **75** (1899) 710.
2. Cavalieri, L. *Chem. Revs.* **41** (1947) 525.
3. Brown, G. M., Norment, H. G. and Levy, H. A. *Acta Cryst.* **10** (1957) 806.
4. Gomberg, M. and Cone, L. H. *Ann.* **376** (1910) 228.

Received March 14, 1960.