

impurities all showed a pyridine hemochromogen spectrum identical to that of protohemin. It seems that these represent some kind of degradation products. No hemin with a pyridine hemochromogen  $\alpha$ -band at  $550 \mu$  was observed. The methyl esters of the two purified components showed on chromatography identical  $R_F$  values with that of standard protoporphyrin in the chloroform:kerosene system as well as in that of propanol:kerosene.

The porphyrins of the two components of Lhb both showed an etio-type spectrum in neutral solvents. The absorption maxima of these porphyrins in neutral and acidic solvents are given in Table 1.

In order to illustrate the definite identity of the hemin derivative of Lhb and protohemin, the apoprotein of Lhb was recombined with the protohemin. Apoprotein was used in excess to obtain as quantitative a recombination of hemin as possible: 0.1 ml of 1.5 mM hemin in 0.01 N NaOH was rapidly mixed into 3 ml of 0.15 mM apoprotein of the slower component of Lhb in a pH 7.0 phosphate buffer ( $\mu$  equal to 0.05). A slight precipitation of apoprotein occurred and was centrifuged off. The spectrum of the recombined slow component of Lhb was identical with that of the intact native slow component of Lhb at pH 7.0.

All results obtained, the spectroscopical as well as chromatographic studies of different derivatives of the hemin of the two main components of Lhb indicate the hemin of the two components to be protohemin. An additional confirmation to this was obtained by a recombination study of protohemin with apoprotein of Lhb. There were no indications of another main hemin derivative forming a part of Lhb except protohemin. The hemin derivative with a pyridine hemochromogen  $\alpha$ -band at  $550 \mu$  found in the root nodules, is not a constituent of Lhb.

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Received January 19, 1965.

## Hydrothermally Grown Crystals of Silver Vanadium Oxide Bronzes

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When vanadium pentoxide is heated with 5–40 weight percent of water in a sealed silver capsule at temperatures between 300–700°C and pressures of 2000 atm, a reaction occurs resulting in the formation of blue-black rod-formed or plate-like crystals up to one mm in size. X-Ray powder patterns of the rods and the plates were identical.

The crystals were found to be monoclinic from X-ray single-crystal studies. The cell dimensions derived from the Guinier powder pattern were:  $a = 11.742 \text{ \AA}$ ;  $b = 3.667 \text{ \AA}$ ;  $c = 8.738 \text{ \AA}$ ;  $\beta = 90.48^\circ$

An X-ray spectrographic analysis revealed considerable silver content in the compound. The crystal structure was determined by means of the Patterson projection on to (010). The atomic arrangement thus obtained was refined by means of electron density projections and indicated the formula to be  $\text{Ag}_{1-x}\text{V}_2\text{O}_5$ . The  $h0l$  and  $h1l$  data were then processed by a full-matrix least-squares refinement using the Busing-Levy

program written for the IBM 7090. The fractional occupancy of the silver atom was included as one of the parameters to be refined by adding a multiplier to its form factor. The fractional  $x$  in  $\text{Ag}_{1-x}\text{V}_2\text{O}_5$  was found to be  $0.32 \pm 0.03$  when the R-value had reached its minimum, 0.10.

The structure consists of layers which are built up of distorted  $\text{VO}_6$  octahedra sharing corners and edges. The layers have the composition  $\text{V}_2\text{O}_5$  and are held together by means of  $\text{Ag}^+$  ions. The structure is of a new kind and different from the structures of the two known bronzes,  $\text{Na}_{2-x}\text{V}_6\text{O}_{15}$  and  $\text{Li}_{1+x}\text{V}_3\text{O}_8$ , given by Wadsley.<sup>1,2</sup> A detailed description of the structure of  $\text{Ag}_{1-x}\text{V}_2\text{O}_5$  will shortly follow.<sup>3</sup>

New vanadium oxide bronzes have been reported by Hagenmuller and Lesaichere<sup>4</sup> and the same compound as reported here has also been prepared by Hardy, Galy, Casalot and Pouchard.<sup>5</sup> Their preparation methods do not involve the presence of water and they characterize this compound as a bronze.

Another silver vanadium oxide bronze was prepared by the present author by heating metallic silver,  $\text{V}_2\text{O}_5$  and water in a gold capsule at high pressure. Single-crystal studies indicate this compound to be isostructural with Wadsley's  $\text{Na}_{2-x}\text{V}_6\text{O}_{15}$ <sup>1</sup> and its composition should thus be written  $\text{Ag}_{2-x}\text{V}_6\text{O}_{15}$ . This compound was also prepared in a dry way by Hardy, Galy, Casalot and Pouchard.<sup>5</sup>

Further studies on the formation of vanadium oxide bronzes with supercritical water are in progress.<sup>6</sup>

For valuable comments on the manuscript I thank Professor A. Magnéli.

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Received January 28, 1965.

## Favorsky Rearrangements

### VII. Attempts to Rearrange 2,2,5-Tribromocyclopentanone; the Preparation of 3-Bromocyclopentanone-1,2-dione

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The Favorsky rearrangement of alicyclic  $\alpha$ -haloketones usually results in ring contraction. Similar to acyclic compounds the alicyclic monohaloketones produce saturated acids,<sup>1</sup> dihaloketones give  $\alpha, \beta$ -unsaturated acids<sup>2</sup> and trihaloketones  $\beta$ -halogen-substituted  $\alpha, \beta$ -unsaturated acids.<sup>2</sup> This ring contraction has been studied for alicyclic ketones with 4, 6, 7, and 8 carbons in the ring.<sup>2-4</sup> However, although attempts have been made<sup>5</sup> only one successful rearrangement of a mono-, di- or trihalocyclopentanone seems to be described, the synthesis of the interesting system cubane.<sup>6</sup>

As a part of a general comprehensive examination of the Favorsky rearrangement of trihaloketones,<sup>7</sup> attempts were made to prepare and rearrange 2,5,5-tribromocyclopentanone.

This tribromoketone was isolated as a crude oil which began to decompose after a few hours at room temperature. It was, therefore, not possible to distill the product.

The weak bases sodium and potassium carbonate or bicarbonate have been useful reagents in the Favorsky rearrangement of polyhaloketones.<sup>7,8</sup> When the crude product from the bromination of cyclopentanone was treated in this way, a very dark-coloured solution was obtained and from this no pure substance could be isolated.

However, it was found by Conia and Salaün that when monobromocyclobutanone was treated with water at 50°C for 30 min the bromoketone rearranged to cyclopropanecarboxylic acid.<sup>3</sup>

Thus, the crude tribromocyclopentanone was treated with water at room temperature for two days. From the reaction mixture an acidic crystalline substance was isolated. After recrystallization (m.p. 153–154.5°C) it was analyzed, and had the empirical formula  $\text{C}_5\text{H}_5\text{BrO}_2$ . The substance had an equiv. wt. 179.