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 $Ag_{1-x}V_2O_5$ was found to be 0.32 ± 0.03 when the R-value had reached its minimum, 0.10.

The structure consists of layers which are built up of distorted VO_6 octahedra sharing corners and edges. The layers have the composition V_2O_5 and are held together by means of Ag^+ ions. The structure is of a new kind and different from the structures of the two known bronzes, $Na_{2-x}V_6O_{15}$ and $Li_{1+x}V_3O_8$, given by Wadsley.[1,2] A detailed description of the structure of $Ag_{1-x}V_2O_5$ will shortly follow.[3]

New vanadium oxide bronzes have been reported by Hagenmuller and Lesaicherre [4] and the same compound as reported here has also been prepared by Hardy, Galy, Casalot and Pouchard.[5] 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, V_2O_5 and water in a gold capsule at high pressure. Single-crystal studies indicate this compound to be isostructural with Wadsley's $Na_{2-x}V_6O_{15}$[1] and its composition should thus be written $Ag_{2-x}V_6O_{15}$. This compound was also prepared in a dry way by Hardy, Galy, Casalot and Pouchard.[5]

Further studies on the formation of vanadium oxide bronzes with supercritical water are in progress.[6]

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Favorsky Rearrangements

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

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

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

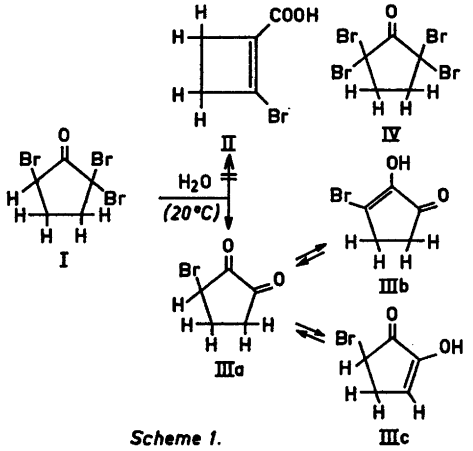
This tribromoketone was isolated as a crude oil which began to decompose after a few hours at room temperature. It was, therefore, not possible to distil the product.

The weak bases sodium and potassium carbonate or bicarbonate have been useful reagents in the Favorsky rearrangement of polyhaloketones.[7,8] 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.[3]

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 $C_5H_5BrO_2$. The substance had an equiv. wt. 179.

Two compounds with empirical formula $C_5H_5BrO_2$ seem to be more plausible than others as possible products from the reaction between 2,2,5-tribromocyclopentanone (I) and water. One, the expected Favorsky product, is 2-bromo-1-cyclobut-



Scheme 1.

ene-1-carboxylic acid (II) and the other 3-bromocyclopentane-1,2-dione (III a) or its two enolic forms (III b, III c); see Scheme 1.

2-Bromo-1-cyclobutene-1-carboxylic acid (II) has been described by Perkin Jr.,[9] m.p. 121—122°C. 3-Bromocyclopentane-1,2-dione (III a) has been prepared by Dieckmann [10] and by Knight and Cram,[11] m.p. 152.5—154°C. By infrared spectral comparison and by mixed melting points

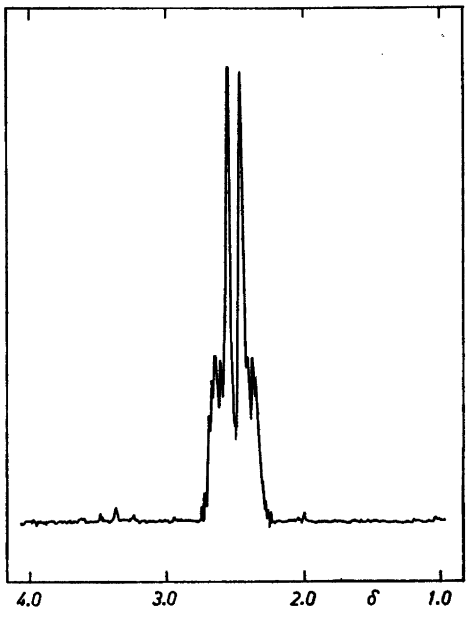


Fig. 2. NMR-spectrum of 3-bromocyclopentane-1,2-dione in trifluoroacetic acid.

it was shown that the present substance and the substance prepared according to Knight and Cram are identical.

A substance with the same empirical formula and m.p. 147°C was obtained by Godchot and Taboury [12] by boiling an unidentified by-product from the preparation

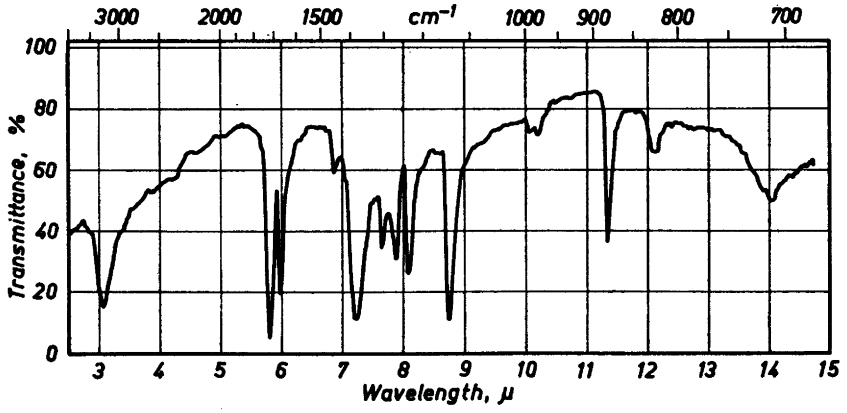


Fig. 1. Infrared spectrum of 3-bromocyclopentane-1,2-dione. Solid in KBr.

of tetrabromocyclopentanone with water. No structure of the compound was given. Repeating the experiment of Godchot and Taboury it was possible to isolate 3-bromocyclopentanone-1,2-dione (III).

The bromoketone was analyzed by infrared (Fig. 1) and by NMR (Fig. 2). The IR-spectrum had a strong band at 6.0 μ indicating a high content of enols (III b, III c). The NMR-spectrum was recorded in trifluoroacetic acid, acetone and chloroform, and in all cases it contained only a A_2B_2-system. From this it could be concluded that, as suggested already by Dieckmann and by Knight and Cram the compound exists in the form III b.[10,11] The enolic hydrogen was acidic and could be titrated. It should be noted that cyclopentane-1,2-dione also exists in the enol form.[13]

The formation of only enol III b suggests that, in general, α-monobromoketones enolize so that the halogenbearing α-carbon forms part of the double bond.

The bromination of cyclopentanone has been performed in various solvents, and the yields of isolated 3-bromocyclopentane-1,2-dione calculated on cyclopentanone, are given in Table 1. The major by-product was 2,2,5,5-tetrabromocyclopentanone IV. The yields of this compound are also given in Table 1.

Table 1.

Solvent	III %	IV %
$HBr + H_2O$	47	24
CH_3COOH	36	13
CCl_4	0	29

Experimental. The micro analyses were carried out by the Analytical Laboratory at the Chemical Institute, University of Uppsala. The NMR-spectrum was recorded on a Varian model A–60 spectrometer.

3-Bromocyclopentane-1,2-dione. To 16.8 g (0.2 mole) of cyclopentanone dissolved in 20 ml of 48 % hydrobromic acid and 50 ml of water was added 31 ml (0.6 mole) of bromine dropwise with chilling. After all the bromine had reacted, 1000 ml of water was added. The heavy organic layer was separated and was vigorously stirred with 1000 ml of water for 48 h. The crystals of 2,2,5,5-tetrabromocyclopentanone were filtered, 19.0 g, m.p. 88–91°C, 24 %. Repeated recrystallization from carbon tetrachloride raised the m.p. to 98–99°C, unstable crystals. Godchot and Taboury reported m.p. 99°C.[12]

The filtrate was continuously extracted with ether, the ether dried and evaporated *in vacuo* leaving 16.8 g of crystals, m.p. 144–146°C, 47 %. Repeated recrystallizations from carbon tetrachloride raised the m.p. to 153–154.5°C. (Found: C 33.93; H 2.85; Br 44.81. Calc. for $C_5H_5BrO_2$: C 33.93; H 2.85; Br 45.15).

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