

it into the vinyl derivative, yellow needles from alcohol, m. p. 107–108°.

Anal. Calcd. for $C_{12}H_5BrNO_2$: Br, 28.7. Found: Br, 28.8.

Attempts to prepare addition products with aniline, phenylhydrazine, etc., were fruitless. Using fuming nitric acid a yellow amorphous substance, apparently containing two added nitro groups, was isolated.

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Anhydrous Tantalum Tribromide

BY RALPH C. YOUNG AND THOMAS J. HASTINGS, JR.

If tantalum pentabromide vapor and hydrogen are passed through a tube at 700°, reduction of the compound occurs and lower bromides are produced prior to the formation of tantalum metal.¹ Complete reduction to the metal occurs, however, if the reaction at 700° is continued for a long enough time.

By the employment of the St. Claire-Déville principle it has been found possible to obtain the anhydrous tribromide of tantalum by a process analogous to that by which the tribromide² of titanium and the tribromide³ of zirconium were formed. A Pyrex tube 27 mm. in diameter and 100 cm. long was used as the reaction tube and the middle section (33 cm. in length) was heated in an electric furnace at 700°. Into the forward end which held the tantalum pentabromide⁴ was passed pure dry hydrogen at a rate of 24 liters per hour. During this interval 18 g. of tantalum pentabromide was volatilized and carried with the hydrogen into the heated zone. The reduction product and unchanged pentabromide collected on the surface of an inner tube through which water at 0° flowed. This inner tube extended to within 15 cm. of the forward end of the furnace.

At the conclusion of the experiment the apparatus was cooled to room temperature and dry carbon dioxide substituted for the hydrogen. The apparatus was so constructed that the products of the reaction could be directed into an arm sealed to the lower side of the reaction tube about 20 cm. from the end. After the arm had been

(1) Van Haagen, *THIS JOURNAL*, **32**, 729 (1910).

(2) Young with Schumb, *ibid.*, **52**, 4233 (1930).

(3) Young, *ibid.*, **53**, 2148 (1931).

(4) Tantalum pentabromide was prepared by the action of bromine on a mixture of sugar charcoal (2 moles) and tantalum oxide (0.1 mole). This mixture was first heated in a silica tube at 700° in a current of nitrogen to remove water. Subsequently the reaction tube was raised to 860°. The sublimate was resublimed at 0.05 mm. pressure and at a temperature of 400°; yield 80%.

sealed off from the apparatus, the outer end which was provided with a stopcock was sealed directly to a high vacuum system and the excess tantalum pentabromide was removed from the reduced product by sublimation at 1×10^{-3} mm. pressure at a temperature of 160°. The residue, which weighed 1 g., was a grayish-green powder which under a lens appeared uniform. *Anal.* Calcd. for $TaBr_3$: Ta, 43.0; Br, 57.0. Found: Ta, 43.4, 45.5; Br, 59.5, 58.3, 55.5.

The analyses indicate the formation of the tribromide, mixed with higher and lower bromides.

The tribromide reacts with water and alkali. Hydrogen is evolved and in the absence of air in an amount that corresponds to a change of the tantalum from an oxidation state of 3 to 4. In accord with this fact a brown tetravalent oxide was formed, the composition of which corresponded to $TaO_2 \cdot 2H_2O$ after it had been washed with water, alcohol, and ether and dried at a pressure of 0.05 mm. for ten minutes. The dioxide is slowly oxidized in the air at room temperature and rapidly at elevated temperatures to the white Ta_2O_5 . The latter is quickly formed from the tribromide and dioxide by the action of strong oxidizing agents such as nitric, permanganic and dichromic acids.

CONTRIBUTION No. 91

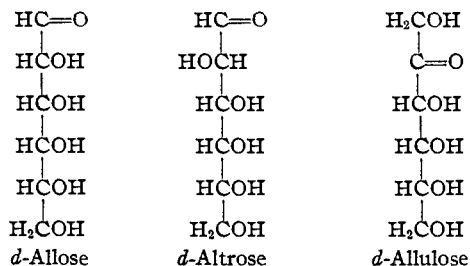
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d-Allulose and Some Methylated Derivatives

BY F. W. ZERBAN AND LOUIS SATTLER

In the industrial fermentation of cane molasses to produce ethyl alcohol, part of the sugar remains unfermented, and we have shown¹ that the unfermentable residue of a molasses distillery contains a ketohexose whose osazone is identical with the osazones of *d*-allose and *d*-altrose. Consequently the ketose must be *d*-psicose. Because of



(1) Presented at the Atlantic City meeting of the American Chemical Society, Sept., 1941.