

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.

PEARSON MEMORIAL LABORATORY  
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MEDFORD, MASSACHUSETTS RECEIVED APRIL 28, 1942

### 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.<sup>1</sup> 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 tribromide<sup>2</sup> of titanium and the tribromide<sup>3</sup> 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 pentabromide<sup>4</sup> 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  $1 \times 10^{-5}$  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

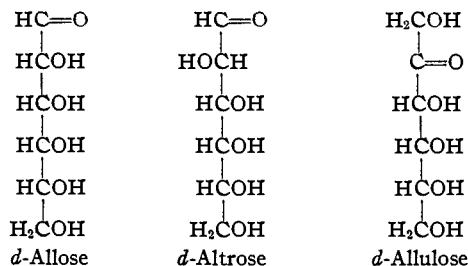
RESEARCH LABORATORY OF INORGANIC CHEMISTRY  
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### *d*-Allulose and Some Methylated Derivatives

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 shown<sup>1</sup> 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.

the relationship of the ketose to the two aldoses, we prefer the name *allulose* proposed by Professor William Lloyd Evans.

From commercial distillery residues we have now obtained *d*-allulose by way of its diacetone derivative. This compound when heated with dilute acetic acid decomposes to form the free sugar. The sirup thus prepared was dissolved in water and read in a saccharimeter.

$$[\alpha]^{20}_D = \frac{+0.05^\circ S \times 100}{1.2044 \times 0.5} \times 0.3462 = +2.9^\circ$$

Steiger and Reichstein<sup>2</sup> reported  $[\alpha]^{20}_D +3.1^\circ$ .

Methylation of the crude allulose concentrate followed by a high-vacuum distillation of the product yielded 1,3,4,6-tetramethyl ( $\alpha \rightleftharpoons \beta$ ) methyl *d*-alluloside which distilled as a thick oil from a bath temperature of 105–140° at a pressure of  $8 \times 10^{-5}$  mm.

*Anal.* Calcd. for  $C_{11}H_{22}O_6$ : C, 52.77; H, 8.86;  $OCH_3$ , 62.00. Found: C, 53.00; H, 9.24;  $OCH_3$ , 59.70;  $n^{21.5}_D$  1.4572.

When 0.3199 g. of the tetramethyl methyl alluloside was dissolved in 25 ml. of methyl alcohol containing four drops of concentrated hydrochloric acid and heated in a pressure bottle for two hours at 100°, the product (probably an equilibrium mixture of tetramethyl methyl allulosides) had a specific rotation in sodium light of +36° at 20°.

Further work with allulose derivatives is in progress.

(2) Steiger and Reichstein, *Helv. Chim. Acta*, **19**, 187 (1936).

THE NEW YORK SUGAR TRADE LABORATORY  
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## NEW COMPOUNDS

### N,N'-Piperazinium Bis-(2-methyl-5-isopropylbenzenesulfonate)

Smith and Pollard<sup>1</sup> have prepared a number of N,N'-piperazinium bis-(arylsulfonates) and found them moderately soluble in cold water, and quite soluble in hot water. McKee and Bahner<sup>2</sup> found that, while the benzenesulfonate and 2,4-dimethylbenzenesulfonate salts of ethylenediamine and also the 2-methyl-5-isopropylbenzenesulfonate salts of diethylenetriamine and triethylenetetramine are all relatively soluble in water at room temperature, the 2-methyl-5-isopropylbenzenesulfonate salt of ethylenediamine is only slightly soluble. This property was used to separate ethylenediamine from mixtures.

We have prepared N,N'-piperazinium bis-(2-methyl-5-isopropylbenzenesulfonate) and have found that, while it is readily soluble in hot water, it is only slightly more soluble at room temperature than the corresponding salt of ethyl-

enediamine. It is soluble only to the extent of 1 part in 80 of water at 30° or 1 part in 200 at 0°.

The salt was prepared by mixing aqueous solutions of recrystallized sodium 2-methyl-5-isopropylbenzenesulfonate and N,N'-piperazinium dichloride, the former being in excess at all times.<sup>3</sup> The product, obtained in almost the theoretical yield, consisted of small, white leaflets which did not melt below 300°. After recrystallization from water and drying at 110° it was analyzed by the Kjeldahl method.

*Anal.* Calcd. for  $C_{24}H_{48}N_2O_8S_2$ : N, 5.45. Found: N, 5.47, 5.58, 5.64.

(3) We are indebted to Carbide and Carbon Chemicals Corporation for piperazine hexahydrate and to Professor Ralph H. McKee for technical sodium cymenesulfonate used as raw materials for this preparation.

(4) Present address: Alabama Ordnance Works, Sylacauga, Ala.

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### N-Substituted Piperonylamides

These compounds were prepared by treating a benzene solution of piperonyl chloride with slightly more than two equivalents of the appropriate amine in the same solvent and heating the solution under reflux for thirty minutes. The mixture was treated with water to dissolve the hydrochloride of the amine and the benzene was removed by distillation under reduced pressure with a water pump. The remaining aqueous solution containing the amide in suspension was filtered and the amide washed with water. This procedure was found preferable to distilling separately the benzene solution of the amide as some amides tended to separate from this solvent as an oil. The yield of crude amide was 90% or more in all cases. Purification of the amide was effected by recrystallization from dilute alcohol. The nitrogen determinations were made by the Kjeldahl method.

Name	Formula	M. p., °C. (cor.)	Nitrogen, % Calcd.	Found
N-Phenylpiperonyl- amide	$C_{14}H_{11}NO_2$	146 -147	5.81	5.83
N-( <i>o</i> -Chlorophenyl)- piperonylamide	$C_{14}H_{10}ClNO_2$	107 -108	5.08	5.27
N-( <i>p</i> -Chlorophenyl)- piperonylamide	$C_{14}H_{10}ClNO_2$	206.5-207.5	5.08	5.16
N- <i>o</i> -Tolylpiperonyl- amide	$C_{15}H_{13}NO_2$	137.5-138.5	5.49	5.44
N- <i>m</i> -Tolylpiperonyl- amide	$C_{15}H_{13}NO_2$	121 -122	5.49	5.46
N- <i>p</i> -Tolylpiperonyl- amide	$C_{15}H_{13}NO_2$	149 -149.5	5.49	5.46
N-(1-Naphthyl)- piperonylamide	$C_{18}H_{15}NO_2$	192.5-193	4.81	4.82
N-(2-Naphthyl)- piperonylamide	$C_{18}H_{15}NO_2$	156.5-157.5	4.81	4.60
N-Benzylpiperonyl- amide	$C_{16}H_{15}NO_2$	126.5-127.5	5.49	5.46
N-Cyclohexyl- piperonylamide	$C_{14}H_{17}NO_2$	167.5-168.5	5.67	5.61

BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE  
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RECEIVED MARCH 9, 1942

(1) Smith and Pollard, *THIS JOURNAL*, **63**, 631 (1941).

(2) McKee and Bahner, U. S. Patent 2,164,587, July 4 1939.