boiling ethanol, and were best purified by leaching out the unreacted amide with boiling ethanol.

Procedure 2.—This process was found to be satisfactory for amides whose mercury derivatives were soluble in hot ethanol, insoluble in cold. It was used successfully with benzamide, *p*-chlorobenzamide, the bromobenzamides, the toluamides, *o*-anisamide and salicylamide. Five grams of yellow mercuric oxide and 4 g. of amide were added to 50 ml. of 95% ethanol, the mixture refluxed for one hour, filtered while hot through a fluted filter, chilled in an ice-bath, and the crystals removed by suction. Purification, where necessary, was accomplished as in Procedure 1.

VENABLE CHEMICAL LABORATORY
UNIVERSITY OF NORTH CAROLINA
CHAPEL HILL, N. C.
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Crystalline Xylitol

BY M. L. WOLFROM AND E. J. KOHN

Fischer[1] and Bertrand[2] prepared xylitol as a sirup in 1891 by the sodium amalgam reduction of *d*-xylose. Xylitol has been prepared subsequently by other investigators but, to our knowledge, no record of its crystallization has appeared in the literature. We wish to report that the crystallization of xylitol now has been effected in this Laboratory. The xylitol was prepared by the high-pressure catalytic reduction of highly purified *d*-xylose and the crystalline reduction product was characterized by elementary analysis, behavior with periodate and by the preparation of two known crystalline derivatives. The crystals were anhydrous, low-melting (61°) and hygroscopic.

Experimental

A solution of 300 g. of highly purified *d*-xylose in 750 cc. of water containing 60 g. of a nickel catalyst supported on kieselguhr was reduced in a steel shaking autoclave (American Instrument Company) at an initial hydrogen pressure of 1700 lb. per sq. in. (113 atm.) at 30°. A maximum temperature of 150° at a pressure of 2400 lb. per sq. in. (160 atm.) was attained in one hour and maintained for an additional four hours. The catalyst was removed from the cooled solution by filtration followed by treatment with an excess of hydrogen sulfide and by heating at 55° with decolorizing charcoal. The clear sirup obtained on solvent removal below 50° under reduced pressure, crystallized on standing for some weeks under absolute ethanol and at icebox temperature; yield 255 g. Pure material was obtained on recrystallization from anhydrous methanol; m. p. 61–61.5° (cor.), optically inactive (H_2O, D line of sodium). The hygroscopic, crystalline product was very soluble in water and was fairly soluble in hot methanol. It did not reduce boiling Fehling solution.

Anal. Calcd. for $C_5H_{12}O_5$: C, 39.47; H, 7.95. Found: C, 39.43; H, 7.85. Sodium periodate analysis[3]: moles periodate consumed, 4.0 (calcd., 4); moles formic acid formed, 2.8 (calcd., 3); moles formaldehyde formed,[4] 1.8 (calcd., 2).

The crystalline substance was further characterized by the preparation of two previously known crystalline derivatives, the pentaacetate[5] (m. p. 62.5–63°, cor.) and the dibenzylidene derivative[6] (m. p. 187.5–188°, cor.). Hockett and Hudson[5] record 61.5–62.5° (cor.) as the melting point of xylitol pentaacetate. Lobry de Bruyn and Alberda van Ekenstein[6] record 175° as the melting point of dibenzylidene-xylitol but previous experience in this Laboratory with sirupy xylitol preparations has indicated the higher melting point of 187.5–188° (cor.).

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[1] E. Fischer and R. Stahel, *Ber.*, **24**, 538 (1891).

[2] G. Bertrand, *Bull. soc. chim.*, [3] **5**, 554 (1891).

[3] R. M. Hann, W. D. Maclay and C. S. Hudson, THIS JOURNAL, **61**, 2432 (1939).

[4] Determined by the dimedon method as per D. Vorländer, *Z. anal. Chem.*, **77**, 321 (1929).

[5] R. C. Hockett and C. S. Hudson, THIS JOURNAL, **57**, 1753 (1935).

[6] C. A. Lobry de Bruyn and W. Alberda van Ekenstein, *Rec. trav. chim.*, **18**, 151 (1899).

CHEMICAL LABORATORY
THE OHIO STATE UNIVERSITY
COLUMBUS, OHIO
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Nitrovinylnaphthalene

BY DAVID E. WORRALL AND ABRAHAM TATILBAUM

Since α,β-unsaturated compounds containing a naphthalene group have not as yet been described, it appeared worth while to prepare 2-(α-nitrovinyl)-naphthalene and some of its derivatives.

2-(α-Nitrovinyl)-naphthalene.—A condensation of 0.1 g. mole each of β-naphthaldehyde and nitromethane in the presence of alcoholic sodium hydroxide yielded 16 g. of the crude product, which, when recrystallized from alcohol, gave yellow needles, m. p. 120.5–122°.

Anal. Calcd. for $C_{12}H_9NO_2$: C, 72.4; H, 4.5. Found: C, 72.3; H, 4.8.

Aliphatic amines instead of alkali proved unsuitable for promoting the reaction because of the formation of polymers. Thus, using amylamine, considerable amounts of an amorphous, tan-colored substance relatively insoluble in common solvents was obtained, which, after digestion with hot nitric acid, washing with alcohol and drying, melted indefinitely with decomposition at about 253°.

Anal. Calcd. for $(C_{12}H_9NO_2)_x$: C, 72.4; H, 4.5. Found: C, 72.2; H, 4.6.

2-(α-Bromo-α-nitrovinyl)-naphthalene.—The dibromide of the original compound was prepared by the action of bromine on a chloroform solution of the unsaturated substance. The bromination which did not go smoothly gave best results on long standing at room temperature in sunlight. Spontaneous evaporation left a crystalline residue which after washing with cold alcohol to remove oily impurities, crystallized from alcohol as white needles, m. p. 125–126°. Warm alcoholic potassium acetate converted it into the vinyl derivative, yellow needles from alcohol, m. p. 107–108°.

Anal. Calcd. for $C_{12}H_8BrNO_2$: 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
TUFTS COLLEGE
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.[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 tribromide[2] of titanium and the tribromide[3] 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[4] 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 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^{-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
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MASS.
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[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%.

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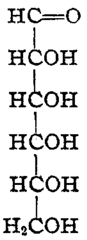
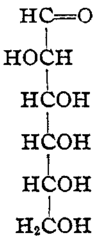
d-Allulose and Some Methylated Derivatives

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[1] 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


d-Allose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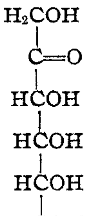
d-Allulose

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[1] Presented at the Atlantic City meeting of the American Chemical Society, Sept., 1941.