

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.

RECEIVED APRIL 23, 1942

### Crystalline Xylitol

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

Fischer<sup>1</sup> and Bertrand<sup>2</sup> 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<sub>2</sub>O, 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.

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

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

*Anal.* Calcd. for C<sub>5</sub>H<sub>12</sub>O<sub>5</sub>: C, 39.47; H, 7.95. Found: C, 39.43; H, 7.85. Sodium periodate analysis<sup>3</sup>: moles periodate consumed, 4.0 (calcd., 4); moles formic acid formed, 2.8 (calcd., 3); moles formaldehyde formed,<sup>4</sup> 1.8 (calcd., 2).

The crystalline substance was further characterized by the preparation of two previously known crystalline derivatives, the pentaacetate<sup>5</sup> (m. p. 62.5–63°, cor.) and the dibenzylidene derivative<sup>6</sup> (m. p. 187.5–188°, cor.). Hockett and Hudson<sup>6</sup> record 61.5–62.5° (cor.) as the melting point of xylitol pentaacetate. Lobry de Bruyn and Alberda van Ekenstein<sup>6</sup> 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.).

(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

RECEIVED APRIL 3, 1942

### Nitrovinyl-naphthalene

BY DAVID E. WORRALL AND ABRAHAM TATILBAUM

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

**2-( $\alpha$ -Nitrovinyl)-naphthalene.**—A condensation of 0.1 g. mole each of  $\beta$ -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<sub>12</sub>H<sub>9</sub>NO<sub>2</sub>: 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<sub>12</sub>H<sub>9</sub>NO<sub>2</sub>)<sub>2</sub>: C, 72.4; H, 4.5. Found: C, 72.2; H, 4.6.

**2-( $\alpha$ -Bromo- $\alpha$ -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