cyanobenzylalcohol by oxidation with nitrogen tetroxide[6,7]) gave, on treatment in alcoholic solution with hydrazine hydrate (50% by wt.), an immediate pale-yellow, microcrystalline precipitate exhibiting the physical properties which might be expected of 4,4′-dicyanobenzaldazine. This product was obtained in almost the theoretical yield, being virtually insoluble in hot alcohol; after crystallization from pyridine or nitrobenzene, from which it separates in yellow needles or plates, it melted at 318–320° (uncor.).

The analyses for nitrogen (Dumas) were consistently slightly low on various samples, but there is little doubt as to the identity of the compound. Calcd. for $C_{16}H_{10}N_4$: C, 74.1; H, 3.75; N, 21.70. Found: C, 74.4; H, 3.88; N, 21.2, 21.5, 21.2, 21.1, 21.2.

Sah describes the azine as being readily soluble in alcohol and having m. p. 118–120°.

Sublimation of our product *in vacuo* (0.5 mm.) resulted in its recovery unchanged but repeated sublimation under normal pressure at 300–320° gave colorless long needles and plates in small yield. Some charring and decomposition to the original aldehyde also occurred at this temperature. Crystallization of the sublimate from glacial acetic acid or nitrobenzene gave slender colorless needles, m. p. 220–223° (uncor.). The melting point of terephthalonitrile[8] was not depressed by this compound.

Although the nature of this decomposition is not clearly understood, there seems little doubt that the compound described is indeed 4,4′-dicyanobenzaldazine: hence, the identity of the product described by Sah is obscure. The possibility of dimorphism cannot be neglected, but a more likely explanation is that the *p*-cyanobenzaldehyde used was impure. It has already been shown in these laboratories that the product obtained from *p*-cyanobenzyl chloride and copper nitrate solution[9,10] is unsatisfactory, being, in fact, a mixture of aldehyde, alcohol and acid.

In this case it is conceivable that other compounds may be isolated (*e. g.*, hydrazine salts), but neither theory explains satisfactorily the production of dicyanostilbene as claimed by Sah.

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(6) Cohen, *J. Chem. Soc.*, 1050 (1897).

(7) J. N. Ashley, *et al.*, *ibid.*, 103 (1942).

(8) British Patent 488,642.

(9) Reinglass, *Ber.*, **24**, 2421 (1891).

(10) Moses, *ibid.*, **33**, 2624 (1900).

A New Form of Crystalline Xylitol

BY J. F. CARSON, S. W. WAISBROT AND F. T. JONES

Wolfrom and Kohn[1] recently succeeded in preparing a hygroscopic crystalline xylitol, m. p. 61–61.5°, by prolonged standing of the sirup in an ice box. In repeating their preparation of this substance from *D*-xylose, the clear viscous sirup which we obtained after concentration *in vacuo*, solidified to a hard, crystalline mass on standing overnight. Recrystallization from either methanol or ethanol yielded colorless crystals melting at 93–94.5°.

From a sample of fused xylitol either type of crystal could be obtained by seeding with the proper nuclei, but the low-melting form, kindly furnished us by Professor Wolfrom, changed in a few days into the high-melting and stable form on exposure to the air of the laboratory.

The low-melting, metastable xylitol separates from alcoholic solution as colorless, lath-shaped crystals with oblique ends similar in appearance to gypsum crystals and is hygroscopic.

The new, high-melting, stable xylitol crystallizes usually as colorless tablets about twice as long as they are wide with symmetrically pointed ends. It is further differentiated from the low-melting form by its ease of crystallization in good yield from methanol, ethanol and even aqueous solution, and by its non-hygroscopic character. Its solubilities at 25° in absolute methanol and ethanol, and in water are, respectively, 6.0, 1.2 and 64.2 g. per 100 g. of solution.

Its identity as anhydrous xylitol was established by the analytical data. *Anal.* Calcd. for $C_5H_{12}O_5$: C, 39.47; H, 7.95. Found: C, 39.52; H, 8.09.

Its identity was further confirmed by conversion to the known pentaacetate.[2] Colorless plates, m. p. 63–64°, were obtained which showed no depression when mixed with an authentic specimen of xylitol pentaacetate, m. p. 62.5–63.5°.

Crystallographic Analysis of Two Crystalline Forms of Xylitol.—The two crystalline modifications were examined under a petrographic microscope, and refractive indices were determined with monochromatic sodium light by the immersion method. The orientation in each case was verified by means of interference figures. The crystallographic properties of the two crystalline forms of xylitol are given in Table I.

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(1) Wolfrom and Kohn, THIS JOURNAL, **64**, 1739 (1942).

(2) R. C. Hockett and C. S. Hudson, *ibid.*, **57**, 1753 (1935).

TABLE I

CRYSTALLINE FORMS OF XYLITOL

Form	Metastable	Stable
M. p., °C.	61–61.5	93–94.5
α	1.519	1.549
γ	1.548	1.566
β	1.521	1.551
Crystal system	Monoclinic	Rhombic
Axial angle and dispersion	$2V = 32 \pm 5°$ $(r > v)$ weak	$2V = 38 \pm 5°$ $(r < v)$ weak
Optical character	(+)	(+)

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Suggested Method for Replaceable Hydrogen

BY HERMAN A. LIEBHAFSKY

Dilute sodium amalgams react rapidly neither with acetonitrile nor with water dissolved therein at low concentrations. If silicon tetrachloride is added, however, the amalgam will, upon violent shaking, rapidly liberate hydrogen derived from the water initially present. Unfortunately, the reaction is not quantitative even under conditions chosen after considerable experimentation: the hydrogen is liberated in amounts ranging from one to two gram atoms for each mole of water.

Samples of known water (or alcohol) content were prepared with acetonitrile that had been distilled from phosphorus pentoxide; the solvent gave a negligible blank. 50 cc. of such a sample was measured into a 100-cc. acetylation flask attached to a mercury-filled gas buret. Ten drops of freshly distilled silicon tetrachloride was added with a dropper and dissolved by shaking the closed flask; 10 cc. of sodium amalgam (about 0.05% by weight) was now poured in, and the closed flask shaken violently for three ten-second periods; a gas buret reading was taken after each period had elapsed, the final reading being taken when temperature equilibrium had been re-established. At water concentrations below 0.05% by weight, more hydrogen could not be liberated by this procedure when amalgam or silicon tetrachloride was subsequently added. At the higher concentrations, these substances had to be added alternately in the amounts given above until no more hydrogen was evolved. Some of the results obtained are given in Table I; here all percentages are by weight, and water is assumed to have two replaceable hydrogens.

Two samples of acetonitrile in which 0.013 and 0.07% water had been obtained with the Karl Fischer reagent by Mr. Stanley Mills, Niacet Chemical Company, gave only 0.003 and 0.02% by the present method when the results were calculated as in the last column of the table. (An empirical correction would, of course, improve the agreement.) Whether the Karl Fischer reagent reacted with substances other than water in these samples is not known.

TABLE I

REPLACEABLE HYDROGEN IN ACETONITRILE SOLUTIONS

No.	Solute	% Solute added	% Solute found
1	Water	0.008	0.004
2	Water	.015	.010
3	Water	.030	.019
4	Water	.045	.031
5	Water	.060	.045
6	Water	.075	.055
7	Water	.13	.08
8	Water	.13	.08
9	Water	.13	.12
10	Ethyl alcohol	.13	.17
11	Ethyl alcohol	.13	.17
12	Methyl alcohol	.13	.12

The method suggested here is subject to complications. Silicon tetrachloride and sodium amalgam are both consumed in side reactions. Table I shows that the stoichiometry is not simple; water gives lower results than the alcohols, but this is not surprising because water (or an —OH group) is the more likely to be retained in an inactive condition by the reaction products. The amalgam becomes covered almost instantly by a film, presumably siliceous, that bars it from reacting when its surface is at rest; this simplifies the manipulation. Sodium amalgam can be slowly oxidized by the air in the system; the occurrence of this reaction, the rate of which is usually negligible, can be turned to account as a signal that the hydrogen chloride has been consumed with amalgam still present.

In spite of these complications, the proposed method may find its place where other methods are inapplicable or too slow. No doubt other substances that react like silicon tetrachloride could be used. One experiment showed that dioxane could replace acetonitrile.

The method grew out of experiments being carried on here by Dr. C. E. Reed. I am grateful also to Dr. R. O. Sauer for supplying the silicon tetrachloride, and to Mr. L. B. Bronk for helping with the determinations.

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The Preparation of β-Primeverose Heptaacetate and β-Vicianose Heptaacetate

BY CHESTER M. MCCLOSKEY[1] AND GEORGE H. COLEMAN

Recently in this Laboratory we have had occasion to prepare primeverose and vicianose in con-

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(1) Research Fellow of the Corn Products Refining Co.