to crystallize. The acid was filtered with suction and dried *in vacuo;* yield 37–41 g. Recrystallization from water gave a nearly white product melting at 199–200°.

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RECEIVED APRIL 15, 1942

Identification of Amides through the Mercury Derivatives

BY JONATHAN W. WILLIAMS, WILLIAM T. RAINEY, JR., AND ROBERT S. LEOPOLD

In characterizing amides the most general procedure is hydrolysis, followed by identification of the two products. With unsubstituted amides, solid derivatives may be prepared directly by reaction with phthalyl chloride.[1] Another procedure, the use of which obviates hydrolysis, is the preparation of the mercury derivative. This procedure is simple and gives satisfactory derivatives for a large number of unsubstituted amides.

The reaction represented by the equation

$$2R{-}\underset{\underset{O}{\|}}{C}{-}NH_2 + HgO \longrightarrow (R{-}\underset{\underset{O}{\|}}{C}{-}NH)_2Hg + H_2O$$

was first reported in 1852 by Dessaignes,[2] who prepared the mercury derivatives of benzamide and acetamide. Mercury derivatives of several other amides have since been described.[3]

Two general procedures were investigated for the preparation of these mercury compounds. Procedure 1, patterned after the work of Dessaignes,[2] consisted of bringing a mixture of yellow mercuric oxide and excess amide to the melting point of the amide, maintaining that temperature and adding more mercuric oxide in small portions until no further reaction occurred, and then purifying the product by recrystallization from ethanol or by leaching with hot ethanol. This process is the more generally applicable one, and the one that must be used with aliphatic amides. Procedure 2, based on the process described by Mann and Saunders,[4] consisted of refluxing about 0.04 mole of amide with excess (around 0.025 mole) yellow mercuric oxide in 50 ml. of 95% ethanol for one hour, filtering while hot, cooling, removing the crystalline mercury derivative, and purifying by recrystallization or leaching.

(1) Evans and Dehn, THIS JOURNAL, **51**, 3651 (1929).

(2) Dessaignes, *Ann.*, **82**, 231 (1852).

(3) For summary and complete references, see Whitmore, "Organic Compounds of Mercury," Chemical Catalog Company (Reinhold Publishing Corporation), New York, N. Y., 1921, pp. 159–161.

(4) Mann and Saunders, "Practical Organic Chemistry," Longmans, Green and Company, London, 1938, p. 79.

In Table I are listed the melting points and mercury analyses[5–7] of the compounds successfully prepared. Due to low solubility in boiling ethanol, the purification of the mercury derivatives of *p*-anisamide and *m*-chlorobenzamide must be accomplished by leaching.

TABLE I

Amide	M. p., °C. (uncor.)	M. p. of mercury derivative, °C. (uncor.)	Mercury, % Calcd.	Found	
Acetamide	82	196–197	..	..	..
Propionamide	79	201	58.2	57.8	58.5
Butyramide	115	222–224	53.8	53.3	53.4
Benzamide	128	222	45.5	45.1	45.2
m-Chlorobenzamide	134	245	39.2	39.0	38.6
p-Chlorobenzamide	178	258	39.2	38.9	39.1
o-Bromobenzamide	155	242	33.5	33.5	..
m-Bromobenzamide	155	235	33.5	33.2	33.2
p-Bromobenzamide	191	266	33.5	33.1	33.5
o-Toluamide	158	196	42.6	42.4	42.5
m-Toluamide	94	200	42.6	43.1	42.3
p-Toluamide	166	260	42.6	42.5	..
o-Anisamide	128	241	40.1	39.8	40.3
p-Anisamide	167	222	40.1	39.9	40.3
Salicylamide	139	190	42.4	42.7	..

Unsuccessful attempts were made to prepare the mercury derivatives of isovaleramide, stearamide, *m*-anisamide and benzenesulfonamide. In the first two cases, decomposition occurred at the temperature used, making isolation of the mercury derivative impossible. With the latter two substances, reaction occurred readily, but the products obtained could not be rendered analytically pure.

Experimental

Procedure 1.—In a test-tube were placed 1.5 g. of the amide and 0.5 g. of yellow mercuric oxide. Using a small flame, the mixture was heated at the melting point of the amide until all mercuric oxide had reacted (disappearance of color) and the water vapor had been dispelled. More mercuric oxide was then added in small portions until no more would react. If an excess of mercuric oxide was obtained, enough of the amide to react with it was added and the yellow color removed completely. The melt was cooled somewhat, then taken up in the minimum amount of boiling ethanol and allowed to cool. The crystals were filtered and washed with cold ethanol or ether. Considerable variations were found in the solubilities of the mercury derivatives in alcohol. The derivatives of aliphatic amides were quite soluble, even in cold ethanol. On the other hand, the derivatives of *p*-anisamide, *m*-chlorobenzamide and benzenesulfonamide were quite insoluble in

(5) Rauscher, *Ind. Eng. Chem., Anal. Ed.*, **10**, 331 (1938).

(6) Shriner, "Quantitative Analysis of Organic Compounds," Edwards Brothers, Ann Arbor, Mich., 1938, p. 31.

(7) Shukis and Tallman, *Ind. Eng. Chem., Anal. Ed.*, **12**, 123 (1940).

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.

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CHAPEL HILL, N. C. RECEIVED APRIL 23, 1942

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.).

(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).

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COLUMBUS, OHIO RECEIVED APRIL 3, 1942

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