

xanthate, an intermediate used by Richtmyer, Carr and Hudson¹ in the preparation of tetraacetyl- β -glucothiose, may readily be desulfurized by Raney nickel to give 1,5-anhydro-D-sorbitol tetraacetate in high yield.

Since ethyl tetraacetyl-D-glucopyranosyl xanthate is readily preparable in high yield by the condensation of acetobromo-D-glucose with potassium ethyl xanthate⁴ and since polygalitol may easily be obtained from its tetraacetate by conventional methods such as the catalytic deacetylation described below, this facile synthesis constitutes an attractive preparative method for polygalitol, preferable to the time-consuming and costly extraction of this anhydrohexitol from its natural source.⁵

The writer is indebted to Dr. Nelson K. Richtmyer of this Laboratory for the gift of a sample of ethyl tetraacetyl-D-glucopyranosyl xanthate.

Experimental

Two grams of ethyl tetraacetyl-D-glucopyranosyl xanthate (m. p. 78.9–79.2° (cor.)) was dissolved in a suspension of about 40 g. of fresh Raney nickel in 100 ml. of absolute alcohol and refluxed gently for six hours. The solution was then cooled, filtered through a fritted glass filter and concentrated *in vacuo* (45° bath) to a thick sirup. After solution in 35 ml. of anhydrous ether and removal of a trace of amorphous, insoluble solid the material was again reduced to a sirup *in vacuo*. Isopentane (50 ml.) was added, the sirup seeded and then left at 3° overnight. The mass of fine, prismatic needles, removed by filtration and washed with isopentane, weighed 1.197 g. (81%) and melted at 69.8–72.0° (cor.). Recrystallization from a mixture of ether and isopentane resulted in negligible loss and gave material which alone or in admixture with authentic tetraacetyl-1,5-anhydro-D-sorbitol melted at 73.6–74.8° (cor.). In chloroform it showed $[\alpha]^{20}_D +38.9^\circ$ (*c*, 0.418) which is the value reported by Richtmyer, Carr and Hudson¹ for the same substance.

1,5-Anhydro-D-sorbitol (Polygalitol).—The tetraacetyl-1,5-anhydro-D-sorbitol (0.9680 g.) was dissolved in 5 ml. of methanol and treated with four drops of 1 *N* sodium methylate solution. After twenty-four hours at room temperature the clear, colorless solution was seeded and there developed the aggregates of thin, plate-like crystals characteristic of polygalitol. After thorough washing with methanol the material (0.478 g.; 63%) melted, either alone or in admixture with polygalitol from *Polygala Senega L.*, at 142–143° (cor.). In water it showed $[\alpha]^{20}_D +42.3^\circ$ (*c*, 0.844) while Richtmyer, Carr and Hudson¹ reported $[\alpha]^{20}_D +42.4^\circ$ (*c*, 2) in water. An additional crop of polygalitol (0.1372 g.) was recovered from the mother liquors, raising the total yield of crystalline material to 89%.

(4) W. Schneider, R. Gille and K. Eisfeld, *Ber.*, **61**, 1244 (1928).

(5) N. K. Richtmyer and C. S. Hudson, *THIS JOURNAL*, **65**, 64 (1943).

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Conversion of Alkaline-Metals Salts of Amino Acids into Free Amino Acids

BY ALEXANDER GALAT

In the course of work with amino acids one is frequently confronted with the problem of

preparing a free amino acid from its alkaline-metal salt. In the case of water-soluble amino acids this conversion is not readily accomplished since treatment with acids yields mixtures the components of which have similar solubility characteristics.

We have found that satisfactory results may be obtained by the use of ethyl isonitrosocynoacetate. This ester is sufficiently acidic to free amino acids from their salts and, since its alkaline-metals salts are freely soluble in alcohol, the separation can be easily accomplished.

Basic, neutral and acidic amino acids have been investigated with good results and the method may be considered of general applicability.

Experimental

Glycine.—To a solution of 0.97 g. (0.01 mole) of the sodium salt of glycine in 1.5 ml. of water was added 1.45 g. (0.01 mole) of ethyl isonitrosocynoacetate¹ in 10 ml. of ethanol (95%). The mixture was allowed to stand for one hour, the crystals filtered off and washed with ethanol until the yellow color due to the sodium salt of ethyl isonitrosocynoacetate was completely removed; yield 0.57 g. (76%), m. p. 230–233° (dec.).

1-Histidine.—To a solution of 1.54 g. (0.0087 mole) of the sodium salt of 1-histidine in 2 ml. of water was added 1.25 g. of ethyl isonitrosocynoacetate in 10 ml. of methanol. The free amino acid precipitated immediately and was filtered off and washed with methanol until the yellow color was removed; yield 1.02 g. (75%), m. p. 280–285° (dec.).

l-Glutamic Acid.—To a solution of 1.87 g. (0.01 mole) of monosodium glutamate in 2 ml. of warm water was added 1.5 g. (ca. 0.01 mole) of ethyl isonitrosocynoacetate in 10 ml. of methanol. There was formed a pasty precipitate which became crystalline on stirring. The crystals were filtered off and washed with methanol until white; yield 1.32 g. (91%), m. p. 200–202° (dec.).

(1) Conrad and Schulze, *Ber.*, **42**, 735 (1909).

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The Heat and the External Work of Vaporization of Ethylbenzene from 0 to 140°

BY J. E. HAGGENMACHER

In previous papers¹ an expression was derived for the volume difference of liquid-vapor equilibria

$$v_g - v_L = \frac{RT}{Mp} \sqrt{1 - \frac{Dp}{T^3}} \quad (1)$$

$$\text{where } D = T^3/p_c$$

The expression leads to relationships for the external work, the heat and the entropy of vaporization.

The external work or the change in the Helmholtz function *A*, becomes

$$p(v_g - v_L) = -\Delta A = \frac{RT}{M} \sqrt{1 - \frac{Dp}{T^3}} \quad (2)$$

Through the Clapeyron-Clausius equation the

(1) Haggmacher, *THIS JOURNAL*, **68**, 1123, 1633 (1946).