xanthate, an intermediate used by Richtmyer, Carr and Hudson[1] in the preparation of tetra-acetyl-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 xanthate[4] 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° (*c*, 0.418) which is the value reported by Richtmyer, Carr and Hudson[1] 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° (*c*, 0.844) while Richtmyer, Carr and Hudson[1] reported $[\alpha]^{20}D$ +42.4° (*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 isonitrosocyanoacetate. 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 isonitrosocyanoacetate[1] 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 isonitrosocyanoacetate 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 isonitrosocyanoacetate 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 isonitrosocyanoacetate 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 papers[1] an expression was derived for the volume difference of liquid–vapor equilibria

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

where $D = T_c^3/p_c$

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

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

Through the Clapeyron–Clausius equation the

(1) Haggenmacher, This Journal, 68, 1123, 1633 (1946).

heat of vaporization or the change in the enthalpy function, becomes

$$\Delta H = \frac{dp}{dT} \frac{RT^2}{Mp} \sqrt{1 - \frac{Dp}{T^3}} \qquad (3)$$

The vapor pressure of ethylbenzene has been measured from 0 to 60° by Guttman, Westrum and Pitzer,[2] and from 60 to 140° by Willingham, Taylor, Pignocco and Rossini.[3] The vapor pressure equation of the first group of observers is of the form

$$\log p = -\frac{a}{T} - b \log T + C \qquad (4a)$$

that of the second group

$$\log p = -\frac{B}{C + t} + A \qquad (4b)$$

Taking $T_c = 619.6°K$, $p_c = 38.1$ atm., icepoint $= 273.16°K$., mol. wt. $= 106.160$, $R = 1.98647$ (15° cal./deg. mole, for p in atm.),[4] and inserting the values of the constants as given by the authors, the heat of vaporization, in cal./g., becomes, respectively

$$\Delta H = (127.495 - 0.10853T) \sqrt{1 - \frac{Dp}{T^3}} \qquad (5a)$$

$$\Delta H = \frac{61.1526T^2}{(T - 60.549)^2} \sqrt{1 - \frac{Dp}{T^3}} \qquad (5b)$$

and the external work of vaporization, in cal./g.

$$-\Delta A = 0.018712T \sqrt{1 - \frac{Dp}{T^3}} \qquad (6)$$

The equations are valid: (5a) from 0 to 60°; (5b) from 60 to 140°; (6) from triple point to critical point.

A comparison of calculated heats of vaporization and measured values is shown in Table I.

TABLE I

T, °K.	ΔH, cal./g. eq. (5a)	Measd.	Observer
294.01	95.47	95.62	Scott, Brickwedde[4]
298.16	95.00	95.08	Osborne, Ginnings[5]

Measured values in int. joules are converted through: 15° cal. = 4.1847 int. joules.[6]

Calculations of the heat and the external work of vaporization give the following values, in cal./g.: at 0° 97.81 and 5.109; at 50° 92.03 and 6.022; at 100° 85.35 and 6.839; at 140° 79.74 and 7.343. In this region the heat of vaporization decreases and the external work of vaporization increases with temperature.

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(2) L. Guttman, E. F. Westrum, Jr., and K. S. Pitzer, THIS JOURNAL, 65, 1246 (1943).

(3) Ch. B. Willingham, W. J. Taylor, J. M. Pignocco and F. D. Rossini, J. Research Natl. Bur. Standards, 35, 219 (1945).

(4) R. B. Scott and F. G. Brickwedde, ibid., 35, 501 (1945).

(5) N. S. Osborne and D. C. Ginnings, private communication in preceding article, p. 511.

(6) R. T. Birge, Rev. Mod. Physics, 13, 233 (1941).

Bromination of 4-Phenylphenol and 4-Phenylphenyl Benzoate

BY STEWART E. HAZLET AND LEE C. HENSLEY

Repeated brominations of 4-phenylphenyl benzoate in glacial acetic acid in an attempt to improve the yield of 4-(4-bromophenyl)-phenyl benzoate led to results comparable to those reported previously.[1] Some "solvent effects" had been noted in other substitution reactions,[2] and, therefore, bromination of the benzoate was attempted in carbon tetrachloride. In this medium, a yield of 35.8% of pure 4-(4-bromophenyl)-phenyl benzoate was obtained, and, in addition, some 2-bromo-4-(4-bromophenyl)-phenyl benzoate was isolated. Although it was rather low, the yield of dibromo compound is sufficient to justify mention of the influence of the solvent.

The preparation of 2-bromo-4-(4-bromophenyl)-phenol by direct bromination of 4-phenylphenol in carbon tetrachloride is another case in point illustrating a "solvent effect." In certain solvents,[3] bromine substitutes in the phenol principally first in one ortho- and then in the other ortho- position with respect to the hydroxyl group.

Experimental

2-Bromo-4-(4-bromophenyl)-phenol. A.—This compound was prepared in approximately 10% yield according to the method of Bell and Robinson.[4]

B.—A considerably higher yield was obtained in the following manner. Ten grams of 4-phenlyphenol was suspended in 300 ml. of hot carbon tetrachloride, a trace of powdered iron was added, and 6.6 ml. (1.08 times the quantity necessary to produce a disubstituted product) of bromine in 35 ml. of carbon tetrachloride was introduced over a period of ninety minutes. Warming (just below boiling) and stirring were continued during this period of time, and after the addition of bromine was completed, the mixture was refluxed for one and one-half hours. The reaction mixture was treated with Norite and filtered, and the volume was reduced to about 25 ml. by distillation. After the oil which separated upon treating the residue with 30–60° ligroin solidified, it was dissolved in boiling 70–90° ligroin; the solution was treated with Norite, filtered and allowed to cool slowly. Long needles separated on cooling. They were recrystallized from the same solvent; m. p. 113–114.5°; yield 9.2 g. (47.6%).

No depression was observed when a mixed melting point determination was made with equal amounts of the material prepared in the two ways.

2-Bromo-4-(4-bromophenyl)-phenyl Benzoate.—Two and two-tenths grams of 2-bromo-4-(4-bromophenyl)-phenol was benzoylated in pyridine solution.[5] The crude product was obtained in almost quantitative yield, and after several crystallizations from 70–90° ligroin, colorless needles resulted; m. p. 147.5–148°.

Anal. Calcd. for $C_{19}H_{12}O_2Br_2$: Br, 36.99. Found: Br, 36.89.

Bromination of 4-Phenylphenyl Benzoate. A. In Glacial Acetic Acid ("Analytical Reagent").—This reaction was carried out as described previously,[1] and 4-(4-bromophenyl)-phenyl benzoate was the only product obtained.

(1) Hazlet, Alliger and Tiede, THIS JOURNAL, 61, 1447 (1939).

(2) Hazlet, Hensley and Jass, ibid., 64, 2449 (1942); Hensley and Hazlet, ibid., 65, 987 (1943).

(3) Ref. 1; cf. especially note 3 in that report.

(4) Bell and Robinson, J. Chem. Soc., 1127 (1927).

(5) Hazlet, THIS JOURNAL, 59, 287 (1937).