was washed thoroughly with ether, the ether layer was separated from the filtrate, decolorized, and evaporated *in vacuo*. Crystallization of the residue from Skellysolve B gave 3.2 g. (67%) of **7-phenoxyquinoline**, m. p. and mixed m. p. with the above-described authentic sample, 72.5–73.5°. The picrate and methiodide derivatives corresponded in m. p. and mixed m. p. with those described above.

4,7-Diphenoxyquinoline. From 7-Bromo-4-chloroquinoline.—To a solution of anhydrous potassium phenolate prepared from 3.1 g. of potassium hydroxide and 20 g. of phenol was added 5.0 g. of 7-bromo-4-chloroquinoline[4,13] and 0.5 g. of copper bronze. The resulting mixture was stirred at 185° for one and one-half hours. Upon working up by the general method described above there was obtained 5.6 g. (86%) of product, white prisms from Skellysolve B, m. 81.5–82.0°.

Anal. Calcd. for $C_{21}H_{15}NO_2$: C, 80.49; H, 4.83; N, 4.47. Found: C, 80.49; H, 4.86; N, 4.49.

The **picrate** formed long, brilliant yellow needles from alcohol, m. p. 185–186°.

Anal. Calcd. for $C_{27}H_{18}N_4O_9$: N, 10.33. Found: N, 10.07.

The **methiodide** formed pale yellow prisms from alcohol, m. p. 262–264° (dec.).

Anal. Calcd. for $C_{22}H_{18}INO_2$: N, 3.08. Found: N, 3.02.

From 4-Chloro-7-phenoxyquinoline.—Treatment of 4-chloro-7-phenoxyquinoline with potassium phenolate and copper bronze by the above method afforded a 90% yield of **4,7-diphenoxyquinoline**, m. p. and mixed m. p. with the above-described authentic sample, 81.5–82.0°. The picrate and methiodide derivatives corresponded in m. p. and mixed m. p. with those previously described.

4-(4-Diethylamino-1-methylbutylamino)-7-phenoxyquinoline.—This compound was prepared in the usual manner.[2,4,5] The product was obtained in 65.5% yield, b. p. 230–235° at 0.1 mm., m. p. 102–102.5° (lit.[2] m. p. 102–104°).

The **citrate** formed rosets of white prisms from alcohol–ether, m. p. 122.5–124.5° (gas evolution).

Anal. Calcd. for $C_{24}H_{31}N_3O \cdot C_6H_8O_7$: N, 7.39. Found: N, 7.41.

(13) Although the original description of this compound did not give a rigorous proof of structure, subsequent work in these laboratories has confirmed the assigned structure. Oxidation of 7-bromo-4-hydroxyquinoline with alkaline sodium hypobromite solution by a method analogous to that of Vaughan (THIS JOURNAL, **68**, 324 (1946)) gave a 62% yield of 4-bromoanthranilic acid. The m. p. and mixed m. p. with an authentic sample (Claus and Scheulen, *J. prakt. Chem.*, [2] **43**, 206 (1891)) was 220–221° (dec.).

STERLING-WINTHROP RESEARCH INSTITUTE
RENSSELAER, NEW YORK RECEIVED OCTOBER 7, 1946

o- and *p*-Nitroacetophenones by Liquid Phase Oxidation

BY WILLIAM S. EMERSON, JOSEF W. HEYD, VICTOR E. LUCAS, JAMES K. STEVENSON AND THOMAS A. WILLS

Ford-Moore and Rydon[1] have recently described two methods for the preparation of *o*- and *p*-nitroacetophenone. One method comprised the nitration and subsequent oxidation of methylphenylcarbinol and the other the treatment of *o*- and *p*-nitroethylbenzene with *t*-butyl nitrite and sodium *t*-butoxide followed by the hydrolysis of the resulting oximes.

(1) Ford-Moore and Rydon, *J. Chem. Soc.*, 679 (1946).

We have found liquid phase oxidation[2,3] to be suitable for the preparation of these compounds. While the conversions are not as high as is usually the case (14% for the *ortho* and 20% for the *para* isomer), the yields are satisfactory (63 and 66%, respectively) and the procedure is comparatively simple.

Experimental

The *o*-nitroethylbenzene[4] used boiled at 116° (22 mm.), $n^{25}D$ 1.5338, and the *p*-nitroethylbenzene at 134–136° (23 mm.), $n^{25}D$ 1.5431.

***o*-Nitroacetophenone.**—*o*-Nitroacetophenone was prepared by blowing air through an alundum disperser for twenty-eight hours, into 250 g. of *o*-nitroethylbenzene held at 135–145° and containing 4 g. of chromium oxide. This mixture was cooled, filtered, washed free of acid with aqueous sodium carbonate, and fractionated to separate the product. The pure *o*-nitroacetophenone boiled at 112.5–113.5° (2 mm.) [159° (16 mm.)],[5] $n^{25}D$ 1.5530, d^{25}_{25} 1.238, yield 39 g. (63%, 14% conversion).

Anal. Calcd. for $C_8H_7O_3N$: C, 58.2; H, 4.24. Found: C, 58.6; H, 4.75.

After two crystallizations from alcohol the oxime melted at 113–115° (115°).[6]

***p*-Nitroacetophenone.**—*p*-Nitroacetophenone was prepared in the same manner as the *ortho* isomer. The product, a solid, was collected at 123–130° (2 mm.) and crystallized from acetone and then from hexane, m. p. 78.5–80.0° (80–81°),[7] yield 29 g. (60%, 10% conversion). In a larger run of 900 g. the conversion rose to 20% with a 66% yield.

(2) Emerson, Heyd, Lucas, Chapin, Owens and Shortridge, THIS JOURNAL, **68**, 674 (1946).

(3) Emerson, Heyd, Lucas, Cook, Owens and Shortridge, *ibid.*, 1665 (1946).

(4) Cline and Reid, *ibid.*, **49**, 3150 (1927).

(5) Camps, *Ber.*, **32**, 3232 (1899).

(6) German Patent 109,663; *Chem. Zentr.*, **71**, II, 458 (1900).

(7) Drewsen, *Ann.*, **212**, 160 (1882).

CENTRAL RESEARCH DEPARTMENT
MONSANTO CHEMICAL COMPANY
DAYTON, OHIO RECEIVED NOVEMBER 9, 1946

A New Synthesis of Polygalitol Tetraacetate (Tetraacetyl-1,5-anhydro-D-sorbitol)

BY HEWITT G. FLETCHER, JR.

Richtmyer, Carr and Hudson[1] found that the reductive desulfurization of either octaacetyl-β,β-diglucosyl disulfide or tetraacetyl-β-glucothiose with Raney nickel afforded the tetraacetate of 1,5-anhydro-D-sorbitol (polygalitol). Recent work by Wolfrom and Karabinos[2] as well as by other authors[3] has further demonstrated the feasibility of reductive desulfurization as a preparative method. In the course of an investigation of sugar–alcohol anhydrides in this Laboratory it was found that ethyl tetraacetyl-D-glucopyranosyl

(1) N. K. Richtmyer, C. J. Carr and C. S. Hudson, THIS JOURNAL, **65**, 1477 (1943); *cf.* J. Bougault, E. Cattelain and P. Chabrier, *Compt. rend.*, **208**, 657 (1939), who introduced the use of Raney nickel for desulfurization.

(2) M. L. Wolfrom and J. V. Karabinos, THIS JOURNAL, **66**, 909 (1944); *ibid.*, **68**, 1455 (1946).

(3) O. Jeger, J. Norymberski, S. Szpilfogel and V. Prelog, *Helv. Chim. Acta*, **29**, 684 (1946); V. Prelog, J. Norymberski and O. Jeger, *ibid.*, 360 (1946); R. Jeanloz, D. A. Prins and T. Reichstein, *ibid.*, 371 (1946).

xanthate, an intermediate used by Richtmyer, Carr and Hudson[1] 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 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).

CHEMISTRY LABORATORY
NATIONAL INSTITUTE OF HEALTH
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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).

GALAT CHEMICAL DEVELOPMENT, INC.
61 SO. BROADWAY
YONKERS, N. Y. RECEIVED DECEMBER 2, 1946

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).