TABLE I

CARBOXYLIC ANILIDES PREPARED USING TETRAETHYL PYROPHOSPHITE

Anilides	Method of purification	Yield, %	M.p., °C.
Benzanilide	Crystallized from toluene	97	160–161[a]
Acetanilide	Washed with saturated sodium bicarbonate	97	110–111[c]
Carbobenzoxy-DL-phenylalanine anilide	Crystallized from toluene	98	158–160[d]
o-Chloroacetanilide	Washed with sodium bicarbonate and recrystallized from ether	75	86–87[e]
N-Methylacetanilide	Crystallized from reaction mixture and recrystallized from alcohol	64	98–99[f]
Salicylanilide[b]	Washed with $^1/_2$ saturated sodium bicarbonate—recrystallized from 50% alcohol	69	134–135[g]
2-Phenylcinchoninanilide	Washed with saturated sodium bicarbonate and reprecipitated from alcohol with water	77	201–202[h]

[a] O. Wallach and M. Hoffmann, *Ann.*, **184**, 80 (1876). [b] No solvent was used in this reaction. [c] Authentic sample U.S.P. grade had m.p. 110–111°. [d] G. W. Anderson, J. Blodinger, R. W. Young and A. D. Welcher, THIS JOURNAL, **74**, 5307 (1952). [e] Doht, *Monatsh.*, **27**, 221 (1906); "Beilstein," Vol. XII, p. 299, gives m.p. 88°. [f] W. Staedel, *Ber.*, 19, 1947 (1886). [g] R. Wanstrat, *ibid.*, **6**, 336 (1873), gives m.p. 134–135°. [h] A. Rojahn and J. Schotten, *Arch. Pharm.*, **264**, 337–347 (1926); *Chem. Zentr.*, **97**, II, 1, 415 (1926), give m.p. 198°.

The preparation of benzanilide was investigated to find optimum conditions. The effect of the order of reagent addition, the period of heating, the relative proportions of reagents and the presence or absence of a solvent upon the ease of isolation and yield of product was determined. The use of a 10% excess of tetraethyl pyrophosphite was favorable, but when increased to 50% the yield was lowered and the product was more difficult to purify. Increasing the period of heating with a 10% excess of tetraethyl pyrophosphite in toluene was favorable, but with a 50% excess the yield was decreased. The order of addition did not affect the yield. The following procedure gave a product that was readily purified and in the higher yield. A solution of 1.22 g. (0.01 mole) of benzoic acid, 0.93 g. (0.01 mole) of aniline and 2.83 g. (0.011 mole) of tetraethyl pyrophosphite in 15 cc. of dry toluene was refluxed for 2 hours. The mixture was cooled in an ice-bath and a solid precipitated. After drying this weighed 1.47 g., m.p. 160–161°. The distillation of the toluene yielded an oil which crystallized after being washed with 10 cc. of saturated sodium bicarbonate solution; wt. 0.45 g., m.p. 160–161°. The total yield was 97%. A control reaction, run under the same conditions in the absence of tetraethyl pyrophosphite, gave no product and a 97% recovery of benzoic acid. The anilides listed in Table I were made using essentially this same procedure.

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The Preparation of Isonicotinic and Picolinic Acids

BY D. J. COOK AND ROLAND S. YUNGHANS[1]

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Although several references appear in the literature concerning the oxidation of 2-picoline to picolinic acid by use of selenium dioxide,[2,3] no experimental references are recorded for a similar preparation of isonicotinic acid from 4-picoline. A recent article[4] makes note of the isolation of this acid when selenium dioxide was used to prepare isonicotinaldehyde from 4-picoline but no details of this reaction are given.

Since another problem in this Laboratory involved the use of selenium dioxide as an oxidizing agent for methyl-substituted nitrogen heterocyclics, it was of interest to apply this reaction to the preparation of isonicotinic acid from 4-picoline. It has been found that oxidations of this type can be carried out successfully using diphenyl ether as the solvent. The following method makes possible a convenient preparation of isonicotinic acid from 4-picoline in 57% yield with no aldehyde contamination. The preparation of picolinic acid gives yields of only 25–30% while similar attempted oxidations of 3-picoline were unsuccessful.

Acknowledgment.—The authors wish to express their appreciation to the Research Corporation for the Frederick Gardner Cottrell Fellowship Grant which made this work possible.

Experimental[5]

Isonicotinic Acid.—Twenty grams (0.216 mole) of 4-picoline was dissolved in 100 ml. of diphenyl ether and placed in a three-neck flask equipped with a stirrer, condenser and glass plug. The solution was heated to 155°. To the stirred mixture 39.6 g. (0.351 mole, 10% excess) of selenium dioxide was added portionwise over a period of 15 minutes. The reaction temperature was then raised to 185° and the reaction continued at this temperature for 30 minutes. At the end of this time the diphenyl ether was decanted from the precipitated selenium–isonicotinic acid residue and the residue brought onto a suction filter and washed with 75 ml. of low boiling ligroin.

The black selenium acid residue was ground to a powder and extracted with three 100-ml. portions of boiling water. The fractions were combined and upon cooling in ice tan crystals of isonicotinic acid formed. The yield was 15.1 g. (57%). No isonicotinic acid was recovered from the diphenyl ether. A melting point of this substance was approximately 310°. Several literature references give the m.p. of this compound from 308 to 317°.

Picolinic Acid.—In a manner analogous to the above preparation 10 g. (0.108 mole) of 2-picoline was dissolved in 50 ml. of diphenyl ether and treated with 17.8 g. (0.16 mole) of selenium dioxide at a temperature of 130° for three hours. At the end of this time the hot diphenyl ether solution was filtered and diluted with 60 ml. of high boiling ligroin. On cooling 3.5 g. (26%) of cream colored crystals, m.p. 132–135°, were obtained. One gram of this substance was recrystallized from a mixture of 40 ml. of benzene and 5 ml. of ligroin (60–75°). The m.p. was 134–135°. Picolinic acid is reported as melting at 134.5–136°.

The precipitated selenium residue was extracted twice with 75 ml. of benzene–ligroin mixture (60 ml.–15 ml.). From the combined extracts was obtained a yellow solid weighing 1.3 g. Recrystallization of this solid from 60 ml. of benzene–alcohol (50 ml.–10 ml.) gave a white solid which melted at 117–119° and which apparently contained selenium

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[1] Abstracted from a thesis by R. S. Yunghans presented to the Graduate Council of DePauw University in partial fulfillment of the requirements for the M.A. degree, June, 1952.

[2] M. Henze, *Ber.*, **67**, 750 (1934).

[3] W. Borsche and H. Hartman, *ibid.*, **73**, 839 (1940).

[4] H. H. Fox, *J. Org. Chem.*, **17**, 555 (1952).

[5] The melting points are uncorrected.

or was contaminated with selenium dioxide. No further attempts were made to purify this substance.

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The Apparent Molal Volume of Barium Chloride in Ethanol–Water Mixtures

BY RICHARD LOUIS BATEMAN

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A previous publication[1] gave the density and apparent molal volume of strontium chloride in ethanol–water mixtures with a discussion of the results. The present report concerns the density and apparent molal volume of barium chloride in ethanol–water mixtures at 25.00°. The apparent molal volume of barium chloride in aqueous solutions at 25° has been reported by Geffcken[2] and at 35° by Chacravarti and Prasad.[3]

TABLE I

APPARENT MOLAL VOLUME OF BARIUM CHLORIDE IN ETHANOL–WATER MIXTURES AT 25°

Molality of $BaCl_2$	Density of soln., g./ml.	Vol. of soln. per 1000 g. solvent, ml.	Apparent molal vol. $BaCl_2$, ml.
	0% Ethanol		
0.5	1.08545	1017.21	28.56
.4	1.06812	1014.21	28.20
.3	1.05066	1011.25	27.73
.2	1.03304	1008.35	27.10
.1	1.01513	1005.59	26.60
.05	1.00615	1004.22	25.80
0	0.99708	1002.93	
	20% Ethanol		
0.5	1.05159	1049.97	30.38
.4	1.03501	1046.67	29.72
.3	1.01818	1043.51	29.10
.2	1.00122	1040.38	28.00
.1	0.98400	1037.42	26.40
.05	.97534	1036.01	24.60
0	.96639	1034.78	
	40% Ethanol		
0.5	1.01151	1091.57	36.02
.4	0.99590	1087.75	35.47
.3	.98005	1084.11	35.17
.2	.96410	1080.44	34.40
.1	.94794	1076.88	33.20
.05	.93985	1075.08	30.40
0	.93148	1073.56	
	50% Ethanol		
0.2	0.94141	1106.49	37.05
.1	.92584	1102.60	35.20
.05	.91791	1100.79	34.20
0	.90985	1099.08	
	60% Ethanol		
0.17710	0.91442	1133.91	36.70
.1	.90273	1130.81	34.00
.05	.89496	1128.99	31.60
0	.88699	1127.41	

For the same solvent, the apparent molal volume of barium chloride is greatest in the more concentrated solutions. In the more dilute solutions, with the same solute concentration, the molal volume reaches a maximum in about 50% ethanol and a minimum in about 10% ethanol in the solvent.

Experimental

Conductance water was prepared by the redistillation of water containing a little potassium permanganate through a block tin condenser and saving only the middle fraction. At 25° the specific conductance of this water was 1.0×10^{-6} ohm^{-1} cm.$^{-1}$.

Ethanol was purified by treating 95% ethanol by the method of Kiczales.[4] The purified ethanol was 99.9% absolute and at 25° the specific conductance was 2.0×10^{-7} ohm^{-1} cm.$^{-1}$.

J. T. Baker C.P. $BaCl_2 \cdot 2H_2O$ was twice recrystallized from conductance water and oven-dried to constant weight.

Ethanol–water solvents were prepared by the weight method and the exact composition determined by density measurement and interpolation with the density values from the "International Critical Tables."

Barium chloride solutions in ethanol–water mixtures were prepared from anhydrous barium chloride by the weight method and the concentrations were expressed as gram-moles per 1000 g. of solvent.

Weights were standardized against a Bureau of Standards certified set and all weighings were corrected to vacuum.

The bath temperature was constant to within 0.01° and was determined by a Beckmann thermometer that had been standardized against a thermometer certified by the Bureau of Standards.

Density determinations were made at each concentration with two pycnometers, one of 45.7941 ml. the other of 46.1905 ml., calibrated with water as a standard and considering the density of water at 25.00° as 0.9970739 g./ml. Each value given in the table was the average of two independent determinations that were interpolated to "round" solvent composition and solute concentration. Limited solubility in the strongly alcoholic solutions confined the determinations to solvents containing 60% or less ethanol.

The results are summarized in Table I. The ethanol percentages are weight percentages ethanol in the solvent.

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[1] R. L. Bateman, THIS JOURNAL, **71**, 2291 (1949).

[2] W. Geffcken, *Z. physik. Chem.*, **A155**, 12 (1931).

[3] A. S. Chacravarti and B. Prasad, *Trans. Faraday Soc.*, **35**, 1469 (1939).

[4] S. Kiczales, *Ind. Eng. Chem.*, **20**, 493 (1928).

Identification and Properties of the Colored Compound Formed in Parathion Estimations[1]

BY R. C. BLINN, F. A. GUNTHER AND M. J. KOLBEZEN

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With the widespread use of the insecticidal material O,O-diethyl O-*p*-nitrophenyl thiophosphate (parathion) has coincided the development and exploitation of a sensitive method for its quantitative estimation upon foodstuffs.[2] This method is based upon the quantitative reduction of the nitro to the amino group with subsequent diazotization and coupling with N-1-naphthylethylenediamine to produce an intense magenta color. It has been established[3] that various substituted nitrobenzenes or anilines also give magenta colors

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[1] Paper No. 732, University of California Citrus Experiment Station, Riverside, California. Presented at the 121st Meeting of the American Chemical Society, Milwaukee, Wisconsin, April, 1952.

[2] (a) P. R. Averell and M. V. Norris, *Anal. Chem.*, **20**, 753 (1948); (b) F. A. Gunther and R. C. Blinn, *Advances in Chemistry Series*, **1**, 72 (1950); (c) J. C. Gage, *Analyst*, **75**, 189 (1950).

[3] (a) F. I. Edwards, Jr., *Anal. Chem.*, **21**, 1415 (1949); (b) R. C. Blinn and F. A. Gunther, *ibid.*, **22**, 1219 (1950); (c) M. V. Norris and P. R. Averell, private communications.