

dried over anhydrous sodium sulfate and evaporated. After some manipulation, 0.3 g. of a solid acid was obtained, which crystallized from aqueous alcohol, m. p. 77–78°. The amide, prepared in the usual way, melted at 158–158.5°, and so the acid was judged to be dimethylphenylacetic acid.

B.—Ten grams of the carbinol mixture was treated with sodium hypoiodide solution (prepared using 30 g. iodine, 60 g. potassium iodide, 240 ml. water and excess 10% sodium hydroxide solution). Only a few tenths of a gram of iodoform was obtained. The reaction was continued using 90 g. of bromine and excess sodium hydroxide solution. Some benzoic acid and a little oily acid with the odor of methylphenylacetic acid were obtained. The amount of the latter however was too small for further identification.

(5) Wallach, *Chem. Zentr.*, **70**, 11, 1047 (1899).

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The Heat of Dilution of Aqueous Hydrochloric Acid at 25°

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Subsequent to the publication of data on the heats of dilution of hydrochloric acid solutions by

TABLE I

INTEGRAL HEATS OF DILUTION OF HYDROCHLORIC ACID SOLUTIONS AT 25°

Square root of concentration (moles per 1000 g. H ₂ O) ^{1/2}			Heat of dilution from initial to final concentration — ΔH , joules (int.) per mole
Initial	Final	Diluent	
1.2513	0.3541	0	1617
1.4840	.4229	0	2069
1.7214	.4757	0	2666
1.7783	.4528	0	2891
1.8267	.0678	0	3798
1.8267	.0943	0	3706
1.8267	.1132	0	3621
1.8267	.1339	0	3574
1.8267	.1919	0	3466
1.8267	.2230	0	3412
1.8267	.2332	0	3381
1.8267	.2676	0	3325
1.8267	.3349	0	3233
1.8267	.3367	0	3217
1.8267	.3454	0	3198
1.8267	.3836	0	3143
1.8267	.4463	0	3041
1.8267	.4748	0	2999
1.8267	.5377	0.3050	2903
1.8267	.5434	0	2883
1.8267	.6128	0.4214	2782
1.8267	.7604	.6264	2532
1.8267	.8623	.7651	2361
1.8267	.9628	.8345	2176
1.8267	.9695	.8917	2164
1.8267	1.0647	.9800	1979
1.8267	1.2179	1.1470	1651

TABLE II

APPARENT AND PARTIAL RELATIVE MOLAL HEAT CONTENT OF SOLUTE AND PARTIAL RELATIVE MOLAL HEAT CONTENT OF SOLVENT IN HYDROCHLORIC ACID SOLUTIONS AT 25°

Square root of molality of hydrochloric acid	Heat content, joules (int.) per mole		
	$\Phi_H - \Phi_H^0$	\bar{L}_1	\bar{L}_1
0.0000	0	0	0
.0500	100		
.1000	199	297	— 0.0177
.1500	295		
.2000	388	570	— .131
.2500	475		
.3000	560	810	— .405
.3500	642		
.4000	722	1039	— .914
.4500	801		
.5000	880	1271	— 1.76
.5500	959		
.6000	1039	1519	— 3.11
.6500	1120		
.7000	1202	1784	— 5.14
.7500	1285		
.8000	1369	2060	— 7.97
.8500	1455		
.9000	1544	2360	— 11.9
.9500	1636		
1.0000	1731	2699	— 17.4
1.0500	1830		
1.1000	1932	3064	— 24.7
1.1500	2038		
1.2000	2147	3467	— 34.2
1.2500	2259		
1.3000	2374	3891	— 46.2
1.3500	2492		
1.4000	2613	4348	— 61.3
1.4500	2739		
1.5000	2870	4857	— 80.5
1.5500	3005		
1.6000	3146	5436	— 106
1.6500	3293		
1.7000	3443	6027	— 135
1.7500	3596		
1.8000	3752	(6628)	(— 168)
1.8267	3838		

the author,¹ Gucker and Pickard² pointed out the necessity for correcting such data for the heat effects resulting from differences in the vapor pressures of the concentrated and diluent solutions. The required corrections have now been made.

The vapor pressure and density data have been taken from the "International Critical Tables." The vapor pressure of hydrogen chloride over the solutions used is small enough so that no correction for vaporization or condensation of hydrogen chloride need be applied. Both the correction for distillation of water into the air space over the more concentrated solution, and that for the con-

(1) Sturtevant, *THIS JOURNAL*, **62**, 584 (1940).

(2) Gucker and Pickard, *ibid.*, **68**, 1464 (1940).

densation of water from the air space over the diluent have been applied. The corrected dilution heats are listed in Table I, and the derived values of the apparent and partial molal heat content of the solute and the partial molal heat content of the solvent are given in Table II. The average deviation of the experimental points from a smooth curve drawn through them is ≈ 3 joules per mole, if the two runs at the lowest concentrations are omitted. One run recorded in the original paper has been discarded.

The chief effect of the application of these corrections is on the extrapolation to infinite dilution, which is an arbitrary procedure at best. Thus the relatively large changes in the values of $\Phi_H - \Phi_H^0$ correspond to considerably smaller changes in the actual heats of dilution.

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Preparation of β -Alanine Methyl Ester¹

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The use of β -alanine ester in the synthesis and "partial synthesis" of pantothenic acid³ has made desirable a rapid and convenient method for the preparation of that substance. Because of the instability of the free ester,⁴ quantities of the material cannot be kept on hand, and must be made up immediately before use. We have found the preparation of the ester from the ester hydrochloride to be inconvenient and the yields poor.

Kuhn and Brydowna⁵ have prepared a number of α -amino acid esters by esterification with diazomethane. This method has been applied to the preparation of the methyl ester of β -alanine, the product being finally obtained in high purity and good yield. The comparative instability of the final product has necessitated working out certain conditions which must be followed closely for good results.

Experimental

To 4 g. of β -alanine was added one-half of an ether solution of diazomethane freshly prepared from 20 g. of

(1) This research is a continuation of preliminary work carried out at Oregon State College, under a grant of the Rockefeller Foundation.

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(3) Woolley, Waisman and Elvehjem, *THIS JOURNAL*, **61**, 977 (1939); Williams, *Science*, **89**, 486 (1939); Williams, Mitchell, Weinstock and Snell, *THIS JOURNAL*, **62**, 1784 (1940); Stiller, Harris, Finkelstein, Keresztesy and Folkers, *ibid.*, **62**, 1785 (1940).

(4) Abderhalden, *Z. physiol. Chem.*, **85**, 118 (1913).

(5) Kuhn and Brydowna, *Ber.*, **70**, 1333 (1937).

nitrosomethylurea.^{6,7} After 1 cc. of water had been added, the reaction mixture was stirred mechanically until the ether solution had become colorless (fifteen to thirty minutes). The remainder of the ether solution of diazomethane was added and stirring continued another two hours. At this time gas evolution was scarcely noticeable, and only a small amount of semi-solid material remained undissolved. Omission of mechanical stirring was found to reduce the yield considerably. The ether solution was decanted and dried over anhydrous sodium sulfate in the refrigerator for one hour. The ether solution was filtered and distilled from a 10 cc. "spitzkolben" under water pump pressure at a water-bath temperature not exceeding 35°. The flask containing the crude amino acid ester was removed from the bath, the bath was warmed quickly to 75–80°, the distillation flask was again immersed and the ester distilled under vacuum utilizing a good condensing system and well-cooled (0°) receivers. A fore-run boiling 40–49° (12 mm.) (0.55 g.) was collected. The main fraction of ester (2.9 g.) came over at 50–52° (12 mm.), 54–55° (13 mm.). Conversion of the ester in the fore run to the hydrochloride indicated an additional 0.2 g. of ester, making the total yield of β -alanine methyl ester 67%.

Identification was effected by heating a small portion of the ester for one hour with water, evaporation almost to dryness and addition of 95% ethanol. The product which crystallized out melted at 194–195°. A mixed melting point with an authentic specimen of β -alanine showed no depression. The ester was further characterized through its chloroplatinate which melted, without recrystallization, at 192°. After one recrystallization from 90% ethanol-ether the m. p. was 193°. The melting point of the crude chloroplatinate is indicative of the purity of the ester.

We are grateful for the suggestions of Dr. Roger J. Williams and Dr. Donald Price who, at different times, directed this research, and to Robert Eakin and Herschel K. Mitchell for preliminary work at Oregon State College.

(6) Gatterman and Wieland, "Laboratory Methods of Organic Chemistry," Macmillan Co., New York, N. Y., p. 272.

(7) The ethereal solution was allowed to stand over a few potassium hydroxide pellets for fifteen minutes.

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p-Nitrobenzoyl-*d*(-)- and *p*-Aminobenzoyl-*d*(-)-glutamic Acid

BY HARRY C. WINTER

Some contradictions exist in the literature as to the properties of the *p*-nitrobenzoyl derivatives of the optical isomers of glutamic acid. J. Van der Scheer and K. Landsteiner¹ reported the preparation of *p*-nitrobenzoyl-1(+)-glutamic acid and

(1) Van der Scheer and Landsteiner, *J. Immunol.*, **29**, 371 (1935).