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 Ester[1]

BY HARRY H. WEINSTOCK, JR.,[2] AND EVERETTE L. MAY[2]

The use of β-alanine ester in the synthesis and "partial synthesis" of pantothenic acid[3] 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 Brydowna[5] 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 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.

(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).

(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. Landsteiner[1] reported the preparation of *p*-nitrobenzoyl-l(+)-glutamic acid and

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

described it as crystallizing from water in the form of platelets, melting point 112–113°. Later, G. Iványovics and V. Bruckner[2] described this compound and also *p*-nitrobenzoyl-*d*(−)-glutamic acid as having melting points of 170°; since no analyses were given, the purity of these products may be open to question. In each instance, the compounds were prepared by the reaction of *p*-nitrobenzoyl chloride with l(+)- or *d*(−)-glutamic acid, a reaction known to produce racemization. Corresponding amino derivatives were obtained by reduction. No optical properties of these compounds have been reported.

p-Nitrobenzoyl-*d*(−)-glutamic acid has been prepared in this Laboratory by resolution of *p*-nitrobenzoyl-*dl*-glutamic acid through repeated recrystallization of the strychnine salt from water. The slightly soluble salt of the *d*(−)-enantiomorph was obtained in good yield. After removal of strychnine, the free acid derivative crystallized from aqueous solution in fine white needles which softened at 77° and melted at 115–116° (*Anal.* Calcd. for $C_{12}H_{12}N_2O_7$: N, 9.46. Found: N, 9.39). This is in good agreement with the melting point of the l(+)-derivative reported by Van der Scheer and Landsteiner.[1] The specific rotation of the aqueous solution containing 2 moles of alkali was −16.02°.

p-Aminobenzoyl-*d*(−)-glutamic acid has been prepared in this Laboratory by the reduction of the nitro compound using the method of Van der Scheer and Landsteiner[1] for the preparation of *p*-aminobenzoyl-l(+)-glutamic acid. The compound crystallized from water in clusters of microscopic needles (*Anal.* Calcd. for $C_{12}H_{14}N_2O_5$: N, 10.53. Found: N, 10.50) melting at 166–167°, somewhat lower than that (175°) reported by Iványovics and Bruckner.[2] Its specific rotation in aqueous solution containing 2 moles of alkali was −27.4°; in 9% hydrochloric acid +15.5°. It is possible that some racemization occurred under the conditions of the reduction.

(2) Iványovics and Bruckner, *Z. Immunitäts.*, **93**, 119 (1938).

BIOCHEMICAL RESEARCH FOUNDATION
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The Preparation of Tetraphenylgermanium

BY DAVID E. WORRALL

Two classical methods for the preparation of organometallic derivatives are those of Grignard and Fittig. Surprising it is, therefore, that both are said to give poor results in the synthesis of tetraarylgermanes.[1] Perhaps that is why most investigators have not reported yields. Morgan and Drew[2] found it necessary to employ 36 molar equivalents of phenylmagnesium bromide, obtaining a 40% yield of tetraphenylgermanium. Kraus and Foster[3] modified the usual procedure by converting the intermediate magnesium compound into diphenylzinc in an atmosphere of nitrogen, subsequently replacing the ether with toluene. Excellent yields are obtainable but the procedure is elaborate and time consuming and a rather large excess of reagent is used.

It has been found in this Laboratory that the presence of zinc compounds or a large excess of the organomagnesium derivative is unnecessary. A good yield of tetraphenylgermanium may be obtained by the usual technique provided only that toluene is substituted for ether. A similar replacement in the Fittig synthesis of the same compound gives fair results.

Experimental

A solution of phenylmagnesium bromide prepared from 29 g. of monobromobenzene was filtered by decantation mixed with 100 cc. of dry toluene and heated on a water-bath to remove ether. While still warm and connected to a reflux condenser, 10 g. of germanium tetrachloride mixed with 10 cc. of toluene was run in with occasional shaking at such a rate that vigorous boiling took place. The mixture was then heated for two hours on an oil-bath. Following hydrolysis using hydrochloric acid, several hundred cc. of warm toluene was added and the filtered toluene layer concentrated to a small bulk. White needle-like crystals separated from the yellow solution. It was filtered by suction, washed first with a few cc. of cold toluene, then with several volumes of alcohol; yield 14.1 g., m. p. 225–226° (uncor.).

In another experiment a mixture containing 10 g. of germanium tetrachloride, 100 cc. of toluene, 9 g. of granulated sodium and 30 g. of monobromobenzene was heated cautiously under a reflux condenser until the reaction started. Once started the reaction became violent so that outside cooling from time to time was necessary. The mixture was heated for an hour after the spontaneous reaction ceased and worked up while still hot. Although the solution was deeper colored than that obtained by the magnesium method, the product was perfectly white; yield 9.6 g. Longer heating or the replacement of toluene with xylene did not noticeably increase the yield.

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(1) Simons, Wagner and Müller, THIS JOURNAL, **55**, 3705 (1933).
(2) Morgan and Drew, *J. Chem. Soc.*, **127**, 1760 (1925).
(3) Kraus and Foster, THIS JOURNAL, **49**, 457 (1927).