In one experiment a sample of 2-methoxybenzoyl peroxide[6] was decomposed in benzene, but no methyl salicylate could be found.

Experimental[7]

2-Phenoxybenzoic Acid.—The preparation of this acid has been described previously,[8] but since devising a procedure for the formation of a pure product in good yield proved troublesome, the procedure is given. Phenol (18.8 g., 0.20 mole), 16.5 g. of 85% potassium hydroxide (0.25 mole), 15.7 g. of *o*-chlorobenzoic acid (0.10 mole), and approximately 0.5 g. of copper bronze were heated with stirring in a 250-ml. three-necked flask (foaming) equipped for distillation. While the temperature was gradually increased a sudden reaction occurred at about 150° and the color of the mixture changed from brown to brick red; phenol began to distil at 180° and by slowly raising the temperature between 200 and 220° a yield-reducing exothermic reaction was avoided. The mixture was cooled to 115° and 20 ml. of water added cautiously to prevent the troublesome caking which occurs in the absence of water. The solution was acidified with sulfuric acid and excess phenol removed by steam distillation. The solid was filtered, dissolved in benzene, and the acidic materials extracted into aqueous sodium bicarbonate. Acidification gave a somewhat reddish solid; this crude 2-phenoxybenzoic acid was dissolved in about 10 ml. of benzene, kept at 55° while 40 ml. of petroleum ether (b.p. 60–70°) was added slowly and with stirring to prevent separation of an oil; then 50 ml. of petroleum ether was added rapidly precipitating a small amount of red oil that quickly solidified. The hot solution was filtered and the pure 2-phenoxybenzoic acid, m.p. 111–112°, crystallized out in 70% yield (15.2 g.). This purification method removes the red-colored impurity and a colorless solid, m.p. 187–198°, possibly diphenic acid.

2-Phenoxybenzoyl Chloride and 2-Phenoxybenzoyl Peroxide.—2-Phenoxybenzoic acid (13 g.) and 7 ml. of thionyl chloride were heated at 50–55° for 40–60 min.; 15 ml. of *n*-heptane was added, the solution filtered and cooled in a Dry Ice bath to cause the acid chloride to crystallize. Sometimes a non-crystallizable oil settled out; in this case the heptane was decanted and replaced by a fresh portion. The 2-phenoxybenzoyl chloride is an almost colorless solid, m.p. 39–40°, and obtained in 94% yield.

To a stirred solution of 2.40 g. of sodium peroxide in 75 ml. of water maintained at 5° was added in dropwise fashion over a half-hour period a solution of 14.9 g. of 2-phenoxybenzoyl chloride in 100 ml. of toluene. Stirring was continued for an additional three hours at 0–5°. After drying the toluene layer, most of the solvent was removed at 30° and 20 mm., and the resulting oil triturated with successive portions of *n*-heptane until it solidified to a light-yellow powder (containing 97.5% of peroxide as determined iodometrically); yield 88%. The product on crystallization from an ether–heptane mixture was obtained in the form of colorless crystals, m.p. 66–67°. The product slowly decomposed at room temperature over a period of several weeks.

Anal. Calcd. for $C_{26}H_{18}O_6$: C, 73.25; H, 4.25. Found: C, 73.16; H, 4.37.

Polymerization of Monomers.—Ten-ml. samples of freshly distilled styrene were placed in each of four test-tubes. To the first tube was added 0.1 g. of 2-phenoxybenzoyl peroxide (2.3 mmoles), to the second was added 0.057 g. of benzoyl peroxide (2.3 mmoles), to the third 0.1 g. of 2-phenoxybenzoyl peroxide plus 0.138 g. (1.25 mmoles) of hydroquinone; the fourth tube contained just styrene. After seven days in the dark at room temperature the contents of the first two tubes had become viscous, but the latter two tubes appeared unchanged.

In a similar experiment with methyl methacrylate the benzoyl peroxide tube had hardened, the 2-phenoxybenzoyl peroxide tube was somewhat viscous, and the other two tubes were still mobile.

Thermal Decomposition of 2-Phenoxybenzoyl Peroxide.—In two experiments 1-g. samples of 2-phenoxybenzoyl peroxide were refluxed with 100-ml. portions of benzene for seven hours while swept with a slow stream of high-purity nitrogen to determine carbon dioxide yields. In the first experiment the Ascarite tube gained 5.5 mg., equivalent to a carbon dioxide yield of 1.4%, but the large quantity of benzene found in the cold trap indicated that the nitrogen sweep rate was too high. The second experiment gave a gain of only 0.3 mg.; the carbon dioxide yield was nil.

Evaporation of the benzene from a run in which 5.4 g. of the peroxide had been refluxed for 15 hours in 500 ml. of reagent grade benzene gave a viscous oil. This was extracted with isoöctane, one portion of which was diluted and the ultraviolet absorption spectral curve obtained, and the other portion of which was evaporated and the infrared curve obtained. The absorption curve of the oil had all the absorption peaks of phenyl salicylate (more than 28 significant peaks) and only one peak at 5.73 μ that was clearly extraneous. Attempts to get the oil to solidify were unsuccessful. This extract was missing some of the peaks characteristic of the phenyl ester of 2-phenoxybenzoic acid. 2-Phenoxybiphenyl has strong peaks at 12.99, 13.33 and 13.57μ; the above oil lacks peaks in these regions. The absence of dibenzofuran was indicated by the ultraviolet spectra; dibenzofuran has peaks at about 250 mμ and at 282 mμ and a minimum at about 259 mμ. The ultraviolet curve of the oil had maxima at 241 and at 310 and a minimum at 278 mμ with no indication of perturbations expected for dibenzofuran. Moreover, the formation of these products would require decarboxylation. Their absence therefore seems well established.

A small amount of solid material, m.p. 271–273°, could be isolated from a benzene concentrate of the decomposition products. It may be some sort of dimer (or polymer) of *o*-phenoxybenzoic acid as indicated by analysis and by the high melting point. The material was recovered unchanged from refluxing sodium hydroxide.

Anal. Calcd. for $C_{26}H_{18}O_6$: C, 73.25; H, 4.25; neut. equiv., 214. Found: C, 73.22; H, 4.89; neut. equiv., 217.5.

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(6) We are indebted to Dr. A. J. Buselli for this sample.

(7) All melting points are corrected.

(8) F. Ullmann and M. Zlokasoff, *Ber.*, **38**, 211 (1905); R. Q. Brewster and F. Strain, THIS JOURNAL, **56**, 117 (1934).

Saturation of Acetyldehydroalanine with Benzylamine

BY S.-C. J. FU AND JESSE P. GREENSTEIN

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The unsaturated character of the dehydropeptides, RCHCONHC(=CHR′)COOH, is revealed in part by several types of addition reactions such as the decolorization of bromine and permanganate,[1,2] and the addition of catalytic hydrogen,[1] of mercaptans,[3] of amides[4] and of amines.[2,5] Not all of the dehydropeptides react alike toward these reagents. Thus, whereas acetyldehydroalanine readily reacts quantitatively with bromine[2] and with amines,[2,5] acetyldehydrovaline reacts only partially, and acetyldehydrophenylalanine not at all with bromine, and neither compound reacts with amines.[2]

Saturation of acetyldehydroalanine (N-α-acetaminoacrylic acid) with benzylamine has led to the identification of α-acetamino-β-benzylaminopropionic acid as one of the products.[2] The low yield obtained made it desirable to study the reaction in more detail, and it was further considered of interest to see if it might serve as a method for the preparation of the relatively difficultly accessible

(1) M. Bergmann and F. Stern, *Ann.*, **448**, 20 (1926).

(2) I. Z. Eiger and J. P. Greenstein, *Arch. Biochem.*, **19**, 467 (1948).

(3) B. H. Nicolet, *Science*, **81**, 181 (1935).

(4) D. Shemin and R. Herbst, THIS JOURNAL, **60**, 1954 (1938).

(5) V. E. Price and J. P. Greenstein, *J. Biol. Chem.*, **173**, 337 (1948).

α-acetamino-β-aminopropionic acid and of the corresponding α,β-diamino acid.

Accordingly, acetyldehydroalanine was refluxed in ethanolic solution with benzylamine. From the reaction mixture three products were isolated in crystalline form. In the order of their isolation there was obtained alanine (16%), α-amino-β-benzylaminopropionic acid (15%) and α-acetamino-β-benzylaminopropionic acid (25%), the figures in parentheses relating to the yields based on the acetyldehydroalanine employed. When absolute methanol was used instead of ethanol in the saturation reaction, no alanine was isolated, and the yields of α-amino-β-benzylaminopropionic acid and of α-acetylamino-β-benzylaminopropionic acid were, respectively, 20 and 32%. Catalytic reduction of α-acetamino-β-benzylaminopropionic acid led to α-acetamino-β-aminopropionic acid which on HCl hydrolysis gave α,β-diaminopropionic acid·HCl in good yield.

The formation of α-amino-β-benzylaminopropionic acid in the saturation reaction was no doubt due to the splitting off of the acetyl group from the addition product. The formation of alanine in this reaction, and to so appreciable an extent, is more difficult to explain, but it is not inconceivable that under the conditions used the amino acid might owe its origin to a reductive reaction among the degradation products of acetyldehydroalanine which would include ammonia and pyruvic acid. The lower refluxing temperature in the presence of methanol than of ethanol might be insufficient to permit this reaction to proceed.

Experimental

Reaction of Acetyldehydroalanine with Benzylamine.—Ten grams of acetyldehydroalanine[6] was suspended in a solution of 100 ml. of freshly distilled benzylamine in 50 ml. of absolute ethanol, and the reaction mixture refluxed for six hours in the absence of atmospheric carbon dioxide. After cooling the solution to 25°, 500 ml. of acetone was added and the mixture chilled at −10° for several hours. The precipitate (1.1 g.) which appeared was filtered off and recrystallized from water by addition of excess acetone. Paper chromatograms in several solvents, together with an infrared spectrogram revealed that the material was alanine, evidence which was confirmed further by the analytical data.

Anal. Calcd. for $C_3H_7O_2N$: C, 40.5; H, 7.9; N, 15.7. Found: C, 40.7; H, 7.8; N, 15.6.

The filtrate from the above precipitate was evaporated *in vacuo* nearly to dryness and 200 ml. of acetone again added. A slightly yellowish crystalline material separated (2.2 g.). The crude product was dissolved in water, the solution clarified with Norit, and after filtration a large volume of absolute ethanol added to the filtrate. The colorless precipitate which appeared was purified again in the same way. Analysis revealed nearly pure α-amino-β-benzylaminopropionic acid.

Anal. Calcd. for $C_{10}H_{14}O_2N_2$: C, 61.8; H, 7.2; N, 14.5. Found: C, 61.6; H, 6.9; N, 14.3.

The filtrate from the above isolation which was a light brown viscous liquid was treated with 200 ml. of 2 *N* NaOH and extracted four times with ethyl ether. Dilute HCl was added to the aqueous layer until the reaction was slightly acid to congo red, the solution was evaporated *in vacuo* to dryness, and the residue extracted three times with absolute ethanol. The combined ethanolic extracts were evaporated *in vacuo* to dryness, and chloride ion removed by addition of a suspension of silver carbonate in water. Silver ion subsequently was removed with H_2S gas and the final filtrate evaporated *in vacuo* to a low bulk. Appearance of crystals at this stage was further facilitated by addition of excess ethanol. The crude yield of α-acetamino-β-benzylaminopropionic acid was 4.5 g. The compound was recrystallized from hot 85% ethanol, and melted at 188°.

Anal. Calcd. for $C_{12}H_{16}O_3N_2$: C, 61.0; H, 6.8; N, 11.9. Found: C, 60.7; H, 6.7; N, 11.9.

Repetition of the above procedure, using methanol instead of ethanol in the saturation reaction of benzylamine with acetyldehydroalanine yielded no alanine but only α-amino-β-benzylaminopropionic acid and α-acetamino-β-benzylaminopropionic acid in yields of 20 and 32%, respectively.

Treatment of α-amino-β-benzylaminopropionic acid with a hot mixture of acetic anhydride in glacial acetic acid yielded the α-acetamino compound which was isolated after pouring the reaction mixture into cold water. After recrystallization from 85% ethanol, the compound melted at 188°. The yield was 60%.

Anal. Calcd. for $C_{12}H_{16}O_3N_2$: C, 61.0; H, 6.8; N, 11.9. Found: C, 61.1; H, 6.9; N, 11.5.

Preparation of α,β-Diaminopropionic Acid.—Three grams of α-acetamino-β-benzylaminopropionic acid, isolated as above from the reaction mixture of benzylamine and acetyldehydroalanine, was dissolved in 75 ml. of 50% methanol, the solution treated with a few drops of acetic acid, and subjected to catalytic hydrogenation at 40 lb. in the presence of palladium. The reaction was ended in two and a half hours, and after removal of the catalyst the solution was evaporated *in vacuo* to a volume of about 10 ml. Addition of acetone caused the separation of a colorless oil which crystallized on chilling to −10°. The compound, α-acetamino-β-aminopropionic acid, sintered at 181° and decomposed at 197°. The yield was 1.2 g.

Anal. Calcd. for $C_5H_{10}O_3N_2$: C, 41.1; H, 6.9; N, 19.1. Found: C, 41.0; H, 7.1; N, 18.8.

When the α-acetamino-β-aminopropionic acid was refluxed with 2 *N* HCl for two hours the acetyl group was hydrolyzed off, and α,β-diaminopropionic acid monohydrochloride isolated by addition of excess ethanol to the condensed reflux mixture. The yield was about 80%.

Anal. Calcd. for $C_3H_9O_2N_2Cl$: C, 25.6; H, 6.5; N, 19.9; Cl, 25.2. Found: C, 25.5; H, 6.6; N, 19.5; Cl, 25.0.

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(6) M. Bergmann and K. Grafe, *Z. physiol. Chem.*, **187**, 187 (1930).

Reactions of the Bromomagnesium Salt of N,N-Dimethyl-β,β-diphenylpropionamide

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The conjugate addition of Grignard reagents to α,β-unsaturated amides has been reported to yield the intermediates I.[2] Maxim and Ioanid claimed that the acylation of these substances formed the enol esters II and that this evidence established the addition as proceeding by a 1,4-mechanism.[3] The structure of the acylated derivatives was proved by hydrolysis with alcoholic potassium hydroxide. Where R was methyl or ethyl, the corresponding anilide of β,β-diphenylpropionic acid was isolated. Where R was phenyl, hydrolysis yielded β,β-diphenylpropionic acid itself.

(1) Medicinal Chemistry Branch, Chemical Corps Medical Laboratories, Army Chemical Center, Md.

(2) N. Maxim and N. Ioanid, *Bull. soc. chim. Romania*, **10**, 116 (1928).

(3) The evidence, however, does not in itself favor any mechanism for the conjugate addition of the Grignard reagent since, for example, it has been shown that the acylation of intermediates formed by addition to unsaturated ketones yields products which vary with the structure of the ketone. See E. P. Kohler, M. Tishler and H. Potter, THIS JOURNAL, **57**, 2517 (1935).