in a 70% yield, and crystallization from ethanol gave the pure amide, m. p. 209–210°.

Anal. Calcd. for $C_{14}H_{11}O_2N$: N, 6.22. Found: N, 6.31.

The 2-dibenzofurylacetic acid was obtained by refluxing the amide with thirty parts of a 15% ethanolic solution of potassium hydroxide for four hours and then crystallizing the precipitated acid from ethanol as colorless needles, m. p. 162–163°; yield 87%.

Anal. Calcd. for $C_{14}H_{10}O_3$: C, 74.33; H, 4.47. Found: C, 74.24; H, 4.61.

2. **Willgerodt Reaction.**—A mixture of 2 g. (0.01 mole) of 2-acetyldibenzofuran, 8 cc. of purified dioxane, and 1 g. of sulfur in 10 cc. of a solution of ammonium sulfide was heated in a sealed tube at 160° for ten hours. The yellow crystals which deposited on cooling were crystallized from ethanol to give 1.5 g. (70%) of 2-dibenzofurylacetamide, m. p. 209–210°. There was no depression in a mixed melting point determination with the amide obtained from the Arndt–Eistert reaction.

3. **From 2-Dibenzofurylmethyl Chloride.**—A solution of 1 g. (0.005 mole) of 2-dibenzofurylmethyl chloride[3] and 0.33 g. (0.006 mole) of potassium cyanide in 10 cc. of ethanol was refluxed for three hours, and then evaporated almost to dryness under reduced pressure. Addition of water precipitated the 2-dibenzofurylmethyl cyanide which, after crystallization from ethanol, melted at 100–102°; yield 0.52 g. (55%).

Anal. Calcd. for $C_{14}H_9ON$: N, 6.76. Found: N, 7.01.

A solution of 0.4 g. (0.002 mole) of 2-dibenzofurylmethyl cyanide in a mixture of 5 cc. of 50% sulfuric acid and 5 cc. of glacial acetic acid was refluxed for one hour, cooled, and diluted with water. Crystallization from ethanol gave the acid melting at 162–163°, which was shown to be identical with the acid prepared by hydrolysis of the acid amide.

4-Dibenzothienylacetic Acid.—First, 5 g. (0.021 mole) of 4-dibenzothiophenecarboxylic acid[4] was converted by thionyl chloride to 4-dibenzothiophenecarboxylic acid chloride which after crystallization from benzene was obtained as colorless needles, m. p. 159–160°; yield 4.9 g. (92%).

Anal. Calcd. for $C_{13}H_7OClS$: Cl, 14.38. Found: Cl, 14.47.

Second, from 4 g. (0.016 mole) of 4-dibenzothiophenecarboxylic acid chloride and diazomethane was obtained an 86% yield of diazomethyl 4-dibenzothienyl ketone as yellow crystals, m. p. 161–162° after crystallization from ethanol.

Anal. Calcd. for $C_{14}H_8ON_2S$: N, 11.11. Found: N, 11.39.

Third, in accordance with the Arndt–Eistert procedure described for 2-dibenzofurylacetic acid, 2.5 g. (0.01 mole) of diazomethyl 4-dibenzothienyl ketone was converted in a 61% yield to 4-dibenzothienylacetamide, m. p. 205–206° after crystallization from ethanol.

Anal. Calcd. for $C_{14}H_{11}ONS$: N, 5.80. Found: N, 5.97.

Fourth, the amide on hydrolysis by refluxing for three hours with a 15% ethanolic potassium hydroxide solution gave, subsequent to acidification and crystallization from ethanol, an 89% yield of 4-dibenzothienylacetic acid, m. p. 161.5–162.5°.

Anal. Calcd. for $C_{14}H_{10}O_2S$: S, 13.22. Found: S, 13.35.

2-Phenoxathiinacetic Acid.—In accordance with the Willgerodt reaction described for 2-dibenzofurylacetic acid, there was obtained from 2 g. (0.008 mole) of 2-acetylphenoxathiin[5] 1.4 g. (68%) of yellow crystals of 4-phenoxathiinacetamide, m. p. 202–203° after crystallization from ethanol.

Anal. Calcd. for $C_{14}H_{11}O_2NS$: N, 5.44. Found: N, 5.61.

Hydrolysis of the acid amide by refluxing with ethanolic potassium hydroxide gave an 85% yield of colorless needles of 2-phenoxathiinacetic acid, m. p. 136–137° after crystallization from benzene.

Anal. Calcd. for $C_{14}H_{10}O_3S$: S, 12.40. Found: S, 12.53.

2-Carbazolylacetic Acid.—First, the modified Willgerodt reaction with 2 g. (0.01 mole) of 2-acetylcarbazole[6] gave 1.3 g. (58%) of 2-carbazolylacetamide, obtained as yellow crystals, m. p. 236–237° after crystallization from ethanol.

Anal. Calcd. for $C_{14}H_{12}ON_2$: N, 12.50. Found: N, 12.39.

Then, hydrolysis of the acid amide by refluxing with ethanolic potassium hydroxide gave an 87% yield of the acid as colorless leaflets, m. p. 270–271° after crystallization from ethanol.

Anal. Calcd. for $C_{14}H_{11}O_2N$: N, 6.22. Found: N, 6.48.

3-Carbazolylacetic Acid.—A mixture of 2.1 g. (0.01 mole) of 3-acetylcarbazole, 1 g. of sulfur, 10 g. of ammonium sulfide and 10 cc. of purified dioxane was heated in a sealed tube for twelve hours at 160°. Recrystallization of the resulting yellow product from dioxane gave 1.9 g. (85%) of 3-carbazolylacetamide, m. p. 295–296°.

Anal. Calcd. for $C_{14}H_{12}ON_2$: N, 12.50. Found: N, 12.48.

Hyodrolysis of the amide by ethanolic potassium hydroxide gave 1.7 g. (90%) of 3-carbazolylacetic acid, m. p. 260–261° after crystallization from ethanol.

Anal. Calcd. for $C_{14}H_{11}O_2N$: N, 6.22. Found: N, 6.37.

2,8-Dibenzofuryldiacetic Acid.—A mixture of 2.5 g. (0.01 mole) of 2,8-diacetyldibenzofuran, 2 g. of sulfur, 20 g. of ammonium sulfide and 20 cc. of dioxane was heated at 160° for twelve hours. The resulting mixture was suspended in 100 cc. of 15% ethanolic potassium hydroxide, refluxed for three hours, filtered, and the filtrate acidified with hydrochloric acid. Recrystallization from acetic acid gave 1.5 g. (53%) of 2,8-dibenzofuryldiacetic acid, m. p. 230–231°.

Anal. Calcd. for $C_{16}H_{12}O_5$: C, 67.60; H, 4.22. Found: C, 67.69; H, 4.34.

Assays and Acknowledgment.—The authors are grateful to Dr. George S. Avery, Jr., of Connecticut College[7] for growth tests on some of the compounds. 2-Carbazolylacetamide, 2-carbazolylacetic acid and 2,8-dibenzofuryldiacetic acid were physiologically inactive in the Avena curved growth test (deseeded method), and in the tomato test (Hitchcock and Zimmerman). In connection with a study of other types, it was observed that triethylleadacetic acid at 1.4 mg./liter gave a suggestion of activity in the Avena straight growth test (Scheer).

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[3] Prepared in accordance with directions provided by Paul T. Parker.

[4] Gilman and Jacoby, *J. Org. Chem.*, **3**, 108 (1938).

[5] Suter, McKenzie and Maxwell, THIS JOURNAL, **58**, 717 (1936).

[6] Meitzner, *ibid.*, **57**, 2327 (1935); Plant and Williams. *J. Chem. Soc.*, 1142 (1934).

[7] Present address: Brooklyn Botanic Garden, New York, N. Y.

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RECEIVED MAY 10, 1946

A Convenient Synthesis of 5-Methyltryptophan

BY MARY E. JACKMAN AND S. ARCHER

In connection with another problem the need arose for a sizeable quantity of 5-methyltryptophan. Robson[1] described a method for preparing

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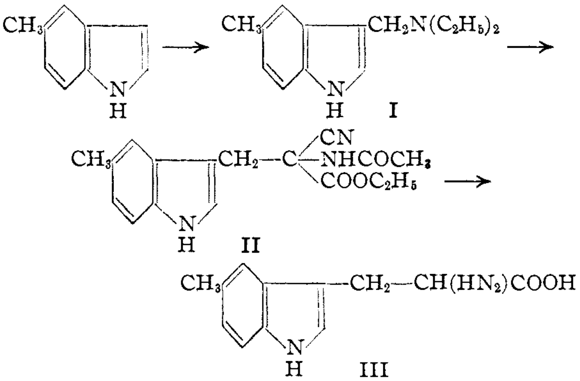
[1] Robson. *J. Biol. Chem.*, **62**, 495 (1924–1925).

this compound but the yields in several of the steps were so low that the procedure proved to be unsatisfactory for our purpose. It was found that syntheses recently developed for the parent substance, tryptophan, could be applied here successfully.[2] The required 5-methylindole was prepared essentially by Robson's method.[1] It was converted to 3-diethylaminomethyl-5-methylindole (I) in 86% yield by treatment with formalin and diethylamine in acetic acid solution. The Mannich base condensed readily with ethyl acetamidocyanoacetate[3] to give II in 86% yield. Hydrolysis to 5-methyltryptophan (III) was effected in 55% of the theoretical yield by refluxing with dilute sodium hydroxide. Robson[1] stated that the amino acid, III, melted at 259–264° and was soluble in water. Our compound was found to melt at 284–288° and could be precipitated from an aqueous solution of its sodium salt by acidification with acetic acid. The analytical data agreed quite well with the theoretical values.



Experimental

5-Methylindole.—The method of Robson[1] was followed except that *p*-tolylhydrazine was prepared by the method described in "Organic Syntheses" for phenylhydrazine.[4]

3-Diethylaminomethyl-5-methylindole (I).—Thirty-five milliliters of a 40% formalin solution and a solution of 73 g. (1 mole) of anhydrous diethylamine in 66.5 ml. of acetic acid were added dropwise and simultaneously to 65.3 g. of 5-methylindole. The flask was swirled during the addition. After standing overnight (all the indole had dissolved), the dark reaction mixture was poured into water and filtered to remove a small amount of insoluble material. The filtrate was made basic with 10% sodium hydroxide solution and the gum that separated soon solidified. It was collected on a filter, washed with water and dried; the yield was 97.7 g. or 86% of the theoretical. It was sufficiently pure for the next step. On crystallization from dilute ethanol it melted at 89–92°.

Anal. Calcd. for $C_{14}H_{20}N_2$: N, 12.95. Found: N, 12.90.

Ethyl α-Acetamido-α-cyano-(5-methylindole)-propionate (II).—To a solution of 10.35 g. of sodium in 800 ml. of dry ethanol there was added 97.7 g. of 3-diethylaminomethyl-5-methylindole and 76.0 g. of ethyl acetamidocyanoacetate. When all the solids had dissolved, 94.6 g. of methyl sulfate was added dropwise to the stirred solution. The reaction mixture was cooled occasionally to prevent the temperature from rising above 40°. After standing overnight the mixture was poured into water with stirring and the solid that separated was collected and thoroughly washed with water. After air drying, the substance weighed 123 g. (87%). A sample crystallized from dilute ethanol with the aid of charcoal melted at 197–198°.

Anal. Calcd. for $C_{17}H_{19}N_3O_3$: N, 13.41. Found: N, 13.41.

5-Methyltryptophan (III).—A mixture of 123 g. of II and 123 g. of sodium hydroxide in 1110 ml. of water was refluxed for fifteen hours and cooled. The solution was carefully acidified to about *p*H 5 and the precipitate filtered. The amino acid was recrystallized from acetic acid containing a small amount of water. The crystals were filtered off and dissolved in dilute sodium hydroxide. The solution was decolorized with Darco G-60, filtered and acidified with acetic acid. The substance that separated was washed with water, ethanol and finally ether. After drying for twenty four hours at 50° it weighed 47 g. (55%), and melted at 284–288°. It was insoluble in water, ethanol and cold acetic acid, soluble in sodium hydroxide solution, hydrochloric acid and hot acetic acid. The purity as determined by a perchloric acid titration[5] was 100.1%.

Anal. Calcd. for $C_{12}H_{14}N_2O_2$: N, 12.84. Found: N, 12.80.

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[2] Snyder and Smith, This Journal, **66**, 350 (1944); Albertson, Archer and Suter, *ibid.*, **66**, 500 (1944); **67**, 36 (1945); Howe, Zambito, Snyder and Tishler, *ibid.*, **67**, 38 (1945); Albertson and Tullar, *ibid.*, **67**, 502 (1945).

[3] Tullar, U. S. Patent 2,393,723 (1946).

[4] "Organic Syntheses," Coll. Vol. I, 442 (1941).

[5] Toennies and Callan, *J. Biol. Chem.*, **125**, 259 (1938).

CONTRIBUTION FROM THE
STERLING-WINTHROP RESEARCH INSTITUTE
RENSSELAER, N. Y.
RECEIVED JULY 22, 1946

Polymerization of *d*-*s*-Butyl *p*-Vinylbenzoate[1]

BY C. S. MARVEL AND C. G. OVERBERGER

d-*s*-Butyl *p*-vinylbenzoate has been prepared and polymerized in bulk. The change in rotation as the monomer is polymerized is too small to make this monomer of use in kinetic studies of polymerization. It is of some interest to note that saponification of the optically active polyester gives an inactive polyacid, hence no asymmetric synthesis occurred during polymerization.

Experimental

_d_-_s_-Butyl _p_-Vinylbenzoate.—In a 300-cc. Erlenmeyer flask were placed 100 g. (1.35 moles) of *d*-*s*-butyl alcohol and 38 g. (0.28 moles) of *p*-vinylbenzoic acid.[2] To this was added 10 g. of dry hydrogen chloride at room temperature and the slurry was allowed to shake for four hours and then to stand overnight. About 600 cc. of dry benzene, containing 0.01 g. of picric acid and 1.0 g. of *p*-*t*-butylcatechol was added and the solution was transferred to a 1-liter, round-bottomed flask equipped with a distilling column with a variable take-off. The water and benzene were removed slowly at a reflux ratio of 15 to 1. After four hours the theoretical amount of water had been collected and the remainder of the benzene was then distilled. The residue was dissolved in 300 cc. of ether, the ether solution was washed twice with 100-cc. portions of water, twice with 100-cc. portions of 10% sodium bicarbonate solution and three times with 100-cc. portions of water. On acidification of the sodium bicarbonate solution with dilute hydrochloric acid, 8 g. of impure *p*-vinylbenzoic acid was recovered. The first water extracts were combined and saturated with powdered sodium carbonate. Thirty grams of impure *d*-*s*-butyl alcohol separated from the water layer and was recovered.

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[1] The work described in this note was done under sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program.

[2] Marvel and Overberger, This Journal, **67**, 2250 (1945).