drides are inferior to those derived from the alkyl-chlorocarbonates[2,3] largely because of the difficulty of freeing the derivatives from the other reaction product, *i.e.*, thiophenol.

EXPERIMENTAL[4]

Acetanilide. *S*-Phenylthiocarbonyl chloride, 1.58 g. (0.009 mole), was added over a 15-min. period to a vigorously stirred solution of 0.6 g. (0.01 mole) of glacial acetic acid and 1.01 g. (0.01 mole) of triethylamine in 20 ml. of water and 15 ml. of ethanol. After 2 hr. at room temperature, 0.93 g. (0.01 mole) of redistilled aniline was added drop-wise whereupon a precipitate formed. The precipitate was collected, washed with 2*N* aqueous hydrochloric acid, dried, and recrystallized from aqueous ethanol to give *N*,*S*-diphenylthiocarbamate, m.p. 126.5–127.7°. Lit.[1], m.p. 125.6–127.6°.

Repetition of the above experiment in anhydrous dioxane, with the first stage being conducted at 0°, gave, after the addition of the aniline, a yellow solid which was washed with 3*N* aqueous sodium carbonate, 2*N* aqueous hydrochloric acid, water, dried, and recrystallized from 60–70° ligroin to give 0.6 g. (44%) of acetanilide, m.p. 112.9–113.9°.

Hippurylanilide. To a cooled stirred solution of 1.79 g. (0.01 mole) of hippuric acid and 1.01 g. (0.01 mole) of triethylamine in 25 ml. of anhydrous dioxane was added, at 0°, 1.73 g. (0.01 mole) of *S*-phenylthiocarbonyl chloride and an additional 15 ml. of dioxane. After 15 min., 0.93 g. (0.01 mole) of redistilled aniline was added and the stirring continued for 90 min. at room temperature. The reaction mixture was then poured into 100 ml. of ice cold 0.3*N* aqueous hydrochloric acid, the precipitate collected by filtration and washed with 200 ml. of 2*N* aqueous hydrochloric acid and 200 ml. of water. The residue which still had a strong odor of thiophenol was stirred for 15 min. with 100 ml. of 10% aqueous sodium hydroxide, the precipitate collected, washed with aqueous acid and water, and finally recrystallized from aqueous ethanol to give 0.43 g. (17%) of hippurylanilide, m.p. 211.5–212.5°. Lit.,[5] m.p. 208.5°.

CONTRIBUTION NO. 2221 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY,
CALIFORNIA INSTITUTE OF TECHNOLOGY,
PASADENA 4, CALIF.

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α-*N*-Trichloroacetyl-L-tyrosinamide

HOWARD F. MOWER AND CARL NIEMANN

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The low yield reported for the preparation of trichloroacetyl-DL-alanine by reaction of the amino acid with trichloroacetyl chloride in the presence of aqueous sodium hydroxide at 0°,[1] presumably because of the rapid hydrolysis of the acid chloride under the above reaction conditions,[2] and the difficulty of achieving a satisfactory selective hydrolysis of *O*,α-*N*-di-trichloroacetyl-L-tyrosinamide, obtained by reaction of trichloroacetyl chloride and triethylamine with L-tyrosinamide in anhydrous tetrahydrofuran, to α-*N*-trichloroacetyl-L-tyrosinamide led us to attempt the direct α-*N*-acylation of L-tyrosinamide with ethyl trichloroacetate in a nonaqueous medium. The reaction of L-tyrosinamide with 1.2 equivalents of ethyl trichloroacetate in anhydrous ethyl acetate at the refluxing temperature of the reaction mixture gave the desired product in a 65% yield. When the reaction was attempted in anhydrous acetone, a reaction product containing no chlorine was obtained. On the basis of an elementary analysis, it appeared to be a condensation product resulting from the reaction of 1 mole of L-tyrosinamide with 1 mole of acetone with the loss of 1 mole of water.

EXPERIMENTAL[3,4]

α-N-Trichloroacetyl-L-tyrosinamide. L-Tyrosinamide, prepared by ammonolysis of the corresponding ester, was placed in the extraction thimble of a Soxhlet extraction apparatus and transferred, by dissolution in ethyl acetate, in the course of 1 hr. to the boiler of the extraction apparatus which was charged with 1.2 equivalents of ethyl trichloroacetate present as a 20% solution in anhydrous ethyl acetate. The reaction mixture was cooled to give 65% of a crude product, m.p. 158–160°, which was successively recrystallized from chlorobenzene, methanol, aqueous methanol, and a mixture of anhydrous ethanol and benzene to give α-*N*-trichloroacetyl-L-tyrosinamide, m.p. 160–161°, $[\alpha]_D^{25}$ + 30.5° (in 30% ethanol).

Anal. Calcd. for $C_{11}H_{11}O_3N_2Cl_3$ (325.5): C, 41.9; H, 3.4; N, 8.9; Cl, 33.8. Found: C, 41.8; H, 3.4; N, 8.9; Cl, 33.7.

The presence of a phenolic hydroxyl group in the above compound was indicated by a positive test with the Folin-Denis[5] reagent and by a comparison of its infrared spectrum, in solid KBr, with that of an authentic sample of α-*N*-acetyl-L-tyrosinamide and of α-*N*-acetyl-D-phenylalaninamide in the same medium.

When the above reaction was attempted with acetone as the solvent, a crystalline product, m.p. 184–185°, separated from the hot reaction mixture. This material, $[\alpha]_D^{25}$ −18.2° (in 30% ethanol) contained no chlorine and on the basis of an elementary analysis, appeared to be a condensation product resulting from the reaction of 1 mole of L-tyrosinamide with 1 mole of acetone with the loss of 1 mole of water.

Anal. Calcd. for $C_{12}H_{16}O_2N_2$ (220): C, 65.5; H, 7.3; N, 12.7. Found: C, 65.2; H, 7.4; N, 12.3.

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PASADENA, CALIF.

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