

ber of the acids were prepared. The esters were prepared by modification of a method previously described,⁴ and the amides were, in general, made from the corresponding esters by reaction with alcoholic ammonia.

Experimental

Benzoyl-DL-valine Ethyl Ester (I).—A solution of 7.25 g. (0.04 mole) of DL-valine ethyl ester hydrochloride in 19 ml. of water was stirred with 90 ml. of 2 *N* sodium carbonate (0.09 mole) and 200 ml. of chloroform. The mixture was cooled in an ice-bath and a solution of 6.5 g. of benzoyl chloride (0.046 mole, 15% excess) in dry chloroform was added with stirring over a 30-minute period. The ice-bath was removed and the stirring continued for an additional 30 minutes. The chloroform layer was separated and the aqueous layer was extracted twice with chloroform (25 ml.) and twice with ether (25 ml.). All extracts were combined and dried over sodium sulfate. After evaporation of the solvent a yellow sirup was obtained. This was dissolved in 25 ml. of benzene and treated with 275 ml. of hexane. A seed, obtained by pre-treating a small quantity of benzene solution, was introduced and the mixture set aside to crystallize in the cold. Filtration gave 8.2 g. (82%) of I; m.p. 65–68°.

Anal. Calcd. for $C_{14}H_{19}O_3N$: N, 5.62. Found: N, 5.42.

Carbobenzoxy-DL-valine Ethyl Ester (II).—Treatment of 5.5 g. (0.03 mole) of DL-valine ethyl ester hydrochloride with a 15% excess of carbobenzoxy chloride,⁵ as described for the benzoyl derivative, yielded an oil which was soluble in benzene–hexane and crystallized on long standing at –12°. Recrystallization from benzene–hexane gave 2.7 g. (32%) of II; m.p. 32–33°.

Anal. Calcd. for $C_{15}H_{21}O_4N$: N, 5.02. Found: N, 5.04.

Carbobenzoxy-DL-leucine Ethyl Ester (III).—This derivative was prepared by treating 5.9 g. (0.03 mole) of DL-leucine ethyl ester hydrochloride with 5.9 g. (0.034 mole) of carbobenzoxy chloride by the same general procedure. The residue obtained after evaporation of the extraction solvent was crystallized from benzene–hexane. The solid was filtered off in the cold; a second crop was obtained from the filtrate; yield 6.9 g. (78%); m.p. 18.5–19°.

Anal. Calcd. for $C_{16}H_{23}O_4N$: N, 4.78. Found: N, 4.79.

Carboallyloxy-DL-valine Ethyl Ester (IV).—Treatment of 5.4 g. (0.03 mole) of DL-valine ethyl ester hydrochloride with 4.2 g. (0.034 mole) of allylchloroformate,⁶ according to the general acylating procedure, yielded an oil which showed no tendency to crystallize from benzene–hexane at –12°. Removal of the solvents yielded solid after chilling at –12°. This was washed with cold hexane. The total yield was 2.5 g. (36%); m.p. 9–11°.

Anal. Calcd. for $C_{11}H_{19}O_4N$: N, 6.11. Found: N, 5.94.

Carbobenzoxyglycinamide (V).—Carbobenzoxyglycyl chloride was synthesized according to the method of Bergmann and Zervas. Addition of the acid chloride, obtained from 4.2 g. (0.02 mole) of carbobenzoxyglycine, to 50 ml. of anhydrous ether previously saturated with ammonia, gave a white precipitate. Ammonia was passed through the mixture for 15 minutes. After cooling overnight, the solid was filtered off. This material was extracted with 40 ml. of boiling ethyl acetate and the residue remaining after the extraction was extracted continuously for 7 hours with ethyl acetate, in a Butt extractor. The ethyl acetate extracts were combined, heated to boiling and filtered hot. The filtrate was evaporated until, upon cooling, crystallization occurred. An additional crop was obtained by adding hexane to the filtrate. The combined yield was 2.4 g. (58%); m.p. 133–136°.

Anal. Calcd. for $C_{10}H_{12}O_3N_2$: N, 13.4. Found: N, 13.3.

A second preparation of V was obtained by treating 1.8 g. (0.0075 mole) of carbobenzoxyglycine ethyl ester, in 20 ml.

(4) S. W. Fox, *This Journal*, **68**, 194 (1946).

(5) M. Bergmann and L. Zervas, *Ber.*, **65**, 1192 (1932).

(6) A generous sample of this compound was furnished by the Columbia Chemical Division, Pittsburgh Plate Glass Co., Pittsburgh, Pa. It was redistilled and stored at –12°.

of absolute alcohol, with a stream of ammonia for 45 minutes. After 4 days at room temperature, crystals appeared. The alcohol was removed under reduced pressure and the solid residue was recrystallized from 15 ml. of boiling water. Filtration gave 1.1 g. (71%) of V, m.p. 136–137.5°. A mixed m.p., run with the above preparation, gave 135–136.5°.

Carboallyloxyglycinamide (VI).—Carboallyloxyglycine ethyl ester was prepared by treating 5.6 g. (0.04 mole) of glycine ethyl ester hydrochloride with 5.6 g. (0.046 mole) of allylchloroformate in 25 ml. of carbon tetrachloride. The general procedure described for benzoyl-DL-valine ethyl ester was used. An oil (7.3 g.) was obtained.

The oil dissolved in 50 ml. of absolute alcohol, and dry ammonia gas was passed into the solution for 15 minutes. The flask was stoppered and after 6 weeks (this period was unnecessarily long) at room temperature the alcohol was distilled off under reduced pressure. The solid residue was dissolved in a small quantity of ethyl acetate, and on the addition of hexane, the material crystallized. The yield of VI was 5.5 g. (87%) based on the 0.04 mole of glycine ethyl ester hydrochloride used in the preparation of the intermediate acylamino acid ester; m.p. 107–107.5°.

Anal. Calcd. for $C_8H_{10}O_3N_2$: N, 17.7. Found: N, 17.2.

Carboallyloxy-DL-leucinamide (VII).—Attempts to prepare the corresponding ester from 5.9 g. (0.03 mole) of DL-leucine ethyl ester hydrochloride, according to the general acylating procedure, yielded an oil (7.1 g.).

The oil was dissolved in 50 ml. of absolute alcohol and treated with gaseous ammonia as described above. The sirupy residue which remained after evaporation of the alcohol was dissolved in 25 ml. of hot ethyl acetate. One hundred ml. of hexane was added and after 4 hours at –12°, crystallization commenced. After filtering, washing with hexane, and drying, 1.5 g. (23%) of VII, m.p. 83–85°, was obtained.

Anal. Calcd. for $C_{10}H_{18}O_3N_2$: N, 13.1. Found: N, 13.1.

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CHEMICAL LABORATORY

IOWA STATE COLLEGE

AMES, IOWA

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The Preparation of Nitrosyl Fluoride and Nitryl Fluoride¹

BY ALBERT V. FALOON AND WILLIAM B. KENNA

The compounds nitrosyl fluoride and nitryl fluoride have been prepared by Ruff, Menzel and Neumann.² The method consisted of the vapor-phase fluorination of nitric oxide and nitrogen dioxide with the reaction products being trapped in a quartz vessel. Since these fluorides attack quartz, silicon tetrafluoride and nitrogen sesquioxide were obtained as impurities.

This investigation has shown that a vapor-liquid fluorination carried out in a Fluorothene³ reaction vessel proceeds very smoothly and without the formation of the above impurities. The fluorinations were carried out at temperatures just above the melting points of the respective oxides.

Experimental

The apparatus used in this investigation is shown in Fig. 1. The reaction vessel (R) was constructed from a block

(1) This document is based on work performed for the Atomic Energy Commission by Carbide and Carbon Chemicals Division, Union Carbide and Carbon Corporation, at Oak Ridge, Tennessee.

(2) Otto Ruff, W. Menzel and W. Neumann, *Z. anorg. allgem. Chem.*, **208**, 293 (1932).

(3) Chlorotrifluoroethylene plastic polymer produced by Carbide and Carbon Chemicals Division, Union Carbide and Carbon Corporation.