

SHORT COMMUNICATIONS

An Improved Synthesis of O-Benzyl-DL-serine

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(Received September 20, 1956)

In the previous paper*, it was reported that O-benzyl-DL-serine was synthesized from methyl acrylate in 51% yields. The method, however, is not profitable for a large scale preparation. In the present work, ethyl acrylate was used in place of methyl acrylate and the method was improved as follows:

α -Bromo- β -benzyloxy-propionic Acid.—To a solution of 115 g. of ethyl acrylate in 100 cc. of absolute ether was added 57 cc. of dry bromine dropwise at 5°C under stirring, and the mixture was allowed to stand over-night at room temperature (Solution-A).

Twenty six grams of metallic sodium was dissolved in an ether-benzylalcohol mixture (500 cc. of ether-300 cc. of benzylalcohol) under reflux-condenser (Solution-B).

Solution-B was added portionwise into the solution -A under strong stirring at -10°C for one hour, the stirring was continued at the same temperature for thirty minutes after the addition was over.

The precipitated sodium bromide was removed from the ether solution by washing with 200 cc. of water and the extract was acidified with

conc. hydrochloric acid. The oily product separated was extracted with ether and both the ether solutions were combined. After removal of the ether, the mixture was shaken with 180 g. of barium hydroxide in 3 l of water for five hours at room temperature. In order to complete the hydrolysis, the residual oil was treated with 100 g. of barium hydroxide in 1.5 l of water under the same conditions. The water layers were collected and acidified with conc. of hydrochloric acid. Then the separated oily product was extracted with ether. After removal of the ether, 370 g. of crude α -bromo- β -benzyloxy-propionic acid was obtained.

O-Benzyl-DL-serine.—The crude product of the α -brom acid was dissolved in 5 l. of aq. ammonia (34%) containing 500 g. of ammonium carbonate and then allowed to stand for 1 week at room temperature. The reaction mixture was concentrated in vacuo until crystals of the amino acid appeared. A small amount of the crystals were obtained from the mother liquor. The fine crystals of O-benzyl-DL-serine (150 g.) were prepared in 67% yields.

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* K. Okawa and H. Tani, *J. Chem. Soc. Japan.*, 75 1197 (1950).