[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ARMOUR AND COMPANY]

THE SYNTHESIS OF LAURIC ACID AND DODECYLAMINE CONTAINING CARBON FOURTEEN[1]

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Compounds labeled by radioisotopes have been shown to be of great value in investigations of chemical and physical mechanisms (1). The application of such compounds to studies involving the behavior of long-chain aliphatic compounds is clearly indicated. Obviously the first step is the synthesis of the labeled substances. This paper describes the preparation of lauric acid and dodecylamine containing C^{14} in the 1-position.

In the proposed application, an activity of approximately 0.02 millicurie per gram of reagent was considered desirable. C^{14} was obtained in the form of barium carbonate having a radioactive isotope ratio of 3.16% and an activity of 1 millicurie in 124.3 mg. The radioactive carbon was introduced into the aliphatic carbon chain by the reaction of carbon dioxide with undecylmagnesium bromide. The radioactive lauric acid so obtained was converted to the nitrile by passage over aluminum oxide in the presence of ammonia (2). Reduction of the nitrile with sodium yielded radioactive dodecylamine which was isolated as the acetate. Successive additions of inert materials at each step of the synthesis served to reduce losses of the active compounds as well as to achieve the desired activity in the final products. Radioactive assay indicated that no appreciable loss of C^{14} had occurred.

EXPERIMENTAL PART

Radioactive lauric acid. Undecylmagnesium bromide was prepared from 14.1 g. of undecyl bromide (from undecanol-1, f.p. 16.2°) and 1.5 g. of magnesium in 125 cc. of anhydrous ethyl ether. The solution containing the Grignard reagent was cooled to about −40° and into it was passed the carbon dioxide liberated from 0.5 g. of barium carbonate by means of concentrated sulfuric acid. This barium carbonate contained 0.0392 g. of the original radioactive salt with an activity of 0.315 millicurie. A stream of nitrogen (25 cc. min.) carried the active carbon dioxide into the Grignard reagent, which was vigorously stirred. After about forty minutes the stream of nitrogen was increased to 100 cc./min. for ten minutes. Carbonation of the Grignard reagent was completed using inert carbon dioxide gas (50–100 cc./min.), and the temperature was allowed to rise to 25° during the process.

After hydrolysis with dilute hydrochloric acid, the ether solution was washed with water until the washings were neutral. Evaporation of the ether yielded a mixture of lauric acid and hydrocarbon (undecane and docosane) which were separated by extraction of the dilute alcohol solution of potassium laurate with petroleum ether (b.p. 60–70°). Partial evaporation of the potassium laurate solution to remove petroleum ether and alcohol, followed by

[1] These compounds were synthesized for use in connection with a fellowship sponsored by Armour and Company under the direction of Professor A. M. Gaudin of Massachusetts Institute of Technology. The project involves the application of radioactive tracer technique to a study of the mechanism of mineral flotation.

acidification, yielded lauric acid, which was filtered off, washed with water, and crystallized from acetonitrile at −20°. The crystallized acid weighed 6.80 g. (f.p. 43.52°). Evaporation of the filtrate yielded 0.7 g. of residual acid. To this residue was added 3.0 g. of inert lauric acid (f.p. 43.95°) and the mixture crystallized from 30 cc. of acetonitrile at −20°. A second crop weighing 3.30 g. was obtained. Evaporation of this filtrate yielded 0.4 g. of residue which was discarded. The combined lauric acid fractions (10.10 g.) had the freezing point 43.40.°

A portion (6.73 g.) of the lauric acid was used in the preparation of lauronitrile, and the remainder (3.37 g.) was further diluted with 1.63 g. of inert lauric acid and crystallized from 25 cc. of acetonitrile at −20°. This acid (4.7 g.) had the capillary melting point 44.2–44.7° (cor.) and an activity of 0.10 millicurie.

Radioactive lauronitrile. The 6.73-g. portion of radioactive lauric acid was converted to nitrile by passage over aluminum oxide catalyst in a stream of ammonia gas. The ammonia rate was 200 cc./min. and the acid was vaporized by being dropped into a flask at 320–340°. Approximately 10 g. of catalyst was used at a temperature of 390°. The catalyst chamber was 22 x 1.6 cm. and contained a 7.25-mm. (O.D.) thermocouple well. A 3.23-g. portion of inert lauric acid was passed through the apparatus after the active sample. A total time of 130 min. was required, and the apparatus was swept with ammonia for an additional 60 min. after all the acid had been added. The product was collected in petroleum ether, washed with water, and dried over potassium carbonate. After removal of the solvent, a yield of 8.82 g. (97.4%) of crude radioactive lauronitrile was obtained. This nitrile was converted to amine without purification.

Radioactive dodecylamine. To 6 g. of finely divided sodium, vigorously stirred in 75 cc. of boiling toluene, was added the 8.82 g. of radioactive lauronitrile in 19 g. of anhydrous butanol-1. The addition required 10 minutes. An additional 25 cc. of toluene and 10 cc. of butanol were added and the mixture heated and stirred until the sodium had all reacted. Water was cautiously added, the lower layer separated, and the toluene solution dried with potassium carbonate.

After removal of the solvent, the crude amine was dissolved in 100 cc. of 50% ethanol containing 4 cc. of concentrated hydrochloric acid. This solution was extracted four times with petroleum ether (b.p. 60–70°) to remove unreduced nitrile. The solution of amine hydrochloride was boiled to remove most of the ethanol, and then made alkaline. The amine was extracted with petroleum ether and the solution dried with potassium carbonate. Evaporation of the solvent yielded 8.25 g. (91.5%) of radioactive dodecylamine. This amine was dissolved in 50 cc. of benzene, 2.5 cc. of glacial acetic acid added, and the acetate crystallized at 15°. After recrystallization from 50 cc. of benzene at 15°, a yield of 9.5 g. of radioactive dodecylammonium acetate was obtained. This salt had the capillary melting point 68.5–69.0° (cor.) and an activity of 0.24 millicurie.

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SUMMARY

The preparation of lauric acid and dodecylamine containing C^{14} has been reported.

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