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1-NAPHTHALENEACETIC-α-C^{14} ACID

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by

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The synthesis of naphthaleneacetic acid has been most readily accomplished by the treatment of a halomethylnaphthalene with potassium or sodium cyanide and hydrolysis of the resulting nitrile.[1,2,3,4,5]

(1) F. Mayer and T. Oppenheimer, Ber., 49, 2137 (1916).

(2) A. Cambron, Can. J. Res., 17B, 10 (1939).

(3) R.H.F. Manske and A.E. Ledingham, Can. J. Res., 17B, 14 (1939).

(4) A. Shmuk and A. Guseva, J. Appl. Chem. (USSR), 14, 1031 (1941); Chem. Abs., 39, 4069 (1945).

(5) A.T. Javeri, G.D. Jadhow and C.R. Shah, J. Univ, Bombay, 17A, 81 (1949); Chem. Abs., 43, 9057a (1949).

The Arndt-Eistert reaction with 1-naphthoyl chloride has also been used[5,6] and recently the direct ferric salt catalyzed condensation between

(6) A.L. Wilds and A.L. Meader, J. Org. Chem., 13, 763 (1948).

naphthalene and chloroacetic acid has been reported.[7]

(7) Y. Ogata and J. Ishiguro, J. Am. Chem. Soc., 72, 4302 (1950).

For purposes of preparing this acid labeled in the methylene group with isotopic carbon, the synthesis initially noted was used. In order to conserve materials, several of the intermediates were not purified and were used directly as obtained.

The general scheme involved carbonation of 1-naphthylmagnesium bromide with radioactive carbon dioxide[8] and reduction to the carbinol with

(8) W.G. Dauben, J.C. Reid and P.E. Yankwich, Anal. Chem., 19, 828 (1947).

lithium aluminum hydride.[9] The carbinol was not isolated but treated directly

(9) R.F. Nystrom and W.G. Brown, J. Am. Chem. Soc., 69, 1197, 2548 (1947).

with gaseous hydrogen bromide to give 1-bromomethyl-C^{14}-naphthalene.[10]. The

(10) H. de Pommereau, Compt. rend., 175, 106 (1922).

halide was treated with potassium cyanide and the nitrile thus obtained hydrolyzed to give 1-naphthaleneacetic-α-C^{14} acid. The yield of purified acid was 35% from carbon dioxide. This yield is in fair agreement with those obtained in several large-scale syntheses.[1,2,4] The specific activity of the purified acid was 4.2 μc/mg.

Experimental

1-Naphthoic-carboxyl-C^{14} Acid: - Carbonation of 1-naphthylmagnesium bromide (aliquot in ether, calculated for 0.007 mole) with the carbon dioxide generated from 0.70 g. (0.0035 mole) of barium carbonate (specific activity 4 μc/mg.) was carried out according to known methods.[8] The acid was isolated in 93% yield (0.563 g.), m.p. 159-160°; specific activity, 4.2 μc/mg.

1-Bromomethyl-C^{14}-naphthalene: - Reduction of the labeled 1-naphthoic acid (0.400 g., 0.0023 mole) was carried out with excess lithium aluminum hydride in ether. The reduction product was washed free of acidic material and the ether solution dried over anhydrous sodium sulfate. When a stream of dry hydrogen bromide[10] was passed into the dry ether solution, two phases appeared. After 30 minutes, the lower, aqueous, layer was separated, thoroughly extracted with ether and the washings added to the upper, ether, layer. The combined ether solutions were dried over anhydrous potassium carbonate. Distillation of the ether left a heavy oil, which was not further characterized.

1-Naphthaleneacetic-α-C^{14} Acid: - The oily bromide was dissolved in 10 ml. of alcohol, then a solution of 0.425 g. (0.006 mole) of potassium cyanide in 5 ml. of water and a crystal of potassium iodide were added. The solution was heated under reflux for 18 hours. The nitrile was extracted with ether, the ether distilled and the residue hydrolyzed by refluxing for 24 hours with 10 ml. of a 10% aqueous solution of potassium hydroxide. Acidification and extraction yielded 1-naphthaleneacetic-α-C^{14} acid. The acid (0.151 g., 35% theory) was obtained as light, white needles from hot water, m.p. 130-131°. Specific activity of the acid was 4.2 μc/mg.

Summary for UCRL Report

The synthesis of 1-naphthaleneacetic-α-C^{14} acid has been carried out using the following reaction scheme:

1-bromonaphthalene $\longrightarrow$ 1-naphthoic-carboxyl-C^{14} acid $\longrightarrow$

1 naphthylcarbinol-C^{14} $\longrightarrow$ 1-bromomethyl-C^{14}-naphthalene $\longrightarrow$

2-(1-naphthyl)-acetonitrile-2-C^{14} $\longrightarrow$ 1-naphthaleneacetic-α-C^{14} acid

Besides the final product, only the 1-naphthoic acid was isolated and characterized.