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A Note on the Synthesis of 1-Naphthyl-^{14}C-Isocyanate and Ethyl β-[3-(1′-naphthyl)-ureido-2-^{14}C] Butyrate

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The most convenient way of obtaining the title ureidoester[1] (II) semed to be the action of 1-naphthyl- ^{14}C-isocyanate (I) on ethyl β-aminobutyrate. A search of the literature revealed that the preparation of 1- or 2-naphthyl- ^{14}C-isocyanate was not described. As 1-naphthoic- ^{14}C-acid was synthesized[2] in a good yield by one step reaction from Ba $^{14}CO_3$ and 1-bromonaphthalene, we investigated the optimal conditions under which I could be obtained from this acid. In inactive runs 1-naphthoyl chloride was treated with sodium azide by the wet and the dry method[3] respectively. Working under anhydrous conditions in absolute toluene was found more suitable because besides higher yields the Curtius rearrangement could be performed without isolating the intermediate azide.

EXPERIMENTAL

1-Naphthyl- ^{14}C-*isocyanate* (I)

1-Naphthoic- ^{14}C-acid[2] (1.013 g., 5.9 mmoles, spec. act. 0.759 μC/mmole) was converted to the chloride[2] and dissolved in absolute toluene (17 ml.) after the excess of thionyl chloride had been carefully removed. Sodium azide (458 mg., 7.06 mmoles) was added and the mixture refluxed and stirred vigorously under anhydrous conditions for 5 hours, whereupon the evolution of nitrogen completely ceased. Sodium chloride and unreacted sodium azide were filtered off, washed with dry toluene and the combined filtrates evaporated *in vacuo* leaving I as a lightly brown oil.

In trial experiments yields on *N,N'*-dinaphthylurea obtained from I and 1-naphthylamine ranged from 80—85% calculated on 1-naphthoic acid.

Ethyl β-[3-(1'-naphthyl)-ureido-2- ^{14}*C] butyrate* (II)

To I dissolved in absolute ether (8 ml.), ethyl β-aminobutyrate[4] (805 mg., 6.14 mmoles) in absolute ether (4 ml.) was gradually added under stirring at 0°. After standing in the ice-box, II was centrifuged off, washed with petroleum ether and dried. Recrystallization from a mixture of chloroform and petroleum ether gave 1.105 g. (62% calc'd. on 1-naphthoic- ^{14}C-acid) of white crystals with spec. act. 0.711 μC/mmole, which remained constant after one further recrystallization. M. p. 134—136°, reported[1]: 134—136°.

Anal. $C_{17}H_{20}N_2O_3$ (300.35) calc'd.: N 9.33%
found: N 9.56%

The radioactivity determinations were made on samples of »infinite thickness« and compared with the ^{14}C Amersham standard of the same size.

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IZVOD

Sinteza 1-naftil- ^{14}C-izocijanata i etil β-[3-(1'-naftil)-ureido-2- ^{14}C] butirata

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Iz 1-naftojeve- ^{14}C-kiseline[2] priređen je suhom metodom preko neizoliranog azida 1-naftil-^{14}C-izocijanat (I) u dobrom iskorištenju. I s etil β-aminobutiratom dao je odgovarajući markirani ureidoester (II).

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