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# IMPROVEMENT IN THE METHOD OF SYNTHESIZING [5-$^{14}$C]-SYDNOCARB

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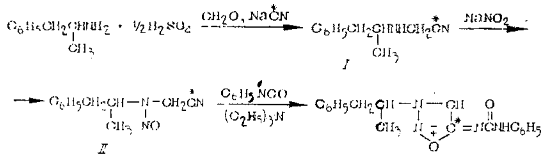
UDC 615.214.31.012.1.07

For the synthesis of sydnocarb, N$^6$-phenylcarbamoyl-3-(1-phenylprop-2-yl)sydnonimine, labeled with $^{14}$C in position 5 of the sydnonimine ring [1] we formerly used a scheme in which the sydnonimine ring was obtained by the action of hydrochloric acid on N-nitroso-N-phenylisopropylaminoacetonitrile (I) [2]. It has been found recently [3] that the formation of the sydnonimine ring may also occur under base catalyzed conditions. Thanks to the simplicity of carrying out this reaction, its good reproducibility, and high yield the new method is more convenient for the synthesis of labeled sydnocarb. Sydnocarb has been obtained by us in preliminary experiments by this method in 60-65% yield calculated on sodium cyanide



## EXPERIMENTAL

[Cyano-$^{14}$C]-β-Phenylisopropylaminoacetonitrile (I). Phenylisopropylamine (0.8 g : 4.34 mmole) was placed in a three-necked 20 ml flask fitted with stirrer, thermometer, and dropping funnel, water (4 ml) and $^{14}$C labeled sodium cyanide (0.233 g: 4.56 mmole) of total activity 40 mCi were added, the funnel washed with water (1 ml), the mixture cooled to 3-5°C, and a 30% solution of formaldehyde (0.45 ml) was added dropwise with stirring. The mixture was maintained for 1 h at 5°C, 1 h at 10-15°C, toluene (0.5 ml) was added, and the mixture stirred at this temperature for 1 h further. The end of the reaction was determined in preliminary work by the absence of a spot for amphetamine on chromatography of a test sample on Silufol plates in the system hexane–ethyl acetate (1 : 1). The product was extracted with toluene (3 × 5 ml), and the extract washed with water (3 × 1.5 ml) to neutral reaction. Toluene was distilled off in the vacuum of a water-jet pump at a bath temperature of 25-30°C to a residue (2-3 ml) in the flask.

[Cyano-$^{14}$C]-N-nitroso-N-phenylisopropylaminoacetonitrile (II). The toluene solution of compound (I) and 2 N hydrochloric acid (to pH 1.0) were placed in a three-necked 20 ml flask fitted with stirrer, thermometer, and dropping funnel, a solution of sodium nitrite (0.311 g) in water (1 ml) was added dropwise with vigorous stirring at 3-5°C, stirred for 1 h at this temperature, and for 1 h at 10-15°C. During the process the reaction medium was periodically checked (pH must be 1.0) for the presence of $NO_2^-$ ions, When required a solution of sodium nitrite and hydrochloric acid was added. The mixture was extracted with toluene (3 × 5 ml), the extract washed with water to neutral reaction, and the solution dried with sodium sulfate for 24 h. Toluene was distilled off in vacuum at a bath temperature of 30-40°C to a residue (2-3 ml) in the flask.

[5-$^{14}$C]-Sydnocarb. N$^6$-Phenylcarbamoyl-3-(1-phenylprop-2-yl)-[5-$^{14}$C]-sydnonimine. The toluene solution of compound (II) was placed in a two-necked 20 ml flask fitted with a mercury sealed stirrer, dry toluene (2 ml) was added, then triethylamine (0.421 g: 4.16 mmole) and phenyl isocyanate (0.495 g: 4.16 mmole) were added with stirring, and the mixture maintained at 50°C for 3 h. The reaction mixture was cooled to 0°C and maintained at this temperature for several hours. Solid was filtered off, washed on the filter with dry toluene (3 × 3 ml) until the solid was decolorized, then with dry hexane, and with ether. [$^{14}$C]-Sydnocarb (0.635 g: 45.2% calculated on phenylisopropylamine) was obtained as a white powder with a yellowish tinge and mp 132-134°C. On chromatography on Silufol UV-254 plates in the system chloroform–acetone (6 : 1) the product disclosed one spot, identical to a spot of an authentic sample, in which 98% total radioactivity was concentrated.

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When contamination by diphenylurea was detected, which was formed by the presence of traces of moisture in the reaction mixture, the product was recrystallized from absolute isopropyl alcohol.

The specific activity of $^{14}$C-sydnocarb was 28 mCi/g. Total activity was 17.78 mCi. The radiochemical yield was 36.3% calculated on $^{14}$C sodium cyanide.

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# INVESTIGATION OF THE KINETICS OF THE SYNTHESIS OF METHYLHEPTENONE UNDER CONDITIONS OF HOMOGENEOUS ACID CATALYSIS

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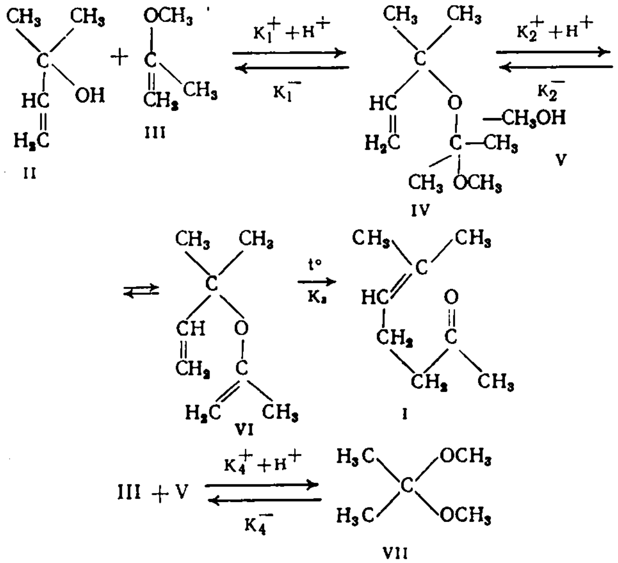
Methylheptenone (I) is an intermediate in the synthesis of pseudo- and beta-ionones used in the manufacture of vitamins A and E. A method for obtaining (I) is known from dimethylvinylcarbinol (II) and methylisopropenyl ether (III) under conditions of homogeneous acid catalysis [1]. According to the data of [1] and in agreement with our results by methods described previously [2] the synthesis proceeds in the presence of orthophosphoric acid according to the following scheme:



(1)

In the absence of kinetic studies on this reaction we have investigated these.

According to the accepted experimental procedure a prepared mixture (about 2 ml) of compounds (II), (III), and orthophosphoric acid in definite proportions is placed at a temperature of −5 to 0°C in glass ampuls. The sealed ampuls of about 10 ml capacity each were transferred to a thermostat at the reaction temperature. One ampul was taken out after definite time intervals, cooled to −5 to 0°C and the contents analyzed. Analysis of the

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