

## NOTE

### FACILE [ $^{14}\text{C}$ ]METHANE PREPARATION USING THE REDUCTION OF [ $^{14}\text{C}$ ]METHYL IODIDE BY SODIUM BOROHYDRIDE.

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#### SUMMARY

[ $^{14}\text{C}$ ]Methane (440 mCi) was prepared using the reduction of [ $^{14}\text{C}$ ]methyl iodide by sodium borohydride in diglyme in quantitative yield. The diborane formed was trapped as nonvolatile 9-BBN. [ $^{14}\text{C}$ ]Methane free of any accompanying gases was conveniently distributed into calibrated glass ampules by the aid of capillary vacuum manifold and freezing out by liquid nitrogen.

Key words: [ $^{14}\text{C}$ ]methyl iodide, [ $^{14}\text{C}$ ]methane, reduction of primary iodides, [ $^{14}\text{C}$ ]alkanes.

#### INTRODUCTION

[ $^{14}\text{C}$ ]Methane with molar activity greater than 1850 MBq.mmol $^{-1}$  (50 mCi.mmol $^{-1}$ ) in total amount around 7 GBq (200 mCi) was required by the Coal Mining R&D Institute in Most (Czechoslovakia) for modeling gas transport processes in coal mines.

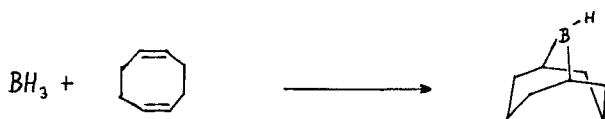
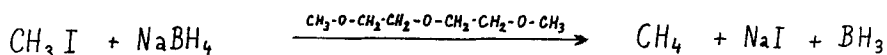
Several approaches to [ $^{14}\text{C}$ ]methane synthesis are described in literature. The first one requires preparation of aluminum [ $^{14}\text{C}$ ]carbide, which upon hydrolysis gives [ $^{14}\text{C}$ ]CH $_4$  (1)(2). The second one inheres on beryllium nitride target bombardment by neutrons which yields beryllium [ $^{14}\text{C}$ ]carbide and this again gives [ $^{14}\text{C}$ ]CH $_4$  upon hydrolysis (3). Reduction of [ $^{14}\text{C}$ ]CO $_2$  by hydrogen over nickel catalyst at 300–350 °C was also described (4). This methods have in common, that the product – [ $^{14}\text{C}$ ]methane – is

accompanied by large amounts of hydrogen from which it cannot be freed out by liquid nitrogen without big losses (the partial pressure of  $\text{CH}_4$  at liquid nitrogen temperature is 2 kPa).

For nonactive preparation of methane the conversion of methyl iodide by magnesium to methyl magnesium iodide and its decomposition by high boiling alcohol - benzyl alcohol (5) or water (6) was described. The yield was 80-85% in the case of (5), no experimental details were given in (6). Conversion of  $[\text{C}^{14}]$ methyl iodide to  $[\text{C}^{14}]$ methyl lithium and its hydrolysis or reaction with diazomethane to yield  $[\text{C}^{14}]$ methane was also described (7). The yield of the reaction with the diazomethane was 70%, the yield of conversion to methyl lithium and of its subsequent hydrolysis was not reported.

#### RESULTS AND DISCUSSION

In this work we decided to use the readily available  $[\text{C}^{14}]$ methyl iodide as a starting material. Hutchins et al. have described the direct reduction of alkyl halides by sodium borohydride in dimethyl sulfoxide (8). If the diborane, formed during this reaction, is trapped quantitatively as for instance as an adduct with 1,5-cyclooctadiene (resulting in nonvolatile 9-borabicyclononane) the only volatile product of this facile one step reaction should be corresponding alkane. As the preparation of Grignard compounds from higher 1-halo alkanes may pose problems on the millimole scale and as the direct reduction, described by Hutchins et al., proceeds readily also with this compounds (and even with the tosylates), we decided to study this reaction as a



Scheme I.

possible general method for the preparation of the [ $^{14}\text{C}$ ]alkanes.

In the "cold" experiments we always encountered greater volume of evolved gases than calculated from the amount of added methyl iodide. Moreover the gas evolution, after rapid formation of methane, has not ceased but slowly continued. When left overnight, the volume of gases was twice of that calculated. As the dimethyl sulfoxide used was dried by calcium hydride, distilled and kept over molecular sieve and even drying of the reagent solution after dissolution of sodium borohydride by molecular sieve did not cure the situation, we concluded, that the surplus gas is hydrogen generated by the reaction of the 9-borabicyclononane with dimethyl sulfoxide. When the reaction was performed in the diethylene glycol dimethyl ether (diglyme), only the theoretical amount of methane gas was formed.

In the "hot" experiment the [ $^{14}\text{C}$ ]methyl iodide was prepared from 20GBq (540 mCi) of barium [ $^{14}\text{C}$ ]carbonate according to lit.(9) by the simple procedure, which is based on the direct breakdown of the methoxy alanate complex (obtained after [ $^{14}\text{C}$ ]CO<sub>2</sub> reduction by LiAlH<sub>4</sub>) with concentrated hydroiodic acid, in the 82% yield.

[ $^{14}\text{C}$ ]Methyl iodide was transferred from the freezing out vessel to the reaction flask 1 (fig. 1) using vacuum manifold. The reaction flask contained 1 M solution of NaBH<sub>4</sub> in diglyme, 1,5-cyclooctadiene and a magnetic stirrer. After thawing the reaction mixture was stirred overnight and then the resulted [ $^{14}\text{C}$ ]methane was distributed to the individual ampoules 3. The compact distribution manifold

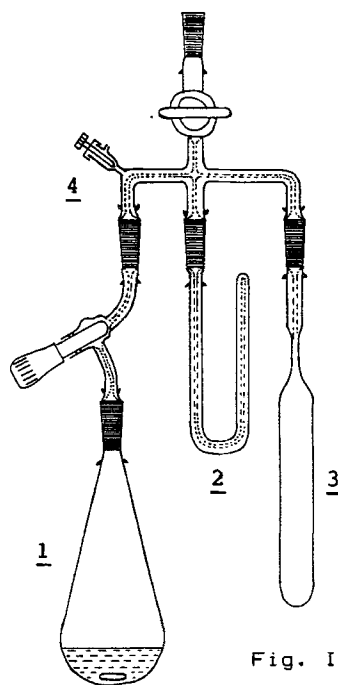


Fig. 1.

(fig. 1, 2 - mercury manometer, 4 - air inlet valve) made from thick-wall glass capillary, had only 13 ml of dead volume and thus the losses of the [ $^{14}\text{C}$ ]methane in the manifold due to the incomplete freezing out of the [ $^{14}\text{C}$ ]methane by the liquid  $\text{N}_2$  were kept under 10%. The total yield of [ $^{14}\text{C}$ ]methane on [ $^{14}\text{C}$ ]methyl iodide was quantitative; its radiochemical purity, checked by radio-gas chromatography, was greater than 99%.

### EXPERIMENTAL

Barium [ $^{14}\text{C}$ ]carbonate (specific activity  $> 50$  mCi/mmol) was purchased from Techsnabexport, USSR. Radio-gas chromatography (RGC) was performed on Packard gas chromatograph model 7409 equipped either by FID or radioactivity detector consisting from combustion tube, water absorber and Berthold proportional counter (volume  $2\text{ cm}^3$ ); methane as a counting gas was added. Signal from the detector was processed on Berthold-Silena 7940 multichannel analyzer coupled with HP-97 S calculator; samples of [ $^{14}\text{C}$ ]methane were analyzed on a  $1\text{ m} \times 3\text{ mm}$  column packed with 10% Apiezon L on Chromosorb W at  $60^\circ\text{C}$ , gas flow of Ar  $35\text{ ml/min}$ . Retention time of [ $^{14}\text{C}$ ]methane ( $1' 20''$ ) corresponded practically to the column dead volume, traces of [ $^{14}\text{C}$ ]methyl iodide could be easily detected by both detectors.

#### [ $^{14}\text{C}$ ]Methane

$16.4\text{ GBq}$  of [ $^{14}\text{C}$ ]methyl iodide prepared according (7) were transferred via vacuum manifold to reaction flask 1 connected with the distribution manifold (fig. 1). The reaction flask contained  $20\text{ ml}$  of  $1\text{ M}$  solution of  $\text{NaBH}_4$  in diglyme,  $5\text{ ml}$  of 1,5-cyclooctadiene and magnetic stirrer. After thawing the reaction mixture was stirred overnight at the room temperature. Part of the [ $^{14}\text{C}$ ]methane was dosed to the ampoule equipped with the the teflon lined silicon septum. Samples for the RGC were withdrawn from the ampoule by gas syringe. RGC gave the evidence of identity of

[<sup>14</sup>C]methane (as compared with the non active standard) and of good radiochemical and chemical purity. No [<sup>14</sup>C]methyl iodide was detected, the impurity detected by both FID and radioactivity detector (0.2%) was identical with that already present in the starting [<sup>14</sup>C]methyl iodide (presumably di[<sup>14</sup>C]methyl ether). [<sup>14</sup>C]Methane was distributed to the 50 ml ampules in 400 MBq portions (pressure in the apparatus 8.25 kPa).

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