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ABSTRACT

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A procedure for converting $C^{14}O_2$ to methanol and methyl iodide by high pressure hydrogenation of the Cd-Ni salt of formic acid is described. A pure product is obtained in good yield and the method was found to be consistently reliable.

(*) The work described in this paper was sponsored by the Atomic Energy Commission.

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The conversion of $BaC^{14}O_3$ or $C^{14}O_2$ to methanol and methyl iodide has been accomplished by numerous procedures since the introduction of radioactive carbon. Many of these procedures are quite capable of giving excellent yield, but oftentimes difficulties are encountered in their use. Thus, direct high pressure hydrogenation of $C^{14}O_2$ (1) requires a special catalyst that may be difficult to prepare. Reduction of $C^{14}O_2$ with lithium aluminum hydride is nearly quantitative on a macro scale (2), but on a semi-micro scale difficulty is encountered because

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(*) The work described in this paper was sponsored by the Atomic Energy Commission.

(1) B. M. Tolbert, J. Am. Chem. Soc. 69, 1529 (1947).

(2) R. F. Nystrom, W. H. Yanko & W. G. Brown, J. Am. Chem. Soc. 70, 411 (1948).

of need for special solvents since splitting of solvent ethers produces contaminants difficult to remove on a small scale, and because the yields have been found to be somewhat erratic. Therefore, alternative methods of preparation of these important intermediates have been explored.

In a recent series of patents (3), the reduction of metal salts of high molecular weight fatty acids are described. The products formed are mixtures of alcohols and esters. This study was extended to the low molecular weight fatty acids, and with several important modifications excellent yields of the alcohols were obtained (4). Since formic acid can be made in good yield by hydrogenating potassium bicarbonate, this offered an excellent method of preparing methanol as follows:

$$\mathrm{BaC^{14}O_3} \longrightarrow \mathrm{C^{14}O_2} \longrightarrow \mathrm{KHC^{14}O_3} \xrightarrow[\mathrm{H_2}]{30\%\ \mathrm{Pd(C)}} \mathrm{HC^{14}O_2K}$$

$$\xrightarrow{\text{Dowex 50}} \mathrm{HC^{14}O_2H} \xrightarrow{\substack{90\%\ \mathrm{Cd(OH)_2} \\ 10\%\ \mathrm{Ni(OH)_2}}} \mathrm{HC^{14}O_2(Cd\text{-}Ni)_{1/2}} \xrightarrow[\text{Copper Chromite}]{\mathrm{H_2},\ \Delta}$$

$$\mathrm{C^{14}H_3OH} \xrightarrow{\mathrm{P_4},\ \mathrm{I_2}} \mathrm{C^{14}H_3I}$$

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(3) A. S. Richardson & J. E. Wyoming, U.S. Patent #2,340,344 and 2,340,687 to 2,340,691 (1944).

(4) P. T. Adams & B. M. Tolbert, unpublished data.

(5) D. B. Melville, J. R. Rachelle & E. B. Keller, J. Biol. Chem. 169, 419 (1947).

In this process no solvents other than water are used at any time and no reagents containing organic carbon (except the ion exchange resins) are introduced to make possible contamination or dilution of the product.

The purity of the product methanol was checked by mass spectrographic analysis and shown to contain no ethyl alcohol or propyl alcohol. The identity of the methyl iodide was confirmed by boiling point and index of refraction measurements. Conversion of the methyl iodide to acetic acid gave a product with the correct equivalent weight, which also indicated the absence of higher molecular weight analogues.

The authors wish to thank Prof. M. Calvin for his interest and help in this work.

Experimental Procedure

Potassium Formate-C^{14}: - Using concentrated sulfuric acid, 20 mmoles (3.94 g.) of $BaC^{14}O_3$ was converted to $C^{14}O_2$ on a vacuum line (6). This carbon dioxide was absorbed in 20 ml. of 1 N carbonate-free potassium hydroxide with stirring over a period of 3-4 hours. At the end of this time the flask was frozen with liquid air to condense the residual carbon dioxide from the line, the stopcock connecting it to the line closed, and the flask warmed to room temperature. After 10-20 minutes of additional stirring, the absorbing flask was opened and the contents washed into a small beaker using 5-10 ml. water.

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(6) M. Calvin, et.al., "Isotopic Carbon," John Wiley & Sons, Inc., New York, New York (1949), p. 142.

The pH of the solution was adjusted with 0.1 N sulfuric acid until it was faintly pink to phenolphthalein. The adjusted solution was transferred to a 300 cc. stainless steel hydrogenation bomb (7) containing 2 g. 30% palladium on charcoal (8). The bomb was then closed and pressured to 1800-2000 psi with electrolytic hydrogen and heated at 70°C with shaking for 20-24 hours.

After the bomb had cooled to room temperature the pressure was released and the contents filtered, with suction, through a #40 Whatman filter paper. The filtrate was then stirred with 10 ml. packed cation exchange resin (9). The volume of the solution here was 200-300 ml.

The resin was filtered off and washed 3-4 times with water. The filtrate was titrated with 1 N sodium or potassium hydroxide to a pH of 9.0-9.5 and evaporated to dryness. Yield on this run of 18.3 mmoles or 91.5%.

The yield by this method varied from 85-90%. The equivalent weight of the product was usually 3-4% high, probably due to impurities in the resin, but these did not interfere with the subsequent chemical steps. If the formic acid is steam distilled a very pure product can be obtained, but the steam distillation of this acid is slow.

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(7) Micro bomb, American Instrument Company, Silver Springs, Maryland.

(8) Commercial product from J.T. Baker & Co., Inc.

(9) Dowex 50 cation exchange resin. Before the resin was used it was washed first with 2 N hydrochloric acid and then repeatedly washed with water to remove all traces of free acid.

Methanol-C^{14}: - The potassium formate (18.3 mmoles, 1.6 g.) was dissolved in 4-5 ml. of water and treated with 10 ml. of wet packed cation exchange resin (9). Meanwhile, 0.30 g. $Ni(NO_3)_2 \cdot 6H_2O$ and 2.08 g. $Cd(Cl)_2 \cdot 2\text{-}1/2\ H_2O$ in solution in a 40 ml. centrifuge tube was treated with sodium hydroxide to precipitate the hydorxides. This precipitate was washed three times with distilled water to remove all traces of Cl^- and NO_3^- ions.

The resin-formic acid mixture was filtered through a coarse sintered glass funnel and the filtrate added to the wet hydroxide slurry. Seven to eight portions of water were then used to wash the rin and this water used to insure complete transfer of the formic acid; about 30 ml. water was used in all. On mixing, most of the hydroxide dissolved; the resulting mixture was evaporated to dryness on a steam bath using an air stream.

The dry mixture was transferred to a 115 ml. stainless steel hydrogenation bomb (7) containing 1.5 g. of copper chromite. The copper chromite was made according to the procedure of Adkins (10) except that the final acid wash was made with dilute (5%) nitric instead of acetic acid to eliminate contamination of the product with ethanol.

The bomb was closed, connected to a vacuum line and pumped 4-8 hours to remove final traces of water. This is especially important if any water has been used to transfer the last of the salts from the centrifuge tube. If the product is not dried well here, yields will be markedly reduced.

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(10) "Organic Syntheses, Vol. II," John Wiley & Sons, Inc., New York, New York, (1943), p. 144.

The bomb was removed from the vacuum line, pressure to 3500 psi with electrolytic hydrogen and heated at 240°C with shaking for 9 hours. After the bomb had cooled, it was transferred to the vacuum line where the hydrogen was passed through a liquid air-cooled spiral trap (11) containing a sintered disk. The bomb was then pumped for 5 hours while warmed at approximately 80°C with an infra-red lamp. The product is a mixture of methanol and water containing 85-90% yield of methanol based on the potassium formate used.

Methyl Iodide-C^{14}: - The methanol-water mixture obtained by hydrogenation was converted to the iodide using 10 g. of iodine, 0.62 g. of red phosphorus and 3 ml. of water as described elsewhere (1). The methyl iodide produced was washed first with 10 ml. of water and then dried over phosphorus pentoxide and weighed. In this preparation the yield was 68% based on the $BaC^{14}O_3$ used to begin the synthesis or 74% based on the formate used. The specific activity of the product was 9.92 μc/mg. in 1.93 g. or 19.15 mc., total. Other preparations gave yields of 85, 78 and 82% based on the formate used.

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(11) B. M. Tolbert, et.al., J. Org. Chem. 14, 527 (1949).