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THE REDUCTION OF C¹⁴ LABELED CARBON DIOXIDE AND FATTY ACIDS
WITH LITHIUM ALUMINUM HYDRIDE

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Berkeley, California

THE REDUCTION OF C¹⁴ LABELED CARBON DIOXIDE AND FATTY ACIDS
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ABSTRACT

Procedures for converting carbon dioxide and the lower fatty acids labeled with C¹⁴ to their corresponding alcohols and halides are described. Pure products are obtained in good yield and the methods were found to be consistently reliable.

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Although the reduction of C^{14} labeled carbon dioxide and fatty acids to the corresponding alcohols has been accomplished by numerous procedures, most of these present certain disadvantages, e.g., difficultly prepared catalysts,¹ special apparatus, low yields, lengthy procedures, or dilution of labeled products.²

Lithium aluminum hydride presents certain advantages over other reducing agents. It reacts rapidly and essentially quantitatively and is relatively free from side reactions. However, splitting of solvent ethers produces contaminants difficult to remove on a small scale.³ This disadvantage has largely been eliminated by the use of tetrahydrofurfuroxytetrahydropyran as a solvent for lithium aluminum hydride as described by Cox.⁴

This paper describes the use of lithium aluminum hydride solutions in this solvent for the reduction of C^{14} labeled carbon dioxide and fatty acids and the conversion of the corresponding alcohols to the halides as done in this laboratory. Most of the procedures are sufficiently different from those of Cox that they require description.

The authors wish to thank Mrs. P. T. Adams for her continued interest and help in this work.

Experimental Procedures

Preparation of the hydride solutions: Tetrahydrofurfuroxytetrahydropyran (TFTP; b.p. $124^{\circ}/14$ mm) was prepared according to the method of Woods and Kramer⁵ from tetrahydrofurfuryl alcohol (TFA; b.p. $82-84^{\circ}/25$ mm) and 2,3-dihydropyran.

Lithium aluminum hydride solutions in TFTP were prepared by stirring the hydride (which had been ground in a mortar) with TFTP for 5-6 hours at $50-60^{\circ}$. The slurry was then filtered through a sintered glass funnel and the clear solution was stored in a flask sealed with a serum bottle stopper. The solutions,

which were 0.7-0.8 M, were analyzed by decomposing an aliquot with butyl carbitol and measuring the volume of the evolved hydrogen. All manipulations were done in a nitrogen atmosphere.

Reduction of carbon dioxide: A pear-shaped, 3-necked flask, fitted with an induction stirrer,⁶ was attached to a vacuum line, evacuated and maintained at reduced pressure until thoroughly dry. The flask was filled with air, charged with hydride solution (1 1/2 moles hydride per mole carbon dioxide) and evacuated cautiously, with stirring. After the foam had broken, evacuation was continued until the pressure became constant. (The hydride solution has a vapor pressure of about 50-100 microns). A bath of water at room temperature was placed around the flask, the system was isolated from the vacuum pump and the stopcock to a storage bulb containing 10-20 millimoles of carbon dioxide was opened. The vigorously stirred solution absorbed most of the carbon dioxide in 10-20 minutes. The residual carbon dioxide was condensed in a liquid nitrogen trap on the vacuum line and the system re-evacuated. The hydride solution was frozen with liquid nitrogen and the carbon dioxide was distilled into the reaction flask. The flask was isolated from the vacuum line and the solution allowed to thaw. The stirrer was started as soon as possible and stirring was continued at room temperature for 1/2 hour.

The flask was transferred to the hood and fitted with a pressure-equalizing dropping funnel and an outlet connected to a spiral trap T₁ (Figure 1). Twelve moles of TFA per mole carbon dioxide were placed in the funnel and dry nitrogen was swept thru the system and out thru a bubbler. The trap was then cooled in liquid nitrogen and the TFA was added dropwise to the vigorously stirred hydride solution. After all the TFA was added, the flask was cooled in an ice-acetone bath. The stirrer was replaced with a stopper and the dropping funnel was replaced with a bubbler tube extending nearly to the bottom of the flask. The end of the bubbler tube was a fritted cylinder. A

heating tape was wrapped around all exposed glass between the flask and the trap and was heated to about 200°. The flask was then placed in an oil bath at 150° and the methanol was swept into the spiral trap with nitrogen at a flow rate of 30-40 ml/min. for 5-6 hours. The product contains TFA and TFTP, but it need not be purified before its conversion to methyl iodide. The yield was not determined at this point.

Methyl Iodide: Methanol from the preceding reduction has been converted to methyl iodide successfully with either of the following procedures:

(a) Hydriodic acid (30-40 ml; d. 1.7) was added to the methanol in trap T₁, and the trap was fitted with a cold finger and connected to trap T₂ (Figure 2). The system was swept with nitrogen thru stopcock S₁ with stopcock S₂ closed. The trap T₂ was then immersed in liquid nitrogen and the reaction vessel (trap T₁) placed in an oil bath at 80°. Nitrogen was then swept at a rate of about 10 ml/min. thru S₂ with S₁ closed. During the next 1/2 hour the temperature was gradually raised to 90°, by which time methyl iodide refluxed from the cold finger. The bath temperature was kept at 90-100° for 2 hours longer. The methyl iodide which had collected in the liquid nitrogen trap T₂ was distilled into a vessel containing 3 ml of 30% potassium carbonate solution. After thawing and thorough shaking, the methyl iodide was distilled from the aqueous solution and dried over phosphorous pentoxide.

(b) A Carius tube, closed at one end with an 8 mm stopcock, was charged with 10 grams of iodine and 640 mg red phosphorous. A mixture of the labeled methanol with 3 ml of water was distilled into the tube. The stopcock was closed and held in place with a couple of strong rubber bands. A water jacket was placed around the upper half of the tube and the tube was heated in a steam bath for 1 hour. The methyl iodide was washed with 10 ml of water and then with 3 ml of 30% potassium carbonate, dried over phosphorous pentoxide on the vacuum line and stored in a weighed storage vessel.

The yield by either method was 80-95% of theory based on barium carbonate.

Conversion of the sodium salts of the lower fatty acids to the free acids:

The sodium salt of the fatty acid (10-20 millimoles) was placed in a porcelain boat in the apparatus shown in figure 3. The tube was wrapped with a heating tape. The system was swept with dry nitrogen and the tape was heated to 150° to drive off residual moisture. The tape was allowed to cool and the trap was cooled in a dry-ice-isopropyl alcohol mixture. Hydrogen chloride gas which had been dried first in concentrated sulfuric acid and then over phosphorous pentoxide was passed thru the system and the tape was heated to approximately the boiling point of the acid. After most of the acid had distilled into the trap, the temperature was gradually raised to 300° over a period of 2 hours.

The system was again swept with nitrogen for 1/2 hour. The trap was removed from the reaction tube and was quickly closed with a ground joint sealed to a stopcock, the trap remaining in the dry-ice bath. The trap was then removed from the dry-ice and the stopcock opened. Hydrogen chloride was given off and when the evolution became too vigorous, the trap was replaced in the dry-ice and the stopcock closed. This process was repeated several times until most of the hydrogen chloride had been given off. The trap was then allowed to warm to room temperature. The residual hydrogen chloride does not interfere with the subsequent reduction. The yield based on total acidity and chloride titrations was better than 95%.

Reduction of Fatty Acids: The apparatus shown in Figure 1 is charged with hydride solution (1 mole of hydride per mole of sodium salt used). The acid from the preceding step is transferred to the dropping funnel with the aid of 10-15 ml of TFTP. Dry nitrogen was then passed thru the system and trap T₁ was immersed in liquid nitrogen. A bath of water at 60-70° was placed around the reaction flask and the acid-TFTP mixture was added dropwise to the rapidly stirred hydride solution. The funnel was rinsed with several 1 ml portions

of TFTP. The mixture was then stirred for 1/2 hour longer. Excess hydride was decomposed and the alcohol swept into the trap as described for methanol above.

The alcohols were converted into the iodides by method (b) above for methyl iodide, except that heating on the steam bath was continued for 1 1/2-2 hours. The yield of isobutyl iodide was 65-75% based on sodium isobutyrate. Normal butyl bromide was made by method (a) above, using 25 ml of 48% hydrobromic acid and heating to 130-135°; the yield was 70-80%.

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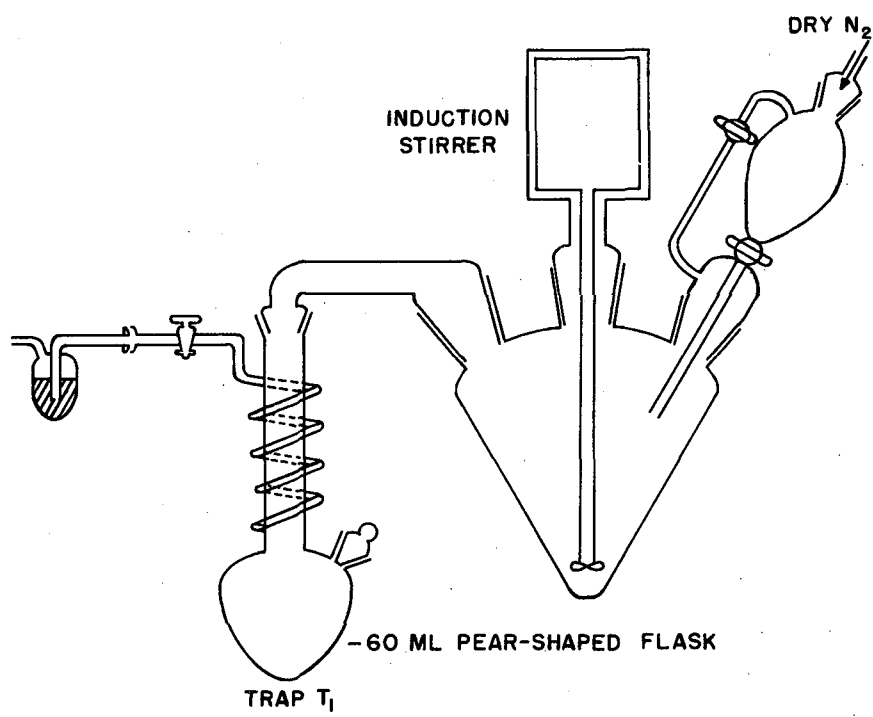


FIG 1

MU 4265

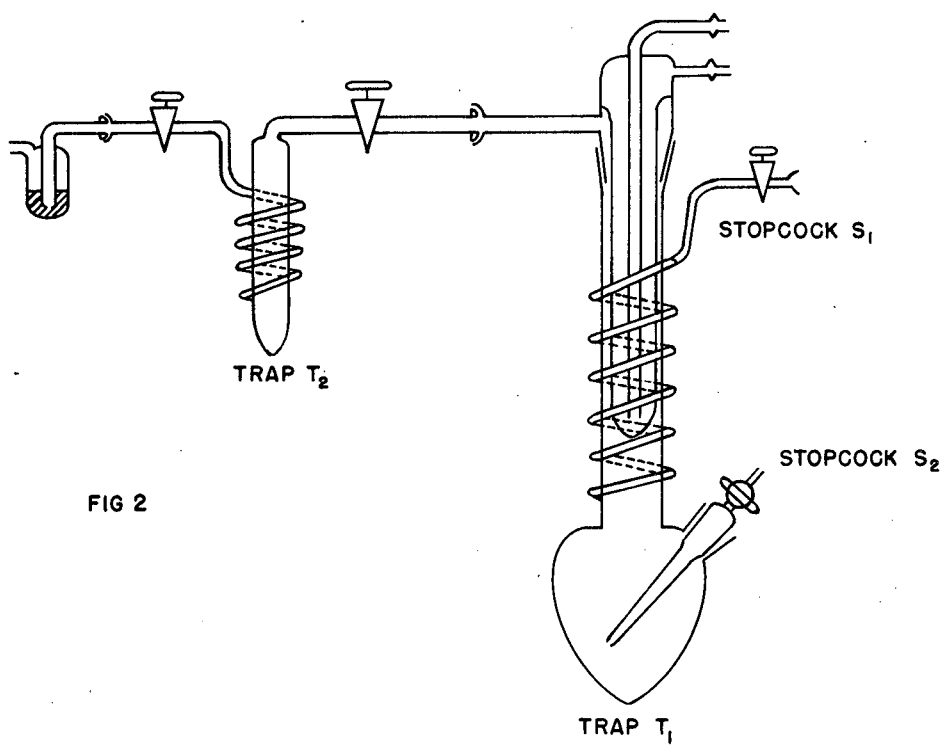


FIG 2

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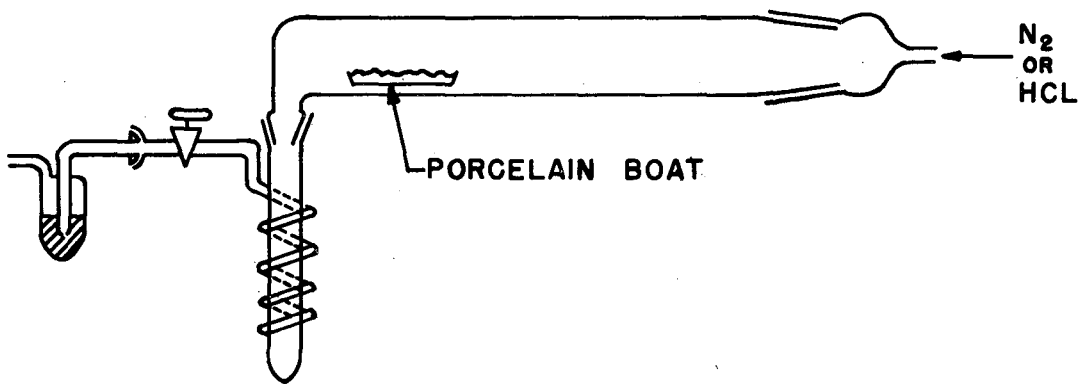


FIG 3

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