yield, including the less pure compound, was approximately 77% calculated on the same basis.

Both samples of IPC were counted as $BaCO_3$, corrected for self absorption. The first sample (m.p. 84–85°) showed an activity of 7.78×10^5 counts/min./mg. The second sample (m.p. 79–80°) showed an activity of 6.69×10^5 counts/min./mg.

Acknowledgment.—Funds for the purchase of the isotopes used were provided by the General Research Council, Oregon State College.

DEPARTMENT OF CHEMISTRY
OREGON STATE COLLEGE
CORVALLIS, OREGON
RECEIVED JANUARY 28, 1952

Synthesis of Carbon-14 Labeled Urea[1,2]

BY ALBERT L. MYERSON[3]

Carbon-14 labeled urea was conveniently synthesized in small quantities through the direct combination of carbon dioxide and ammonia at room temperature, to form ammonium carbamate. The latter compound was sealed in a capillary and heated to 135°, to form urea. The first reaction is quantitative, while the second reaches equilibrium at 40% conversion.

This synthesis constitutes one of the simplest operations by which radioactive carbon dioxide can be incorporated into an organic compound on a micro scale. The preparation of urea from carbon dioxide and ammonia was originally reported[4] using 10 to 20 g. quantities, where maximum conversion was obtained by heating 16 g. of carbamate in a volume of 37 cc. In the present work, two radioactive syntheses were carried out employing 30 and 300 mg. of barium carbonate, respectively, the total activity in each case being 0.35 mc. The m.p. of the white crystals of urea was 131.5° without recrystallization, compared to reported values of 132 to 133°.

[1] For experimental details of this synthesis order Document 3493 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35-mm. motion picture film) or $1.00 for photocopies (6 × 8 inches) readable without optical aid.

[2] Reported at a symposium "Isotopes and Medicine," at the University of Wisconsin, Madison, Wis., in September, 1948.

[3] The Franklin Institute, Philadelphia, Pa.

[4] F. Fichter and B. Becker, *Ber.*, **44**, 3473 (1911).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WISCONSIN
MADISON, WIS.
RECEIVED DECEMBER 22, 1951

A Synthesis of Formaldehyde-C^{14} [1]

BY A. R. JONES AND W. J. SKRABA

Methanol-C^{14} has been converted to formaldehyde-C^{14} by the chlorination of methyl-C^{14} acetate followed by hydrolysis of the chlorinated product. The reactions, first studied by Henry[2] and Michael[3] gave a 60% yield of product when isolated with the aid of inert formaldehyde.[4]

Since the hydrolysis of carefully purified chloromethyl acetate[5] gave a quantitative yield of formaldehyde, efforts to improve the over-all yield of formaldehyde from methanol were confined to the acetylation and chlorination steps. The over-all yield was not improved by conducting the acetylation at atmospheric pressure under reflux, and was considerably decreased when a mole proportion of pyridine was added before acetylation.

The chlorination yield was not affected by ultraviolet irradiation of the reaction mixture, nor by varying the reaction temperature from 20–60°. The over-all yields of formaldehyde were best when a slightly less than molar proportion of chlorine was used.

To avoid the competing chlorination of the methyl group of the acetate moiety, the methyl esters of chlorocarbonic, oxalic, chloroacetic, trichloroacetic, bromoacetic, benzoic and *p*-toluenesulfonic acids were chlorinated. Poor yields were obtained in all cases. A mixture of methyl bromoacetate and bromine was decolorized after two days at room temperature, but hydrolysis of the product yielded only a small amount of formaldehyde.[6]

Experimental

Acetylation.—Methanol-C^{14}, 332 mg., 10.4 mmoles, 21.43 microcuries (2.06 microcuries/mmole) and acetyl chloride, 816 mg., 10.4 mmoles, were consecutively high-vacuum distilled[7] into the liquid nitrogen cooled nipple of a one-liter bulb. The reaction vessel was isolated from the manifold and the frozen reagents were warmed to 40–50° for 45 minutes with a heat lamp. The contents were then frozen into the nipple by immersing the latter in liquid nitrogen. To remove a part of the hydrogen chloride, the nipple was warmed to −80° (Dry Ice and trichloroethylene) and the bulb was evacuated to 10^{-4} mm.

Chlorination.—The Dry Ice–trichloroethylene-bath was replaced by liquid nitrogen and 1400 ml. (27° and 12.9 cm. pressure), 9.6 mmoles, of commercial chlorine gas, from which impurities non-condensable with liquid nitrogen had been removed, was distilled into the reaction bulb. The pressure of chlorine was determined with a manometer in which the mercury was protected by a layer of sulfuric acid. The bulb was isolated from the manifold and the contents were allowed to warm to room temperature in subdued light. Loss of the chlorine color began while the reactants were still quite cold. The contents of the bulb were recondensed and allowed to return to room temperature several times to ensure thorough mixing. When all trace of chlorine color had disappeared, one to two hours, part of the hydrogen chloride was removed as described above.[8]

Hydrolysis.—A 25-ml. hydrolysis bulb containing 3 ml. of distilled water and equipped with a spring-loaded 4-mm. straight-bore stopcock was attached to the manifold, im-

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[1] This document is based upon work performed under Contract Number W-7405 eng. 26 for the Atomic Energy Commission at the Oak Ridge National Laboratory.

[2] L. Henry, *Ber.*, **6**, 739 (1873).

[3] A. Michael, *Am. Chem. J.*, **1**, 418 (1879).

[4] Since the preliminary report of this procedure (Jones and Skraba, *Science*, **110**, 332 (1949)), another synthesis has been proposed by A. Murray and A. R. Ronzio, AECU-991; LADC-778.

[5] M. Descude, *Compt. rend.*, **132**, 1567 (1901).

[6] Radioactive paraformaldehyde was prepared by treating chloromethyl-C^{14} acetate with sufficient commercial formalin solution to furnish the water for hydrolysis. This procedure produced a paste which left a residue of dry polymeric formaldehyde when the volatile material was removed under high vacuum.

In attempts to prepare an isolable solid derivative from which formaldehyde would be easily recoverable, formaldehyde oxime, hexamethylenetetramine and the methylol derivatives of saccharin and phthalimide were investigated. None gave sufficiently high yields of derivative from reaction with aqueous formaldehyde.

Direct oxidation of dilute methanol to formaldehyde with potassium persulfate (P. D. Bartlett and J. D. Cotman, THIS JOURNAL, **71**, 1419 (1949)) was attempted as a preparative method, but was not found feasible because of the difficulty of recovering formaldehyde from the dilute aqueous solution necessary for reaction to take place.

[7] All joints and stopcocks were greased with Dow-Corning silicone vacuum grease.

[8] After a number of runs the reaction bulb contained a trace of white non-volatile material and the over-all yields of formaldehyde decreased. Replacement of the bulb corrected the matter.