3,6-Dimethoxy-9,10-dimethyl-9,10-dihydrophenanthrenediol (I).—3,6-Dimethoxyphenanthraquinone[6] (1.5 g.) was added to the Grignard reagent prepared from 1 g. of magnesium, 5 ml. of methyl iodide and 50 ml. of dry ether. The reaction mixture was refluxed for one hour. Dry benzene (50 ml.) was then added and refluxing was continued for two hours. The reaction mixture afforded 1.2 g. of crude diol with m. p. 115–125°. Two crystallizations from benzene–heptane gave a product with m. p. 125–126°. For analysis it was dried for three hours at 80° *in vacuo.*

Anal. Calcd. for $C_{18}H_{20}O_4$: C, 72.0; H, 6.7. Found: C, 71.4; H, 6.9.

3,6-Dihydroxy-9,10-dimethylphenanthrene.—A mixture of 3,6-dimethoxy-9,10-dimethylphenanthrene (1.5 g.), 15 ml. of acetic acid and 4 ml. of concentrated hydriodic acid was refluxed for one hour. The reaction mixture afforded crude 3,6-dihydroxy-9,10-dimethylphenanthrene which, after crystallization from toluene, melted at 238–239°; yield, 0.35 g.

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.6; H, 5.9. Found: C, 80.5; H, 6.3.

---

[6] Prepared by the excellent procedure outlined by Fieser, THIS JOURNAL, **51**, 2471 (1929).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ALBERTA
EDMONTON, ALBERTA, CANADA

RECEIVED OCTOBER 3, 1949

Preparation of Ethyl Acetate-2-C^{14} and *n*-Butyl Acetate-2-C^{14} Using Alkyl Phosphates[1]

BY GUS A. ROPP

For the conversion of C^{14}-labelled sodium acetate samples to alkyl esters of acetic acid, the use of alkyl phosphates has been found to be somewhat superior to the use of the corresponding alkyl sulfates[2] which boil slightly lower and are much less stable at temperatures near 200°.

Sodium acetate-2-C^{14} was converted to ethyl acetate-2-C^{14} in 93% yield by heating to 170–220° with excess triethyl phosphate. The high purity of the ethyl acetate was indicated by its vapor pressure.

Sodium acetate-2-C^{14} was converted in 82% yield to *n*-butyl acetate-2-C^{14} by heating at 140–220° with tributyl phosphate. That the *n*-butyl ester was of high purity was shown by dilution technique. A sample was diluted one hundredfold with C. P. *n*-butyl acetate, and the diluted ester was converted to pure N-benzylacetamide having essentially the specific activity calculated from the specific activity of the sodium acetate.

Experimental

Ethyl Acetate-2-C^{14}.—Approximately 4 mg. of sodium acetate-2-C^{14} having a specific activity of about 25 μc. per mg. was mixed with 0.4018 g. (4.90 mmoles) of anhydrous sodium acetate. The mixture was dissolved in 5 ml. of distilled water, the solution was evaporated to dryness, and the residue was dried several hours at 100–120° at 0.5 micron pressure. One and one-half milliliters of distilled triethyl phosphate and a small piece of glass wool were added to the dried sodium acetate in a 10-ml. pear-shaped flask, and the mixture was heated one hour under reflux in an oil-bath at 170–220°. The reaction mixture was cooled at room temperature, and the upper end of the reflux condenser was sealed to a vacuum line through (A), a trap cooled to −18°, and (B) a second trap cooled to −190° in liquid nitrogen. The reaction mixture was warmed to 70° at a pressure of 0.1–0.01 micron. A small amount of triethyl phosphate collected in trap (A). In trap (B) 0.400 g. (4.54 mmoles, 93% yield) of ethyl acetate-2-C^{14} was collected. Vapor pressures of the ethyl acetate were obtained at several temperatures: 31 mm. at 0°, 95 mm. at 20°, and 122 mm. at 30° (Dreisbach[3] gives 30 mm. at 0.6°).

***n*-Butyl Acetate-2-C^{14}.**—Sodium acetate, 0.464 g. (5.66 mmoles) having a specific activity of 23.6 μc. per mmole, was mixed with 2.0 ml. of Eastman C. P. *n*-butyl phosphate. The mixture was heated under reflux for one hour in an oil-bath at 140–220°. The viscous mixture was cooled to room temperature, the upper end of the reflux condenser was sealed through a liquid nitrogen cooled trap to a vacuum line, and the product ester was distilled into the cold trap by heating the pot two hours to 80–140° at 0.5 micron pressure while cold water was kept running in the vertical reflux condenser. *n*-Butyl acetate, 0.540 g. (4.66 mmoles, 82% yield) was obtained.

N-Benzylacetamide-2-C^{14}.—A 100 λ sample of *n*-butyl acetate-2-C^{14} was diluted to 10.0 ml. with C. P. *n*-butyl acetate. From the well-mixed diluted ester sample, 2.0 ml. was pipetted into 4 ml. of C. P. benzylamine, and 4 ml. of distilled water was added. The mixture was heated[4] under reflux three and one-half hours at a bath temperature of 100–130°. Then the mixture was distilled at 15 mm. pressure with a bath temperature of 190° until only a brown solid remained in the flask. The solid was twice recrystallized from hot ligroin (b. p. 90–120°) with charcoal treatment. About 0.5 g. of N-benzylacetamide, m. p. 60–61.5°, was obtained. Duplicate samples were burned by the van Slyke wet combustion method[5] and the resulting carbon dioxide samples were counted in an ion chamber.[5] Specific activity values of 0.244 μc. per millimole and 0.236 μc. per millimole were obtained.

---

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

[2] Sakami, Evans and Gurin, THIS JOURNAL, **69**, 1110 (1947); Tolbert, Christensen, Chang and Sah, *J. Org. Chem.*, **14**, 525 (1949).

[3] R. Dreisbach, "Vapor Pressure–Temperature Data for Organic Compounds," second edition, The Dow Chemical Company Midland, Michigan, 1946.

[4] Buehler and Mackenzie, THIS JOURNAL, **59**, 421 (1937).

[5] Neville, *ibid.*, **70**, 3501 (1948).

CHEMISTRY DIVISION
OAK RIDGE NATIONAL LABORATORY
OAK RIDGE, TENNESSEE

RECEIVED NOVEMBER 16, 1949

The Preparation of Acrylyl Chloride

BY GUIDO H. STEMPEL, JR.,[1] ROBERT P. CROSS AND RAYMOND P. MARIELLA

We have had occasion to prepare considerable quantities of acrylyl chloride for use in making various acrylic esters and acrylamides. Attempts to use thionyl chloride with acrylic acid gave negligible yields, a result which is confirmed by observations made at The General Tire and Rubber Company[2] and at Rohm and Haas[3], who also reported poor results with phosphorus oxychloride and with phosphorus pentachloride. The use of phosphorus trichloride suggested by Rehberg[4] did not appear to be entirely suitable for

---

[1] Present address: The General Tire and Rubber Co., Akron, O.

[2] Unpublished work of Harold Barker.

[3] Rohm and Haas Co., Report PB 30751, "Combustible Nitro Polymers," to Division 8, National Research Committee, Office of Scientific Research and Development, pp. 38–39, March 6, 1944.

[4] Rehberg, Dixon and Fisher, THIS JOURNAL, **67**, 209 (1945).