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
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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
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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).

our purposes because the boiling points of phosphorus trichloride and acrylyl chloride are within a degree of one another. We therefore adopted the method using benzoyl chloride for the preparation of aliphatic acid chlorides first reported by Brown.[5] This synthesis gave us good yields of a pure product.

Acknowledgment.—This work was performed as a part of a research project sponsored by The General Tire and Rubber Company of Akron, Ohio.

Experimental

A mixture of 216 g. (3 moles) of acrylic acid, 844 g. (6 moles) of benzoyl chloride, and 0.5 g. of hydroquinone was distilled at a fairly rapid rate through an efficient 25-cm. distilling column. The distillate was collected in a receiver containing half a gram of hydroquinone, immersed in ice. When the temperature at the top of the column, which remained between 60 and 70° for most of the distillation, had reached 85° the distillation was discontinued. The crude product, weighing between 215–225 g., was then redistilled through the same column and the fraction boiling at 72–74° at 740 mm. was collected. The weight of the final product was 185–195 g., or 68–72%.

(5) Brown, THIS JOURNAL, **60**, 1325 (1938).

DEPARTMENT OF CHEMISTRY
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Preparation of 1-Phenyl-6-methylhendecane

BY WILLIAM E. TRUCE AND JOHN T. WISE

A pure sample of 1-phenyl-6-methylhendecane was desired for infrared and ultraviolet absorption studies. It was prepared by treating 1-phenyl-5-pentylmagnesium bromide with 2-heptanone, followed by dehydration and subsequent hydrogenation.

Experimental

1-Phenyl-5-pentanol[1] was prepared by treating 1-phenyl-3-propylmagnesium bromide with a two-fold excess[2] of ethylene oxide; yield 68%, b. p. 136° (5 mm.), $n^{20}D$ 1.5158.

1-Phenyl-5-bromopentane was prepared by treating the corresponding alcohol with anhydrous hydrogen bromide[3]; yield 80.3%, b. p. 144° (12 mm.), $n^{20}D$ 1.5332. *Anal.* Calcd. for $C_{11}H_{15}Br$: Br, 35.1. Found: Br, 35.1.

To the Grignard reagent prepared from 319.5 g. (1.40 m.) of 1-phenyl-5-bromopentane, 34.1 g. (1.40 m.) of magnesium and 600 ml. of ether, 159.6 g. (1.40 m.) of 2-heptanone was added over a period of five hours. After standing for thirty-six hours, the reaction mixture was hydrolyzed with cold, dilute hydrochloric acid. The alcohol was extracted with ether. After removing the ether, the crude product was refluxed for twenty hours with twice its volume of 90% formic acid.[4] The mixture was made alkaline with aqueous sodium hydroxide and the crude olefin(s) was extracted with ether. After removing the ether, the residue was distilled over sodium in an atmosphere of nitrogen; b. p. 158° (5 mm.), $n^{20}D$ 1.4979; 40.1% conversion based on 1-phenyl-5-bromopentane. The product gave positive tests for unsaturation with bromine and potassium permanganate. *Anal.* Calcd. for $C_{18}H_{28}$: C, 88.45; H, 11.55. Found: C, 88.9; H, 11.1.

A portion of the material (24.4 g.) was reduced practically quantitatively in the presence of Raney nickel catalyst in a Parr type hydrogenerator at 90–100° and 51 p. s. i. hydrogen pressure for four hours. The resulting hydrocarbon, 1-phenyl-6-methylhendecane, was filtered and distilled, b. p. 136–137° (1 mm.), $n^{20}D$ 1.4874. It gave negative tests for unsaturation with bromine and potassium permanganate. *Anal.* Calcd. for $C_{18}H_{30}$: C, 87.8; H, 12.2. Found: C, 88.0; H, 12.3.

Retention of the benzene ring was demonstrated by infrared analysis, and the ultraviolet absorption spectrum of the compound agreed well with that expected of a monoalkylbenzene.[5]

Acknowledgment.—Our thanks are due to the Procter and Gamble Company for financial assistance in this work.

(5) We are indebted to the Chemical Division of the Procter and Gamble Company for this information.

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Basic Ketals of Benzophenone

BY PRICE TRUITT AND W. D. COMPTON[1]

The recent success of Benadryl[2] as a potent histamine antagonist suggested the possibility that the structurally related diphenyl-di-(2-dialkylaminoethoxy)-methane might exhibit a similar potency.

Although Fourneau and Chantalou[3] have reported certain similar cyclic acetals, namely, 2-phenyl-4-dialkylaminomethyldioxalane-1,3, their method of synthesis was unsuccessful when applied to preparation of the compounds reported in this paper.

Even though other procedures gave some of the desired ketals, the preferred method of synthesis was by the addition of anhydrous potassium carbonate to a refluxing solution of diphenyldichloromethane and the appropriate 2-dialkylaminoethanol. The diphenyl-di-(2-dialkylaminoethoxy)-methanes prepared in this manner were very viscous liquids which hydrolyzed rapidly when in contact with diluted hydrochloric acid. Benzophenone was obtained from this hydrolysis. It was necessary to prepare the disuccinates or dimethiodides of these basic ketals in order to obtain pure crystalline products.

Neither of the disuccinate salts prepared in this work showed appreciable antihistamine activity.

Experimental[4]

The 2-dimethylaminoethanol, 2-diethylaminoethanol and 2-piperidinoethanol were obtained from Eastman Kodak Company and distilled before use.

(1) v. Braun, *Ber.*, **44**, 2872 (1911).

(2) Huston and Langham, *J. Org. Chem.*, **12**, 90 (1947).

(3) v. Braun, Deutsch and Schmatloch, *Ber.*, **45**, 1258 (1912); "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 246.

(4) Soffer, Strauss, Trail and Sherk, THIS JOURNAL, **69**, 1684 (1947).

(1) Present address: Department of Chemistry, Arlington State College, Arlington, Texas.

(2)(a) Parke, Davis & Co. Trade Mark. (b) Rieveschl and Huber, Paper 41, Division of Medicinal Chemistry, American Chemical Society Meeting, Atlantic City, 1946.

(3) Fourneau and Chantalou, *Bull. soc. chim.*, **12**, 845 (1945).

(4) Melting points were taken with a Fisher-Johns melting point apparatus.