

distillation of the reaction mixtures. From Run 4 its yield was 78%, corresponding to the oxygen uptake. In other experiments yields as high as 85% were encountered. Attempts to obtain crystalline products from the cholesterol oxidation products which had taken up from 0.7–2.0 atoms of oxygen were unsuccessful. The total oxygen uptake of cholesterol was not measured, the rate in Run 5 having diminished only slightly when the reaction was stopped.

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The Synthesis of β -Oxoesters from Acyl Pyruvates

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β -Oxoesters were prepared by several methods for intermediates in the synthesis of thiouracils.² Another method used in this investigation was the decarbonylation of methyl acyl pyruvates. The procedure involved pyrolyzing the pyruvates by heating with powdered soft glass. In the case of the compounds which readily decomposed, a flash distillation procedure was used instead of batch heating.

The mechanism of this decarbonylation is not known but it is presumably similar to that by which ethyl pyruvate is pyrolyzed to ethyl acetate. In this latter case Calvin and Lemmon³ found, by using C¹⁴, that the carbon monoxide was evolved from the carbethoxy group.

Experimental

Pyruvates: The methyl acyl pyruvates were all prepared from methyl ketones by the method of Royals.⁴ His method was slightly modified in that the alcohol was removed before working up the sodium salt. The methyl pyruvates prepared were: pivalo, b. p. 111–112° (11 mm.) (76% yield)⁵; butyl, b. p. 107–108° (5–6 mm.) (55%); propiono, b. p. 86–87° (2–3 mm.) (35%); and myristyl, a new compound, m. p. 52–53° (cor.).

Anal. Calcd. for C₁₈H₃₂O₄: C, 69.19. Found: C, 68.91.

β -Oxoesters: Methyl β -oxo- γ -dimethylvalerate⁶ was prepared by heating a mixture of 18.62 g. (0.1 mole) of methyl pivalopyruvate and 2 g. of ground soft glass at 175°. In five hours approximately 95% of the theoretical volume of carbon monoxide was collected, so heating was discontinued and the residual liquid distilled. An 80% yield of the β -oxoester, b. p. 91–96°, chiefly 91–93°, at 20 mm. was obtained. A run using 950 g. (5.1 moles) of methyl pivalopyruvate yielded 80.1% of β -oxoester.

Methyl β -oxopalmitate was prepared by heating a mixture of 3.2 g. (0.01 mole) of methyl myristylpyruvate and 0.3 g. of ground soft glass at 185°. After twenty minutes heating was discontinued when more than the theoretical amount of gas had been collected. Most of the residue dissolved in alcohol. The alcoholic solution was evaporated and the residue distilled at 155–165° at 1 mm. The distillate solidified in the condenser. After recrystallization from dilute alcohol, the solid melted at 34–35°.

(1) Present address: Cutter Laboratories, Berkeley, Calif.

(2) (a) Anderson, Halverstadt, Miller and Roblin, *THIS JOURNAL*, **67**, 2197 (1945); (b) Miller, Dessert and Anderson, *ibid.*, **70**, 560 (1948).

(3) Calvin and Lemmon, *ibid.*, **69**, 1232 (1947).

(4) Royals, *ibid.*, **67**, 1508 (1945).

(5) A 87.5% yield was obtained from a run using 9 moles of pinacolone.

(6) Baumgarten, Levine and Hauser, *ibid.*, **66**, 864 (1944).

The copper salt was made and recrystallized from petroleum ether, m. p. 78–81°.

Anal. Calcd. for C₃₄H₆₄CuO₆: Cu, 10.1. Found: Cu, 10.3.

In a typical run for the preparation of methyl β -oxocaproate,⁷ 17.2 g. (0.1 mole) of methyl butyropyruvate was flash distilled over 2 g. of ground soft glass. The flask containing the glass was heated in a metal-bath kept at 365°. The pyruvate was forced over the hot glass in 0.5-cc. portions and distilled as rapidly as possible at 240° to prevent side reactions. On fractional distillation of the mixture, 4.46 g. (31% yield) of the β -oxoester, b. p. 85–95° at 14 mm. and 9.09 g. of methyl butyropyruvate, b. p. 110–112° at 7 mm., were collected. The yield corrected for recovered pyruvate was 65%.

Methyl β -oxovalerate⁸ was prepared by flash distillation as was the methyl β -oxocaproate. On fractional distillation, in the most successful run, 4.44 g. (31% yield) of β -oxoester, b. p. 60–65° at 14 mm. and 6.52 g. of pyruvate were obtained. The yield corrected for recovered pyruvate was 50%. The crude copper salt, m. p. 155–157°, checked the melting point of the crude salt given in the literature.⁸

(7) Levine and Hauser, *ibid.*, **66**, 1768 (1944).

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The Removal of Aluminum Chloride from Friedel-Crafts Mixtures Containing Water-Labile Phosphorus Halides

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The most useful of three methods developed by Michaelis for the synthesis of aromatic phosphine halides is the Friedel-Crafts reaction of aromatic hydrocarbons and phosphorus trichloride.^{2,3} This method has one serious drawback, its incomplete and malodorous method of product isolation by extraction. Two new methods of separating the product have been developed. One is an adaptation of Robinson's method⁴ to the recovery of phosphine halides. The other depends upon the precipitation of the complex Al₂Cl₆·2POCl₃.³ Although both of these methods have been successfully used in the preparation of several aromatic phosphine halides, only the application to phenyl-dichlorophosphine is presented in detail.

Experimental

Reagents.—The aluminum chloride, benzene (dried over phosphorus pentoxide) and phosphorus trichloride were J. T. Baker C. P. quality.

Preliminary Procedure.—In all experiments, various molar proportions of aluminum chloride, benzene and phosphorus trichloride were refluxed in three-neck flasks fitted with a rubber-sealed glass stirrer, thermometer, reflux condenser, hydrogen chloride trap, and mantle heater. Reaction times, usually one to four hours, were only long enough for practical cessation of hydrogen chloride evolution. The catalyst was then removed by either of the following methods.

(1) Present address: Central Research Laboratories, Monsanto Chemical Co.

(2) Michaelis, *Ber.*, **12**, 1009 (1879).

(3) Michaelis, *Ann.*, **293**, 198–200 (1896).

(4) Robinson, U. S. Patent 2,211,704; *C. A.*, **35**, 468 (1941).