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

BY ALICE M. DESSERT AND I. F. HALVERSTADT[1]

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 Lemmon[3] found, by using C^{14}, 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 $C_{18}H_{32}O_4$: C, 69.19. Found: C, 68.91.

β-Oxoesters: Methyl β-oxo-γ-dimethylvalerate[6] 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°. The copper salt was made and recrystallized from petroleum ether, m. p. 78–81°.

Anal. Calcd. for $C_{34}H_{64}CuO_6$: 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-oxovalerate[6] 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.[6]

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(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 67.5% yield was obtained from a run using 9 moles of pinacolone.

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

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

CHEMOTHERAPY DIVISION
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RECEIVED APRIL 29, 1948

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

BY WILLIAM T. DYE, JR.[1]

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 method[4] to the recovery of phosphine halides. The other depends upon the precipitation of the complex $Al_2Cl_6 \cdot 2POCl_3$.[3] Although both of these methods have been successfully used in the preparation of several aromatic phosphine halides, only the application to phenyldichlorophosphine 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.

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(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).

With Water.—The reaction mixture was cooled to room temperature and diluted with benzene or low-boiling petroleum ether. An optimum quantity of 3 moles of water per mole of catalyst was stirred in as rapidly as foam control would allow. (Water was added either pure or as concentrated hydrochloric acid.) About 50 cc. more of solvent was then added. During the following brief period in which hydrogen chloride evolution ceased, the supernatant liquid was decanted. The solvent was then removed and the product vacuum-distilled.

Table I shows the effect of stirring different quantities of water, as concentrated hydrochloric acid, into 0.1:0.4:0.4-mole reaction mixtures of aluminum chloride, benzene and phosphorus trichloride.

TABLE I

YIELD OF PHENYLDICHLOROPHOSPHINE AFTER REMOVAL OF CATALYST WITH WATER

Moles water added	Yield $C_6H_5PCl_2$, g.
0.25	10.7
.275	15.3
.30	20.6
.325	20.9
.35	20.2
.40	16.8

The yield of phenyldichlorophosphine rose rapidly as the critical point of 3 moles water per mole aluminum chloride was approached, and as much as a 10% excess of water did no harm. When sufficient water was added, the hydrated catalyst separated as soft slightly coherent granules, free of product and easily filtered or decanted.

With Phosphorus Oxychloride.—One mole of phosphorus oxychloride per mole of aluminum chloride was added to the hot reaction mixture (with a temperature rise of about 5°), excess phosphorus trichloride and benzene were recovered by vacuum-stripping, the residue was cooled to 40° or below, the catalyst complex was completely precipitated by dilution with about three volumes of light petroleum, and the liquid layer was decanted and distilled. (Caution: In a few instances, involving large excess of phosphorus trichloride and benzene, the mixture separated into two layers when the oxychloride had been partly added, with consequent vigorous boiling of the more volatile layer. This can be prevented by stripping the excess of reactants before addition of phosphorus oxychloride.)

The utility of the latter procedure in Friedel–Crafts reactions in general seems limited only by the provision that the phosphorus oxychloride–aluminum chloride complex must be the most stable one possible in any given reaction mixture. The method has the advantage over the foregoing hydration process that there is no evolution of hydrogen chloride and consequently no tendency for the precipitate to float. Both of these methods appear suitable for isolating other Friedel–Crafts products decomposed by the conventional catalyst quenching process.

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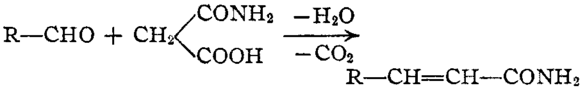
(5) Original manuscript received May 26, 1947.

A Synthesis of α,β-Unsaturated Amides

BY ALEXANDER GALAT

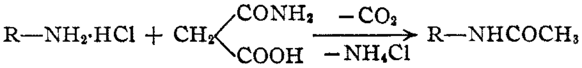
In a previous communication[1] we have reported a synthesis of α,β-unsaturated esters which involved the condensation of an aldehyde with a monoester of malonic acid. It appeared that a similar direct synthesis of α,β-unsaturated amides could be accomplished by condensing an aldehyde with the mono-amide of malonic acid



$$\mathrm{R{-}CHO + CH_2}\left\langle\begin{matrix}\mathrm{CONH_2}\\ \mathrm{COOH}\end{matrix}\right. \xrightarrow[-\mathrm{CO_2}]{-\mathrm{H_2O}} \mathrm{R{-}CH{=}CH{-}CONH_2}$$

It was found that malon-monoamide did, in effect, readily condense with several representative aldehydes (benzaldehyde, *p*-dimethylaminobenzaldehyde, naphthaldehyde and furfural) to give satisfactory yields of the expected unsaturated amides.

The monoamide of malonic acid was prepared by treating diethyl malonate with one mole of potassium hydroxide in methanol, followed by ammonolysis of the monoester thus formed. The amide is a white, crystalline solid which melts at 110–115° with evolution of carbon dioxide and quantitative formation of acetamide. Its solution in water is strongly acid and can be accurately titrated. Heated with salts of primary amines, malon-monoamide reacts as an acetylating agent



$$\mathrm{R{-}NH_2{\cdot}HCl + CH_2}\left\langle\begin{matrix}\mathrm{CONH_2}\\ \mathrm{COOH}\end{matrix}\right. \xrightarrow[-\mathrm{NH_4Cl}]{-\mathrm{CO_2}} \mathrm{R{-}NHCOCH_3}$$

Experimental

Malon-monoamide.—To a solution of 160 g. (1 mole) of diethyl malonate in 450 ml. of methanol was added slowly with stirring 280 ml. (1 mole) of 20% methanolic potassium hydroxide. After the addition was completed the mixture was stirred until the reaction became neutral. The crystalline precipitate was filtered off and the filtrate evaporated to dryness *in vacuo*. The combined solids weighed 132 g. (85%). The product is the potassium salt of mono-methyl malonate (ester interchange takes place when working in methanol).

The potassium salt was dissolved in 500 ml. of concentrated ammonium hydroxide and the solution kept at room temperature for one week. It was then evaporated to dryness *in vacuo*, treated with 76 ml. of concentrated hydrochloric acid and stirred until homogeneous. To the mixture was added 275 ml. of isopropanol, the precipitated potassium chloride filtered off, washed with isopropanol and the filtrate evaporated to dryness *in vacuo*. To the resulting sirup was added 150 ml. of hot isopropanol and an additional amount of potassium chloride removed by filtration. Malonmonoamide crystallized upon cooling and was filtered off, washed with isopropanol and dried at room temperature; yield, 52 g. (61%), m. p. 110–115° (dec.).

Anal. Calcd.: N, 13.59; neut. equiv., 103. Found: N, 13.4.; neut. equiv., 103.5.

Cinnamamide.—One gram of benzaldehyde (*ca.* 0.01 mole), 2 g. (*ca.* 0.02 mole) of malon-monoamide, 2 drops of piperidine and 5 ml. of pyridine were heated on a water-bath until the evolution of gas ceased. To the mixture was added 25 ml. of boiling water, the solution cooled and the precipitated amide recovered by filtration; yield, 0.8 g. (57%), m. p. 146–147° (cor.), lit. 142°.

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[1] Galat, THIS JOURNAL, 68, 376 (1946).

Preparation of Aliphatic Fluorides

BY FRIEDRICH W. HOFFMANN

The exchange of halogen in aliphatic —CHX— and –CH_2X groups (X = Cl, Br) by means of an-