

aldehyde derivatives. Aldol and propionaldol formed aldehyde resins and isobutyraldol apparently underwent a simultaneous dealdolization and Cannizzaro reaction since the glycol was isolated but only isobutyric acid could be found in the acid fraction. In the other examples the normal Cannizzaro reaction occurred.

Obviously it cannot be concluded from this work that a displacement reaction such as the one shown in equation 1 does not occur, but it is quite clear that even in what appears to be the most favorable case (the quaternary amino aldehydes) the displacement shown in equations 3 and 4 does not proceed at a rate comparable to the Cannizzaro reaction.

Summary

A study of the products obtained by carrying out a Cannizzaro reaction on a number of hydroxy and amino aldehyde derivatives revealed that aldol and propionaldol formed aldehyde resins. Isobutyraldol gave the corresponding glycol and isobutyric acid, but in the other cases which were investigated the Cannizzaro reaction proceeded normally. These reactions are of interest since the occurrence of an intramolecular hydride ion displacement similar to one postulated for the Cannizzaro reaction would be expected to result in the formation of unsubstituted acids of the same carbon skeleton.

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RECEIVED MARCH 29, 1948

NOTES

Catalytic Oxidation of Alcohols at Low Temperatures

By ROBERT H. BAKER AND DAVID STANONIS

By making use of the ease of oxidation of anthrahydroquinone by air, it has been possible to modify the usual Oppenauer reaction¹ and to demonstrate a catalytic oxidation of the alcohols. Thus, instead of anthraquinone being used as the oxidant in the reversible reaction,² $\text{RCH(OH)R} + \text{quinone} \rightleftharpoons \text{RCOR} + \text{hydroquinone}$, it is used only in catalytic amounts, and the progress of the reaction is followed manometrically. The conventional catalyst, aluminum *t*-butoxide, must be used in sufficient quantity to react with the water produced in the reaction, but this amount is no larger than that which is generally used.¹ The catalytic oxidation fails with aluminum *t*-butoxide made from certain batches of metal, but this is

Cholesterol was found to take up more than two atoms of oxygen while 4-cholesten-3-one with the same catalyst took up none. This is in agreement with the observations of Bergstrom and Wintersteiner³ on the emulsion oxidation of steroid derivatives, in which those containing the 5,6 double bond are oxidized more extensively than those with 4,5 unsaturation.

Experimental

Apparatus.—The reactions were carried out in flasks shaken by a motor-driven eccentric and connected to a 100-ml. buret by means of a spiral of copper tubing bearing standard taper brass connections. Rubber connections were found to be unsatisfactory because of the rapid uptake of oxygen.

Oxidations.—The conditions of typical runs are shown in Table I. The amount of solvent used was 5 ml. per millimole of alcohol. Unpurified aluminum *t*-butoxide was used and the cupric salt was added only when necessary. The oxygen pressure was maintained at one atmosphere by means of a leveling bulb containing mercury.

TABLE I

Run	Compound	Milli- moles	Al- (O- <i>t</i> -Bu) ₃ , milli- moles	Cupric oleate, mg.	Quinone, millimoles	Solvent	T, °C.	O ₂ , atoms/mole compound	Time, hr.
1	Benzohydrol	50	30	..	5	<i>m</i> -Xylene	60	..	56
2	Same	3	4	50	0.3	Toluene	35	0.3	71
3	Fluorenol	3	4	50	0.3	Benzene	30	0.5	65
4	Same	3	4	..	0.3	Benzene	25	0.78	114
5	Cholesterol	15	20	..	15	Benzene	30	2.0	407
6	Cholestenone	3	4	..	15	Benzene	30	0.04	144

remedied by the addition of anhydrous cupric sulfate, or better cupric oleate, to the reaction mixtures.

(1) Oppenauer, *Rec. trav. chim.*, **56**, 137 (1937); *Org. Syn.*, **31**, 13 (1941).

(2) Baker and Adkins, *This Journal*, **62**, 3805 (1940).

In numerous experiments fluorenol was found to take up oxygen more rapidly than benzohydrol, but duplicate rates on either compound could not be obtained. The yield of benzophenone from Run 1 was 56% (determined polarographically³). Fluorenone was isolated by steam

(3) Bergstrom and Wintersteiner, *J. Biol. Chem.*, **145**, 327 (1942).

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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RECEIVED FEBRUARY 2, 1948

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**, 590 (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).

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 butyropyrivate 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 butyropyrivate, 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.⁶

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

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RECEIVED APRIL 29, 1948

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).