equally good but no better than water for the reduction of uracil. Various strengths of hydrochloric acid when added to the reduction solution produced no effect on the reduction. Of course, in each of the experiments except those carried out in alkaline solution some hydrochloric acid was present resulting from the reduction of the chloroplatinic acid.

Experiments carried out under identical conditions showed that the reduction proceeded more rapidly with colloidal platinum than with colloidal palladium when equal weights of the two materials were used; however, the differences were never large and both are applicable for the reduction of uracil to hydro-uracil.

Summary

1. Uracil is converted quantitatively into hydro-uracil (β-lactylurea) by treatment with hydrogen in the presence of colloidal platinum or palladium.

2. Since hydro-uracil has been shown to undergo hydrolysis smoothly to β-alanine[6] our method of reduction, therefore, offers an easy and practical method of converting uracil directly into β-alanine. From a biochemical point of view this result is one of especial interest and importance.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WASHINGTON]

BETA-PHENOXYPROPIONIC ACID AND SOME OF ITS DERIVATIVES. CHROMANONE

BY S. G. POWELL

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In the course of an investigation of certain unsaturated phenyl ethers, which is to be reported later, a considerable quantity of β-phenoxypropionic acid was required. The only method then available for the preparation of this compound was that of Bischoff[1] which depends upon the action of sodium phenoxide on sodium β-iodopropionate. Unfortunately, the latter is difficult to obtain; moreover, the yield of β-phenoxypropionic acid under the most favorable conditions is only 20%. This paper describes a convenient method for obtaining this acid from the corresponding alcohol.

In preparing some derivatives of the acid, an attempt to purify a sample of β-phenoxypropionyl chloride by distillation resulted in the isolation of the hitherto unknown chromanone. This compound and some of its derivatives are also described.

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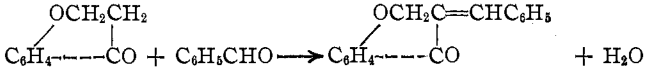
[6] Weidel and Roithner, *Monatsh.*, **17,** 183 (1986). Lengfeld and Stieglitz, *Am. Chem. J.*, **15**, 221, 517 (1893).

[1] Bischoff, *Ber.*, **33,** 928 (1900).

Attempts to oxidize γ-phenoxypropyl alcohol with alkaline permanganate by the method of Fournier[2] were not successful. Oxidation with neutral permanganate, however, gave results which were highly satisfactory, although by no means quantitative. It should be mentioned here that this method is being further investigated, not only as applied to this acid, but also to other β-aryloxy fatty acids. The yield by the method described in this paper varies between 32 and 45% when 10 g. or less of the alcohol is oxidized at one time, but falls off materially when larger quantities are used. Thus 10 g. of the alcohol gave 5 g. of the acid, whereas 40 g. gave only 7 g. As the success of the oxidation depends upon keeping the temperature low, the poorer yield in the larger runs may be due to imperfect cooling of the larger volume of solution. In the smaller runs the yield was not improved by using an excess of permanganate, although about half of the alcohol was recovered unchanged.

As mentioned above, β-phenoxypropionyl chloride decomposes on distillation, yielding chromanone: $C_6H_5OCH_2CH_2COCl \longrightarrow \underbrace{C_6H_4OCH_2CH_2CO}$ + HCl. This compound is more readily obtained, however, by the dehydration of the free acid by means of phosphorus pentoxide. It resembles very closely the 6-methyl-chromanone described by V. Auwers and Krollpfeiffer.[3] Thus, it reacts normally as a ketone with hydroxylamine forming an oxime, and condenses with benzaldehyde to benzalchromanone.



$$C_6H_4\begin{cases}OCH_2CH_2\\ \quad\;\;|\\ \text{-----}CO\end{cases} + C_6H_5CHO \longrightarrow C_6H_4\begin{cases}OCH_2C{=}CHC_6H_5\\ \quad\;\;|\\ \text{-----}CO\end{cases} + H_2O$$

The preparation of other chromanones and their derivatives by this same general method will be described in a later paper.

Experimental Part

γ-Phenoxypropyl Alcohol, $C_6H_5OCH_2CH_2CH_2OH$.—The γ-phenoxypropyl alcohol used in this work was prepared by a modification of the method described by Rindfusz[4] who obtained it in 75% yield by treating an absolute alcoholic solution of sodium phenoxide with trimethylene chlorohydrin. By using an aqueous solution of sodium phenoxide, in which the chlorohydrin is completely soluble, the use of metallic sodium and absolute alcohol is avoided, the reaction is completed in a much shorter time, and slightly better yields are obtained.

To a solution of 250 g. of phenol in 1000 g. of 10% aqueous sodium hydroxide is added 188 g. of trimethylene chlorohydrin, and the clear solution is heated to boiling under a reflux condenser. About 3 minutes after the solution begins to boil it separates into two layers and the reaction is practically complete at this point. To insure com-

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[2] Fournier, *Bull. soc. chim.*, [4] **5**, 920 (1909).

[3] Auwers and Krollpfeiffer, *Ber.*, **47**, 2585 (1914).

[4] Rindfusz, THIS JOURNAL, **41**, 668 (1919).

plete reaction, however, the boiling is continued for 30 minutes. The mixture is cooled, the phenoxypropyl alcohol taken up in ether, the ether solution washed with dil. sodium hydroxide solution, then with water, and finally dried over sodium sulfate. After removing the ether, the oily residue is heated when the phenoxypropyl alcohol distils at 160° (25 mm.); yield, 240 g., or 80%.

β-Phenoxypropionic Acid, $C_6H_5OCH_2CH_2COOH$.—This compound has been prepared by Bischoff[1] who obtained it by treating sodium β-iodopropionate with sodium phenoxide. It is more conveniently prepared by the oxidation of the corresponding alcohol by the following method.

Ten g. of γ-phenoxypropyl alcohol is added to a solution of 30 g. of crystallized magnesium sulfate in 100 cc. of water contained in a narrow bottle immersed in a pan of cold water. The mixture is kept well stirred with a mechanical stirrer, and 280 cc. of 5% potassium permanganate solution is added drop by drop over a period of several hours, while the temperature is maintained at about 15–20°. The stirring is continued until the color of the permanganate disappears. A slight excess of sodium bisulfite is then added and the mixture is acidified with 50% sulfuric acid, when the β-phenoxypropionic acid separates as an oil which partially solidifies as it cools. The oily mass is dissolved in ether and the ether solution extracted with 5% sodium hydroxide solution. The alkaline extract is acidified with dil. sulfuric acid when the phenoxypropionic acid separates in shiny, needle-like crystals. After the mixture has cooled, the acid is filtered off and recrystallized from hot water from which it separates in long needles melting at 98°. The yield varies between 3.5 g. (32%) and 5 g. (45%). The ether solution from which the acid has been extracted contains unoxidized alcohol, which is recovered and treated again.

Ethyl β-Phenoxypropionate, $C_6H_5OCH_2CH_2COOC_2H_5$.—Forty g. of the acid is dissolved in 400 cc. of absolute alcohol previously saturated with dry hydrogen chloride and the solution boiled under a reflux condenser for one hour. Most of the alcohol is then distilled, the residue diluted with water, and the ester taken up in ether. The ether solution is washed with dil. sodium carbonate solution, then with water, and finally dried over sodium sulfate. After removal of the ether, the residue is heated, when the ester distils to the last drop at 170° (40 mm.). The product is a colorless oil with a characteristic, very persistent odor; yield, 42 g., or 90%.

Analysis. Subs., 0.2009: CO_2, 0.5020; H_2O, 0.1432. Calc. for $C_{11}H_{14}O_3$: C, 68.1; H, 7.2. Found: C, 68.1; H, 7.9.

β-Phenoxypropionyl Chloride, $C_6H_5OCH_2CH_2COCl$.—A solution of 20 g. of β-phenoxypropionic acid in 60 g. of thionyl chloride is heated to 100° for 30 minutes, and then distilled. Two main fractions are obtained, one boiling at 159–160° (50 mm.) and the other boiling at 237° (50 mm.). The lower-boiling fraction is chromanone, while the higher-boiling has not been further investigated except to determine that it is halogen-free. When, however, the acid is gently warmed for a few seconds with only a slight excess of thionyl chloride, a liquid of irritating odor is produced which yields the corresponding amide with ammonia.

β-Phenoxypropionamide, $C_6H_5OCH_2CH_2CONH_2$.—The crude reaction mixture from 3 g. of the acid and 3 g. of thionyl chloride is added drop by drop to an excess of concd. aqueous ammonia. After standing overnight, the precipitated amide is filtered off and recrystallized from hot water, from which it separates in shiny needles melting at 119°.

Analysis. Subs., 0.5110: 30.6 cc. of 0.1 *N* H_2SO_4. Calc. for $C_9H_{11}O_2N$: N, 8.48. Found: 8.38.

Chromanone.—To a solution of 25 g. of β-phenoxypropionic acid in 200 cc. of dry benzene, 50 g. of phosphorus pentoxide is added, and the mixture is refluxed for one hour. The benzene solution is decanted and the dark colored mass of phosphorus compounds extracted several times with boiling benzene. The united benzene solutions are washed with a little dil. sodium hydroxide solution, then with water and finally dried with a little calcium chloride. The benzene is removed by distillation from the water-bath and the residue distilled. The chromanone forms a colorless, highly-refracting liquid, with a very pleasant lemon-like odor. It boils at 160° (50 mm.) and on standing solidifies to a mass of hard crystals melting at 38.5°.

Analysis. Subs., 0.2554: CO_2, 0.6810; H_2O, 0.1287. Calc. for $C_9H_8O_2$: C, 73.0; H, 5.4. Found: C, 72.7; H, 5.6.

Chromanone Oxime.—Three g. of chromanone and 3 g. of hydroxylamine hydrochloride are dissolved in 50 cc. of alcohol, 6 g. of potassium carbonate is added and the whole boiled under a reflux condenser on the water-bath for 6 hours. The product is poured into water when the oxime separates and is filtered off. It is purified by dissolving it in hot benzene and precipitating with petroleum ether. It forms glistening, needle-like crystals melting at 140°.

Analysis. Subs., 0.2416: (Kjeldahl) 14.5 cc. of 0.1 N H_2SO_4. Calc. for $C_9H_9O_2N$: N, 8.6. Found: 8.4.

Benzal-chromanone.—Three g. of chromanone and 4 g. of benzaldehyde are dissolved in 50 cc. of alcohol, the solution is heated almost to boiling, and 10 cc. of concd. hydrochloric acid added drop by drop. After standing for several days the benzal-chromanone which has separated is filtered off and recrystallized from alcohol, from which it separates in long yellow needles melting at 112°.

Analysis. Subs., 0.2130: CO_2, 0.6314; H_2O, 0.1034. Calc. for $C_{16}H_{12}O_2$: C, 81.4; H, 5.1. Found: C, 80.9; H, 5.4.

Summary

1. The method of preparation of γ-phenoxypropyl alcohol has been simplified.
2. β-Phenoxypropionic acid has been prepared by oxidation of the corresponding alcohol.
3. Some derivatives of β-phenoxypropionic acid have been prepared.
4. Chromanone and some of its derivatives have been prepared.

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