naphthoyl)-propionic acid. It forms small, silvery-white crystals from toluene–methanol, or methanol alone, and melts at 232–232.5°.

Anal. Calcd. for $C_{14}H_{12}O_4$: C, 68.84; H, 4.95. Found: C, 68.72; H, 5.29.

The methyl ether, prepared from the acid with dimethyl sulfate, melted at 170–170.5° and gave no depression of the melting point when mixed with an authentic sample.[8]

The same acid was obtained in tetrachloroethane solution at 100–105° (5–10%). Above that temperature the yield was lower. Between 80–90° in tetrachloroethane, there was obtained, instead of the 4-acid, an isomeric acid which forms yellowish prisms from chloroform and a little methanol, and melts at 173.4–174°. It gives a blue color with ferric chloride and is perhaps β-(1-hydroxy-2-naphthoyl)-propionic acid.

Anal. Calcd. for $C_{14}H_{12}O_4$: C, 68.84; H, 4.95. Found: C, 68.91; H, 5.18.

DEPARTMENT OF CHEMISTRY
BRYN MAWR COLLEGE
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RECEIVED MARCH 19, 1951

The Reaction of Silver Acetate with 8-Quinolinol[1]

BY B. P. BLOCK,[2a] JOHN C. BAILAR, JR., AND D. W. PEARCE[2b]

In connection with another problem we found it desirable to confirm the report by Nakatsuka that an aqueous solution of silver acetate will react with an alcoholic solution of 8-quinolinol at 60° to yield bis-(8-quinolinolo)-silver(II) and silver.[3] Nakatsuka established the oxidation state of the silver by the interpretation of a bromine titration of the product in which seven equivalents of bromine reacted per atom of silver, rather than the eight equivalents expected for a silver(I) compound containing two 8-quinolinol molecules. The supposed silver(II) compound is green, while the corresponding silver(I) compound, also prepared by Nakatsuka, is yellow.

We were able to duplicate the physical description of the preparations as reported by Nakatsuka, but our analysis of the green solid indicates that it, too, is a silver(I) compound. Each of our preparations required 8 equivalents of bromine per atom of silver in the usual titrimetric determination of 8-quinolinol, and all were diamagnetic, as expected for silver(I) compounds. All other established silver(II) coördination compounds are paramagnetic, presumably because they contain one unpaired electron.[4] Further, we found that the green solid is formed at 60° only if the silver acetate solution is not filtered before addition of the 8-quinolinol. If the traces of silver present in silver acetate are removed prior to the addition, the yellow silver(I) compound is formed at 60° also.

There are objections to expecting a silver(II) compound to be formed in the reaction mixture in question. First, of course, in the preparation of all other silver(II) compounds a powerful oxidizing agent is required to promote silver above the plus one level,[5] and none is present here. Secondly, potassium permanganate oxidizes 8-quinolinol to quinolinic acid,[6] but silver(II) is an even more powerful oxidizing agent than the permanganate ion[7] and would therefore be expected to cause the same oxidation. The conclusion that 8-quinolinol should be oxidized by silver(II) can be drawn also from the report that silver(II) oxidizes quinoline to quinolinic acid.[8] Another objection to the hypothesis of the formation of silver(II) in the manner reported is that the ethyl alcohol present would almost certainly reduce any silver(II) as rapidly as it was formed.

The silver is probably formed by the reduction of some silver acetate by 8-quinolinol, rather than by a disproportionation. There is some precedent for such an explanation in that Freeman and Lions reported the reduction of silver acetate to silver by the action of 1-acridol,[9] a homolog of 8-quinolinol. Hein and Regler have reported the conversion of the yellow silver(I) compound to an olive green silver(I) compound by recrystallization from concentrated ammonia.[10] We were able to repeat this experiment. There are, then, two forms of 8-quinolinol-8-quinolinolo-silver(I), yellow and green; the yellow is the more readily formed, but it may be converted to the green by heating to 60° in water with a trace of silver, or by recrystallization from ammonia.

Experimental

Nakatsuka's Green Compound.[3]—The procedure reported by Nakatsuka[3] was followed. A yellow solid was first precipitated, but almost immediately a dark green metallic-appearing mirror started to form. From 1 g. of 8-quinolinol and 1.2 g. of AgOAc, 1.1 g. of a yellow green solid mixed with a dark solid was obtained. *Anal.* Found: Ag, 27.9, 27.8; Br/mole, 8.04, 8.06. Calcd. for $Ag''(C_9H_6NO)_2$: Ag, 27.2; Br/mole, 7.00. For $Ag'(C_9H_6NO)(C_9H_7NO)$: Ag, 27.2; Br/mole, 8.00. The solid, in a modified Curie–Cheveneau balance, gave a deflection in the diamagnetic direction. Some of the solid was treated with pyridine, the mixture filtered, and the filtrate evaporated to give the compound reported to be $Ag''(C_9H_6NO)_2\cdot py$.[3] *Anal.* Found: Br mole, 7.95. Calcd. for $Ag''(C_9H_6NO)_2\cdot py$: Br/mole, 7.00. For $Ag'(C_9H_6NO)(C_9H_7NO)\cdot py$: Br/mole, 8.00. The substance gave a diamagnetic deflection.

Nakatsuka's Yellow Compound,[3] Hein and Regler's Compounds.[10]—The experimental procedures in the literature were followed. The only difficulty encountered was in dissolving the yellow silver(I) compound in concentrated ammonia[10]; the compound was difficultly rather than readily soluble.

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[1] This investigation was begun under a grant from the Purdue Research Foundation and completed at the University of Illinois.

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[3] Y. Nakatsuka, *Bull. Chem. Soc. Jap.*, **11**, 45 (1936).

[4] P. W. Selwood, "Magnetochemistry," Interscience Publishers, Inc., New York, N. Y., 1943, pp. 102 and 182.

[5] J. C. Bailar, Jr., *J. Chem. Education*, **21**, 523 (1944).

[6] S. Hoogewerff and W. A. van Dorp, *Ber.*, **12**, 747 (1879).

[7] A. A. Noyes and A. Kossiakoff, THIS JOURNAL, **57**, 1238 (1935).

[8] A. Burada, *Ann. sci. univ. Jassy*, **20**, 71 (1935).

[9] D. H. Freeman and F. Lions, *J. Proc. Roy. Soc. N. S. Wales*, **74**, 520 (1941).

[10] F. Hein and H. Regler, *Ber.*, **69B**, 1692 (1936).

NOYES CHEMICAL LABORATORY
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RECEIVED MARCH 15, 1951

A New Synthesis of Croweacin Aldehyde

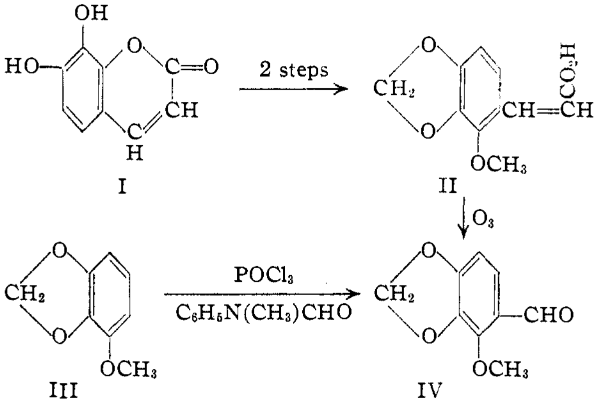
BY WM. B. BROWNELL AND ARTHUR W. WESTON

In a study associated with a previous investigation,[1] a simplified synthesis of croweacin aldehyde, 2-methoxy-3,4-methylenedioxybenzaldehyde (IV),

[1] K. E. Hamlin and A. W. Weston, THIS JOURNAL, **73**, 2210 (1949).

was desired. This aldehyde has been prepared[2] from daphnetin (I) by methylenation, followed by treatment with sodium hydroxide and dimethyl sulfate and ozonization of the resulting cinnamic acid (II).

As an approach to the synthesis of IV, 1-methoxy-2,3-methylenedioxybenzene (III) was treated with phosphorus oxychloride and N-methylformanilide.[3] The aldehyde (IV) was obtained in a 46% yield.



Since III is readily prepared from *o*-vanillin by the method of Baker and co-workers,[4] the present work offers a convenient synthesis of croweacin aldehyde (IV).

Experimental

Croweacin Aldehyde (IV).—To 13.5 g. (0.1 mole) of N-methylformanilide there was added 15.3 g. (0.1 mole) of phosphorus oxychloride. The solution was allowed to stand for 30 minutes and then 6 g. (0.04 mole) of 1-methoxy-2,3-methylenedioxybenzene[4a] (III) was added. The reaction mixture was heated at 100° for two hours, cooled to room temperature and poured into ice-water. The solid product was collected by filtration and crystallized from dilute alcohol. The weight of material melting at 103° (lit.[2] 104°) was 3.3 g. (46%).

The 2,4-dinitrophenylhydrazone was prepared in the conventional manner and crystallized from ethyl acetate; m.p. 254–255° (lit.[2] 254°).

A portion of the aldehyde was oxidized with potassium permanganate to give croweacic acid, 2-methoxy-3,4-methylenedioxybenzoic acid, melting at 155° (lit.[2] 153°).

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[2] A. R. Penfold, G. R. Ramage and J. L. Simonsen, *J. Chem. Soc.*, 756 (1938).

[3] L. N. Ferguson, *Chem. Revs.*, **38**, 231 (1946).

[4] (a) W. Baker, L. V. Montgomery and H. A. Smith, *J. Chem. Soc.*, 1281 (1932); (b) W. Baker and R. I. Savage, *ibid.*, 1607 (1938).

ABBOTT LABORATORIES
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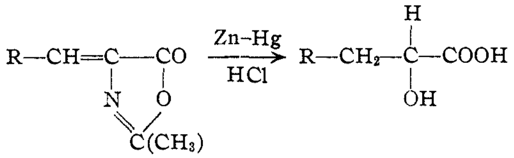
RECEIVED APRIL 16, 1951

A Method of Synthesis of Phenyllactic Acid and Substituted Phenyllactic Acids[1]

BY EDWARD C. BUBL AND JOSEPH S. BUTTS

The need for large quantities of phenyllactic acid for the continuation of metabolic studies was met by the application of a reductive hydrolysis of the azlactone. The azlactones were prepared from the aldehyde and acetylglycine using the well known general procedure.[2] When the azlactones were refluxed with amalgamated zinc and hydrochloric acid, they were converted into aryllactic acids in good yields.



If the aldehydes required for the preparation of the azlactones are available, this reaction has distinct advantages in comparison with procedures described previously.[3,4,5]

Phenyllactic Acid.—This process illustrates the general procedure. A mixture of 50 g. of azlactone (2-methyl-4-benzal-5-oxazalone), 100 g. of amalgamated zinc and 200 ml. of 6 *N* hydrochloric acid was refluxed for eight hours. The cold solution was saturated with sodium chloride and extracted repeatedly with ether. The ether was removed by distillation after drying over anhydrous sodium sulfate. The crude acid recrystallized from carbon tetrachloride had m.p. 95.5–96.5° (uncor.).

Anal. Calcd. for $C_9H_{10}O_3$: C, 65.06; H, 6.02; neut. equiv., 166. Found: C, 64.81; H, 5.93; neut. equiv., 167.

p-Hydroxyphenyllactic acid prepared using a similar procedure had m.p. 139–140° (uncor.).

Anal. Calcd. for $C_9H_{10}O_4$: C, 59.34; H, 5.49; neut. equiv., 182. Found: C, 59.25; H, 5.39; neut. equiv., 178.

A number of benzene-substituted phenyllactic acids have been prepared; physical constants and microbial activity will be reported in a later paper.

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[1] Published as Technical Paper Number 658 with the approval of the Director of Oregon Agricultural Experiment Station.

[2] "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 1.

[3] V. K. La Mer and J. Greenspan, THIS JOURNAL, **56**, 1492 (1934).

[4] F. F. Blicke and H. H. Kaplan, *ibid.*, **65**, 1967 (1943).

[5] E. Erlenmeyer, *Ber.*, **13**, 303 (1880).

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RECEIVED APRIL 23, 1951

Amine-catalyzed Condensations of Benzaldehydes with Phenylacetic Acids[1]

BY ROBERT E. BUCKLES, M. PETER BELLIS AND WILLIAM D. CODER, JR.

In an earlier report[2] the use[3] of triethylamine and tripropylamine as catalysts in the condensations of benzaldehyde and *p*-nitrobenzaldehyde with phenylacetic acid to yield the corresponding α-phenylcinnamic acids was described. At the same time similar condensations with *p*-nitrophenylacetic acid were reported to give little or no product. Since that time improved methods for the isolation of products from these condensations have been developed, so that the yields of the few condensations originally reported have been raised substantially. A much more extensive survey of the condensations of phenylacetic acid and the nitrophenylacetic acids with various benzaldehydes in the presence of trialkylamines has now been carried out. The results of the reactions are summarized in Table I.

The method appears to be of general value for synthesizing α-phenylcinnamic acids. The yields obtained were not always as high as those few reported for the Oglialoro[4] modification of the

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[1] From the Ph.D. thesis of M. Peter Bellis and the M.S. thesis of William D. Coder, Jr.

[2] R. E. Buckles and E. A. Hausman, THIS JOURNAL, **70**, 415 (1948).

[3] M. Bakunin and D. Peceriillo, *Gazz. chim. ital.*, **65**, 1145 (1935).

[4] (a) A. Oglialoro, *ibid.*, **9**, 428, 533 (1879); (b) A. Oglialoro and E. Rosini, *ibid.*, **20**, 396 (1890).