was added over 0.5 min and the reaction was allowed to proceed for 8 min during which time the temperature rose from 10 to 24°. Next, 40 ml of water was added over 2.5 min. The slurry was cooled to 9° over the next 7 min. In order to get as quantitative a recovery as possible, the 9 was not filtered, but the whole reaction mixture was extracted with four 50-ml portions of methylene chloride which was washed with 50 ml of saturated sodium bicarbonate and half-saturated sodium chloride solutions. After removal of the solvent, under reduced pressure, the residue was dried under 0.01 mm at 60° to give 791 mg of solids. Analysis by quantitative tlc[25] showed this material to be composed of 13% 11 and 60% 9 by weight based on 791 mg of material. Based on 1.000 g of 5 this corresponds to a 48% yield of cortisone acetate (9) and a 14% yield of adrenosterone (11).

**Oxidation of 5 in the Absence of Manganese.**—Using exactly the same procedures and amounts as in the experiment reported above but without added manganous nitrate gave 764 mg of product. Quantitative tlc showed that 54% of the weight of this product was adrenosterone and 39% cortisone. These values correspond to a yield of 56% of adrenosterone (11) and 30% of cortisone acetate (9).

(25) Private communication, E. J. Kubiak and A. J. Taraska, Control Research and Development Department, The Upjohn Co.

**Oxidation of 1 in the Presence of Cerous Nitrate.**—A slurry of 10.00 g of 1, 67.5 ml glacial acetic acid, 24.26 g cerous nitrate hexahydrate, and 30.1 ml of water was prepared. To the slurry was added over 4 min an aqueous solution of 12.02 g of chromium trioxide and 6.9 ml of sulfuric acid (20.4 ml of water). An immediate precipitate formed on mixing the oxidant with the slurry. The temperature rose to 30° and was maintained there by cooling during the 8-min reaction. Over the next 10 min, 300 ml of water was added. The slurry was cooled to 10°, filtered, washed white with water (600 ml), and dried to give 4.28 g of pure cortisone acetate (9) as determined by paper chromatography.

**Registry No.**—**1**, 10026-44-5; **2**, 2871-71-8; **5**, 7738-89-8; **6**, 1758-06-1; **3**, 2481-66-5; **4**, 2483-33-2; **7**, 2300-23-4; **8**, 2483-34-3; **9**, 50-04-4; **10**, 125-10-0; **11**, 382-45-6; **12**, 7738-93-4; **13**, 566-38-1; chromic acid, 7738-94-5.

**Acknowledgments.**—We wish to thank Dr. Wm. Struck and associates for the analytical and spectral data, particularly Mr. F. A. MacKellar for the nmr data. Thanks are also due to Mr. E. A. Hughes and Mr. W. G. DeWitt, III, for able technical assistance.

# On the Reactions of Carbonyl Compounds with N-Salicylideneglycinatoaquocopper(II). Syntheses of β-Hydroxy α-Amino Acid from Glycine[1]

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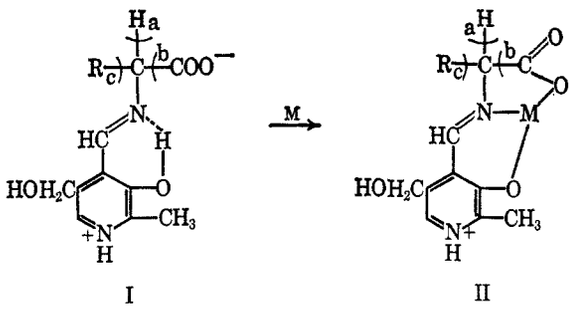
*Received November 2, 1966*

Several forms of N-salicylideneglycinatoaquocopper(II) were synthesized. These complexes were found to be the same in structure except for combining with water. Carbonyl compounds react rather easily with these complexes to form N-salicylidene-β-hydroxy amino acid–copper complex under conditions of aqueous solution, at room temperature (25 ± 1°) and at neutral to weakly alkaline pH. Threonine, β-phenylserine, β-hydroxyaspartic acid, and serine were synthesized. The yields dependent on reaction time and the ratios of *threo* and *erythro* isomers were studied. The reactions are similar to those nonenzymatically catalyzed by pyridoxal and the complexes could be regarded as the benzene analogs of pyridoxalamino acid complexes.

It has been found that many naturally occurring enzymes contain pyridoxal 5-phosphate as a coenzyme.[2] Nonenzymatic reactions catalyzed by pyridoxal or pyridoxamine have been studied extensively by Metzler and Snell.[3] The chemistry of pyridoxal was reviewed by Snell,[3] Westheimer,[4] and Braunstein.[5] Aldimines (I) are formed from pyridoxal with amino acids, and their metal chelating compounds will be illustrated as II in Scheme I.[3c]

In both structures I and II, chemical bonds a, b, and c combined with the α-carbon atom of the amino acid could be weakened by the aldimine formation. In structure I, bond b might be the weakest and decarboxylation might take place. On the other hand, in structure II, the carboxyl group could be stabilized by the formation of a chelate, and bond c could be

SCHEME I




weakened. Metzler, Longenecker, Ikawa, and Snell[6,7] reported the reversible catalytic cleavage of β-hydroxy α-amino acids using pyridoxal and metal ions by heating in aqueous solution. These nonenzymatic reactions catalyzed by pyridoxal seem to be similar in reaction mechanism to those catalyzed by enzymes which contain pyridoxal as a coenzyme. Ikawa and Snell[8] have studied the chemical properties of benzene analogs of pyridoxal with amino acids. They found 4-nitrosalicyaldehyde simulates pyridoxal in its reactions with

(1) Contribution No. 078 of the Institute of Molecular Evolution, University of Miami.

(2) Some of the pyridoxal-containing enzymes are amino acid decarboxylase, transaminase, tryptophanase, kynureninase, tyrosinase, serine deaminase, cysteine desulfhydrase, and hydroxy amino acid aldolase.

(3) (a) E. E. Snell, Special Lectures in Biochemistry," University College, London, H. K. Lewis, Distributors, 1954–1955, pp 1–16; (b) E. E. Snell, *Vitamins Hormones*, **16**, 78 (1960); (c) "Chemical and Biological Aspects of Pyridoxal Catalysis," E. E. Snell, P. M. Fasella, A. Braunstein, and A. Rossi Fanelli, Ed., The Macmillan Co., New York, N. Y., 1963, p 1.

(4) F. H. Westheimer, "The Enzymes," Vol. 1, P. D. Boyer, H. Lardy, and K. Myrback, Ed., Academic Press Inc., New York, N. Y., 1959, p 259.

(5) A. E. Braunstein, "The Enzymes," Vol. 2, Academic Press Inc., New York, N. Y., 1960, p 113.

(6) D. E. Metzler, J. B. Longenecker, and E. E. Snell, *J. Am. Chem. Soc.*, **75**, 2786 (1953); **76**, 639 (1954).

(7) D. E. Metzler, M. Ikawa, and E. E. Snell, *ibid.*, **76**, 648 (1954).

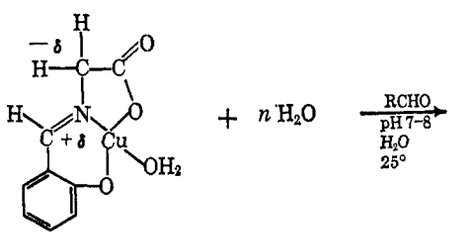
(8) M. Ikawa and E. E. Snell, *ibid.*, **76**, 653 (1954).

several amino acids. 4-Nitrosalicylaldehyde catalyzes the dehydration of serine, the desulfhydration of cysteine, and the splitting of threonine to glycine as pyridoxal. In each of these reactions metal ions were found to be necessary. However, salicylaldehyde was found to be ineffective.

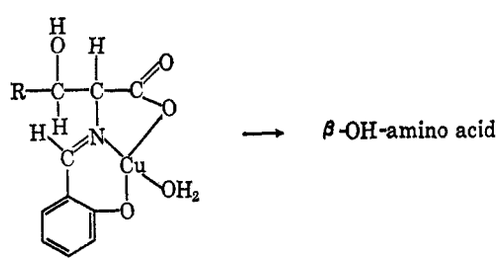
In this investigation, N-salicylideneglycinatoaquocopper(II), which could be recognized as a benzene analog of pyridoxal–aminometal complex (II), illustrated in Scheme I (R = H), was prepared. By the use of the N-salicylideneglycinatocopper(II) complex, the syntheses of various β-hydroxy α-amino acids have been studied.

The complex was first prepared in solution by Eichhorn and Marchand.[9] In their study, the coordination of copper(II) ion to the Schiff base formed from glycine and salicylaldehyde resulted in a stabilization of the Schiff base which would hydrolyze in the absence of a metal. Recently Nakahara[10] synthesized the complex in a crystalline state and he investigated the complex spectroscopically. Nakahara concluded that the complex is the copper(II) chelate of N-salicylideneglycine and the structure is the same as postulated by Eichhorn and Marchand[9] analytically and spectroscopically as illustrated below (structure III, Scheme II).

SCHEME II




III




IV

Nakahara prepared the complex in an acidic aqueous solution and obtained a yellow-green complex (crystal A-1). However, when we prepared the complex under neutral or weakly alkaline conditions (pH 7.5–8.0), different colored complexes were obtained. When the reaction mixture was at pH 8, dark blue crystals (crystal A-2) were obtained. These were recrystallized from water and ethanol and blue-green crystals were obtained (crystal A-3). Crystal A-3 was again recrystallized from the same solvent and dark green crystals were obtained (crystal A-4). Crystal A-4 seems to be a stable form in the recrystallization solvent system and the color, crystalline form, and infrared absorption spectra do not change by further recrystallization. According to the visible and long ultraviolet absorption spectra of these four complexes in sodium hydrogen carbonate solutions, they were the same and showed absorption maxima at 667 and at 350 mμ. This suggests that the complexes have the same structure and are different in how they combine with water in quality or in its amount. Quantitative analyses of glycine in these complexes were carried out by the use of the automatic amino acid analyzer after decomposition of complexes by hydrochloric acid. These results indicate the possible molecular formulas of complexes A-1, A-2, A-3, and A-4 which are shown in Table I.

TABLE I

POSSIBLE MOLECULAR FORMULA OF N-SALICYLIDENEGLYCINATOAQUOCOPPER(II)

| Crystal type, color | Mol wt found | Possible molecular formula | Calcd mol wt |
|---|---|---|---|
| A-1, yellow-green | 282.7 | $C_9H_7NO_3Cu \cdot 2H_2O$ | 276.7 |
| A-2, dark blue | 409.4 | $C_9H_7NO_3Cu \cdot 9H_2O$ | 402.9 |
| A-3, blue-green | 350.7 | $C_9H_7NO_3Cu \cdot 6H_2O$ | 348.8 |
| A-4, dark green | 276.7 | $C_9H_7NO_3Cu \cdot 2H_2O$ | 276.7 |

The reactions of the complexes with carbonyl compounds were carried out under conditions similar to physiological conditions: aqueous solution at pH 7.0–8.0 and at room temperature (25 ± 1°) (Scheme II). Acetaldehyde and the complex resulted in a mixture of N-salicylidene–copper (II) complex of threonine and of glycine. Observed results of the threonine syntheses are summarized in Table II. The results show that complex A-4 is more reactive than A-1 and the yield of (threonine and allothreonine) reached almost 90% based on starting complex A-4. The ratios of threonine and allothreonine were measured colorimetrically by a Beckman–Spinco Analytrol after paper chromatography.[11] The ratios of threonine and allothreonine in the products were in a relatively narrow range in all reactions: threonine 31–34%, allothreonine 66–69%. From this reaction mixture, allothreonine was isolated (see the Experimental Section).

TABLE II

FORMATION OF THREONINE

| Reacn time, hr | A-1 Thr, %[a] | A-1 Gly, %[a] | A-1 Yield of Thr, %[b] | A-4 Thr, %[a] | A-4 Gly, %[a] | A-4 Yield of Thr, %[b] |
|---|---|---|---|---|---|---|
| 24 | 60.7 | 39.3 | (56.3) | 95.6 | 4.4 | (84.3) |
| 48 | 62.2 | 37.8 | (58.5) | 97.7 | 2.3 | (87.5) |
| 72 | 63.5 | 36.5 | (55.8) | 95.5 | 4.5 | (89.2) |
| 96 | 63.9 | 36.1 | (52.8) | 97.7 | 2.3 | (79.1) |
| 120 | 65.2 | 34.8 | (51.3) | 97.2 | 2.8 | (72.8) |

[a] Amino acid compositions of the reaction mixture are shown in molar per cent. [b] Calculated yields are based on the starting complexes A-1 and A-4.

In a similar way, phenylserine formation from complex A-1 and A-4 with benzaldehyde was studied under similar conditions. Summarized results are listed in Table III.

The ratios of *threo*- and *erythro*-phenylserine of the product were measured colorimetrically after paper chromatographic separation.[12] A larger amount of

(9) G. L. Eichhorn and N. D. Marchand, *J. Am. Chem Soc.*, **78**, 2688 (1956).
(10) A. Nakahara, *Bull. Chem. Soc. Japan*, **32**, 1195 (1959).
(11) T. L. Hardy and P. O. Holland, *Chem. Ind.* (London), 517 (1954).
(12) K. N. F. Shaw and S. W. Fox, *J. Am. Chem. Soc.*, **75**, 3421 (1953).

TABLE III

FORMATION OF β-PHENYLSERINE

| Reacn time, hr | A-1 Phe-Ser, %[a] | A-1 Gly, %[a] | A-1 Yield of Phe-Ser, %[b] | A-4 Phe-Ser, %[a] | A-4 Gly, %[a] | A-4 Yield of Phe-Ser, %[b] |
|---|---|---|---|---|---|---|
| 24 | 42.7 | 57.3 | (38.9) | 54.2 | 45.8 | (42.5) |
| 48 | 45.2 | 54.8 | (42.5) | 59.2 | 40.8 | (45.1) |

[a] Amino acid compositions of the reaction products are expressed in molar per cent. [b] Yields are calculated based on the starting complexes A-1 and A-4.

*threo*-phenylserine was synthesized in the reactions: (A-1) *threo*, 77.4–82.2%, *erythro*, 22.6–17.8%; (A-4) *threo*, 79.2–84.1%, *erythro* 20.8–15.9%. From the reaction mixture, pure *threo*-phenylserine was isolated (see the Experimental Section).

β-Hydroxyaspartic acid was prepared from the complexes and glyoxylic acid. In this reaction, however, refluxing conditions were employed. Products were analyzed to determine the yields and amino acid compositions of the products by an automatic amino acid analyzer. Table IV shows the summarized results of β-hydroxyaspartic acid formation.

TABLE IV

FORMATION OF β-HYDROXYASPARTIC ACID

| Reacn time, min (of refluxing) | Yield of β-OH-Asp, %[a] | Amino acid compn of reacn product,[b] % *threo*-β-OH-Asp | *erythro*-β-OH-Asp | Gly |
|---|---|---|---|---|
| 10 | 49.4 | 43.0 | 24.5 | 32.5 |
| 10 (without $NaHCO_3$) | 50.6 | 42.9 | 23.3 | 33.8 |
| 15 | 50.9 | 42.9 | 23.5 | 33.6 |
| 60 | 28.4 | 29.3 | 13.2 | 57.5 |

[a] Calculated yields are based on the starting complex A-4. [b] Amino acid compositions of the reaction mixtures are expressed in molar per cent.

Synthesis of serine from the complexes was studied. The yield of serine, however, was found to be very low under the reaction conditions (pH 7–8, at room temperature in aqueous solution). Summarized results are shown in Table V.

TABLE V

| Reacn time, hr | Ser, %[a] | Gly, %[a] | Yield of Ser, %[b] |
|---|---|---|---|
| 24 | 4.6 | 95.4 | (2.6) |
| 120 | 4.7 | 95.3 | (1.1) |

[a] Amino acid compositions of the reaction products are expressed in molar per cent. [b] Calculated yields are based on the starting complex A-4.

## Experimental Section[13]

**N-Salicylideneglycinatocopper(II).**—N-Salicylideneglycinatocopper(II) complex (A-1) was prepared by the same method described by Nakahara, and a yellow-green complex was obtained.

Other preparations of the complex are as follows. Glycine (7.50 g, 0.10 mole), and sodium hydroxide (8.0 g, 0.20 mole), were dissolved in 30 ml of water and the temperature was brought to 40°. To this solution, 12.0 ml (0.1 mole) of salicylaldehyde in 10 ml of ethanol was added. Then a hot solution of 19.9 g (0.1 mole) cupric acetate monohydrate in 80 ml of water was added to the reaction mixture. After 10 min of agitation, a mixture of ethanol (120 ml) and ether (120 ml) was added to complete the precipitation. After 1 hr of standing at room temperature, the precipitated crystals were filtered to yield 29.0 g (71.9%). The crystals were dark blue (crystal A-2). These crystals (A-2) were recrystallized from water and ethanol (1:1) and blue-green crystals were obtained (crystal A-3) yielding 21.1 g (60.3%). Crystals (A-3) were recrystallized again from water and ethanol (1:2) and dark green crystals were obtained (crystal A-4), yielding 13.4 g (48.3%). Elemental analysis of A-4 is as follows.

*Anal.* Calcd for $C_9H_7NO_3Cu \cdot 2H_2O$: C, 39.06; H, 4.01; N, 5.06. Found: C, 39.18; H, 3.90; N, 5.07.

The glycine content of these complexes, A-1, A-2, A-3, and A-4 was measured. A known amount of these complexes was decomposed with 1 *N* hydrochloric acid and the solutions were applied to the Phoenix K-5000 automatic amino acid analyze to determine glycine content.

Visible and long ultraviolet absorption spectra of A-1, A-2, A-3, and A-4 were measured. Each of the complexes (5.0 mg) was dissolved in 10 ml of water containing 84 mg of sodium hydrogen carbonate. Absorption maxima were found at 667 and 350 mμ.

**Threonine and Allothreonine.**—Complexes A-1 and A-4 (64 mg each, 250 μmoles) were suspended in 4 ml of water, and 84 mg of sodium hydrogen carbonate and 0.4 ml of acetaldehyde each were added to the suspensions. The mixtures were shaken for 24, 48, 72, 96, and 120 hr at room temperature (25°). Then 1 ml of 6 *N* hydrochloric acid was added to each of the samples to decompose the copper complex, and the resulting amino acids were analyzed by the amino acid analyzer. Results are summarized in Table II.

Threonine and allothreonine were resolved by paper chromatography.[11,12] After staining with ninhydrin, the color density was measured by a Beckman–Spinco Analytrol intensitometer. $R_f$ values of amino acids are as follows: threonine, 0.54; allothreonine, 0.41; glycine, 0.15.

**Isolation of Allothreonine.**—Complex A-4 (2.76 g, 0.01 mole) was suspended in 120 ml of water, and 3.3 g of sodium hydrogen carbonate and 16 ml of acetaldehyde were added. This mixture was shaken for 24 hr at room temperature. After reaction, the excess acetaldehyde was removed *in vacuo*. This reaction mixture was acidified with 6 *N* hydrochloric acid. Then the liberated salicylaldehyde was extracted with ether. The aqueous solution concentrated to dryness *in vacuo*. The residue was extracted with absolute ethanol. The resulting sodium chloride was removed by filtration. Ethanol was removed under reduced pressure. The residue was dissolved in 5 ml of water, then applied to a column of Dowex 50 × 2 (H-form, 100–200 mesh, 2 × 20 cm) and washed with water to neutrality, then eluted with 1 *N* ammonia. The effluent was evaporated *in vacuo* and treated with active carbon. This solution was again concentrated and 95% ethanol was added. After being kept in a refrigerator overnight, the crystals were filtered. The crystals (450 mg, 38%) were recrystallized from water and ethanol three times yielding 340 mg (29%), mp 239° dec. By paper chromatography, the crystals were identified as allothreonine containing trace amounts of glycine. Comparison of the infrared spectrum of the allothreonine agreed with authentic allothreonine in all absorption maxima.

*Anal.* Calcd for $C_4H_9NO_3$: C, 40.33; H, 7.62; N, 11.76. Found: C, 40.31; H, 7.36; N, 11.90.

***threo*- and *erythro*-Phenylserine.**—Complexes A-1 and A-4 (69 mg each, 250 μmoles), were suspended in a mixture of 3 ml of water and 3 ml of 95% ethanol. To these were added 84 mg of sodium bicarbonate and 0.75 ml of benzaldehyde. These mixtures were shaken for 24 and 48 hr at room temperature. Hydrochloric acid (6 *N*, 1 ml) was added to this reaction mixture to decompose the copper complex. The reaction mixture was then analyzed by the amino acid analyzer.

*threo*- and *erythro*-phenylserine were resolved by paper chromatography.[12] The color density was measured after staining with ninhydrin by a Beckman–Spinco Analytrol intensitometer. *R* values of amino acids are as follows: *threo*-phenylserine, 0.42; *erythro*-phenylserine, 0.27; glycine, 0.12. Results are summarized in Table III.

**Isolation of *threo*- and *erythro*-Phenylserine.**—Complex A-4 (2.76 g, 0.01 mole) was suspended in a mixture of 60 ml of water and 60 ml of 95% ethanol. To this was added 3.3 g of sodium hydrogen carbonate and 29 ml of benzaldehyde. The mixture was shaken for 24 hr at room temperature. The reaction mixture was acidified with 6 *N* hydrochloric acid. The salicylaldehyde

(13) Elemental analyses were done by Micro-Tech Laboratories, Skokie, Ill. Amino acid analyses were carried out by Phoenix K-5000 automatic amino acid analyzer.

and excess benzaldehyde were extracted with ether. The aqueous solution was evaporated to dryness *in vacuo*. The residue was extracted with absolute ethanol and insoluble sodium chloride was removed by filtration. The ethanolic solution was evaporated to dryness. The residue was dissolved in 5 ml of water and this was applied to a column of Dowex 50 × 2 (H-form, 100–200 mesh, 2 × 20 cm). The column was washed with water until the effluent water became neutral. Then the amino acid was eluted with 1 *N* ammonia. Fractions containing the amino acid were combined and concentrated to about 5 ml, and were kept in a refrigerator overnight. Precipitated crystals were filtered and were recrystallized from water and 95% ethanol twice yielding 480 mg (24%), mp 195° dec.

*Anal.* Calcd for $C_9H_{13}NO_4$: C, 54.26; H, 6.58; N, 7.03. Found: C, 54.52; H, 6.54; N, 7.33.

These crystals were identified as pure *threo*-phenylserine by paper chromatography[12] and by the infrared spectrum.

The mother liquor, from which the *threo*-phenylserine was already removed, was evaporated to dryness *in vacuo*. This was dissolved in 1.4 ml of hot water and 2 ml of hot dioxane was added. Crystallization began after a few minutes. The suspension was kept in a refrigerator overnight and the crystals were collected by filtration. The crystals were washed with a mixture of water and dioxane (1:1). These crystals, 230 mg (10%), were recrystallized from water and dioxane three times yielding 170 mg (7.6%), mp 192° dec. These crystals were found to be *erythro*-phenylserine dioxane adduct and did not contain *threo*-phenylserine. However, they contained a small amount (3%) of glycine. Comparison of the spectrum of these crystals with the authentic dioxane adduct of *erythro*-phenylserine showed no difference.

*threo*- and *erythro*-**β-Hydroxyaspartic Acid.**—Complex A-4 (27.6 g, 100 μmoles), sodium glyoxylate (9.6 mg, 100 μmoles), and sodium hydrogen carbonate (42 mg) were dissolved in 10 ml of water and refluxed for 10,15, and 60 min. These solutions were analyzed after decomposing the copper complex by hydrochloric acid by the amino acid analyzer. Effluent volume of amino acids are as follows: *threo* isomer, 52.5 ml; *erythro* isomer, 63.0 ml; glycine, 116.7 ml.

**Serine.**—Complex A-4 (69 mg, 250 μmoles) was suspended in 4 ml of water, then 84 mg of sodium hydrogen carbonate and 2 ml of 35% formaldehyde solution were added. These mixtures were shaken for 24 and 120 hr at room temperature. The reaction products were analyzed by the amino acid analyzer. Results are shown in Table V.

**Registry No.**—Glycine, 56-40-6; threonine, 72-19-5; allothreonine, 72-19-5; *threo*-phenylserine, 7695-56-9; *erythro*-phenylserine, 7687-36-7; *threo*-β-hydroxyaspartic acid, 5174-55-0; *erythro*-β-hydroxyaspartic acid, 1186-90-9; serine, 56-45-1.

**Acknowledgments.**—This work was supported by Grant No. NsG-689 of the National Aeronautics and Space Administration. The authors wish to express their thanks to Dr. S. W. Fox for his encouragement, to Dr. H. B. Powell for discussion, and to Dr. A. Nakahara for literature information. Thanks are extended to Mr. C. R. Windsor for amino acid analyses.

# Intramolecular Trapping of Hydroxylamines from the Catalytic Hydrogenation of 2-Nitrobiphenyls[1]

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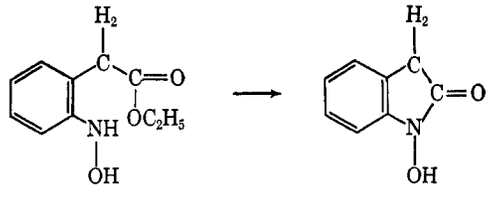
*Received October 10, 1966*

Catalytic hydrogenation of 2-nitro-2′-carboxybiphenyl (**3a**) and carboxy derivatives of **3a** in ethanol in the presence of platinum has led to products resulting from the intramolecular trapping of hydroxylamino and amino groups. In the presence of mineral acid the order of hydroxylamino trapping abilities is carbamoyl > carbomethoxy > carboxy. With no added mineral acid the order of trapping abilities is reversed. Compounds containing the cyano group were found to yield only hydroxylamino-trapped products.

In contrast to chemical and electrical reductions of nitro compounds from which several products intermediate to the formation of the amine often have been isolated,[3] seldom have compounds other than amines or their derivatives been isolated from the catalytic hydrogenation of nitro compounds. In one exception ethyl 2-nitrophenylacetate when subjected to catalytic hydrogenation yielded in addition to the expected lactam a small amount of a cyclic hydroxamic acid



1 2

(2)[4] which can be accounted for by the trapping of a hydroxylamino group by a carboethoxy group.

## Hydroxylamino Trapping By Carboxy, Carbomethoxy, and Carbamoyl Groups

In the current study some nitrobiphenylcarboxylic acids and derivatives were subjected to hydrogenation in absolute ethanol in the presence of platinum. The results are summarized in Table I. For those cases in which hydrogenation data are listed the percentages of hydroxylamino trapping are based on the assumption that a mole ratio of 2:1 for hydrogen consumed to compound reduced indicates 100% hydroxylamino trapping and that a mole ratio of 3:1 for the same reagents indicates 0% hydroxylamino trapping. In all cases the indicated hydrogenation products were isolated and the absence of starting material was established. The percentages (where available) of the compounds isolated from the hydrogenations are in good agreement with values calculated from the mole ratio of hydrogen to the compound being reduced.

As can be seen in Scheme I the results may be explained by assuming that the hydroxylamine (**4**),

(1) Presented in part before the Organic Division at the 151st National Meeting of the American Chemical Society, March 1966, Pittsburgh, Pa., and in part before the 40th Meeting of the West Virginia Academy of Science, April 1965, Fairmont, W. Va.

(2) (a) From Ph.D. Dissertation (1966); (b) from M.S. Thesis (1961); (c) from M.S. Thesis (1959).

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(4) F. J. DiCarlo, *J. Am. Chem. Soc.*, **66**, 1420 (1944).