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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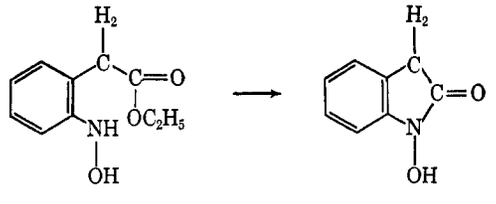
Catalytic hydrogenation of 2-nitro-2′-carboxybiphenyl (**3a**) and carboxy derivatives of **3a** in ethanol in the presence of platinum has led to products resulting from the intramolecular trapping of hydroxylamino and amino groups. In the presence of mineral acid the order of hydroxylamino trapping 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).

(3) J. D. Roberts and M. C. Caserio, "Basic Principles of Organic Chemistry," W. A. Benjamin, Inc., New York, N. Y., 1964, p 867.

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

TABLE I

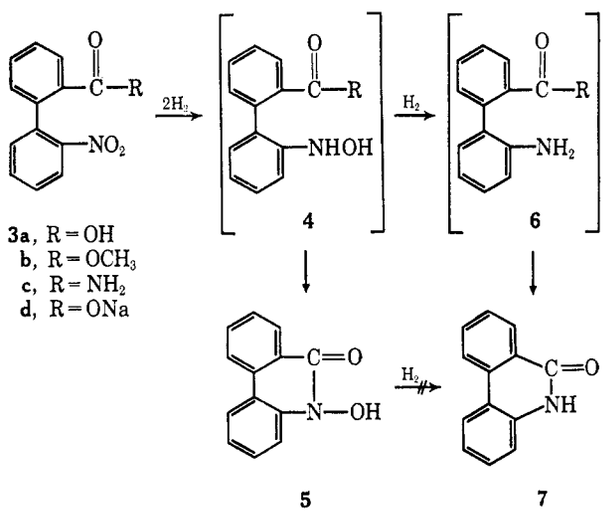
HYDROGENATION OF SOME 2-NITROBIPHENYLS

Compd	Mp, °C	Mole ratio of H_2:compd	Hydroxylamino trapping, %	Compd isolated, %[a]
3a	164–166[b]	2.49 ± 0.03	51	**5, 7**
3a (H^+)[c]	164–166[b]	2.33 ± 0.04	67	**5** (70%), **7** (23%)
3b	54–56	2.60 ± 0.03	40	**5, 7**
3b (H^+)[c]	54–56	2.25 ± 0.03	75	**5** (66%), **7** (27%)
3c[d]	138–140[e]	...	0	**7**
3c (H^+)[c]	138–140[e]	2.14 ± 0.12	86	**5, 7** (13%)
3a (Na salt)[f]		...	0	**7**
8	128–129[g]	...	0	**12**
8 (H^+)[c]	128–129[g]	...	100	**10**
13	127–129	2.34 ± 0.08	66[h]	**14**
16	257–259	...	100	**18**

[a] Based on starting material. [b] Prepared by the method of R. G. Shuttleworth, W. S. Rapson, and E. T. Stewart, *J. Chem. Soc.*, 71 (1944). [c] In the presence of sulfuric acid. [d] Only phenanthridone (**7**) was isolated. [e] Mp 140–141, C. W. Muth, W. L. Sung, and Z. B. Papanastassiou, *J. Am. Chem. Soc.*, **77**, 3393 (1955); mp 138–139, C. Angelini, *Ann. Chim.*, 879 (1957). [f] Phenanthridone (**7**) was isolated and sodium 2-amino-2′-biphenylcarboxylate was detected. [g] Prepared according to the method of D. C. Iffland and H. Siegel, *J. Am. Chem. Soc.*, **80**, 1947 (1958). [h] The infrared spectrum of the product indicates that **14** was the only compound produced.

formed from the addition of 2 moles of hydrogen to the nitro group, can undergo one or both of the two reactions. The hydroxylamino group can either undergo reaction with the acid function, or the hydroxylamino group can add a 3rd mole of hydrogen to form an amine (**6**), which can undergo reaction with the acid function. Under the conditions of the reaction, N-hydroxyphenanthridone (**5**) did not undergo reaction to yield phenanthridone (**7**).

SCHEME I



Two features of the results need emphasis. First, in all cases a higher percentage of hydroxylamino trapping occurs in the presence of mineral acid. Second, in the absence of mineral acid the hydroxylamino trapping abilities of the functional groups are $CO_2H > CO_2CH_3 > CONH_2$ with no trapping in the last case, whereas this order is reversed in the presence of mineral acid.

The higher percentages of hydroxylamino trapping in the presence of mineral acid can be interpreted to mean that the trapping group is protonated and thereby becomes a better electrophile. The carbamoyl group is the strongest base of those being compared;[5] consequently, its conjugate acid is the weakest acid and should be the best electrophile. It seems possible that the hydroxylamino group could be trapped as it comes off the catalyst by an adjacent carbonyl group before the hydroxylamino group is protonated.

For those hydrogenations in which no mineral acid was present, the amount of hydroxylamino trapping increased as the basicity of the leaving group decreased. In these cases the basicity of the leaving groups decrease in the order $NH_2^- > OCH_3^- \gtrsim OH^-$.[5]

No hydroxylamino trapping occurred from the hydrogenation of sodium 2-nitro-2′-biphenylcarboxylate (**3d**); phenanthridone (**7**) and sodium 2-amino-2′-biphenylcarboxylate were formed. The fact that the foregoing salt could be isolated demonstrates that the carboxylate ion is a poor electrophile. Heating a solution of the foregoing salt in water or ethanol resulted in the formation of phenanthridone (**7**).

The compound assigned structure **5**, N-hydroxyphenanthridone, conceivably could be in equilibrium with or could be 6-hydroxyphenanthridone 5-oxide. The results of an ultraviolet study support structure **5**: the compound in question has a spectrum in the region examined, 280–350 mμ, which is very similar to the spectrum of phenanthridone (**7**) and unlike the spectra of phenanthridine 5-oxide and 6-carbomethoxyphenanthridine 5-oxide.

Confirmation of the hydroxyl stretching band[6,7] of N-hydroxyphenanthridone (**5**) has been obtained by comparing its infrared spectrum with that of its potassium, cupric and ferric salts. Compound **5** has a series of diffuse bands between 3100 and 2800 cm^{-1} (in KBr and as a mull in halocarbon) which are assigned to hydroxyl stretching because these bands are absent in the spectra of the salts.

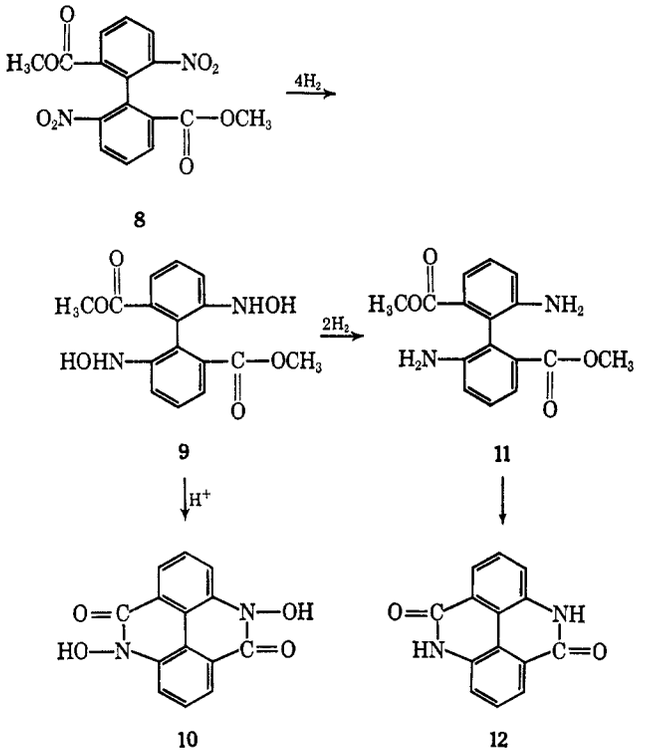
From the hydrogenation of 2,2′-dinitro-6,6′-dicarbomethoxybiphenyl (**8**) under neutral conditions no hydroxylamino trapping occurred. In this case diamino diester **11** was isolated which readily underwent ring closure on heating or in the presence of mineral acid to form dilactam **12**. The fact that diamino diester **11** does not spontaneously undergo ring closure to yield **12** is undoubtedly due to steric hindrance.

In the hydrogenation of dinitro diester **8** under acidic conditions, two hydroxylamino groups were trapped with the formation of 4,9-dihydroxy-5,10-dioxo-4,9-diazapyrene (**10**). In this case, both nitro groups must be hydrogenated nearly simultaneously to two hydroxylamino groups which undergo reaction with the carbomethoxy groups. This result again demonstrates that the hydroxylamino trapping ability of a carbonyl function is enhanced by the presence of mineral acid. (See Scheme II.)

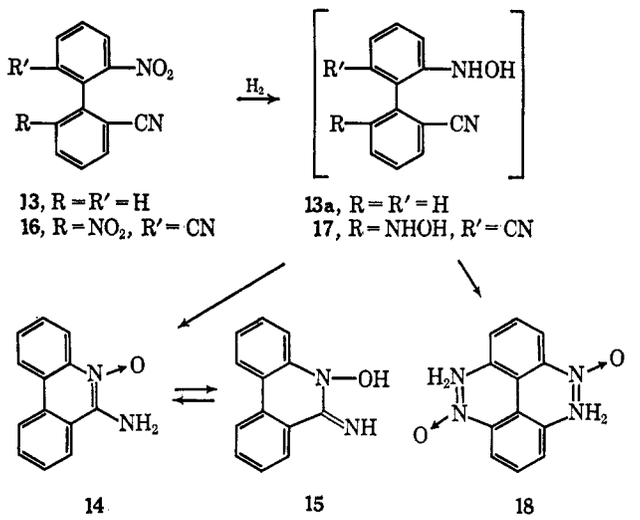
The spectral properties of authentic **10**[8] and the product from the catalytic hydrogenation of **8** in the presence of mineral acid were identical. Compound **10** when treated with ferric chloride gave a wine-colored

(5) M. L. Bender, *Chem. Rev.*, **60**, 53 (1960).
(6) D. H. Hey, J. A. Leonard, and C. W. Rees, *J. Chem. Soc.*, 4579 (1962).
(7) F. Mathis, *Compt. Rend.*, **232**, 505 (1951).
(8) R. F. Robbins, *J. Chem. Soc.*, 2553 (1960).

SCHEME II



SCHEME III



solution and **10** reacted with cupric chloride to form a pale green precipitate.

The structures assigned for compounds **10** (4,9-dihydroxy-5,10-dioxo-4,9-diazapyrene) and **12** (4,9-dihydro-5,10-dioxo-4,9-diazapyrene) are supported by the fact that their ultraviolet spectra are similar and unlike the spectrum of the compound which was assigned structure **18** (5,10-diamino-4,9-diazapyrene4,9-dioxide).

Hydroxylamino Trapping by Cyano Group

There are few examples of intramolecular trapping of a hydroxylamino group by a cyano group as a result of the catalytic hydrogenation of a nitro group.[9,10] The current study involved 2-nitro-2′-cyanobiphenyl (**13**) (Scheme III) and 2,2′-dinitro-6,6′-dicyanobiphenyl (**16**).

From the catalytic hydrogenation of **13** in ethanol with platinum as the catalyst only the hydroxylamino-trapped oroduct, 6-aminophenanthridine-5 oxide (**14**) was isolated and this, based on the infrared spectrum of the reaction product, was the sole compound produced.

The most convenient method examined for the preparation of **14** was the catalytic hydrogenation (2 atm) of **13** in tetrahydrofuran in which **13** is more soluble than in ethanol. The yield of **14** as a monohydrate was 90%.

Although the compound assigned structure **14** was insoluble in concentrated potassium hydroxide, this compound did give an emerald green ferric chloride test and an olive green cupric salt; consequently, the compound assigned structure **14** is probably in equilibrium with **15**. Analogous compounds in the pyridine series exist almost exclusively in the form of the N-oxide.[11]

A spectral examination of the catalytic hydrogenation product of 2,2′-dinitro-6,6′-dicyanobiphenyl (**16**) showed that 2,2′-dihydroxylamino-6,6′-dicyanobiphenyl (**17**) was present. When attempts were made to recrystallize the foregoing hydrogenation product any **17** present underwent ring closure to form 5,10-diamino-4,9-diazapyrene 4,9-dioxide (**18**). It was surprising that the hydroxylamino groups were not reduced when they were not immediately trapped.

Solvent Effect

From the catalytic hydrogenation (2 atm) of 2-nitro-2′-carbamoylbiphenyl (**3c**) in tetrahydrofuran using platinum as the catalyst a 70% yield of recrystallized N-hydroxyphenanthridone (**5**) was isolated. In contrast, when all conditions and reagents were the same except that ethanol was the solvent instead of tetrahydrofuran, a 91% yield of phenanthridone (**7**) was isolated.

There is also a large solvent effect in the hydrogenation of **3b** because from this compound in tetrahydrofuran under 2 atm of hydrogen there were obtained **5** and **7** with only a 13% yield of the latter. From **3b** in ethanol under 1 atm of hydrogen the yields of **5** and **7**, based on hydrogen uptake, were 40 and 60%, respectively.

A possible partial explanation for these results is that the hydroxylamino group can not hydrogen bond with tetrahydrofuran, whereas it can hydrogen bond with ethanol; therefore, in tetrahydrofuran the hydroxylamino group is more available to react with a trapping group. It is to be noted, however, that the hydrogenations proceed faster in ethanol than in tetrahydrofuran. Coutts[12] recently reported that palladium-catalyzed sodium borohydride reductions of *o*-nitrophenylthio acids yield more hydroxylamino-trapped product in a nonhydrogen bonding solvent (dioxane) than in methanol.

(9) K. H. Bauer, *Chem. Ber.*, **71**, 2226 (1938).
(10) G. D. Buckley and T. J. Elliott, *J. Chem. Soc.*, 1508 (1947).
(11) J. M. Gardner and A. R. Katritzky, *ibid.*, 4375 (1957); A. R. Katritzky, *ibid.*, 191 (1957); A. R. Katritzky and A. R. Hands, *ibid.*, 2195 (1958); A. R. Katrizky and R. A. Jones, *J. Chem. Soc.*, 3674 (1959).
(12) R. T. Coutts, D. L. Barton, and E. M. Smith, *Can. J. Chem.*, **44**, 1733 (1966).

Experimental Section[13]

Hydrogenation Procedure.—The 100-ml hydrogenation apparatus employed was like that described by Wiberg[14] with the following three modifications. First, heavy-walled rubber tubing was used in place of glass tubing. Second, a pressure-equalizing separatory funnel was placed in the system; this enables one to add solvent and reactant to the system (but out of contact with the catalyst) prior to equalizing the pressure of the system. Third, a reservoir was incorporated in the system into which the solution of the hydrogenation product could be poured, leaving the catalyst behind. This change allowed the same catalyst to be used several times and greatly speeded up the hydrogenations since more solvent and reactant could be added and hydrogenated without opening the system.

A typical experiment will be described. To a 250-ml erlenmeyer flask was added 0.037 g (0.016 mmole) of platinum oxide,[15] 20 ml of absolute ethanol, and a magnetic stirring bar. This was placed in the system which was then successively evacuated and filled with hydrogen three times. Stirring was started and continued for 5 min by which time no more hydrogen was absorbed by the system. A 50-ml aliquot (0.9942 mmole) of *p*-nitrotoluene (Eastman Organic Chemicals) in absolute ethanol was added through a separatory funnel into the pressure equalizing separatory funnel of the system and the pressure was equalized. The initial volume, temperature, and pressure were recorded. The reactant and solvent were added to the catalyst, and stirring was started and continued until hydrogen uptake had ended (15–30 min); the final volume, temperature, and pressure were recorded. The number of millimoles of hydrogen taken up was then calculated from the ideal gas equation after corrections were made for the vapor pressure of absolute ethanol and for the deviation of the barometric reading caused by the mercury column not being at standard temperature. The mole ratio of hydrogen to *p*-nitrotoluene was then calculated. The product was then poured into the reservoir and a new aliquot of *p*-nitrotoluene was added to the system and treated as the first. A total of seven aliquots was hydrogenated. The solution of the hydrogenation product was filtered free of platinum with suction and evaporated to dryness on a steam bath. The infrared spectrum of the product was the same as that of known *p*-toluidine (Eastman Organic Chemicals); therefore, the theoretical mole ratio of hydrogen to *p*-nitrotoluene was 3.00. The average mole ratio of hydrogen to *p*-nitrotoluene was 3.01 ± 0.04 as determined from the mole ratios of the individual runs by dropping the two values farthest from the median and averaging the other five.

The data recorded in Table I were obtained in a similar manner. One drop (0.05 ml) of concentrated sulfuric acid was added in those experiments in which sulfuric acid was present. In all cases the products indicated in Table I were isolated and in all cases an exmination of the infrared spectra of the products showed the absence of the nitro group.

Preparation of New Compounds Which Were Hydrogenated. A. 2-Nitro-2′-carbomethoxybiphenyl (3b).—This ester was prepared in the usual manner from **3a** and methanol with sulfuric acid as the catalyst. The yield of **3b**, mp 56–57.5°, was 85% after recrystallization from methanol. *Anal.* Calcd for $C_{14}H_{11}NO_4$: N, 5.44. Found: N, 5.30.

B. 2-Nitro-2′-cyanobiphenyl (13).—Compound **3c** (27 g, 0.11 mole) was heated under reflux with 70 ml of thionyl chloride for 12 hr. The excess thionyl chloride was removed by distillation under reduced pressure and the residue was dissolved in benzene. The benzene solution was washed successively with 2% sodium carbonate solution and with water. The benzene was removed by distillation to form a solid residue which was recrystallized from methanol and then twice from benzene to yield 22.5 g (90%) of pale yellow crystals: mp 128–131°; ν_{max} 2220 (CN), 1520, and 1340 (NO_2) cm^{-1}.

The analytical sample, mp 128–130°, was prepared by successive crystallizations from methanol and benzene. *Anal.* Calcd for $C_{13}H_8N_2O_2$: C, 69.57; H, 3.57; N, 12.60. Found: C, 69.56; H, 3.59; N, 12.50.

C. 2,2′-Dinitro-6,6′-dicyanobiphenyl (16).—2,2′-Dinitro-6,6′-dicarbamoylbiphenyl (5.0 g, 0.015 mole, mp 274–276° dec) (lit.[16] mp 276° dec) was refluxed for 24 hr with a mixture of 20 g of phosphorous pentachloride and 30 ml of redistilled phosphoryl chloride. The mixture was concentrated using reduced pressure and the residue was treated with cold, concentrated ammonium hydroxide. The resulting solid was filtered and dried to yield 3.5 g (86%) of crude 2,2′-dinitro-6,6′-dicyanobiphenyl (**16**) which formed fine golden needles, mp 257–259°, ν_{max} 2215 (CN) and 1520 and 1340 (NO_2) cm^{-1}, upon recrystallization from methanol. *Anal.* Calcd for $C_{14}H_6N_4O_4$: C, 57.15; H, 2.06; N, 19.05. Found: C, 57.31; H, 2.06; N, 18.85.

Separation and/or Identification of Products. A. From Hydrogenation of 2-Nitro-2′-Carboxybiphenyl (3a). Isolation of N-Hydroxyphenanthridone (5) and Phenanthridone (7).—The hydrogenation product mixture was concentrated and the residue was treated with hot dilute potassium hydroxide; the resulting mixture was filtered and washed with water until neutral.

The insoluble material from the base treatment was washed with dilute sulfuric acid and then with water until neutral to yield phenanthridone (**7**), which was recrystallized from absolute ethanol to give tan flakes, mp 290–292° (lit.[17] mp 288–290°). The infrared spectrum was the same as that of phenanthridone.

The cooled filtrate from the base treatment contained a gelatinous gray precipitate which was filtered and shown to be the potassium salt of N-hydroxyphananthridone, mp 312–314°, by conversion on acidification to N-hydroxyphenanthridone (**5**). The remainder of the filtrate was acidified to yield N-hydroxyphenanthridone (**5**) which formed pale pink crystals from acetic acid: mp 254–256° (lit.[6] mp 258–259° and lit.[17] mp 251–254°); ν_{max} 3085 m, 2880 m, 2760 sh, 1630 s, 1608 s, and 1580 s cm^{-1}.

Products from the hydrogenation of **3b** and **c** were examined similarly. N-Hydroxyphenanthridone in ethanol gave a wine red color with ferric chloride. The beet-colored ferric salt of N-hydroxyphenanthridone, mp 279–280° dec, was prepared by dissolving N-hydroxyphenanthridone in concentrated sulfuric acid, adding an excess of 5% ferric chloride, and precipitating with water.

Compound **5** in ethanol in the presence of Raney nickel and 30 psi of hydrogen was converted during 2 hr to **7**, mp 285–287°.

B. From Hyrogenation of Sodium 2-Nitro-2′-biphenylcarboxylate (3d). Identification of 2-Amino-2′-biphenylcarboxylate and Phenanthridone (7).—Concentration of the hydrogenation product mixture under reduced pressure at room temperature gave a residue the infrared spectrum of which indicated that both the sodium salt of 2-amino-2′-carboxybiphenyl [ν_{max} 3450 m (as NH_2), 3350 (sym NH_2), 1580 s (sym CO_2^-), and 1395 (as CO_2^-) cm^{-1}] and phenanthridone [**7**, ν_{max} 1670 m (C=O) cm^{-1}] were present. The mixture upon heating in water or ethanol was completely converted to **7**. Attempts to prepare the benzenesulfonamide of 2-amino-2′-carboxybiphenyl in the usual manner were not successful. Phenanthridone was formed upon acidification.

C. From Hydrogenation of 2,2′-Dinitro-6,6′-dicarbomethoxybiphenyl (8) in Absence of Sulfuric Acid. Identification of 11 and Isolation of 12.—The yellow ethanolic solution of the hydrogenation product gave a negative ferric chloride test; therefore, no hydroxylamine trapping had occurred. Treatment of the ethanolic solution with water followed by extraction with ether gave a yellow ether extract which was divided into two portions. The first portion was washed with a saturated sodium chloride solution, filtered through sodium sulfate, and evaporated to dryness with an air jet to yield 2,2′-diamino-6,6′-dicarbomethoxybiphenyl (**11**) as yellow crystals [ν_{max} 3425 m (as NH_2), 3350 m (sym NH_2), 2950 w (as CH_3), 1720 s (C=O) cm^{-1}] which ring closed upon heating in ethanol to yield 4.9-dihydro-5,10-dioxo-4,9-diazapyrene (**12**) as tan flakes [mp >405° (lit.[16] mp >300°, and lit.[8] mp >360°); ν_{max} 3120 m (d), 3000 m (d) 2880 m (d), 1660 s, 1615 m, and 1570 m cm^{-1} (lit.[8] in KBr 3100, 1670, 1615, and 1575 cm^{-1})], which dissolved in concentrated sulfuric acid to give a blue fluorescence.[8,16] An analytical sample of pale yellow flakes was prepared by sublimation at

(13) All melting points were determined with a Mel-Temp apparatus and are uncorrected. All elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. All infrared measurements were made in potassium bromide with a Perkin-Elmer Infracord spectrophotometer. The abbreviations used to record the infrared spectra follow: ν_{max} absorption maxima in reciprocal centimeters (cm^{-1}); s, strong; m, medium; w, weak; d, doublet; as, asymmetric; and sym, symmetric. All ultraviolet measurements were made in 95% ethanol with either a Perkin-Elmer Model 350 or Beckman DU spectrophotometer. All ϵ values were determined by using the latter instrument.

(14) K. B. Wiberg, "Laboratory Technique in Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p 227. .

(15) Krishell Laboratories, Inc., Portland, Ore. 97202.

(16) J. Kenner and W. V. Stubbings, *J. Chem. Soc.*, **119**, 593 (1921).

(17) E. Hayashi and Y. Hotta, *Yakugaku Zasshi*, **80**, 834 (1960); *Chem. Abstr.*, **54**, 24597 (1960).

300° (0.5 mm). *Anal.* Calcd for $C_{14}H_8N_2O_2$: C, 71.18; H, 3.41; N, 11.86; O, 13.55. Found: C, 71.02; H, 3.56; N, 11.71; O, 13.34.

Attempts to form the diacetyl derivative of diamine **11** by stirring it with acetic anhydride at room temperature for 2 hr resulted in the precipitation of **12**.

The second portion of the ether extract was extracted with dilute hydrochloric acid. The hydrochloric acid extract gave a white, flocculent precipitate upon standing at room temperature for a few minutes. The precipitate was filtered, washed with water, and dried to give **12**.

D. From Hydrogenation of 2,2′-Dinitro-6,6′-dicarbomethoxybiphenyl(8) in the Presence of Sulfuric Acid. Isolation of 4,9-Dihydroxy-5,10-dioxo-4,9-diazapyrene (10).—The hydrogenation product gave a wine-colored ferric chloride test, a pale green cupric salt with cupric chloride in ethanol[8] and a blue fluorescence when dissolved in concentrated sulfuric acid and subjected to ultraviolet light. The hydrogenation product was dissolved in 10% sodium hydroxide and filtered with suction. The filtrate was acidified to give a precipitate which was filtered with suction and dried to yield 4,9-dihydroxy-5,10-dioxo-4,9-diazapyrene (**10**) as tan flakes. Sublimation at 250° (0.5 mm) gave **10** as pale yellow flakes [mp >405° (lit.[8] mp >360°); ν_{max} 3060 m, 2850 m, 2700 m, 1660 s, 1590 s, and 1570 m cm^{-1}; λ_{max} 367, 350, 337 sh, 290 sh, 258 sh, 244, and 237 sh mμ (log ε 4.08, 3.98, 3.69, 3.72, 4.33, 4.53, and 4.44)], which gave an infrared spectrum identical with that of **10** prepared by the method of Robbins.[8]

Compound **10** was also prepared by treating a solution of 0.5 g (1.5 mmoles) of **8** in 100 ml of ethanol with 3 g (25 mmoles) of tin and 10 ml of concentrated hydrochloric acid. The mixture was shaken until all the tin dissolved at which time it was refluxed on a steam bath for 0.5 hr. The resulting precipitate was filtered, washed free of acid with water, and dried to give **10** as pale yellow flakes.

Attempts to deoxygenate **10** with acetic anhydride or phosphorous trichloride according to the methods used for the deoxygenation of N-hydroxyphenanthridone (**5**) were unsuccessful, maybe because of the low solubility of **10**.

E. From Hydrogenation of 2-Nitro-2′-Cyanobiphenyl (13). Isolation of 6-Aminophenanthridine 5-Oxide (14).—Concentration of the hydrogenation product gave a residue which was recrystallized from ethanol to yield yellow crystals, mp 246–248°, of 6-aminophenanthridine 5-oxide (**14**) (lit.[18] mp 244–245°): ν_{max} 3400 m, 3290 m, 3100 m, 1625 s, 1580 sh, (in Nujol) 3450, 3300, 3150, and 1640 cm^{-1}; λ_{max} 2.92 (log ε 3.93), 330 (3.92), and 341 sh mμ (3.88). Although **14** was insoluble in concentrated potassium hydroxide, it did give an emerald green ferric chloride test and an olive green cupric salt [mp 342° dec, ν_{max} 3490 (=NH) cm^{-1}] which was precipitated with water from an ethanolic solution of 6-aminophenanthridine-5-oxide and cupric chloride. *Anal.* Calcd for $C_{26}H_{18}N_4O_2Cu \cdot H_2O$: C, 62.45; H, 4.03; N, 11.21. Found: C, 62.27; H, 4.01; N, 10.98.

2-Nitro-2′-cyanobiphenyl (9.33 g, 0.046 mole) in 150 ml of tetrahydrofuran when treated with 0.2 g of platinum oxide and 30 psi of hydrogen in a Burgess Parr hydrogenation apparatus for 40 min yielded after recrystallization from methanol 8.75 g (90%) of a white solid, mp 238–241°, which is a monohydrate of 6-aminophenanthridine 5-oxide. *Anal.* Calcd for $C_{13}H_{10}N_2O \cdot H_2O$: C, 68.42; H, 5.30; N, 12.28. Found: C, 68.39, 68.23; H, 5.21, 5.24; N, 12.14, 12.34. Calcd for monohydrate (perchloric acid in acetic acid and acetic anhydride): neut equiv, 228.2. Found: neut equiv, 227.

Heating the white solid gave a yellow solid, mp 245–249°, which is anhydrous **14**. Treatment of the white solid with dilute hydrochloric acid yielded a monohydrochloride of **14**: mp 210° dec; ν_{max} 3310 m, 3150 m, 2625 m, and 1650 s cm^{-1}. *Anal.* Calcd for $C_{13}H_{10}N_2O$: neut equiv, 210. Found: neut equiv, 212. Calcd for $C_{13}H_{10}N_2O \cdot HCl$: neut equiv, 247. Found: neut equiv, 248.

In the presence of Raney nickel under 30 psi of hydrogen **14** in ethanol during 2 hr was converted to 6-aminophenanthridine, mp 191–194° (lit.[19] mp 193–194°), which had the same infrared spectrum as the authentic material; also a mixture melting point showed no depression.

F. From Hydrogenation of 2,2′-Dinitro-6,6′-dicyanobiphenyl (16). Identification of 2,2′-Dihydroxylamino-6,6′-dicyanobiphenyl (17) and Isolation of 5,10-Diamino-4,9-diazapyrene 4,9-Dioxide (18).—The hydrogenation product was a dark orange solid which showed the presence of cyano band (2210 cm^{-1}) but the absence of nitro groups in its infrared spectrum; therefore, hydrogenation was complete but ring closure was not. Extraction with ether left an olive green solid. Evaporation of the ether extract gave canary yellow crystals which showed an absorption band at 2210 (cyano) and at 3330 cm^{-1} (sharp) superimposed on or adjacent to an broader band 3300–3450 cm^{-1} (NH and OH of hydroxylamino). Crystallization attempts of the canary yellow crystals from methanol gave more of the olive green solid; therefore, the olive green solid was being formed from a ring closure of the canary yellow crystals. Since the olive green solid gave a mossy green ferric chloride test and since the canary yellow crystals gave the olive green solid, hydrogenation stopped at the hydroxylamine state to yield **17** as yellow crystals which ring closed upon heating in methanol or ethanol to form **18** as olive green flakes, which were insoluble in common organic solvents, hot 6 *N* hydrochloric acid, and hot 10% sodium hydroxide. An analytical sample of 5,10-diamino-4,9-diazapyrene 4,9-dioxide (**18**) was prepared by dissolving it in concentrated sulfuric acid. The sulfuric acid solution which gave a blue fluorescence when exposed to ultraviolet light was filtered through a sintered-glass filter. The filtrate was diluted with water and neutralized with solid potassium carbonate to give a precipitate which was filtered with suction, washed with water until neutral, and dried to give **18** as olive green flakes: mp >405°; ν_{max} 3400 s, 3100 s, 1630 s, 1600 s, 1460 s, 1440 m, 1190 m, 1095 m, 825 m, 800 m, and 715 m cm^{-1}; λ_{max} 388, 380, 294, 288, 250 sh, 240 sh, and 225 sh mμ (log ε 3.99, 3.97, 4.24, 4.23, 4.33, 4.37, and 4.46). *Anal.* Calcd for $C_{14}H_{10}N_4O_2$: C, 63.15; H, 3.79; N, 21.04; O, 12.02. Found: C, 63.01; H, 3.90; N, 20.97; O, 11.82.

Registry No.—**3b**, 7605-67-6; **13**, 7605-68-7; **16**, 7605-69-8; potassium salt of **5**, 7605-70-1; **5**, 7605-71-2; **7**, 1015-89-0; sodium salt of 2-amino-2′-carboxybiphenyl, 7605-73-4; **11**, 7605-74-5; **12**, 727-48-0; **10**, 791-76-4; **14**, 7605-77-8; copper salt of **14**, 7605-78-9; **14**, hydrochloride, 7605-79-0; **18**, 7605-80-3.

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