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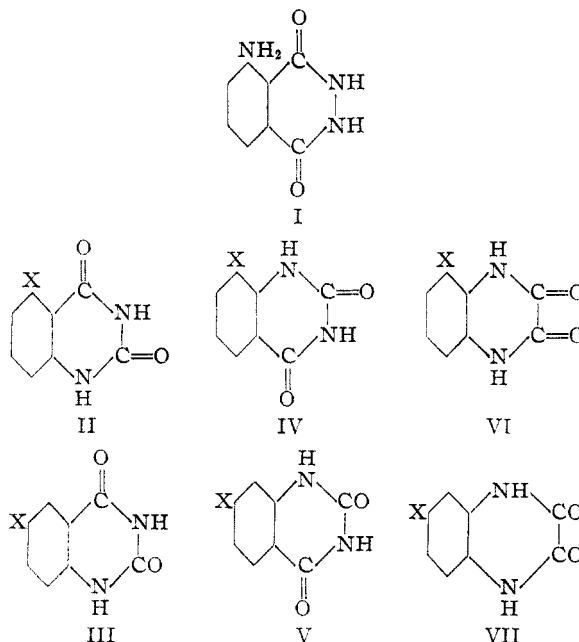
The Synthesis of Aminobenzoyleneureas and of Dihydroxyquinoxalines Isomeric with "Luminol"

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The brilliant chemiluminescence produced during alkaline oxidation of 3-aminophthalhydrazide ("Luminol"³) has long been the subject of investigation by many workers. Some of these workers have been concerned with the influence of structural changes upon the chemiluminescent properties. With such progress as has been made in this direction this paper cannot in general be concerned in detail. However, Drew⁴ has pointed out that since hydrazides in five-membered rings do not show chemiluminescence, a six-membered hetero ring may be essential. It has also been established^{4c} that in 3-aminophthalhydrazide both imino hydrogens of the cyclohydrazide ring must be free to enolize. It does not appear, however, that any attempt has been recorded to show that in the heterocyclic portion of 3-aminophthalhydrazide the two imino groups must be adjacent to each other, *i. e.*, that a hydrazine derivative is imperative for the possession of chemiluminescent properties on oxidation.

The work reported in this paper is primarily concerned with the preparation of certain hitherto unreported compounds isomeric with 3-aminophthalhydrazide and whose carbocyclic nucleus is precisely the same as in "Luminol," but in which although the heterocyclic ring is varied it still retains the characteristic of being a six-membered ring with two potentially enolizable hydrogen atoms. The particular individual compounds thus constituting the primary interest of this work are the two aminobenzoyleneureas II and IV ($X = NH_2$) together with the aminodihydroxyquinoxaline VI ($X = NH_2$). Syntheses of the two other possible aminobenzoyleneureas III and V and the one other possible aminodihydroxyquinoxaline VII ($X = NH_2$) have been

included, although admittedly in them the amino group of the carbocyclic ring is not in the same relationship to the heterocyclic nucleus as in 3-aminophthalhydrazide.



All six of these new compounds have been prepared and characterized. Each amino compound has been obtained by reduction of the corresponding nitro relative. The three nitro compounds corresponding to structure II, IV and V ($X = NO_2$) were obtained from the correspondingly substituted nitroanthranilic acids. The first (II, $X = NO_2$) was prepared by condensation of 6-nitroanthranilic acid with potassium cyanate in acetic acid, the second (IV, $X = NO_2$) and third (V, $X = NO_2$) by fusion of 3-nitro- and of 4-nitroanthranilic acids, respectively, with urea. 6-Nitrobenzoyleneurea (III, $X = NO_2$) was prepared by nitration of benzoyleneurea according to Bogert and Scatchard.⁵

The position of the nitro group in 6-nitrobenzoyleneurea had already been established⁵ by its preparation from methyl 2-(ω -nitrocarbamido)-5-nitrobenzoate. The position of the nitro group in the other three isomers is here estab-

(5) Bogert and Scatchard, *THIS JOURNAL*, **41**, 2058-2059 (1919).

(1) This paper is constructed from part of a dissertation submitted in June, 1941, by Miss Jeanne V. Kitenplon (Mrs. E. K. Gladding) to the Faculty of the Massachusetts Institute of Technology in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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(3) Huntress, Stanley and Parker, *J. Chem. Education*, **11**, 142-145 (1934).

(4) (a) Drew, *Sci. J. Roy. Coll. Sci.*, **8**, 33-38 (1938). (b) Drew and Pearman, *J. Chem. Soc.*, 586-592 (1937). (c) Drew and Garwood, *ibid.*, 1841-1846 (1937).

lished by their mode of preparation from the corresponding anthranilic acids. In the case of 8-nitrobenzoyleneurea (IV, $X = NO_2$) this evidence is also supported by its further nitration to the same 6,8-dinitrobenzoyleneurea previously obtained by nitration of 6-nitrobenzoyleneurea.

All four mononitrobenzoyleneureas are pale yellow crystalline solids with high melting or decomposition points. They are all phenolic in character and are therefore soluble in dilute aqueous alkalis forming deeply colored solutions from which the parent compounds are reprecipitated by carbon dioxide. They are but sparingly soluble in organic solvents.

The four aminobenzoyleneureas (II, III, IV, V, $X = NH_2$) have been obtained by stannous chloride reduction of the corresponding nitro compounds. Their hydrochlorides separated from the hot reduction solution in high purity and no complexes with the reagent have been observed. From the salts the amines were released by dilute ammonia. The free amines are white crystalline solids, some melting at high temperatures, others decomposing before true fusion. The free bases are amphoteric and readily dissolved in dilute aqueous alkalis or carbonates. The presence of the amino group was evidenced by the formation of colored coupling products when the diazotized amines were treated with alkaline β -naphthol.

The results of tests for possible chemiluminescence on oxidation, however, were uniformly negative. No significant light evolution occurred. Formation of highly colored red to brown solutions occurred in all cases and suggested that oxidation was taking place. Since no light was observed, however, and since such colored solutions would be poorly adapted for study if there had been, the nature of the reaction products was not further examined.

Experimental Work

All melting points were taken in a Berl and Kullmann copper block on a 360° rod form melting point thermometer set in the block up to its zero point.

The Nitrobenzoyleneureas

5-Nitrobenzoyleneurea (II, $X = NO_2$).—Potassium cyanate (5.25 g., 0.065 mole) dissolved in water (25 ml.) was added dropwise to a stirred suspension of 6-nitro-2-aminobenzoic acid (9.1 g., 0.05 mole) in water (300 ml.) and glacial acetic acid (4.5 ml., 0.08 mole). After the orange colored solution had been stirred for half an hour, it was treated with flaked sodium hydroxide (80 g., 2 moles) in small portions the temperature being kept below

40° and the alkaline solution allowed to stand overnight in a refrigerator. After removal of any precipitate by filtration the product was precipitated by acidification with sulfuric acid. It separated from these solutions in fine, light yellow crystals or from boiling water in pale tan, thin, regular hexagons. After treatment with decolorizing carbon it was thrice recrystallized from boiling 50% acetic acid; weight, 7.0 g., representing 67% of theoretical; m. p. 339–340° dec. uncor. in sealed tube, 357–358° cor.

Anal. Calcd. for $C_8H_5O_4N_3$: N, 20.3. Found: N, 21.0, 21.1.

5-Nitrobenzoyleneurea is insoluble in ether, benzene, carbon tetrachloride, ligroin, carbon disulfide or toluene; slightly soluble in cold water, ethyl acetate, chloroform or 95% ethanol; moderately soluble in boiling water, boiling 50% acetic acid, methanol, acetone, or pyridine. Its solutions in aqueous sodium hydroxide, sodium carbonate or concentrated ammonium hydroxide are bright yellow, but the compound is precipitated on saturation with carbon dioxide.

5-Nitrobenzoyleneurea N,N'-Dimethyl Ether.—Treatment of 5-nitrobenzoyleneurea (1.03 g., 0.005 mole) dissolved in 5% potassium hydroxide (15 ml.) by shaking with dimethyl sulfate (1.5 g. = 0.010 mole) for half an hour caused evolution of heat and separation of a pale yellow precipitate of the N,N'-dimethyl ether; weight 0.905 g., representing 77% of the theoretical. From boiling 50% ethanol this material separated in fine white needles.

This material was refluxed for twenty minutes with concentrated hydrochloric acid (to hydrolyze any O-ethers) washed with 5% potassium hydroxide, filtered and recrystallized from boiling methanol. Its melting point was 263–265° uncor. (275–277° cor.).

Anal. Calcd. for $C_{10}H_9O_4N_3$: N, 17.9; for $C_{10}H_9O_4N_3 \cdot H_2O$: N, 16.6. Found: N, 16.5, 16.8.

6-Nitrobenzoyleneurea (III, $X = NO_2$).—This was prepared from benzoyleneurea by nitration with a mixture of concentrated sulfuric acid and fuming nitric acid according to the directions of Bogert and Scatchard.⁵ The yield was 86% of theoretical and the product showed a melting point of 315–316° dec. uncor., 331–332° dec. cor. (recorded 330–331° cor.).

6-Nitrobenzoyleneurea-N,N'-dimethyl Ether.—By treatment with dimethyl sulfate exactly as for the 5-nitro isomer, the dimethyl ether was obtained in 85% yield. Although from boiling 50% ethanol this separated in fine white crystals, yet after boiling with concentrated hydrochloric acid (to split any O-ethers) and treatment with potassium hydroxide, recrystallization of the alkali insoluble product from boiling methanol yielded bright yellow needles, melting at 204–205° uncor. (213–214° cor.).

Anal. Calcd. for $C_{10}H_9O_4N_3$: N, 17.9. Found: N, 18.3, 18.5.

7-Nitrobenzoyleneurea (V, $X = NO_2$).—A mixture of 4-nitro-2-aminobenzoic acid (3.0 g., 0.0165 mole) and urea (3.0 g., 0.05 mole) was heated from room temperature to 200° during thirty minutes and then fused at 200° for one hour. The material was contained in a large Pyrex test-tube suspended within an air-bath, the temperature of the melt being measured by a thermometer inserted directly into the fused material.

During fusion ammonia was evolved and a feathery yellow sublimate formed at the top of the test-tube. After cooling the porous yellow-brown mass was washed with water (50 ml.) to remove ammonium salts. The residual solid was then extracted with warm 5% aqueous sodium bicarbonate (50 ml.) followed by warm 10% aqueous sodium carbonate (50 ml.). This treatment converted the 7-nitrobenzoyleneurea into the sparingly soluble sodium salt and removed unchanged 4-nitro-2-aminobenzoic acid or other acidic material. The solid residue was then treated with dilute sulfuric acid (50 ml.) and small amounts of by-product 4-nitro-2-aminobenzamide extracted with boiling methanol (50 ml.) from the free 7-nitrobenzoyleneurea. Crystallization from boiling 50% acetic acid gave fine cream-colored needles; weight 2.6 g. (76% theoretical); m. p. 323° uncor. or 337° cor. dec. in a sealed capillary tube. Further crystallizations from 50% acetic acid accompanied by the use of decolorizing carbon gave lustrous white plates.

For analyses the potassium salt was recrystallized from very dilute potassium hydroxide solution, followed by acidification with 10% acetic acid and final recrystallization from boiling 50% acetic acid.

Anal. Calcd. for $C_8H_5O_4N_3$: N, 20.3. Found: N, 20.4, 20.5.

7-Nitrobenzoyleneurea is slightly soluble in boiling water, cold 95% ethanol, ether or ethyl acetate. It is moderately soluble in boiling methanol, 95% ethanol or pyridine. Its solutions in aqueous alkali are deep yellow and from them 7-nitrobenzoyleneurea is precipitated by carbon dioxide.

A long series of experiments on the influence of time and temperature on this fusion showed clearly that below 170° both 7-nitrobenzoyleneurea and 4-nitro-2-aminobenzamide were formed as a result of which the yields of former were low. At 170° or above, however, no amide was detectable and the yield of 7-nitrobenzoyleneurea was very satisfactory. The best conditions are given above, but a similar fusion at 170° for seven hours gave 67% yield, showing that the temperature rather than prolonged time is the critical governing factor. This was confirmed by the observation that 4-nitro-2-aminobenzamide (1.0 g., 0.006 mole) fused with urea (1.0 g., 0.017 mole) for two hours at 180–200°, gave 35% yield of purified 7-nitrobenzoyleneurea, m. p. 337° dec. cor.

7-Nitrobenzoyleneurea-N,N'-dimethyl Ether.—This was obtained (85% yield) from its parent with dimethyl sulfate and alkali essentially as for the preceding isomers; from boiling methanol it separates in pale yellow needles, m. p. 229–230° uncor.

8-Nitrobenzoyleneurea (IV, X = NO₂).—The preparation of this compound was effected by fusion of 3-nitro-2-aminobenzoic acid with urea according to the general procedure used for the 7-nitro isomer. Both the desired 8-nitrobenzoyleneurea and the by-product 3-nitro-2-aminobenzamide were always formed, their yields varying considerably with fusion temperature, time and proportion of reactants. Conditions were finally established for obtaining satisfactory yields of the 8-nitrobenzoyleneurea, but (unlike the corresponding 7-nitro isomer) it was always accompanied by at least a small amount of the amide from which it had to be separated

A mixture of 3-nitro-2-aminobenzoic acid (5.0 g., 0.0274 mole) and urea (10.0 g., 0.167 mole) was heated at 180–190° (thermometer in melt) for five hours. Ammonia was evolved and a yellow sublimate formed at the mouth of the tube. After cooling the yellow-brown solid was extracted with warm 5% aqueous potassium hydroxide and the filtered solution treated with carbon dioxide until precipitation was completed. The resultant small brown crystals were recrystallized from boiling 50% acetic acid; weight 3.9 g. (68% theoretical); m. p. 263–264° uncor. (272–273° cor.) in a sealed capillary tube.

Anal. Calcd. for $C_8H_5O_4N_3$: N, 20.3. Found: N, 20.0, 20.2.

8-Nitrobenzoyleneurea after three crystallizations from boiling 50% acetic acid using decolorizing carbon was obtained in hard yellow-green prisms. It is moderately soluble in methanol, 95% ethanol, acetone, or pyridine; insoluble in ether, benzene, toluene, carbon tetrachloride or carbon disulfide. Its solutions in cold aqueous sodium hydroxide, sodium carbonate or ammonium hydroxide are yellow but from these the original compound is precipitated by carbon dioxide.

6,8-Dinitrobenzoyleneurea.—8-Nitrobenzoyleneurea (0.90 g. = 0.0043 mole) dissolved in concentrated sulfuric acid (10 ml.) was slowly treated with concentrated nitric acid (6 ml., d. 1.42). After heating the solution at 100° for one hour, cooling, and pouring onto ice, the pale yellow solid was filtered, washed with water and dried at 110°. From boiling 50% acetic acid it separated as light yellow prisms; weight 1.10 g. (100% theoretical); m. p. 263–265° uncor.; recorded,⁶ 274–275° cor. dec.

Anal. Calcd. for $C_8H_4O_6N_4$: N, 22.2. Found: N, 22.1, 22.3.

The melting point of a 50–50 mixture of this product and authentic 6,8-dinitrobenzoyleneurea was not depressed. The melting point of a 50–50 mixture of 8-nitrobenzoyleneurea and either this product or the authentic sample of 6,8-dinitrobenzoyleneurea was depressed to 219–227° uncor.

8-Nitrobenzoyleneurea-N,N'-dimethyl Ether.—8-Nitrobenzoyleneurea (1.03 g., 0.005 mole) dissolved in 5% aqueous potassium hydroxide (15 ml.) first gave a clear red solution which soon solidified to an orange paste. After dilution with water this was shaken for half an hour with dimethyl sulfate (1.5 g., 0.01 mole) at room temperature, then heated at 100° for an hour, cooled and filtered. After washing with water and drying at 100° the crude product weighed 1.035 g. Recrystallization from boiling 50% ethanol gave light tan needles which were refluxed fifteen minutes with concentrated hydrochloric acid (15 ml.), treated with 5% aqueous potassium hydroxide (25 ml.), and finally recrystallized again from boiling methanol; yield, 0.54 g. (45% theoretical); m. p. 217–218° uncor.

Anal. Calcd. for $C_{10}H_9O_4N_3$ (dimethyl ether): N, 17.9. Found: N, 17.8. Calcd. for $C_8H_7O_4N_3$ (monomethyl ether): N, 19.0.

3-Nitro-2-aminobenzamide.—This compound constituted the residue from alkali extraction of the fusion of 3-nitro-2-aminobenzoic acid with urea. From boiling methanol, 95% ethanol or acetone it crystallized in long

⁶ Bogert and Scatchard. *THIS JOURNAL*, **38**, 1612 (1916).

lustrous orange needles, m. p. 226–227° uncor. (234–235° cor.).

Anal. Calcd. for $C_7H_7O_3N_3$: C, 46.4; H, 3.87. Found: C, 46.3, 46.6; H, 3.70.

Its identity was further supported by hydrolysis on long boiling with either dilute sodium hydroxide or 6 *N* hydrochloric acid which gave 3-nitro-2-aminobenzoic acid and ammonia. Furthermore, on refluxing with acetic anhydride followed by warming of the intermediate 3-nitro-2-acetylaminobenzoic acid with 5% aqueous potassium hydroxide, treatment with carbon dioxide precipitated 8-nitro-2-methyl-4-ketodihydroquinazoline in 36% yield. After recrystallization from boiling 50% acetic acid this separated as hard brown-red crystals; m. p. 260–261° dec. uncor. (267–268° dec. cor.); recorded,⁷ m. p. 264° dec. Finally it was observed that 3-nitro-2-aminobenzamide (4.0 g., 0.022 mole) fused with urea (8.0 g., 0.134 mole) for five hours at 200° gave 8-nitrobenzoyleurea (4.0 g. or 87.0% theoretical), m. p. 262–263° uncor. (271–272° cor.).

3-Nitro-2-aminobenzoic Acid.—This compound was prepared in two ways, *viz.*, by oxidation of 3-nitro-2-aminotoluene and by Hofmann degradation of 3-nitrophthalamic-2-acid-1.

The first sequence started with 3-nitro-*o*-toluidine, converted⁸ it to 3-nitro-2-acetylaminotoluene (91% yield), m. p. 156° uncor. (recorded⁸ 156°), oxidized⁸ with neutral potassium permanganate to 3-nitro-2-acetylaminobenzoic acid (74% yield), and finally by hydrolysis with boiling 50% sulfuric acid gave 3-nitro-2-aminobenzoic acid (87% yield), m. p. 202–203° uncor. (recorded, 205°, 208–9°).⁹ The over-all yield by this method was therefore 58.6%.

The alternative procedure started from 3-nitrophthalic acid, converted¹⁰ it to the anhydride (78% yield), ammonolyzed in warm concentrated ammonium hydroxide to 3-nitrophthalamic-2-acid-1 (70% yield), followed by Hofmann degradation⁹ to 3-nitro-2-aminobenzoic acid (90% yield), m. p. 201–203° uncor. By this sequence the over-all conversion of 3-nitrophthalic acid to the 3-nitroanthranilic acid was 48%.

6-Nitro-2-aminobenzoic Acid.—This was prepared by starting with 3-nitrophthalic acid, converting it to the acid ammonium salt in 100% yield, fusing this at 235–250°¹¹ to obtain 94% yield of 3-nitrophthalimide, converting this imide to 6-nitrophthalamic-2-acid-1 by solution in 2 equivalents of 0.5 *N* sodium hydroxide and precipitation at 0° with excess concentrated hydrochloric acid (yield 76%), and finally degrading the amide group to amino (90% yield) via the Hofmann method as employed by Kahn.¹² The over-all yield of this preparation thus represented 64.3% of the theoretical and gave a product melting at 181° dec. uncor.

The Aminobenzoyleureas

All four isomeric nitrobenzoyleureas on reduction with stannous chloride in boiling concentrated hydrochloric

acid gave the corresponding aminobenzoyleureas in the form of their hydrochlorides. These were all sparingly soluble in the excess acid and separated during the reduction. No tin double salts were observed. The general method was based upon the procedure reported¹³ for the reduction of 6,8-dinitrobenzoyleurea. It was worked out specifically for the reduction of 6-nitrobenzoyleurea (see below) and applied without change to the other isomers.

5-Aminobenzoyleurea (II, $X = NH_2$).—The hydrochloride separated in very fine white needles from the hot concentrated hydrochloric acid solution. It was also sparingly soluble in cold water. When dissolved in boiling water and treated with ammonium hydroxide, the free base separated in pale green needles which after four recrystallizations from hot water (using decolorizing carbon) became lustrous white needles, m. p. 284° dec. uncor. (295° dec. cor.), in sealed capillary tubes. The yield of amine hydrochloride was 71% theoretical.

Anal. Calcd. for $C_8H_7O_2N_3$: N, 23.7. Found: N, 24.4, 24.6.

The free base was somewhat soluble in hot water, methanol, ethanol or ethyl acetate, the solutions possessing a purple fluorescence. The base is also soluble in dilute sodium hydroxide, dilute sodium carbonate, or concentrated ammonium hydroxide and these solutions were pale yellow. Diazotization of the amine and coupling with alkaline β -naphthol gave a deep brown-red solution.

6-Aminobenzoyleurea (III, $X = NH_2$).—6-Nitrobenzoyleurea (10.5 g., 0.05 mole) was added gradually to a boiling solution of stannous chloride dihydrate (50 g., 0.22 mole) in concentrated hydrochloric acid (160 ml.). After refluxing for four hours the mixture was cooled, the insoluble amine hydrochloride filtered, washed with water, and dried at 110°. To remove any occluded tin salts this material was refluxed with concentrated hydrochloric acid (40 ml.) for fifteen minutes, water (40 ml.) was added, and the mixture boiled five minutes more. The amine hydrochloride separated in fine light tan needles, weight 9.8 g. (91% theoretical).

This salt is only sparingly soluble in cold water, cold dilute acids or hot concentrated hydrochloric acid. When dissolved in a large volume of freshly boiled water (to avoid oxidation) and ammonium hydroxide added to the boiling solution, the free base separated in pinkish-tan needles, which after three recrystallizations from boiling water (using decolorizing carbon) separated as fine lustrous white needles. This base does not show a melting point, but becomes black above 330°.

Anal. Calcd. for $C_8H_7O_2N_3$: N, 23.7. Found: N, 24.0, 24.2.

The free base was only slightly soluble in cold water, but moderately soluble in hot water, in methanol or 95% ethanol. Its alcoholic solutions showed a green fluorescence. Solutions of the amine in dilute aqueous sodium hydroxide, 10% sodium carbonate or in concentrated ammonium hydroxide were light yellow. Diazotization of the amine and coupling with alkaline β -naphthol gave deep red solutions.

7-Aminobenzoyleurea (V, $X = NH_2$).—The hydrochloride separated in fine light tan needles from boiling

(7) Zacharias, *J. prakt. Chem.*, [2] **48**, 441 (1891).

(8) James, Kenner and Stubbings, *J. Chem. Soc.*, **117**, 775 (1920).

(9) Chapman and Stephens, *ibid.*, 1795 (1925).

(10) Nicolet and Bender, *Organic Syntheses*, Coll. Vol. I, (1932), p. 402.

(11) Bogert and Boroschek, *THIS JOURNAL*, **23**, 747 (1901).

(12) Kahn, *Ber.*, **35**, 3863 (1902); *cf.* Bogert and Chambers, *THIS JOURNAL*, **27**, 652–653 (1905).

(13) Ref. 5, p. 2060.

concentrated hydrochloric acid. This salt was also sparingly soluble in either cold or hot water. The yield of hydrochloride was 90% theoretical.

The free base was obtained from boiling water as a white flocculent precipitate from hot water. Above 200° it colored yellow, but did not melt up to 350°.

Anal. Calcd. for $C_8H_7O_2N_3$: N, 23.7. Found: N, 24.0, 24.1.

The amine is almost insoluble in cold water, slightly soluble in boiling water, or in methanol, 95% ethanol, acetone or pyridine. Solutions in concentrated sulfuric acid had a purple fluorescence. Diazotization and coupling with alkaline β -naphthol gave a deep red solution.

8-Aminobenzoyleneurea (IV, X = NH₂).—By the stannous chloride method the base hydrochloride separated from the boiling solution in light tan needles (55% yield). This hydrochloride was sparingly soluble in cold water or in either hot or cold concentrated hydrochloric acid; it was moderately soluble in hot water.

When its solution was treated with dilute ammonium hydroxide and saturated with carbon dioxide, the free base was precipitated in light tan needles, purified by recrystallization from boiling water, m. p. 270–272° dec. uncor. (279–281° cor.).

The free base was also obtained by reduction of a glacial acetic acid solution of 8-nitrobenzoyleneurea in the presence of Adams catalyst with hydrogen at atmospheric pressure, yield 40% of the theoretical.

Diazotization of this amine yielded a clear yellow solution which with aqueous alkali turned a yellow-brown and with alkaline β -naphthol gave a heavy yellow-green precipitate.

The Nitro- and Amino-2,3-dihydroxyquinoxalines

5-Nitro-2,3-dihydroxyquinoxaline (VI, X = NO₂).—3-Nitro-*o*-phenylenediamine (2.03 g., 0.0132 mole) was treated with diethyl oxalate (25 ml.). The solid diamine slowly became red-orange and heat was evolved but solution did not occur. The mixture was therefore refluxed until (after about two hours) its color had faded. After heating about five minutes a heavy precipitate of lustrous tan plates separated. After cooling the solid was filtered, washed with alcohol and dried at 100°. After three recrystallizations from boiling 50% acetic acid (using decolorizing carbon) the product was obtained in fine bright yellow plates, m. p. 284° dec. uncor. (295° dec. cor.) in sealed capillary tubes, weight 1.60 g. (60% theoretical).

Anal. Calcd. for $C_8H_5O_4N_3$: N, 20.3. Found: N, 19.8, 19.6.

The compound was only slightly soluble in benzene, toluene, ether, chloroform, carbon tetrachloride or carbon disulfide; was moderately soluble in methanol, 95% ethanol, acetone, ethyl acetate or pyridine. From its deep red solutions in dilute sodium hydroxide, potassium carbonate or concentrated ammonium hydroxide, carbon dioxide precipitated the free base.

6-Nitro-2,3-dihydroxyquinoxaline (VII, X = NO₂).—4-Nitro-*o*-phenylenediamine (7.15 g., 0.0465 mole) mixed with anhydrous oxalic acid (10.7 g., 0.12 mole) was finely powdered, placed in a Pyrex test-tube, the latter arranged for heating in an air-bath. After slowly raising the temperature of the melt to 150°, it was maintained for one

hour, then raised to 180–200° for another hour. After cooling the light brown to black product was extracted with warm 5% aqueous sodium hydroxide from which red solution carbon dioxide precipitated small brown crystals. After four recrystallizations from boiling 50% acetic acid (using decolorizing carbon) the product separated in clusters of white needles, m. p. 329–330° dec. uncor. (343–344° dec. cor.) both in sealed capillary tubes. The yield was 7.1 g. (73% theoretical).

Anal. Calcd. for $C_8H_5O_4N_3$: N, 20.3. Found: N, 19.6.

This compound was moderately soluble in methanol, 95% ethanol, ethyl acetate, acetone or pyridine; it was almost insoluble in ether, benzene, toluene, chloroform, carbon tetrachloride or petroleum ether. Its solutions in dilute aqueous sodium hydroxide, potassium carbonate or concentrated ammonium hydroxide were deep orange-red and from these carbonation precipitated the parent compound.

The Amino-2,3-dihydroxyquinoxalines

5-Amino-2,3-dihydroxyquinoxaline (VI, X = NH₂).—5-Nitro-2,3-dihydroxyquinoxaline (1.6 g., 0.008 mole) suspended in a solution of sodium sulfide (nonahydrate) (5 g. = 0.021 mole) in water (25 ml.) was refluxed for one and one half hours. The deep orange suspension gradually dissolved, yielding a clear brown solution. After cooling the solution was strongly acidified, boiled and filtered (to remove free sulfur). Upon neutralization with sodium bicarbonate the flocculent orange precipitate was filtered. After two recrystallizations from boiling water the amine separated in fine light-yellow crystals, blackening at 336° uncor. with decomposition about 344° uncor. in sealed m. p. tubes. The yield was 0.6 g. (44% theoretical). This compound was also prepared by stannous chloride reduction.

Anal. Calcd. for $C_8H_7O_2N_3$: N, 23.7. Found: N, 23.1, 22.9.

Diazotization in hydrochloric acid yielded a clear yellow solution which with alkali turned clear brown and with alkaline β -naphthol gave a yellow-green precipitate.

6-Amino-2,3-dihydroxyquinoxaline (VII, X = NH₂).—6-Nitro-2,3-dihydroxyquinoxaline (5.0 g., 0.024 mole) suspended in a solution of sodium sulfide crystals (20 g., 0.083 mole) in water (100 ml.) was refluxed for two hours, yielding a deep red solution which gradually turned brown. After cooling and diluting with 100 ml. of water, and strongly acidifying with hydrochloric acid, the solution was boiled and filtered from sulfur. Addition of sodium bicarbonate precipitated the free amine as flocks of pale yellow microscopic needles. On heating the compound becomes black at about 330°, but does not melt up to 350°. The yield was 3.22 g. (75% theoretical).

Because the amine is insoluble in almost all ordinary solvents, it cannot be satisfactorily crystallized and analyses are low.

Anal. Calcd. for $C_8H_7O_2N_3$: N, 23.7. Found: N, 23.3, 23.1.

The amine hydrochloride is moderately soluble in either cold or hot water, but the sulfate is sparingly soluble in cold though moderately soluble in hot water. The amine dissolves in aqueous sodium or potassium hydroxides.

sodium carbonate or concentrated ammonium hydroxide to give clear yellow-brown solutions from which the base is reprecipitated by carbon dioxide.

Aqueous solutions of the salts give with ferric chloride a clear blue color. Diazotization and treatment with alkaline β -naphthol gives a deep red solution.

Test for Chemiluminescence.—The four aminobenzoyleureas and the two amino-2,3-dihydroxyquinoxalines were tested at 28° for possible chemiluminescence on oxidation by visual observation in a dark room. A 10-ml. sample of a 0.04 molar solution of each compound in 0.5 *N* sodium hydroxide was successively treated with 1 ml. of 3% hydrogen peroxide, 1 ml. of 3% potassium ferricyanide. In a second series of tests each 10-ml. sample was treated first with a trace of the catalytic salicylaldehyde ethylenedimine ferric chloride complex,¹⁴ followed by 1 ml. of 3% hydrogen peroxide. In a third series

(14) Thielert and Pfeiffer, *Ber.*, **71**, 1401 (1938).

of tests each 10-ml. sample was treated with 10 ml. of 8% sodium hypochlorite solution.

Summary

1. All four isomeric aminobenzoyleureas and both possible amino-2,3-dihydroxyquinoxalines have been prepared by reduction of the corresponding nitro compounds.

2. None of them shows significant chemiluminescence under conditions which with the isomeric 3-aminophthalhydrazide give intense effects.

3. Previous assumption regarding the indispensability of the hydrazine residue for chemiluminescent power has thus been demonstrated.

CAMBRIDGE, MASS.

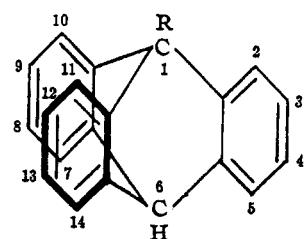
RECEIVED MAY 14, 1942

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

Triptycene¹ (9,10-*o*-Benzenoanthracene)

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Previous publications from this Laboratory have brought out the special properties of substituents located on the bridgehead of a bicyclic ring system.² These findings would lead us to



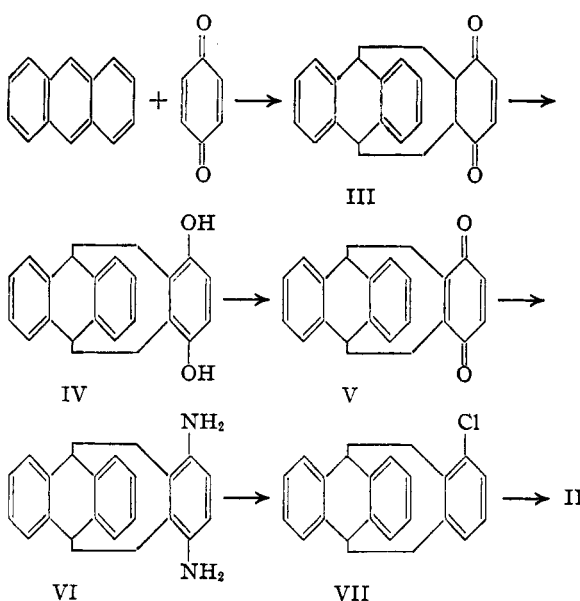
I, R absent

II, R = H

predict that the analog (I) of the triphenylmethyl radical in which the ortho positions of the three phenyl groups are united to a common CH should have much less tendency to exist as a free radical than triphenylmethyl itself, as a result of its inability to assume the coplanar form demanded by the usual resonance structures.³ With the eventual purpose of testing this prediction we have prepared the parent hydrocarbon II (9,10-*o*-benzenoanthracene, or tribenzobicyclo(2,2,2)octatriene) and studied some of its chemical properties. For

convenience, the name "triptycene" is suggested for this symmetrical hydrocarbon.¹

The steps in the synthesis of triptycene are as follows



The removal of the functional groups was achieved only after very many unsuccessful attempts. We tried to dehydroxylate the hydroquinone IV with zinc dust, to convert it into a dibromide or diiodide with phosphorus halides, to reduce the quinone by hydrogenation, by the

(1) This name is proposed because the shape of this ring system suggests the triptych of antiquity, which was a book with three leaves hinged on a common axis. We are indebted to Professor Mason Hammond of the Harvard Department of Classics for this suggestion.

(2) Bartlett and Knox, *THIS JOURNAL*, **61**, 3184 (1939); Bartlett and Cohen, *ibid.*, **62**, 1183 (1940); Bartlett and Woods, *ibid.*, **62**, 2933 (1940).

(3) Pauling and Wheland, *J. Chem. Phys.*, **1**, 362 (1933).