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PRODUCTS OF NUCLEOPHILIC DISPLACEMENT REACTIONS IN THE ANTHRAQUINONE SERIES

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Abstract—Several unusual products are described, obtained from the reactions of 1-chloro-2-nitroanthraquinone, 2-bromo-3-nitroanthraquinone, etc with hydrazine, acylhydrazines, pyridine, 2-aminopyridine and toluenesulfonamide.

ALTHOUGH the displacement of either a halogen atom or a sulfo or nitro group from anthraquinone compounds by various reagents (particularly amines) is well known, relatively little has been reported concerning such reactions upon halonitroanthraquinones. The halogen atom of 1,5- or 1,8-chloronitroanthraquinones is displaced upon reaction[1] with *p*-toluenesulfonamide, as are, reportedly, those of 1,5-dichloro-4,8-dinitro- and 1,8-dichloro-4,5-dinitroanthraquinones upon treatment[2] with diethylamine, although in the latter two compounds the nitro groups also were displaced under more vigorous conditions, or upon reaction[3] with *p*-toluidine. Both the chlorine and the nitro group of 1-chloro-4-nitroanthraquinone were displaced[4] by *p*-toluidine, whereas only the chlorine was displaced by 1-amino-4-nitroanthraquinone.[5] Replacement of the chlorine atom was reported[6] in the reaction of 1-chloro-2-nitroanthraquinone with sodium acetate, diethylamine or 2-aminoanthraquinone, while aniline displaced the nitro group of 1-nitro-2-chloroanthraquinone.

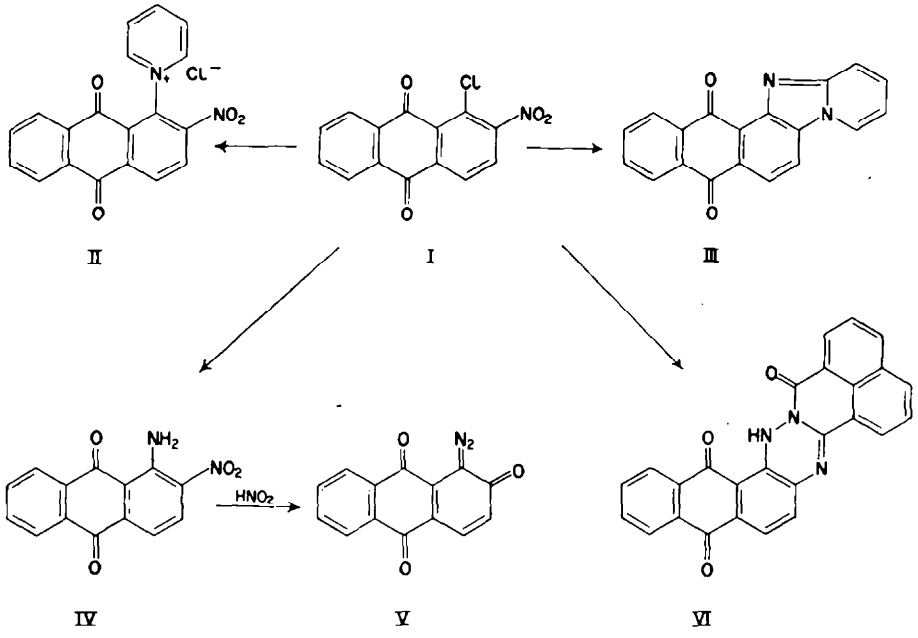
With halonitroanthraquinones now conveniently available[7] via the peracetic acid oxidation of aminohaloanthraquinones, we began a study of their reactions with nucleophilic reagents, particularly those capable of forming more complex products, and those leading to selective displacement.

A. Reactions of 1-chloro-2-nitroanthraquinone

When 1-chloro-2-nitroanthraquinone[7] (I) was heated in pyridine, the quaternary salt II was formed rapidly. While many halogen compounds react in this manner with pyridine, this reaction in the anthraquinone series is apparently novel. Even anthraquinones containing an "activated" halogen (e.g. 2-carbomethoxy-1-chloroanthraquinone or 1-chloro-2-cyanoanthraquinone) give no sign of reaction when heated briefly in pyridine. We therefore attempted the preparation of III, since it was known[8] that 2,4-dinitrochlorobenzene reacts readily with 2-aminopyridine to yield 3-nitropyrido[1,2-*a*]benzimidazole. In amyl alcohol, no reaction occurred

[1] F. Ullman and P. Kertész. *Ber. Dtsch. Chem. Ges.* **52**, 545 (1919).
[2] Bayer, *Ger. Pat.* 137,782; *Frdl.* **6**, 1304 (1904).
[3] Bayer, *Ger. Pat.* 127,458/9; *Frdl.* **6**, 363/4 (1904).
[4] Bayer, *Ger. Pat.* 126,803; *Frdl.* **6**, 362 (1904).
[5] Meister, Lucius and Brüning, *Ger. Pat.* 254,186; *Frdl.* **11**, 614 (1915).
[6] W. Bradley and E. Leete, *J. Chem. Soc.* 2129 (1951).
[7] W. L. Mosby and W. L. Berry, *Tetrahedron* **5**, 93 (1959).
[8] G. Morgan and J. Stewart, *J. Chem. Soc.* 1057 (1939).

between I and 2-aminopyridine, and in dichlorobenzene decomposition supervened. However, in glycol diacetate, a low yield of III was produced.



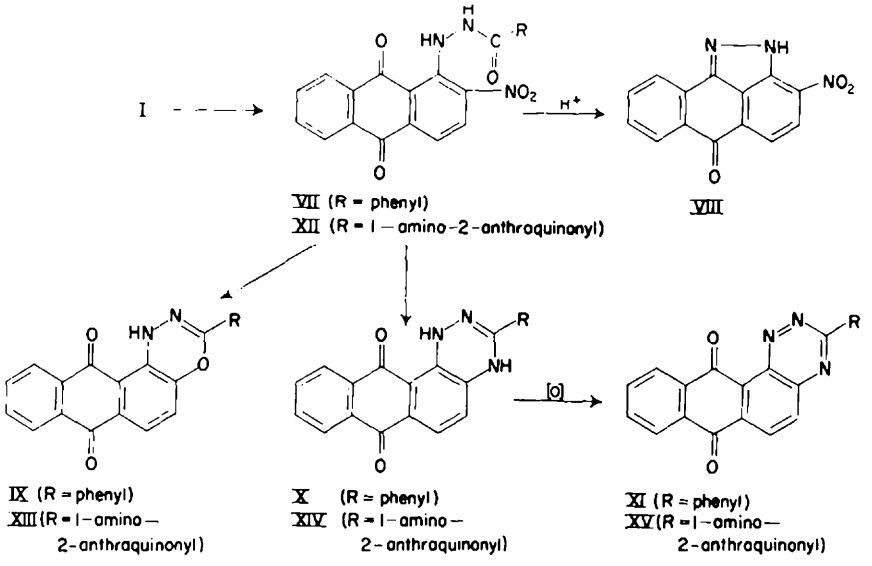
The reaction of I with *p*-toluenesulfonamide readily afforded the toluenesulfonamido intermediate from which the amine IV was obtained upon hydrolysis. Compound IV has been obtained, together with the 1,4-isomer, by the nitration of 1-aminoanthraquinone[9] or 1-anthraquinonylurethane,[10] and by the peracetic acid oxidation of 1,2-diaminoanthraquinone.[11] Treatment of IV with nitrous acid produced the diazo oxide V, which, because of its instability, could not be obtained analytically pure. However, the infrared spectrum of the compound and its ability to couple with H-acid indicate its structure.

When I was allowed to react with N-aminonaphthalimide,[12] N-(2-nitro-1-anthraquinonylamino)naphthalimide was formed. Reduction of the nitro group with sodium sulfide (or upon vatting) was accompanied by closure of the 1,2,4-triazine ring to yield the deep blue product VI.

The reaction of I with benzhydrazide afforded VII, which underwent acidic hydrolysis to yield VIII. Heating VII with potassium hydroxide in methyl Cellosolve produced two products: the oxadiazine IX, and 1-benzoylhydrazino-2-(2-methoxyethoxy)-anthraquinone formed by displacement of the nitro group by the solvent.

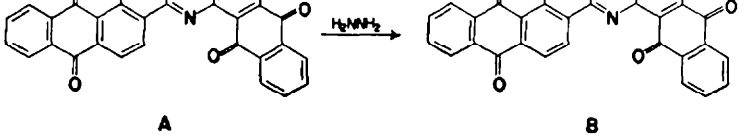
[9] Badische Anilin- und Sodafabrik, *Ger. Pat.* 279,866; *Frdl.* **12**, 419 (1917).
[10] Bayer & Co. *Ger. Pat.* 167,410; *Frdl.* **8**, 297 (1908).
[11] I. G. Farbenindustrie, A. G., *P.B, Report No.* 70341, frame 14040.
[12] Previously prepared by heating naphthalic anhydride with hydrazine in ethanol[13] or aqueous acetic acid.[14] These solvents offer disadvantages in preparing more than small amounts of material however, and we found aqueous pyridine[15] or, better still, dimethylformamide to give superior results. The use of glacial acetic acid as a solvent produced only N-acetamidonaphthalimide.
[13] A. Bistrzycki and J. Risi, *Helv. Chim. Acta* **8**, 810 (1925).
[14] A. Ostrogovich and M. Mihailescu, *Gazz. Chim. Ital.* **41**, II, 757 (1912); *Chem. Zentr.* I, 813 (1912).
[15] K. Wilke, *P.B. Report No.* 70339, frame 10986.

Treatment of VII with aqueous sodium sulfide gave the deep blue dihydrotriazine X, which was easily oxidized to XI. An analogous reaction sequence was completed from XII (obtained by reacting I with 1-amino-2-anthraquinone carbohydrazide[16]). Attempts to purify XII by recrystallization, produced compound XIII, and the latter accompanied XIV in the reduction of XII with sodium sulfide. Possibly catalytic hydrogenation would have given superior results, but this was not investigated.

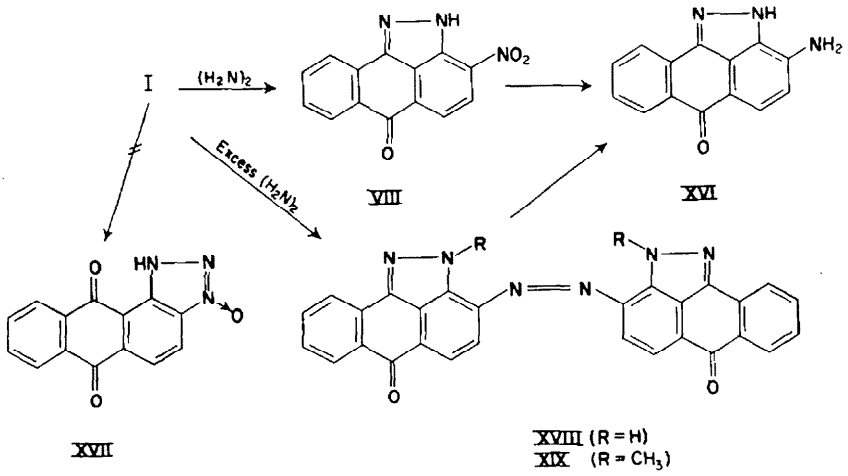


The conversion of VII and XII into X and XIV is similar to the method employed by Bischler[17,18] for the synthesis of benzo-1,2,4-triazine and its 3-methyl homolog. Despite its simplicity, the method does not appear to have been used since, with one exception. Raab[19] described the preparation of the 5-chloro homolog of X from the reaction of 2-benzamido-1,3-dichloranthraquinone with hydrazine. With this exception, anthra-[2,1-*e*][1,2,4]triazines and anthra[1,2-*e*][1,3,4]oxadiazines have not previously been described, although 2-(2-anthraquinonyl)-[1,2,4]triazines were prepared[20,21] recently.

[16] F. Ebel and R. Randebrock, *U.S. Pat.* 2,717,898.
[17] A. Bischler, *Ber. Dtsh. Chem. Ges.* **22**, 2801 (1889).
[18] A. Bischler and S. Brodsky, *Ber. Dtsch. Chem. Ges.* **22**, 2809 (1889).
[19] H. Raab, *P.B. Report No.* 70339, frame 11446.
[20] P. V. Laakso, R. Robinson and H. P. Vandrewala, *Tetrahedron* **1**, 103 (1957).
[21] In the preparation of the "anhydride" of 1-amino-anthraquinone-2-carboxylic acid[20] no structure was shown, although G. Stein [*P.B. Report No.* 70340, frame 12853] indicated the anhydride to have structure A. This suggests structure B for the product of "unknown identity" obtained[20] by treating A with hydrazine. This possibility is strengthened by recent work [N. S. Dokunikhin and I. D. Pletneva, *Zh. Obschei Khim.* **28**, 1019 (1958)] demonstrating the preparation of anthra[1,2-*d*]pyrimidones from anthra[1,2-*d*][1,3]oxazinones.



Next, the reactions of I with hydrazine were examined. Although 1-hydrazino-2-nitroanthraquinone undoubtedly is formed, only products of its further reaction were isolated. The addition of two molar equivalents of hydrazine to a solution of I in dimethylformamide afforded an excellent yield of 3-nitropyrazolanthrone (VIII). Reduction of VIII yielded XVI, which also was prepared from 2-benzamido-1-chloroanthraquinone. Structure XVII, initially considered along with VIII for the reaction product, seems unlikely in view of (1) similarities between the infrared spectrum of this product and those of other pyrazolanthrones, and (2) the reduction under mild conditions to XVI, unlikely to occur in the case of XVII. The reaction of I with less than two moles of hydrazine hydrate gave mixtures of I and VIII.



Treatment of I with an excess of hydrazine (ten moles) produced a different product. Microanalyses indicated the empirical formula $C_{14}H_7N_3O$, and alkaline reduction yielded XVI. The deep blue color of the vat solution of this substance recalled the colors of the vat solutions of the N,N′-dialkyl-3,3′-bispyrazolanthronyls,[22] and particularly of the N,N′-dimethyl-3,3′-vinylenebispyrazolanthronyls.[23] The product formed a copper chelate derivative when treated with cupric acetate in dimethylformamide. Accordingly, structure XVIII was assigned to the product Methylation of XVIII yielded XIX.

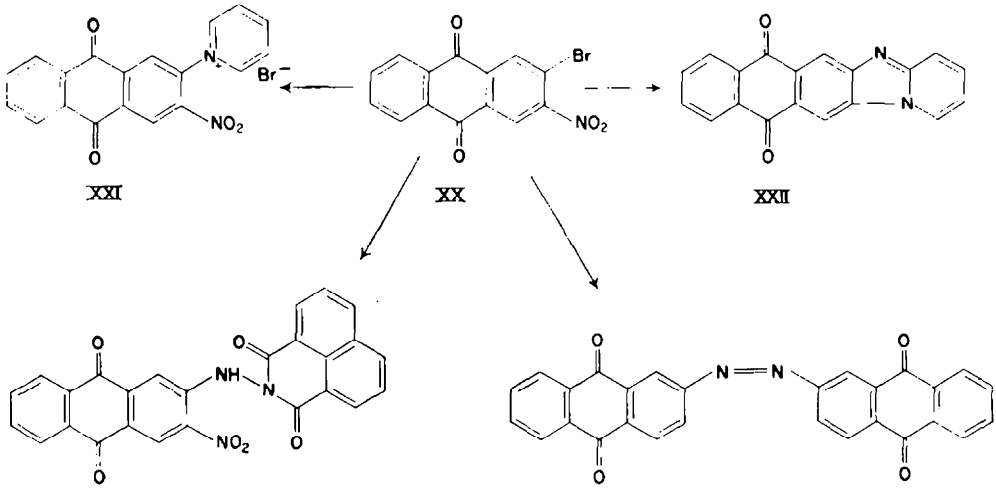
B. Reactions with 2-bromo-3-nitroanthraquinone

Heating 2-bromo-3-nitroanthraquinone[7] (XX) with pyridine readily afforded the pyridinium salt XXI, while with 2-aminopyridine, the linear quinone XXII resulted. The reaction of XX with *p*-toluenesulfonamide, followed by hydrolysis of the resulting toluenesulfonamido intermediate, yielded 2-amino-3-nitroanthraquinone. This compound has been obtained previously, together with other products, by the nitration of 2-amino-anthraquinone[24] or 2-anthraquinonylurethane.[25]

When XX was condensed with N-aminonaphthalimide, compound XXIII was obtained. However, reduction of this product (by vatting) did not produce the

[22] W. Bradley and K. W. Geddes, *J. Chem. Soc.* 1636 (1952).
[23] G. Kalischer and H. Scheyer, *Ger. Pat.* 517,845; *Frdl.* 17, 1275 (1932).
[24] R. Scholl, G. Schneider and F. Eberle, *Ber. Dtsch. Chem. Ges.* 37, 4427 (1904).
[25] F. Ullman and R. Medenwald, *Ber. Dtsch. Chem. Ges.* 46, 1798 (1913).

linear analog of compound VI, but gave only 2,3-diaminoanthraquinone. The reasons for cleavage of the hydrazide in this instance, but not in the case of the angular isomer, are not apparent.



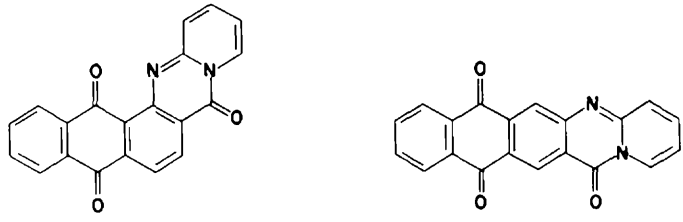
XXI XX XXII

XXIII XXIV

Another anomalous reaction appeared when XX was treated with hydrazine. The major product formed was 2-amino-3-bromoanthraquinone, but a halogen-free by-product also was isolated. Upon the bases of microanalyses and infrared spectrum, structure XXIV was assigned tentatively to this substance.

C. Miscellaneous

Reaction of 2-chloro-1-nitroanthraquinone[7] with benzhydrazide occurred slowly, and always yielded mixtures of the chloronitroanthraquinone with N′-(2-chloro-anthraquinonyl)-benzhydrazide. Treatment of the latter substance with sulfuric acid afforded 3-chloropyrazolanthrone.



XXV XXVI

In the course of these studies, a number of other displacement reactions were run. Three of these, although not involving halonitroanthraquinones, may be reported here. The reaction of 2-carbomethoxy-1-chloroanthraquinone[26] with 2-aminopyridine yielded a product assigned structure XXV, insomuch as the condensation of 2-chlorobenzoic acid with 2-aminopyridine has been reported[27,28] to

[26] F. Ullmann and H. Bincer, *Ber. Dtsch. Chem. Ges.* **49**, 732 (1916).
[27] O. A. Seide, *Liebigs Ann.* **440**, 311 (1924).
[28] O. A. Seide and G. W. Tschelinzew, *J. Gen. Chem. U.S.S.R.* **7**, 2314 (1937); *Chem. Zentr.* I, 601 (1938).

yield 11*H*-pyrido[1,2-*b*]quinazol-11-one. An attempt to prepare XXVI by an analogous reaction with 2-carbomethoxy-3-chloroanthraquinone, gave only dark decomposition products, although the reactivity of the chlorine atom in this ester was demonstrated by its displacement with *p*-toluenesulfonamide.

EXPERIMENTAL

1-(2-Nitro-1-anthraquinonyl)-pyridinium chloride (II). A slurry of 1·44 g 1-chloro-2-nitroanthraquinone[7] (I) in 25 ml dry pyridine was heated rapidly to the boil. The resulting clear brown solution quickly deposited a yellow precipitate. The mixture was cooled and the solid was filtered and washed with pyridine and ethyl acetate. The yield of greenish-yellow product was 1·64 g (89·5%). Crystallization from a methanol–ethyl acetate mixture gave 1·20 g m.p. 214–216° d.

(Found: C, 61·70; H, 2·88; Cl, 9·85; N, 7·41; O, 17·63. Calc. for $C_{19}H_{11}ClN_2O_4$: C, 62·21; H, 3·00; Cl, 9·68; N, 7·43; O, 17·44%).

8H,13H-Anthra[1',2',4,5]imidazo[1,2-a]pyridine-8,13-dione (III). A mixture of 1·44 g I, 0·47 g 2-aminopyridine, a few mg cupric acetate and 10 ml glycol diacetate was stirred and boiled under reflux for 3 hr. A dark solid deposited and nitrous fumes were evolved. The mixture was cooled, and the solid was separated, washed with ethyl acetate and dried, giving 0·60 g of dark product. Vacuum sublimation afforded 0·25 g (16·8% yield) of orange needles m.p. >360°, which gave a red vat solution.

(Found: C, 76·47; H, 3·44; N, 8·94; O, 10·81. Calc. for $C_{19}H_{10}N_2O_2$: C, 76·50; H, 3·36; N, 9·40; O, 10·72%).

1-Amino-2-nitroanthraquinone (IV). A mixture of 5·80 g I, 5·00 g *p*-toluenesulfonamide, 1·70 g anhydrous sodium acetate, 0·50 g cuprous chloride and 150 ml amyl alcohol was stirred and heated at 125° for 6 hr, then was cooled, diluted with petroleum ether and filtered. The dry toluenesulfonamido derivative was dissolved in 50 ml conc H_2SO_4 and the solution warmed on a steam bath for ½ hr, then poured onto ice and filtered. The bright red solid was washed well and dried. Crystallization from acetic acid gave 4·05 g (72·5% yield) of red needles, m.p. 226–228°. A further crystallization from acetic acid raised the m.p. to 228–229·5° (lit[11] 223°).

(Found: C, 62·53; H, 2·85; N, 10·55; O, 24·28. Calc. for $C_{14}H_8N_2O_4$: C, 62·65; H, 3·01; N, 10. 45; O, 23·85%).

Antraquinone-1-diazo-2-oxide (V). To a solution of 3·00 g 1-amino-2-nitroanthraquinone in 10 ml H_2SO_4 was added 1·10 g powdered sodium nitrite. The solution was then heated at 60° for 6 hr. Dilution with ice gave 2·50 g (100% yield) or orange product, having $\lambda\lambda$ 4·70, 5·98 and 6·01 μ. As the diazo oxide proved sensitive to heat and light, it could not be purified for analysis.

(Found: C, 65·09; H, 2·55; N, 11·98. Calc. for $C_{14}H_6N_2O_3$: C, 67·20; H, 2·44; N, 11·20%).

N-Aminonaphthalimide. To a stirred solution of 10·0 g commercial naphthalic anhydride in 50 ml hot dimethylformamide, was added (as rapidly as the vigor of the reaction permitted) a solution of 5 ml 85% hydrazine hydrate in 10 ml dimethylformamide. A thick slurry formed immediately. The cold mixture was filtered and the solid was washed with ethanol and water, and dried. The yield was 8·97 g (84%) of yellow crystals, m.p. 262–264°. Crystallization from dimethylformamide raised the melting point to 264–266° (lit[13] 262°); λ_{max}^{EtOH} 236·5 and 333 mμ (log ε 4·63 and 4·13); $\lambda\lambda$ 3·00, 3·16 and 6·00 μ.

N,N-Naphthaloyl-N'-(2-nitro-1-anthraquinonyl)-hydrazine. A slurry of 1·50 g I, 1·25 g N-aminonaphthalimide,[11] 0·41 g sodium acetate, 0·10 g cuprous chloride and 75 ml amyl alcohol was stirred and boiled under reflux for 1·5 hr then cooled and filtered. The solid was crystallized from chlorobenzene to give 1·40 g (58% yield) of orange microneedles, m.p. 305–315°. A portion for analysis, recrystallized from chlorobenzene, melted at 314–315°.

(Found: C, 67·32; H, 2·66; N, 8·89. Calc. for $C_{26}H_{13}N_3O_6$: C, 67·39; H, 2·86; N, 9·08%).

10H, 15H, 16H, 18H-Anthra[2,1-e]benz[4,5]isoquinolo[2,1-b]-[1,2,4]triazine-10, 15, 18-*trione* (VI). To a solution of 2·0 g sodium sulfide nonahydrate in 40 ml pyridine and 60 ml water, was added 1·00 g N,N-naphthaloyl-N'-(2-nitro-1-anthraquinonyl)-hydrazine, and the mixture was boiled under reflux for 2 hr. The cooled mixture was filtered giving 0·60 g (66% yield) of blue solid, m.p. >360°. The product was purified by solution in sulfuric acid and precipitation with water.

(Found: C, 73·48; H, 2·95; N, 9·82; O, 12·63. Calc. for $C_{26}H_{13}N_3O_3$: C, 75·15; H, 3·15; N, 10·14; O, 11·56%).

N-*Benzoyl*-N'-(2-*nitro*-1-*anthraquinonyl*)-*hydrazine* (VII). A mixture of 2·88 g I, 1·60 g benzhydrazide and 150 ml amyl alcohol was stirred and boiled under reflux for 4 hr. The cooled mixture was filtered, giving 2·50 g (64% yield) of brown solid, m.p. 260–271°. Two crystallizations from acetic acid gave 1·90 g of golden felted microneedles m.p. 277–278° d.

(Found: C, 65·12; H, 3·18; N, 10·87; O, 20·46. Calc. for $C_{21}H_{13}N_3O_5$: C, 65·12; H, 3·38; N, 10·85; O, 20·65%).

Basic hydrolysis of VII. A slurry of 1·5 g VII in 60 ml methyl Cellosolve containing 0·50 g potassium hydroxide was stirred at 80° for ½ hr then was drowned and filtered, giving 0·90 g of deep red solid. Crystallization from acetic acid afforded 0·30 g of purple needles, m.p. 255–256° of 3-*Phenyl*-2*H*, 7*H*, 12*H*-*anthra*[1,2-*e*][1,3,4]*oxadiazine*-7,12-*dione* (IX).

(Found: C, 74·01; H, 3·53; N, 8·70; O, 14·24. Calc. for $C_{21}H_{12}N_2O_3$: C, 74·08; H, 3·56; N, 8·23; O, 14·13%).

Dilution of the above acetic acid mother liquor with ligroin gave an orange product, which, after two crystallizations from amyl alcohol, melted at 245–246°, weighed 0·21 g and appears to be 1-(N'-*Benzoyl*-N-*hydrazino*)-2-(2-*methoxyethoxy*)-*anthraquinone*.

(Found: C, 69·35; H, 4·93; N, 6·78; O, 18·74. Calc. for $C_{25}H_{22}N_2O_5$: C, 69·75; H, 5·15; N, 6·51; O, 18·59%).

3-*Phenyl*-1,4-*dihydro*-7*H*,12*H*-*anthra*[2,1-*e*][1,2,4]*triazine*-7,12-*dione* (X). A solution of 5·0 g sodium sulfide nonahydrate in 90 ml water was added to a solution of 1·00 g VII in 60 ml pyridine, and the slurry was stirred and boiled under reflux for 2 hr. The cooled mixture was diluted with water and filtered, giving 0·60 g (68% yield) of product. Crystallization from an acetic acid–water mixture yielded 0·36 g of deep blue X, m.p. 260–265° d.

(Found: C, 73·9; H, 3·79; N, 11·85. Calc. for $C_{21}H_{11}N_3O_3$: C, 74·2; H, 3·85; N, 12·37%).

3-*Phenyl*-7*H*,12*H*-*anthra*[2,1-*e*][1,2,4]*triazine*-7,12-*dione* (XI). A mixture of 0·20 g X, 15 ml glacial acetic acid and 5 drops of 40% peracetic acid was warmed slightly, whereupon the initial blue color changed to yellow. The mixture was diluted with water, and the product was filtered and crystallized twice from amyl alcohol, giving 0·11 g of yellow crystals, m.p. 255–257° d.

(Found: C, 74·84; H, 3·39; N, 12·55. Calc. for $C_{21}H_{11}N_3O_3$: C, 74·77; H, 3·29; N, 12·46%).

3-(1-*Amino*-2-*anthraquinonyl*)-1*H*,7*H*,12*H*-*anthra*[1,2-*e*][1,3,4]-*oxadiazine*-7,12-*dione* (XIII). A mixture of 2·10 g I, 2·00 g 1-aminoanthraquinone-2-carbohydrazide[16] and 150 ml dry *o*-dichlorobenzene was stirred at 160° for 6 hr. The cooled reaction mixture was filtered, giving 2·50 g (63·6% yield) of dull red XII (brown vat solution), m.p. ~340° d. No method was found to purify this hydrazide without converting it into XIII. Crystallization from pyridine and two recrystallizations from *o*-dichlorobenzene gave a 45% recovery of reddish-black (yellow-brown vat solution) XIII, m.p. >360°.

(Found: C, 71·33; H, 3·38; N, 8·99; O, 16·25. Calc. for $C_{29}H_{16}N_3O_5$: C, 71·74; H, 3·13; N, 8·66; O, 16·47%).

3-(1-*Amino*-2-*anthraquinonyl*)-1,4-*dihydro*-7*H*,12*H*-*anthra*[2,1-*e*][1,2,4]*triazine*-7,12-*dione* (XIV). A slurry of 3·00 g XII, 5·00 g sodium sulfide nonahydrate, 40 ml pyridine and 60 ml water was allowed to stir at room temp overnight. Filtration afforded 2·20 g of deep blue-black solid, m.p. >360°. A sample for analysis was crystallized from trichlorobenzene.

(Found: C, 71·98; H, 3·97; N,1 0·97. Calc. for $C_{29}H_{16}N_4O_4$: C, 71·89; H, 3·33; N, 11·57%).

3-(1-*Amino*-2-*anthraquinonyl*)-7*H*,12*H*-*anthra*[2,1-*e*][1,2,4]-*triazine*-7,12-*dione* (XV). Crystallization of XIV from nitrobenzene effected oxidation to XV, a burgundy-red solid with a light brownish-yellow vat.

(Found: C, 72·26; H, 2·94; N, 11·59. Calc. for $C_{29}H_{14}N_4O_4$: C, 72·19; H, 2·92; N, 11·61%).

3-*Nitropyrazolanthrone* (VIII). To a stirred solution of 2·87 g I in 50 ml dimethylformamide was added 1·20 ml 85% hydrazine hydrate. The reaction temperature rose to 40°, and after the mixture had been cooled, the product was filtered, giving brownish-yellow crystals m.p. 278–291°. Four crystallizations from amyl alcohol and two from glacial acetic acid gave 1·80 g (68% yield) of orange needles, m.p. 297–298°.

(Found: C, 63·33; H, 2·56; N, 15·88; O, 17·81. Calc. for $C_{14}H_7N_3O_3$: C, 63·40; H, 2·66; N, 15·84; O, 18·10%).

This product also was obtained when VII was warmed for ½ hr on the steam bath with sulfuric acid (0·3 g/15 ml), then diluted with water.

3-Aminopyrazolanthrone (XVI). To a solution of 3·61 g 2-benzamido-1-chloroanthraquinone[9] in 150 ml pyridine was added 2·80 ml 85% hydrazine hydrate, and the reaction was stirred and boiled under reflux for 4 hr. The fluorescent green solution was cooled, diluted with water and filtered, providing 2·90 g of dark brown solid. This was dissolved in 50 ml sulfuric acid and warmed for 1 hr on the steam bath, then the solution was cooled, diluted well with water and filtered, giving 1·90 g of orange-brown solid, m.p. 340–350°. Three crystallizations from aqueous ethanol afforded yellow-brown needles, m.p. 352–353° d.

(Found: C, 70·90; H, 4·15; N, 18·02. Calc. for $C_{14}H_9N_3O$: C, 71·48; H, 3·86; N, 17·86%).

This product (XVI) also was produced when either VII or XVIII was vatted and the vat solution was reoxidized and acidified.

3,3'-Azopyrazolanthrone (XVIII). To a solution of 2·87 g I in 50 ml dimethylformamide was added 5·70 ml 85% hydrazine hydrate. The reaction was heated at 130° for ½ hr, then was poured into water and filtered, giving 1·80 g of dark brown solid, m.p. >360°. Three crystallizations from nitrobenzene afforded 0·90 g (21·5% yield) of black powder, m.p. >360°, which dyed cotton a dark red from a deep blue vat.

(Found: C, 72·35; H, 3·28; N, 17·74; O, 6·76. Calc. for $C_{28}H_{14}N_6O_2$: C, 72·09; H, 3·03; N, 18·02; O, 6·86%).

2,2'-Dimethyl-3,3'-azopyrazolanthrone (XIX). A mixture of 0·50 g XVIII, 0·50 g sodium hydroxide, 5·0 ml methyl benzenesulfonate and 100 ml *o*-dichlorobenzene was stirred at 145° for 9 hr. The cooled solution was filtered and the solid was washed with ethanol and water, giving 0·35 g of dark solid (green vat solution), m.p. >360°. A sample for analysis was crystallized from nitrobenzene.

(Found: N, 17·13; Calc. for $C_{30}H_{18}N_6O_2$: N, 16·99%).

2-Nitro-3-(4-toluenesulfonamido)-anthraquinone. A mixture of 3·60 g 3-bromo-2-nitroanthraquinone (XX), 3·40 g *p*-toluenesulfonamide, 8·0 g anhydrous sodium acetate, 0·02 g cupric acetate and 60 ml methyl Cellosolve was stirred and boiled under reflux for 18 hr. The cooled reaction mixture was diluted with water and filtered, giving 3·60 g of solid, m.p. 182–187°. Crystallization from amyl alcohol followed by two recrystallizations from acetonitrile afforded 1·65 g of orange crystals, m.p. 207·5–212·5°.

(Found: C, 59·60; H, 3·32; N, 6·69. Calc. for $C_{21}H_{14}N_3O_6S$: C, 59·70; H, 3·32; N, 6·65%).

3-Amino-2-nitroanthraquinone. The above toluenesulfonamido derivative (1·45 g) was dissolved in 10 ml sulfuric acid and warmed gently (~50°) for 10 min. The cooled solution was diluted with water and filtered, giving 0·99 g of light yellow product, m.p. 297–302° d. Three crystallizations from chlorobenzene gave 0·47 g m.p. 307–310·5°. Recrystallization from pyridine gave 0·30 g of felted orange microneedles, m.p. 310·5–314° (lit[25,24] 316–317° and 305–306°).

1-(3-Nitro-2-anthraquinonyl)-pyridinium bromide (XXI). A solution of 1·16 g 2-bromo-3-nitroanthraquinone (XX) in 25 ml dry pyridine was boiled for a few minutes and cooled. Filtration yielded 1·10 g of crude product, which crystallized from methanol in tan needles (0·42 g), m.p. 244–245° d.

(Found: C, 55·89; H, 3·23; N, 7·08. Calc. for $C_{19}H_{11}BrN_2O_4$: C, 55·47; H, 2·67; N, 6·82%).

7H,12H-Anthra[2',3',4,5]imidazo[1,2-a]-pyridine-7,12-dione (XXII). A solution of 1·66 g XX 1·41 g 2-aminopyridine, and 0·04 g cupric acetate in 10 ml glycol diacetate was stirred and boiled under reflux for 18 hr. The cooled mixture was filtered, giving 1·35 g of brownish-yellow solid. Vacuum sublimation and two crystallizations from trichlorobenzene afforded 0·34 g of orange needles, m.p. >360°.

(Found: C, 76·30; H, 3·67; N, 10·04; O, 10·69. Calc. for $C_{19}H_{10}N_2O_2$: C, 76·50; H, 3·36; N, 9·40; O, 10·72%).

N,N-Naphthaloyl-N'-(3-nitro-2-anthraquinonyl)-hydrazine (XXIII). A mixture of 1·66 g XX, 1·10 g N-aminonaphthalimide, 0·41 g anhydrous sodium acetate, 0·25 g cuprous chloride and 60 ml amyl alcohol was stirred and boiled under reflux. Filtration of the cooled reaction mixture, and washing the solid with ethanol and water gave 2·17 g of crude solid. Crystallization (charcoal) from 1-chloronaphthalene or nitrobenzene afforded 1·20 g of fluffy yellow needles, m.p. >360°

(Found: C, 67·38; H, 2·75; N, 9·12. Calc. for $C_{26}H_{13}N_3O_6$: C, 67·39; H, 2·86; N, 9·08%).

An attempt to convert this substance, by vatting, into the linear analog of compound VI gave (in 78% yield) only 2,3-diaminoanthraquinone, identified by microanalyses and by comparison of the infrared spectrum with that of an authentic sample.

2,2'-Azoanthraquinone (XXIV). Hydrazine hydrate (1·14 ml of an 85% solution) was added to a slurry of 3·62 g XX in 50 ml dimethylformamide at 110°, and the resulting solution was stirred at this temp for 2 hr. The cooled solution was diluted with water and filtered, giving 2·34 g of brown solid. The solid was boiled with 15 ml acetic acid and filtered hot. The insoluble portion was extracted with a little hot dimethylformamide and filtered hot. The residue was crystallized from trichlorobenzene giving 0·15 g of tan solid, m.p. >350°.

(Found: C, 76·07; H, 3·01; N, 6·25; O, 14·49. Calc. for $C_{28}H_{14}N_2O_4$: C, 76·01; H, 3·19; N, 6·33; O, 14·47%).

The major product, isolated from the acetic acid extracts, was shown to be 2-amino-3-bromoanthraquinone by comparison with an authentic specimen.

N'-(2-Chloro-1-anthraquinonyl)-benzhydrazide. A solution of 0·72 g 2-chloro-1-nitroanthraquinone[7] and 0·50 g benzhydrazide in 10 ml dry pyridine was boiled under reflux for 6 hr, then most of the pyridine was allowed to boil away. The cooled residue was filtered, washed with methanol and dried. Crystallization from glycol diacetate afforded 0·49 g of bright yellow needles, m.p.~ 256–264°, shown by infrared analysis to be a mixture of the product with the halonitro compound. Repeated crystallization from glycol diacetate gave the pure product, m.p. 278·5–279·5°; $\lambda\lambda$ 3·11, 6·02 and 6·10 μ.

(Found: C, 66·70; H, 3·51; Cl, 9·39; N, 7·56; O, 13·00. Calc. for $C_{21}H_{13}ClN_2O_3$: C, 66·91; H, 3·45; Cl, 9·43; N, 7·43; O, 12·75%).

3-Chloropyrazolanthrone. Crude N'-(2-Chloro-1-anthraquinonyl)-benzhydrazide (0·42 g, m.p. 256–264°) was dissolved in 10 ml conc H_2SO_4 and kept at 50° for 1 hr. The solution was diluted with water and filtered, and the resulting solid was crystallized from n-butanol, giving 0·21 g of yellow needles. The product was warmed with dil NaOHaq and the resulting red solution was filtered from an insoluble portion and acidified. The yellow precipitate was crystallized from chlorobenzene, giving 0·12 g of golden platelets, m.p. 285·5–286·5°.

(Found: C, 65·85; H, 2·89; N, 11·16. Calc. for $C_{14}H_7ClN_2O$: C, 65·95; H, 2·75; N, 11·00%).

6H,9H,14H-Anthra[1,2-d]pyrido[1,2-ap]yrimidine-6,9,14-trione (XXV). A solution of 0·75 g 1-chloro-2-carbomethoxyanthraquinone.[36] 0·25 g 2-aminopyridine and 0·01 g cupric acetate in 5 ml glycol diacetate was stirred and boiled under reflux for 3 hr. The mixture was cooled and filtered, giving 0·34 g of dark solid. Vacuum sublimation, then crystallization from trichlorobenzene gave 70 mg of brownish-orange needles, m.p. 336–338·5°; λ 5·98 and 6·02 μ. (poorly resolved).

(Found: C, 73·62; H, 2·81; N, 8·75. Calc. for $C_{20}H_{10}N_2O_3$: C, 73·61; H, 3·07; N, 8·59%).

2-Carbomethoxy-3-chloroanthraquinone. To a slurry of 5·73 g of 3-chloroanthraquinone-2-carboxylic acid [29] in 50 ml dichlorobenzene were added 3·5 ml thionyl chloride and 4 drops pyridine. The mixture was heated gently, producing a clear yellow solution, and the excess thionyl chloride was blown off by an air stream. Methanol (5 ml) was then added, the excess again being removed from the hot solution by a stream of air. The cooled solution was poured onto a 2 × 7 cm column of alumina, and developed with benzene. The effluent solution was stripped of solvents *in vacuo*, giving 4·38 g (73% yield) of crude ester, m.p. 151–153°. A sample for analysis was crystallized from acetonitrile in pale yellow needles, m.p. 154·5–155·5°.

(Found: C, 64·13; H, 3·01; Cl 11·60; O, 21·14. Calc. for $C_{16}H_9ClO_4$: C, 63·89; H, 2·95; Cl, 11·81; O, 21·25%).

2-Carbomethoxy-3-(4-toluenesulfonamido)-anthraquinone. A mixture of 1·52 g 2-carbomethoxy-3-chloroanthraquinone, 1·00 g *p*-toluenesulfonamide, 0·41 g anhydrous sodium acetate, 0·01 g cupric acetate and 5 ml methyl Cellosolve was stirred and boiled under reflux for 7 hr. The reaction mixture was cooled, and diluted with water. The resulting oil was washed with hot water, dissolved in benzene and chromatographed upon acid-washed[30] alumina. Evaporation of the eluate gave 0·65 g of golden platelets, m.p. 177–183°. Two crystallizations from acetonitrile gave 0·44 g of yellow crystals, m.p. 184–186°.

(Found: C, 63·23; H, 4·16; N, 2·99. Calc. for $C_{23}H_{17}NO_6S$: C, 63·45; H, 3·91; N, 3·22%).

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