Oxidation of Glycols A and B.—Glycol A (43 mg.) was oxidized with excess chromic acid–sulfuric acid in acetone.[10] After the dilution of the reaction mixture with water, the product was extracted with ether. Evaporation of the dried (magnesium sulfate) solution gave 26 mg. of crude diketone A′. An analytical sample was collected from a Viton A-HV column at 220°, $n^{25}D$ 1.4743. A similar oxidation of glycol B (81 mg.) afforded 28 mg. of crude diketone B′. An analytical sample, $n^{25}D$ 1.4775, was collected on the same chromatographic column.

Anal. Calcd. for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found, A′: C, 68.45; H, 8.71. Found, B′: C, 68.72; H, 8.41.

N.m.r. Spectra of Diketones A′ and B′.[11]—Diketone A′: τ = 8.95 (doublet, J = 11 c.p.s.), τ = 8.05 (multiplet), τ = 7.57 (multiplet), τ = 6.33 (quartet, J = 11 c.p.s.). Diketone B′: τ = 9.00 (doublet, J = 3 c.p.s.), τ = 8.21 (multiplet), τ = 7.51 (multiplet).

2-Methyl-1,3-cyclohexanedione (A′).—A solution of 1.97 g. of 3-hydroxycycloheptene oxide[5] in 10 ml. of ether was added dropwise with stirring in a nitrogen atmosphere to a filtered solution of methyllithium, prepared from 1.4 g. of lithium wire and 5 ml. of methyl iodide in *ca.* 100 ml. of ether. The solution was stirred at room temperature for 24 hr., then poured onto ice and extracted with four 20-ml. portions of ether. The combined extracts were washed with water until neutral and then dried (magnesium sulfate). Removal of the solvent under reduced pressure left 1.12 g. (50%) of an oil. It was dissolved in 50 ml. of acetone, 4 g. of anhydrous copper sulfate was added, and the suspension was stirred for 42 hr. at room temperature in a stoppered flask. The solids were removed by filtration and the filter cake was washed several times with acetone. Evaporation of the combined filtrates left 1.16 g. of an oil which was chromatographed on 50 g. of Woelm alumina (activity I). The isopropylidene ketal (0.87 g.) was eluted with 1:1 pentane–ether and a glycol fraction (0.21 g.) was eluted with 1:4 methanol–ether. The glycol fraction (98 mg.) was oxidized with chromic acid–sulfuric acid in acetone[10] and gave 41 mg. (43%) of a diketone mixture. Gas chromatography (Viton A-HV, 245°) showed a peak with the same retention time as diketone A′. Another peak was found to be the 1,2-diketone resulting from 1,2-glycol that had failed to form an isopropylidene ketal. Oxidation of the glycol mixture before treatment with acetone and copper sulfate gave the same compound (1,2-diketone) in a larger proportion to the 1,3-diketone. The compound with the same retention time as diketone A′ was isolated by gas chromatography; its infrared spectrum was identical to that of diketone A′.

5-Methyl-1,4-cycloheptanedione (B′).—1,4-Cyclohexanedione[12] (1.80 g.), dissolved in 160 ml. of ether to which *ca.* 20 mg. of aluminum chloride had been added, was treated at room temperature with an ethereal solution of diazoethane, generated from 5.7 g. of nitrosoethylurea and aqueous potassium hydroxide solution.[7] The solution was stirred for 4.5 hr., then washed with 30-ml. portions of 5% sodium carbonate, dilute hydrochloric acid, and 5% sodium carbonate. After drying over magnesium sulfate, the ether was evaporated, giving 0.34 g. of an oil which was shown by gas chromatography (silicone grease, 159°) to contain at least six materials. The major peak (34% of the product mixture) had a retention time identical to that of the diketone B′. Starting material (11%) also was detected. The infrared spectra of the diketone B′ derived from the *trans*-cycloöctene oxide solvolysis product and the major product, isolated by gas chromatography, were identical.

(10) K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).

(11) The spectra were obtained for 20% solutions in carbon tetrachloride using a Varian 4300B spectrophotometer with a 60-Mc. oscillator frequency. Tetramethylsilane was the internal standard.

(12) J. R. Vincent, A. F. Thompson, and L. I. Smith, *J. Org. Chem.*, **3**, 603 (1939).

Polynuclear Heterocycles. III. The Chlorination and Nitration of Benzo[*b*]phenazine[1]

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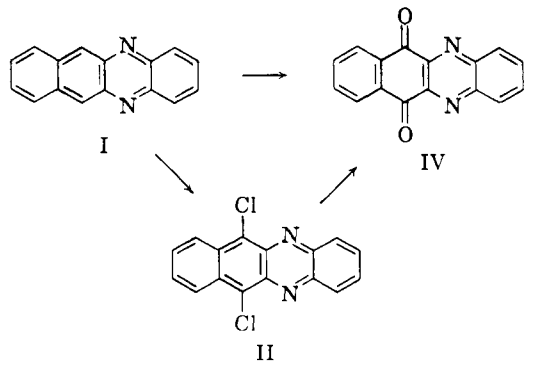
The structures of several chlorinated and nitrated benzo[*b*]phenazines have been determined. It is shown that substitution occurs exclusively in the 6,11-positions. Benzo[*b*]phenazine-6,11-quinone, a key intermediate in the above structural determinations, has been prepared by the thermal decomposition of 2-azido-3-anilino-1,4-naphthoquinone. Under similar conditions of chlorination and nitration, dibenzo[*a*,*i*]phenazine gives products with substituents in the 8,13-positions.

In a previous communication,[2] it was shown that the *meso* positions of benzo[*b*]phenazine (I) are reactive toward electrophilic reagents. As an extension of this investigation, I was chlorinated[3] with sulfuryl chloride to give 6,11-dichlorobenzo[*b*]phenazine (II), m.p. 263°. Zincke and Fries[4] have described a substance (m.p. 265°) which they obtained by the condensation of 1,4-dihydro-1,1,4,4-tetrachloro-2,3-naphthoquinone with *o*-phenylenediamine and to which they assign the structure II. To elucidate the structure of our product, we made numerous attempts to repeat their work, but obtained a mixture of chlorophenazine derivatives of which the main component was a trichlorobenzo[*b*]-phenazine (III) (m.p. 239°). Since this method of determining the structure failed, II was oxidized with chromic acid in acetic acid to give 6,11-benzo[*b*]phenazinequinone (IV) which was identical with the oxidation product of I. The structure of IV is proved later by an unambiguous synthesis.



Leicester[5] claimed to have obtained 6,11-benzo[*b*]-phenazinequinone (IV) by heating 2-(2′-nitroanilino)-1,4-naphthoquinone (V) in a sealed tube with ammonium sulfide. However, Badger and Pettit[6] have dis-

(1) Contribution no. 2306 from the Kodak Research Laboratories.

(2) J. A. VanAllan, R. E. Adel, and G. A. Reynolds, *J. Org. Chem.*, **27**, 2873 (1962).

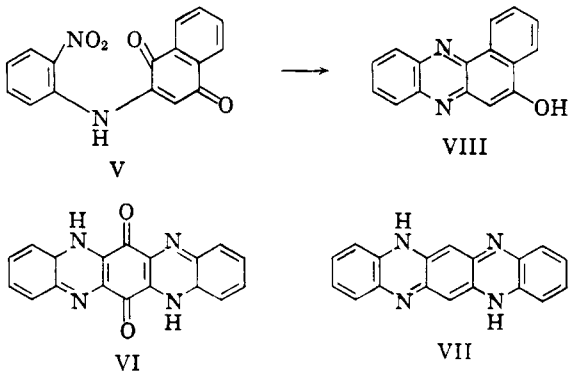
(3) In place of I, the corresponding 5,12-dihydrobenzo[*b*]phenazine may be used. Oxidation of the dihydro compound gives I.

(4) T. Zincke and K. Fries, *Ann.*, **334**, 360 (1904).

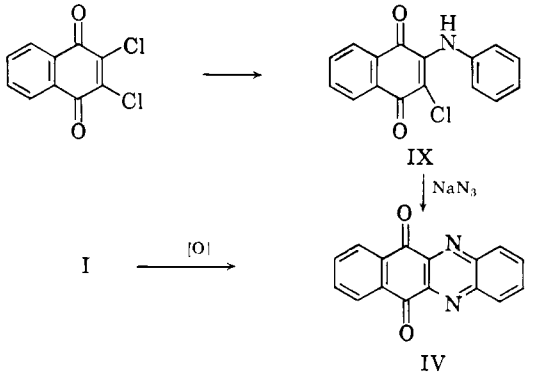
(5) J. Leicester, *Ber.*, **23**, 2793 (1890).

(6) G. M. Badger and R. Pettit, *J. Chem. Soc.*, 3211 (1951).

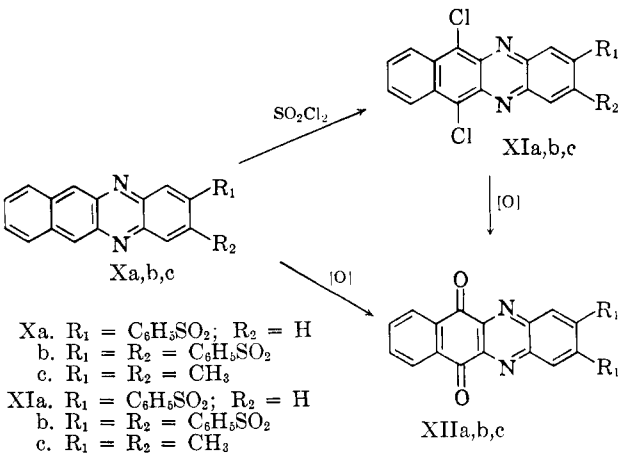
proved Leicester's claim that 5,12-dihydro-5,7,12,14-terazapentacene-6,13-quinone (VI) is prepared by a similar reduction of 2,5-bis(2′-nitroanilino)-1,4-benzoquinone. They showed that the nitro groups, upon reduction, react with the quinone oxygen to yield 5,12-dihydro-5,7,12,14-tetrazapentacene (VII). If the same mechanism is operative here, the product should be 5-hydroxybenzo[*a*]phenazine (VIII), as suggested by Swan and Felton.[7] A product identical with Leicester's was obtained by the condensation of 2-hydroxy-1,4-naphthoquinone with *o*-phenylenediamine.[8]



Since Leicester's procedure failed to give the desired quinone, IV, and because the structure of IV is the key to other structural proofs, it seemed desirable to synthesize IV by an alternative method. To this end, 2,3-dichloronaphthoquinone was condensed with aniline to give 2-anilino-3-chloronaphthoquinone (IX).[9a] When heated in dimethylformamide in the presence of sodium azide, IX gave a product identical with the oxidation product of benzo[*b*]phenazine, presumably by formation of 2-anilino-3-azidonaphthoquinone, which underwent thermal decomposition and oxidative ring closure.

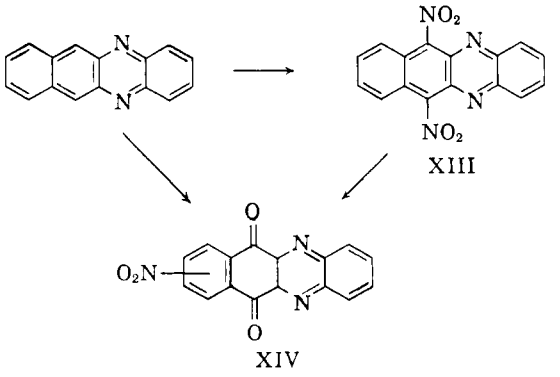


To test the generality of the chlorination in the *meso* positions, 2-phenylsulfonylbenzo[*b*]phenazine (Xa),[2] 2,3-bis(phenylsulfonyl)benzo[*b*]phenazine (Xb),[2] and 2,3-dimethylbenzo[*b*]phenazine (Xc)[2] were treated with sulfuryl chloride to give 6,11-dichloro-2-phenylsulfonylbenzo[*b*]phenazine (XIa), 6,11-dichloro-2,3-bis(phenylsulfonyl)benzo[*b*]phenazine (XIb), and 6,11-dichloro-2,3-dimethylbenzo[*b*]phenazine (XIc), respectively. These structures are assigned because, upon oxidation, the compounds yield the quinones XIIa, XIIb, and XIIc, respectively. The quinones are also obtained by the oxidation of the parent compounds, Xa, Xb, and Xc. The similarity of the ultraviolet spectra of XIIa, XIIb, and XIIc to the spectrum of 6,11-benzo[*b*]phenazinequinone (IV) confirms their close structural relationship.



Xa. $R_1 = C_6H_5SO_2$; $R_2 = H$
b. $R_1 = R_2 = C_6H_5SO_2$
c. $R_1 = R_2 = CH_3$
XIa. $R_1 = C_6H_5SO_2$; $R_2 = H$
b. $R_1 = R_2 = C_6H_5SO_2$
c. $R_1 = R_2 = CH_3$
XIIa. $R_1 = C_6H_5SO_2$; $R_2 = H$
b. $R_1 = R_2 = C_6H_5SO_2$
c. $R_1 = R_2 = CH_3$

Benzo[*b*]phenazine with nitric acid in acetic acid at 95–100° gives a dinitro compound which is believed to be 6,11-dinitrobenzo[*b*]phenazine (XIII) for reasons to be discussed. If the nitration is conducted in concentrated nitric acid at 95°, a mononitrobenzo[*b*]phenazine-6,11-quinone (XIV) is obtained. This quinone is also obtained by treatment of XIII with nitric acid at 95°, whereas 6,11-benzo[*b*]phenazinequinone is unaffected under these same conditions. These observations may be explained by assuming a nitration at some intermediate stage in the oxidation of XIII to XIV.



Attempts to add maleic anhydride to XIII were unsuccessful. This failure to react with maleic anhydride is additional evidence of the presence of nitro groups in the 6,11-positions.[9b]

2-Phenylsulfonylbenzo[*b*]phenazine (Xa), 2,3-bis(phenylsulfonylbenzo[*b*]phenazine (Xb), and 2,3-dimethylbenzo[*b*]phenazine (Xc) were nitrated in acetic acid at 95–100° to give, by analogy with the behavior of the parent compound, 6,11-dinitro-2-phenylsulfonylbenzo[*b*]phenazine (XVa), 6,11-dinitro-2,3-bis(phenylsulfonyl)benzo[*b*]phenazine (XVb), and 6,11-dinitro-2,3-dimethylbenzo[*b*]phenazine (XVc), respectively.

(7) G. A. Swan and D. G. I. Felton, "Heterocyclic Compounds, Vol. 11, Phenazines," Interscience Publishers, Inc., New York, N. Y., 1957, p. 215.
(8) F. Kehrmann, *Ber.*, **23**, 2446 (1890).
(9) (a) R. V. Acharya and B. D. Tilak, *J. Sci. Ind. Res.* (India), **14B**, 221 (1955); (b) "Newer Methods of Preparative Organic Chemistry," Interscience Publishers, Inc., New York, N. Y, 1948, p. 484, wherein it is stated that substituents in the *meso* position act as inhibitors toward the addition of maleic anhydride.

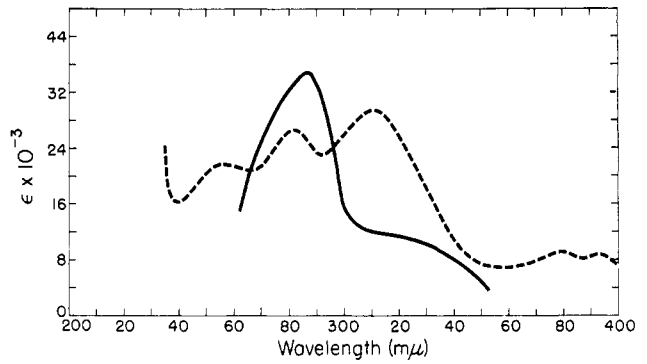
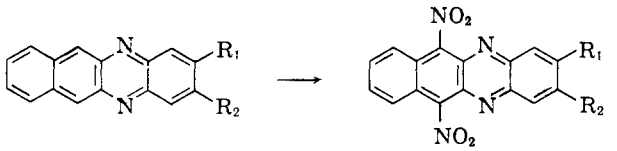


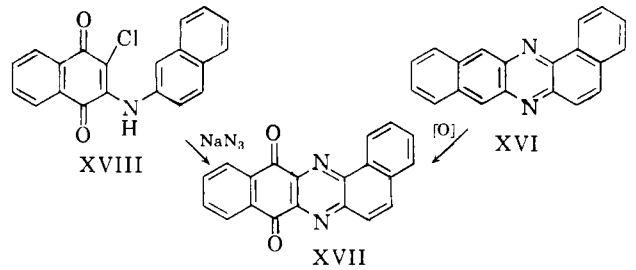
Fig. 1.—Ultraviolet absorption spectra of (1) benzo[*b*]phenazine-6,11-quinone (IV) ——— (in dioxane); (2) dibenzo[*a,i*]-phenazine-8,13-quinone (XVII) - - - - (in dioxane).



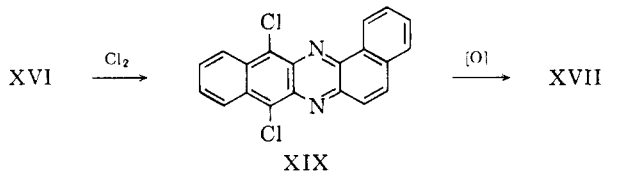
Xa, b, c

XVa. $R_1 = C_6H_5SO_2$; R = H
b. $R_1 = R_2 = C_6H_5SO_2$
c. $R_1 = R_2 = CH_3$

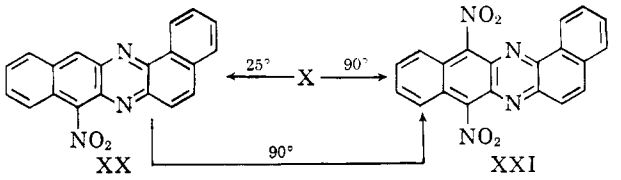
The oxidation of dibenzo[*a,i*]phenazine (XVI) with chromic acid in acetic acid gives 8,13-dibenzo[*a,i*]-phenazinequinone (XVII). The structure assigned to XVII is confirmed by the fact that 2-(2-naphthylamino)-3-chloronaphthoquinone (XVIII),[9a] on treatment with sodium azide in dimethylformamide, also gives XVII, presumably by a mechanism similar to that described for the preparation of IV. The quinone XVII is also obtained on treatment of the 1-naphthylamino analog of XVIII[10] with sodium azide.



The chlorination of XVI with sulfuryl chloride in carbon tetrachloride gives 8,13-dichlorodibenzo[*a,i*]-phenazine (XIX). This latter structure is assigned because XIX, on oxidation with chromic acid, gives XVII.



The nitration of XVI at room temperature in acetic acid gives 8-(or 13)-nitrodibenzo[*a,i*]phenazine (XX). Nitration of either XVI or XX at 95–100° gives 8,13-dinitrodibenzo[*a,i*]phenazine (XXI). The structures tentatively assigned to these compounds are analogous

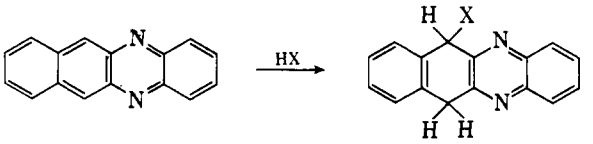


to the products obtained by the nitration of benzo[*b*]-phenazine.

Finally, dibenzo[*b,i*]phenazine (XXII), on oxidation with chromic acid in acetic acid, gives dibenzo[*b,i*]-phenazine-5,14,7,11-diquinone (XXIII). This series was not investigated further owing to the great insolubility of its members.

Discussion

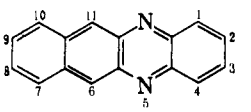
It is suggested that chlorination and nitration of benzo[*b*]phenazine, its derivatives, and dibenzo[*a,i*]-phenazine take place by the addition of the reagent to the *meso* positions, followed by the transannular elimination of hydrogen chloride and water, respectively. This process is again repeated to give the bisadducts. On the addition of the chlorinating or nitrating agent to a suspension of the reactant, a pronounced color change is observed, followed by solution of the reactant. After an interval of five to ten minutes, the product separates. These observations suggest the formation of an intermediate compound. By analogy with the chemistry of anthracene, these intermediate compounds are addition compounds.



Both benzo[*b*]phenazine and dibenzo[*a,i*]phenazine and their derivatives have complicated absorption spectra, but these may be divided into three groups, as suggested by Jones.[11] There is some loss of fine structure in the azahydrocarbons, but the three regions can be identified without difficulty, as shown in Tables I and II. Conversion of the aza carbons to the quinones

TABLE I

ABSORPTION SPECTRA OF SUBSTITUTED BENZO[*b*]PHENAZINES



Substituent[a]	$\lambda_{max.}$,[b] mμ	$\lambda_{max.}$, mμ	$\lambda_{max.}$, mμ
6,11-Dichloro	255 (31)		500 (1.94)
	288 (100)	410 (1.86)	534 (1.92)
2,3-Dimethyl-6,11-	262 (25)		500 (1.78)
dichloro	292 (86)	426 (1.76)	532 (1.71)
2,3-Bis(phenylsul-		414 (18.1)	
fonyl)-6,11-di-	290 (81)	480 (5.2)	518 (4.2)
nitro			
6,11-Quinone	288 (36.5)	~325 (11)	
2,3-Dimethyl-6,11-	303 (34.0)		
quinone			

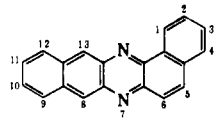
[a] Solvent in all cases is dimethylformamide. [b] Extinction coefficients are reported as $\epsilon \times 10^{-3}$.

(10) N. G. Buü-Hoi, *Bull. soc. chim. France*, [5] **11**, 578 (1944).

(11) R. N. Jones, *J. Am. Chem. Soc.*, **62**, 148 (1940).

TABLE II

ABSORPTION SPECTRA OF SUBSTITUTED DIBENZO[*a*,*i*]PHENAZINES



Substituent[a]	λ_{max}, mμ	λ_{max}, mμ	λ_{max}, mμ
None		300 (80)	
		310 (80.4)	460 (2.2) broad
8,13-Dichloro	225 (32.5)		
	242 (27.5)		
	262 (20)	298 (68.5)	400–520 (*ca.* 1.9) broad
8,13-Dinitro		292 (11.5)	
	240 (5.8)	305 (13.8)	400–500 (*ca.* 6.0) broad
8,13-Quinone	255 (22)	312 (30)	
	282 (27)	388 (8.3)	
		395 (8.6)	

[a] Solvent in all cases is dimethylformamide.

results in a complete loss of fine structure, as illustrated by 6,11-benzo[*b*]phenazinequinone, which has a single, well defined peak at 288 mμ and 8,11-dibenzo[*a*,*i*]phenazinequinone, which has three broad, high-intensity peaks (Fig. 1).

Experimental

The following general methods illustrate the procedure used in the chlorination, oxidation, and nitration of the benzophenazines. The analytical data are collected in Table III.

Method A. Chlorination.—Sulfuryl chloride, 5 ml. (0.062 mole), was added to a suspension of the benzophenazine (0.022 mole) in 50 ml. of carbon tetrachloride, and the reaction mixture heated on the steam bath for 1 hr. The reaction mixture was cooled. The product was collected by filtration. Crystallization of the product from a suitable solvent gave the pure dichlorobenzophenazine in a yield of 55 to 65%.

Method B. Oxidation of Benzophenazines to Benzophenazinequinones.—A boiling solution of 15 g. of chromic acid in 75 ml. of acetic acid was added gradually to a warm solution of the benzophenazine (0.022 mole) in 40 ml. of acetic acid and 12 ml. of acetic anhydride. Warming was continued on the steam bath for 0.5 hr. after the addition was completed. The reaction mixture was cooled. The product was collected by filtration. Crystallization of the product from a suitable solvent gave the pure quinone in 60–70% yield.

Method C. Nitration.—Nitric acid (*d* 1.42), 7.5 ml., was added at room temperature to a solution of the benzophenazine (0.025 mole) in 60 ml. of acetic acid. The mixture was then heated on the steam bath for 2 hr. The reaction was cooled and the product collected by filtration and purified by crystallization; yield, 60–70%.

Method D. Preparation of Quinones by the Azide Procedure.—To a solution of 0.1 mole of 2-arylamino-3-chloro-1,4-naphthoquinone in 250 ml. of dimethylformamide was added 0.15 mole of sodium azide dissolved in the minimum quantity of water. The mixture was heated 4 hr. on the steam bath, chilled, and the solid collected and washed on the filter with benzene and then alcohol, and finally recrystallized from the appropriate solvent.

TABLE III

ANALYTICAL DATA

Compound no.	M.p., °C.	Solvent of recrystallization	Empirical formula	Calcd. C	Calcd. H	Calcd. N	Calcd. Cl	Found C	Found H	Found N	Found Cl	Method of preparation
II	263	Toluene	$C_{16}H_8Cl_2N_2$	64.3	2.7	9.4	23.7	64.4	3.0	9.4	24.5	A
III	235	Toluene/ligroin	$C_{16}H_7Cl_3N_2$	57.8	2.1		31.6	57.6	2.1		30.9	
IV	334	Trichlorobenzene	$C_{16}H_8O_2N_2$	73.9	3.1	10.7		73.7	3.0	10.7		B and D
XIa	284	Cyclohexanone	$C_{22}H_{12}O_2Cl_2N_2S$	60.2	2.7		16.0	60.6	3.0		15.8	A
XIb	219	Butanol	$C_{28}H_{16}O_4Cl_2N_2S_2$	58.0	2.8	4.8	12.2	57.9	2.5	5.0	12.3	A
XIc	>400		$C_{18}H_{12}Cl_2N_2$	66.2	3.7	8.6	21.5	65.7	3.8	8.8	21.8	A
XIIa	310	Dimethylformamide	$C_{22}H_{12}O_4N_2S$	66.0	3.0	7.0		66.2	3.3	7.1		B
XIIb[a]	321	Acetic anhydride	$C_{28}H_{16}O_6N_2S_2$									B
XIIc	335	Trichlorobenzene	$C_{18}H_{12}O_2N_2$	75.0	4.2			74.3	4.2			B
XIII	285	Cyclohexanone	$C_{16}H_8O_4N_4$	60.0	2.6	17.5		59.5	2.8	17.0		C
XIV	312	Trichlorobenzene	$C_{16}H_7O_4N_4$	62.9	2.3	13.8		62.7	2.0	13.3		
XVa	*ca.* 320	Trichlorobenzene	$C_{22}H_{12}O_6N_4S$	57.4	2.6	12.2		57.4	2.7	12.5		C
XVb	*ca.* 300	Trichlorobenzene	$C_{28}H_{16}O_8N_4S_2$	56.2	2.7	9.4		56.5	2.5	9.4		C
XVc	288 dec.	Chlorobenzene	$C_{18}H_{12}O_2N_4$	62.2	3.5	16.1		62.3	3.1	15.3		C
XVII	340	Trichlorobenzene	$C_{20}H_{10}O_2N_2$	77.1	3.2	9.0		76.7	3.5	8.8		B and D
XIX	232	Chlorobenzene	$C_{20}H_{10}Cl_2N_2$	68.9	2.9	8.1	20.1	68.4	3.1	7.7	20.8	A
XX	300	Trichlorobenzene	$C_{20}H_{11}O_2N_3$	73.9	3.4	12.9		73.5	3.2	12.6		C
XXI	314	Trichlorobenzene	$C_{20}H_{10}O_4N_4$	64.9	2.7	15.1		65.2	2.5	14.7		C
XXIII[b]	400		$C_{20}H_{10}O_4N_2$	70.4	2.4	8.2		69.1	2.8	7.4		B and D

[a] We were unable to obtain a satisfactory analytical sample, but ultraviolet and infrared spectra indicated the presence of the quinone.
[b] Insoluble in all organic solvents.

X,X,X-Trichlorobenzo[*b*]phenazine (III).—A mixture of 1 g. of 1,4-dihydro-1,1,4,4-tetrachloro-2,3-naphthoquinone hydrate and 0.5 g. of *o*-phenylenediamine in 5 ml. of acetic acid was heated on the steam bath for 15 min., cooled, and the solid collected. The solid was boiled in 100 ml. of toluene, the insoluble material filtered off, and the filtrate diluted with ligroin and chilled. The solid that separated was collected and recrystallized from chloroform to give 0.2 g. of red product, m.p. 235°.

Mononitrobenzo[*b*]phenazine-6,11-quinone (XIV).—Benzo[*b*]-phenazine (I) (20 g.) was added, with stirring, to 200 ml. of nitric acid (*d* 1.42). The reaction mixture was then heated on the steam bath for 2 hr. After cooling, 50 ml. of water was added. The bright yellow product was collected by filtration and crystallized twice from cyclohexanone to give 12 g. of XIV, m.p. 312°. If 6,11-dinitrobenzo[*b*]phenazine (XIII) is substituted for I in the above reaction, XIV is again obtained.

Polynuclear Heterocycles. IV. The Synthesis of Some New Heterocyclic Quinones[1]

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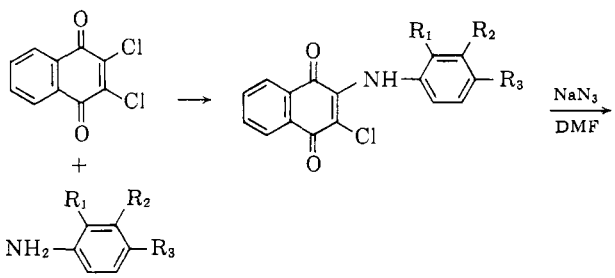
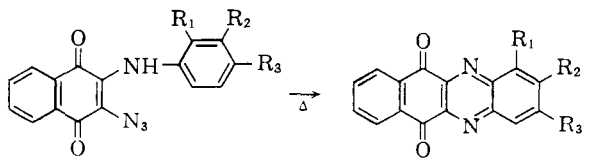
2-Arylamino-3-azido-1,4-naphthoquinones, on heating, undergo a ring closure to give 6,11-benzo[*b*]phenazine-quinones. The corresponding 2-cycloalkylamino-3-azido-1,4-naphthoquinones undergo an analogous transformation to yield 5,10-dioxo-4a,11-diazabenzo[*b*]fluorenes. The secondary product obtained in these reactions is a 2-aryl(or cycloalkyl)amino-3-amino-1,4-napthoquinone.

It has been shown[2] that 2-anilino-3-chloro- (Ie), 2-(2-naphthylamino)-3-chloro- (I. R_1 = H; R_2R_3 fused benzo), and 2-(1-naphthylamino)-3-chloro-1,4-naphthoquinone (I. R_1R_2 fused benzo; R_3 = H) react with sodium azide in dimethylformamide at 90–100° to give 6,11-dihydro-6,11-dioxo-5,12-diazanaphthacene (IIe) and 8,13-dihydro-8,13-dioxo-7,14-diazabenzo[*a*]-naphthacene, respectively. The over-all reaction is represented by the following general equations, in which R_1, R_2, and R_3 are hydrogen, a fused benzene ring, or various other substituents.



I

Ia. $R_1 = R_2 = H$; $R_3 = NO_2$
b. $R_1 = R_2 = H$; $R_3 = OCH_3$
c. $R_1 = R_2 = H$; $R_3 = Cl$
d. $R_1 = R_2 = H$; $R_3 = CH_3$
e. $R_1 = R_2 = R_3 = H$
f. $R_1 = CH_3$; $R_2 = H$; $R_3 = N(C_2H_5)_2$

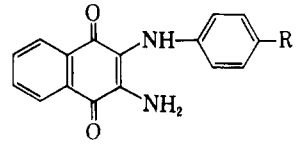


II

IIa. $R_1 = R_2 = H$; $R_3 = NO_2$
b. $R_1 = R_2 = H$; $R_3 = OCH_3$
c. $R_1 = R_2 = H$; $R_3 = Cl$
d. $R_1 = R_2 = H$; $R_3 = CH_3$
e. $R_1 = R_2 = R_3 = H$
f. $R_1 = CH_3$; $R_2 = H$; $R_3 = N(C_2H_5)_2$

In this paper, further work on the scope of this reaction is reported. The effect of electron-withdrawing and electron-attracting substituents in the arylamino moiety of I on ring closure was first examined. During the course of synthesizing such compounds, it was found that the reaction of 2,3-dichloro-1,4-naphthoquinone with aromatic amines was sensitive to steric[3] as well as electronic effects. The preparation of 2-(4-nitroanilino)-3-chloro-1,4-naphthoquinone (Ia) could not be achieved by direct interaction of the components, presumably because of the weak basicity of the amine.[4] Ia was prepared by nitration[5] of 2-anilino-3-chloronaphthoquinone (Ie), and compounds Ib,[6] Ic,[7] and Id[8] as described in the literature.

Treatment of Ia with sodium azide in dimethylformamide at 90–100° gave 2-(4-nitroanilino)-3-amino-1,4-naphthoquinone (IIIa) and none of the heterocyclic quinone (IIa). In contrast, Ib gave the quinone, IIb (in 46% yield), and a 32% yield of IIIb. The ring closure of Ic, Id, and If also proceeded readily to give the quinones IIc, IId, and IIf, respectively. No attempt was made to isolate the secondary product in the latter three reactions.



IIIa. R = NO_2
b. R = OCH_3
e. R = H

The reaction of 2-anilino-3-chloronaphthoquinone (Ie) with sodium azide described previously[2] was repeated and a second product obtained which was identical with the 2-anilino-3-amino-1,4-naphthoquinone (IIIe) prepared according to Fries.[5] A comparison of the ultraviolet spectrum of IIIe with the spectra

(1) Communication no. 2307 from the Kodak Research Laboratories.

(2) J. A. VanAllan, G. A. Reynolds, and R. E. Adel, *J. Org. Chem.*, **27**, 2873 (1962).

(3) Aromatic amines in which there is an *ortho* substituent, such as *o*-chloroaniline and 2,4-dichloroaniline, did not react with 2,3-dichloronaphthoquinone, whereas the reaction proceeded smoothly with 3,4-dichloroaniline.

(4) The reaction of 2,3-dichloro-1,4-naphthoquinone with *p*-nitroaniline in trichloropropane with dimethylaniline as base gave 2-(4-nitroanilino)-naphthoquinone that was identical with the product obtained from 2-hydroxynaphthoquinone and *p*-nitroaniline.

(5) K. Fries and K. Billig, *Ber.*, **58**, 1128 (1925).

(6) N. G. Buü-Hoi, *Bull. soc. chim. France*, **11**, 578 (1944).

(7) K. Fries and P. Ochwat, *Ber.*, **56**, 1291 (1923).

(8) A. Plagemann, *ibid.*, **15**, 484 (1882).