652. *The Oxidation of Derivatives of* o-*Phenylenediamine. Part VII.*[1] *Bromination of Anilinoaposafranines and Related Compounds.*

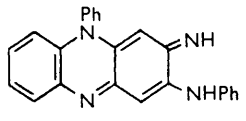
By VINCENT C. BARRY, J. G. BELTON, J. F. O'SULLIVAN, and DERMOT TWOMEY.

It has been established that anilinoaposafranine, on bromination in chloroform and subsequent treatment with alkali, yields a tetrabromo-derivative. No bromine enters the phenazine nucleus. Arguments are advanced which prove that bromine has replaced the hydrogen of the 2- and 3-imino-groups atached to the phenazine nucleus, and that the third and fourth bromine atoms have substituted the *ortho*- and the *para*-position of the N^2-phenyl group. The isomer of anilinoaposafranine yields the dibromo-derivative, 2-bromoamino-3-*p*-bromophenylimino-3,5-dihydro-5-phenylphenazine.

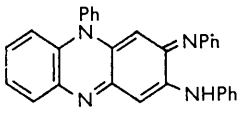
Aposafranone forms a monobromo-derivative, the bromine entering the 2-position *ortho* to the carbonyl group. With anilinoaposafranone four bromine atoms again enter the molecule, one replacing the imino-hydrogen atom, and the remaining three the 2-, 4-, and 6-hydrogen atoms of the anilino-group.

The structures of a number of other brominated derivatives of anilinoaposafranine have been elucidated.

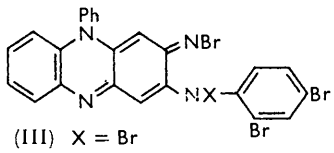
IN Part I [2] treatment of anilinoaposafranine (I) and its isomer (XVIII) was described as leading to tribromo- and dibromo-derivatives respectively. The bromine was thought to have entered the *ortho*-positions of the quinonoid system, and to have replaced the hydrogen of the =NH group in anilinoaposafranine. As indicated in Part V,[3] a continuing investigation of the bromination studies has shown the situation to be complex, and it is now clear that the formulations of the bromo-derivatives in Part I are incorrect. When bromination of the compounds is carried out under our conditions, no bromine enters the phenazine nucleus.



(I)



(II)



(III) X = Br
(IV) X = H

When derivatives of anilinoaposafranine are treated in chloroform with excess of bromine, an unexpectedly large proportion of bromine is taken up (*ca.* 7 bromine atoms per mole). Treatment of the brominated products in ethanol with ammonia or alkali results in a loss of some bromine, and we are concerned in this paper with the structure of the alkali-stable brominated compounds.

Addition of a large excess of bromine (12 mols.) to anilinoaposafranine (I) gave a product which, on treatment in ethanol with ammonia, gave a tetrabromo-derivative (III). In the bromination of anilinoaposafranine (I), described in Part I,[2] carbon tetrachloride was used as solvent and a tribromo-derivative resulted. The use of chloroform as solvent enabled a fourth bromine atom to substitute the molecule. Unless a large excess of bromine is employed the product will contain some di- and tri-brominated compounds which are difficult to eliminate by column chromatography. The tetrabromo-derivative (III), on being heated under reflux with aniline, was converted into the bromine-free rimino-compound (II).[3] The four bromine atoms, therefore, in compound (III) must be present in the groups substituting the 2- and the 3-position of the phenazine nucleus.

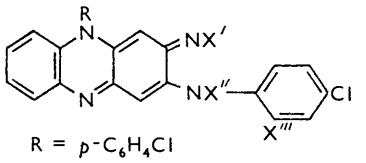
[1] Part VI, Barry, Belton, O'Sullivan, and Twomey, *J.*, 1958, 4495.
[2] *Idem*, *J.*, 1956, 888.
[3] *Idem*, *J.*, 1958, 859.

The tribromoanilinoaposafranine described in Part I [2] was thought to be the 1,4,N^3-tribromo-compound which on degradation in a sealed tube with ethanolic sulphuric acid yielded a bromine-free hydroxy-derivative. The analytical data for this compound fitted a 1,4-dihydroxyanilinoaposafranone, and the failure to introduce more than one acetyl group into it was attributed to hydrogen-bonding. It is now clear that the degradation product was hydroxyaposafranone which also results from anilinoaposafranine itself under the same degradative conditions. The reinterpretation of these facts affords further evidence that no bromination occurs in the phenazine nucleus.

The tetrabromoanilinoaposafranine (III), when heated under reflux with cyclohexylamine, gave a mixture from which a tribromoanilinoaposafranine (IV) was isolated by chromatography on alumina. One of the four bromine atoms is thus somewhat labile although stable to alkali, and for reasons which will be made clear during the discussion we have assigned this bromine to the –NH– group of the 2-anilino-substituent in the phenazine nucleus.

As already shown,[3] anilinoaposafranines may be converted into rimino-compounds by heating them with the appropriate alkyl- or cycloalkyl-amines, the =NH group being replaced by alkyl- or cycloalkyl-imino-groupings. However, in the conversion of the tetrabromoanilinoaposafranine (III) into the tribromo-derivative (IV), a rimino-compound was not formed, and we attribute this failure to the fact that =NH has been converted by bromination into =NBr which, although replaceable by boiling aniline, is stable to boiling cyclohexylamine. Further evidence will be given below in favour of our contention that a second bromine atom is present as =NBr in the tetrabromo-compound (III).

The third and the fourth bromine atom are in the *ortho*- and the *para*-position of the anilino-group substituting position 2 of the phenazine nucleus. This deduction is based on the following facts:

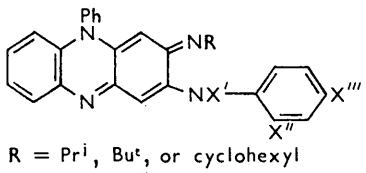


R = *p*-C_6H_4Cl

(V) X′=X″ = X‴ = H

(VI) X′=X″ = X‴ = Br

(VII) X′=X‴ = Br ; X″= H

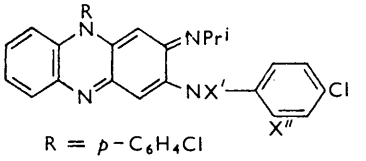


R = Pr^i, Bu^t, or cyclohexyl

(VIII) X′ = X″=X‴ = H

(IX) X′ = X″=X‴ = Br

(IXa) X′=H ; X″=X‴= Br ; R = cyclohexyl

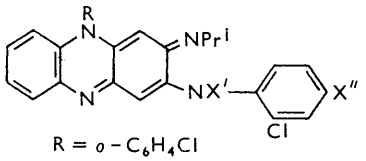


R = *p*-C_6H_4Cl

(X) X′=X″= H

(XII) X′=X″= Br

(XIV) X′=H ; X″= Br



R = *o*-C_6H_4Cl

(XI) X′= X″= H

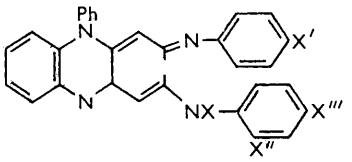
(XIII) X′= X″= Br

(XV) X′= H, X″= Br

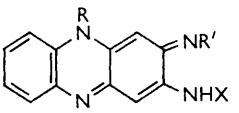
The rimino-compounds (VIII), in which the hydrogen of the =NH group has been replaced by alkyl or cycloalkyl gave tribromo-derivatives (IX), in contrast to the tetrabromo-derivative (III), obtained from anilinoaposafranine. The tribromo-derivative (IX; R = cyclohexyl) lost one bromine atom in boiling cyclohexylamine, to yield the dibromo-derivative (IXa). Again the dichlorinated rimino-compounds (X and XI) yielded only dibromo-derivatives (XII and XIII), respectively, and these are converted by boiling cyclohexylamine into the monobromo-derivatives (XIV and XV). Further, the

dichloro-anilinoaposafranine (V) on bromination gave a tribromo-compound (VI), which was converted by boiling cyclohexylamine into the dibromo-dichloro-anilinoaposafranine (VII), with the elimination of a bromine atom. It is clear therefore that the failure to introduce more than two bromine atoms into compounds (XI and X) is due to the fact that the *ortho*- and the *para*-position respectively of the anilino-group are already occupied by chlorine. A repetition of the degradation experiment with the tetrabromo-compound (III) yielded, as before, the bromine-free hydroxyaposafranone, but on this occasion it proved possible to isolate also a small amount of the dibromo-compound (XXIX). This is a further confirmation that two bromine atoms are present in the 2,4-positions of the N^2-phenyl group, and that no bromine has entered the phenazine nucleus.

We have now indicated the positions occupied by the four bromine atoms in tetrabromo-anilinoaposafranine (III), and in the various rimino-compounds (IX, XII, XIII). The

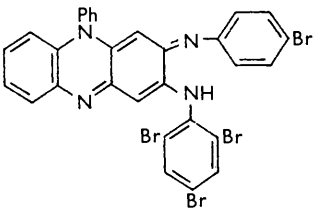


(XVI) X = X″=H , X′= X‴= Br
(XVII) X = X′= X″ = X‴ = Br

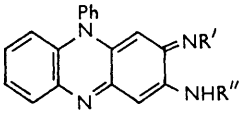


	R	R′	X
(XVIII)	Ph	Ph	H
(XIX)	*p*-C	*p*-C	H
(XX)	ch	ch	H
(XXI)	*p*-C	*p*-C	Br
(XXII)	ch	ch	Br
(XXIII)	Ph	*p*-Br	Br

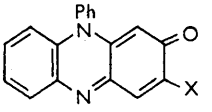
p-C = *p*-C_6H_4Cl
p-Br = *p*-C_6H_4Br
ch = cyclohexyl



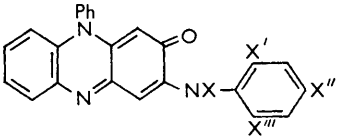
(XXIV)



(XXV) R′= R″= cyclohexyl
(XXVI) R′= cyclohexyl; R″= Br



(XXVII) X = Br
(XXVIII) X = NHPh



	X	X′	X″	X‴
(XXIX)	H	H	Br	Br
(XXX)	H	Br	Br	Br
(XXXI)	Br	Br	Br	Br

phenyl rimino-compound (II), however, unlike the alkyl or cycloalkyl compounds of this class, formed a tetrabromo-derivative, and the evidence here favours the placing of the fourth bromine atom in the *para*-position of the =NPh group in position 3 of the phenazine nucleus. This evidence is provided by synthesis of the dibromo-compound (XVI), by condensation of *o*-aminodiphenylamine and 4,5-di-*p*-bromoanilino-*o*-quinone, which on further bromination yielded the identical tetrabromo-derivative (XVII), already obtained from compound (II), by direct bromination. Supporting evidence is afforded by the behaviour on bromination of the isomers of the anilinoaposafranines. Thus the isomer (XVIII) gave under the usual conditions a dibromo-derivative which is stable to boiling cyclohexylamine. With aniline under reflux it gave the bromine-free phenyl rimino-compound (II), showing that again with this group of compounds only the 2- and 3-substituents of the phenazine nucleus are concerned in the bromination. Compound

(XVIII) has already been shown[1] to form a monoacetyl derivative. The dibromo-derivative, however, could not be acetylated. It is presumed, therefore, that one of the bromine atoms has substituted in the NH_2– group and, by analogy from compound (XVII), the second bromine atom must be placed in the *para*-position of the =NPh residue. This is confirmed by the results obtained from bromination of compounds (XIX) and (XX), both of which yielded monobromo-derivatives (XXI and XXII). The fact that the dibromo-derivative (XXIII), on degradation with ethanolic sulphuric acid in a sealed tube, gave a bromine-free product (cf. Part I [2]) which we now know to be hydroxyaposafranone, is readily understood on the basis of the structure here advanced for compound (XXIII).

The bromine linked to nitrogen in the 2-arylamino-substituent of the phenazine nucleus is remarkably stable, resisting alcoholic potassium hydroxide and boiling dilute acetic acid. It is labile in boiling cyclohexylamine, in part being eliminated from the molecule and in part, we suspect, being transferred to the 6-position of the already brominated phenyl nucleus. Thus in one experiment it was possible to separate chromatographically a second tetrabromo-compound from the product resulting from the treatment of the tetrabromo-derivative (XVII) with cyclohexylamine. This tetrabromo-compound was much paler, had a sharp melting point and altered colour reactions in acid, and probably has the structure (XXIV). In many other experiments, boiling with cyclohexylamine gave mixtures of bromo-compounds which it was impossible to separate chromatographically. The bromination of compound (XXV) gave an interesting result, one bromine atom entering the molecule with the simultaneous displacement of a cyclohexyl group. As it has already been shown that the =N· cyclohexyl group in position 3 is stable under these conditions, the monobromo-derivative must have the structure (XXVI).

Bromination experiments were also performed with aposafranone and some of its derivatives. Under the same conditions of bromination, aposafranone gave a monobrominated derivative which was converted by warm aniline into anilinoaposafranone (XXVIII). It seems probable, therefore, that structure (XXVII) represents the monobromo-compound. Anilinoaposafranone (XXVIII), however, gave a tetrabromo-derivative from which treatment with cyclohexylamine eliminated one bromine atom, yielding a tribromo-compound. For reasons already given we consider that this bromine atom has been removed from a bromoimino-grouping. The positions of two of the remaining bromine atoms have been fixed by brominating the 2,4-dibromoanilinoaposafranone (XXIX), which had been synthesised unambiguously by condensation of aposafranone with 2,4-dibromoaniline. Bromination of the dibromo-compound (XXIX) gave the same tetrabromo-derivative as was already obtained by direct bromination of anilinoaposafranone (XXVIII). The fourth bromine atom has probably substituted the 6-position of the anilino-group. It was not possible to confirm this as 2,4,6-tribromoaniline could not be condensed with aposafranone. The tri- and tetra-bromoanilinoaposafranone are formulated as (XXX) and (XXXI).

Experimental

Light petroleum had b. p. 40—60°; ligroin had b. p. 100—120°.

Bromination of Anilinoaposafranine.—A solution of bromine (2·5 c.c.) in chloroform (10 c.c.) was added dropwise with stirring to anilinoaposafranine (2·0 g.) in chloroform (200 c.c.). The solution, when kept for 3 hr., deposited dark green crystals which were suspended in ethanol and treated with dilute sodium hydroxide solution. The base was purified chromatographically on alumina. 3-*Bromoimino*-3,5-*dihydro*-5-*phenyl*-2-(N,2,4-*tribromoanilino*)*phenazine* (1·0 g.) (III) was obtained as bronze glistening needles (from benzene), m. p. >310° (Found: C, 44·1; H, 2·1; N, 8·4; Br, 46·0. $C_{24}H_{14}N_4Br_4,\frac{1}{3}C_6H_6$ requires C, 44·3; H, 2·3; N, 8·0; Br, 45·5%). Its solution in concentrated sulphuric acid has a deep blue colour which changes to red on dilution.

Heating of Tetrabromoanilinoaposafranine.—(a) *With cyclohexylamine.* The hydrochloride of the bromo-compound (1·0 g.) was heated under reflux with cyclohexylamine (25·0 c.c.) for ½ hr. Excess of amine was steam-distilled and the residue purified on an alumina column. 3-*Bromoimino*-2-(2,4-*dibromoanilino*)-3,5-*dihydro*-5-*phenylphenazine* (IV) was obtained as dark

red needles (from benzene–methanol), m. p. 210° (decomp.) (0·4 g.) (Found: C, 48·6; H, 2·7; N, 9·3; Br, 39·7. $C_{24}H_{15}N_4Br_3$ requires C, 48·1; H, 2·5; N, 9·3; Br, 40·1%). Its solution in concentrated sulphuric acid is petunia-purple.

(b) *With aniline.* The product which crystallised from the chloroform solution above was heated under reflux with aniline for 15 min. The solution was poured into ether, and the precipitated salts converted into the base which was purified on alumina. 2-Anilino-3,5-dihydro-5-phenyl-3-phenyliminophenazine (II) was obtained as dark red needles, m. p. and mixed m. p. 234—236°.

(c) *With ethanolic sulphuric acid.* Tetrabromoanilinoaposafranine (0·8 g.), ethanol (10·0 c.c.), and dilute sulphuric acid (5·0 c.c.) were heated in a sealed tube at 160—170° for 4 hr. The mixture was made alkaline with dilute sodium hydroxide solution. The precipitate was washed repeatedly with warm dilute alkali, and the residue was chromatographed in benzene on alumina. The eluate was evaporated to dryness and the residue recrystallised from ethanol, yielding 2,4-dibromoanilinoaposafranone (50 mg.) (XXIX), m. p. 257—258° not depressed on admixture with an authentic sample (see below).

The combined alkaline extracts were acidified with acetic acid, giving the orange-yellow flocculent precipitate of hydroxyaposafranone.[2]

3-Bromoimino-2-(N,2-dibromo-4-chloroanilino)-5-p-chlorophenyl-3,5-dihydrophenazine (VI).—2-*p*-Chloroanilino-5-*p*-chlorophenyl-3,5-dihydro-3-iminophenazine (V) (1·2 g.) was brominated, and the product purified, as described for anilinoaposafranine. The *tribromo-compound* was obtained as red-brown needles (0·3 g.) (from benzene), m. p. >320° (Found: C, 44·3; H, 1·9; N, 8·3; Cl, 10·4; Br, 35·4. $C_{24}H_{13}N_4Cl_2Br_3,\frac{1}{4}C_6H_6$ requires C, 44·5; H, 2·1; N, 8·1; Cl, 10·3; Br, 34·9%). This bromo-compound (0·3 g.) on refluxing with cyclohexylamine yielded 2-(2-*bromo-4-chloroanilino*)-3-*bromoimino*-5-p-*chlorophenyl*-3,5-*dihydrophenazine* (VII), an orange-brown powder (0·1 g.) (from benzene–methanol), m. p. 206° (decomp.) (Found: C, 49·8; H, 2·5; N, 9·3; Cl, 11·7; Br, 26·5. $C_{24}H_{14}N_4Cl_2Br_2$ requires C, 48·9; H, 2·4; N, 9·5; Cl, 12·1; Br, 27·2%).

3-Cyclohexylimino-3,5-dihydro-5-phenyl-2-(N,2,4-tribromoanilino)phenazine (IX; R = cyclohexyl).—2-Anilino-3-cyclohexylimino-3,5-dihydro-5-phenylphenazine (VIII; R = cyclohexyl) (1·3 g.) in chloroform (16 c.c.) was stirred during the dropwise addition of bromine (1 c.c.) in chloroform (8 c.c.). The solution was kept overnight, ligroin added, and the precipitate converted into the base with ethanolic ammonia. The *base* was purified on alumina and obtained as a black powder (0·3 g.), m. p. 200—205° (decomp.) (from chloroform–ligroin) (Found: C, 52·7; H, 4·0; N, 7·7; Br, 36·0. $C_{30}H_{25}N_4Br_3$ requires C, 52·9; H, 3·7; N, 8·2; Br, 35·2%).

3-Cyclohexylimino-2-(2,4-dibromoanilino)-3,5-dihydro-5-phenylphenazine (IXa).—The hydrochloride of the tribromo-base (0·6 g.) (IX; R = cyclohexyl) was heated under reflux for 90 min. with cyclohexylamine (20 c.c.). The precipitate obtained with methanol was chromatographed in benzene on alumina, and the single band collected in two fractions. The second fraction was rechromatographed, and the second half of the eluate yielded the *dibromo-compound* as brown needles (0·1 g.), m. p. 222—224° (Found: C, 60·3; H, 4·4; N, 9·2; Br, 25·9. $C_{30}H_{26}N_4Br_2$ requires C, 59·8; H, 4·3; N, 9·3; Br, 26·6%).

5-p-Chlorophenyl-2-(N,2-dibromo-4-chloroanilino)-3,5-dihydro-3-isopropyliminophenazine (XII).—2-*p*-Chloroanilino-5-*p*-chlorophenyl-3,5-dihydro-3-isopropyliminophenazine (X) (5·0 g.) in chloroform (300 c.c.) was treated dropwise with bromine (3 c.c.) in chloroform (20 c.c.). The *product* (5·2 g.), purified as above, was obtained as dark red needles, m. p. 193—195° (decomp.) (from benzene) (Found: C, 51·4; H, 3·2; N, 8·9; Cl, 11·2; Br, 25·4. $C_{27}H_{20}N_4Cl_2Br_2$ requires C, 51·3; H, 3·2; N, 8·9; Cl, 11·3; Br, 25·4%).

2-(2-Bromo-4-chloroanilino)-5-p-chlorophenyl-3,5-dihydro-3-isopropyliminophenazine (XIV).—The hydrochloride of the dibromo-base (XII) (2·0 g.) was heated under reflux with cyclohexylamine (25 c.c.) for 1 hr. The excess of cyclohexylamine was steam-distilled and the product (0·2 g.) purified chromatographically. The *monobromo-compound* was obtained as red-brown needles, m. p. 205—208° (from benzene–ligroin) (Found: C, 59·9; H, 4·2; N, 9·7; Cl, 12·6; Br, 14·1. $C_{27}H_{21}N_4Cl_2Br,\frac{1}{2}C_6H_6$ requires C, 60·2; H, 4·0; N, 9·7; Cl, 12·3; Br, 13·9%).

5-o-Chlorophenyl-2-(N,4-dibromo-2-chloroanilino)-3,5-dihydro-3-isopropyliminophenazine (XIII).—2-*o*-Chloroanilino-5-*o*-chlorophenyl-3,5-dihydro-3-isopropyliminophenazine (XI) (1·0 g.) gave with the usual treatment the *dibromo-base* (0·3 g.), m. p. 200° (decomp.) (from benzene–methanol) (Found: C, 51·5; H, 3·2; N, 9·1; Cl, 11·1; Br, 25·1. $C_{27}H_{20}N_4Cl_2Br_2$ requires C, 51·3; H, 3·2; N, 8·9; Cl, 11·3; Br, 25·4%).

2-(4-*Bromo*-2-*chloroanilino*)-5-o-*chlorophenyl*-3,5-*dihydro*-3-*isopropyliminophenazine* (XV).—The hydrochloride of the dibromo-base (XIII) (0·2 g.) with the usual cyclohexylamine treatment gave the *monobromo-compound* (50 mg.), m. p. 231—233° (from benzene–methanol) (Found: C, 60·1; H, 4·2; N, 9·5; Cl, 12·0; Br, 13·7. $C_{27}H_{21}N_4Cl_2Br$ requires C, 60·9; H, 4·1; N, 9·5; Cl, 12·0; Br, 13·5%).

3,5-*Dihydro*-3-*isopropylimino*-5-*phenyl*-2-(N,2,4-*tribromoanilino*)*phenazine* (IX; R = Pr^i) (0·3 g.) was obtained by the usual bromination method from 2-anilino-3,5-dihydro-3-isopropylimino-5-phenylphenazine (VIII; R = Pr^i) (1·1 g.). It was a black powder, m. p. 200—201° (decomp.) (from ethanol) (Found: C, 50·8; H, 3·4; N, 8·6; Br, 37·5. $C_{27}H_{21}N_4Br_3$ requires C, 50·5; H, 3·3; N, 8·7; Br, 37·4%).

3,5-*Dihydro*-5-*phenyl*-3-*t*-*butylimino*-2-(N,2,4-*tribromoanilino*)*phenazine* (IX; R = Bu^t) (0·1 g.) was obtained by the bromination of 2-anilino-3,5-dihydro-5-phenyl-3-t-butyliminophenazine (VIII; R = Bu^t) (0·35 g.). It formed dark green needles, m. p. 218—220° (from benzene–ethanol) (Found: C, 51·3; H, 3·8; N, 8·7; Br, 37·0. $C_{28}H_{23}N_4Br_3$ requires C, 51·3; H, 3·5; N, 8·5; Br, 36·6%).

4,5-*Di*-p-*bromoanilino*-o-*quinone*.—Catechol (2·2 g.) and *p*-bromoaniline (6·8 g.) were dissolved in ethanol (150 c.c.) and sodium iodate (4·4 g.) in water (150 c.c.) added. The mixture was stirred for 3 hr. and kept overnight. The bright red *quinone* (5·1 g.) which separated had m. p. 245—247° (from chloroform) (Found: C, 48·2; H, 2·6; N, 6·2; Br, 36·1. $C_{18}H_{12}O_2N_2Br_2$ requires C, 48·2; H, 2·7; N, 6·3; Br, 35·7%).

2-p-*Bromoanilino*-3-p-*bromophenylimino*-3,5-*dihydro*-5-*phenylphenazine* (XVI).—The above quinone (4·9 g.) and 2-aminodiphenylamine hydrochloride (2·5 g.) were heated under reflux with ethanol (200 c.c.) for 2 hr. The mixture on treatment with excess of dilute ammonia gave, after chromatographic purification, brown needles (2·0 g.) (from benzene), m. p. 235—236° (Found: C, 60·7; H, 3·4; N, 9·5; Br, 26·7. $C_{30}H_{20}N_4Br_2$ requires C, 60·4; H, 3·4; N, 9·4; Br, 26·8%). Bromination of the above compound, or of 2-anilino-3,5-dihydro-5-phenyl-3-phenyliminophenazine (II), gave 3-p-*bromophenylimino*-3,5-*dihydro*-5-*phenyl*-2-(N,2,4-*tribromoanilino*)*phenazine* (XVII). It formed almost black needles, m. p. >310° (from benzene) (Found: C, 47·5; H, 2·4; N, 7·1; Br, 42·6. $C_{30}H_{18}N_4Br_4$ requires C, 47·7; H, 2·4; N, 7·4; Br, 42·4%). The identity of the two products was established by examination in the infrared region, and by their blue colour in concentrated sulphuric acid. The tetrabromo-compound (0·4 g.) was heated for 1 hr. with cyclohexylamine (20 c.c.) and cyclohexylamine hydrochloride (0·4 g.). The solution was diluted with methanol and kept overnight. The precipitate was purified in benzene in an alumina column, yielding brown needles (0·1 g.), m. p. 265—267° (from benzene–methanol) (Found: C, 48·1; H, 2·3; N, 7·4; Br, 41·7. $C_{30}H_{18}N_4Br_4$ requires C, 47·7; H, 2·4; N, 7·4; Br, 42·4%). This compound is isomeric with the starting material and probably has the structure (XXIV). It has a violet colour in concentrated sulphuric acid. Repetition of this experiment has always given mixtures which we have failed to purify by chromatography. For example one product, m. p. 242—244° (from benzene–methanol), had C, 51·1; H, 2·8; N, 8·4; Br, 38·4 ($C_{30}H_{19}N_4Br_3$ requires C, 53·3; H, 2·8; N, 8·3; Br, 35·6%).

2-*Bromoamino*-3-p-*bromophenylimino*-3,5-*dihydro*-5-*phenylphenazine* (XXIII).—2-Amino-3,5-dihydro-5-phenyl-3-phenyliminophenazine (XVIII) (2·4 g.) by the usual bromination method gave the *dibromo-base* as dark red needles (1·6 g.), m. p. 242—244° (from benzene) (Found: C, 57·6; H, 3·2; N, 10·0; Br, 28·9. $C_{24}H_{16}N_4Br_2,\frac{1}{2}C_6H_6$ requires C, 57·9; H, 3·6; N, 10·0; Br, 28·6%). Boiling this compound with acetic anhydride gave unaltered material. When heated under reflux for 25 min. with aniline (25 c.c.) and aniline hydrobromide (0·6 g.), and purified as described earlier, 0·7 g. of the dibromo-base (XXIII) yielded the bromine-free compound (II).

2-*Bromoamino*-5-*cyclohexyl*-3-*cyclohexylimino*-3,5-*dihydrophenazine* (XXII) (0·3 g.), m. p. 225—227° (from ethanol) (Found: C, 63·7; H, 6·4; N, 12·4; Br, 17·6. $C_{24}H_{29}N_4Br$ requires C, 63·6; H, 6·4; N, 12·4; Br, 17·7%), was obtained by bromination of the amino-compound (XX) (0·4 g.). Similarly the *p*-chlorophenyl analogue (XIX) gave, on bromination, 2-*bromoamino*-5-p-*chlorophenyl*-3-p-*chlorophenylimino*-3,5-*dihydrophenazine* (XXI) in 50% yield. It formed red needles, m. p. 278—280° (from benzene-methanol) (Found: C, 56·5; H, 3·0; N, 11·1; Cl, 14·1; Br, 15·8. $C_{24}H_{15}N_4Cl_2Br$ requires C, 56·5; H, 2·9; N, 11·0; Cl, 13·9; Br, 15·7%).

2-*Bromoamino*-3-*cyclohexylimino*-3,5-*dihydro*-5-*phenylphenazine* (XXVI) (0·15 g.) was obtained by bromination of 2-cyclohexylamino-3-cyclohexylimino-3,5-dihydro-5-phenylphenazine

(XXV) (0·4 g.). It formed orange-yellow needles, m. p. 235—237° (from ethanol–benzene) (Found: C, 64·2; H, 4·9; N, 12·2; Br, 17·8. $C_{24}H_{23}N_4Br$ requires C, 64·4; H, 5·1; N, 12·5; Br, 17·9%). This decomposes on the alumina column.

2-Bromo-3,5-dihydro-3-oxo-5-phenylphenazine (XXVII) was got in 60% yield by bromination of aposafranone. It was a dark brown powder, m. p. 228—230° (from ethanol) (Found: C, 61·1; H, 3·1; N, 8·3; Br, 22·0. $C_{18}H_{11}ON_2Br$ requires C, 61·5; H, 3·1; N, 8·0; Br, 22·8%). Its solution in concentrated sulphuric acid is vivid green, becoming amber-coloured on dilution. The hydrobromide of this compound when heated with aniline for 4 hr. on the water-bath yielded anilinoaposafranone (XXVIII).

2,4-Dibromoanilinoaposafranone (XXIX).—Aposafranone (0·7 g.), 2,4-dibromoaniline hydrochloride (1·0 g.), and 2,4-dibromoaniline (1·8 g.) were heated together on the water-bath for 3 hr. The product was recrystallised from benzene–ligroin, to give 2-(2,4-*dibromoanilino*)-3,5-*dihydro*-3-*oxo*-5-*phenylphenazine* (XXIX) as a red-brown powder (0·4 g.), m. p. 257—259° (Found: C, 57·0; H, 2·8; N, 8·0; Br, 29·6. $C_{24}H_{15}ON_3Br_2,\frac{1}{3}C_6H_6$ requires C, 57·0; H, 3·1; N, 7·7; Br, 29·3%). On bromination this compound gave the tetrabromo-derivative (XXXI), 3,5-*dihydro*-3-*oxo*-5-*phenyl*-2-(N,2,4,6-*tetrabromoanilino*)*phenazine*, as a red powder, m. p. 205—206° (from ligroin–benzene) (Found: C, 44·6; H, 2·2; N, 6·0; Br, 45·5. $C_{24}H_{13}ON_3Br_4,\frac{1}{3}C_6H_6$ requires C, 44·3; H, 2·1; N, 6·0; Br, 45·4%). This tetrabromo-derivative (XXXI) was also got by direct bromination of anilinoaposafranone.

Treatment of Tetrabromoanilinoaposafranone (XXXI) *with Cyclohexylamine.*—The base (0·1 g.) was heated under reflux for 90 min. with cyclohexylamine (12 c.). The product obtained from the cooled solution on addition of methanol was obtained as red-brown crystals (80 mg.) (from benzene–methanol), m. p. 236—237° (Found: C, 48·7; H, 2·3; N, 6·8; Br, 39·8. $C_{24}H_{14}ON_3Br_3$ requires C, 48·0; H, 2·3; N, 7·0; Br, 40·0%). 3,5-*Dihydro*-3-*oxo*-5-*phenyl*-2-(2,4,6-*tribromoanilino*)*phenazine* (XXX) is purple-red in concentrated sulphuric acid, becoming grey-green on dilution.

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