25 ml. of water to 225 ml. of methanol and storing the resulting solvent in the thermostat. Commercial 12 *N* hydrochloric acid was diluted to *ca.* 0.1 *N*, and mixed with methanol as described above to give a stock acid solution, which was standardized by titration with sodium hydroxide solution, and diluted as necessary for kinetic runs. More concentrated acid solutions were prepared as needed. Solutions of quinamines were prepared on the day they were to be used. For each run, the acid solution was added to a measured volume of the quinamine solution from a rapid flow pipet, the mixture quickly shaken in a volumetric flask, and the solution transferred to a jacketed ultraviolet absorption cell kept at 26.0°. The rate of disappearance of the cyclohexadienone peak at 247–258 mμ was followed on a Cary Model 11 spectrophotometer. The concentration of acid was usually at least twenty times as great as that of quinamine, to allow pseudo-first-order rates to be calculated.

[CONTRIBUTION FROM THE CHEMISTRY RESEARCH DEPARTMENT, AGRICULTURAL CENTER, AMERICAN CYANAMID CO., PRINCETON, N. J.]

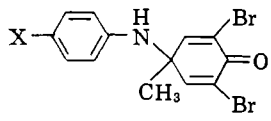
A Re-examination of Some Reported Rearrangements of Quinamines[1]

BY BERNARD MILLER

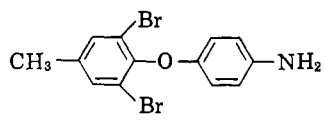
RECEIVED SEPTEMBER 18, 1963

The rearrangement of Ia in acid has been shown to give a mixture of IIIa and IIIb rather than IIIc as previously reported. Yields of IIIa and IIIb were increased by increasing acid concentrations. A by-product of the rearrangement of Ib, which had been assigned structure V, has been shown to have structure VI. Quinamine VIIIa gives largely 2,6-dibromo-4-methylaniline and X on reaction with acid, while VIIIb gives the same amine and 2,6-dibromo-4-methylphenol. No evidence has been found for occurrence of a dienone-phenol rearrangement. These results are interpreted in terms of the formation of a "π-complex" as an intermediate.

In the preceding paper[2] it was shown that the acid-catalyzed rearrangement of *p*-quinamines (I) to 4-aminodiphenyl ethers (II) proceeds by an intramolecular path, and a mechanism was proposed involving a transition state resembling a π-complex of two aromatic rings.

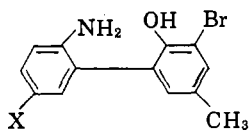


Ia, X = H
b, X = Br
c, X = Cl

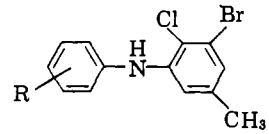


II

The conversion of I to II proceeds in excellent yield when the *p*-position of the aniline ring of I is unsubstituted. When the *p*-position is substituted, *p*-quinamines react with mineral acids to give phenols of type III or oxygen-free diphenylamines of type IV.[3]



IIIa, X = H
b, X = Br
c, X = Cl



IV

While there is no direct evidence concerning the mechanism by which I is converted to III and IV, it is tempting to regard these reactions as being intramolecular rearrangements analogous to the rearrangement of I to II. A particularly satisfying mechanism would involve the production of II, III, and IV from a common intermediate π-complex, as is outlined in the preceding paper.[2]

Although all the major products of quinamine rearrangements can be explained by the "π-complex" mechanism, several minor products isolated by Fries and his co-workers were assigned structures which cannot be easily rationalized by this mechanism.

These minor products have now been re-examined, and new structures have been assigned to them. As a result, the structures assigned to all the known products of quinamine rearrangements are consistent with those which might be expected to result from collapse or rearrangement of a single intermediate complex.

Minor Products from the Rearrangement of Ia.—Rearrangement of Ia in glacial acetic acid containing high concentrations of hydrochloric acid was reported to give, in addition to II, a side product, m.p. 168°, whose analysis corresponded to the formula $C_{13}H_{11}NOBrCl$ and which was assigned structure IIIc. This unusual reaction was explained by assuming that Ia was first cleaved to give aniline hydrochloride and a 4-chlorocyclohexadienone. The 4-chlorocyclohexadienone was believed to act as a chlorinating agent, converting quinamine Ia to Ic; Ic could then rearrange to IIIc.[3]

Although mechanisms proposed 30 years ago often seem strange to us today, it is indeed difficult to explain the production of IIIc without assuming the occurrence of a 4-chlorocyclohexadienone as an intermediate. Once the existence of such cleavage products are assumed, however, it becomes possible to rationalize the production of products such as III and IV by intermolecular paths, rather than the intramolecular path which was shown to be exclusively followed in the formation of II.[2] A reinvestigation of the structure of the 168° product was therefore of more than usual interest. We initially attempted to confirm Fries' assignment of structure IIIc to his 168° product by forming IIIc by rearrangement of Ic. When Ic was treated with acid, however, the diphenyl derivative IIIc which was obtained had a melting point of 198–199°, and did not seem likely to be identical with Fries' product

Fries' procedure for the preparation of his 168° material was therefore repeated, and a 9% yield of a side product, m.p. 153–173°, was obtained. This proved, after a rather tedious separation, to be composed of approximately equal amounts of two compounds: A, m.p. 202–203°, whose analysis fit the formula $C_{13}H_{11}ONBr_2$, and B, m.p. 147–148°, with the formula $C_{13}H_{12}OBrN$. No chlorine-containing product corresponding to that reported by Fries could be obtained. It seems probable that Fries' "compound" was, in fact, a mixture of A and B, which would give a total halogen content agreeing reasonably well with that required for the formula $C_{13}H_{11}NOBrCl$.

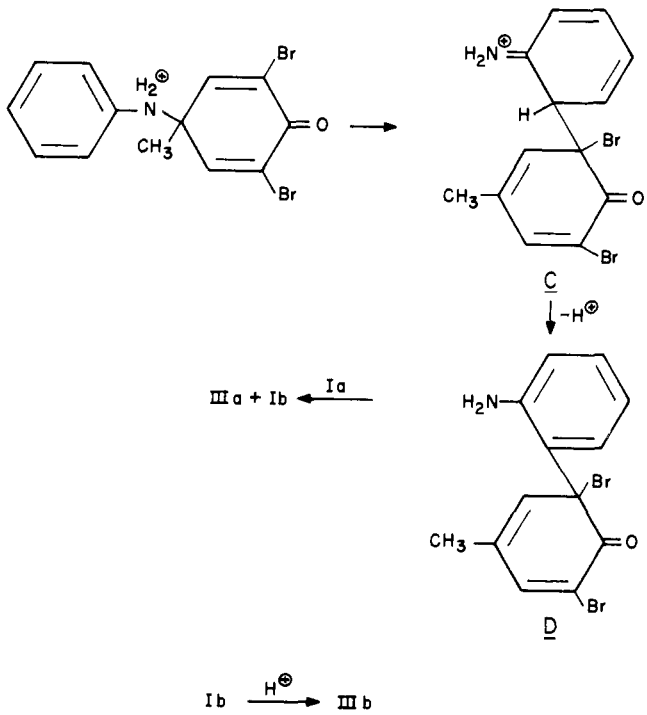
Both A and B showed split N–H stretching peaks at 2.92 and 3.02 μ. as would be expected for primary amines, and in addition showed broad phenolic hydroxyl peaks at 3.8–3.9 μ, indicating that the hydroxyl group forms strong hydrogen bonds. Compound IIIc showed similar absorption in its infrared spectrum, as would be expected of a compound in which strong interaction can occur between the hydroxyl and amino groups. Other

(1) Reactions of Cyclohexadienones. V. For paper IV, see ref. 2.
(2) B. Miller, *J. Am. Chem. Soc.*, **86**, 1127 (1964).
(3) K. Fries, R. Boeker, and F. Wallbaum, *Ann.*, **509**, 73 (1934).

2,6-disubstituted phenols, in which strong hydrogen bonding cannot occur, show sharp peaks at *ca.* 2.8 μ.[4]

It seemed probable, therefore, that A had the structure IIIb, and B the structure IIIa. Synthesis of IIIb by rearrangement of Ib gave a product which was shown by melting point, mixture melting point, and infrared spectrum to be identical with A. Bromination of B with dioxane dibromide again yielded A, thus confirming the postulated structure IIIa for B.

The formation of A and B as side products in the rearrangement of Ia can be explained by the mechanism



The preceding paper[2] presented arguments favoring formation of "C" by collapse of a π-complex intermediate, rather than directly from I by a Claisen rearrangement.

The intermediate 2-bromocyclohexadienone D need not, of course, react directly with Ia in order to yield the observed products, but could react with acetic acid to form acetyl hypobromite, which would then serve as the brominating agent.

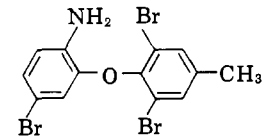
Although the observed yield of IIIa and IIIb accounted for 9% of the starting material, half of this was presumably derived from rearrangement of Ib produced by bromination of Ia, so that the direct rearrangement of Ia to IIIa amounts to only some 5% of the amount of Ia rearranging to IIa.

Fries reported that the amount of phenolic product obtained was increased by the use of higher hydrochloric acid concentrations and longer reaction times.[3] We did not observe any change in the yield of phenols on increasing the reaction time from 5 min. to 65 hr. This is as expected, since all the products of the reaction are quite stable in the acetic acid–hydrochloric acid mixture. However, reducing the volume of hydrochloric acid from one-half to one-twenty-fifth of the acetic acid volume and adding the hydrochloric acid slowly to the reaction mixture reduced the yields of phenols to 5%, while adding a slurry of the quinamine in acetic acid slowly to an equal volume of hydrochloric acid increased the yield to 12%. That these differences are actually due to changes in hydrogen ion concentration rather than the change in the solvent composition from acetic acid to acetic acid–water was shown by carrying out the rearrangement in 50% aqueous acetic acid, to which was slowly added concentrated hydrochloric acid amounting to one-twenty-fifth of the volume of the solvent. Rearrangement under these conditions was quite slow, probably owing to the insolubility of the quinamine in aqueous acid, but the yield of phenolic side products again amounted to just 5%.

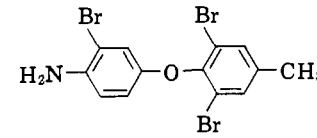
It seems, therefore, that the rearrangement of Ia to IIIa and IIIb involves, at least in part, reactions which are higher than first order in hydrogen ion. This behavior resembles the acid-catalyzed benzidine rearrangements of hydrazonaphthalenes, the products of which have been shown by Ingold and his co-workers to change as the acid concentration increases.[5] These rearrangements are first order in hydrogen ion concentration at low acid strengths, but change to higher orders at high acid concentrations.[5]

It does not appear, however, that the rearrangement of *p*-quinamines to III necessarily proceeds only under such high acid concentrations as those used in the preceding rearrangement of Ia, since qualitative experiments show that quinamines with substituents in the *p*-position of the aniline ring rearrange quite readily in 10^{-3} *M* solutions of hydrochloric acid in methanol.[6]

Structure of the By-product from the Rearrangement of Ib.—Since quinamine Ib had been prepared as an intermediate in the preparation of IIIb, we took the opportunity to reinvestigate the structure of a by-product of the rearrangement of Ib. Fries had assigned structure V to this product (m.p. 105°) on the basis of its elemental analysis, the absence of phenolic properties, and the presence of a primary amine function.

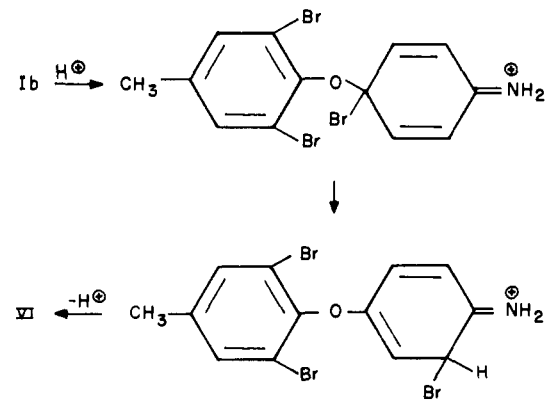


V



VI

Compound V would indeed appear to be a reasonable product of the collapse of a π-complex of two aromatic rings, but its structure is not completely defined by the evidence given above. An alternative structure is VI, which agrees with Fries' evidence and is more in accord with the known tendency of both the quinamine[3] and benzidine[7] rearrangements to give products which are coupled at the *p*-positions. VI could rise *via* the route shown below.



The displacement of bromine atoms from 4-bromohydrazobenzenes to give benzidines has frequently

(4) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1956, Chapters 6 and 14.

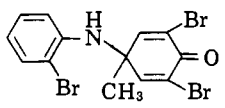
(5) D. V. Banthorpe, E. D. Hughes, and C. Ingold, *J. Chem. Soc.*, 2386 (1962), and succeeding papers.

(6) B. Miller, to be published.

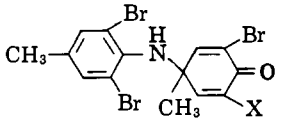
(7) (a) P. Jacobson, *Ann.*, **428**, 76 (1922); (b) R. B. Carlin and W. O. Forshey, Jr., *J. Am. Chem. Soc.*, **72**, 793 (1950).

been observed.[7] The shift of the bromine from the *p*- to the *o*-position of the aniline ring could be either an intramolecular or an intermolecular process.[8]

Repetition of Fries' procedure gave a 14% yield of an amino ether, m.p. 102–103°, which is presumably identical with Fries 105° product. Its n.m.r. spectrum shows a methyl group at 7.68 τ, two protons adjacent to the methyl group at 2.66 τ, and a single aromatic proton adjacent to the bromine atom at 3.19 τ, which is consistent with both structure V and VI. The two adjacent hydrogens on the aniline ring, however, show no *ortho* coupling. The peak at 3.47 τ has only weak side peaks for the outer lines of the "AB" pattern. This pattern is similar to that of *p*-methoxyaniline, but quite different from that of *p*-chloroaniline, in which the different electronegativities of the chlorine atom and the amino group induce strong coupling.[9] The n.m.r. spectrum therefore favors structure VI over structure V. That the product was, in fact, VI was shown by its identity with a sample of VI prepared by rearranging quinamine VII in acid.

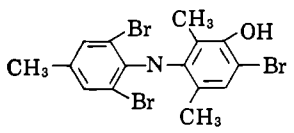


VII

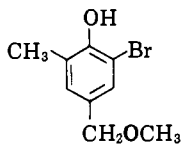


VIIIa, X = CH_3
b, X = Br

The Reaction of VIII with Acid.—Since we have shown that the by-product of the reaction of Ia with acid is a mixture of IIIa and IIIb rather than IIIc, the only evidence for cleavage of quinamines on reaction with acid is the reported isolation of a 40% yield of 2,6-dibromo-4-methylaniline and unstated amounts of 2-bromo-4,6-dimethylphenol from the reaction of quinamine VIIIa with acid. The only other reported product (obtained in unstated yield) was a phenol, m.p. 110°, which was assumed to arise from a normal dienone–phenol rearrangement and was assigned structure IX.[3]



IX



X

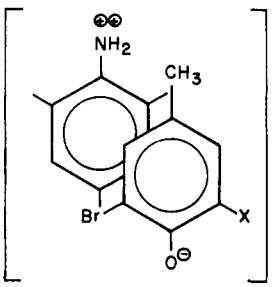
Repetition of the reported reaction of hydrochloric acid with a methanolic solution of VIIIa gave a 75% yield of dibromotoluidine, a 20% yield of 2-bromo-4,6-dimethylphenol, and a 23% yield of a second phenol, $C_9H_{11}O_2Br$, which darkened rapidly on standing and decomposed significantly on distillation. The infrared spectrum of the crude mixture of phenols before distillation indicated that it consisted preponderately of this second phenol.

This phenol was assigned structure X on the basis of its elemental analysis and the presence of a strong methyl ether band at 9.0 μ in its infrared spectrum. X was independently synthesized from sodium methoxide and 2-bromo-4-bromomethyl-6-methylphenol.[10] The product of this reaction was identical in infrared spectrum and retention time in thin layer chromatography on silica gel with the product obtained from VIIIa and acid.

No evidence could be found for any rearrangement of VIIIa to IX or other products of a dienone–phenol rearrangement.

Reaction of VIIIb with methanolic acid gave an 80% yield of dibromotoluidine and a 77% yield of dibromocresol. A very small yield (*ca.* 3%) of 3,5-dibromo-4-hydroxybenzaldehyde was obtained and was identified by comparison with a sample prepared by bromination of *p*-hydroxybenzaldehyde.[11] Again, no evidence for a dienone–phenol rearrangement could be observed.

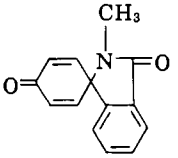
It does not appear likely that the cleavages of VIIIa and VIIIb could have proceeded by initial cleavage to form 4-chlorocyclohexadienones, since methanolic solutions of 4-bromocyclohexadienones give 4-methoxycyclohexadienones as their major solvolysis products.[12] While discussion of the mechanism at this point can only be speculative, it is tempting to regard these reactions as proceeding through an intermediate π-complex (XI), similar to that proposed for the rearrangement of quinamines to *p*-aminodiphenyl ethers.[2]



XI a, X = CH_3
b, X = Br

Transfer of a hydride ion within complex XIa would give an anilinium ion and a quinone methide, which would add methanol to give X. The more stable phenolate ion in complex XIb, however, would transfer a hydride ion less readily; XIb, therefore, might reasonably be expected to oxidize a solvent molecule to give an anilinium ion and dibromocresol.

It is quite interesting that the presence of a dienone–phenol rearrangement product could not be confirmed, even though all normal quinamine rearrangements were precluded by the structure of VIII. This reluctance to undergo the "normal" rearrangement must be due to preferential protonation of the amino nitrogen rather than the carbonyl oxygen. A dienone–phenol rearrangement would thus either require migration of a positively charged nitrogen atom, or, if the methyl group migrates, would place two positive charges on adjacent carbons, in a situation reminiscent of that found in 4-polyhalomethylcyclohexadienones.[13] The very slow dienone–phenol rearrangements of the spirocyclic quinamine XII prepared by Hey and his co-workers[14] can similarly be attributed to protonation of the amide group in preference to the carbonyl



XII

(8) Rearrangement of a bromine from the *o*- to the *p*-positions of cyclohexadienones has been observed: L. Denivelle and R. Fort, *Compt. rend.*, **238**, 1132 (1954).

(9) N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "NMR Spectra Catalog," Varian Associates, Palo Alto, Calif., 1962, Spectra 123 and 171.

(10) K. Fries and G. Oehmke, *Ann.*, **462**, 1 (1928).

(11) C. Paal, *Ber.*, **28**, 2407 (1895).

(12) B. Miller, unpublished work; see also G. M. Coppinger and T. W. Campbell, *J. Am. Chem. Soc.*, **75**, 734 (1953).

(13) *I.e.*, S. M. Bloom, *Tetrahedron Letters*, **No. 21**, 7 (1959).

(14) D. H. Hey, J. A. Leonard, T. M. Moynehan, and C. W. Rees, *J. Chem. Soc.*, 232 (1961); D. H. Hey, J. A. Leonard, and C. W. Rees, *Chem. Ind.* (London), 1025 (1962).

group. In the absence of alternative convenient reaction paths, such as those available to N-arylquinamines, XII does undergo a dienone–phenol rearrangement, presumably *via* the small fraction of its molecules which are protonated on the carbonyl rather than the amide functions.

Experimental[15]

Rearrangement of 4-Anilino-2,6-dibromo-4-methyl-2,5-cyclohexadien-1-one (Ia).—A mixture of glacial acetic acid (30 ml.) and concentrated hydrochloric acid (15 ml.) was added to Ia.[10] (5.5 g., 0.0154 mole). A white precipitate formed immediately. The mixture was stirred for 5 min., then filtered, and the solid washed with glacial acetic acid. The combined acetic acid solutions were evaporated to dryness to give 1.1 g. of a cream colored solid, which was dissolved in 20 ml. of ethyl alcohol; 50 ml. of a 5% sodium hydroxide solution was added, and the mixture extracted with methylene chloride and acidified with glacial acetic acid. A white precipitate formed which was extracted with methylene chloride. The methylene chloride layer was washed with water, dried over magnesium sulfate, and evaporated to give 0.53 g. of a white solid, m.p. 153–173°. Fractional crystallization from benzene–hexane gave a less soluble product as felted needles, m.p. 202–203°.

Anal. Calcd. for $C_{13}H_{11}Br_2NO$: C, 43.70; H, 3.08; Br, 44.80; N, 3.92. Found: C, 45.22; H, 3.25; Br, 43.78; N, 4.01.

The mother liquors afforded a second product, m.p. 147–148°.

Anal. Calcd. for $C_{13}H_{12}BrNO$: C, 56.1; H, 4.32; N, 5.03. Found: C, 55.97; H, 4.34; N, 5.17.

The infrared spectra of mixtures of the two solids showed that they were present in roughly equal amounts in the crude product.

Preparation of 4-(*p*-Chloranilino)-2,6-dibromo-4-methyl-2,5-cyclohexadien-1-one (Ic).—A suspension of 2,4,6-tribromo-4-methyl-2,5-cyclohexadien-1-one[10] (30.0 g., 0.087 mole) in ethanol was cooled to −10°, and a solution of *p*-chloraniline (20.0 g., 0.178 mole) was added slowly with continual stirring. No apparent reaction occurred at −10°, but the quinamine separated slowly as the temperature rose to +10°. Filtration gave 9.5 g. of the quinamine (0.0243 mole, 28%) as a yellow powder, m.p. 118–120° dec. after recrystallization from acetone–water.

Anal. Calcd. for $C_{13}H_{10}Br_2ClNO$: C, 39.87; H, 2.57; Br, 40.80; Cl, 9.06; N, 3.58. Found: C, 40.01; H, 3.19; Br, 40.94; Cl, 8.88; N, 3.74.

Preparation of 2-Amino-3'-bromo-5-chloro-2'-hydroxy-5'-methylbiphenyl (IIIc).—Compound Ic (2.0 g., 0.00510 mole) was suspended in 15 ml. of glacial acetic acid and 5 ml. of concentrated hydrochloric acid was added. The quinamine dissolved immediately, and a precipitate settled slowly out of the solution, which was filtered after 3 hr. The precipitate was rubbed with a 10% sodium hydroxide solution, which was acidified with acetic acid to give 1.0 g. (0.00319 mole, 63%) of IIIc as a cream colored powder, m.p. 196–198°. Recrystallization from benzene gave white felted needles, m.p. 198–199°.

Anal. Calcd. for $C_{13}H_{11}NOBrCl$: C, 50.08; H, 3.53; Br, 25.64; Cl, 11.37; N, 4.49. Found: C, 50.15; H, 3.67; Br, 25.87; Cl, 11.23; N, 4.64.

Rearrangement of 2,6-Dibromo-4-(*p*-bromoanilino)-4-methyl-2,5-cyclohexadien-1-one (Ib).—Compound Ib[3] (4.8 g., 0.00109 mole) was rearranged as described for Ic. The reaction mixture was filtered and the precipitate stirred in 20 ml. of ethyl alcohol and heated with 50 ml. of 10% sodium hydroxide solution. The solution was filtered free of a black, tarry, insoluble material and acidified with glacial acetic acid, to give a white precipitate, which was extracted from the aqueous layer with methylene chloride. The methylene chloride solution was washed with water, dried over magnesium sulfate, and evaporated to give 0.90 g. (0.000252 mole, 25%) of 2-amino-3'5-dibromo-2'-hydroxy-5'-methylbiphenyl (IIIb) as a tan solid. Recrystallization from benzene–hexane gave white felted needles, m.p. 202–203° (reported[3] m.p. 205°).

The sodium hydroxide-insoluble tar was taken up in methylene chloride, washed with water, dried, and decolorized with charcoal. Evaporation of the solvent left 2.0 g. of a brown gum which was extracted with hot hexane. The hexane solution, on cooling, deposited a gum which crystallized on standing. Recrystallization from ethanol gave 0.70 g. (0.0016 mole, 14%) of 4-(2,6-dibromo-4-cresyloxy)-2-bromoaniline, m.p. 90–93°. Recrystallization from hexane raised the melting point to 102–103° (reported[3] m.p. 105°).

(15) Melting points are corrected. Microanalyses were by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

Preparation of 2,6-Dibromo-4-(*o*-bromoanilino)-4-methyl-2,5-cyclohexadien-1-one (VII).—Reaction of *o*-bromoaniline with 2,4,6-tribromo-4-methyl-2,5-cyclohexadien-1-one as described for the preparation of Ic gave the desired quinamine in 23% yield as light yellow plates, m.p. 131–132° (from acetone–water).

Anal. Calcd. for $C_{13}H_{10}Br_3NO$: C, 35.82; H, 2.31; Br, 54.99; N, 3.21. Found: C, 35.76; H, 2.21; Br, 55.23; N, 3.26.

Preparation of 4-(2,6-Dibromo-4-cresyloxy)-2-bromoaniline (VI).—2,6-Dibromo-4-(*o*-bromoanilino)-4-methyl-2,5-cyclohexadien-1-one (2.50 g., 0.00573 mole) was suspended in 20 ml. of glacial acetic acid and 3 ml. of concentrated hydrochloric acid was added. A white precipitate formed immediately, which was filtered, washed with acetic acid, and suspended in 15 ml. of ethyl alcohol. The solution was neutralized with dilute sodium hydroxide. The white precipitate which formed (2.20 g., 0.00505 mole, 88%) was recrystallized from hexane to give white needles, m.p. 103–104°.

Preparation of 2,6-Dibromo-4-(2,6-dibromo-4-methylanilino)-4-methyl-2,5-cyclohexadien-1-one (VIIIb).—To a suspension of 8.0 g. of 2,4,6-tribromo-4-methyl-2,5-cyclohexadien-1-one (0.0232 mole) in 20 ml. of ethyl alcohol at 0° was added a warm solution of 2,6-dibromo-4-methylaniline (12.0 g., 0.0453 mole) in 75 ml. of ethyl alcohol. The solution was allowed to come to room temperature and gently warmed on the steam bath until formation of the quinamine began, and then removed, stirred for 15 min., and cooled in ice. Filtration gave 4.2 g. (0.00795 mole, 34%) of a pink solid, which was recrystallized from acetone–water to give a white powder, m.p. 112–113°.

Anal. Calcd. for $C_{14}H_{11}Br_4NO$: C, 31.79; H, 2.08; Br, 60.44; N, 2.65. Found: C, 31.69; H, 1.97; Br, 61.77; N, 2.92.

Reaction of 2-Bromo-4-(2,6-dibromo-4-methylanilino)-4,6-dimethyl-2,5-cyclohexadien-1-one (VIIIa) with Acid.—Concentrated hydrochloric acid (10 ml.) was added to a solution of 10.0 g. (0.0215 mole) of VIIIa[10] in 100 ml. of methanol. The solution turned bright yellow on addition of the acid, but turned red after a few minutes. The mixture was stirred overnight. Water was added until precipitation of solid was complete. The product was filtered, the red solid obtained was dissolved in methylene chloride, and the methylene chloride solution was extracted with 3 *N* sodium hydroxide solution. The methylene chloride layer was washed with water, dried over magnesium sulfate, and the solvent evaporated to give 4.3 g. (0.0150 mole, 75%) of 2,6-dibromo-4-methylaniline. The sodium hydroxide solution was combined with the filtrates from the crude reaction mixture to give an acidic solution which was extracted with methylene chloride. The methylene chloride layer was washed with water, dried over magnesium sulfate, and evaporated to give 4.02 g. of red liquid. Distillation at 0.5 mm. gave 0.89 g. (0.000443 mole, 20%) of 2-bromo-4,6-dimethylphenol, b.p. 110–114°, and 1.06 g. (0.0046 mole, 23%) of 2-bromo-4-methoxymethyl-4-methylphenol, b.p. 150–160°.

Preparation of 2-Bromo-4-methoxymethyl-4-methylphenol (X).—A solution of 2-bromo-4-bromomethyl-4-methylphenol[3] (9.0 g., 0.0322 mole) in 50 ml. of methanol was cooled in ice and a solution of 1.74 g. (0.0332 mole) of sodium methoxide added. Addition of water gave a heavy white precipitate which was filtered and washed with methylene chloride. The filtrate was extracted with methylene chloride, and the combined methylene chloride solutions were washed with water, dried over magnesium sulfate, and evaporated to give 3.0 g. (0.0130 mole, 40%) of X as a yellow oil, which showed one spot on a thin layer silica gel film.

Anal. Calcd. for $C_9H_{11}O_2Br$: C, 46.99; H, 4.78; Br, 34.74. Found: C, 46.80; H, 4.77; Br, 34.64.

Reaction of 2,6-Dibromo-4-(2,6-dibromo-4-methylanilino)-4-methyl-2,5-cyclohexadien-1-one (VIIIb) with Acid.—To a solution of 5.0 g. (0.0094 mole) of VIIIb in 50 ml. of methanol was added 10 ml. of concentrated hydrochloric acid. The mixture was stirred for 18 hr. to give a dark brown solution which was made basic with 2 *N* sodium hydroxide solution. Filtration gave 2.0 g. (0.00755 mole, 80%) of 2,6-dibromo-4-methylaniline. The filtrate was neutralized with acetic acid and extracted with methylene chloride. Evaporation of the methylene chloride solution gave a red oil, which partially crystallized. Filtration gave 0.150 g. of cream colored powder and a red oil, which crystallized on seeding to give 1.92 g. (0.00734 mole, 77%) of 2,6-dibromo-4-methylphenol. The cream colored powder, which showed three spots on thin layer chromatography, was recrystallized four times from ethanol to give 0.050 g. (0.18 mmole, 1.9%) of 3,5-dibromo-4-hydroxybenzaldehyde, m.p. 174–176° (reported[11] m.p. 178–179°).

Acknowledgment.—We thank Dr. J. Lancaster for the n.m.r. spectra.