

981. Amine Oxidation. Part II.* Reactions of Aliphatic Tertiary Amines with Quinones. Detection of Dehydrogenation by the Formation of Coloured Dialkylaminovinylquinones.

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This and the following papers are concerned with the oxidation of tertiary amines by organic oxidising agents, which often proceed readily at room temperature. In this paper structural factors influencing the reactions of tertiary amines with *p*-quinones are discussed. These reactions may proceed particularly readily owing to prior formation of molecular complexes, for which spectroscopic evidence is presented. Reactions between tertiary amines containing a flexible $\text{>N}\cdot\overset{\text{H}}{\text{C}}\cdot\text{CH}<$ grouping and some halogenated quinones can result in dehydrogenation to enamines $\text{>N}\cdot\overset{\text{H}}{\text{C}}\cdot\text{C}<$. If the enamine contains a β -CH grouping, coupling with a second molecule of halogenated quinone can occur, to give a blue or purple dialkylaminovinylquinone. From the viewpoint of the isolation of the coloured quinone the two-stage reaction proceeds best with simple *N*-ethyl compounds. Some of the properties of these new coloured quinones are described.

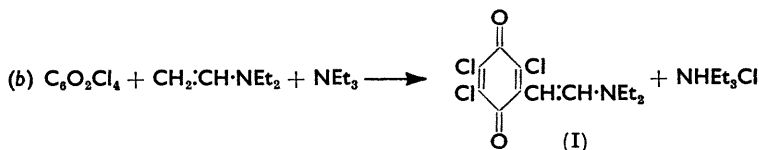
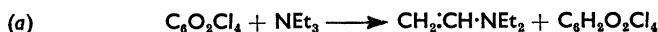
THE observation was made¹ that when triethylamine was added to a solution of chloranil in benzene, the mixture became green and then blue with the simultaneous precipitation of a colourless crystalline product. The compound responsible for the blue colour was

* Part I, *J.*, 1957, 3032.

¹ Cf. *Chem. and Ind.*, 1956, 1096; the initial observations were made by one of us (H. B. H.) in the Converse Memorial Laboratories, Harvard, where very generous facilities were placed at our disposal by Professor R. B. Woodward.

readily obtained crystalline (m. p. 131—132°), and the colourless product was shown to be triethylamine hydrochloride. The production of green or blue colours from aliphatic tertiary amines and chloranil has been recorded before.²

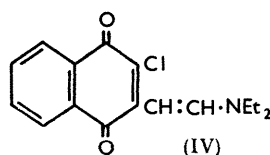
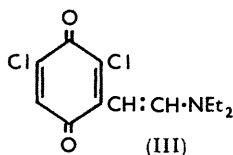
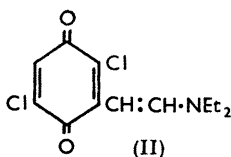
Analysis of the blue compound suggested the formula $(C_{12}H_{12}O_2NCl_3)_n$, corresponding, when $n = 1$, to the loss of one molecule each of hydrogen and of hydrogen chloride from a 1 : 1 reaction between the amine and the quinone. Molecular-weight determinations confirming this degree of complexity and the infrared absorption showing the presence of conjugated carbonyl groups, the blue compound was formulated as the diethylaminovinyl-quinone (I), the first member to be characterised of this group of coloured quinones.



The formation of the blue quinone (I) is believed to take place in two steps. First (a), the amine is dehydrogenated to diethylvinylamine—in agreement, tetrachloroquinol was isolated from the final reaction solution. Secondly (b), the diethylvinylamine acts as a nucleophile, displacing chlorine from a second molecule of chloranil (cf. following paper). This second stage has an electronic analogy to the *C*-alkylation of β -dialkylaminocrotonic esters and cyclic enamines³ by alkyl halides. The structure (I) for the blue quinone is confirmed by its properties (some of which are given at the end of this paper), and by the synthesis of this and related compounds by alternative methods (two following papers).

Scope of the Dehydrogenation-Coupling Reaction.—(i) *Quinone component.* The reaction between chloranil (a nearly saturated solution in benzene) and triethylamine (2.5 mol.) was complete within 24 hr. at 22° in the dark, the yield of blue quinone (based on above equations) being approx. 50%. Losses occurred during isolation, as spectroscopic examination of the reaction solution showed that more than 70% of the blue quinone was actually formed, the absorption of the blue quinone at 6400 Å (ϵ 8800 for the pure compound) being used for this computation. The reaction between bromanil and triethylamine was similar, the spectroscopic yield of the blue tribromo-analogue being 60%: again the reactivity of the coloured quinone resulted in losses during isolation. Under the same conditions iodanyl did not react appreciably with triethylamine. This must be due to inhibition of the dehydrogenation step (a) (see below), as tests with diethylvinylamine generated by other methods (following papers) showed that the coupling reaction could occur with the iodo-quinone.

Other halogenated quinones gave lower yields of blue quinones than those obtained from chloranil and bromanil. Thus, low yields of the blue quinones (II) and (III) were obtained from 2 : 5- and 2 : 6-dichloro-*p*-benzoquinone (even allowing for the fact that the



enamine is attacking CH positions on the quinones and hence more initial dichloroquinone is required in each case for oxidation of the intermediate condensation products to give the final blue quinones). 2-Chloro- and 2 : 3-dichloro-naphthaquinone reacted slowly

² Sivadjian, *Bull. Soc. chim. France*, 1935, 2, 623; Stahl, *Analyt. Chem.*, 1953, 25, 1725.

³ Hamilton and Robinson, *J.*, 1916, 1029, 1038; Stork *et al.*, *J. Amer. Chem. Soc.*, 1954, 76, 2029; 1956, 78, 5128.

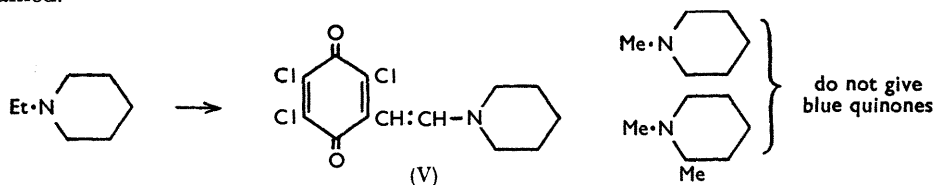
with triethylamine, giving a low yield of the purple quinone (IV) in each case: from the viewpoint of synthesis the method given in the following paper is much preferable.

Electron-donating methoxyl groups are known⁴ to reduce the oxidation potentials of quinones and 2:5-dichloro-3:6- and 2:6-dichloro-3:5-dimethoxy-*p*-benzoquinone did not react appreciably with triethylamine in the dark [the former compound was chosen as a convenient detector for the dehydrogenation of triethylamine by other agents, as a methoxyl group is displaced by diethylvinylamine to give a blue quinone (two following papers)].

The reaction took another course when quinones containing adjacent unsubstituted positions were used. Black, apparently amorphous, materials separated (together with triethylamine hydrochloride) from the reactions of chloro- and 2:3-dichloro-*p*-benzoquinone with triethylamine in benzene at room temperature. The insolubility of these products indicated high molecular weights and analyses showed that several molecules of quinone to each molecule of amine were involved in their formation. No appreciable reaction took place between *p*-benzoquinone and triethylamine at room temperature in the dark, but, on heating, a similar insoluble black material separated.

No ready reaction occurred between triethylamine and *p*-toluquinone, α -naphthoquinone, or 2:5-dichloroanthraquinone and it may be concluded that the presence of halogen on the *p*-benzoquinone ring is necessary for oxidation at room temperature.

(ii) *Amine component.* Various tertiary amines were added to chloranil in benzene solution at room temperature in the dark. Judged by the rate of formation of blue colours, the reactions of tri-*n*-butylamine and *NN*-diethylcyclohexylamine with the quinone were slower than that of triethylamine. The blue product from tributylamine could not be purified satisfactorily owing to its reactivity; in general, alkyl substituents on the vinyl side-chain enhance the reactivity (*e.g.*, towards aqueous reagents) of the compounds. With 1-ethylpiperidine a blue colour developed, and the quinone (V) resulting from dehydrogenation of the ethyl group was isolated (an alternative synthesis is given in following paper). The difficulty of dehydrogenating the piperidine ring was confirmed by the non-production of blue quinones on treatment of 1-methylpiperidine and 1-methyl- α -pipercoline with chloranil [the coupling reaction can take place with the endocyclic enamine from the former amine (*cf.* Part III)]. 1-Methylpyrrolidine and nicotine behaved similarly in not giving blue quinones. Dimethylisopropylamine (related in structure to 1-methyl- α -pipercoline) reduced chloranil slowly, but no blue quinone was obtained.



Simple dialkylanilines have long been known⁵ to give *immediate* blue colours with chloranil in benzene solution, owing to reversible formation of molecular complexes (*cf.* below). When the blue solutions given by dimethyl- and diethyl-aniline were heated and then cooled, no colour changes were apparent but after each had been shaken with dilute acid to extract the dialkylanilines the former solution reverted to the yellow colour of chloranil, whereas the latter remained greenish-blue, indicating that some dehydrogenation of ethyl groups (and thence coupling) had taken place.

In tetramethylethylenediamine, $\text{Me}_2\text{N}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NMe}_2$, the group to be dehydrogenated is flanked by nitrogen on both sides. Chloranil was reduced by this amine but a blue quinone was not formed.

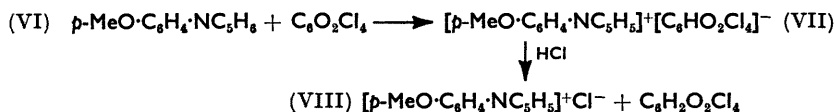
⁴ Fieser, *J. Amer. Chem. Soc.*, 1928, **50**, 439.

⁵ *Cf.* Pfeiffer, "Organische Molekülverbindungen," Enke, Stuttgart, 1927.

The structure of *isobutyldimethylamine* $\text{Me}_2\text{CH}\cdot\text{CH}_2\cdot\text{NMe}_2$ permits dehydrogenation, but the absence of a CH group β to nitrogen in the resulting enamine $\text{Me}_2\text{C}:\text{CH}\cdot\text{NMe}_2$ prevents formation of a blue quinone. This amine reduced chloranil (more slowly than triethylamine), and the isolation of *isobutyraldehyde* 2 : 4-dinitrophenylhydrazone from the reaction solution indicated that the expected enamine was formed.

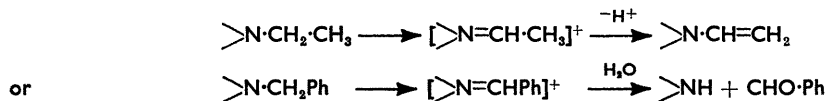
Another group to be considered consists of amines lacking an alkyl group β to nitrogen so that the formation of an enamine is impossible. The simplest compound of this type, trimethylamine, reduced chloranil more slowly than triethylamine, but the reaction has not been closely scrutinised. Attack on the central methylene group of tetramethylmethylenediamine $\text{Me}_2\text{N}\cdot\text{CH}_2\cdot\text{NMe}_2$ could be followed by the decrease in the yield of formaldehyde formed on hydrolysis. Under the chosen conditions the yield of formaldehyde had fallen to 50% after about 60 hr. The reactions of benzyldimethylamine $\text{Ph}\cdot\text{CH}_2\cdot\text{NMe}_2$ and tribenzylamine with chloranil were very slow at room temperature, and they were therefore studied in boiling benzene solutions. After 24 hr. the former amine had reduced about half of the quinone: addition of 2 : 4-dinitrophenylhydrazine reagent then gave the derivative of benzaldehyde (26% based on a 1 : 1 reaction between the quinone and amine). For tribenzylamine the yields of benzaldehyde 2 : 4-dinitrophenylhydrazone were determined after different times, a 60% yield being obtained after 60 hr.

Loss of hydrogen (overall as hydride) from dihydro-1-*p*-methoxyphenylpyridine (VI) ⁶ should receive encouragement from the simultaneous production of an aromatic pyridinium structure. The reaction between the amine and chloranil was very rapid at room temper-

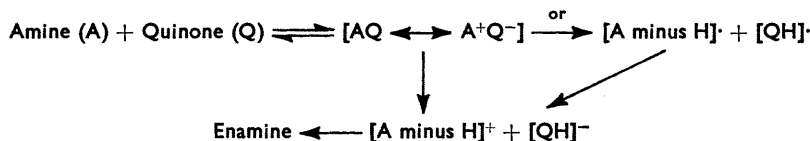


ature, a greenish precipitate separating. From its insolubility in benzene, its lack of infrared carbonyl absorption, and its conversion into the methoxyphenylpyridinium chloride (VIII) and tetrachloroquinol in good yields on treatment with dilute hydrochloric acid, this greenish compound appears to be a salt (cf. VII), although satisfactory analyses could not be obtained.

Mechanism(s) of the Tertiary-amine-Quinone Reactions.—On the simplest analysis, the oxidation level of enamine formation is reached by the transfer of hydride ion from the amine to the quinone, loss of a proton from the resulting conjugate acid of the enamine presumably being rapid and without influence on the rate, *e.g.*:



For the formation of an enamine, hydride-ion transfer therefore represents the overall reaction, but not necessarily the rate-determining step for which a single-electron step (also occurring in a bimolecular process) must also receive consideration. Various possible steps in the reactions may be expressed as follows:



Of simple functional groupings lacking possibilities for hydrogen bonding, tertiary amines are the most easily oxidised by quinones (and by many other reagents). The

⁶ Karrer, Schwarzenbach, and Utzinger, *Helv. Chim. Acta*, 1937, **20**, 72.

relatively rapid rates of these reactions must clearly depend on favourable redox potentials (see below). A second factor in promoting the reactions with quinones may be initial (reversible) association of the reactants in the form of a molecular (charge-transfer) complex ⁷ represented as $[AQ \longleftrightarrow A^+Q^-]$ in the above scheme. In other words, the initial (probably rate-determining) hydrogen-transfer step may be considered to take place within suitably activated complex molecules present in significant concentration.

The best evidence for the initial production of molecular complexes from tertiary amines and quinones comes from light-absorption measurements; complex formation is however often readily observed visually.

As stated already, many dialkylanilines give immediate blue colours with halogenated quinones, and in suitable cases the coloured complexes can be obtained crystalline. The complexes from trialkylamines apparently differ from those from dialkylanilines only in their lower stability and different absorption properties. Thus the immediate colour produced on adding a trialkylamine to a solution of chloranil in benzene is normally reddish-brown and, as with the blue complexes from dialkylanilines, treatment with dilute acid regenerates the original quinone and amine (salt). When suitably dilute solutions of pure reagents are used the initial reddish-brown colour from triethylamine and chloranil can be seen before the formation of the blue dialkylaminovinylquinone becomes apparent.

The available evidence suggests that the following structural factors promote the association of tertiary amines and quinones to molecular complexes (in which oxidation of the amine can take place if the redox potentials are suitable): (a) chlorine or bromine substituents on the *p*-benzoquinone ring, (b) an unsaturated (aromatic) ring linked directly to nitrogen in the amine, and (c) steric accessibility of the nitrogen atom. These factors are next discussed in turn.

(a) Earlier work ⁸ has shown that the presence of chlorine on the quinone ring enhances the stability of the complexes obtained with dimethylaniline, the more stable complex from chloranil absorbing more strongly and at a longer wavelength than that from *p*-benzoquinone (Beer's law not obeyed in either case). Some further measurements are now given in the following Table.

Absorption maxima (Å) for complexes formed in benzene solutions, 0.1M in amine and in quinone (determined in a 1 mm. cell).

Quinone	Amine		
	Me ₃ N	N[-CH ₂ -CH ₂] ₃ N	NPhMe ₂
<i>p</i> -Benzoquinone	—	No max. (orange-red)	No max.* (red)
2 : 6-Dichloro- <i>p</i> -benzoquinone	No max. (red)	5450 (purple)	5900 (blue)
Chloranil	No max. (red)	6000 (blue)	6500 (blue)

* In more concentrated solutions this complex gives a max. at 5050 Å.⁸

With dimethylaniline the two chlorinated quinones gave well-defined absorption maxima, whereas this amine and benzoquinone gave only enhanced general absorption at the concentrations studied.

These results parallel the chemical findings, the chloroquinones, but not benzoquinone, reacting with triethylamine at room temperature in dilute benzene solution.

As mentioned earlier, iodanyl differs from its bromo- and chloro-analogues in not giving a blue dialkylaminovinylquinone on treatment with triethylamine. As the oxidation potentials of these quinones are very similar (E° 0.737, 0.746, 0.742 v respectively), the lack of reactivity of iodanyl appears to be caused by the bulkiness of the iodine atoms,

⁷ For a recent review of charge-transfer complexes, see Orgel, *Quart. Rev.*, 1954, **8**, 422. Other references pertaining to quinones are given by Kuboyama and Nagatara, *J. Amer. Chem. Soc.*, 1955, **77**, 2644, and to charge-transfer complexes by Kosower, *ibid.*, 1956, **78**, 3493, 5700.

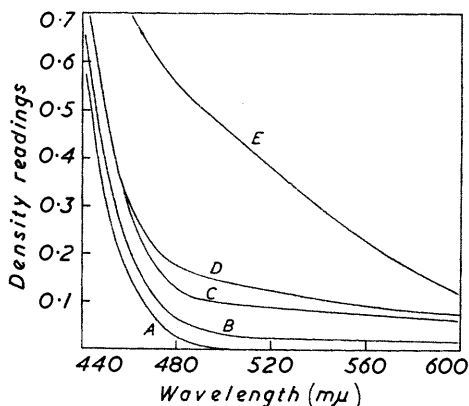
⁸ Briegleb and Czekalda, *Z. Electrochem.*, 1954, **58**, 249.

preventing the necessary association with the trialkylamine for reaction to occur. The poorer association of chloranil with hexaethylbenzene than with hexamethylbenzene has also been attributed to steric factors.⁹ In agreement, iodanil gave no appreciable immediate colour with dimethylaniline, whereas bromanil and chloranil gave blue colours. This may be expressed in a more general form, for quinones which dehydrogenate (say) triethylamine (and thence give coloured dialkylaminovinylquinones) are those which give immediate mauve to blue colours with dimethylaniline due to strong complex formation.

(b) The stabilising effect of an aromatic group attached to nitrogen can be seen by comparing the behaviour of dimethylaniline and trimethylamine with chloranil (Table). The dialkylaniline complex, which can easily be obtained crystalline, is represented by strong absorption near 6500 Å, whereas the complex from trimethylamine cannot be isolated at room temperature and gives a relatively weak general absorption.

(c) Steric factors for the amine component were investigated by adding various trialkylamines to a standard solution of chloranil and recording the changes of absorption in the 4500–6000 Å region (Figure), which correspond to the reddish-brown colours observed immediately with more concentrated solutions. The absorption due to complex formation

Absorption (0.2 cm. cell) of chloranil (0.04M) with (A) no additive, (B) tribenzylamine (0.09M), (C) tri-*n*-propylamine (0.08M), (D) 1-methylpiperidine (0.08M), and (E) trimethylamine (0.08M), all in benzene.



fell in the order Me_3N , $\text{Me}\cdot\text{C}_5\text{H}_{10}\text{N}$, $(n\text{-C}_3\text{H}_7)_3\text{N}$, and $(\text{Ph}\cdot\text{CH}_2)_3\text{N}$, corresponding to inhibition of association by the increasing bulk of the substituents. Like the stronger absorptions given by dialkylanilines, those from trialkylamines did not obey Beer's dilution law. Addition of more trialkylamine (all of those studied are virtually transparent in the 4500–6000 Å region) led to an increase in the level of absorption in line with the suggested reversible association. The interaction of quinones and triethylenediamine, $\text{N}[\cdot\text{CH}_2\cdot\text{CH}_2\cdot]_3\text{N}$, was examined as the nitrogen atoms in this type of amine are much less hindered than that in trimethylamine.¹⁰ Compared with the latter amine, triethylenediamine gave more strongly absorbing solutions (too strong to include in the Figure), the position of λ_{max} for the complex approaching those given by dimethylaniline (Table).

In suggesting that the oxidation–reduction step takes place within a molecular complex it must be remembered that the other condition of a suitable redox potential must be fulfilled before ready reaction will take place. Thus dimethylaniline is not appreciably oxidised by chloranil at room temperature in dilute solution in the dark, in spite of the obvious presence of a large concentration of complex. Similarly 2:5-dichloro-3:6-dimethoxy-*p*-benzoquinone gives an immediate brown colour with triethylamine but no dehydrogenation takes place in the dark (see below) as the oxidation potential of this quinone must be considerably lower than that of chloranil.

More detailed discussion of redox potentials is hampered by the lack of knowledge of the nature of the rate-determining hydrogen-transfer step in the amine–quinone reactions;

⁹ Foster, Hammick, and Parsons, *J.*, 1956, 555.

¹⁰ Cf. Brown, *J.*, 1956, 1248.

and the possibility that different pairs of components may react by different mechanisms must also be kept in mind.

The oxidation potentials of halogenated *p*-benzoquinones have only been determined for the overall two-electron reaction: $Q + 2e + 2H^+ \longrightarrow QH_2$. The fact that quinones with highest potentials¹¹ on this scale are also the most generally effective in dehydrogenating olefins and amines does not prove that a hydride-transfer mechanism is necessarily operating,* as the (unknown) potentials for single-electron steps (*e.g.*, acceptance of a hydrogen atom by the quinone) may run in a similar order. As mentioned above, a quinone, such as iodanyl, which does not readily form complexes may not oxidise an amine despite its apparently suitable high potential.

For the amine component it seems that complex formation with quinones and the susceptibility of an $\text{>N}\cdot\text{CH}<$ grouping towards oxidation are often in opposition. Thus triethylamine is oxidised more readily than trimethylamine, although for steric reasons the latter is likely to form a higher concentration of complex. Also, the slow oxidation of substituted benzylamines may be due to poor association for steric reasons (Figure), and not because of any particular difficulty in attack of a C-H bond in the $\text{N}\cdot\text{CH}_2\text{Ar}$ grouping. On the other hand, it is probable that the reduction potential and complex-forming power of dihydro-1-*p*-methoxyphenylpyridine (VI) act together to give the very rapid reaction observed with chloranil.

The tertiary-amine-quinone reactions discussed above were carried out in the dark, or in subdued light if the reaction was fast. Some reactions which did not proceed under these conditions were promoted by daylight: this may be attributed to photochemical activation of the molecular complex. Thus 2 : 5-dichloro-3 : 6-dimethoxy-*p*-benzoquinone and triethylamine gave a reddish-brown solution in benzene which slowly became blue on exposure to light. Similarly 1-methylpiperidine and chloranil gave a blue colour owing to dehydrogenation of the ring, a reaction which did not take place in the dark. The "dark reaction" in which the ethyl group of 1-ethylpiperidine is selectively dehydrogenated shows that attack on the annular α -CH group is relatively difficult in the absence of light; this could be rationalised in terms of a homolytic or a heterolytic mechanism, no decision being possible at present.

This paper has been confined to the reactions of *p*-benzoquinones; it may be noted that *o*-chloranil reacts readily with trialkylamines¹³ but the products have not yet been determined.

Molecular Complex Formation in the Indole Series.—The production of a blue colour from chloranil and 1-methylindole in ether has been reported.¹⁴ Pure 1-methylindole¹⁵ (kindly supplied by Dr. G. F. Smith) immediately gave a magenta colour in ether and a dull violet colour in benzene, neither colour changing on storage. It seems probable that the earlier workers used an impure amine. Two groups of workers^{16,17} have observed that the dehydrogenation of 2 : 3-cycloalkylindoles proceeds better with chloranil than by other methods. Clearly such reactions may be assisted by molecular-complex formation between the quinone and the substituted indoles.

Properties of the Dialkylaminovinylquinones.—The quinonoid structure for the blue compound (I) was indicated by its ease of reduction to colourless products and by its infrared absorption, carbonyl peaks appearing near 1670 and 1640 cm^{-1} . The latter band is relatively weak and this, together with its low frequency, suggests that it arises from the

* A hydride-transfer mechanism has been favoured for olefin-quinone reactions.¹²

¹¹ Values given in this paper are for solutions of the quinones in benzene (Kvalnes, *J. Amer. Chem. Soc.*, 1934, **56**, 667).

¹² Braude, Jackman, and Linstead, *J.*, 1954, 3548.

¹³ Horner and Spietschka, *Annalen*, 1955, **591**, 1.

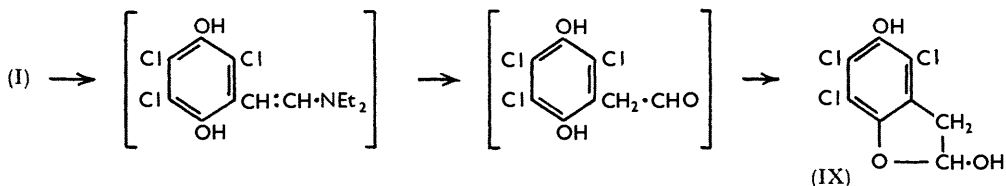
¹⁴ Ciusa and Ciamician, *Gazzetta*, 1909, **41**, 667.

¹⁵ Cf. Potts and Saxton, *J.*, 1954, 3548.

¹⁶ Treibs, Steinert, and Kirchof, *Annalen*, 1953, **581**, 54.

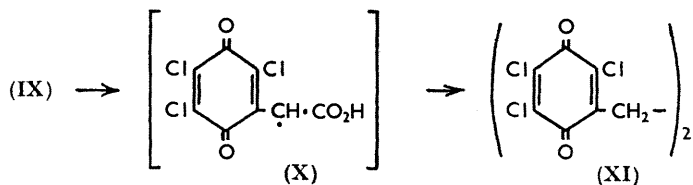
¹⁷ Barclay and Campbell, *J.*, 1945, 530.

carbonyl group conjugated with the electron-donating side-chain. The other band (at 1670 cm.^{-1}) has the normal quinone position and intensity and represents the non-conjugated carbonyl function.

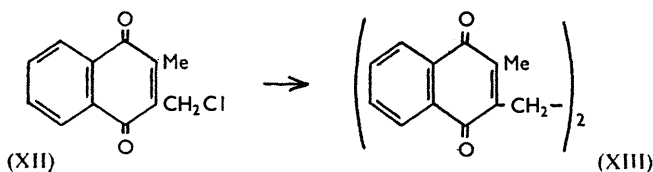


Catalytic hydrogenation (2 mols. of hydrogen) of the blue quinone (I) gave a colourless solution, but the product was difficult to purify. The blue colour of the quinone was also rapidly discharged by aqueous sodium dithionite and a crystalline compound free from nitrogen was isolated. The lactol structure (IX) is proposed for this on the basis of analytical data and infrared and ultraviolet absorption, the last resembling closely that of an alkyltrichloroquinol. Its formation may take place as indicated, hydrolysis of the enamine group occurring readily after the quinone-carbonyl system has been reduced.

Oxidation of the lactol with chromic acid in acetone gave a yellow, high-melting compound, $(\text{C}_7\text{H}_2\text{O}_2\text{Cl}_3)_n$, obviously a quinone. The low solubility of this compound (rendering molecular-weight determination by solution techniques difficult) indicated that it was not a simple alkyltrichloroquinone. The infrared absorption in the C-H bending region suggested that only methylene groups were present, and the compound is therefore formulated as (XI). This compound could arise by dimerisation of an intermediate radical, *e.g.*, (X), decarboxylation occurring at some stage ($\beta\gamma$ -unsaturated acids). Stabilisation of radicals (and so dimerisation) by groups containing a carbonyl function has been encountered previously, notably in the formation of succinic acids by dimerisation of radicals.¹⁸ Somewhat similar reactions to those in which the quinone (XI) is formed appear to be involved in the preparation of the quinone (XIII) by successive hydrogenation and oxidation of the chloromethyl compound (XII).¹⁹



A solution of the blue quinone (I) in benzene was unaffected when shaken with dilute aqueous acids, but the colour of an acidified methanol solution was slowly discharged; the expected hydrolysis product containing an aldehydic grouping proved difficult to purify.



This blue quinone was very reactive towards dilute alkaline reagents, but the reactions are undoubtedly caused by replacement of chlorine *para* to the unsaturated side-chain (see following paper) as the naphthaquinone compound (IV) was relatively stable.

¹⁸ Kharasch and Gladstone, *J. Amer. Chem. Soc.*, 1943, **65**, 15; Kharasch, Jensen, and Urry, *J. Org. Chem.*, 1945, **10**, 386.

¹⁹ Thomson, *J.*, 1953, 1190.

EXPERIMENTAL

M. p.s were determined on a Kofler hot stage. Alumina deactivated with dilute acetic acid ²⁰ was generally used for chromatography of the quinones. Light petroleum had b. p. 40—60°.

2 : 3 : 5-Trichloro-6-2'-diethylaminovinyl-*p*-benzoquinone (I).—A solution of chloranil (0.99 g.) in redistilled benzene (160 c.c., deoxygenated by nitrogen) was treated with triethylamine (1 g.), then kept at 20° in the dark for 24 hr. under nitrogen. The deep blue solution was filtered, to give triethylamine hydrochloride (0.33 g.), m. p. and mixed m. p. in a sealed tube 253—254° (from propan-2-ol). One half of the filtrate was concentrated under reduced pressure and adsorbed on deactivated alumina (80 g.). Rapid elution with benzene gave the *vinyl-quinone* (0.21 g.), m. p. 127—131° (raised to 131—132° on crystallisation from benzene-light petroleum) (Found: C, 46.8; H, 3.85; N, 4.35; Cl, 34.45. C₁₂H₁₂O₂NCl₃ requires C, 46.7; H, 3.9; N, 4.55; Cl, 34.45%). The second half was extracted with 5% sodium hydroxide solution (150 c.c.), dried, and evaporated under reduced pressure to give the *vinyl-quinone* (0.153 g.), m. p. 125—129°, raised to 131—132° on crystallisation. Acidification of the alkaline extract and extraction with ether gave a brown solid (0.33 g.) which on sublimation *in vacuo* gave impure tetrachloroquinol (0.2 g.), m. p. 210—214°, raised to 226—230° by crystallisation from benzene. Acetylation afforded the diacetate, m. p. and mixed m. p. 252—253° (from benzene).

The molecular weight of the blue quinone, determined in benzene solution by isothermal distillation, was 350 (calc., 308); the somewhat high value is probably due to partial decomposition during the several days necessary for the attainment of equilibrium.

Reduction of the Diethylaminovinylquinone (I).—The quinone (0.6 g.) in "AnalaR" ethyl acetate (250 c.c.) was shaken with hydrogen in the presence of pre-reduced Adams catalyst (0.1 g.). Absorption was rapid until 110 c.c. had been taken up (calc. for 2H₂: 100 c.c.). The resulting pale yellow solution became blue on exposure to air. Evaporation of the filtered solution under nitrogen gave an impure white solid (0.62 g.), m. p. 155—160°, which decomposed on attempted crystallisation.

Solutions of the quinone (1 g.) in acetone (150 c.c.) and sodium dithionite (10 g.) in water (200 c.c.) were mixed under nitrogen. When the mixture became colourless, water and ether were added. The product from the dried ethereal layer was crystallised from water, to give material (0.45 g.), m. p. 162—167°. The pure *lactol* (IX) had m. p. 166—167° (from benzene) (Found: C, 37.85; H, 1.95; Cl, 41.4. C₆H₅O₃Cl₃ requires C, 37.6; H, 2.0; Cl, 41.6%). The compound showed infrared hydroxyl absorption. Ultraviolet absorptions (in EtOH) were:

	Trichloro- <i>p</i> -toluquinol	Lactol	Tetrachloro- <i>p</i> -quinol
λ_{\max} . (Å)	3020	3060	3090
ϵ_{\max}	4800	5100	9300

A solution of the lactol (0.28 g.) in acetone (20 c.c.) was treated with 8N-chromic acid until oxidation was complete. The product (0.22 g.) was isolated with ether and adsorbed on deactivated alumina (20 g.) from benzene. Elution with benzene gave the *quinone* (XI) (0.15 g.), m. p. 268—273° (raised to 275—276° on crystallisation from benzene-acetone) (Found: C, 37.2; H, 0.95; Cl, 47.45. C₁₄H₄O₄Cl₆ requires C, 37.45; H, 0.9; Cl, 47.4%), having (in perfluoro-carbon) carbonyl peaks at 1687 and 1670 cm.⁻¹ and a methylene peak at 1456 cm.⁻¹, and (in dioxan) λ_{\max} . 2815 Å (ϵ 26,300). The related trichloro-*p*-toluquinone had (in dioxan) λ_{\max} . 2800 Å (ϵ 16,500).

2 : 3 : 5-Tribromo-6-2'-diethylaminovinyl-*p*-benzoquinone.—A solution of bromanil (2.0 g.) and triethylamine (3.5 g.) in benzene (400 c.c.) was kept at 20° under nitrogen in the dark for 24 hr. Triethylamine hydrobromide (0.6 g.) was removed and the solution evaporated. The residue was chromatographed in benzene on deactivated alumina, to give the blue *quinone* (0.47 g.), m. p. 114—116° (from light petroleum-benzene) (Found: C, 32.6; H, 2.9; N, 3.45. C₁₂H₁₂O₂NBr₃ requires C, 32.7; H, 2.75; N, 3.15%), λ_{\max} . (in dioxan) 3210 and 6450 Å (ϵ 28,900 and 8800 respectively).

Triethylamine and Other Quinones.—*p*-Benzoquinone, 2 : 5-dichloro-3 : 6-dimethoxy- and 2 : 6-dichloro-3 : 5-dimethoxy-*p*-benzoquinone were recovered in about 90% yields from attempted reactions with triethylamine in benzene, as described for chloranil. No blue colours were formed.

²⁰ Farrar, Hamlet, Henbest, and Jones, *J.*, 1952, 2657.

2 : 6-Dichloro-3-2'-diethylaminovinyl-p-benzoquinone.—A solution of 2 : 6-dichloro-*p*-benzoquinone (2.6 g.) and triethylamine (5 g.) in benzene (100 c.c.) was heated under reflux for 20 min. Filtration of the cooled solution removed dark insoluble material (2 g.). The filtrate was evaporated under reduced pressure and adsorbed on deactivated alumina (50 g.). Rapid elution with benzene followed by crystallisation of the product from ligroin gave the blue quinone (0.25 g.), m. p. 97—99° raised to 100—102° on recrystallisation (Found: C, 52.2; H, 4.8; N, 5.05; Cl, 25.55. $C_{12}H_{13}O_2NCl_2$ requires C, 52.6; H, 4.8; N, 5.1; Cl, 25.85%).

In a similar experiment with the quinone (0.71 g.) and triethylamine (0.81 g.) in benzene (80 c.c.) under nitrogen at 20° for 24 hr. in the dark, triethylamine hydrochloride (0.13 g.) and the blue quinone (25 mg.), m. p. 100—101°, were obtained.

2 : 5-Dichloro-3-2'-diethylaminovinyl-p-benzoquinone.—A solution of 2 : 5-dichloro-*p*-benzoquinone (3 g.) and triethylamine (6 g.) in benzene (100 c.c.) was heated under reflux for 1 hr. The solution was filtered to remove black material (3.5 g.), and evaporated under reduced pressure to give a product which, in benzene, was adsorbed on deactivated alumina (50 g.). Rapid elution with benzene and crystallisation from ligroin yielded the blue quinone (0.26 g.), m. p. 88—95°. Recrystallisation gave the pure quinone, m. p. 96—98° (decomp.) (Found: C, 53.05; H, 4.8; N, 5.45; Cl, 24.85%).

2-Chloro-3-2'-diethylaminovinyl-naphtha-1 : 4-quinone (IV).—A solution of 2 : 3-dichloro-naphtha-1 : 4-quinone (6 g.) and triethylamine (9 g.) in benzene (300 c.c.) was heated under reflux for 72 hr. The amine hydrochloride (0.3 g.) was filtered off and the filtrate evaporated under reduced pressure. The product was chromatographed on deactivated alumina (130 g.). Elution with benzene–light petroleum (1 : 3) yielded unchanged quinone (5.1 g.). Elution with benzene–light petroleum (1 : 1) gave red material (15 mg.). Elution with benzene gave the vinyl-quinone (0.2 g.), m. p. 91—95° (raised to 93—95° by recrystallisation from light petroleum, b. p. 40—60°) (Found: C, 66.2; H, 5.6; N, 4.45. $C_{18}H_{16}O_2NCl$ requires C, 66.3; H, 5.55; N, 4.85%). The quinone in ethyl acetate in the presence of Adams catalyst absorbed 2 mols. of hydrogen. A similar yield of the vinyl-quinone was obtained on reaction of 2-chloronaphtha-1 : 4-quinone and triethylamine in boiling benzene.

2 : 3 : 5-Trichloro-6-piperidinovinyl-p-benzoquinone (V).—A solution of 1-ethylpiperidine (1.13 g.) and chloranil (1.23 g.) in benzene (150 c.c.) was kept in the dark under nitrogen at 20° for 24 hr. The blue solution was washed with *n*-sodium hydroxide, then evaporated under reduced pressure to give the crude product (0.35 g.). This in benzene was filtered through deactivated alumina (20 g.). Crystallisation from aqueous acetone gave the vinyl-quinone (0.20 g.) as needles, m. p. 145—146° (decomp.) (Found: C, 48.5; H, 4.1. $C_{13}H_{12}O_2NCl_3$ requires C, 48.7; H, 3.8%).

General Properties of Dialkylaminovinylquinones.—The benzoquinone compounds decomposed to brown materials on melting, and their m. p.s depended on the rate of heating. The blue colour was rapidly discharged by alkaline reagents in homogeneous solution. Deactivated, neutral alumina was necessary for chromatography but appreciable losses occurred unless elution was rapid. The colour of a blue solution in methanol faded slowly on the addition of *n*-sulphuric acid. The naphthaquinone (IV) was more stable thermally and towards alkaline reagents.

Reaction of Chloranil with Dihydro-1-*p*-methoxyphenylpyridine (VI).—The amine (0.125 g.) in benzene (5 c.c.) was added to chloranil (0.165 g.) in benzene (10 c.c.), a green precipitate immediately being formed. After 30 min. the salt (cf. VII) (0.274 g., 95%) was collected. A thoroughly dried sample had m. p. 111—114° (dependent on rate of heating) (Found: C, 47.6, 47.5; H, 2.7, 2.85; N, 3.5, 3.5; Cl, 35.6, 35.4. Calc. for $C_{18}H_{13}O_3NCl_4$: C, 49.9; H, 3.0; N, 3.25; Cl, 32.8%). It was thought that the low carbon and the high chlorine analyses might be due to coprecipitation of chloranil, but repetition of the experiment with a deficiency (0.85 equiv.) of chloranil gave material with almost the same analysis (second set of figures above). The infrared spectrum of the salt (in Nujol) indicated that no appreciable amount of chloranil or of tetrachloroquinol could be present. The green salt (0.146 g.) was shaken with dilute hydrochloric acid and ether. The ether extract gave a solid (82.4 mg., theor. 83.5 mg.) which on crystallisation from benzene–light petroleum afforded tetrachloroquinol (50 mg.), m. p. and mixed m. p. 233—234°, whose infrared spectrum was identical with that of authentic material. The aqueous solution was evaporated to give a solid (75.2 mg., theor. 74.6 mg.) which on crystallisation from propan-2-ol–*isopropyl* ether gave 1-*p*-methoxyphenylpyridinium chloride (49.2 mg.) (infrared spectrum identical with that of authentic material).

Dehydrogenation of isoButyldimethylamine.—A solution of the amine (0.404 g.) and chloranil (0.492 g.) in pure peroxide-free dioxan (10 c.c.) was kept under nitrogen in the dark at 20° for 24 hr. The solution was then purple and a small precipitate of amine hydrochloride had been formed. The whole was acidified with dilute sulphuric acid and filtered and the filtrate treated with 2 : 4-dinitrophenylhydrazine reagent. The derivative was extracted with benzene and chromatographed on kieselguhr-bentonite. Chloroform eluted isobutyraldehyde 2 : 4-dinitrophenylhydrazone (55 mg., 22% based on chloranil), m. p. 183—188°. Crystallisation from propan-2-ol gave the pure compound as orange needles, m. p. and mixed m. p. 187—188°.

In a similar experiment with benzene (50 c.c.) as solvent, 48% of chloranil was recovered.

Reactions of Chloranil with Other Amines.—The following experiments were carried out under nitrogen in the dark at 20° for 24 hr. None of the amines gave blue quinones.

Trimethylamine. The amine (0.118 g.) and chloranil (0.246 g.) in benzene (25 c.c.) gave a reddish-brown solution. After 24 hr. the solution had become purple and some amine hydrochloride had separated. Chloranil (0.134 g., 55%) was recovered. From absorption measurements the yield of 2 : 3 : 5-trichloro-6-dimethylaminobenzoquinone was estimated to be 4% (based on initial chloranil). This *quinone*, isolated from a larger-scale experiment, had m. p. 120—122° [from light petroleum (b. p. 60—80°)] (Found: C, 38.25; H, 2.4; N, 5.6. $C_8H_6O_2NCl_3$ requires C, 37.75; H, 2.4; N, 5.5%); for its ultraviolet absorption see the following paper. Whether the formation of the dimethylaminoquinone depends on the presence of traces of water has yet to be determined.

Dimethylisopropylamine. A brownish colour was formed immediately on adding the amine (0.174 g.) to chloranil (0.246 g.) in benzene (25 c.c.). After 24 hr. the solution had become greenish-brown and some amine hydrochloride had separated. Chloranil (0.125 g., 51%) was recovered.

Tetramethylethylenediamine. A deep red-brown colour was formed on adding the amine (0.464 g.) to chloranil (0.492 g.) in benzene (60 c.c.), and a dark precipitate began to separate after 10 min. After 24 hr. the precipitate (mixture of amine hydrochloride and black material, m. p. >350°) was collected and chloranil (31 mg., 6%) was isolated from the filtrate.

Tetramethylmethylenediamine. A solution of the amine (0.204 g.) and chloranil (0.492 g.) in benzene (100 c.c.) was kept at 26°. After various times, 10 c.c. portions were withdrawn and washed with 0.04N-hydrochloric acid and water. The combined washings were adjusted to pH 5—6 and treated with dimedone [12 c.c. of a 0.04M-solution in methanol-water (1 : 19)] at 90° for 10 min. and then kept at 20° for 24 hr. The yield of formaldehyde derivative is a measure of attack on the central methylene group:

Time (hr.)	1	2.5	4	24	48	120
Formaldehyde dimethone (%)	99	83	72	62	57.	36

Benzyl dimethylamine. A solution of chloranil (0.492 g.) and the amine (0.27 g.) in benzene (50 c.c.) was heated under reflux for 24 hr. in nitrogen which thence passed into dimedone solution (no formaldehyde derivative was precipitated). The purple solution was filtered from dark brown material containing some amine hydrochloride and divided in halves. One portion was treated with an excess of 2 : 4-dinitrophenylhydrazine reagent, to give benzaldehyde derivative (26%). The other portion was washed with dilute hydrochloric acid and chromatographed on deactivated alumina, chloranil (50%; contaminated with some purple 2 : 3 : 5-trichloro-6-dialkylaminoquinone) being recovered.

Tribenzylamine. A solution of the amine (0.576 g.) and chloranil (0.492 g.) in benzene (40 c.c.) was heated under reflux, the yield of benzaldehyde (as its 2 : 4-dinitrophenylhydrazone) being estimated at different times:

Time (hr.)	18	28	72	98	120
Ph-CHO deriv. (%)	18	30	45	53	60

Reactions of Triethylamine with Other Chloroquinones.—A solution of the amine (4.04 g.) and 2 : 3-dichlorobenzoquinone (3.54 g.) in benzene (100 c.c.) was kept under nitrogen in the dark for 24 hr. A black precipitate (4.6 g.) which separated was washed with water to remove amine hydrochloride (1.77 g.). The black solid (insoluble in the common organic solvents), m. p. >320°, was dried *in vacuo* at 50° (Found: C, 49.0; H, 3.4; N, 2.0; Cl, 24.9%). Apart from analytical differences this material was not the quinhydrone (from the original quinone and the related quinol) which had m. p. 100—104°. No crystalline compounds were obtained from the benzene solution.

A similar reaction with chloro-*p*-benzoquinone (2.89 g.) gave a black precipitate (3.85 g.), and unchanged quinone (0.34 g.) was recovered from the benzene solution. Amine hydrochloride (0.69 g.) was removed by aqueous extraction of the black solid, leaving material, m. p. >320°, which was dried *in vacuo* at 50° (Found: C, 54.55; H, 2.5; N, 1.3; Cl, 16.25%).

The analyses of these black products did not fit with any simple compositions, but indicated that the products were formed from several molecules of quinone per molecule of amine, with loss of some hydrogen chloride.

Reaction of Triethylamine with p-Benzoquinone.—A solution of the amine (0.404 g.) and quinone (0.216 g.) in benzene (25 c.c.) was kept under nitrogen in the dark at 20° for 24 hr. The pale orange solution was evaporated to give unchanged quinone (0.190 g., 88%; almost certainly low owing to some loss of the volatile compound).

The amine (1.01 g.) and quinone (1.08 g.) in benzene (25 c.c.) were heated under reflux for 4.5 hr. with the exclusion of light. Filtration of the cooled mixture gave black solid and a red solution. The solid, washed with warm benzene and warm water and dried (0.69 g.), had m. p. >320° [Found: C, 63.85; H, 5.4; N, 2.5. (C₃₀H₃₁O₁₀N)_n requires C, 63.7; H, 5.55; N, 2.5%].

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